RHODE ISLAND

WATER RESOURCES CENTER

FIRST ANNUAL REPORT

UNIVERSITY OF RHODE ISLAND

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THE RHODE ISLAND WATER RESOURCES
RESEARCH PROGRAM

FIRST PROGRESS REPORT

OFFICE OF THE DIRECTOR
RHODE ISLAND WATER RESOURCES CENTER
UNIVERSITY OF RHODE ISLAND
KINGSTON, RHODE ISLAND

OCTOBER, 1965

Issued Under Provisions of the
Water Resources Research Act of 1964
PL 88-379

WATER RESOURCES CENTER
University of Rhode Island

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INTRODUCTION

The establishment of a Water Resources Center at the University of Rhode Island was formally proposed in May of 1964. One year later the proposal became a reality when the President of the United States signed, in May of 1965, a supplemental appropriation for Water Resource Institutes under the Water Resources Research Act of 1964 (P. L. 88-379).

The proposal for the establishment of a Center was made to the then Vice-President and Provost, Ernest W. Hartung, by an ad hoc Committee. This committee was charged with the task of making an investigation of the water resources research capabilities at the University and requested to submit the plans for carrying out water resources research. In general the proposals of the ad hoc committee were accepted.

Administration:

Responsibility for the Water Resources Research program is vested in a five man "Water Resources Coordinating Committee" whose Chairman is the Director of the Center. The Center is University wide and its membership consists of permanent university faculty appointments. For the period covered by this report, the faculty consisted of personnel from the Colleges of Agriculture, Arts and Science, Business Administration and Engineering.

Need for Research:

The problem in Rhode Island, as with the rest of the nation, is a result of the conflict in alternative uses of water. Research is needed

Need for Research - Continued

to resolve these conflicts in such a way so as to assure the greatest public benefit from our water resources.

In its original report the ad hoc Committee recommended five general areas of investigation where it appeared there was the greatest need for research. These were: (1) a determination of the future water needs of the state and of the surrounding area; (2) the problem of water pollution, including industrial and residential contaminants; (3) economic analysis of water supply and a determination of measures for increasing the economic efficiency of providing water; (4) the problem of conflict in water use which would encompass recreational use of water and (5) the development of information retrieval systems.

While the ad hoc Committee felt that a governing body was needed to review research proposals, it was the opinion of that committee that the quality of the research would be enhanced with a minimum of direction. For this reason, research proposals were accepted from all members of the University Faculty without areas being specifically delineated. In addition, it was believed that it was in the best interests of research to encourage as many projects as possible with the available funds.

RESEARCH PROJECTS FOR FISCAL YEAR 1965

In its first year of operation, the Water Resources Coordinating Committee gave approval to nine research proposals. These projects, with a statement of their accomplishments, are given below:

A. Analysis of the Effluent (non-radioactive) from a Nuclear Fuel Recovery Plant

The purpose of this investigation was to develop suitable quantitative atomic absorption techniques for the analyses of complex industrial waste effluents of a non-radioactive nature. It was necessary to determine what effects the presence of various cations and anions had on the determination of the metals in question.

Such a study is needed because the binding, moderating and clodding components of a nuclear fuel contain a number of the heavy metals which are poisonous to human and marine life. The recovery process isolates the uranium and thorium fractions and discharges an effluent that probably contains at least the following cations: beryllium, lead, cadmium, aluminum, iron, zirconium, chromium, nickel, sodium, molydenum and some rare earths.

Thus far, calibration curves have been obtained for seven of the above metals. The effects of eleven impurities have been determined at two different levels (20 and 40 ppm). Finally, since it is known that lime (CaO) is used extensively to precipitate metal impurities from industrial wastes, the effect of relatively large amounts of calcium (250 and 2,500 ppm) were determined for each of the metals.

B. The Effect of Obstructions on the Aeration of Flowing Streams

It is well known that most organic pollutants drastically reduce the oxygen content of a flowing stream. It is essential that the oxygen content be maintained above a certain minimum level in order that the plant and animal life in the stream be sustained and that offensive conditions be prevented from developing. The oxygen content of a polluted stream can be increased by providing for increased contact of the water with the atmosphere. This is done naturally by rapids and waterfalls.

The purpose of this project is to perform a systematic investigation of the effect of obstructions on the aeration of flowing streams. There are reports in the literature on the effect of weirs on the aeration of rivers, but to our knowledge there have not been any laboratory studies of weirs and systems of weirs, or of other types of obstructions. We hope, from this project, to develop some design criteria that will enable a person to design an obstruction that will produce the greatest amount of aeration for given flow conditions.

The work, thus far, has consisted of an extensive literature search and some preliminary experiments on single weirs and two weirs in series. The experiments were conducted in a laboratory flume. Other kinds of obstructions will also be tested in the laboratory flume. The obstructions that appear promising will be further tested in the field.

The oxygen concentration of the flowing water is being determined by a Clark type oxygen sensor that allows continuous readout of the oxygen concentration to within 0.5%. Check determinations are made using the standard Winkler chemical method.

The data from the weir experiments are now being processed and further experiments are being planned.

C. Static and Dynamic Behavior of Soils

Soil mechanics and foundation engineering play a vital role in water resource development since many hydraulic structures (embankments, dams and canals) are made entirely of earth and almost all are founded on soil. An extremely wide range of soil types are encountered in these structures and of great importance with respect to soil properties are those concerned with strength and deformation characteristics. In recent years improvement in measuring techniques has led to refined strength characteristics. However, relatively little attention has been given to the response of earthen masses to shear stresses short of failure or to the immediate response of soils to suddenly applied loads.

The primary purpose of this study is to ascertain whether shear strength properties are unique or are a function of the strain rate. Two experimental approaches are to be used. The first, is a study of the strength and deformation characteristics of compacted and natural soils under conditions of vibrational loads, impact loads and repeated loads. Secondly, small amplitude dynamic waves will be used to determine elastic constants, correlate soil properties such as type, consolidation, pressure and porosity and to determine damping capacity and effects of frequency on different soils.

Static application using the Geonor loading press, constant chamber pressure system in underway to determine the strength parameters of a laboratory sedimented silt. Shear strain rates of .046% per minute and .094% per minute.

The application of impact or vibrational loads has required the

Static and Dynamic Behavior of Soils - Continued from Page 7

modification of existing equipment or the fabrication of new equipment. Preparation of plans and specifications as well as the purchase of the component parts of needed equipment has been accomplished.

D. Factors Affecting the Solution of Manganese in Well Water.

The gradual increase in manganese content of well water supplies has been attributed by some people to nearby surface waters which have become increasingly polluted. Others have suggested the possibility that biologic activity, temperature stratification and chemical stratification are factors influencing the solution of manganese in water supplies.

This study proposes to determine the causes for the increase in the manganese content of the well water through the use of both a laboratory and field program of study. Closely controlled laboratory studies will first be run to study the effect of pertinent variables upon the solution of manganese, such as initial quality of the water, manganese content of the leaching soils, water flow rate through the soil, etc. The laboratory studies will be correlated to the field situations in three different locations. Two of these locations will be where the well waters contain an abnormally high concentration of manganese and the wells are located near polluted streams. The third location will be where the wells do not contain an appreciable amount of manganese at present but are located near a surface water which is being increasingly polluted by the presence of new industry.

Laboratory percolation studies of representative soils will be carried out in order to determine what characteristics of the flowing fluid affect

Factors Affecting the Solution of Manganese in Well Water - Continued.

the solution of manganese, and give the results found in the field. Chemical analyses of both the soil and water will be carried out using standard procedures. In particular the dissolved oxygen content, redox potential, acidity, and the presence of reducing substances that have an effect on the solubility of the manganese in water will be studied.

The analysis for manganese will be conducted using atomic absorption spectrophotometry. For this purpose, an atomic absorption attachment has been ordered to be used in conjunction with our Beckman model DU spectrophotometer. Until this unit arrives use will be made of equipment in another building on the campus.

At the time of this writing, the laboratory experiments using manganese salts are being conducted. Other work to be done includes percolation studies through soil under varying conditions and a series of analyses of the ground water and the surface water at the well site where this problem exists.

E. Structural Chemistry of Yellow Organic Matter in Fresh Water.

The presence of soluble iron and organic matter in surface water supplies is a widespread problem. In spite of extensive study the nature of the iron-organic matter complex remains an almost complete mystery. Although previous investigators have assumed that the organic fraction was either aliphatic or aromatic in nature, recent work by the principal investigator has suggested that materials extracted from soils and having many properties similar to the yellow organic matter from fresh water were more probably pyronic in nature. As such, these materials are probably synthesized by either soil or aquatic microflora and are not directly derived from plant residues.

It is proposed to examine the yellow organic matter extracted from surface fresh water supplies by a method of high pressure hydrogenolysis previously developed by the principal investigator. From analyses of the products of the hydrogenolysis degradation, hypotheses on the molecular structure of the yellow organic matter will be formulated. Attempts will be made to synthesize compounds with structure identical or similar to the formulated hypotheses and properties of these synthetic compounds compared with those of naturally occurring compounds.

Concurrent with the above study will be an examination of the water-soluble, yellow-colored products synthesized by various soil and aquatic microflora. Comparison of the microbial products and known plant residue with the organic matter extracted from fresh water should help in determining the origin of the water substances. Such knowledge should greatly facilitate steps to remove the water contaminants.

The yellow organic matter from colored surface water will be extracted by means of vacuum filtration, freezing, and solvent extraction. Elemental analyses, functional group determination, infrared spectra, and nuclear magnetic resonance spectra will be determined on the original, unmodified organic fractions. The samples will then be degraded by high pressure hydrogenolysis and the products fractionated as previously described. Following characterization of the degradation products, they will be compared with similar products obtained from various soil fractions and the appropriate molecular structural hypotheses formulated.

Following establishment of suggested structures, attempts will be made, using known methods of organic syntheses, to synthesize similar

Structural Chemistry of Yellow Organic Matter in Fresh Water - Continued

compounds with known structures. The properties of these synthetic compounds will be compared with those of the naturally occurring materials.

Mass cultures of microflora known to produce high-molecular weight, water-soluble, yellow organic substances (most probably members of *Aspergilli*, *Fusaria*, and *Streptomyces*) will be grown, and the organic substances extracted from these cultures will be examined by the methods described above.

E Impact and Incidence of Taxation on Water Utilities in Rhode Island

(Completed September, 1965)

This study was undertaken (1) to determine the effect of the tax burden of water utilities in Rhode Island on growth, development, and service to the consuming public, and (2) to find whether stockholder owned water works or the government owned public water utility serves the public more efficiently. The problem of the effect of the tax burden on investors, the cost to the stockholder, and tax shelter to the government-owned utility was analyzed.

This study, now being completed, will be published in the near future. Below is an abstract of the thesis prepared under this project.

ABSTRACT

This thesis problem is a study of the effect of taxation on water utilities in Rhode Island. It involves a detailed study of the six private or quasi-municipal water utilities in Rhode Island although the comparative size differential of each utility is often quite striking.

The method of descriptive research was used to develop and solve this problem by obtaining and interpreting the necessary information and data. The facts used in this approach were obtained principally from the Rhode

Island Utilities Commission; annual reports of the six utilities; articles in daily newspapers; and interviews with local water authorities.

The important conclusions reached in this study were: (1) Taxes do not detract from the private or quasi-municipal water utilities development. (2) Utility taxation does not lessen the quality of service to the consuming public. (3) The private or quasi-municipal water utility bears the impact of utility taxation. (4) The incidence of utility taxation is borne by the consuming public. (5) Rate increases must be slightly higher due to utility taxation. (6) The Utilities Commission protects the consumer from unwarranted rate increases. (7) Utility taxation does not prevent water utilities from servicing expanding areas.

G Ground Water Characteristics by Resistivity Criteria

The objective of this study is to investigate, by direct application in the field, the correlation of subsurface hydrologic characteristics, (specifically ground water supply aquifiers and ground-water subsurface reservoirs) with data that can be acquired by surface electric resistivity tests. Because of the importance of unconsolidated glacial deposits as potential water-supply reservoirs for the northern United States, this research project will concentrate on the correlation of hydrologic characteristics of glacial deposits with resistivity data to develop suitable resistivity-hydrologic correlation criteria for determining the ground-water supply potential of glacial deposits.

The field area chosen, Block Island, Rhode Island, is an offshore island underlain almost exclusively by glacial deposits of clay, silt, sand, and gravel of variable thickness and extent. It provides an ideal

Ground Water Characteristics by Resistivity Critera - Continued

site to study and isolate those factors of glacial drift influencing resistivity data. In addition, sea cliffs, around the perimeter of the island, expose subsurface deposits for study and lessens the need for extensive drilling for subsurface sampling. Sampling drilling in the interior of the island will be necessary only for subsurface correlation and completing the resistivity study network. By setting up this resistivity network it will also be possible to correlate the resistivity data and geohydrologic characteristics of the glacial deposits with the subsurface structure of the glacial deposits.

Similar resistivity-correlation studies of undeformed glacial deposits have been done by some Mid-west states; little has been done with this technique in the more deformed and highly structured glacial deposits of the Eastern United States.

Preliminary work has been completed on the choice of test sites and the mapping of these areas.

H The Water Economy of Turf Grass

This project is to supply information on the relationship between use of water and the management of turf grass. The water economy of several commonly used species and varieties of turf grasses will be evaluated in relation to soil type maintenance practices (fertilization, cutting, management, etc.) and environmental conditions (temperature, sunlight, rainfall, fog and atmospheric humidity).

The turf to be used will be suitable areas of established turf or new seedings planted for this project. The grass species will include those species or mixture that have been found useful for fine turf or for utility turf. Variation in water will range from controlled and measured amounts applied by irrigation, to natural moisture from rainfall, fog and dew.

To date plots have been established on an area seeded to Kentucky bluegrass with three different cutting heights and three different moisture regimes. The cover equipment which will cover the plots automatically when rain falls is almost completed but not yet in operation. Some preliminary work has also been done with measurements of soil atmosphere. When the equipment is operating, data will be collected on quality of the grass cover as related to rainfall, fog and dew, soil moisture, and soil atmosphere.

I. Water Loss Through Interception by Mixed Oak Forests in Rhode Island

The primary objective of this study will be to determine the amount of precipitation intercepted by the mixed oak forest type. The large proportion of the upland area in Rhode Island in this forest type makes it of particular interest in regard to watershed protection and water yield.

The procedure will entail locating stands within the mixed oak forest. Total precipitation received will be recorded using rain and snow guages placed in the open. Sample plots will be established within the stands and the amount of throughfall (precipitation passing through the crown) and stemflow (precipitation reaching ground by flowing down stems) will be determined. Canopy interception (total precipitation - stemflow and throughfall) will then be determined and correlated with size of storm, season, type of precipitation, and stand density.

At the time of this report, one stand has been selected for study and three (3) one-tenth acre plots have been established within the stand. Data on tree age, tree height, species composition and density have been obtained for each plot. Three additional stands will be selected and three (3) one-tenth acre plots established in each stand. Rain guages and stem flow collection devices will be assembled and set up in the established plots. Accumulation of data will commence in February, 1966.

BUDGET SUMMARY, FISCAL YEAR 1965

PROJECT TITLE	EXPENDITURES
Analysis of the Effluent from a Nuclear Recovery Plant.	$ 7,478.47
Effects of Obstruction on Aeration of Flowing Streams.	1,881.03
Static and Dynamic Behavior of Soils.	4,617.32
Movement of Manganese into Ground Water Supplies.	8,006.90
Structural Chemistry of Yellow Organic Matter in Fresh Water.	11,995.94
Impact and Incidence of Taxation on Water Utilities in Rhode Island.	908.00
Ground Water Characteristics - by Resistivity Criteria.	3,384.22
Water Economy of Turf Grass.	2,284.17
Water Loss through Interception by Mixed Oak Forests in Rhode Island.	465.11
Center Direction, Administration, Supplies, Services and Equipment.	7,741.07
Total Expended............$	48,762.23

BREAKDOWN OF EXPENDITURES

Non-expendable Property (Equipment)	$ 21,453.62
Expendable Supplies and Materials	4,599.15
Salaries (Professional Staff, Graduate Students, P. I.)	21,488.00
Travel	1,171.46
Publication	50.00
Total - Cost Categories	$ 48,762.23

ADDITIONAL PROJECTS

Not supported by the Water Resources Research Act of 1964

Economics of Use and Distribution of Water in Rhode Island

ABSTRACT OF THESIS

This study was concerned with the present and future public water supply in the State of Rhode Island. Confusion about the present water supply was prevalent because of restrictions placed on water users. Uncertainty characterized the future situation because only surface water has been considered as a method of fulfilling future requirements.

Two hypotheses evolved from the present situation. The first postulated that the present "water shortages" the state's water systems were undergoing during peak periods and the restrictions placed on the system's water users were not the result of a deficient supply of water. The second hypothesis stated that using an economic supply function would offer a least cost solution to the state's future water problems.

The first hypothesis was tested by analyzing primary data obtained from a questionnaire distributed to the operators of the state's water systems and through use of secondary data. It was found that seventeen systems supplied approximately 98 percent of the population served by public systems. When the average daily demand was compared to the dependable yield, it was discovered that one system had a supply deficiency, however, the total supply of water is in excess of the present requirement and the one system facing a shortage of water can alleviate its problem by the development of an additional source of supply. Many systems experienced problems during peak periods, but this was a result of the limited capacity of one or more components of the system. It was

Abstract of Thesis - Continued

also found that most of the components of the systems, listed as inadequate for the operations, were in the process of being corrected. The first hypothesis, then, was tested and verified.

The testing of the second hypothesis began with an investigation of the general economic characteristics of water systems. This was accomplished by gathering cost data from five public water systems and comparing expenses between systems with special emphasis on determining the magnitude of expenditure for the various supply costs in regard to predominantly surface and ground water systems. A projection of water requirements for 1985 contrasted with present and planned increase in the dependable yield of public supplies made possible an estimate of the future public water situation. Several regions of the state showed a deficient supply of water for the future.

Two methods were available for satisfying future requirements. The first consisted of fuller utilization of present supplies and the second, ground water, surface water, and desalination development. These last three modes of supply were compared to each other in an effort to determine costs of development and operation associated with these sources of supply.

Desalination was found not to be competitive with ground water and surface water development based on the most recent information that was available. Conversly, ground water which was omitted from the analysis because of lack of information in the state's most recent engineering report, was found to be an extremely competitive source of supply along with surface water developments. It was concluded then that ground water as well as surface water, should be considered when new requirements make the development of new sources of supply necessary in the State of Rhode Island.

PLANS FOR THE FUTURE

The future research activities at the Center promise to move toward greater emphasis in the social sciences than at present. Looking ahead at this time, it appears that the fields of economics and sociology will be the specific areas to be developed.

This trend is in keeping with suggestions that have been offered for regional water resources research. This Center cooperated in the regional supply-demand conference held at Cornell University in Jene, 1965. In addition through the Center's association with the Northeast Regional Resource Economic Committee, it seems likely that work in the problem aspects of water law will be supported. This work may involve cooperative effort between the Water Resource Centers and the Agricultural Experiment Stations.

A faculty symposium on the present research activities of the Center is planned for the early part of 1966. Guests will be invited from State and Federal agencies and from the other Water Resource Institutes or Centers in the Northeast. The symposium will be concerned only with the research projects supported by the Center.

The Rhode Island Water Resources Coordinating Committee has indicated its approval of the Center's participation in the activities of the Northeast Water Resource Directors Association. The publication of this report is the first in a series to further the exchange of information relative to water resources research.

The Water Resources Center is not directly involved in the curriculum of the University. However, the existence of the Center has stimulated interdisciplinary collaboration in the development of a Graduate Program

Plans for the Future - Continued

in Water Resources Management. Plans are now being formulated between the Departments of Civil and Sanitary Engineering and the Department of Food & Resource Economics for course offerings that would lead to a Master of Science degree.

TECHNICAL AND FINANCIAL SECTIONS
OF THE ANNUAL REPORT OF THE
RHODE ISLAND WATER RESOURCES CENTER
FISCAL YEAR 1972

RHODE ISLAND WATER RESOURCES CENTER

DIRECTOR'S REPORT FOR FISCAL YEAR 1972

Current Research

Along with projects of importance to the state in the field of water resources planning and engineering, much of the research conducted by the Rhode Island Water Resources Center again this year was concerned with either the detection or correction of pollution in water.

Obviously before removal can be effected, it is imperative that the nature and amount of the pollutants be determined. Methods for the recognition and analysis of various types of pollutants have occupied the efforts of several investigators. Continuation of project B-026-RI has shown that periphyton algae can provide a feasible indication of water quality. Project B-036-RI has as its primary goal the development of a system for detecting water pollutants remotely by Raman spectroscopy. This research may provide a single method for monitoring water impurities on location, thus eliminating the problem of sample collecting. New fluorescent tracer detection techniques are being developed in project B-039-RI for use in polluted natural waters.

No positive correlation was found, in project A-035-RI, to exist between the number of coliform bacteria, fecal streptococci, coliphage and enteric viruses, as had been expected. The first year of project A-039-RI has been spent chiefly in the extraction of endotoxins from Escherichia Coli to be injected into rainbow trout to determine their effect. Two projects have been concerned

Current Research (Continued)

with the transfer of pesticides: Project A-038-RI followed their movement through water, sediments and aquatic life, while A-044-RI began work on their interception and degradation by aquatic algae. Due to a loss of manpower, it was necessary to terminate early, project A-042-RI, which was studying the fate of humic materials and their associated trace metals in water.

Satisfactory treatment of industrial wastes to remove pollutants was the area of two projects during the year. Project A-037-RI showed that synthetic organic polyelectrolytes have the ability to remove metal ions and cyanides contained in metal plating wastewater. An electrochemical cell is being developed in project A-040-RI to effectively remove nitrogen and phosphorus nutrients from wastewater. During the first year it was shown that removal of orthophosphate up to 98% can be attained consistently with a detention time of approximately 30 minutes in a cell of this type.

Two engineering projects have reported results which should be useful in water resources construction projects. The results of project A-036-RI indicate that a minimum safe distance of a disposal field from a water supply source is greatly dependent upon the soil condition and the groundwater table. An analytical model was developed during the second year of project B-028-RI which predicts the behavior of warm water discharges in moving water streams when the discharge is in the form of a slot jet. This information should be of value in the design of nuclear power plants such as that being contemplated for Rome Point, R. I.

Current Research (Continued)

Two projects, with entirely different approaches, considered the treatment of water polluted with hydrocarbons (or oil). Project A-043-RI was interested in improvements in primary oil-water separation through the control of droplet size. The first phase of project B-033-RI has been concerned with the effects of dissolved oxygen and carbon dioxide concentrations on the biological degradation of hydrocarbons. This information is basic to the development of a method involving bacteria for the control of oil spills.

Project A-041-RI has already indicated some rather startling results. It is investigating the effect of chlorination on water polluted with organic compounds which may form chlorinated compounds hazardous to human health and have other effects on the ecological system. The results imply the possibility that contact of foods or drink with water containing active residual chlorine may form toxic chlorinated compounds.

The one-year project B-038-RI, concerned with water resources planning, has produced information which should prove to be very useful to the State of Rhode Island. The study claims that modification of water supply and sewer rate structures should be considered both as a variable in estimating future water use levels and as a means of implementing state water supply and pollution control policy.

State Cooperation

The State of Rhode Island Water Resources Board provides for the coordinated development, conservation and use of Rhode Island's water resources through the formulation and maintenance of a long range, comprehensive plan and implementation program. The plan outlines developments necessary to insure that Rhode Island has an adequate water supply equitably apportioned throughout the state for domestic, industrial, and municipal purposes. Since inception of the Board, the Rhode Island Water Resources Center has cooperated fully with it to provide information, research studies and manpower whenever necessary.

During the year, the Water Resources Board implemented the licensing of well drillers operating in the State of Rhode Island. The main purpose of licensing is to obtain additional geological data on Rhode Island's groundwater reservoirs through the mandatory completion of well driller's reports which are supplied by the Board.

The Water Resources Board agreed to allow the University of Rhode Island the use of the Big-Wood River Reservoir areas, specifically those adjacent to the W. Alton Jones campus, for the pursuit of research investigations.

Regional Studies

The Rhode Island Water Resources Center has continued its interest in regional water resources studies. The Title II project (C-2034), which began in October 1970, entitled, "The Feasibility of Optimizing Multi-University Regional Water Resources Research", Regional Studies (Continued)

with the Rhode Island Director as principal investigator, has been extended to December 31, 1972. In connection with this project, a meeting sponsored by the New England Council of Water Center Directors, was held at Amherst, Mass. in May 1972, involving all six New England states, for the purpose of deciding on the nature of a research study on lakes to which all states could contribute. Administrative members of the Rhode Island Water Resources Board and the Department of Natural Resources were invited to attend this conference. It is planned that a regional research project concerned with some aspect of lake problems in the New England area will be initiated in the near future.

A. Ralph Thompson
Director, Rhode Island
Water Resources Center

ADDITIONAL STATEMENTS REGARDING THE RHODE ISLAND WATER RESOURCES CENTER

Examples of Research Findings and Their Actual or Potential Application to Water Resource Problems

During its seven years of operation, the Rhode Island Water Resources Center has made many contributions to the solving of local, state and even regional water problems.

As an example of a local problem solved through the center's research might be cited the development of methods for controlling the copper content in water. In a few sections of Rhode Island the agressive nature of groundwater from wells caused so much copper to be dissolved from piping that it was a serious health hazard. The research on this problem indicated methods of neutralization or demineralization which reduced the metal content to a satisfactory level, thereby protecting the health and perhaps the lives of many residents.

The presence of high concentrations of iron and manganese in groundwater supplies has been an important problem in many sections of the state of Rhode Island. Working in close cooperation with the Water Resources Board of the state and with the U.S. Geological Survey, the Rhode Island Water Resources Center, through two earlier projects, made definite contributions in the alleviation of this problem. A current project is making excellent progress in the development of cartridges for the filtration of iron and manganese from small groundwater supplies. This accomplishment should go a long way to overcoming a serious deterrent to making use of many water sources in the state.

Problems Encountered in Administering a Center

The establishment and organization of a research center of this type takes considerable time and with the rather modest funds available to it the Center has conducted many valuable research projects as is evident in its excellent annual reports. The Center is now geared up to do a real comprehensive job in the solution of water resources problems if sufficient financial support were available to it. We are all aware now of the tremendous magnitude of this environmental problem which can be solved only if the research centers are provided with a large enough base to be able to muster sufficient personnel to work on all necessary projects.

Regional Cooperation in Research and Training

For a number of years the six New England states have endeavored to initiate regional water resources research. The six institute directors have been extremely cooperative and have worked closely together through the organization, the New England Council of Water Center Directors, formed by them in 1966. The group has managed to sponsor four excellent conferences on water rights law, water resources planning, ecological effects and river diversions but to date it has not been possible to undertake regional research projects. With a view to improving this situation a Title II proposal was submitted to investigate the possibility of using a regional research corrdinator to plan, coordinate and report on research undertaken by several research centers. This project is underway, with the Rhode Island Director

<u>Regional Cooperation in Research and Training</u> (Continued)

as principal investigator, and it is expected that valuable information will be obtained which should be of use to all regions of the country which are contemplating multi-center research.

Scientific Information Dissemination:

The Rhode Island Water Resources Center gave considerable thought and effort to the expansion of its activities in the area of information dissemination. With this in mind, during the year the Center acquired approximately 900 square feet of additional space in Crawford Hall primarily for office use and the establishment of a water resources library. The present office of 350 square feet will be retained by the Center for the Director and a secretarial assistant.

The Center will continue to have the technical section of its Annual Report printed and widely distributed as well as reprints of technical articles based on research supported through the Center. During the next year it is hoped that an Editiorial Assistant can be added to the staff so that newsletters may be issued on a regular basis and the entire effort in information dissemination can be increased considerably. Approximate statistics for the past year are as follows:

Items	Number of Events	Total Numbers Issued or Audience Size
Technical Publications Issued	7	610 (average)
Press Releases	6	
Technical Lectures	3	150
Sponsorship of Seminars	1	100
Correspondence and Telephone Inquiries (Estimate)	1500(30 per/wk)	

Costs:	Dollars	Source of Funds
Printing and page Charges	5348.00	75% OWRR 25% Non-Federal

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-035-RI

Agreement No. 14-31-0001-3240

FCST-COWRR Research Category: VA

Project Title:

Significance of Fecal Streptococci, Coliform Bacteria and Coliphage in relation to enteric Virus Pollution in Sewage and Rivers.

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: July ; Year: 1971 | To Be Completed--Month: June ; Year: 1972

Principal Investigators	Degree	Discipline
Pei W. Chang	Ph.D.	Animal Virology
Vance J. Yates	Ph.D.	Microbiology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Patricia I. Boyle	B.S.	Microbiology
Dennis C. Chi	B.S.	Agronomy (student)
Margaret Y. Hsin	B.S.	Accounting (student)
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A. RESEARCH PROJECT ACCOMPLISHMENTS.

1. Summary.

No correlation existed between the number of coliform bacteria, fecal streptococci, coliphage and enteric viruses isolated. Daily variation between samples was found to be extremely great and statistical analysis showed no positive correlation.

Enteric virus was difficult to isolate. Of the 181 sewage samples studied this year and last year, only four yielded virus.

2. Collection and assay of sewage samples.

During the previous year two ways of collecting sewage were compared; the grab method and the swab sampling technique. In all cases the swab sampling technique showed higher counts of coliform bacteria, streptococci and coliphage and it was felt that the swab sampling technique probably represents bacteria trapped in the gauze and multiplication of bacteria and coliphage probably occurred within the gauze pad. Since this hardly represents the actual count of bactaria and coliphage in sewage, the method was not used.

The method used for collecting sewage throughout this period was the grab method, where 1000 ml of sewage was collected from the affluent of the University sewage plant at approximately 9 o'clock in the morning.

The sewage was then assayed for coliform bacteria and fecal streptococci by the multiple tube fermentation test.

The test used for quantitation of coliphage was the plaque count technique.

For virus isolation, sewage was concentrated by reducing the volume from 1000 ml to 5 ml, by dialysis using carbowax 4000.

The concentrate was then treated with penicillin and streptomycin and then assayed for enteric viruses. The assays were carried out in Rhesus monkey kidney cell cultures by the plaque technique. In earlier trials, sewage concentrates were inoculated into Rhesus monkey kidney cell cultures. Following one hour of adsorption, the cell cultures were overlaid with agar for plaque formation; it was found that the concentrates were toxic to the cell cultures. To avoid this the concentrates were allowed to be adsorbed onto the cell cultures for one hour at room temperature. The cell cultures were then washed three times with phosphate buffered saline (PBS) solution, and followed by agar overlay. No toxic effects were observed after the washing.

To detect the possible presence of animal viruses, ten sewage concentrates were also inoculated onto chicken embryo kidney cells. Following one hour of adsorption and three times of washings as described previously, the cell cultures were overlaid with agar. No virus was isolated.

A total of 51 sewage samples from the sewage plant, University of Rhode Island, was collected. The date of collection, bacteria and coliphage counts are presented in Table 1. In contrast to the previous year, no virus was isolated.

3. Analysis of data.

The data of coliform, fecal streptococci and coliphage counts from 181 sewage samples (Table 1 and Table 2) collected in a two-year period were analyzed to determine their correlation. The method used was product moment correlation. The results are summarized as follows (For calculation, see Appendix).

CORRELATION BETWEEN THE COUNTS OF COLIFORM BACTERIA, FECAL STREPTOCOCCI AND COLIPHAGE

	Coliform	Streptococci	Coliphage
Coliform		0.02	-0.02
Streptococci			-0.03

These correlations appear to be small and negative. The independent counts do not correlate in any way.

B. PUBLICATIONS.

None.

C. PROJECT STATUS.

The project was completed during the fiscal year ending June 30, 1972. A completion report is being written and will be submitted prior to July 31, 1972.

D. APPLICATION OF RESEARCH RESULTS.

The primary objective of the present project is to correlate the concentration of coliform bacteria, fecal streptococci or coliphage in polluted water to viral pathogens. It was hoped that a correlation could be established between the two so that the measurement of one might provide a quantitative estimate of the other. This did not materialize. Virus was only isolated on four occasions out of 181 sewage samples and was, therefore, too few for meaningful correlation. The concentration of coliform bacteria, fecal streptococci or coliphage was highly variable in number on different days and showed no correlation.

E. WORK REMAINING.

Though no correlation was shown in the quantitative relationship of fecal coliform, streptococci, coliphage and viruses and the results were negative, a manuscript is still being prepared to be submitted for publication in 1972.

TABLE 1. COUNTS OF COLIFORM BACTERIA, FECAL STREPTOCOCCI AND COLIPHAGE IN SEWAGE COLLECTED IN 1971-1972.

Date	Coliforms (MPN) $1x10^6$ per 100 ml	Streptococci (MPN) $1x10^6$ per 100 ml	Coliphage per ml
12/14/71	23.0	0.43	3
12/15/71	.023	0.0023	0
12/20/71	.043	0.0023	0
12/21/71	9.3	0.23	0
12/22/71	0.43	0.43	10
12/29/71	2.3	0.75	2
12/30/71	43.00	0.43	1
1/6/72	0.11	0.0023	12
1/18/72	9.30	2.30	5
1/20/72	23.00	0.043	1
1/24/72	0.43	0.023	0
1/26/72	0.093	0.0015	0
2/1/72	4.30	0.093	9
2/3/72	43.00	0.23	1368
2/8/72	0.23	0.23	1
2/10/72	150.00	0.21	27
2/15/72	240.00	15.00	11
2/17/72	0.43	0.43	0
2/22/72	9.30	0.43	16
2/24/72	15.00	0.23	520
2/29/72	23.00	0.93	55
3/2/72	43.00	2.30	13
3/7/72	23.00	0.93	58
3/9/72	4.30	0.093	5
3/14/72	43.00	9.30	19
3/16/72	43.00	24.00	25
3/21/72	240.00	0.43	7
3/24/72	43.00	0.043	1
3/29/72	0.23	0.23	2
3/30/72	9.30	0.15	72
4/4/72	1.50	0.093	3
4/6/72	4.30	0.023	30
4/8/72	43.0	0.21	3
4/11/72	9.30	1.50	21
4/13/72	9.30	0.15	3
4/20/72	23.00	2.30	2
4/26/72	2.30	0.75	0
4/27/72	93.00	0.93	0

5/2/72	43.00	0.21	3
5/4/72	43.00	0.43	6
5/9/72	23.00	0.43	8
5/11/72	23.00	0.43	24
5/18/72	9.3	0.93	84
5/19/72	43.00	0.43	10
5/24/72	23.00	0.75	0
5/26/72	4.3	0.043	0
5/30/72	1.2	0.021	0
6/1/72	15.00	0.23	4
6/2/72	23.00	0.93	16
6/5/72	23.00	0.23	36
6/7/72	0.23	0.23	6

TABLE 2. COUNTS OF COLIFORM BACTERIA, FECAL STREPTOCOCCI AND COLIPHAGE IN SEWAGE COLLECTED IN 1970-1971.

Date	Coliforms (MPN) $1x10^6$ per 100 ml	Streptococci (MPN) $1x10^5$ per 100 ml	Coliphage per ml
8/17/70	9.3	0.43	156
8/18/70	7.5	1.20	20
8/19/70	4.3	0.23	24
8/24/70	9.3	0.23	0
8/25/70	15.0	.43	8
8/26/70	43.0	.43	72
8/31/70*	24.0	.23	0
9/1/70*	15.0	.75	1072
9/2/70	2.3	.43	28
9/8/70	4.3	9.3	0
9/9/70	2.3	.75	4
9/14/70	2300.0	2.3	16
9/15/70	23.0	.75	24
9/16/70	93.0	.43	8
9/21/70	9.3	2.3	4
9/22/70	110.0	4.3	16
9/23/70	110.0	2.3	20
10/5/70	43.0	.75	84
10/6/70	23.0	.23	736
10/13/70	93.0	1.5	20
10/15/70	93.0	.023	28
10/19/70	23.0	23.0	16
10/20/70	43.0	.23	24
10/21/70	93.0	.43	168
10/26/70	93.0	1.5	84
10/27/70	4.3	.15	204
11/2/70	93.0	.93	0
10/28/70	43.0	.93	120
11/4/70	9.3	2.3	0
11/10/70	23.0	.43	308
11/9/70	93.0	.93	320
11/16/70	23.0	2.3	12
11/18/70	230.0	.43	72
11/23/70	930.0	1.5	0
11/24/70	9.3	.93	0
11/30/70	43.0	2.3	0

12/2/70	23.0	.93	680
12/3/70	2400.0	.43	0
12/14/70	230.0	23.0	0
12/15/70	4.3	.23	24
12/16/70	2.3	.43	12
12/17/70	9.3	.93	20
12/22/70	.43	.23	12
12/23/70	.43	.023	14
12/24/70	.23	.0043	38
12/29/70	.0430	.0023	0
12/31/70	.023	.0023	0
1/4/71	4.3	.43	20
1/5/71	7.5	1.20	20
1/6/71	4.3	.23	24
1/7/71	15.0	.43	8
1/11/71	43.0	.43	72
1/12/72	15.0	.75	118
1/13/71	2.3	.75	4
1/14/71	93.0	.75	8
1/18/71	.24	.0023	0
1/19/71	.110	.0024	16
1/20/71	.023	.0043	16
1/21/71	.015	.0043	30
1/25/71	.24	.0023	0
1/26/71	.093	.0015	20
1/27/71	.043	.0023	24
2/1/71	93.0	.43	18
2/2/71*	43.0	.43	21
2/3/71	.75	.023	0
2/4/71	.110	.0043	32
2/5/71	4.3	.023	30
2/8/71	93.0	1.5	40
2/9/71	23.0	.23	720
2/10/71	7.5	1.2	40
2/11/71	.43	.43	32
2/12/71	9.3	.23	0
2/15/71	15.0	.43	24
2/16/71	2.3	.43	4
2/18/71	4.3	9.3	16
2/23/71	9.3	2.3	12
2/24/71	110.0	4.3	36
2/25/71	75.0	.75	1072

3/2/71	23.0	2.3	22
3/8/71	.75	.0023	0
3/9/71	.150	.0023	0
3/10/71	75.0	.23	30
3/15/71	93.0	.75	48
3/16/71	.24	.0023	36
3/17/71	.110	.0043	16
3/19/71	.0024	.00043	20
3/22/71	2.3	.75	4
3/23/71	15.0	.75	16
3/24/71	2400.0	.43	84
3/25/71	.023	.023	76
3/26/71	4.3	.23	28
3/29/71	9.3	.93	32
3/30/71	0.43	.0023	36
3/31/71	.023	.0023	4
4/1/71	93.0	.43	32
4/5/71	23.0	.43	16
4/6/71	.75	.0023	8
4/7/71	.15	.0043	34
4/8/71	43.0	.23	224
4/9/71	.93	.0023	0
4/2/71	.23	.0093	0
4/13/71	15.0	.75	12
4/14/71	43.0	.75	4
4/15/71	7.5	.023	16
4/16/71	15.0	.0093	36
4/19/71	110.0	43.0	96
4/20/71	2.3	.43	36
4/21/71	7.5	12.0	8
4/22/71	24.0	.75	42
4/26/71	.23	.15	0
4/27/71	43.0	.023	16
4/28/71	15.0	.75	0
4/29/71	.93	.15	8
5/3/71	.023	.0023	0
5/4/71	93.0	1.5	40
5/5/71	93.0	.23	36
5/6/71	9.3	.023	32
5/7/71	9.3	.23	0
5/10/71	9.3	.93	24
5/11/71	43.0	2.3	4
5/12/71	.43	.035	16
5/13/71	43.0	.093	0
5/14/71	2400.0	.43	0
5/17/71	.043	.23	32
5/18/71	9.3	2.3	36
5/19/71	110.0	4.3	100
5/20/71	75.0	.75	22
5/21/71	24.0	.75	0
5/24/71	93.0	.43	8
5/25/71	23.0	2.3	20

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*Isolations of enteric virus were obtained on August 31, Sept. 1, Sept. 2 and Oct. 2. The number of viruses were 28, 16, 14, and [illegible] respectively.

APPENDIX

Calculation for the correlation of coliform bacteria, streptococci and coliphage.

Let N = Total number of sewage samples

X_1 = Counts of coliform bacteria

X_2 = Counts of fecal streptococci

X_3 = Counts of coliphage

N = 181 (Inclusive of Table 1 and Table 2)

$\sum X_1^2 = 23951928.2279$

$\sum X_2^2 = 4289.1612$

$\sum X_3^2 = 6466784.00$

$\sum X_1 = 15739.7034$

$\sum X_2 = 275.064$

$\sum X_3 = 10878$

$\sum X_1 \cdot X_2 = 30068.8131$

$\sum X_2 \cdot X_3 = 11842.9446$

$\sum X_1 \cdot X_2 = 647559.924$

$$\sum X_1^2 - \frac{(\sum X_1)^2}{N} = 23951928.2279 - \frac{247738263.119}{181}$$

$$= 23951928.2279 - 1368719.6857$$

$$= 22583208.5422$$

$$\sum X_2^2 - \frac{(\sum X_2)^2}{N} = 4289.1612 - \frac{75660.22060}{181}$$

$$= 4289.1612 - 418.0123$$

$$= 3871.1489$$

$$\sum X_3^2 - \frac{(\sum X_3)^2}{N} = 6466784 - \frac{118330884}{181}$$

$$= 6466784 - 653761.7901$$

$$= 5813022.2100$$

$$\sum (X_1 \cdot X_2) - \frac{(\sum X_1)(\sum X_2)}{N} = 30068.8131 - \frac{4329426.2482}{181}$$

$$= 30068.8131 - 23919.4820$$

$$= 6149.331$$

$$\sum (X_1 \cdot X_3) - \frac{(\sum X_1)(\sum X_3)}{N} = 647559.924 - \frac{171216493.585}{181}$$

$$= 647559.924 - 945947.4784$$

$$= -298387.5544$$

$$\sum (X_2 \cdot X_3) - \frac{(\sum X_2)(\sum X_3)}{N} = 11842.9446 - \frac{2992146.5183}{181}$$

$$= 11842.9446 - 16531.1962$$

$$= -4688.2516$$

$$r_{X_1 X_2} = \frac{6149.3330}{\sqrt{(22583206.5422)\ (3871.1489)}}$$

$$= \frac{6149.3330}{295673.7444} = 0.0208$$

$$r_{X_1 \cdot X_3} = \frac{-298387.5544}{\sqrt{(22583206.5422)\ (5813022.2100)}}$$

$$= \frac{-298387.5544}{11457604.3456} = -0.0260$$

$$r_{X_2 \cdot X_3} = \frac{-4688.2516}{\sqrt{(3871.1469)\ (5813022.2100)}}$$

$$= \frac{-4688.2516}{150010.2483} = -0.0313$$

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-036-RI Agreement No. 14-31-0001-3240 FCST-COWRR Research Category: IIF	Project Title: Groundwater Flow in Partially Saturated Soils

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R.I. 02881

Proj. Began--Month: July ; Year: 1970	To Be Completed--Month: June ; Year: 1972

Principal Investigators	Degree	Discipline
Mian-Chang Wang	Ph.D.	Soil Mechanics
Vito A. Nacci	M.S.	Civil Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Chan-Feng Tsai	B.S.	Civil Engineering

RESEARCH PROJECT ACCOMPLISHMENTS

Work in the past year involved (1) verification of analytical solution from the finite element computer program by using model tests, and (2) determination of the rate of seepage from a sewage disposal field to a water supply source for various spacings between the source and the field, and for various hydraulic conditions.

The model test tank which had an 8 ft. diameter by 6 ft. height contained a 4 ft. thick bed of coarse sand. A layer of gravel was installed between the sand and the tank wall to maintain a constant water head during pumping. The water was pumped out from a wellpoint at center of the tank and recharged into the tank through the gravel layer. A ring installed at various distances from the wellpoint was used for water infiltration which simulated a sewage disposal field. The drawdown curve due to pumping was determined by using 12 electrical resistivity probes located at various places in the test tank. Comparisons of the theoretical drawdown curve generated from the developed computer program with the measured drawdown curve were made. It was found that the theoretical solution was surprisingly close to the experimental results.

The computer program was used to determine the rate of seepage from disposal fields to a water supply source for various soil parameters and hydraulic conditions. Results indicated that the minimum safe distance of a field from a source is greatly dependent upon the soil condition and groundwater table. Detailed information will be presented in the final report.

PUBLICATIONS

A master's thesis entitled "Finite Element Solutions to Groundwater Flow with Infiltration" by Wen-Hsiung Chen has been prepared from the results of the first-year study; the material from the second-year study is being prepared for an M.S. thesis entitled "Experimental Studies of Underground Seepage toward Wells" by Chan-Feng Tsai.

PROJECT STATUS

Work on this project was completed as of June 30, 1972. A completion report is being prepared and will be submitted in the near future.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-037-R I

Agreement No. 14-31-0001-3240

FCST-COWRR Research Category: V D

Project Title: Chemical and Physical Factors in the Flocculation of Metal Plating Wastes with Polyelectrolytes

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1970 To Be Completed--Month: June ; Year: 1972

Principal Investigators	Degree	Discipline
Donald L. Sussman	Ph.D.	Civil and Environmental Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Edward C. Wang	B.S.	Civil and Environmental Engineering

RESEARCH PROJECT ACCOMPLISHMENTS

INTRODUCTION

Flocculation is a process wherein individual colloidal particles in a water suspension are caused to unite as loosely bound, considorably larger agglomerates, or flocs, by a flocculant. The phenomena involved in the flocculation of colloidally dispersed solids by polyelectrolytes has been interpreted by a process of adsorption of polymers on the colloid surface, and of bridging of polymer chains between solid particles.(1)

It has already been proposed by Sommerauer, Sussman and Stumm(2) that the anionic polymers form coorination complexes with cations, like calcium or copper. At polymer concentrations larger than those required for flocculation, restabilization or colloid protection occurs. In order to be effective in destabilization a polymer molecular must contain chemical groups (as $-COO^-$, or $-SO_3^-$) which can interact with sites on the surface of the colloidal particles.

The performance of these polymers is in general aggrement with the predictions of the bridging model; there is a direct relationship between optimum polymer dosage and colloid concentration, and restabilization due to overdosing can occur. The presence of divalent metal ions greatly enhances the ability of polymers to absorb on colloids.

The purpose of the study was to define the chemical and physical factors involved in the flocculation of colloids in an industrial waste by different kind of polymers. The use of synthetic organic polymers which are cationic, anionic, and nonionic to destabilize colloids in water has been done in this study. Two different cations, e.g. calcium and copper, were used. The specific resistance of sludge produced in the flocculation process is also studied.

EXPERIMENTAL

The study is defined in terms of the flocculation kinetics which is measured by the rate of change of absolute turbidity with time and the degree of turbidty removal,(2) and also in terms of the rate of refiltration as determined by the Kozeny-Carman equation. The latter experiments give us particle sizes which relate to the degree of flocculation.(3)

The preliminary experiments were conducted in the jar test apparatus at room temperature to find the opitium polymer concentrations. After the appropriate colloid concentrations have been made, the following order of addition of the other chemicals was followed: metal ion, polyelectrolyte.

The flocculation kinetics was measured by the using of Brice-Phoenix Light Scattering Instrument. The Light-Scattering Instrument measures turbidity which is a consequence of light scattering as a function of particle concentration, at a given solute molecular weight, solvent refractive index and wavelength.

The refiltration rate apparatus was set up as suggested by Smellie, et.al.(4) A 50-ml aliquot was filtered under a constant pressure differential of 80 mm Hg through a Millipore filter having a diameter of 47 mm. and an average pore size of 0.45μ. The filtrate was collected and refiltered through the cake under identical conditions. The Kozeny-Carman equation was applied and the efficiency of a flocculating system could be gauged by the size of the floc produced. The more thorough the flocculation, the larger would be the floc size and the higher the rate of refiltration. The refiltration rate data is reported in Table 1.

Specific resistance of sludge which produced in the flocculatic process was determined by the modified Buchner funnel technique developed by Coackley and Jones.(5) The specific resistance is a valid indicator of sludge filterability and is a better parameter for evaluating the effect of chemical conditioning than is the time required for the cracking of a filter cake. Specific resistance is defined as the resistance of a unit weight of cake per unit area at a given pressure and is calculated by the equation:

$$r = \frac{2PA^2b}{\mu c}$$

where:

r = specific resistance (sec^2/gram)

A = filter area (sq. cm)

P = pressure (gm/sq.cm)

μ = filtrate viscosity (gm/cm. sec)

c = solids content of feed sludge (gm solids/ml. liquid)

b = filtering rate, slope of plot of T/V vs. V (sec/cm^6)

V = ml of filtrate collected in T seconds.

All experiments were done at different pH values and sodium hydroxide was used to adjust the pH value. Concentration of polymer is reported as percentage of solution.

Tables 2 - 4 show the specific resistance data using different polymers.

EXPERIMENTAL RESULTS AND DISCUSSION

The effect of different polymer type and dosage on the rate of refiltration and specific resistance of the sludge produced in the flocculation process is given in Table 1 through 4. The improvement in filterability resulting from the polymer conditioning is very clearly evident from these data. These six different kinds of polymers which include cationic, anionic and nonionic appeared to be little difference. But we can say the two cationic polymers WT-2580 and WT-2640, have the best result in the flocculation of metal plating waste.

The polymers were effective over a reasonably wide pH range. The performance of all experiments were adjusted to pH around 9 in order to improve the flocculation results.

Results of cationic polymer WT-2640 are summarized in figures 1 through 5. The first two figures represent the effect of metal ions (Ca^{++} and Cu^{++}) on the rate of refiltration and specific resistance. Best flocculation occurred for the cationic polymer at the presence of 10^{-3}M concentration of calcium ion. And there was positive correlation between the rate of refiltration and the specific resistance.

The results of filtrating rate of cationic polymer WT-2640 are in figures three through five. These three figures just coincide with the results obtained in figures 1 and 2.

The results of this investigation indicate the ability of synthetic organic polyelectrolytes to treat the metal plating waste. All the polymers investigated show the ability of removing metal ions and cyanides which contained in the metal plating wastewater. And also the polymers improved the drainage rates of the sludge.

The data for the change in trubidty with time is being analyzed at the present time. These results will be reported in the future.

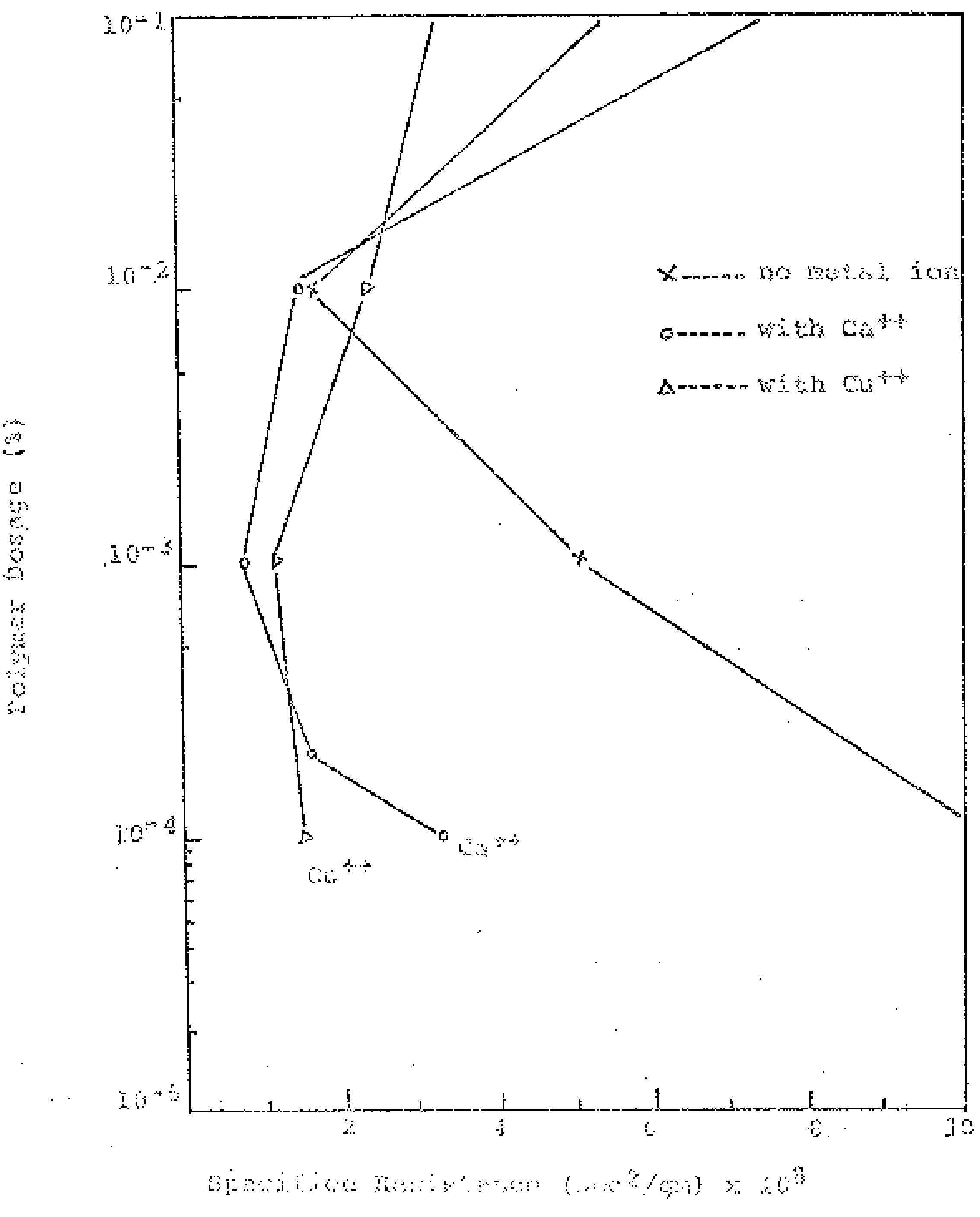

Figure 1: Effect of Metal Ions on Specific Resistance of Cationic Polymer [illegible]

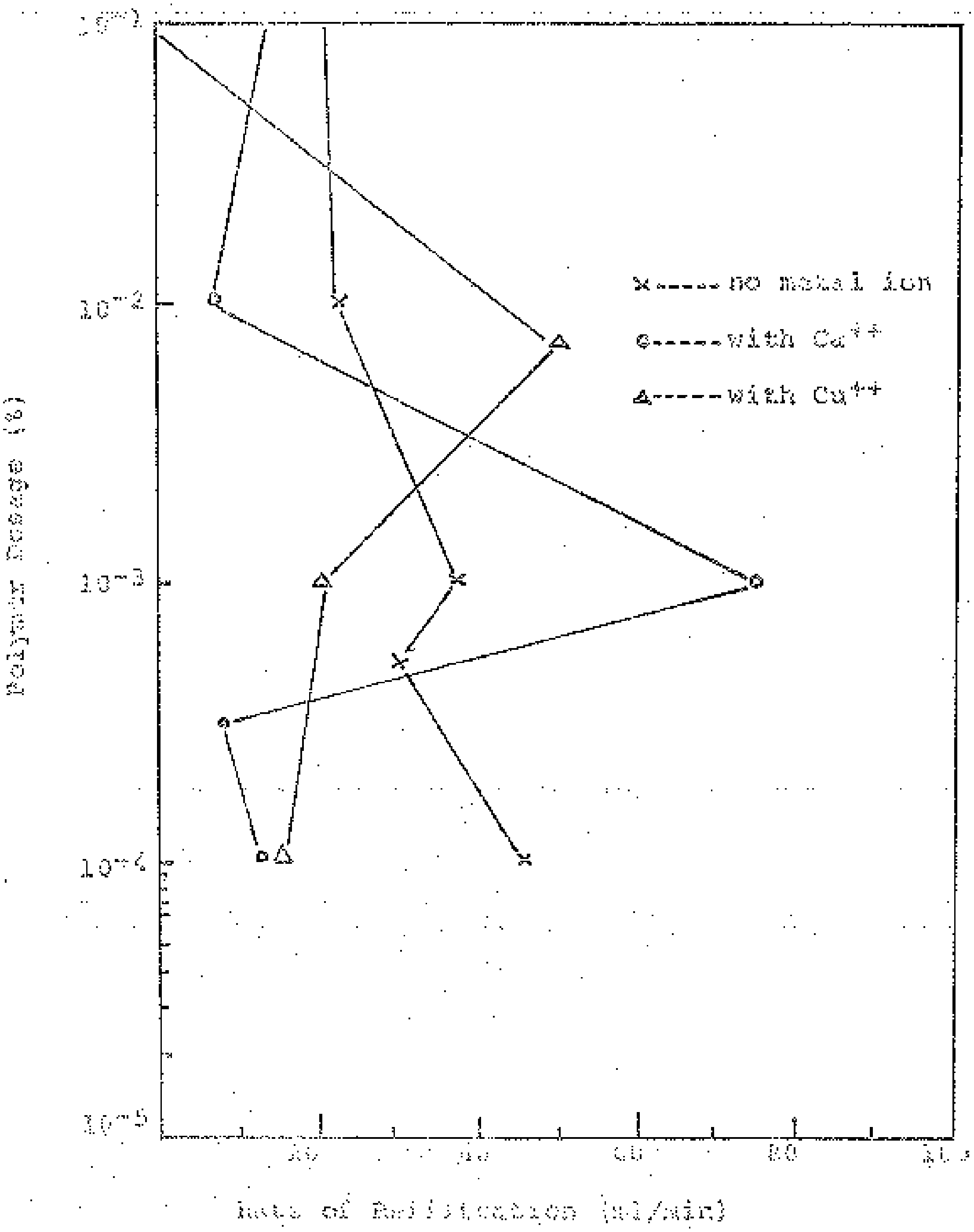

Figure 2: Effect of Metal Ions on Specific Resistance of Cationic Polymer WT-2640

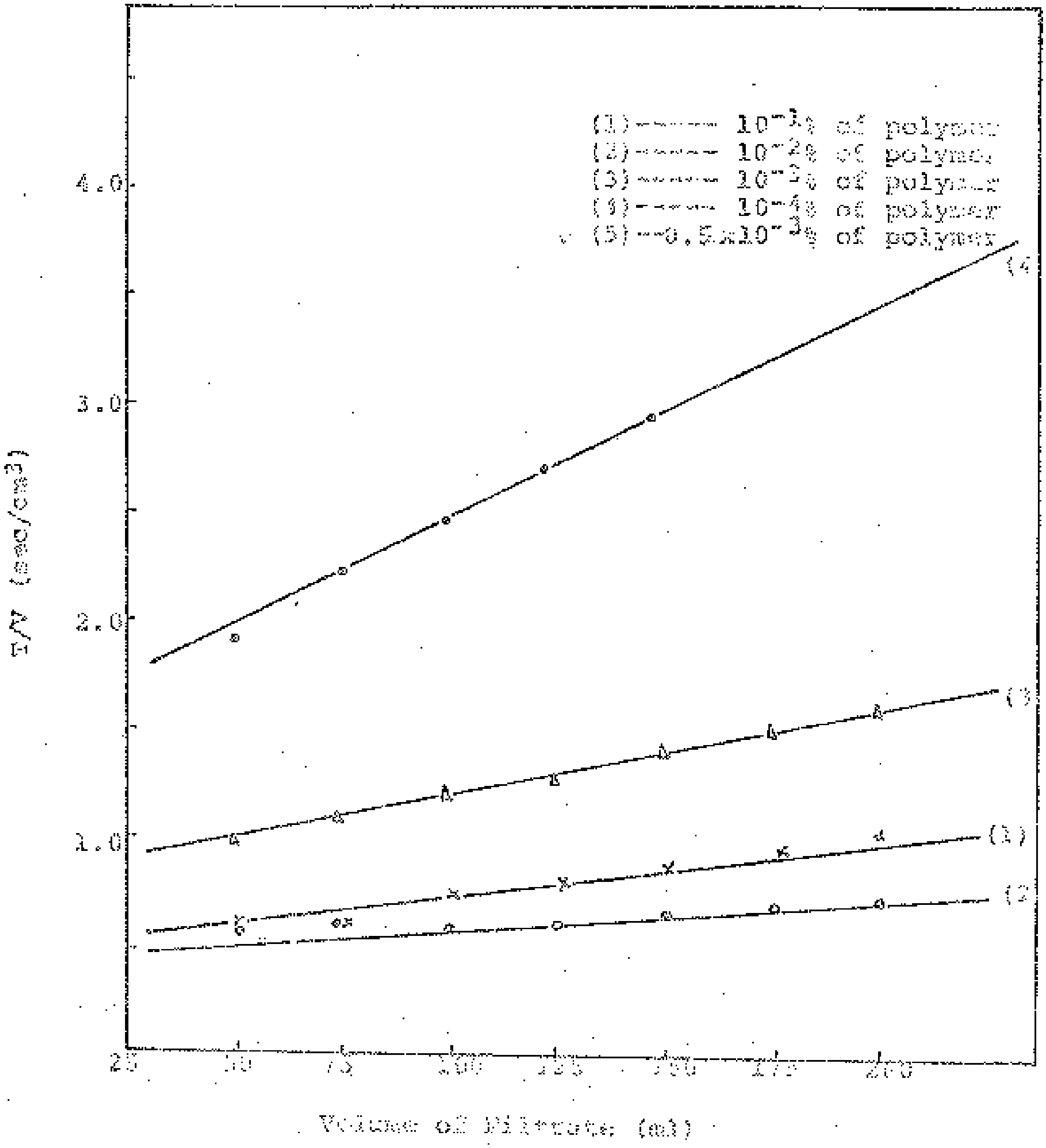

Figure 3: Filtering Rate of Cationic Polymer NP-2640

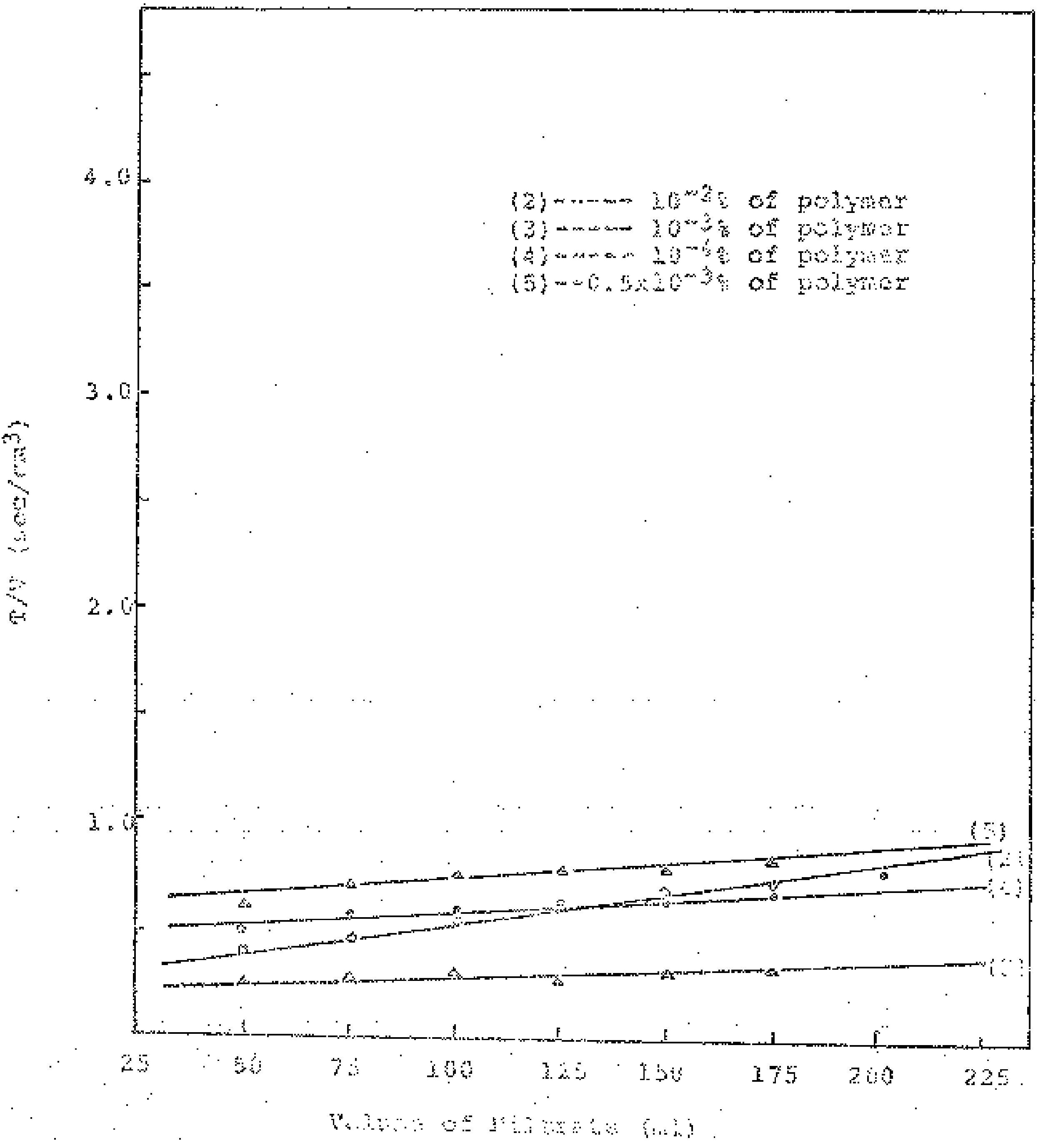

Figure 4: Effect of Metal Ion (Cu++) on Filtering Rate of Cationic Polymer WT-2640

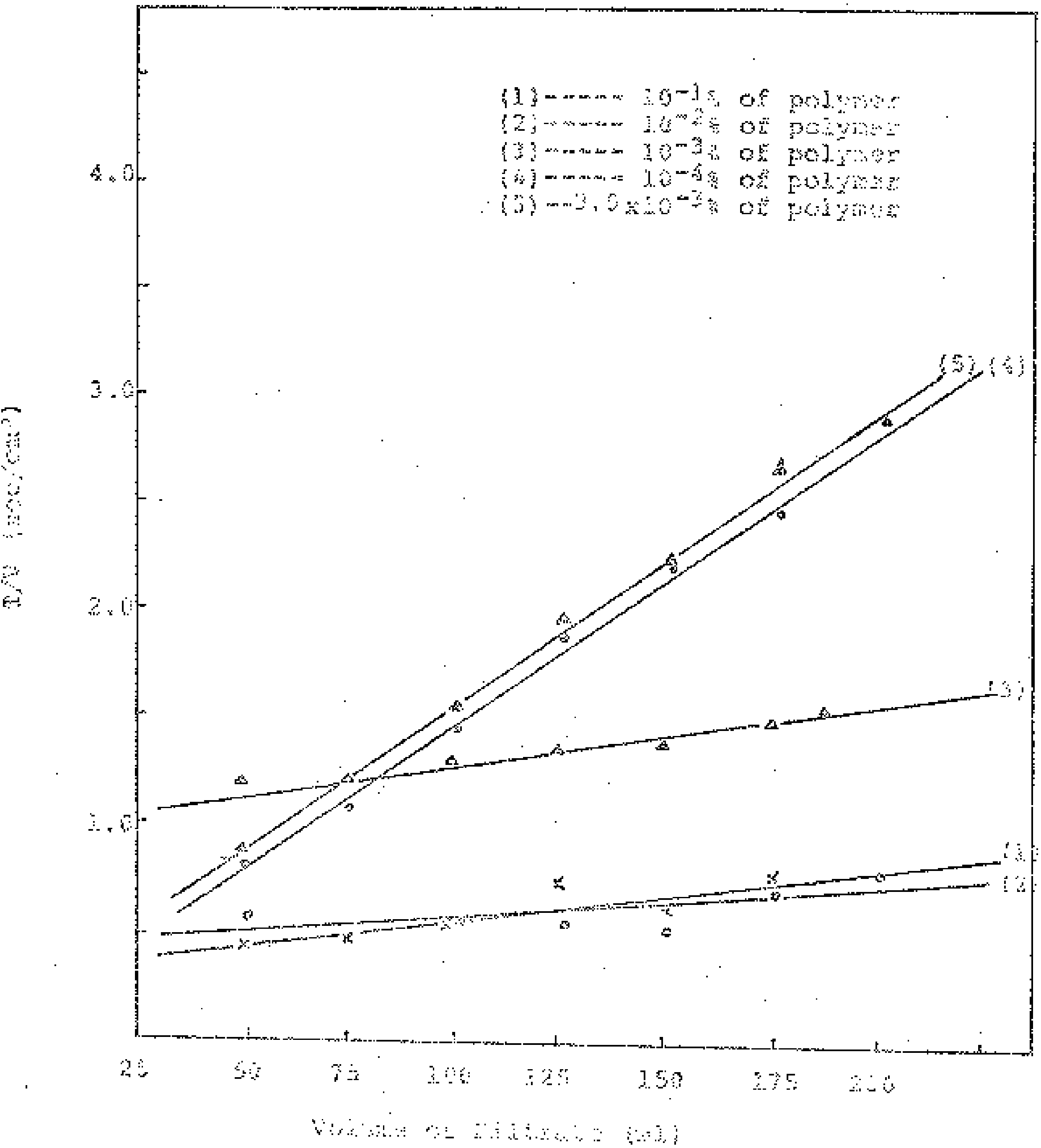

Figure 5: Effect of Metal Ion (Cu^{++}) on Filtering Rate of Cationic Polymer NT-2640

Table 1

Polymer	Dosage	Rate of Refiltration in Milliliters/ Minute		
Q / Metal Ions		Polymer and no salt	Polymer and 10^{-3} M $CaCl_2$	Polymer and 10^{-3} M $CuCl_2$
NaPSS (A)	$10^{-1}\%$	-	-	-
	$10^{-2}\%$	2.60	15.00	-
	$10^{-3}\%$	12.29	28.30	12.24
	$.5\times10^{-3}\%$	28.84	75.00	20.00
	$10^{-4}\%$	10.75	60.00	13.33
PC-2040 (C)	$10^{-1}\%$	20.10	7.79	-
	$10^{-2}\%$	23.52	11.53	50.00
	$10^{-3}\%$	37.28	75.00	40.00
	$.5\times10^{-3}\%$	45.75	8.57	17.64
	$10^{-4}\%$	39.05	11.32	20.00
WT-2580 (C)	$10^{-1}\%$	23.80	25.00	45.00
	$10^{-2}\%$	30.00	83.23	60.00
	$10^{-3}\%$	78.94	150.00	33.33
	$.5\times10^{-3}\%$	28.84	88.23	24.32
	$10^{-4}\%$	45.45	100.00	27.27
PAM (N)	$10^{-1}\%$	2.06	4.86	6.81
	$10^{-2}\%$	2.60	33.33	46.87
	$10^{-3}\%$	60.00	75.00	60.00
	$.5\times10^{-3}\%$	50.00	30.00	25.30
	$10^{-4}\%$	7.89	68.18	38.46
PVP (N)	$10^{-1}\%$	1.29	6.25	2.14
	$10^{-2}\%$	5.00	25.00	2.50
	$10^{-3}\%$	5.76	27.01	2.72
	$.5\times10^{-3}\%$	6.50	31.42	3.75
	$10^{-4}\%$	15.00	37.50	4.28
Gantrez-AN (A)	$10^{-1}\%$	-	7.79	-
	$10^{-2}\%$	4.44	12.00	17.64
	$10^{-3}\%$	57.69	75.00	20.00
	$.5\times10^{-3}\%$	50.00	7.79	50.00
	$10^{-4}\%$	10.52	11.32	50.00

A = Anionic, C = Cationic, N = Nonionic

Table 2

Poly-mer	Do-	Filtrating Rate e of Plot of T/V vs. V	Specific Resistance (Without Metal Ion)
NaPSS (A)		–	–
		–	–
		23.40×10^{-3}	26.0×10^{6}
	.1	16.70×10^{-3}	18.5×10^{6}
		9.20×10^{-3}	10.20×10^{6}
WT-2640 (C)		5.05×10^{-3}	5.60×10^{6}
		1.67×10^{-3}	1.84×10^{6}
		4.55×10^{-3}	5.05×10^{6}
	.5	–	–
		9.70×10^{-3}	10.60×10^{6}
WT-2880 (C)		6.12×10^{-3}	6.75×10^{6}
		11.70×10^{-3}	12.80×10^{6}
		1.45×10^{-3}	1.60×10^{6}
	.5	7.33×10^{-3}	8.05×10^{6}
		4.35×10^{-3}	4.79×10^{6}
PAM (N)		–	–
		–	–
		41.0×10^{-3}	45.0×10^{6}
	.5	1.19×10^{-3}	1.31×10^{6}
		4.4×10^{-3}	4.85×10^{6}
PVP (K)		31.25×10^{-3}	34.2×10^{6}
		3.66×10^{-3}	4.06×10^{6}
		1.66×10^{-3}	1.83×10^{6}
	.5	3.66×10^{-3}	4.06×10^{6}
		5.10×10^{-3}	5.66×10^{6}
Sanfloc-AH (A)		–	–
		114×10^{-3}	126×10^{6}
		32×10^{-3}	35.5×10^{6}
	.5	4.07×10^{-3}	4.55×10^{6}
		4.70×10^{-3}	5.20×10^{6}

Table 3

Effect Polymer \ Dosage		Filtrating Rate Slope of Plot of T/V vs. V	Specific Resistance (With 10^{-3} M $CaCl_2$)
NaPSS (A)	10^{-1}%	–	–
	10^{-2}%	22.2×10^{-3}	24.64×10^{6}
	10^{-3}%	6.0×10^{-3}	6.66×10^{6}
	$.5\times10^{-3}$%	1.93×10^{-3}	2.14×10^{6}
	10^{-4}%	3.50×10^{-3}	3.08×10^{6}
WP-2640 (C)	10^{-1}%	–	–
	10^{-2}%	3.00×10^{-3}	3.33×10^{6}
	10^{-3}%	0.80×10^{-3}	0.88×10^{6}
	$.5\times10^{-3}$%	1.53×10^{-3}	1.09×10^{6}
	10^{-4}%	1.47×10^{-3}	1.67×10^{6}
WP-2580 (C)	10^{-1}%	5.00×10^{-3}	5.55×10^{6}
	10^{-2}%	2.32×10^{-3}	2.57×10^{6}
	10^{-3}%	0.50×10^{-3}	0.55×10^{6}
	$.5\times10^{-3}$%	1.14×10^{-3}	1.26×10^{6}
	10^{-4}%	1.14×10^{-3}	1.26×10^{6}
PAN (N)	10^{-1}%	–	–
	10^{-2}%	4.08×10^{-3}	4.52×10^{6}
	10^{-3}%	1.02×10^{-3}	1.13×10^{6}
	$.5\times10^{-3}$%	4.68×10^{-3}	5.19×10^{6}
	10^{-4}%	2.81×10^{-3}	2.00×10^{6}
PVP (N)	10^{-1}%	4.02×10^{-3}	4.46×10^{6}
	10^{-2}%	1.33×10^{-3}	1.47×10^{6}
	10^{-2}%	1.32×10^{-3}	1.47×10^{6}
	$.5\times10^{-3}$%	1.08×10^{-3}	1.19×10^{6}
	10^{-4}%	0.50×10^{-4}	0.55×10^{6}
Gantrez-AN (A)	10^{-1}%	–	–
	10^{-2}%	73.0×10^{-3}	81.03×10^{6}
	10^{-3}%	1.00×10^{-3}	1.11×10^{6}
	$.5\times10^{-3}$%	51.60×10^{-3}	57.27×10^{6}
	10^{-4}%	32.00×10^{-3}	35.52×10^{6}

Table 4

Polymer	Effect Dosage	Filtrating Rate Slope of Plot of T/V vs. V	Specific Resistance (With 10^{-3} M $CuCl_2$)
NaPSS (A)	$10^{-1}\%$	–	–
	$10^{-2}\%$	12.2×10^{-3}	24.64×10^{6}
	$10^{-3}\%$	21.3×10^{-3}	23.64×10^{6}
	$.5\times10^{-3}\%$	9.52×10^{-3}	10.56×10^{6}
	$10^{-4}\%$	19.4×10^{-3}	21.53×10^{6}
WT-2540 (C)	$10^{-1}\%$	2.22×10^{-3}	2.46×10^{6}
	$10^{-2}\%$	1.17×10^{-3}	1.29×10^{6}
	$10^{-3}\%$	3.00×10^{-3}	3.33×10^{6}
	$.5\times10^{-3}\%$	14.0×10^{-3}	15.50×10^{6}
	$10^{-4}\%$	12.50×10^{-3}	13.87×10^{6}
WT-2560 (C)	$10^{-1}\%$	5.50×10^{-3}	6.10×10^{6}
	$10^{-2}\%$	3.05×10^{-3}	3.39×10^{6}
	$10^{-3}\%$	11.30×10^{-3}	12.54×10^{6}
	$.5\times10^{-3}\%$	16.10×10^{-3}	17.87×10^{6}
	$10^{-4}\%$	21.50×10^{-3}	23.80×10^{6}
PAM (N)	$10^{-1}\%$	–	–
	$10^{-2}\%$	5.0×10^{-3}	5.55×10^{6}
	$10^{-3}\%$	2.3×10^{-3}	2.55×10^{6}
	$.5\times10^{-3}\%$	6.6×10^{-3}	7.39×10^{6}
	$10^{-4}\%$	8.88×10^{-3}	9.85×10^{6}
PVP (N)	$10^{-1}\%$	17.6×10^{-3}	19.53×10^{6}
	$10^{-2}\%$	–	–
	$10^{-3}\%$	12.5×10^{-3}	13.87×10^{6}
	$.5\times10^{-3}\%$	8.0×10^{-3}	8.88×10^{6}
	$10^{-4}\%$	10.5×10^{-3}	11.65×10^{6}
Suntrac-AN (A)	$10^{-1}\%$	–	–
	$10^{-2}\%$	10.8×10^{-3}	11.98×10^{6}
	$10^{-3}\%$	18.7×10^{-3}	20.78×10^{6}
	$.5\times10^{-3}\%$	5.35×10^{-3}	5.93×10^{6}
	$10^{-4}\%$	5.75×10^{-3}	6.39×10^{6}

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PUBLICATIONS:

None

PROJECT STATUS:

The work on this project was completed as of June 30, 1972. A completion report is being prepared and will be submitted in the near future.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-038-RI

Agreement No. 14-31-0001-3240

FCST-COWRR Research Category: V B

Project Title:

TRANSFER OF PESTICIDES THROUGH WATER, SEDIMENTS AND AQUATIC LIFE

Name and Location of University Where Project is Being Carried Out:

UNIVERSITY OF RHODE ISLAND, KINGSTON, R.I.

Proj. Began--Month: July ; Year: 1970

To Be Completed--Month: June ; Year: 1972

Principal Investigators	Degree	Discipline
Charles E. OLNEY	Ph.D.	Food and Resource Chemistry

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Harry DAY	M.S.	Food and Resource Chemistry
Charry VILLEGAS	M.S.	Food and Resource Chemistry (9 mos)

(A) RESEARCH PROJECT ACCOMPLISHMENTS

Methods

Samples were collected from various rivers and ponds of the State. Some water and sediment samples were taken close to the water's edge. Most fish samples were obtained with a gill net and an aluminum boat with outboard motor was used to set and collect the net. Sediment and water samples were also collected from the boat.

Water: Samples were collected by submerging a gallon bottle at least 50 cm below the water surface and analyzed by the EPA method (1). The samples were extracted with two portions of petroleum ether containing 15% ethyl ether. To minimize pesticide loss the first portion was added and the bottle shaken immediately upon receipt at the laboratory. The combined extract was dried by passage through anhydrous sodium sulfate, concentrated in a Kuderna-Danish evaporative concentrator and made to a 10 ml volume for gas chromatography.

Sediment: Samples were collected with a spade or with an Ekman dredge and stored at -18°C until analyzed. Some early samples were stored in polyethylene bags; the majority were transported in glass bottles and wrapped in aluminum foil for storage. Fifty gram samples of wet sediment were extracted with 2:1 hexane: acetone in a Soxhlet extractor. The acetone was removed by washing with distilled water and the petroleum ether phase was dried with sulfate, concentrated, and passed through a Florisil column (2), collecting a 6%

(6% ethyl ether in petroleum ether) and 15% eluate. This column removes some of the lipids and pigments, and separates the pesticides into two fractions, which aids in identification.

The 6% eluate was concentrated and chromatographed on a short silicic acid column. PCB and ppDDE were eluted with petroleum ether and other pesticides with methylene chloride. The various fractions were concentrated and analyzed by electron capture gas chromatography. A separate moisture determination of the wet sediment was made and sediment results are reported on a dry weight basis.

Fish: Samples were obtained with a gill net and stored at -18°C. Some early samples were stored in polyethylene bags; most were individually wrapped in aluminum foil. Single fish were analyzed by the method of Porter, Young and Burke (3). A 50 gram sample of ground fish was extracted by adding sodium sulfate and blending with petroleum ether. Clean-up was accomplished by petroleum ether -- acetonitrile partitioning to remove most of the fat, followed by Florisil column chromatography. The 6% eluate was fractionated into a PCB and a pesticide fraction prior to gas chromatography.

Gas Chromatography: A Tracor MT-220 gas chromatograph equipped with two Ni-63 electron capture detectors and two electrometers was used in the determinative step. Samples were routinely injected into two 6' x 1/4" glass columns, one containing 1.5% OV-17/1.95% QF-1 on 100/120 mesh Supelcoport and the other 4% SE-30/6% QF-1 on 80/100 mesh Supelcoport. At 200° and with carrier gas (nitrogen) flow rates of 60 and 100 ml/min the retention time of ppDDT is approximately 16 minutes. Peaks were identified by retention times and quantitated using peak heights. In addition to direct comparisons with pesticide and Aroclor standards, the retention and response data of Thompson (1) for 50 pesticides on these two columns were also used to identify and quantitate unknowns.

Results

In many samples of sediment and fish, op-isomers of DDE, DDD and DDT were found. They have been totalled with the respective pp-isomer in order to simplify presentation of the data in this report. The residue results are presented in Table I. In attempting to compare sediment and fish residues, it should be kept in mind that the sediments are on a dry weight basis, while fish are on a wet weight basis. Dry weight values for fish would be approximately 4 to 5 times higher than the values listed. In general it may be seen that DDE is the predominant DDT species in fish while DDD predominates in sediments. Although DDT's were detected in almost all samples, the levels are not alarmingly high and may be expected to decline as the ban on chlorinated hydrocarbon insecticides continues. The highest total DDT levels in fish was 1.2 ppm.

Chlordane and dieldrin were also found in many samples. Although chlordane has been used by commercial farmers and has been used extensively on lawns and around buildings it is generally considered to be quite immobile in the soil. Soil run-off and dumping into streams are possible, however.

In some cases, such as Waterman Reservoir, Hundred Acre Pond, and Thirty Acre Pond, residues of dieldrin can be accounted for by proximity to agricultural areas. In other cases wastes from textile mills or aerial transport following co-distillation from water surfaces may account for its presence in streams or ponds distant from agricultural applications. DDT is also believed to be transported via co-distillation and association with atmospheric particulate matter.

PCB's are manufactured and sold as mixtures of polychlorinated biphenyls. A mixture such as Aroclor 1242 may contain a dozen components, which give a characteristic pattern on a gas chromatogram. The last two digits of the Aroclor designation indicate the chlorine percentage of the mixture. Thus, 1260 contains more highly chlorinated molecules than 1242. These materials have been widely used over the past 40 years in a variety of products such as heat exchangers, hydraulic fluids, electrical transformers and plastics. PCB's were found in almost all sediment and fish samples. In all cases, levels in the fish were below the FDA action level which is 5 ppm.

Aroclor 1242 accounts for 70% of the total PCB production in the U.S.A. Some sediments had PCB patterns resembling Aroclor 1242, but, as others have noted, the peak pattern in fish invariably resembles more closely the pattern in 1248, 1254 and 1260. One explanation is that 1248, 1254 and 1260 are preferentially absorbed by fish. A more likely explanation is that the less chlorinated molecules of Aroclor 1242 are degraded or metabolized more rapidly than the highly chlorinated members and thus do not accumulate in fish. The highest PCB residue found was in a bluegill from Print Works Pond. Many dead fish were present in the vicinity of the sampling site. This fish was also high in chlordane. However, visual observation of the site indicated other types of pollution, and PCB or pesticides may not have been the cause of death. Water samples from the Pawtuxet River contained a number of compounds which were not PCB's or pesticides. If, as is likely, some of these compounds are not chlorinated, their levels may be quite high.

No chlorinated hydrocarbons were found in the majority of water samples. Dieldrin was detected in several water samples, one taken at the edge of an orchard, the other in Thirty Acre Pond, adjacent to potato fields and the University turf plots. Dacthal and chlordane were also detected in Thirty Acre Pond water and analysis of the sediment near the turf plot drain (which is no longer used) suggests that this may be the source.

This experiment was designed primarily to determine the levels of chlorinated hydrocarbons present in the fresh water environment of Rhode Island since there has been no published information of this nature. The study indicates that some pesticides are indeed associated with the muds at pond and stream bottoms, and that fish living in the ponds also contain residues of PCB, DDT and occasionally other chlorinated hydrocarbons.

Because of sampling and analytical limitations, detailed studies at one site were not possible. Rather, an attempt was made to check many different sites to obtain an overall picture for the State. To complete the present project selected fish samples will be analyzed to fill in gaps in Table I, with special emphasis on larger fish higher up the food chain.

For future studies, it is recommended that one watershed be studied intensively.

TABLE I

PCB and pesticide residues in streams and ponds of Rhode Island, 1970-71

Location		PCB		Pesticides (ppt)[ab]					Notes
		type	ppb	DDE	DDD	DDT	chlordane	dieldrin	
Slatersville Reservoir, North Smithfield									
Water	7-18-71		ND[c]						
Sediment	"	1242	103	5	35		8		
Nichols Pond, Burrillville									
Water	7-18-71		ND						
Sediment	"				11	3			
Keech Pond, Glocester									
Water	8-21-71		ND						
Sediment	"	1242	286	3	12	10	16	5	lindane-1
Perch	"	1254	10	10	5	4	2	1	a-BHC-1, endosulfan-1
Waterman Reservoir, Glocester									
Water	7-17-71		ND						
Sediment	"	1248	155	17	46	5		4	
Perch	"	1260	65	413	29	32		8	
Water - directly behind orchard	"								dieldrin-160 ppt
Sediment - " " "	"	1248	210	28	292	40		6	
Woonasquatucket Reservoir, Smithfield									
Water	7-18-71		ND						
Sediment	"	1242	334	273	155	11	10		
Olney Pond, Lincoln									
Water	8-20-71		ND						
Sunfish	8-21-71	1254	58	69	50	8			

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[a] Sediment residues are on a dry weight basis, fish on a whole fish, wet weight basis.

[b] DDE, DDD and DDT values are sum of op- and pp-isomer estimates. Chlordane values are sum of α- and γ-isomers.

[c] ND- None detected. For water samples, PCB is less then 50 ppt and pesticides less than 10 ppt. For sediments and fish, PCB is less than 10 ppb and pesticides are less than 1 ppb.

TABLE I (continued)

Location		PCB		Pesticides (ppb)					Notes
		type	ppb	DDE	DDD	DDT	chlor-dane	diel-drin	
Scituate Reservoir, Scituate									
Water - Bridge 251, Route 116	7-17-71		ND						
Sediment " " " "	"	1242	73	9	10	4			
Water - stream from Barden Res.	8-21-71		ND						
Sediment " " " "	"	1254	80	6	20	2	2		
Perch " " " "	"	1260	131	120	28	56			
Water - stream from Westconnaug R.	"		ND						
Stream from Flat River Reservoir, Coventry									
Water	7-18-71		ND						
Sediment	"			13	2				
Pond off Route 3, Coventry									
Sediment	7-17-71	1254	220		107		363	2	
Pawtuxet River and tributaries, Cranston									
Water - at mouth	7-4-71	Chromatograms of these three samples contained many peaks which did not match PCB or pesticides. Sample at mouth of river was highest in these organics.							
Water - Elmwood Ave. Bridge	"								
Water - Print Works Pond	"								
Sediment - at mouth	"	Many peaks in chromatogram. Maximum possible PCB -10 ppm, maximum DDD- 860 ppb.							
Sediment - Elmwood Ave. Bridge	"	1254	300	50	34	37	480	4	
Sediment - Blackamore Pond	"	1254	115	20	85	27	278	5	hydroxychlordene-80
Sediment - Print Works Pond	"	1254	55	13	8		14	5	
Bluegill - " " "	8-1-71	1254	2580	374	270	215	210	64	hydroxychlordene-27 a-BHC-16, lindane-10
Alton Jones Pond, West Greenwich									
Water	10-24-70		ND						
Sediment	"	1248	159	20	6				
Weeds	"	1254	4						
Pumpkinseed	"	1254	26	16	17	8	2		a-BHC-5
Yellow perch	"	1248	28	21	9	7	5	4	a-BHC-2

TABLE I (continued)

Location		PCB		Pesticides (ppb)					Notes
		type	ppb	DDE	DDD	DDT	chlor-dane	diel-drin	
Belleville Pond, North Kingstown									
Water	7-3-71		ND						
Sediment	"		ND						
Yellow perch	"	1254	100	573	130	142	38	1024	
Annaquatucket River, North Kingstown									
Water - at Route 1	7-3-71		ND						
Sediment " "	"				27	1	2	4	
Sediment - Estuary at mouth	"	1248	115	1	3	1			
Bissells Cove, North Kingstown									
Sediment	3-24-70			28	85	3	4	50	
Indian Lake, South Kingstown									
Water	5-14-71		ND						
Sediment	"	1254	40	5	6				
Perch	"	1254	80	79	16	20	6	6	
Cards Pond, South Kingstown									
Water	6-5-71		ND						
Herring	"	1254	165	114	43	62	27	6	
Yawgoog Pond, Hopkington									
Water	7-30-71		ND						
Pickerel	7-31-71	1260	419	1022		22	4	1	a-BHC-3, lindane-1
Ell Pond, Hopkington									
Water	7-30-71		ND						
Moscow Brook, Hopkington									
Water	7-30-71		ND						
Locustville Pond, Hopkington									
Water	9-20-70		ND						
Sediment	"	1254	76	16	34	16	2		hydroxychlordene-7
Yellow perch	"	1254	34	74	25	33	13	3	

TABLE 5 (continued)

Location		PCB type	PCB ppb	Pesticides (ppb) DDE	DDD	DDT	chlordane	dieldrin	Notes
Yawgoo Pond, North Kingstown									
Water	11-11-70		ND						
Water	5-14-71		ND						
Weeds	"			23	26	11	2		a-BHC-1, lindane-1
Sediment	"	1242	400	78	127	26	10	8	endosulfan-5
Hundred Acre Pond, South Kingstown									
Sediment - middle	11-22-70	1254	140	298	341	60	27	17	
Sediment - South end	"	1254	91	40	45	16	4	6	hydroxychlordene-1
Yellow perch	"	1260	103	907	144	126	56	139	dacthal-4
Yellow perch	5-1-71	1254	25	422	55	84	22	255	dacthal-1, endrin-4 endosulfan-1
Thirty Acre Pond, South Kingstown									
Water - North end	9-26-70							20ppt	dacthal-39 ppt
Water - below turf plot drain pipe	"						60ppt	32ppt	
Sediment - North end	"	1248	250	130	250	69	50	6	
Sediment - below drain pipe	"	*	*	50	1150	1330	5680	994	*Many peaks (petroleum?) masking PCB, dacthal-258, endosulfan-2230
Yellow shiner	"	1254	100	864	109		100	175	dacthal-53
Yellow perch	5-1-71	1254	180	473	125	239	30	12	dacthal-8, a-BHC-2
Larkins Pond, South Kingstown									
Yellow perch	2-7-71	1254	47	145	24	23	9		
Yellow perch	"	1248	88	238	41	53	6		a-BHC-3
Wordens Pond, South Kingstown									
Sediment - center	10-13-70	1242	100	3	4		1	1	hydroxychlordene-2 endosulfan-4
Weeds	"	1242	33	2	1	2			a-BHC-1, lindane-1
Pumpkinseed	"	1260	77	40	3	8			endosulfan-15
Perch	5-11-71	1254	40	43	15		4	37	

TABLE I (continued)

Location		PCB		Pesticides (ppb)					Notes
		type	ppb	DDE	DDD	DDT	chlor-dane	diel-drin	
Tuckers Pond, South Kingstown									
Water	11-7-70		ND						
Sediment	"	1248	105	6	15	2			
Perch	"	1254	36	66	12	8	4		a-BHC-1, lindane-1
Yellow perch	5-29-71	1254	62	73	21	16	4	7	a-BHC-6, lindane-3 hydroxychlordene-3
Wood River Pond, Richmond									
Water	12-5-70		ND						
Sediment	"	1248	300	140	189	70	33		poor PCB match
Weeds	"	1248	10	7	12	14			
Perch	"	1254	56	694	93	33	7		a-BHC-2
Brickyard Pond, Barrington									
Water	8-14-71		ND						
Sediment	"	1242	263	42	117	15			
Perch	"	1254	60	112	212	14	13		
One Hundred Acre Cove, Barrington									
Water	8-14-71		ND						
Sediment	"	1248	20	54	122	4			
Melville Pond, Portsmouth									
Water	10-30-70		ND						
Sediment - edge	"	1254	96	10	13	3	8	2	
Sediment - middle	"	1254	40	49	48	8			
Easton Pond, Newport									
Water - West side of dyke	8-14-71		ND						
Water - East side of dyke	"		ND						
Sediment - West side of dyke	"	1242	100	10	9	8	6		
Sediment - East side of dyke	"	1242	105	9	5	8	2	5	
Jamestown Reservoir, Jamestown									
Water	8-14-71		ND						
Sediment	"	1248	20	4	2	4			

References

(1) Manual of Analytical Methods. Primate Research Laboratory, EPA, Perrine, Florida (1971).

(2) Pesticide Analytical Manual. Food and Drug Administration, Washington, D.C. (1971).

(3) Porter, M. L., Young, S. J. U. and Burke, J. A. JAOAC 53:1300 (1970).

(B) NO PUBLICATIONS. MANUSCRIPT IN PREPARATION.

(C) PROJECT TERMINATES JUNE 30, 1972.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-039-R I Agreement No. 14-31-0001-3540 FCST-COWRR Research Category: VC	Project Title: The effects of differently extracted endotoxins from *Escherichia coli* on rainbow trout (*Salmo gairdneri*)

Name and Location of University Where Project is Being Carried Out:

Providence College, Providence, Rhode Island 02918

Proj. Began--Month: July 1, Year: 71 To Be Completed--Month: June 30 Year: 73

Principal Investigators	Degree	Discipline
Gerard P. O'Leary	Ph.D.	Microbiology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Henry R. Vaillancourt	B.S.	Biology
Michael S. Flood	B.S.	Biology

Research Project Accomplishments

To date the research project has progressed mainly along the lines of adapting the extraction procedures of different workers to the two project organisms, Escherichia coli 0111:B4 and E. coli K12 . We have found no problems with the growth of E. coli 0111:B4 on Bacto tryptic Soy Broth, however we have added the E. coli K12 for comparative reasons and found that the published defined medium was not as satisfactory as the T-Soy broth. We have therefore been routinely cultivating both organisms on the T-Soy broth with aeration.

The two organisms have been extracted by these four methods: (1) ethylenediamine - tetraacetatic acid, (2) distilled water, (3) trichloroacetic acid, (4) and aqueous ether. We have found that each organism yields approximately the same dry weight of endotoxin using the same extraction procedure. From the EDTA, TCA, and ether methods approximately 20-30 mg of freeze dried endotoxin was obtained from 200 g wet weight of cells or 18 g dry weight. This means that our percent recovery of endotoxin from whole cells is averaging approximately 0.15%. We, however, have not tried extracting the remaining culture medium itself for excreated endotoxin which would certainly improve the total yield.

To date, the water extracted material has given the best yield. We have obtained approximately 100 mg to 150 mg from E. coli K12 which would be a 1% yield on a dry weight basis. We, however, have found this water preparation to be partly contaminated with amino acids and ribose. The ribose probably came from DNA and RNA leakage during the extraction procedure. However, this has not been mentioned in the literature as far as we know. We still have the water extraction procedure to run on the E. coli 0111:B4 organism.

The carbohydrate chromatographic profile on the E. coli K12 material has been completed. The profile showed the typical monosaccharide components of glucose, galactose, glucosamine and heptose which seemed to be in low concentrations. Initial indications from chromatograms seem to indicate that the monosaccharide concentrations vary with the different extraction procedures employed. The E. coli 0111:B4 has not yet been completely tested and one extraction procedure (water extraction) remains to be performed. These results should be completed by July 1, 1972. The chromatographic picture on the E. coli 0111:B4 has been performed on two extractions products and the initial patterns seem the same as the E. coli K12 endotoxin.

These procedures are giving the same endotoxic profiles as those published by other authors.

Project Status

The project will continue in progress during the next fiscal year, 1972-1973.

Work Remaining, and Progress Contemplated During Next Year.

The project work remaining to be accomplished falls into two catagories. First, we must obtain sufficient quantities of each endotoxin preparation for inoculation into the trout. Secondly, and the main objective of the project, the trout must be tested for the lethal effect and lethal dosage of endotoxin at the two prescribed temperatures 15° C and 20° C.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-040-RI Agreement No. 14-31-0001-3240 FCST-COWRR Research Category: V D	Project Title: Electrochemical Process for the Removal of Nitrogen and Phosphorous from Wastewater

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1971 | To Be Completed--Month: June ; Year: 1973

Principal Investigators	Degree	Discipline
Calvin P.C. Poon	Ph.D.	Civil and Environmental Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Thomas Brueckner	B.A.	Mathematics (B.A.) M.S. Degree Candidate in Civil and Environmental Engineering

RESEARCH PROJECT ACCOMPLISHMENTS

The objective of this project is to construct an electrochemical cell which will effectively remove nitrogen and phosphorus nutrients from wastewater. Work completed in the first year has been directed primarily toward the removal of phosphate in the orthophosphate form.

The first cell constructed was of 10 liter capacity, operated in a batch process mode. The anode consisted of 15 carbon rods 1/4 inch in diameter and 6 inches long, spaced 1/2 inch apart. Various cathodes were tried and it was found that a 3/8 inch iron plate with holes 1/8 inch in diameter, spaced at 1/4 inch intervals gave the most satisfactory results. Seawater was the anolyte and raw sewage from the University Treatment Plant was the catholyte.

When a D.C. current is passed through the cell, chloride ions present in the seawater are oxidized to Cl_2 at the anode and hydrogen ions are reduced to H_2 gas at the cathode. The removal of hydrogen ions results in an excess of hydroxyl ions at the cathode which causes the magnesium ions present in the seawater to precipitate as $Mg(OH)_2$. These flocculent particles are than floated to the surface on the gas bubbles, resulting in a subsequent decrease in phosphate concentration.

Early attempts at phosphate removal met with failure due to an inability to generate the $Mg(OH)_2$ floc. It was found that floc formation could be attained by keeping the seawater and sewage separated; the seawater beneath the cathode and the sewage above it. This was accomplished by first adding the seawater to the cell, then suspending the cathode on top of the seawater. Sewage was then gently added from a hose, using the cathode as a barrier to prevent mixing. When this stratification was achieved, a large portion of the Cl_2 generated dissolved in the seawater lowering the pH from neutral to pH2-3. The pH of the sewage above the cathode increased markedly, from neutral to pH 11, resulting in the formation of a dense white floc.

A second cell was constructed in March of 20 liter capacity, similar to the first, and also operated in the batch process mode. A few other modifications were made in its design to facilitate maintenance of the seawater-sewage stratification and to reduce the overall electrical resistance of the cell. The larger capacity also allowed for greater variation in the sewage to seawater loading ratio.

Results of experiments performed with these two cells indicate that orthophosphate removal up to 98% can be attained consistently with a detention time of approximately 30 minutes. (TABLE 1). Besides the high phosphate removal the sewage becomes visibly clearer with excellent froth flotation and suspended solids removal.

Orthophosphate removal is dependent on detention time and current. In the experiments performed it was found that 2l of seawater, resulting in an electrode spacing of 3 cm, was sufficient to treat up to 18 l of sewage. This is a sewage to seawater ratio of 9 to 1. This was the maximal sewage dosage obtainable with a 20 liter cell. At higher sewage loadings, it is necessary to increase the current through the system in order to attain the desired phosphate removal in the 30 minute detention time. The maintenance of a current to sewage ratio of 0.5 amp/l gave the desired results for this detention time. A comparison between a current to sewage ratio of 0.5 amp/l and 0.33 amp/l is shown in figures 1 and 2. Voltages for this cell vary between 3.5 volts and 7.0 volts (TABLE 1) depending on sewage loading and current. A lower current to sewage ratio requires a longer detention time, to achieve the same phosphate removal as with a higher ratio. However, running the cell at 8 amperes or more will lead to a breakdown of the seawater-sewage stratification between 40 and 60 minutes detention time, with a resultant decrease in the pH of the sewage and lessening of phosphate removal efficiency.

Test are now being run to determine if the mechanism for phosphate removal is by adsorption on the $Mg(OH)_2$ floc. Early results indicate that this may be the primary mechanism for orthophosphate removal.

WORK REMAINING

In the next year total phosphor us removal and nitrogen removal will be determined.

A continuous flow cell has been designed and is currently under construction which, when completed and put into operation will indicate the feasibility of this process under actual operating conditions. It has been designed to permit the removal of the flotated scum which will be analyzed for composition, dewaterability, solids content, and amount of sludge produced. It will be capable of treating 25 liters of sewage per hour with a 30 minute detention time.

An investigation of the amounts of residual Cl_2 in the seawater and sewage will also be conducted.

If time permits, the use of a synthetic electrolyte in place of seawater will be examined to see whether this process would be feasible in areas where seawater is not available.

			TIME (minutes)							
			0		35			60		
Sewage loading	amps	volts	PO_4 (ppm)	pH	PO_4 (ppm)	pH	% removal	PO_4 (ppm)	pH	% removal
6 l.	2	3.5	10.10	6.8	0.98	10.9	90.5	0.13	11.40	99
6 l.	3	4.0	11.0	6.7	0.23	11.4	98	0.14	11.75	99
6 l.	4	4.2	10.6	7.0	0.07	11.4	99.5	0.14	11.75	98.7
6 l.	6	5.0	10.7	7.0	0.09	11.45	99.5	0.19	10.70	98.5
6 l.	8	5.8	11.1	7.1	0.16	10.85	98.7	----	6.25	100
12 l.	4	6.0	9.30	6.8	0.24	11.10	97.5	0.17	11.20	98.3
12 l.	6	5.0	8.50	6.75	0.13	10.75	98.5	0.23	9.40	97.5
12 l.	8	6.0	9.30	6.80	0.09	10.80	99	0.54	3.40	94.5
18 l.	4	5.0	8.30	6.50	1.07	11.0	87	0.15	11.10	98.3
18 l.	6	5.0	9.10	6.70	0.30	10.80	96.7	0.35	10.0	96
18 l.	8	7.0	9.70	5.40	0.28	10.10	97	----	6.30	100

TABLE 1. All pH values are pH values of sewage at given time.

Phosphate values are orthophosphate readings.

Seawater loading is 2 l. for all cases.

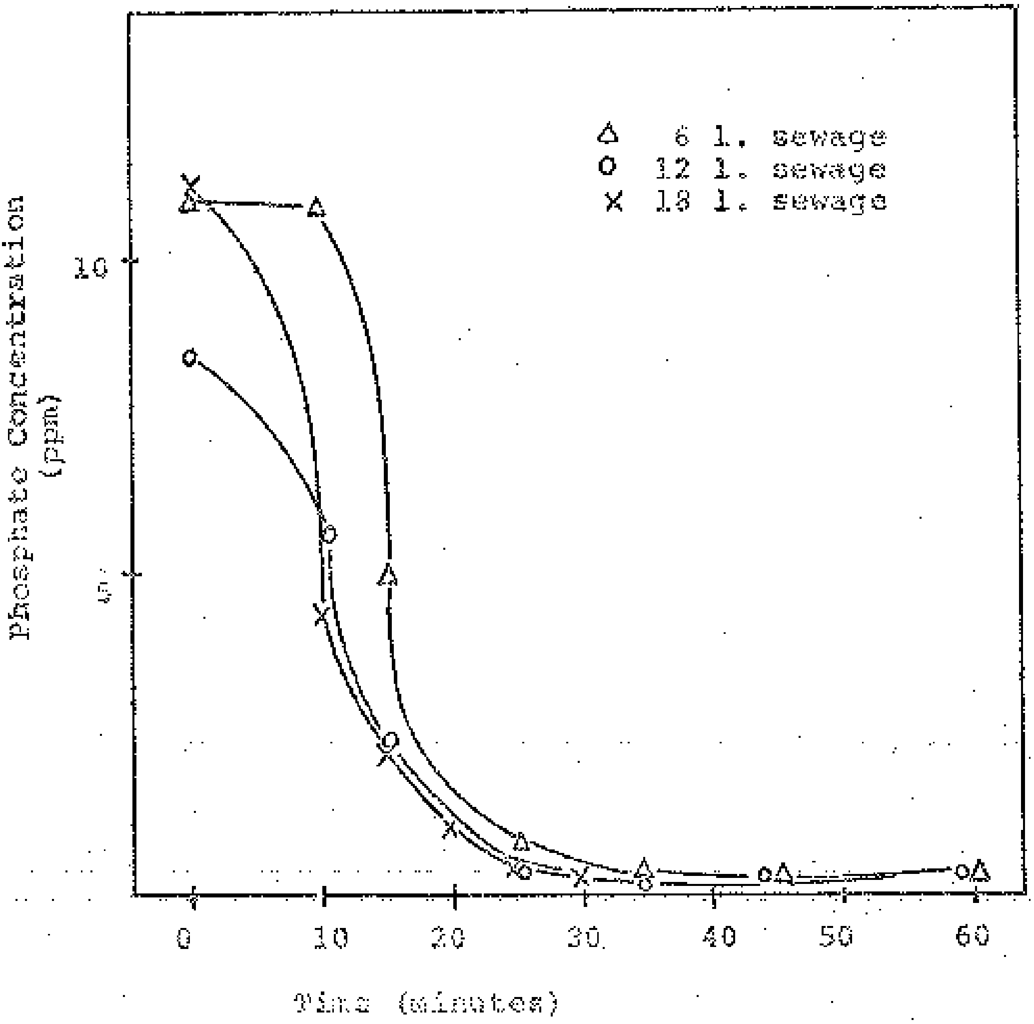


Fig. 1. Phosphate Remaining with Time at 0.5 amp/liter Current To Sewage Ratio

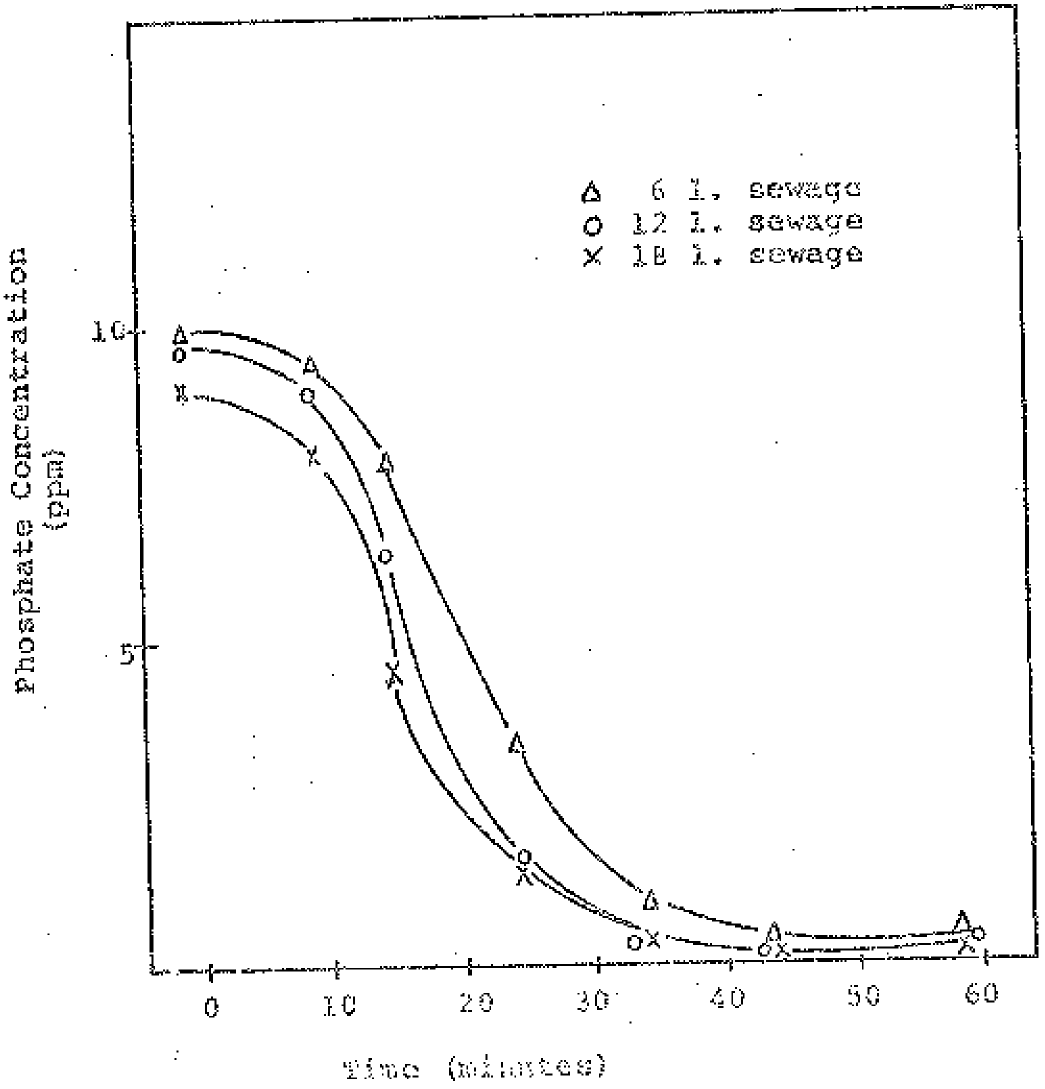


Fig. 2. Phosphate Remaining with Time at 0.33 amp/liter Current to Sewage Ratio

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-042-RI Agreement No. 14-31-0001- 3540 FCST-COWRR Research Category: II K	Project Title: Trace Metals in the Precipitation of Humic Materials.

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Graduate School of Oceanography, Kingston, R.I. 02881

Proj. Began--Month: July 1 ; Year: 1971 | To Be Completed--Month: June 30 ; Year: 1972

Principal Investigators	Degree	Discipline
John McN. Sieburth	Ph.D.	Oceanography and Bacteriology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
A. David McNab	M.S.	Chemistry

RESEARCH PROJECT ACCOMPLISHMENTS:

The purpose of this project was to study the fate of humic substances and their associated trace metals as they are carried into the marine environment. Most data has been collected on the intracoastal waterway between Norfolk, Virginia and West Palm Beach, Florida. Trace metals are definitely associated with the larger molecular weight fraction of water soluble humic substances, commonly referred to as fulvic acid. Using salinity as an index of dilution of terrestrial waters, it was shown that reduction in color and, therefore, humic substances is much more rapid and greater than one would expect by dilution alone. This salting out of the humic substances concentrated trace metals in the resulting sediment.

PROJECT STATUS:

Unfortunately Mr. McNab took a leave from graduate study in the early spring and this project has been terminated before studies on the fate of sedimented humic substances and their trace metals could be completed. A manuscript for publication to be used as a final report is in preparation.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-041-RI Agreement No. 14-31-0001-3540 FCST-COWRR Research Category: V A	Project Title: Plant Phenols and Related Organic Compounds in Public Water Sources, Their Relationship to Chlorination

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1971 | To Be Completed--Month: June ; Year: 1973

Principal Investigators	Degree	Discipline
Shimizu, Yuzuru	Ph. D.	Pharmaceutical Sciences

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Hsu, Rong Y.	M. S.	Pharmacognosy

(A) Research Project Accomplishments

Chlorination is the most common method for the treatment of public water and sewage systems. When chlorination is required, in most cases, the water is polluted with organic compounds, and it is highly conceivable that chlorine atoms work not only oxidatively but they react with certain organic molecules to form chlorinated compounds which may be hazardous to human health and also may have impacts upon the ecological system.

In an attempt to clarify this problem, plant phenol analogs which are likely to exist in water systems polluted with organic materials are treated with various amounts of chlorine in aqueous media at different pH and concentrations. The resulting products were analyzed and fractionated chromatographically. With each purely isolated compound, structure determination was done by chemical and physico-chemical methods.

Chlorination of Hydroxycinnamic Derivatives - Hydroxycinnamic acid derivatives are abundant in plants as free and conjugated forms, and also they are major pollutants as degradation products of lignoids. Their presence in public water systems was reported in the past. Specifically, chlorination of p-hydroxycinnamic acid (I), p-methoxycinnamic acid (II), caffeic acid (III) and ferrulic acid (IV) was studied. The reaction products of the compounds were thoroughly analyzed and the structures of the isolated chlorine compounds were unequivocally established. It is summarized in Table I and II. The speculative reaction mechanisms for the formation of the products are shown in Scheme 1.

Chlorination of Flavonoids - Flavonoids are also expected pollutants derived from dried leaves and pollens which contain a large amount of such compounds. As a simple model, epigenin (XII) was chlorinated. The products are shown in Table III and IV, and the possible reaction mechanism in Scheme 2.

Chlorination of Tyrosine and its Derivatives - Tyrosine (XIV) is a major aminoacid in most proteins and its presence in polluted water is well known. Chlorination of tyrosine and its conjugated derivative (XV) was investigated. The results are shown in Tables V and VI. Scheme 3 shows the possible mechanism for the formation of the products.

Chlorination Experiments at High Dilutions - The reactions were also run in very diluted solutions (ca. 10 ppm) to realize the naturally existing conditions, and the products were analyzed by gas chromatography using the pure compounds as references. The formation of such compounds as VII, X, XVI, and XVII was positively confirmed.

Discussion - As expected, active chlorine atoms are easily "fixed" to form various chlorinated organic compounds. In the case of öxycinnamic acid derivatives chlorination takes place in the side-chain as well as in the nucleus. Compounds resulted from addition of chlorine on the side-chain quickly undergo decarboxylation forming multi-chlorinated styrene derivatives. Further chlorination finds chlorinated benzoquinone derivatives which are homologs of known strong antimicrobial agents. Flavones also take the similar

Table I. Chlorination of Oxycinnamic Acid Derivatives

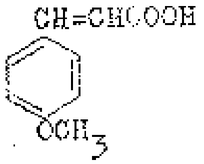
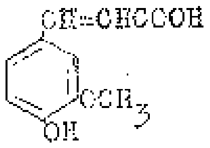
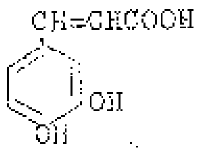
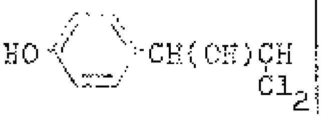
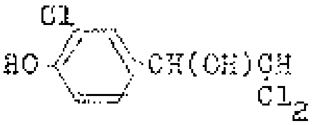
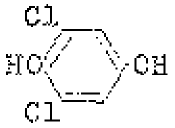
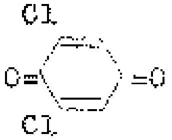
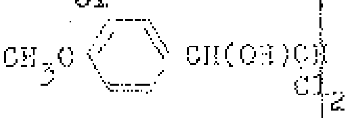
Phenolic Compounds	Chlorine Water (moles)	Solvent	Products	Approximate Percentage in total extract
p-hydroxy-cinnamic acid (I) 	3	H_2O	V VI VII	17.2% 42.6% 6.6%
	5	H_2O	VIII IX	8.3% 69.8%
	5	H_2O Dioxane	VIII IX	7.1% 28.4%
	3	Phosphate Buffer 0.2M NaOH 0.2M KH_2PO_4	IX	3.3%
p-methoxy-cinnamic acid (II) 	5	H_2O Dioxane	IX	45.8%
	4	H_2O Dioxane	IX X XI	11.0% 22.1% 9.8%
	3	H_2O Dioxane	X	47.0%
Ferulic Acid (III) 	3	H_2O	Under investigation	
Caffeic Acid (IV) 	3	H_2O	Under investigation	

Table II. Structures and Physical Constants of Chlorinated Products of Oxycinnamic Acid Derivatives.

Compound Number	Structure	Molecular Formula	M. P.	Mass Spectrum
V		$C_8H_8O_2Cl_2$	90-92°	M/e 206 M^+ (11%) 123 M^+-83 (100%)
VI		$C_8H_7O_2Cl_3$	85-86°	M/e 240 M^+ (9%) 157 M^+-83 (100%)
VII		$C_8H_6O_2Cl_4$	108-110°	M/e 274 M^+ (7%) 191 M^+-83 (100%)
VIII		$C_6H_4O_2Cl_2$	161-162°	M/e 178 M^+ (100%) 180 M^++2 (65%) 182 M^++4 (11%)
IX		$C_6H_2O_2Cl_2$	120-122°	M/e 176 M^+ (100%) 141 M^+-35 (23%)
X		$C_9H_{10}O_2Cl_2$		M/e 220 M^+ (13%) 137 M^+-83 (100%)
XI		$C_9H_9O_2Cl_3$		M/e 254 M^+ (6%) 171 M^+-83 (100%)

Scheme 1

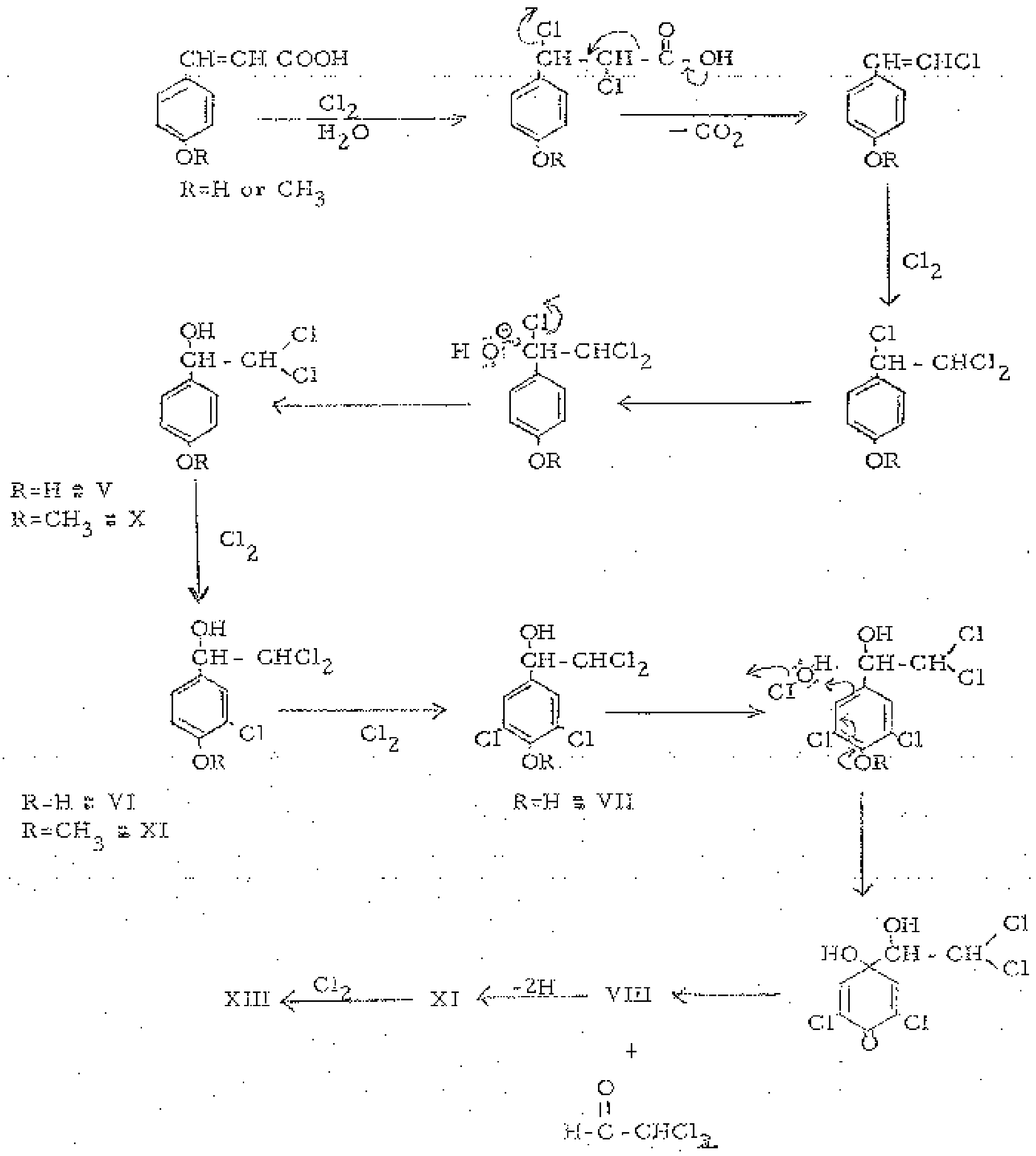

CH=CH COOH
OR
R=H or CH_3
Cl_2
H_2O
Cl
CH - CH - C - OH
Cl
O
OR
$- CO_2$
CH=CHCl
OR
Cl_2
Cl
CH - $CHCl_2$
OR
H O: Cl
CH-$CHCl_2$
OR
OH
CH - CH
Cl
Cl
OR
R=H = V
R=CH_3 = X
Cl_2
OH
CH - $CHCl_2$
Cl
OR
R=H = VI
R=CH_3 = XI
Cl_2
OH
CH-$CHCl_2$
Cl
Cl
OR
R=H = VII
Cl O H
OH
CH-CH
Cl
Cl
Cl
Cl
OR
OH
HO
CH - CH
Cl
Cl
Cl
Cl
O
VIII
-2H
XI
Cl_2
XIII
+
O
H-C -$CHCl_2$

Table III. Chlorination of Epigenin

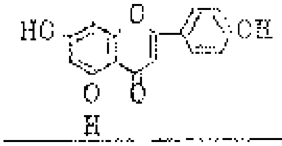
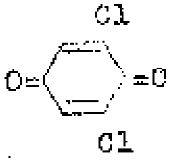
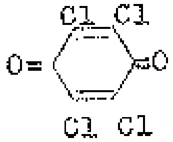
Phenolic Compounds	Choline water (Moles)	Solvent	Products	Approximate Percentage in total extract
Epigenin XII 	5	H_2O suspension	IX	2.5%
	7	H_2O suspension	XIII	2.6%

Table IV. Structures and Physical Constants of Chlorinated Products of Epigenin

Compound Number	Structure	Molecular Formula	M. P.	Mass Spectrum
IX		$C_6H_2O_2Cl_2$	120-122	M/e 176 M^+ (100%) 141 M^+-35 (23%)
XIII		$C_6O_2Cl_4$	290-292	M/e 212 M^+ (100%)

Scheme 2

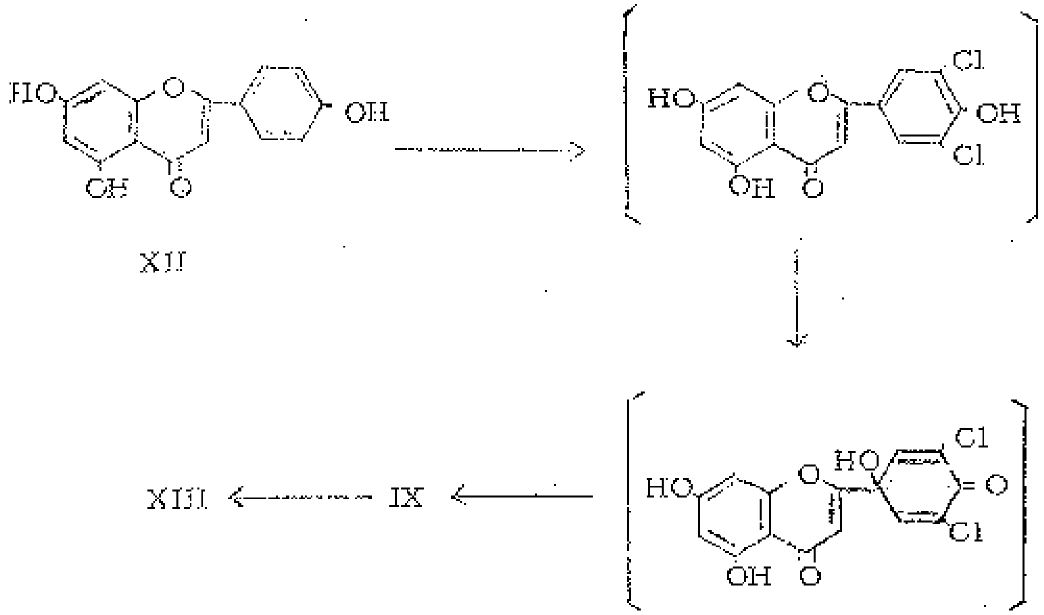


Table V. Chlorination of Tyrosine and its Derivatives

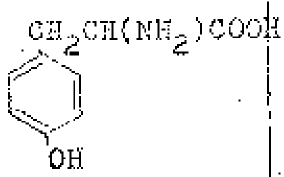
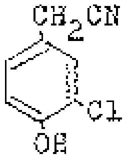
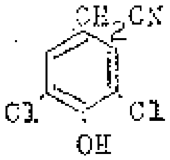
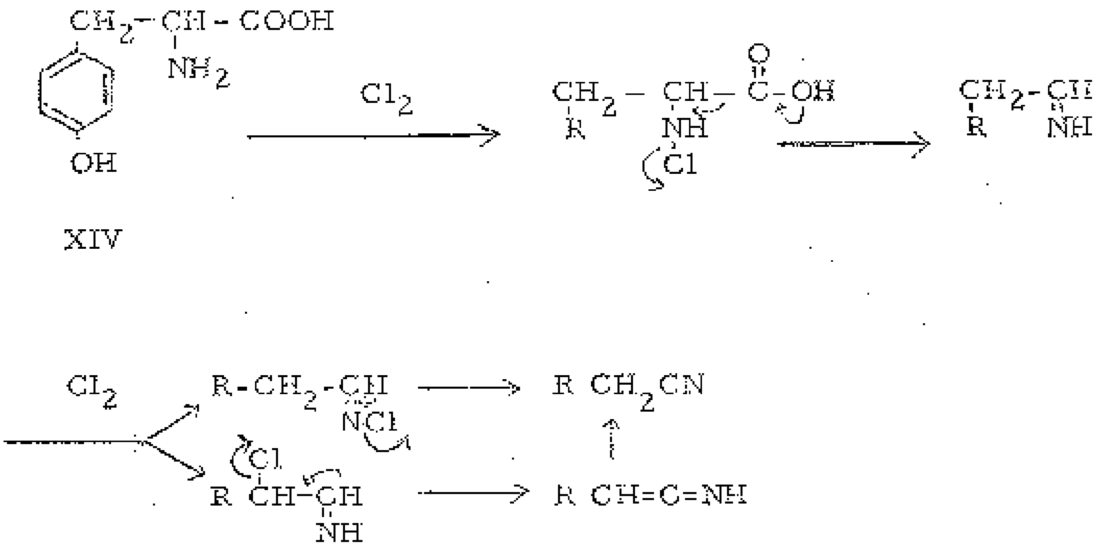
Phenolic Compounds	Chlorine Water (moles)	Solvent	Product	Approximate Percentage in total residue
L-Tyrosine (XIV)  	4	H_2O	XVI XVII	12.8% 19.6%
N-Acetyl-DL-Tyrosine (XV)  	3	H_2O	Under investigation	

Table VI. Structures and Physical Constants of Chlorinated Products of L-Tyrosine

Compound Number	Structure	Molecular Formula	M. P.	Mass Spectrum
XVI		C_8H_6ClNO	102-103	M/e 167 M^+ (47%) 132 M^+-35(100%)
XVII		$C_8H_5Cl_2NO$	162-163	M/e 201 M^+ (38%) 166 M^+-35(100%)

Scheme 3


CH2 - CH - COOH
NH2
OH
Cl2
CH2 - CH - C - OH
R NH O
Cl
CH2 - CH
R NH
Cl2
R-CH2-CH
NCl
R CH2CN
Cl
R CH-CH
NH
R CH=C=NH

XIV

destination to chlorinated benzoquinone derivatives. One of the products, chloranil, is a synthetic herbicide which is being used widely.

Tyrosine afforded unexpected products. Contrary to the initial expectation that Strecker Reaction of the amino acid would give chlorinated aldehyde or acid derivatives, chlorinated nitriles were formed in fairly good yields. The bromo-isomers of such nitriles are naturally occurring antibiotics, and the similar activity is expected to these products.

It is very important to note that these reactions were shown to take place at a very dilute concentration. It implies a possibility that contact of foods or drink with water containing active residual chlorine can form the chlorinated compounds.

Significance of the formation of these polychlorinated compounds as a result of chlorination is still to be investigated. However, most chlorinated phenols are known to possess strong physiological activities including toxicities. Also, due to their strong antimicrobial activities, chlorination may be giving strong secondary effects on microorganism flora in water. The fate of those chlorinated molecules in water; the rate of degradation, accummulation in biological systems, etc. is yet to be studied.

(B) Publication and Report

Y. Shimizu and R. Y. Hsu, Fate of Organic Molecules I, Effects of Chlorination on Cinnamic Acid Derivatives in Water, to be presented at American Society of Pharmacognosy at Columbus, Ohio, July 22, 1972.

(C) Project Status

Project will continue for next fiscal year.

(D) Application of Research Results

This research will be helpful to evaluate chlorination method in the treatment of water contaminated with organic materials of natural and artificial origins.

(E) Work Remaining and Progress Contemplated During Next Year

1) Evaluation of biological activities of the isolated chloro-compounds is now under progress and will continue. The work involves a study of the effects of the compounds to experimental animals and micro-organisms.
2) Further investigation of the chlorination products known to exist in water.
3) Analysis of phenolic materials in water before and after chlorination.

Because of the very interesting preliminary results, the work seems to expand more than planned originally.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-043-RI

Agreement No. 14-31-0001-3540

FCST-COWRR Research Category: VD

Project Title:

Improvements in primary oil-water separation through droplet size Control.

Name and Location of University Where Project is Being Carried Out:

Brown University, Providence, R. I. 02912

Proj. Began--Month: July ; Year: 1971

To Be Completed--Month: June ; Year: 1972

Principal Investigators	Degree	Discipline
R. I. Tanner	Ph.D.	Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
R. W. Fisk	Sc.B.	Engineering

(A) Research Project Accomplishments

A survey of methods of assessing oil droplet sizes was made and it became clear that the most convenient method was the Coulter counter. (Some preliminary work using direct counting from a photographed microscope slide was made for comparitive purposes, but it does not seem that this tedious method is suitable for more complex investigations such as the present one).

We attempted to verify the accuracy of our Coulter counter and immediately found that it was very difficult to obtain satisfactory size distributions even from the suppliers "mono-sized" calibration samples (blood, pollen). Eventually it became clear that only about 8% accuracy (not 2% as advertized) on sample sizing can be achieved. Much better results on calibration were obtained by using polystyrene latex spheres which have a very well defined diameter of 3.195 microns. With these particles we obtained the required single-spike calibration. It is felt that the effort expended in obtaining proper calibration is necessary because otherwise one is faced with some complex data reduction problems.

After considerable testing we found that the calibration of the Coulter counter was highly time dependent. The settling processes occurring in the calibration sample tended to lessen the counts at any window with increasing time. This was especially evident with the larger diameter pollen specimens, and therefore a low speed stirrer was designed to maintain a steady state emulsion.

The problems involved with the stirrer were threefold. First, the impellor and shaft must be non-metallic, as metal would act as an antenna and receive undesirable noise. Second, the driving device, if electrical, had to be sufficiently distant from the apparatus so as not to introduce electrical interference. Lastly, the shaft could not be supported by the test apparatus as the vibrations introduced would seriously effect the internal resistances producing large scale error.

The low speed, flexible shaft stirrer produced a steady state emulsion. The exact rotational speed of the impellor to obtain a constant count at any window was about 30 rev/minute.

A standard oil-water emulsion has been generated by high pressure water spraying. Drop diameter against count frequency graphs have been made and the dependence investigated for water/oil emulsions. Under similar conditions, a dilute polymer solution has been used to generate comparable emulsions. The addition of the polymer shifts the mean diameter and lowers the number of particles at each window.

(C) Project Status

The project is comoleted (in its preliminary stages) but further work is planned. The Sc.M. thesis of R. W. Fisk will contain final details of the project.

(D) Work Remaining

We have yet to examine practical asoects of drop size control for tank washing operations. This will be done in the next three months as part of R. W. Fisk's thesis.

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ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-044-RI

Agreement No. 14-31-0001-3540

FCST-COWRR Research Category: V C

Project Title:

Interception and Degradation of Pesticides by Aquatic Algae

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: April ; Year: 1972 | To Be Completed--Month: June ; Year: 1973

Principal Investigators	Degree	Discipline
Leonard R. Worthen	Ph.D.	Pharmacognosy-Microbiology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Technician		
Steven Zelenski	B.S.	Pharmacognosy

Narrative Statements

A. Research Project Accomplishments

A number of bodies of fresh water in Rhode Island have been examined in an attempt to obtain an overview of the interrelationship between general pollution runoff, localized use of pesticides (by interview with neighboring farmers) and the presence or absence of any Cyanophyta.

Seventeen samples representing twelve widely dispersed areas were collected during the summer of 1971. In only one of these was a specimen of a Cyanophytan found. It was indicated by the end of the summer that a better picture could be obtained by collecting many samples in a restricted area.

During the past several months, 48 sites have been examined in the southern Rhode Island area for blue-green algae. To date, they have been found at nine of these areas and samples have been collected and are currently being examined for their pesticide content. Due to an excessively wet and cold spring the usual bloom of the Cyanophyta has been delayed.

The second part of the project, involves the rates and selectivity of uptake of C^{14}-DDT and C^{14}-Dieldrin by various Cyanophytan cultures. The initial phase of this work undertaken has involved the development of optimum culture conditions and the isolation of pure cultures of local species of blue-green algae.

B. Publications

None to the present time.

C. Project Status

This project will continue for one more year (June 30, 1973).

D. Application of Research Results

Undoubtedly one of the big questions concerning pesticides involves their persistence in the environment and the need to know how they may be naturally degraded as a means of reducing the amounts present. Organisms such as blue-green algae may be able to reduce the levels of accumulation even if only slowly requiring a long period of time. The results of this research will hopefully contribute to such knowledge.

E. Work Remaining and Progress Contemplated During Next Year

During the next two months repeated samplings will be conducted in southern Rhode Island in order to determine whether there will be a bloom of blue-green algae this year. If not, samples of green algae will be collected to ascertain their pesticide levels. This will be correlated with the proximity of the bodies of water in which they were found to adjacent land upon which pesticides have been employed.

The major emphasis of the research will be on the culture experiments to determine the fate of labelled DDT and Dieldrin in unialgal and mixed algae cultures. This will involve the feeding of the isotopes to the cultures and the subsequent examination of the labelled products of metabolism.

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ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-022-RI Agreement No. 14-31-0001- 3125 FCST-COWRR Research Category: VI G	Project Title: Potential Benefits of Integrating a New Community and a Power Reactor with Special Reference to the Water Ecology

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R. I. 02881

Proj. Began--Month: July ; Year: 1969 | To Be Completed--Month: Sept. ; Year: 1971

Principal Investigators	Degree	Discipline
Dieter Hammerschlag	B.Arch., M.C.P.	Urban Design
Vincent C. Rose	Ph.D.	Associate Professor of Nuclear and Ocean Engineerin College of Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background

RESEARCH PROJECT ACCOMPLISHMENTS

The final report was completed and 355 printed copies of "Nuclear Energy for a New Town", 60 pages, was sent out.

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ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-026-RI

Agreement No. 14-31-0001-3338

FCST-COWRR Research Category: V C

Project Title:

Periphyton and Phytobenthon as Indicators of Water Quality

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: July ; Year: 1970

To Be Completed--Month: June ; Year: 1972

Principal Investigators	Degree	Discipline
Richard D. Wood	Ph.D.	Botany

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Louis Ventura	B.S.	Botany

RESEARCH PROJECTS ACCOMPLISHMENTS

The work previously conducted showed that the chemical-physical tests detected changes in water quality in the vicinity of the industrial outfalls, that the relationship among the variables could be measured by computer-processed correlation coefficients, that the periphyton which grew on submerged slides in a two-week period differed in total flora in different rivers, that the change (reduction) in total periphyton flora below the outfall was greater in the case of the more polluted river, that the periphyton flora was greater in the river with the higher domestic pollution (as shown by elevated coliform counts), and that certain genera of periphyton appeared to be restricted to upstream cleaner water while others seemed restricted to downstream more contaminated water.

Work on Saugatucket River in the Peacedale area, R.I., was continued for the second year, while efforts on Hunt River were discontinued because upstream-downstream differences in factors and periphyton were insufficient (Wood, 1972: 34, Tab. 1, 35, Tab. 3). In place of it, the Pawcatuck River at Kenyon, where another textile dying industry is located, was investigated.

During this year, efforts were made to streamline the sampling and analyzing programs, to perfect a routine for biological analysis, to increase the sensitivity of the chlorophyll pigment concentration measurement, to push ahead with identification of algae, to test the method in two pairs of river stations, and to determine whether periphyton and phytobenthon can offer a feasible indicator for water quality.

The field testing program was nearly the same as that done last year, but measurement of light intensity was omitted. Instrumental changes were 1) Hach turbidimeter replacing Hach colorimeter, 2) Beckman Solu Bridge replacing home-assembled research conductivity bridge unit, 3) Hellige color measuring unit replacing Hach colorimeter and the use of spectrophotometer readings on raw water. Tests were run more frequently during active seasons, but in all cases were recorded no less than once a month. The details of these and subsequent procedures are as described by Wood (1970). The data for the rivers are summarized in Tables 1, 2, 3, and 4.

Biological sampling was done on 2-week-immersed glass slides, and study in all cases included fresh examination at 100X (later at 400X as a water immersion lens became available), a duplicate slide was permatized by Karo solidification, and a scraped sample was acid-cleaned for diatoms which were mounted in hyrax for examination by phase contrast microscopy. Counts on four fields were made, omitting a Sedgwick-Rafter chamber count of a blended sample, but this proved to be an error which is being corrected. A set of type slides has been assembled, with marked individual specimens; and these vouchers have been recorded by photomicrography.

Pigment measurements on acetone extracts were not sufficiently accurate with a Spectronic 20, a longer light path (10 cm) being needed. Measuring with the Turner fluorometer increased the sensitivity some tenfold and shows linearity

TABLE 1

Monthly values of chemical-physical, hydrologic and coliform data for 1971/72 at the upstream station ("Pawk A") in the Pawcatuck River at Route 2, Kenyon, R.I.

	March	April	May	June	July	August
Temperature, C	2.0	9.1	13.0	19.0	22.3	25.2
pH	5.28	6.10	5.85	6.10	6.25	6.15
Alkalinity, ppm	0.7	2.7	2.5	4.4	6.0	4.1
Dissolved oxygen, ppm	9.72	8.64	7.62	5.20	4.20	4.04
% oxygen saturation	-	75	72	55	52	49
Conductivity, μ mhos	55	71	-	80	97	90
PO_4, ppm	-	0.008	0.026	0.091	0.076	0.071
NO_3, ppm	-	0.000	0.000	0.000	0.128	-
Color	60	65	100	130	80	80
Turbidity, JTU	-	-	-	-	3.1	-
Velocity, ft/sec	-	-	0.35	0.55	0.39	0.39
Discharge, ft^3/sec	-	-	113.96	85.84	56.67	56.63
Coliform, cells/100 ml	-	336.8	-	2,496.1	3,095	3,215

(continued)

TABLE 1 (Continued)

	September	October	November	December	January	February
Temperature, C	19.0	13.0	3.2	3.0	0.0	0.0
pH	6.41	6.41	6.60?	5.88	5.20	5.30
Alkalinity, ppm	6.2	4.1	5.0	1.8	1.4	1.2
Dissolved oxygen, ppm	6.03	6.40	11.20	10.40	11.04	10.80
% oxygen saturation	65	60	83	-	-	-
Conductivity, µ mhos	90	99	115	93	91	70
PO_4, ppm	0.028	0.002	0.010	0.021	0.017	0.008
NO_3, ppm	0.407	0.191	0.518	0.000	0.226	0.010
Color	35	50	30	60	40	15
Turbidity, JTU	-	-	-	1.0	1.0	1.0
Velocity, ft/sec	0.20	0.22	0.14	0.37	0.61	1.22
Discharge, ft^3/sec	27.94	30.78	20.34	62.80	105.05	232.5
Coliform, cells/100 ml	2,200	3,379	1,222	60	111	104

TABLE 2

Monthly values of chemical-physical, hydrologic and coliform data for 1971/72 at the downstream station ("Pawk C") in the Pawcatuck River ca. 30 yd below railroad bridge, Kenyon, R.I.

	March	April	May	June	July	August
Temperature, C	-	9.6	12.7	19.3	22.5	24.8
pH	-	6.60	5.75	6.28	6.49	6.87
Alkalinity, ppm	-	5.5	2.8	6.0	9.5	8.4
Dissolved oxygen, ppm	-	9.20	7.46	6.30	6.06	5.06
% oxygen saturation	-	80	69	68	68	70
Conductivity, µ mhos	-	74	-	89	118	120
PO_4, ppm	-	0.020	0.042	0.103	0.176	0.067
NO_3, ppm	-	0.000	0.000	0.000	0.289	-
Color	-	105	110	135	100	85?
Turbidity, JTU	-	-	-	-	4.2	-
Velocity, ft/sec	-	-	0.50	0.39	0.34	0.64
Discharge, ft^3/sec	-	-	114.91	80.22	44.39	52.63
Coliform, cells/100 ml	-	5,777	-	14,824	12,800	37,734

(continued)

TABLE 2 (Continued)

	September	October	November	December	January	February
Temperature, C	21.0	14.5	3.7	3.4	0.0	0.0
pH	7.15	6.69	6.67	6.00	5.41	5.25
Alkalinity, ppm	13.9	7.6	6.0	2.0	1.6	1.0
Dissolved oxygen, ppm	7.92	7.14	11.39	10.80	11.66	11.60
% oxygen saturation	87	70	85	-	-	-
Conductivity, µ mhos	145	128	115	98	91	85
PO_4, ppm	0.154	0.011	0.050	0.054	0.033	0.027
NO_3, ppm	0.293	0.202	0.253	0.000	0.246	0.010
Color	-	55	35	75	45	45
Turbidity, JTU	-	-	-	1.0	1.0	1.2
Velocity, ft/sec	0.19	0.19	0.13	0.40	0.82	1.28
Discharge, ft^3/sec	37.11	37.16	25.68	86.49	186.9	310.5
Coliform, cells/100 ml	66,490	over 50,000	22,563	3,600	2,616	1,250

TABLE 3

Monthly values of chemical-physical, hydrologic and coliform data for 1971/72

at the upstream station ("Saug A") in the Saugatucket River at Saugatucket Road, Peacedale, R.I.

	March	April	May	June	July	August
Temperature, C	-	-	9.1	15.1	16.9	19.8
pH	-	6.20	5.89	6.13	6.59	6.31
Alkalinity, ppm	-	3.8	1.6	4.8	10.7	10.1
Dissolved oxygen, ppm	-	9.76	9.76	7.62	6.78	5.78
% oxygen saturation	-	78	84	80	69	64
Conductivity, μ mhos	-	77	69	90	136	120
PO_4, ppm	-	0.010	0.004	0.011	0.009	0.142
NO_3, ppm	-	0.126	0.019	0.190	-	0.613
Color	-	40	80	85	60	55
Turbidity, JTU	-	-	-	-	4.3	-
*Velocity, ft/sec	-	0.83	1.36	0.83	0.20	0.23
Discharge, ft^3/sec	-	9.816	21.198	10.782	1.727	1.550
Coliform, cells/100 ml	-	-	763	937	2,320	4,500

(continued)

TABLE 3 (Continued)

	September	October	November	December	January	February
Temperature, C	19.4	12.0	5.2	3.5	2.0	2.0
pH	6.40	6.61	6.697	6.10	5.99	5.40
Alkalinity, ppm	9.6	12.5	9.1	3.1	3.9	1.3
Dissolved oxygen, ppm	6.88	7.38	10.02	11.20	11.82	12.60
% oxygen saturation	74	68	78	84	85	91
Conductivity, µ mhos	100	130	120	103	98	100
PO_4, ppm	0.097	0.002	0.010	0.010	0.005	0.004
NO_3, ppm	0.533	0.517	0.700	0.219	0.652	0.104
Color	50	60	40	70	55	40
Turbidity, JTU	-	-	-	0.9	0.8	0.6
*Velocity, ft/sec	0.17	0.36	0.43	0.40	0.83	1.23
Discharge, ft^3/sec	0.974	3.023	3.035	5.310	8.410	21.88
Coliform, cells/100 ml	1,800	200	380	50	75	66

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* Velocity of water immediately above east conduit.

TABLE 4

Monthly values of chemical-physical, hydrologic and coliform data for 1971/72 at the downstream station ("Saug B") in the Saugatucket River ca. 100 ft below Palisades Ind., Peacedale, R.I.

	March	April	May	June	July	August
Temperature, C.	-	-	10.1	20.4	21.1	23.3
pH	-	6.4	6.3	6.45	6.71	6.52
Alkalinity, ppm	-	6.2	4.9	6.5	13.9	14.0
Dissolved oxygen, ppm	-	10.22	10.22	7.68	6.62	5.78
% oxygen saturation	-	87	90	84	73	67
Conductivity, μ mhos	-	170	130	140	188	239
PO$_4$, ppm	-	0.418	0.415	0.056	2.101	0.871
NO$_3$, ppm	-	0.094	0.082	0.386	-	0.657
Color	-	45	65	85	65	70
Turbidity, JTU	-	-	-	-	3.7	-
Velocity, ft/sec	-	0.90	1.33	1.66	0.40	0.63
Discharge, ft^3/sec	-	28.19	54.25	38.18	5.17	9.55
Coliform, cells/100 ml	-	-	over 50,000	24,000	over 50,000	over 50,000

(continued)

TABLE 4 (Continued)

	September	October	November	December	January	February
Temperature, C	22.0	12.0	6.2	5.6	4.0	1.0
pH	6.91	6.61	6.80	6.11	5.87	5.95
Alkalinity, ppm	22.2	14.9	14.9	3.6	3.5	2.5
Dissolved, oxygen, ppm	6.48	7.18	9.10	11.18	11.20	12.60
% oxygen saturation	73	68	73	88	85	68
Conductivity, μ mhos	245	130	260	140	168	140
PO_4, ppm	0.933	0.889	2.020	0.366	0.998	0.047
NO_3, ppm	0.445	0.839	0.083	0.028	0.309	0.130
Color	125	60	-	80	85	40
Turbidity, JTU	-	-	-	2.8	3.9	1.5
Velocity, ft/sec	0.70	0.46	0.33	0.76	0.93	2.13
Discharge, ft^3/sec	12.30	11.37	8.01	20.48	28.02	62.95
Coliform, cells/100 ml	over 50,000	over 50,000	over 50,000	over 50,000	over 50,000	over 50,000

with spectrophotometric measurements at low concentrations (Fig. 1). The results also appear to be independent of turbidity problems.

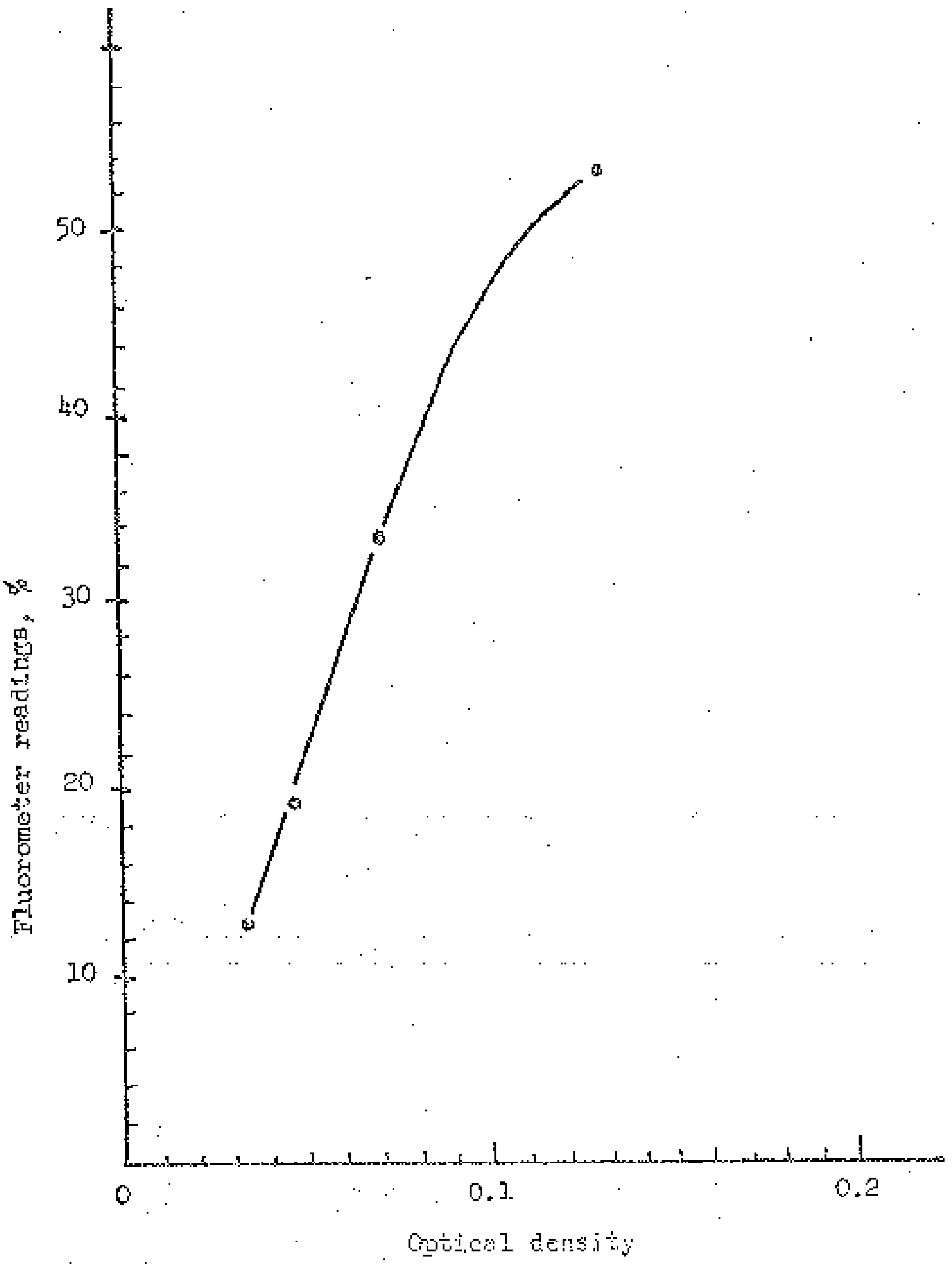

Figure 1   Relationship between fluorometer readings (% as 1 X window, sensitivity) and spectrophotometer optical density values. On 80% acetone extract of 1 in^2 surface of periphyton slide (71-9-2-3, Saug B)

Identification of periphyton was pushed ahead with the gracious preliminary refresher training by Dr. Hannah Croasdale (Dartmouth College) on desmids, Dr. G. W. Prescott (Montana) for general algae, and Drs. Ruth Patrick and C. W. Reimer (Philadelphia) on diatoms. In a totally independent effort, the literature was searched, and published records of freshwater algae of the Northeast in the vicinity of Rhode Island were compiled. Over 1300 taxa have been entered, and a computer printout is assembled. When completed, the card set (or tape file) will print out either alphabetically or systematically. For the present project, the regular collections have been analyzed while fresh, and later studied critically to identify all forms possible. A flora of somewhat over 150 species has been named for the river stations (Table 5).

TABLE 5

Periphyton algae found at the study stations in the Pawcatuck and Saugatucket Rivers, Kenyon and Peacedale, R.I., during 1970-71. Unconfirmed taxa are marked "?", and usually are those not yet reported from the Northeast.

Achnanthes lanceolata (Breb.) Grun. in Cl. & Grun.

A. ?*linearis* (W.Sm.) Grun. in Cl. & Grun. var. *pusilla* Grun.

A. *minutissima* Kutz.

A. ?*pinnata* Hust. in Hedin.

A. ?*peragalli* Brun & Herib. in Herib. var. *fossilis* Temp. & Perag.

A. sp. #1

A. sp. #2

Actinastrum hantzschii Lagerh. var. *fluviatile* Lemm.

Amphora pediculus Grun. var. *minor* Grun.

Anabaena sp. #1

A. sp. #2

(continued)

TABLE 5 (Continued)

Ankistrodesmus falcatus (Corda) Ralfs

Anomoeoneis ?serians (Breb. ex Kutz.) Cl. var. *brachysira* (Breb. ex Kutz.) Hust. in Pasch.

A. vitrea (Grun.) Ross in Patr. & Reim.

Asterionella formosa Hass.

Caloneis ?oregonica (Ehr.) Patr. in Patr. & Reim. var. *quadrilineata* (Grun. ex Cl.) Patr. in Patr. & Reim.

Closterium cynthia De Not.

C. dianae Ehr.

C. kuetzingii Breb.

C. moniliferum (Bory) Ehr.

C. regulare Breb.

C. venus Kutz.

Cocconeis placentula Ehr.

C. ?rugosa Sov.

Coleochaete orbicularis Pringsh.

C. sp. #1

Cosmarium nitidulum De Not.

C. reniforme (Ralfs) Arch.

C. sp. #1

Cyclotella stelligera Cl. & Grun.

Cymatopleura solea (Breb.) W. Sm.

Cymbella affinis Kutz.

C. hauckii van Heurck

C. naviculiformis Auerswald

C. ventricosa Kutz.

(continued)

TABLE 5 (Continued)

Euastrum oblongum (Grev.) Ralfs

Eudorina elegans Ehr.

Euglena sp.

Eunotia ?carolina Patr.

E. curvata (Kutz.) Lagerst.

E. ?elegans Østr.

E. exigua (Breb. ex Kutz.) Rabh.

E. flexuosa Breb. ex Kutz.

E. formica Ehr.

E. hexaglyphis Ehr.

E. incisa W. Sm. ex Greg.

E. ?naegelii Mig. in Thome

E. pectinalis (O.F.Mull.) Rabh.

E. pectinalis var. *biarcuata* A. Berg.

E. pectinalis var. *minor* (Kutz.) Rabh.

E. serra Ehr. var. *diadema* (Ehr.) Patr.

E. tautoniensis Hust. ex Patr.

E. ?valida Hust. in Pasch.

E. vanheurckii Patr. var. *intermedia* (Krasske ex Hust. in Rabh.) Patr.

Fragilaria constricta Ehr.

F. construens (Ehr.) Grun. var. *binodis* (Ehr.) Grun.

F. crotonensis Kitton

F. ?sinuata M. Perag. in Temp. & Perag.

F. virescens Ralfs

F. sp. #1

Frustulia rhomboides (Ehr.) DeT.

F. rhomboides var. *capitata* (A.Mayer) Patr. in Patr. & Reim.

F. vulgaris (Thwaites) DeT.

(continued)

TABLE 5 (Continued)

Gloeotheca sp. #1

Golenkinia sp. #1

Gomphonema acuminatum Ehr. var. *coronata* (Ehr.) W. Sm.

G. angustatum (Kutz.) Rabh. var. *producta* Grun.

G. constrictum Ehr. var. *cuneata* A. Schmidt

G. gracile Ehr.

G. parvulum Kutz.

G. sphaerophorum Ehr.

Hyalotheca dissiliens (Sm.) Breb.

Melosira ambigua (Grun.) O. Mull.

M. granulata (Ehr.) Ralfs

M. granulata var. *angustissima* O. Mull.

Meridion circulare (Grev.) Ag. var. *constricta* (Ralfs) van Heurck

Microcystis ?*flos-aquae* (Wittr.) Kirchn. (*Anacystis cyanea* Dr. & Dail.)

Mougeotia sp. #1

M. sp. #2

M. sp. #3

M. sp. #4

Navicula ?*anglica* Ralfs

N. crucicula W. Sm.

N. cryptocephala Kutz.

N. elginensis (Greg.) Ralfs

N. minima Grun.

N. ?*mutica* Kutz.

N. pupula Kutz. var. *capitata* Hust.

N. rhynchocephala Kutz.

Neidium iridis (Ehr.) Cl. var. *amphigomphus* (Ehr.) A. Mayer (continued)

TABLE 5 (Continued)

Nitzschia acicularis W. Sm.

N. obtusa W. Sm. var. *scalpelliformis* Grun.

N. plana W. Sm. var. *americana* Hust. in A. Sm.

N. scalaris (Ehr.) W. Sm.

N. sublinearis Hust.

N. vermicularis (Kutz.) Grun.

N. sp. #2

Oedogonium sp. #1

O. sp. #2

Oscillatoria princeps Vauch.

O. sp. #2

Pediastrum duplex Meyen var. *gracillimum* W. & W.

Phacus sp. #1

Pinnularia abaujensis (Pant.) Ross var. ?*rostrata* (Patr.) Patr. in Patr. & Reim.

P. abaujensis var. ?*subundulata* (A.Mayer ex Hust. in Pasch.) Patr. in Patr. & Reim.

P. acrosphaeria W. Sm.

P. acrosphaeria var. *turgidula* Grun. ex Cl.

P. acuminata W. Sm. var. ?*bielawskii* (Herib. & Perag.) Patr. in Patr. & Reim.

P. biceps Greg.

P. borealis Ehr.

P. braunii (Grun. in van Heurck) Cl.

P. brebissonii (Kutz.) Rabh.

P. flexuosa Cl.

P. formica (Ehr.) Patr. in Patr. & Reim.

P. hilseana Jan. in Hilse

(continued)

TABLE 5 (continued)

P. *legumen* (Ehr.) Ehr.

P. *maior* (Kutz.) Rabh.

P. *maior* var. *pulchella* Boyer

P. *mesogongyla* Ehr.

P. *mesolepta* (Ehr.) W. Sm.

P. *stomatophora* (Grun. in A.S.) Cl.

P. *subcapitata* Greg. var. *paucistriata* (Grun. in van Heurck) Cl.

P. *sudetica* Hilse

P. *termitina* (Ehr.) Patr. in Patr. & Reim.

P. *viridis* (Nitz.) Ehr.

Pleurotaenium *minutum* (Ralfs) Delp.

Protoderma ?*viride* Kutz.

Scenedesmus *bijuga* (Turp.) Lagerh.

S. *dimorphus* (Turp.) Kutz.

S. *quadricauda* (Turp.) Breb.

Schizothrix sp.

Selenastrum *westii* G. M. Sm.

Spirogyra sp.

Staurastrum sp. #1

S. sp. #2

Stauroneis *anceps* Ehr.

S. *phoenicenteron* (Nitz.) Ehr. f. *gracilis* (Ehr.) Hust. in Pasch.

Stigeoclonium ?*subsecundum* Kutz.

S. sp. #2

Surirella *angustata* Kutz.

S. *ovata* Kutz.

(continued)

TABLE 5 (Continued)

S. moelleriana Grun.

S. patella Ehr. var. *neupaueri* (Pant.) Cl.-Eul.

S. robusta Ralfs in Pritch.

S. sp.

Synedra amphicephala Kutz.

S. delicatissima W. Sm.

S. ?filiformis Cl. var. *exilis* Cl.-Eul.

S. ?incisa Boyer

S. ulna (Nitz.) Ehr.

Synura uvella Ehr.

Tabellaria fenestrata (Lyngb.) Kutz.

T. flocculosa (Roth) Kutz.

Tetraspora lubrica (Roth) C. Ag.

(A series of unidentified taxa are filed as Sp. xx, Sp. x1, Sp. x3, Sp. x6, Sp. x8, Sp. x9, Sp. x10, Sp. x12, Sp. x14, Sp. x15, Sp. x16.)

(A series of questionable organisms, largely nonalgal, are filed as unknowns A through V)

It became apparent that the population, though routinely similar in appearance and density, changed with the season. The periphyton records were therefore scanned, and a sequence of seasonal populations was detected (Table 6).

TABLE 6

Seasonal periodicity among the more prevalent periphyton species in 1971, on slides in the Pawcatuck and Saugatucket River study areas, Kenyon and Peacedale, R.I.

Permanent flora (present throughout the year):

Achnanthes linearis var. *pusilla*
Cocconeis placentula
Eunotia elegans
E. pectinalis
E. pectinalis var. *biarcuata*
E. pectinalis var. *minor*
Fragilaria virescens
Gomphonema angustatum var. *producta*
Melosira ambigua
Meridion circulare var. *constricta*
Nitzschia sublinearis
Pinnularia biceps
Stigeoclonium subsecundum (prostrate colonies)
Tabellaria fenestrata
T. flocculosa

Spring flora (increasing in spring, some (marked S or F) continuing into the summer and/or fall):

Asterionella formosa +S
Coleochaete sp. #1 +S,F
Cymbella ventricosa
Eunotia elegans
E. exigua
Fragilaria crotonensis
Gloeothece sp. #1
Gomphonema acuminatum var. *coronata* +F
G. parvulum +S,F
Melosira granulata
Navicula mutica
Pinnularia viridis
Scenedesmus quadricauda
Surirella sp. +S

Summer flora (increasing in summer, some (marked F) continuing into fall):

Achnanthes lanceolata
Coleochaete orbicularis
C. sp. #1 +F
[illegible]
Navicula cryptocephala
Nitzschia vermicularis +F
Oscillatoria princeps +F
O. sp. #2

(continued)

TABLE 6 (Continued)

Fall flora (increasing in fall, some (marked Sp) continuing into spring):

Achnanthes minutissima

Cymbella ventricosa +Sp

Eunotia incisa

Navicula rhynchocephala

The recognition of the seasonal aspect of these species is important in evaluating the significance to be attached to those not represented in a particular sample.

The periphyton data were searched to detect which species were restricted to cleaner water above the pollution outfall and which to dirtier water below the effluent release site. Nine such taxa were found (Table 7) and constitute indicator species for textile mill effluent.

TABLE 7

Indicator periphyton species, or those restricted to slides upstream or downstream from the textile dyeworks outfalls in the Pawcatuck and Saugatucket Rivers, Kenyon and Peacedale, R.I.

I. Clean water species, restricted to area above the pollution outfall:

- *Achnanthes lanceolata*
- *Closterium moniliferum*
- *C. venus*
- *Gomphonema gracile*
- *Oedogonium* sp. #1

II. Dirty water species, restricted to area below the pollution outfall:

- *Nitzschia obtusa* var. *scapelliformis*
- *Scenedesmus bijuga*
- *S. dimorphus*
- *S. quadricauda*

Of these sensitive species, two which are both sufficiently common and easily recognized (and noticeable among the mass of other algal cells) to be practical indicators for textile mill effluent are Scenedesmus dimorphus and S. quadricauda.

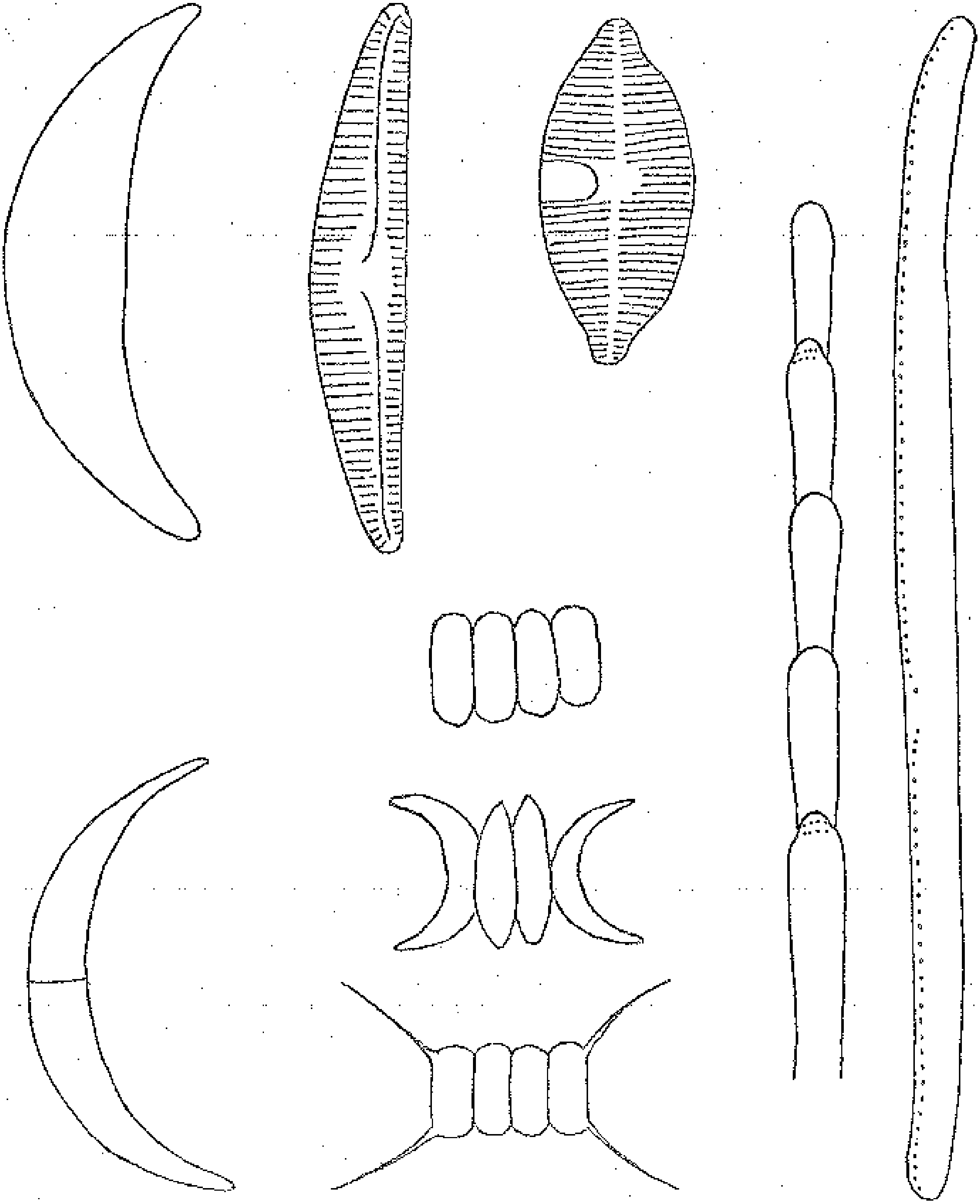

Figure 2 Indicator species for local textile mill effluent: 1. *Closterium moniliferum*, 2. *Gomphonema gracile*, 3. *Achnanthes lanceolata*, 4. *Closterium venus*, 5. *Scenedesmus bijuga*, 6. *S. dimorphus*, 7. *S. quadricauda*, 8. *Oedogonium* sp., 9. *Nitzschia obtusa* var. *scalpelliformis*

Computer analysis of relationship among the factors (Table 8) as well as among periphyton species and also among factors and species was undertaken. The program is expanded to handle 50 variables and 50 observations, thus allowing combined analysis.

TABLE 8

Summary of more significant correlations among chemical-physical factors, including coliform count, calculated from data from the upstream station of the Pawcatuck River at Kenyon for 1971. Values are correlation coefficients, r; and r = 1.00 at perfect agreement.

I

Factor	r =
Temperature:	
coliforms	.784
light	.779
phosphates	.710
alkalinity	.660
pH	.611
color	.610
discharge	-.525
dissolved oxygen	-.974
pH:	
alkalinity	.898
conductivity	.625
discharge	-.797
Color:	
day length	.805
phosphates	.679
temperature	.610
nitrates	-.609
dissolved oxygen	-.625

Factor	r =
Discharge:	
nitrates	-.609
alkalinity	-.765
pH	-.797
conductivity	-.842
Dissolved oxygen:	
color	-.625
phosphates	-.627
coliforms	-.760
temperature	-.974
Coliforms:	
phosphates	.790
temperature	.784
day length	.645
color	.593
dissolved oxygen	-.760

(continued)

TABLE 8 (Continued)

Factor	r =
Day length:	
color	.805
temperature	.779
coliforms	.645
phosphates	.627
dissolved oxygen	-.763

II

Factor	r =
Day length versus temperature:	
coliforms:	
temperature	.764
day length	.645
phosphates:	
temperature	.779
day length	.627

From these data, it can be seen that temperature, coliforms and phosphates have a common value and peak in the heat of the summer. Their peaking in summer is related inversely to discharge; thus, a low volume of flow exaggerates the pollutants. The light-related process of photosynthesis appears not to be very effective since dissolved oxygen shows higher correlation with temperature than day length.

In conclusion, chemical-physical, hydrological, and biological data for upstream and downstream stations from textile mill effluent sources have been obtained; interrelationships among the factors have been quantitatively evaluated; a list of algal taxa of the stations has been compiled, and to a sizeable degree identified; the seasonal progression of algae in these habitats has been tabulated; and nine indicator species which are restricted to either upstream or downstream stations have been detected. Among these, the species of cleaner upstream water were *Achnanthes lanceolata*, *Closterium moniliferum*, *C. venus*, *Gomphonema gracile*, and *Oedogonium* sp. #1; while those of more polluted downstream water were *Nitzschia obtusa*, *Scenedesmus bijuga*, *S. dimorphus*, and *S. quadricauda*. The last two, *S. dimorphus* and *S. quadricauda*, are suggested as practical indicator species. It is thus shown that periphyton algae can provide a feasible indication of water quality.

REFERENCES CITED

Wood, R. D. 1970. Hydrobotanical methods. Available at Bookstore, University of Rhode Island, Kingston. 176 p.

Wood, R. D. 1972. Periphyton and phytobenthos as indicators of water quality. Rhode Island Water Resources Center, 7th ann. rept., pp. 33-36.

PUBLICATIONS:

None

PROJECT STATUS:

The work on this project was completed as of June 30, 1972. A completion report is being prepared and will be submitted in the near future.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-028-RI

Agreement No. 14-31-0001-3329

FCST-COWRR Research Category: VIII A

Project Title:

Diffusion of Thermally Buoyant Water Jets Into a Moving Water Stream

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R.I.

Proj. Began--Month: July ; Year: 1970

To Be Completed--Month: June ; Year: 1972

Principal Investigators	Degree	Discipline
Frederick L. Test	Ph.D	Mechanical Engineering
Warren M. Ragist	M.S.	Mechanical Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Alexander J. Patton	M.S.	Mechanical Engineering

[illegible]

The project was completed during the past year which was the second year of a two-year project. An analytical model has been developed which predicts the behavior of warm water discharges in moving water streams when the discharge is in the form of a slot jet.

Analytical Model

The analytical model is based on an integral technique for which it is necessary to assume a velocity profile. The velocity profile is skewed about the jet centerline and takes on the following form:

$$u(r,s) = U_a \cos\theta + u(s)\, e^{-r^2/b^2} \quad \text{above the centerline} \; - - \; (1)$$

and

$$u(r,s) = U_a \cos\theta + u(s)\, e^{-r^2/b^2} - (r^2/2b^2)\, U'_a \cos\theta \quad \text{below the centerline} \; - - \; (2)$$

All of the terms are defined in the nomenclature.

A similar form is used for the density profile and these equations are then used in the integral form of the continuity, momentum and energy equations. The momentum equation for the x-direction is of particular interest and has the following form:

$$\frac{d}{ds}\left[\int_{0}^{\sqrt{2}b} \rho(r,s)\ u(r,s)\ (u(r,s)\cos\theta)\ dA\right] = \alpha b\ \rho_a\ U_a \left[U_a^2 \sin^2\theta + u(s)^2\right]^{1/2}$$

$$+ C_f\ \rho_a\ U_a^2 \sin^3\theta\ \sqrt{2}b \qquad -\ -\ (3)$$

There are two parameters in this equation, α and C_f, which must be obtained by matching the results of this equation to the experimental data. From the application of the results of the integral equation to the experimental data it is possible to obtain relations for α and C_f as a function of V_j/V_c for a particular entrance angle. It is also necessary to know the jet half-width and angle at the end of the zone of establishment. The zone of establishment extends eight jet entrance widths beyond the jet inlet. This information can be obtained from the experimental data as a function of V_j/V_c and jet entrance angle. Figures 1 and 2 show the agreement between experimental and analytical results for a 90° jet angle and a 30° jet angle, respectively.

Curves for α and C_f in addition to initial conditions at the end of the zone of establishment are given in reference 1. A computer program to determine jet behavior is also given in reference 1.

Thermal Stratification

The previous section discussed the modeling of the jet behavior as the jet expanded and was carried downstream with the moving stream. Under certain conditions the jet will tend to stratify on the surface and move upstream against the flowing main stream. This will tend to happen more readily when the velocity of the main stream is very low. The movement of warm water upstream along the surface is known as a "thermal wedge" and the correct modeling parameter is the densimetric Froude number which is defined as:

$$F_d = \frac{V_c}{\sqrt{g\Delta\rho/\rho_c}} \qquad -\ -\ (4)$$

The terms are defined in the nomenclature but the $\Delta\rho$ term should be discussed. This term represents the magnitude of the density difference between the ambient main stream and the main stream after it has been thoroughly mixed with the jet. Fig. 3 shows isotherms when a thermal wedge has just begun to form. The temperature indicated is the temperature excess above the ambient main stream temperature. Fig. 3 corresponds to a channel velocity of 0.067 ft/sec and a 90° jet angle with a velocity of 0.57 ft/sec. The jet inlet temperature was 38.5°F above the ambient main stream. The results of the study indicate that a thermal wedge will form when the densimetric Froude number is less than 0.7. This criteria is valid for both 90° and 30° jet injection angles.

NOMENCLATURE

A	Cross sectional area of the jet
b	Characteristic jet dimension, $\sqrt{2}b$ is the jet half-width
C_f	Dimensionless force coefficient
D	Jet gap
F_d	Densimetric Froude number (See Eq. 4.)
g	Gravitational acceleration
H	Channel depth
r	Distance measured perpendicular to jet axis
s	Distance along the jet axis
U_a	Ambient velocity
U_a'	A constant to give skewed effect to lower half of velocity profile
$u(r,s)$	Velocity of the jet
$u(s)$	Centerline velocity of the jet
V_c	Channel velocity
α	Entrainment coefficient
ρ_c	Density of the channel fluid
$\Delta\rho$	Density difference between the channel fluid and the downstream mixed fluid
θ	Angle of the jet centerline with the horizontal.

PUBLICATION:

BIBLIOGRAPHY

1. Patton, A. J., "Turbulent Thermal Diffusion of a Slot Jet Flowing into a Moving Stream," thesis submitted to the University of Rhode Island, Kingston, R.I., June 1972 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

PROJECT STATUS:

The work on this project was completed as of June 30, 1972. A completion report is being prepared and will be submitted in the near future.

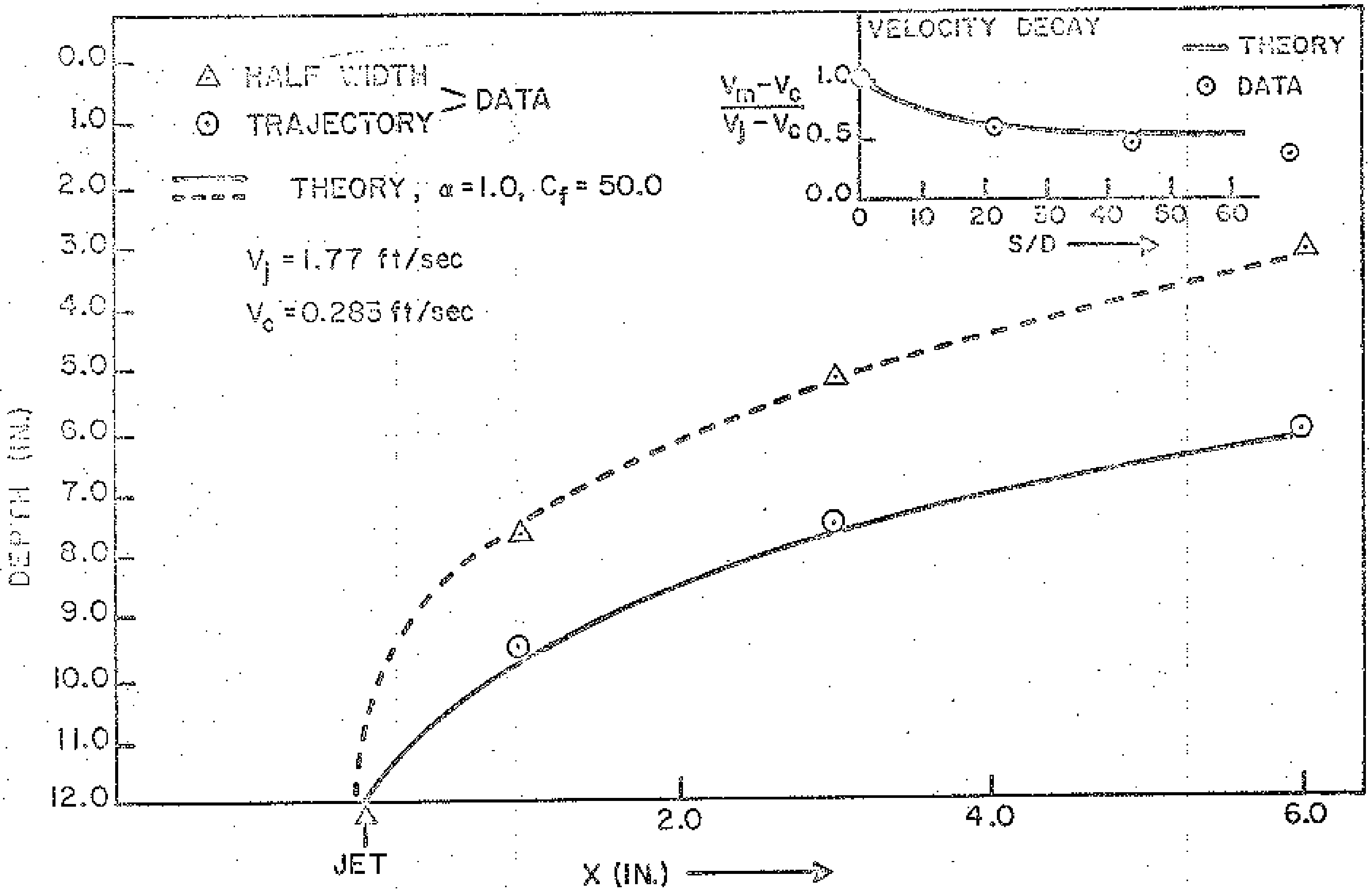

FIGURE 1 EXPERIMENTAL AND THEORETICAL TRAJECTORIES AND HALF WIDTHS

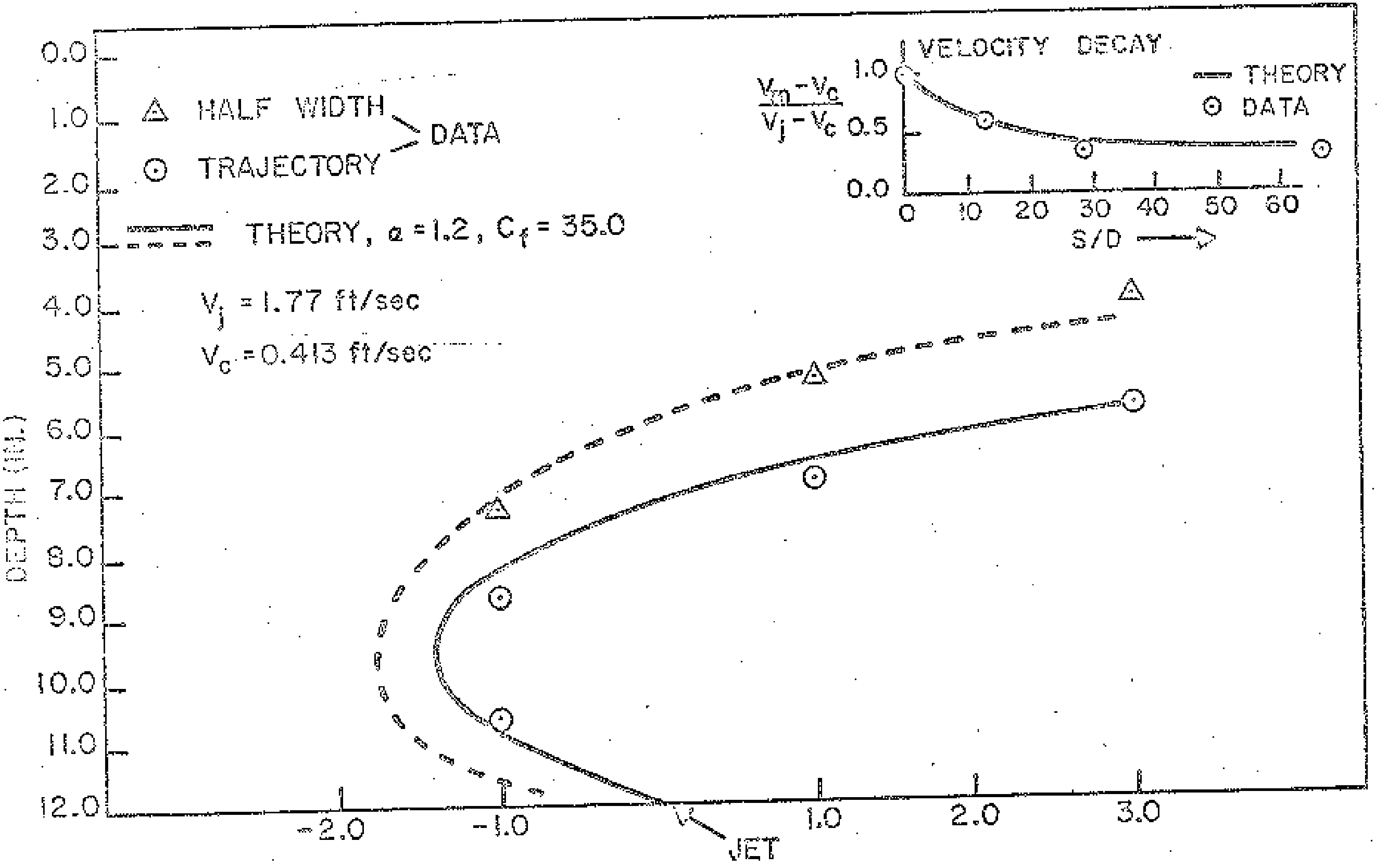

FIGURE 2 EXPERIMENTAL AND THEORETICAL TRAJECTORIES AND HALF WIDTHS

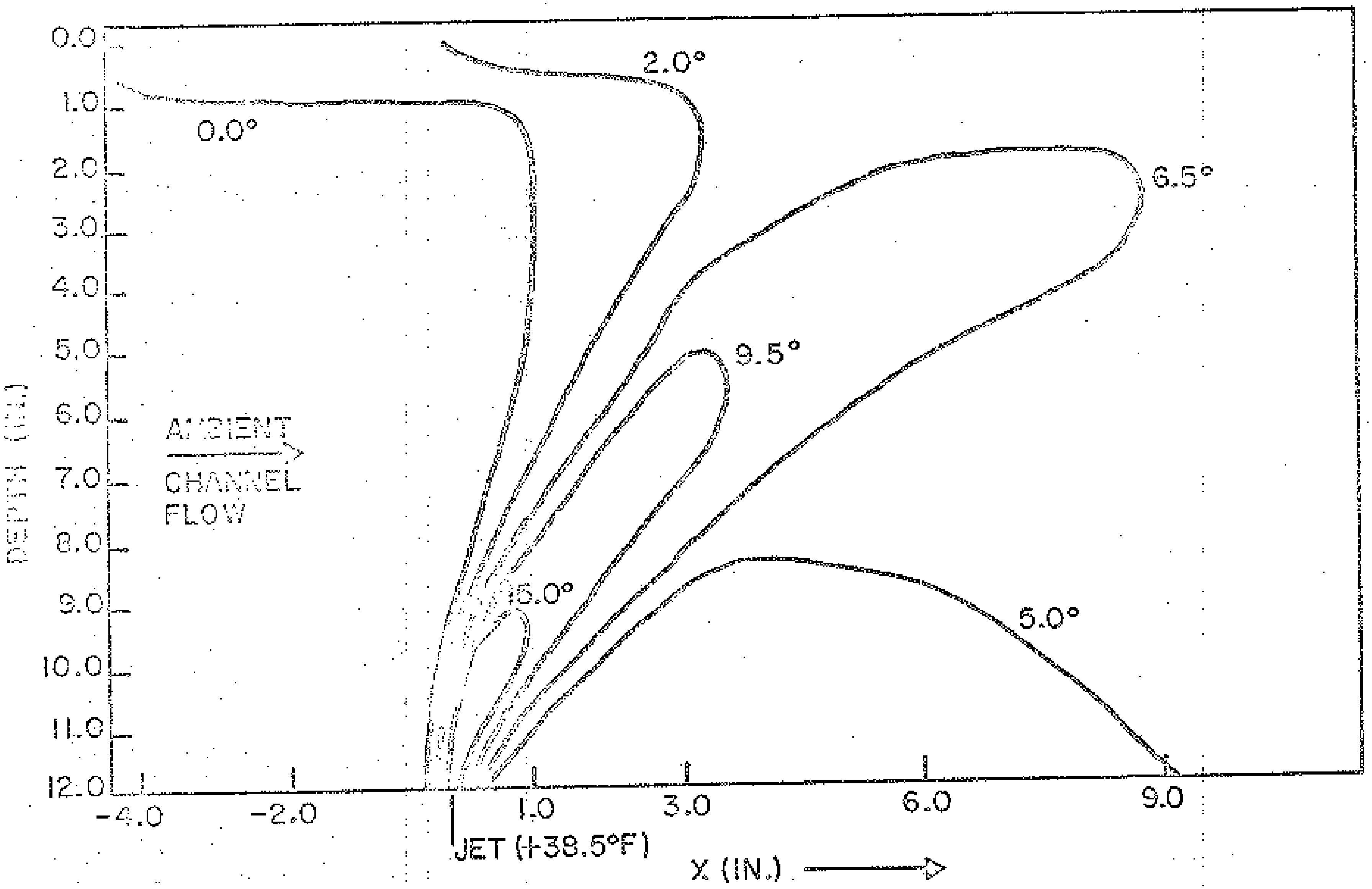

FIGURE 3 ISOTHERMS $F_d = 0.47$

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-033-RI

Agreement No. 14-31-0001-3640

FCST-COWRR Research Category: V D

Project Title:

Biological Degradation of Hydrocarbons In Water

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R. I. 02881

Proj. Began--Month: July ; Year: 1971 To Be Completed--Month: June ; Year:1

Principal Investigator	Degree	Discipline
Chester W. Houston	Ph.D.	Bacteriology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Satish Velankar	M.S.	Chemical Engineering
Peter Paolella	Ph.D.	Bacteriology

RESEARCH PROJECT ACCOMPLISHMENTS:
Narrative Statements.

This project is concerned with the effects of the dissolved oxygen and carbon dioxide concentrations on cultural parameters of hydrocarbon degradation. The oxidation of n-heptane by a strain of *Pseudomonas aeruginosa* which was previously isolated in this laboratory is being studied. Early work of the project was the determination of the aeration capacity of the fermentor (New Brunswick Scientific Company Microferm Fermentor, Model MF 105, modified for an agitation rate of 1500 RPM). The Oxygen Transfer Rate (O.T.R.), a measure of aeration capacity, was determined by three methods: 1) the sulfite oxidation method (Cooper *et al.*, 1944), 2) the glucose oxidase method (Hsieh *et al.*, 1969) and 3) the measurement of oxygen consumption of the bacterial culture.

The results determined by the sulfite oxidation method are shown in Fig. 1. O.T.R. was determined at various RPM and for various flow rates. Results obtained by the different methods varied. For example, under the usual operating conditions of 1500 RPM and an air flow rate of one l/min., the O.T.R. was found to be, on the average, 240 mmoles oxygen/liter-hour using sulfite oxidation; whereas by the other methods it was about 180 mmoles oxygen/liter-hour. The difference is attributed to changes in the physical properties brought about by the presence of organic compounds. Measurement of the rate in the bacterial culture is further complicated by the presence of cells and the silicone antifoam oil.

The effect of agitation on growth rate in this system with an immiscible growth substrate was determined. The air flow rate was set at one l/min. A constant heptane feed rate, in excess of that utilized, was used. As expected, at low cell concentrations (< 1 gm/l), the growth rate was exponential. At higher cell concentrations (1-5 gm/l), the growth rate as determined from measurements of cell mass was linear and is attributed to limitation in heptane transfer rate to cells. The relationship of this linear growth rate to power input per unit volume is shown in Fig. 2. It is seen that the growth rate increases with increasing agitation. Since monitoring of dissolved oxygen concentration showed that it was always above the critical value, the effect is probably due to increased surface area which increases contact between cells and heptane droplets. It appeared that oxygen limitation would be possible only with high cell densities when an air flow rate of one l/min and the maximum agitation rate are used. Efforts to obtain cell concentrations at which oxygen would be limiting have been unsuccessful because of excessive foaming.

It is hoped that some method of foam control will be found so that the effect of oxygen concentration on growth rate at high cell densities can be studied.

Only preliminary work with the system in continuous culture has been carried out. In the work thus far, a dilution rate, D = 0.2 hour^{-1}, was used with an air flow rate of one l/min, but at different oxygen concentrations. The oxygen content of the sparging gas was varied from 3% to 32% by adding nitrogen or oxygen as required. In the range of 8% to 21%, no effect on steady state cell concentration was observed, indicating that oxygen was not limiting. Below 8%, the cell concentration was proportional to the oxygen supplied. In these preliminary runs, a slight but consistent increase in cell concentration was observed when the oxygen content of the sparging gas exceeded 21%. The dissolved oxygen is well above the critical value in the system at much lower percentages. Further work is needed to confirm and perhaps explain this interesting observation.

This study will also be concerned with the products of growth of Pseudomonas aeruginosa during the degradation of n-heptane as they may change or vary in concentration as a result of variation in dissolved oxygen concentration. Work of the first year has involved a study of methods of extraction and identification of products by gas chromatography.

Investigation during the second year will be concerned with further study of the effect of dissolved oxygen on the degradation of n-heptane and its effect on the end products of the fermentation. A means to inhibit foaming of high cell density cultures will be sought so that the effect of oxygen limitation under these conditions can be studied.

References

Cooper, C. M., Fernstrom, G. A. and Miller, S. A. 1944. Performance of agitated gas-liquid contactors. Indust. Eng. Chem. 36:504-509.

Hsieh, D. P. H., Silver, R. S., and Mateles, R. I. 1969. Use of glucose oxidase system to measure oxygen transfer rates. Biotech. & Bioeng. 11:1-18.

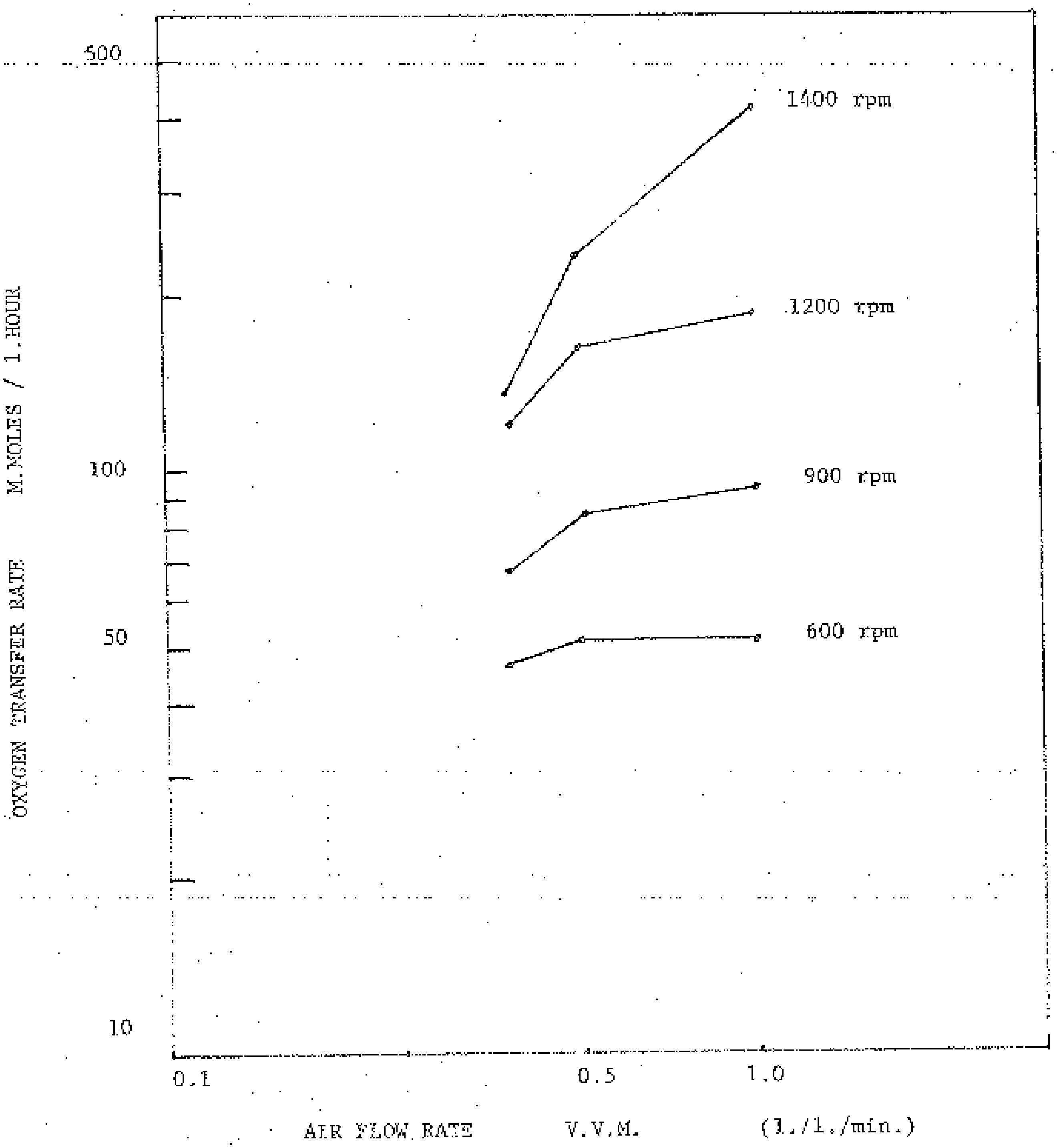

Figure 1. Oxygen Transfer Rate determined by sulfite oxidation method in New Brunswick Scientific Company Microferm Fermentor MF 105

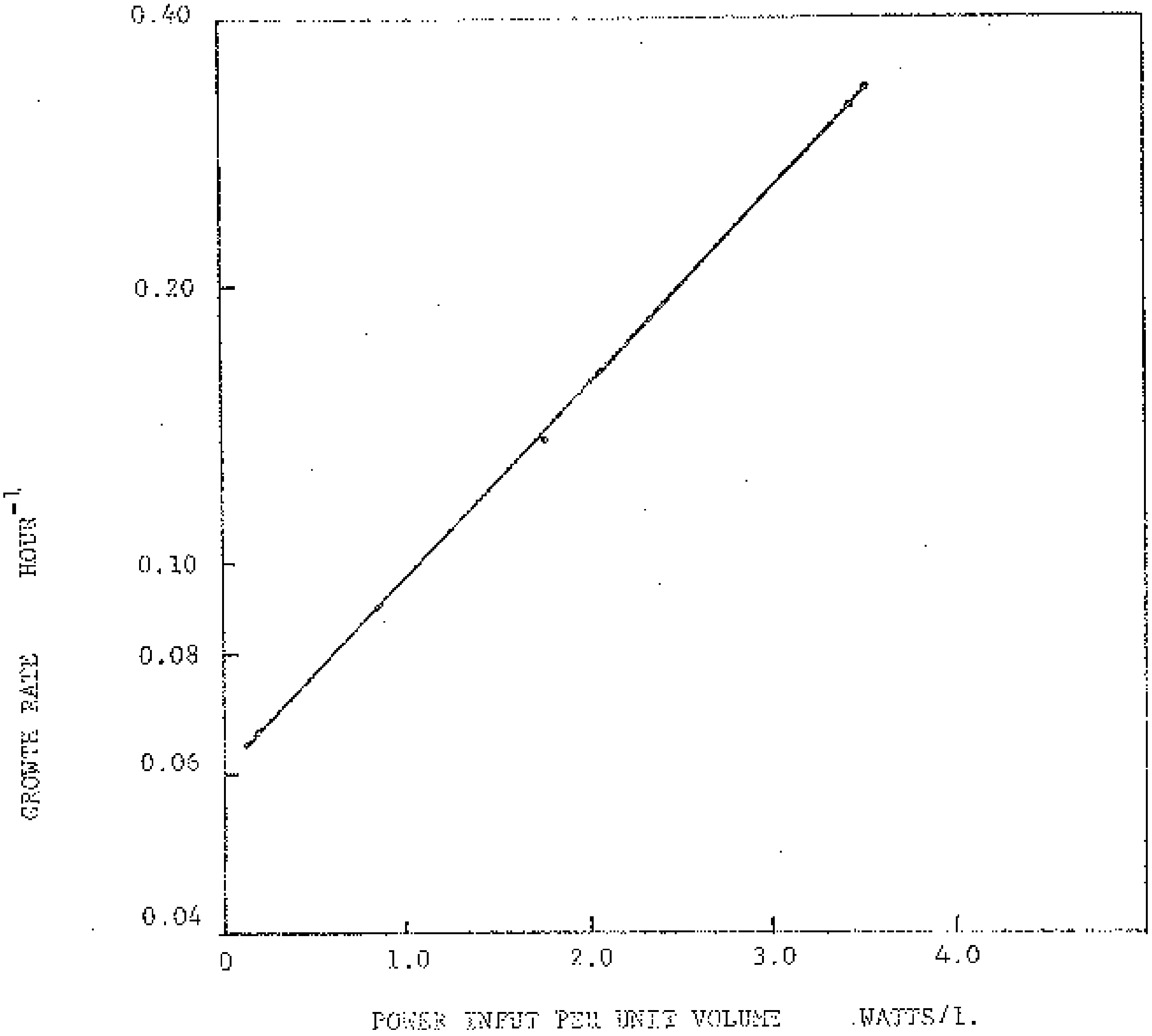

Figure 2. Growth rate of Pseudomonas aeruginosa on n-heptane as a function of power input per unit volume

PUBLICATIONS:

NONE

PROJECT STATUS:

This project will continue through the next year and will be completed by June 30, 1973.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-036-RI

Agreement No. 14-31-0001-3641

FCST-COWRR Research Category: VA

Project Title:
Laser Raman Spectroscopy of Solutes Dissolved in Water from a Remote Platform

Name and Location of University Where Project Is Being Carried Out:

University of Rhode Island, Kingston, R.I. 02881

Proj. Began--Month: July ; Year: 1971

To Be Completed--Month: June ; Year: 1973

Principal Investigators	Degree	Discipline
Chris W. Brown	Ph.D.	Chemistry

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Stuart F. Baldwin	B.S.	Chemistry
Ahmad Azima	B.S., M.S.	Chemistry
W.P. Lee	B.S.	Chemistry
M. Ahmadjian	---	Chemistry

A. Research Project Accomplishments.

The primary goal of this research is to develop a system for detecting water pollutants remotely by Raman spectroscopy. The initial research performed during the first year was devoted to determining the minimum level of detectivity by Raman spectroscopy, to exploring the applications of the technique, and to developing a preliminary optical system for detecting remote Raman scattering.

Raman Spectra of Ionic Water Pollutants (1).

Raman spectra of known aqueous samples have been measured using a conventional laser-excited Raman spectrometer. Sodium salts of NO_3^{-1}, SO_4^{-2}, PO_4^{-3}, and CO_3^{-2} (the latter anion was used to simulate actual situations) were dissolved in water to form 1 M solutions, and their Raman spectra were recorded. The samples were then diluted to 50% of their original concentration and their spectra recorded again. This process of dilution was continued until the minimum detectable concentration was reached.

Portions of typical spectra of NO_3^{-1}, SO_4^{-2}, and PO_4^{-3} at concentrations $\leq$75 ppm. are shown in Figure 1. Each of these anions has only one strong band in its Raman spectrum, which makes identification relatively easy. The minimum concentrations detected with the present

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(1) S. F. Baldwin and C. W. Brown, Water Research, in press.

experimental arrangement are listed in Table I along with the desired level of detectability.

In order to determine the feasibility of using Raman scattering to detect ionic pollutants in real situations, we have examined mixtures of anions. In Figure 2 portions of the Raman spectra of a PO_4^{-3}-NO_3^{-1} mixture and a CO_3^{-2}-SO_4^{-2} mixture are shown. All of the anions are present in concentrations of 100 ppm. As can be seen from the spectra the bands are well separated and are strong enough to be easily identified.

Applications of Raman Spectroscopy in the Determination of Chemical Properties of Aqueous Systems.

As the second phase in this study we have examined several important aqueous systems in order to demonstrate the power of Raman spectroscopy in elucidating the chemical nature of aqueous systems. As a starting point we measured the Raman spectrum of sea water taken from Narragansett Bay at the Graduate School of Oceanography. The spectrum is shown in Figure 3. The sharp, strong band at 980 cm^{-1} is due to SO_4^{-2} and the broad band at 1650 cm^{-1} is due to water. The concentration of SO_4^{-2} in sea water is reported to be 2700 ppm.; thus we would expect the strong band due to SO_4^{-2}. In this experiment we made no effort to detect the anions of lesser concentrations.

As an additional application we have used Raman spectroscopy to demonstrate the presence of ion-pairs in aqueous solutions (2).

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(2) F. P. Daly, C. W. Brown, and D. R. Kester, J. Phys. Chem., submitted for publication.

Initially, we obtained spectra of aqueous solutions of sodium and magnesium sulfates. Mg is known to ion-pair with SO_4^-, but neither Mg nor Na exhibited any evidence of ion-pairing in the Raman spectra of the sulfate solutions. Only one strong band was observed at 980 cm^{-1}. However, a new band appeared in the spectrum of sulfate when HCl was added. This new band, at 1053 cm^{-1}, has been previously assigned to the HSO_4^- ion-pair in dilute sulfuric acid solutions. The addition of small amounts of NaCl or $MgCl_2$ to this solution reduced the intensity of the 1053 cm^{-1} band and increased the intensity of the 980 cm^{-1} band. This strongly indicates that both Mg^{+2} and Na^+ compete with H^+ for the sulfate ion, and that $MgSO_4^0$ and $NaSO_4^-$ ion-pairs are important in aqueous solutions.

Remote Raman Scattering.

A schematic of the preliminary optical system for obtaining Raman spectra of samples located remotely to the instrument is shown in Figure 4. This is essentially a "light pipe" system. The collimated laser beam is reflected by three flat mirrors (M_1, M_2, and M_3) and is focused by a lens (L_1) onto the sample. The scattered light is collected by the same lens, over a large angle, and is returned to the monochromator and analyzed. The trick to this technique is that the laser beam has a very small diameter (~1 mm), whereas the collimated scattered beam has a large diameter (~10 cm). In this manner both can traverse the same optical path to and from the sample.

There are several distinct advantages to this optical system. Since both the laser beam and the scattered beam are collimated over most of the optical path, it is possible to extend the optical path to almost any realistic distance. Presently, we have the sample located 21 feet from the spectrometer, but it should work equally as well up to 100 ft. By enclosing the optical path in a light tight pipe, such as 4 inch plastic plumbing pipe, interferences from daylight or other external lights can be avoided. In addition, the pipe can penetrate the surface of the water, and eliminate surface irregularities. This would be especially important for obtaining remote scattering from natural waters where waves or floating objects would produce abnormal scattering.

During the past two months we have obtained our first Raman spectrum of a sample located remotely from the spectrometer. Using CCl_4 as the sample, located 21 feet from the instrument, we obtained the spectrum shown in Figure 5. Even though CCl_4 is a good Raman scatterer, the fact that we obtained a decent spectrum with little difficulty, increased our confidence in the technique. Currently, we are replacing the preliminary optics with better optics and shortly we should be able to try the system on dilute aqueous samples.

B. Publications.

1) "Detection of Ionic Water Pollutants by Laser Excited Raman Spectroscopy," S. F. Baldwin and C. W. Brown, Water Research, in press.

2) "Sodium and Magnesium Sulfate Ion-Pairing: Evidence from Raman Spectroscopy," F. P. Daly, C. W. Brown and D. R. Kester, J. Phys. Chem., submitted for publication.

C. Project Status.

Will continue in progress in the next fiscal year.

D. Applications of Research Results.

Publication (1) (above) was submitted to and accepted by Water Research. Just recently, we heard from the executive editor of this journal, Dr. S. H. Jenkins, expressing interest in publishing our future results in Water Research. In addition, Dr. Dana Kester of the University of Rhode Island Graduate School of Oceanography has been very enthusiastic about using the method to elucidate the chemical nature of aqueous solutions. We have already collaborated with him on one project (publication 2 above), and are currently working on two other projects with him, all of which stem from the work reported herein.

Raman spectroscopy, whether it be done remotely or in a conventional instrument, offers a rapid means for detecting and identifying pollutants. Both organic and inorganic pollutants have characteristic Raman bands and can be easily identified. The sensitivity of the method needs to be increased; however, it is on the threshold of the desired range, and with some modifications Raman spectroscopy can become a powerful tool in the detection of water pollutants.

E. Work Remaining, and Progress Contemplated During Next Year.

We plan to concentrate on the following three areas during the next year:

i) Increasing the sensitivity of the instrumentation. The greatest problem in this area is background. Aqueous samples have an inherently strong Rayleigh scattering, which extends into the spectral range of interest. We can easily amplify the Raman scattering to increase the sensitivity of the technique, but we also amplify the Rayleigh background. To get around this problem, we are going to optically filter out the dominant Rayleigh scattering intensity, and electronically reduce the background using a single channel analyzer. We recently installed the latter instrument and will try it shortly. This instrument can be set to accept only signals above a certain level; therefore, the lower level Rayleigh scattering can be reduced.

ii) Raman spectra of actual field samples. Currently, we are collecting samples from several areas of known pollution in Rhode Island, and we will measure the Raman spectra of these samples in the conventional spectrometer. Thus far, our investigations have concentrated on inorganic pollutants, but we also intend to analyze the samples for organics.

iii) Remote Detection. The "light pipe" optical system described above has already been tested and we are currently refining it for use during the coming year. In addition, we have designed a telescopic system, which does not use optics between the instrument and the sample. All of the optics are adjacent to the spectrometer. In essence, the laser beam is aimed at a distant sample. The light scattered from the sample is collected by a telescope and directed into the spectrometer. We are collecting the optics for this system and will test it during the coming year.

TABLE I. Desired Level of Detectability and that Achieved in the Present Investigation

ANION	Desired Level[a] ppm	Detected by Raman in ppm	Observed Raman Frequency (cm^{-1})
NO_3^-	10±0.5	25	1049
PO_4^{-3}	20±0.5	50	989
SO_4^{-2}	100±2	50	982
CO_3^{-2}		75	1063

[a] R.S. Green, Analysis Instrumentation, Proc. of 12th Annual Symposium, Houston, 1966, Vol. 4, pp. 1-10, Plenum Press, New York.

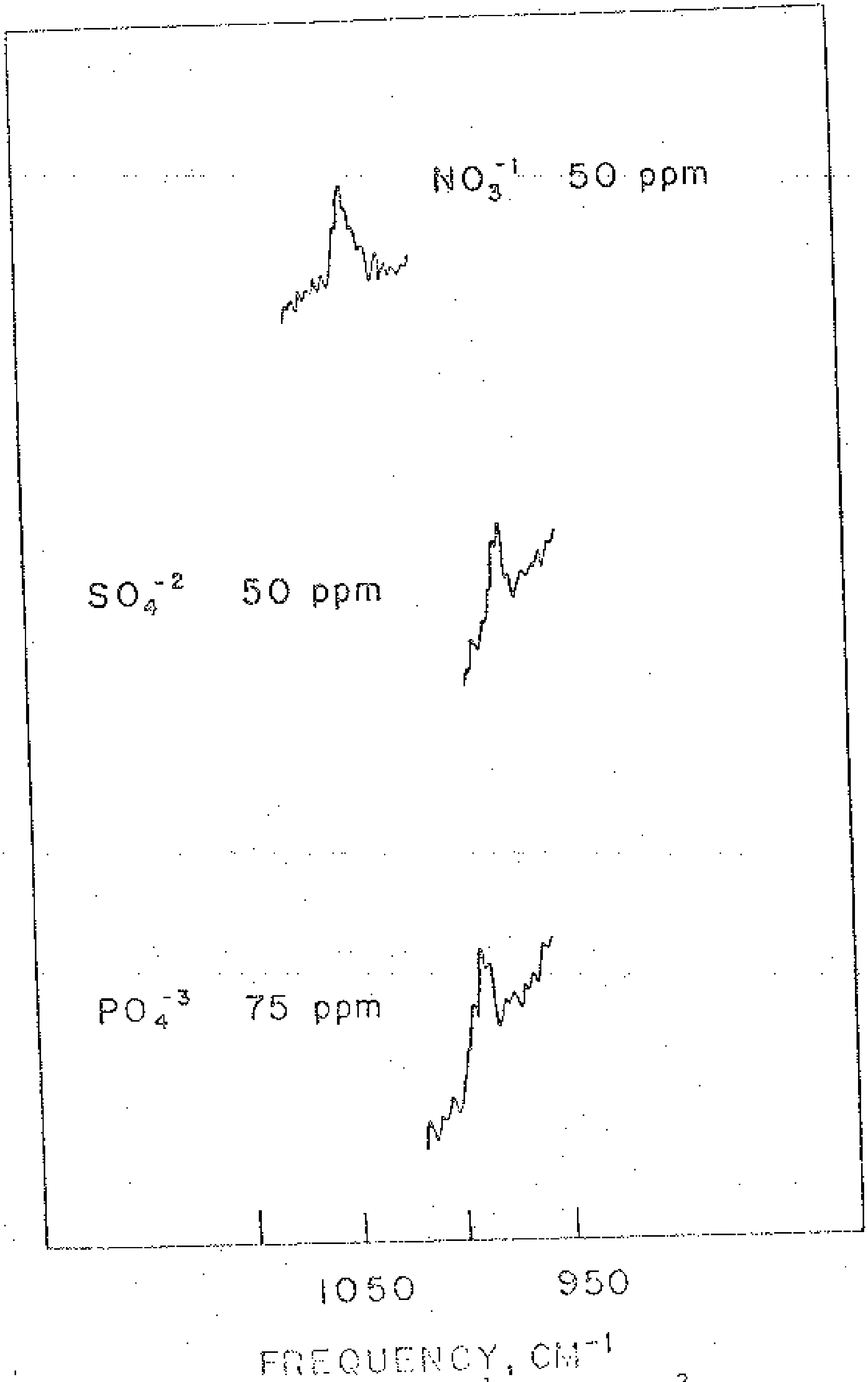

Fig. 1 Raman spectra of NO_3^{-1} (50ppm), SO_4^{-2} (50ppm) and PO_4^{-3} (75 ppm).

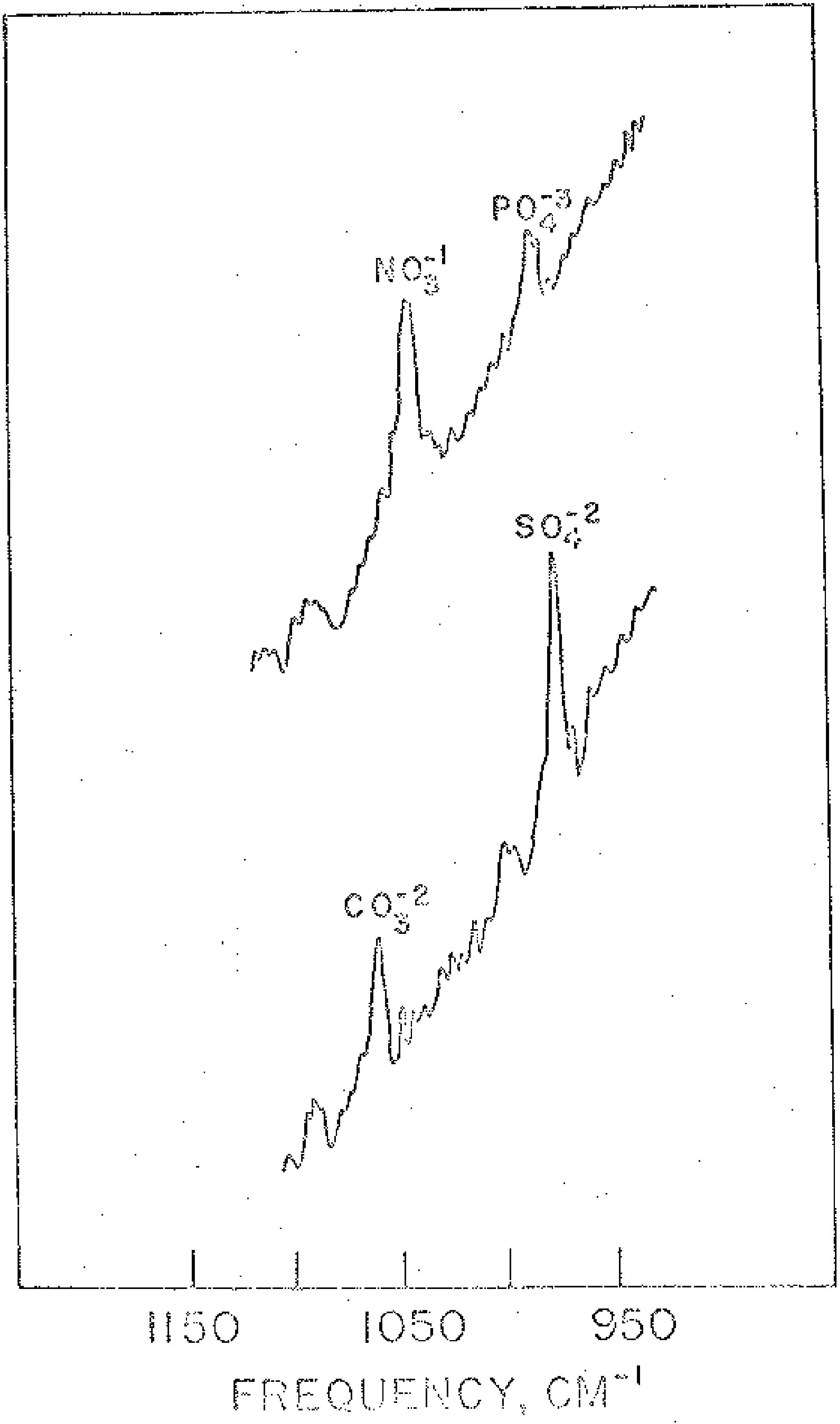

Fig. 2 Raman spectra of NO_3-PO_4 and CO_3-SO_4 solutions. The anions are all present in concentrations of 100 ppm.

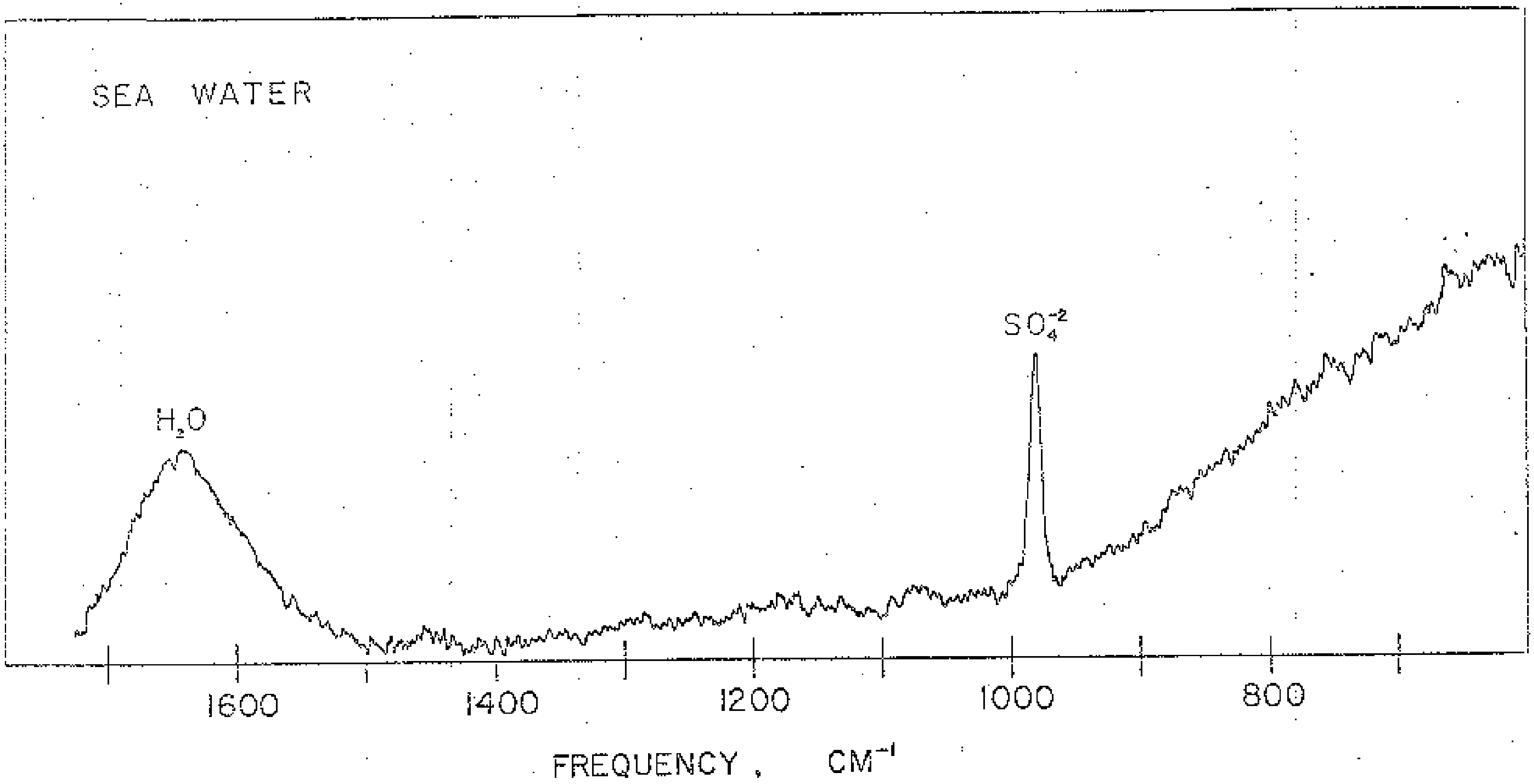

Fig. 3 Raman spectrum of sea water showing a strong SO_4^{-2} band at 980 cm^{-1}.

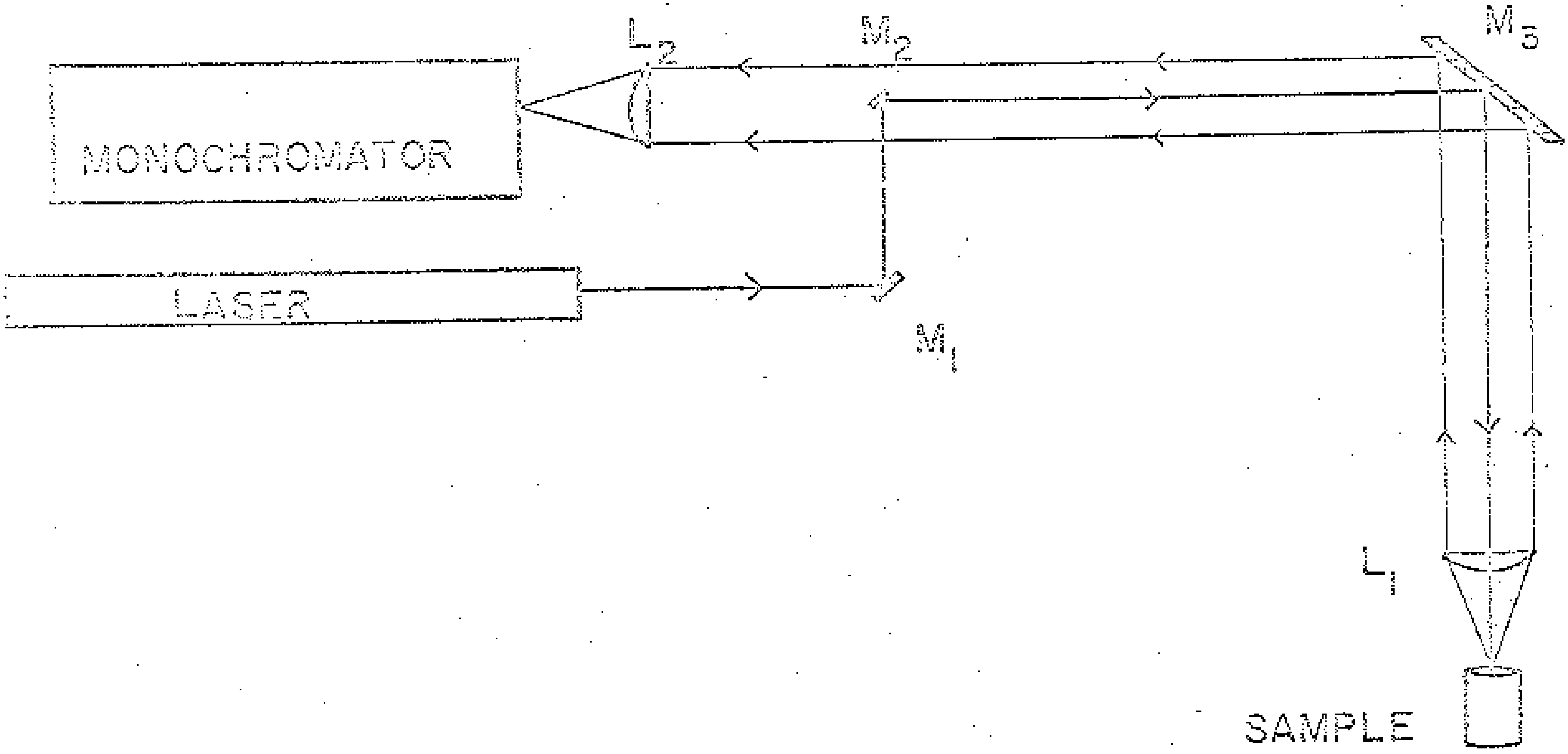

Fig. 4 Optical system used for obtaining Raman spectra of samples located 21 feet from instrument.

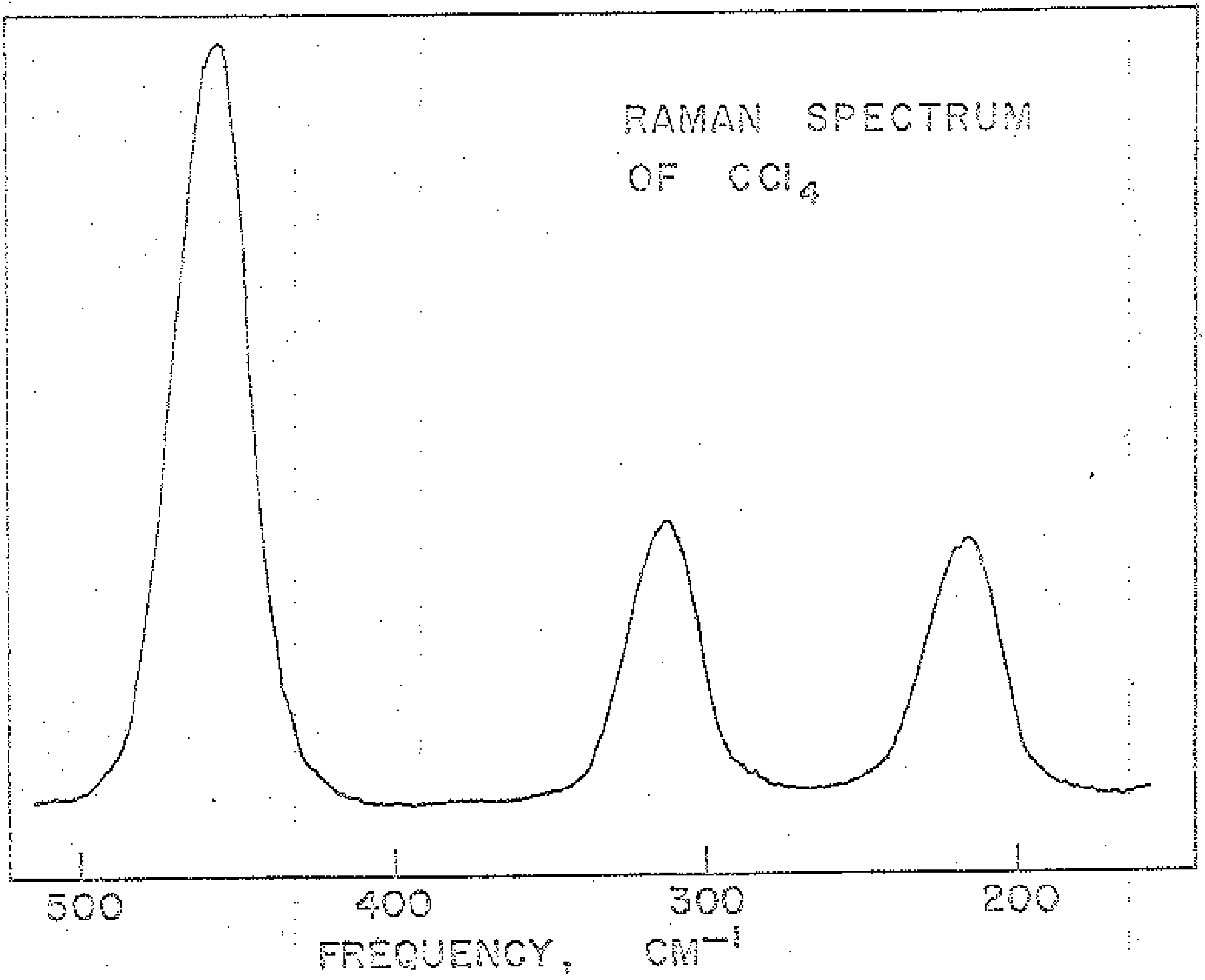

Fig. 5 Raman spectrum of CCl_4. Sample located 21 feet from instrument.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-038-RI

Agreement No. 14-31-0001-3642

FCST-OWRR Research Category: VI F

Project Title:

Planning for Uncertainty in Water Use: A Least-cost Policy for Rhode Island.

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, RI

Proj. Began--Month: June ; Year: 1971

To Be Completed--Month: June ; Year: 1972

Principal Investigators	Degree	Discipline
Arthur D. Jeffrey, Professor of Economic Development and Regional Planning	Ph.D.	Land Economics Community Planning

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Roger S. Hoch	B.A., M.A.	Political Science Community Planning

(A) Research Project Accomplishments

It is determined in this study that the traditional approach contributes to the creation of three undesirable conditions: high implementation costs, reduced development alternatives and increased levels of pollution. To a considerable extent these consequences can be traced to the principal assumptions on which such planning is based. The literature surveyed, however, challenges each of these assumptions and indicates that more efficient use of available supplies is a feasible alternative to new supply development.

Efforts to encourage such use focus on the pricing mechanism and on the integration of water supply and sewage services. Presently, the pricing mechanism encourages inefficient water use and fails to reflect total utilization costs. Modification of water supply and sewer rate structures should be considered both as a variable in estimating future water use levels and as a means of implementing state water supply and pollution control policy.

(B) Publications

A thesis for fulfillment of the degree of Master of Community Planning by Roger S. Hoch has been completed entitled "Impact of Pricing and Administrative Variables in Planning the Use and Development of Water Resources in Rhode Island."

(C) Project Status

Project has been completed.

(D) Application of Research Results

The results of this study will be used by the Natural Resource Group of Rhode Island to bring about changes in the structure and methods of controlling water supply and sewage treatment. This group has previously been successful in implementing change in state government.

(E) Work Remaining, and Progress Contemplated During Next Year

While the work has been completed it is planned to publish the findings of the study in a research publication.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-039-RI

Agreement No. 14-31-0001- 3643

FCST-COWRR Research Category: VII B

Project Title:

"New Fluorescent Tracer Detection Techniques for Use in Polluted Environments"

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: July ; Year: 1971 | To Be Completed--Month: June ; Year: 1973

Principal Investigators	Degree	Discipline
Dr. J.A. Northby	Ph.D.	Physics
Dr. A. Choudry (Assoc. Investigator- July-August '71)	Ph.D.	Physics

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
M. Sarkes (July - Sept. '71)	B.S.	Ocean Engineering
R. Sierra (Sept.'71 to date)	B.S.	Physics

(A) Project Accomplishments:

The first eleven months of this project have been primarily devoted to developing the instrumentation necessary to measure the low background fluorescence of natural water samples, and to determine its polarization properties. Our instrument will be capable of operating in three separate configurations: first, as a scanning fluorimeter, in which the wavelength dependence of the fluorescent intensity is measured; second as a filter fluorimeter which measures the integrated intensity; and third as a polarization fluorimeter in either of the above configurations. The scanning and filter instruments are complete and have been calibrated for use with Rhodamine B dye in water. Conservative estimates of the sensitivities are 5×10^{-5} and 5×10^{-6} mg/liter respectively. The latter number may be compared with a published sensitivity of the commonly used commercial filter instrument of 5×10^{-5} mg/liter. The polarization configuration has been built and operated and gives results in good qualitative agreement with other published results for various Rhodamine solutions in glycerol and water. Modifications currently in progress are expected to improve the quantitative agreement.

Some qualitative measurements on natural water samples have been made to aid in design of the apparatus, but no systematic studies have yet been made.

(B) Publications:

None

(C) Project Status:

We are presently working on the fluorescence polarization instrument. Specifically, we are attempting to improve its accuracy and sensitivity to the point where it can be used to measure the polarization excitation spectrum of the background fluorescence of natural samples.

(D) Applications of Results:

N.A.

(E) Work Remaining:

(1) We will soon begin a study of the fluorescence of water samples taken from the Providence River, utilizing the instrumentation previously described.

(2) We will then undertake a study of tracer materials in natural water samples with a view to optimizing detectability. The method and materials adopted will depend on the results of (1) above.

(3) We expect to continue to improve our instrumentation simultaneously with (1) and (2) above. In particular, we intend to provide a flow cell arrangement, and more automation in data taking.

FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate form for each Sec. 100 project in progress in FY 1972)

State where institut is located: Rhode Island

Report as of June 30, 1972

OWRR Project No. A-035-R I

Annual Allotment Agreement No. 14-31-0001- 3240

Principal Investigator(s):
Vance J. Yates
Pei W. Chang

Project Title: Significance of Fecal Streptococci, Coliform Bacteria and Coliphage in Relation to Enteric Virus Pollution in Sewage and Rivers

Project Began-- Month: July ; Yr: 1970

Scheduled Completion--Month: June ; Yr: 1972

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied	No:	Man-yrs:	Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			3700.00	4068.16
Prin. Investigators:	2		( )	( )
Other Prof. Staff:			( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	2	1.25	(3700.00)	(4068.16)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)			( )	( )
Technicians & Others: (NON-STUDENTS)			( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL				
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			3600.00	3317.51
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			75.00	
Publication			(75.00)	( )
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			7375.00	7385.67

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Resources Research. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

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FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate for: for each Sec. 100 project in progress in FY 1972)

State where institute is located: Rhode Island

Report as of June 30, 1972

OWRR Project No. A-036-RI
Annual Allotment Agreement
No. 14-31-0001- 3240
Principal Investigator(s):
Mien-Chang Wang
Vito A. Nacci

Project Title: Groundwater Flow in Partially Saturated Soils

Project Began-- Month: July ; Yr: 1970

Scheduled Completion--Month: June ; Yr: 1972

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied	Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL	6365.00	6234.19
Prin. Investigators: No: 1 - Man-yrs: 0.05	(880.00)	(880.00)
Other Prof. Staff: No: 1 - Man-yrs: 0.05	(955.00)	(954.19)
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS) No: 1 - Man-yrs 0.625	(4530.00)	(4400.00)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS) No: - Man-yrs:	( )	( )
Technicians & Others: (NON-STUDENTS) No: - Man-yrs:	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL		
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL	2185.00	2688.71
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL		
	( )	( )
	( )	( )
	( )	( )
	( )	( )
E. TOTALS:	8550.00	8922.90

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FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate form for each Sec. 100 project in progress in FY 1972)

State where institute is located: Rhode Island

Report as of June 30, 1972

OWRR Project No. A-037-RI

Annual Allotment Agreement No. 14-31-0001- 3280

Principal Investigator(s):

Donald L. Sussman

Project Title: Chemical and Physical Factors in the Flocculation of Metal Processing Wastes with Polyelectrolytes

Project Began-- Month: July ; Yr: 1970

Scheduled Completion--Month: June ; Yr: 1972

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied			Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			7240.00	7096.48
Prin. Investigators:	No: 1	Man-yrs: 0.2	(2625.00)	(2626.50)
Other Prof. Staff:	No:	Man-yrs:	( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No: 1	Man-yrs: 0.625	(4615.00)	(4469.98)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No:	Man-yrs:	( )	( )
Technicians & Others: (NON-STUDENTS)	No:	Man-yrs:	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL				
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			600.00	340.83
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			100.00	
Publication			(100.00)	( )
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			7940.00	7437.31

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FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate for for each Sec. 100 project in progress in FY 1972)

State where institute is located: Rhode Island

Report as of June 30, 1972

OWRR Project No. A-038-RI

Annual Allotment Agreement No. 14-31-0001- 3240

Principal Investigator(s):

Charles E. Olney

Project Title: Transfer of Pesticides Through Water, Sediments and Aquatic Life

Project Began-- Month: July ; Yr: 19 70

Scheduled Completion--Month: June ; Yr: 1972

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied	No.	Man-yrs	Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			4790.00	4792.00
Prin. Investigators:	1		( )	( )
Other Prof. Staff:			( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	3	1.125	(4790.00)	(4792.00)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)			( )	( )
Technicians & Others: (NON-STUDENTS)			( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL				
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			780.00	761.60
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			180.00	180.00
Travel			(180.00)	(180.00)
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			5750.00	5733.60

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FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate for for each Sec. 100 project in progress in FY 1972)

State where institute is located: Rhode Island

Report as of June 30, 1972

OWRR Project No. A-039-RI

Annual Allotment Agreement No. 14-31-0001- 3540

Principal Investigator(s):

Gerard P. O'Leary

Project Title: The Effects of Differently Extracted Endotoxins from Escherichia Coli on Rainbow Trout (Salmo Gairdneri)

Project Began-- Month: July ; Yr: 1971

Scheduled Completion--Month: June ; Yr: 1973

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied	Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL	3860.00	3848.00
Prin. Investigators: No: 1 - Man-yrs: 0.2	(2500.00)	(2488.00)
Other Prof. Staff: No: __ - Man-yrs: __	( )	( )
Graduate Student Assistants: No: 1 - Man-yrs: 0.40 (INCLUDES STUDENT TECHNICIANS)	(1360.00)	(1360.00)
Undergrad. Student Assistants: No: __ - Man-yrs: __ (INCLUDES STUDENT TECHNICIANS)	( )	( )
Technicians & Others: No: __ - Man-yrs: __ (NON-STUDENTS)	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL	5505.00	5427.72
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL	1765.00	1749.57
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL		
	( )	( )
	( )	( )
	( )	( )
	( )	( )
E. TOTALS:	11130.00	11025.29

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FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate form for each Sec. 100 project in progress in FY 1972)

State where institute is located: Rhode Island | Report as of June 30, 1972

OWRR Project No. A- 040-RI
Annual Allotment Agreement No. 14-31-0001- 3540
Principal Investigator(s):
Calvin C. Poon

Project Title: Electrochemical Process for Nutrient Removal

Project Began-- Month: July ; Yr: 1971 | Scheduled Completion--Month: June ; Yr: 1973

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied			Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			7610.00	7395.84
Prin. Investigators:	No: 1	Man-yrs: 0.20	(3110.00)	(3020.86)
Other Prof. Staff:	No:	Man-yrs:	( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No: 1	Man-yrs: 0.625	(4500.00)	(4374.98)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No:	Man-yrs:	( )	( )
Technicians & Others: (NON-STUDENTS)	No:	Man-yrs:	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL				
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			1000.00	1348.02
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL				
			( )	( )
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			8610.00	8743.86

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FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate form for each Sec. 100 project in progress in FY 1972)

State where institute is located: Rhode Island | Report as of June 30, 1972

OWRR Project No. A- 041-RI
Annual Allotment Agreement No. 14-31-0001- 3540
Principal Investigator(s): Yuzuru Shimizu

Project Title: Plant Phenols and Related Organic Compounds in Public Water Sources, Their Relationship to Chlorination

Project Began-- Month: July ; Yr: 1971 Scheduled Completion--Month: June ; Yr: 1973

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied	No:	Man-yrs:	Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			4565.00	4621.30
Prin. Investigators:	1		( )	( )
Other Prof. Staff:			( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	3	1.25	(4245.00)	(4358.50)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)	1	0.1	(320.00)	(262.80)
Technicians & Others: (NON-STUDENTS)			( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL			3155.00	3155.00
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			2000.00	2031.46
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			250.00	250.00
Travel			(250.00)	(250.00)
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			9970.00	10057.76

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FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate form for each Sec. 100 project in progress in FY 1972)

State where institute is located: Rhode Island

Report as of June 30, 1972

OWRR Project No. A-042-RI

Annual Allotment Agreement
No. 14-31-0001- 3540

Principal Investigator(s):
John McN. Sieburth

Project Title:
Trace Metals in the Precipitation of Humic Materials

Project Began-- Month: July ; Yr: 1971

Scheduled Completion--Month: March ; Yr: 1972

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied	No.	Man-yrs	Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			2925.00	3036.48
Prin. Investigators:	1		( )	( )
Other Prof. Staff:			( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	1	0.4	(2925.00)	(3036.48)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)			( )	( )
Technicians & Others: (NON-STUDENTS)			( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL			515.00	137.71
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			400.00	942.61
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL				
			( )	( )
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			3840.00	4116.80

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FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate forr for each Sec. 100 project in progress in FY 1972)

State where institute is located: Rhode Island

Report as of June 30, 1972

OWRR Project No. A-043-RI

Annual Allotment Agreement No. 14-31-0001- 3540

Principal Investigator(s):

Roger I. Tanner

Project Title: Improvements in Primary Oil-Water Separation Through Droplet Size Control

Project Began-- Month: July ; Yr: 1971

Scheduled Completion--Month: June ; Yr: 1972

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied			Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			6525.00	6523.41
Prin. Investigators:	No: 1	Man-yrs: 0.10	(1800.00)	(1800.00)
Other Prof. Staff:	No:	Man-yrs:	( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No: 1	Man-yrs: 0.625	(4500.00)	(4498.41)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No: 1	Man-yrs: 0.05	(225.00)	(225.00)
Technicians & Others: (NON-STUDENTS)	No:	Man-yrs:	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL			1850.00	1762.81
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			1275.00	1364.73
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL				
			( )	( )
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			9650.00	9650.95

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Resources Research. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted," an explanation of such variance should be provided on an attachment to this sheet.

FORM OW-2
(1972)

FY 1972 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepared separate form for each Sec. 100 project in progress in FY 1972)

State where institute is located: Rhode Island

Report as of June 30, 1972

OWRR Project No. A- 044-RI

Annual Allotment Agreement No. 14-31-0001- 3540

Principal Investigator(s):

Leonard R. Worthen

Project Title: Interception and Degradation of Pesticides by Aquatic Algae

Project Begun-- Month: July ; Yr: 1971

Scheduled Completion--Month: June; Yr: 1973

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied	No:	Man-yrs:	Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			2510.00	1847.52
Prin. Investigators:	1		( )	( )
Other Prof. Staff:			( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)			( )	( )
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)			( )	( )
Technicians & Others: (NON-STUDENTS)	1	0.25	(2510.00)	(1847.52)
B. NON-EXPENDABLE PROPERTY: TOTAL			1000.00	1004.50
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			805.00	666.22
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL				
			( )	( )
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			4315.00	3518.24

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Resources Research. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted," an explanation of such variance should be provided on an attachment to this sheet.

FY 1972 ANNUAL REPORT -- FOR THE INSTITUTE DIRECTOR'S OFFICE

FORM OW-3
(1972)

State Where Institute is Located: Rhode Island

Report as of June 30, 1972

Director's Name:
A. Ralph Thompson

Annual Allotment Agreement No. 14-31-0001- 3540

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied	No.	Man-yrs	Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			17,350.00	17,157.76
Institute Director:		0.2	(5,535.00)	(5,523.30)
Other Prof. Staff:			( )	( )
Graduate Student Assistants: (Includes Student Technicians)	2	0.635	(5,450.00)	(5,127.51)
Undergrad. Student Assistants: (Includes Student Technicians)			( )	( )
Technicians & Others: (Non-Students)	1	1.0	(6,365.00)	(6,506.95)
B. NON-EXPENDABLE PROPERTY: TOTAL				
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			970.00	992.85
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			4,550.00	4,564.91
Printing			(2,800.00)	(2,749.91)
Travel			(1,750.00)	(1,815.00)
			( )	( )
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			22,870.00	22,715.52

Notes: Amount Budgeted is as set forth in the allotment program budget (and revisions) submitted to the Office of Water Resources Research.

Actual Expenditures includes firm outstanding commitments including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted," an explanation of such variance should be provided on an attachment to this sheet.

FY 1972 ANNUAL REPORT -- FOR THE INSTITUTE DIRECTOR'S OFFICE

FORM OW-4
(1972)

Estimated Functional Distribution of FY 1972 Allotment (Sec. 100) Funds Expended for Operation of the Office of the Institute Director

1. Research program (P.L. 88-379) planning and development, including review and analysis of research project proposals - - - - - - - - - - -	$ 2,000.00
2. Coordinating the approved Institute P.L. 88-379 research and related training activities, including evaluation of progress, coordination with State agencies, etc. -	$ 5,338.30
3. Water research and training program symposia relating to current or projected P.L. 88-379 activity but not directly associated with (or included in) the budgets of specific projects - - - - - - - - - -	$ 5,127.51
4. Supplies, Postage, Telephone (long distance) stationery	992.85
5. Printing Costs (reprint of Annual report which is sent to federal and state agencies, and other Water Centers	2,749.91
6.	
7.	
8. Administrative expenses, including such housekeeping activities as the preparation of Institute time and attendance reports, requisitioning miscellaneous office supplies and equipment, operating Institute mails and files systems, general Institute record keeping, etc. -	$ 6,506.95 1/
TOTAL Expenses for the Institute Director's Office - - - - - - -	$22,715.52 2/

1/ If a cost of the Institute Director's Office can be attributed to a research program activity, such as described in items 1, 2, and 3 above, then that cost should be included in that program activity and not as "administrative expenses". For example, that portion of the Institute Director's salary cost, as well as related stenographic-clerical costs, that are attributable to program planning and development activity of the Office of the Institute Director should be included in item 1 above rather than in item 8 above.

2/ This dollar figure should be equal to the total "actual expenditures FY1972" as shown on line "E" of Form OW-3, FY 1972 Annual Report--For the Institute Director's Office.

SUMMARY SHEET FOR FY 1972 ANNUAL ALLOTMENT PROGRAM (SEC. 100) EXPENDITURES

FORM OW-5
(1972)

ummary of information from forms OW-2 and OW-3 covering Institute Director's Office and nnual allotment program projects utilizing FY 1972 allotment program (Sec. 100) funds

State: Rhode Island

Total no. of allotment projects underway, FY 1972: 10

Of these, indicate no. completed during year, if any: 4

Annual Allotment Agreement No. (FY1972): 14-31-0001- 3540.

Cost Categories to Which FY1972 Federal Sec. 100 Funds Applied	No.	Man-yrs	Amount Budgeted FY1972	Actual Expenditures FY1972
A. SALARIES & WAGES: TOTAL			67440.00	66621.14
Institute Director:		0.2	(5535.00)	(5523.30)
Principal Investigators:	11	0.75	(10915.00)	(10815.36)
Other Professional Staff:	1	0.05	(955.00)	(954.19)
Graduate Student Assistants: (Includes Student Technicians)	16	7.56	(40615.00)	(40486.02)
Undergraduate Student Assistants: (Includes Student Technicians)	5	0.15	(545.00)	(487.80)
Technicians & Others: (Non-Students)	2	1.25	(8875.00)	(8354.47)
B. NON-EXPENDABLE PROPERTY: TOTAL			12025.00	11487.74
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			15380.00	16204.11
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			5155.00	4994.91
Publications & Printing			(2975.00)	(2749.91)
Travel			(2180.00)	(2245.00)
			( )	( )
			( )	( )
			( )	( )
			( )	( )
			( )	( )
			( )	( )
E. TOTALS[2]			100000.00	99307.90

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[1] The OWRR project numbers for completed annual allotment projects are as follows:

A-035-RI, A-036-RI, A-038-RI, A-043-RI

[2] Ordinarily, the Total of "Amount Budgeted FY1972" should equal $100,000.

FORM OW-6
(1972)

FY 1972 ANNUAL REPORT -- ESTIMATE OF NON-FEDERAL CONTRIBUTIONS
(Relating to Annual Allotment Program)

State: Rhode Island	Report covering FY 1972

The legislative history leading to passage of the Water Resources Research Act of 1964 emphasizes the importance of State-Federal cooperation in the conduct of the program and indicates that there will be substantial amounts of non-Federal cost participation. Pursuant thereto, please provide an estimate of non-Federal cost participation in the FY 1972 research and training activities carried out pursuant to your institute's FY 1972 annual allotment, Sec. 100, program. (Note: Similar information is needed, relating to compliance with Bureau of the Budget Circular No. A-74.)

The following types of non-Federal cost participation items are suggested for your consideration. Use these, or others, as you deem appropriate.

1. Estimated non-Federal contributions to salaries and wages of professional staff who participated in the FY 1972 annual allotment, Sec. 100, program:-	$37,000.00
2. Estimated non-Federal contribution to indirect costs and employee fringe benefits relating to the FY 1972 annual allotment, Sec. 100, program:-	$30,778.97 *
3. Estimated FY 1972 fair-use-value non-Federal contribution relating to equipment, facilities, etc., used in the FY 1972 annual allotment, Sec. 100, program:-	$50,000.00
4. Tuition and fees for graduate students working on water resources projects	12,000.00
5. * Indirect Costs (excluding the costs of permanent buildings) - 35% of total salaries ** Fringe Benefits - 11.2% of salaries	
6.	
7.	
TOTAL	$129,778.97

FY 1972 ANNUAL REPORT -- MATCHING GRANT (SEC. 101) PROJECT FORM OW-7 (197

(Prepare a separate form for each Sec. 101 project in progress during FY 1972

State where institute located: Rhode Island

Report as of June 30, 1972

OWRR Proj. No. B026-RI

Matching Grant Agreement Number 14- -0001- 3328

Total Federal Amount of the M.G.A.- $11850.

Project Title: Periphyton and Phytobenthon As Indicators of Water Quality

Prin. Investigator(s): Richard D. Wood

Proj. Began--Mo: July; Yr: 1970 Actual or Scheduled Completion--Mo: June; Yr: 1972

Cost Categories Man-Year Information FY1972 1/	Expenditures in FY 1972		
	Federal $	Non-Fed. $	Total $
A. SALARIES & WAGES: Total	6406.22	1653.06	8059.28
Principal Investigator(s) No: 1 Man-Years: 0.20	(4196.22)	( )	(4196.22)
Other Professional Staff: No: ___ Man-Years: ___	( )	( )	( )
Graduate Student Assistants: INCLUDES STUDENT TECHNICIANS No: 1 Man-Years: 0.30	(2210.00)	(1653.06)	(3863.06)
Undergraduate Student Assistants INCLUDES STUDENT TECHNICIANS No: ___ Man-Years: ___	( )	( )	( )
Technician and Others: NON-STUDENTS No: ___ Man-Years: ___	( )	( )	( )
B. NON-EXPENDABLE PROPERTY:			
C. EXPENDABLE PROPERTY: (Supplies, Materials, Etc.)		656.58	656.58
D. OTHER COSTS (SPECIFY): TOTAL (Travel, Indirect costs, Etc.)	155.10	3624.26	3779.36
Travel	(84.60)	( )	(84.60)
Publication	(70.50)	( )	(70.50)
Indirect Costs (34.17% Salaries)	( )	(2753.86)	(2753.86)
Fringe Benefits (10.8% Salaries)	( )	(870.40)	(870.40)
	( )	( )	( )
E. TOTALS for FY 1972	6561.32	5933.90	12495.22

F. Cumulative Total Project Expenditures from Start of Project to June 30, 1972 - - - - - Federal--$11172.64; Non-Fed--$14988.68

1/ Man-Years relate to time paid from Federal funds only.

Other Notes: Firm outstanding commitments (or obligations) are considered as expenditures including, for example, unliquidated orders for equipment.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

FY 1972 ANNUAL REPORT -- MATCHING GRANT (SEC. 101) PROJECT

FORM OW-7 (197

(Prepare a separate form for each Sec. 101 project in progress during FY 1972

State where institute located: Rhode Island

Report as of June 30, 1972

OWRR Proj. No. B-028-RI

Matching Grant Agreement Number 14- -0001- 3329

Total Federal Amount of the M.G.A.- $11360.00

Project Title:

Diffusion of Thermally Buoyant Water Jets Into a Moving Water Stream

Prin. Investigator(s): Frederick Test

Proj. Began--Mo: July; Yr: 1970 Actual or Scheduled Completion--Mo: June; Yr: 19 72

Cost Categories Man-Year Information FY1972 1/	Expenditures in FY 1972		
	Federal $	Non-Fed. $	Total $
A. SALARIES & WAGES: Total	2689.95	4521.16	7211.11
Principal Investigator(s) No: 2 Man-Years: 0.15	(2689.95)	( )	(2689.95)
Other Professional Staff: No: ___ Man-Years: ___	( )	( )	( )
Graduate Student Assistants: INCLUDES STUDENT TECHNICIANS No: 1 Man-Years: ___	( )	(3614.96)	(3614.96)
Undergraduate Student Assistants INCLUDES STUDENT TECHNICIANS No: 1 Man-Years: ___	( )	(906.20)	(906.20)
Technician and Others: NON-STUDENTS No: ___ Man-Years: ___	( )	( )	( )
B. NON-EXPENDABLE PROPERTY:			
C. EXPENDABLE PROPERTY: (Supplies, Materials, Etc.)	359.29		359.29
D. OTHER COSTS (SPECIFY): TOTAL (Travel, Indirect costs, Etc.)	484.24	4538.23	5022.47
Computer	(308.89)	(1295.39)	(1604.28)
Publication	(60.00)	( )	(60.00)
Travel	(115.35)	( )	(115.35)
Indirect Costs (34.17% Salaries)	( )	(2464.04)	(2464.05)
Fringe Benefits (10.8% Salaries)	( )	(778.80)	(778.80)
E. TOTALS for FY 1972:	3533.48	9059.39	12592.87

F. Cumulative Total Project Expenditures from Start of Project to June 30, 1972 - - - - - Federal--$10794.44; Non-Fed--$17899.33

1/ Man-Years relate to time paid from Federal funds only.

Other Notes: Firm outstanding commitments (or obligations) are considered as expenditures including, for example, unliquidated orders for equipment.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

FY 1972 ANNUAL REPORT -- MATCHING GRANT (SEC. 101) PROJECT FORM OW-7 (197

(Prepare a separate form for each Sec. 101 project in progress during FY 1972

State where institute located: Rhode Island Report as of June 30, 1972

OWRR Proj. No. B-033-RI

Matching Grant Agreement Number 14- -0001- 3640

Total Federal Amount of the M.G.A.- $15900.

Project Title: Biological Degradation of Hydrocarbons in Water

Prin. Investigator(s): Chester Houston

Proj. Began--Mo: July; Yr: 1971 Actual or Scheduled Completion--Mo: June ; Yr: 1973

Cost Categories Man-Year Information FY1972 1/	Expenditures in FY 1972		
	Federal $	Non-Fed. $	Total $
A. SALARIES & WAGES: Total	3440.20	5046.12	8486.32
Principal Investigator(s) No: 1 Man-Years: 0.10	(1695.63)	( )	(1696.63)
Other Professional Staff: No: Man-Years:	( )	( )	( )
Graduate Student Assistants: INCLUDES STUDENT TECHNICIANS No: 1 Man-Years:	( )	(5046.12)	(5046.12)
Undergraduate Student Assistants INCLUDES STUDENT TECHNICIANS No: 1 Man-Years: 0.40	(1743.57)	( )	(1734.57)
Technician and Others: NON-STUDENTS No: Man-Years:	( )	( )	( )
B. NON-EXPENDABLE PROPERTY:	2119.73		2119.73
C. EXPENDABLE PROPERTY: (Supplies, Materials, Etc.)	977.91		977.91
D. OTHER COSTS (SPECIFY): TOTAL (Travel, Indirect costs, Etc.)		3816.30	3816.30
Indirect Costs (34.17% Salaries)	( )	(2899.78)	(2899.78)
Fringe Benefits (10.8% Salaries)	( )	(916.52)	(916.52)
	( )	( )	( )
	( )	( )	( )
	( )	( )	( )
E. TOTALS for FY 1972:	6537.84	8862.42	15400.26

F. Cumulative Total Project Expenditures from Start of Project to June 30, 1972 - - - - - Federal--$ 6537.84 ; Non-Fed--$ 8862.42

1/ Man-Years relate to time paid from Federal funds only.

Other Notes: Firm outstanding commitments (or obligations) are considered as expenditures including, for example, unliquidated orders for equipment.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

FY 1972 ANNUAL REPORT -- MATCHING GRANT (SEC. 101) PROJECT FORM OW-7 (1972)

(Prepare a separate form for each Sec. 101 project in progress during FY 1972

State where institut. located: Rhode Island Report as of June 30, 1972

OWRR Proj. No. B-036-RI

Matching Grant Agreement Number 14- -0001- 3641

Total Federal Amount of the M.G.A.- $ 9100

Project Title: Laser Raman Spectroscopy of Solutes Dissolved in Water from a Remote Platform

Prin. Investigator(s): Christopher Brown

Proj. Began--Mo: July; Yr: 1971 Actual or Scheduled Completion--Mo: June ; Yr: 1973

Cost Categories Man-Year Information FY1972 1/	Expenditures in FY 1972		
	Federal $	Non-Fed. $	Total $
A. SALARIES & WAGES: Total	2391.66	1500.00	3891.66
Principal Investigator(s) No: 1 Man-Years: 0.20	( )	( )	( )
Other Professional Staff: No: ___ Man-Years: ___	( )	( )	( )
Graduate Student Assistants: INCLUDES STUDENT TECHNICIANS No: 1 Man-Years: 0.30	(2391.66)	(500.00)	(2891.66)
Undergraduate Student Assistants INCLUDES STUDENT TECHNICIANS No: 2 Man-Years: ___	( )	(1000.00)	(1000.00)
Technician and Others: NON-STUDENTS No: ___ Man-Years: ___	( )	( )	( )
B. NON-EXPENDABLE PROPERTY:			
C. EXPENDABLE PROPERTY: (Supplies, Materials, Etc.)	488.42		488.42
D. OTHER COSTS (SPECIFY): TOTAL (Travel, Indirect costs, Etc.)		1748.30	1748.30
Indirect Costs (34.17% Salaries)	( )	(1328.00)	(1328.00)
Fringe Benefits (10.8% Salaries)	( )	(420.30)	(420.30)
___	( )	( )	( )
___	( )	( )	( )
___	( )	( )	( )
. TOTALS for FY 1972:	2880.08	3248.30	6128.38

F. Cumulative Total Project Expenditures from Start of Project to June 30, 1972 - - - - - Federal--$ 2880.08 ; Non-Fed--$ 3248.30

Man-Years relate to time paid from Federal funds only.

her Notes: Firm outstanding commitments (or obligations) are considered as expenditures luding, for example, unliquidated orders for equipment.

on-expendable property is defined as property which has continuing use as a self-con-ned unit; is not consumed in use; does not ordinarily become a fixture or lose its ntity, or form a component of equipment, machine, plant, etc.

FY 1972 ANNUAL REPORT -- MATCHING GRANT (SEC. 101) PROJECT FORM OW-7 (1972)

(Prepare a separate form for each Sec. 101 project in progress during FY 1972

State where institute located: Rhode Island

Report as of June 30, 1972

OWRR Proj. No. B- 038-RI

Matching Grant Agreement Number 14- -0001- 3642

Total Federal Amount of the M.G.A.- $ 4300.

Project Title: Planning for Uncertainty in Water Use: A Least-Cost Policy for Rhode Island

Prin. Investigator(s): Arthur Jeffrey

Proj. Began--Mo: July Yr: 1971 Actual or Scheduled Completion--Mo: June; Yr: 1972

Cost Categories Man-Year Information FY1972 1/	Expenditures in FY 1972		
	Federal $	Non-Fed. $	Total $
A. SALARIES & WAGES: Total	3756.07	2660.00	6416.07
Principal Investigator(s) No: 1 Man-Years: 0.10	(1956.07)	( )	(1956.07)
Other Professional Staff: No: ___ Man-Years: ___	( )	( )	( )
Graduate Student Assistants: INCLUDES STUDENT TECHNICIANS No: 1 Man-Years: 0.30	(1800.00)	(2660.00)	(4460.00)
Undergraduate Student Assistants INCLUDES STUDENT TECHNICIANS No: ___ Man-Years: ___	( )	( )	( )
Technician and Others: NON-STUDENTS No: ___ Man-Years: ___	( )	( )	( )
B. NON-EXPENDABLE PROPERTY:			
C. EXPENDABLE PROPERTY: (Supplies, Materials, Etc.)	4.00		4.00
D. OTHER COSTS (SPECIFY): TOTAL (Travel, Indirect costs, Etc.)		2885.30	2885.30
Indirect Costs (34.17% Salaries)	( )	(2192.37)	(2192.37)
Fringe Benefits (10.8% Salaries)	( )	(692.93)	(692.93)
___	( )	( )	( )
___	( )	( )	( )
___	( )	( )	( )
E. TOTALS for FY 1972	3760.07	5545.30	9305.37

F. Cumulative Total Project Expenditures from Start of Project to June 30, 1972 - - - - - Federal--$ 3760.07; Non-Fed--$5545.30

lan-Years relate to time paid from Federal funds only.

ier Notes: Firm outstanding commitments (or obligations) are considered as expenditures luding, for example, unliquidated orders for equipment.

on-expendable property is defined as property which has continuing use as a self-conued unit; is not consumed in use; does not ordinarily become a fixture or lose its ntity, or form a component of equipment, machine, plant, etc.

FY 1972 ANNUAL REPORT -- MATCHING GRANT (SEC. 101) PROJECT

FORM OW-7 (1972)

(Prepare a separate form for each Sec. 101 project in progress during FY 1972

State where institute located: Rhode Island

Report as of June 30, 1972

OWRR Proj. No. B-039-RI

Matching Grant Agreement Number 14- -0001- 3643

Total Federal Amount of the M.G.A.- $16090

Project Title: New Fluorescent Tracer Detection Techniques for Use in Polluted Environment

Prin. Investigator(s): Jan Northby

Proj. Began--Mo: July; Yr: 1971 Actual or Scheduled Completion--Mo: June; Yr: 1973

Cost Categories Man-Year Information FY1972 1/	Expenditures in FY 1972		
	Federal $	Non-Fed. $	Total $
A. SALARIES & WAGES: Total	3900.00	5120.10	9020.10
Principal Investigator(s) No: 1 Man-Years: 0.20	(2640.00)	( )	(2640.00)
Other Professional Staff: No: 1 Man-Years: 0.20	(1260.00)	(387.00)	(1647.00)
Graduate Student Assistants: INCLUDES STUDENT TECHNICIANS No: 2 Man-Years: 0.30	( )	(4733.10)	(4733.10)
Undergraduate Student Assistants INCLUDES STUDENT TECHNICIANS No: Man-Years:	( )	( )	( )
Technician and Others: NON-STUDENTS No: Man-Years:	( )	( )	( )
B. NON-EXPENDABLE PROPERTY:	3727.20		3727.20
C. EXPENDABLE PROPERTY: (Supplies, Materials, Etc.)	1145.15		1145.15
D. OTHER COSTS (SPECIFY): TOTAL (Travel, Indirect costs, Etc.)		4056.34	4056.34
Indirect Costs (34.17% Salaries)	( )	(3082.17)	(3082.17)
Fringe Benefits (10.8% Salaries)	( )	(974.17)	(974.17)
	( )	( )	( )
	( )	( )	( )
	( )	( )	( )
. TOTALS for FY 1972:	8772.35	9176.44	17948.79

F. Cumulative Total Project Expenditures from Start of Project to June 30, 1972 - - - - - - Federal--$ 877.35; Non-Fed--$9176.44

Man-Years relate to time paid from Federal funds only.

er Notes: Firm outstanding commitments (or obligations) are considered as expenditures luding, for example, unliquidated orders for equipment.

on-expendable property is defined as property which has continuing use as a self-con-
ned unit; is not consumed in use; does not ordinarily become a fixture or lose its
tity, or form a component of equipment, machine, plant, etc.

FORM OW-8
(1972)

SUMMARY SHEET FOR MATCHING GRANT (SEC. 101) PROGRAM ACTIVITIES - FY 1972

his sheet provides summary information covering all Sec. 101 projects in progress during Y 1972 using FY 1972 or prior years Sec. 101 funds. Hence, it is a summarization of formation set forth on the separate project report forms OW-7.

State: Rhode Island Total No. of Sec. 101 Projects in Progress During FY 1972 6

Cost Categories Man-Year Information FY 1972	Expenditures in FY 1972		
	Federal $	Non-Fed. $	Total $
SALARIES & WAGES: TOTAL	22,584.10	20,500.44	43,084.54
Principal Investigator(s) No: 7 Man-Years: 0.95	(13,178.87)	( )	(13,178.87)
Other Professional Staff: No: 1 Man-Years: 0.20	(1,260.00)	(387.00)	(1,647.00)
Graduate Student Assistants: INCLUDES STUDENT TECHNICIANS No: 7 Man-Years: 1.20	(6,401.66)	(18,207.24)	(24,608.90)
Undergrad. Student Assists: INCLUDES STUDENT TECHNICIANS No: 4 Man-Years: 0.40	(1,743.57)	(1,906.20)	(3,649.77)
Technicians & Others: NON-STUDENTS No: ____ Man-Years: ____	( )	( )	( )
NON-EXPENDABLE PROPERTY:	5,846.93		5,846.93
EXPENDABLE PROPERTY:	2,974.77	656.58	3,631.35
OTHER COSTS (SPECIFY): TOTAL	639.34	20,668.73	21,308.07
Travel	(199.95)	( )	(199.95)
Indirect (overhead)	(/////////)	(14,720.22)	(14,720.22)
Employee benefits	(/////////)	(4,653.12)	(4,653.12)
Printing	(130.50)	( )	(130.50)
Computer	(308.89)	(1,295.39)	(1,604.28)
	( )	( )	( )
	( )	( )	( )
	( )	( )	( )
	( )	( )	( )
	( )	( )	( )
	( )	( )	( )
	( )	( )	( )
Other Miscellaneous Costs	( )	( )	( )
TOTALS for FY 1972	32,045.14	41,825.75	73,870.89

Cumulative Total Sec. 101 Expenditures from Start of Projects to June 30, 1972 - Federal--$ 32045.14; Non-Fed-$ 41825.75

Form OW-9 (1972)
Page 1 of 7

ANNUAL REPORT - TRAINING AND EDUCATION ASPECTS OF THE WATER RESEARCH PROGRAM UNDER P.L. 88-379

Name of University:
(or College) University of Rhode Island

SUBMIT THE INFORMATION SPECIFIED BELOW FOR THE UNIVERSITY AT WHICH THE WATER RESOURCES RESEARCH INSTITUTE OR CENTER APPROVED UNDER P.L. 88-379 IS LOCATED, AND FOR OTHER UNIVERSITIES WITH WHICH THE INSTITUTE OR CENTER IS COOPERATING. KEEP THE STATISTICS ON ENROLLMENTS, NUMBER OF STUDENTS GRADUATING, EMPLOYMENT STATUS OF GRADUTES, NEW COURCES, ETC., SEPARATE FOR EACH UNIVERSITY. IT IS RECOGNIZED CERTAIN OF THE REQUESTED DATA ON STUDENTS MAY NOT BE READILY AVAILABLE. IF SO, PROVIDE BEST ESTIMATE FIGURES. IN OW-9, DATA ON STUDENTS ARE REQUESTED ONLY FOR THOSE STUDENTS WHO RECEIVED EMPLOYMENT AS RESEARCH PROJECT OR PROGRAM ASSISTANTS THROUGH THE P.L. 88-379 PROGRAM. IF EXTRA SPACE IS NEEDED, ADD PAGES AND NUMBER EACH CONTINUATION ITEM IN THE ORDER SHOWN BELOW.

A. During period since last annual report was submitted provide information on: (See footnote 1/ below.)

(1) New water resources related courses developed. (Give title, state whether interdisciplinary, and give brief description of course. Please indicate if any of these were outgrowths of P.L. 88-379 program activities.)

(2) Water resources related staff members added to fill new positions. (List highest degree obtained and scientific discipline. Indicate which ones received any salary from P.L. 88-379 funds. Do not list staff replacements.)

Gerard P. O'Leary, Ph.D.	Biology, Providence College Providence, R. I.
Roger I. Tanner, Ph.D.	Mechanical Engineering Brown University Providence, R. I.

1/ Our intent here is to obtain information on improved academic capability for water resources research and training. Indicate for each position, research facility or other item, whether support was provided in whole or in part through P.L. 88-379 funds, or from other sources; however, also list improvements supported by State or other funds.

A. (Continued)

(3) Water resources related staff members employed to replace those who retired, died, or moved. (List highest degree obtained and scientific discipline. Indicate which ones received any salary from P.L. 88-379 funds.)

NONE

(4) New water resources research and training facilities other than research equipment items. (Include only major facilities such as new laboratories, buildings, etc.)

During the year, the Rhode Island Water Resources Center acquired approximately 900 square feet of additional space primarily for office use and the establishment of a Water Resources Library.

(5) Interdepartmental interuniversity or regional agreements consummated with respect to improved research and training capabilities. (To be answered only by institutes under P.L. 88-379. If copies of such institute-related agreements have not been provided OWRR, please provide.)

The Rhode Island Center, with its Director as principal investigator continued to cooperate with the other five New England centers on the regional Title II OWRR project (C-2034), "The Feasibility of Optimizing Multi-University Regional Water Resources Research".

B. Number of students receiving employment as research project or program assistants through the P.L. 88-379 program. (Include only those students, both continuing and graduating, paid wholly or in part with P.L. 88-379 funds during the past fiscal year.)

Category of Students	No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc. 2/	
	Scientific Discipline of Student	Number
(1) Undergraduates	Animal Pathology	2
	Bacteriology&Biophysics	1
	Chemistry	2
	Mechanical Engineering	1
	Pharmacognosy	1
		7
(2) Master's Students	Animal Pathology	2
	Biology	1
	Botany	1
	Chemistry	2
	Civil & Environmental Engr.	8
	Economics	1
	Food & Resource Chemistry	1
	Mechanical Engineering	2
	Pharmacognosy	1
	Physics	1
	Ocean Engineering	1
		21

2/ This refers to educational background prior to employment as research assistant on P.L. 88-379 projects--not to departments in which projects are being conducted.

B. (Continued)

Category of Students	No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc.) Scientific Discipline of Student	Number
(3) Doctoral Students	Bacteriology & Biophysics	1
	Chemical Engineering	3
	Food & Resource Chemistry	1
	Mechanical Engineering	1
	Oceanography	1
	Pharmacognosy	1
		8
(4) Postdoctoral Students		None

C. Employment status of majors in water-related fields who graduated during the school year ending about June and who receive P.L. 88-379 support.

EMPLOYMENT STATUS	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1. No. employed in water-related positions in: Total----	2	2	0	4
Federal Agencies-------------	( )	( )	( )	( )
State & Local Agencies--------	( )	( )	( )	( )
University or College---------	( )	( )	( )	( )
Other - Including private enterprise-----------------	(2)	( )	( )	( )
2. No. graduates returning to school for advanced degree-------------	2	3	0	5
3. No. going into military service---------------------	0	0	0	0
4. No. unemployed or working in other fields---------------------	2	2	1	5
5. No. status unknown------------------	1	1	0	2
6. Totals-------------------------	7	8	1	16

D. Type of employment of those school year graduates who received P.L. 88-379 support and who are known to have gone into water-related positions. (Number should agree with total listed under item 1 of the preceding paragraph "C". Graduates enrolled for further course work or training should not be listed here as employed.)

Number of Graduates Engaged in Water-Related Work In:	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1A. Federal Agencies:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1B. State & Local Agencies:				
a. Primarily Research		1		1
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1C. University or College: 3/				
a. Primarily Teaching				
b. Primarily Research				
c. Primarily Research & Teaching				
d. Other or not known				
1D. Other - Including Private Enterprise:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development	1	1		2
d. Primarily Operations	1			1
e. Primarily Management				
f. Other or not known				
Totals	2	2		4

Selected summary of above data — from the "Total" column:

Research (1Aa, 1Ba, 1Cb, 1Cc& 1Da)	1
Planning (1Ab, 1Bb & 1Db)	
Development (1Ac, 1Bc & 1Dc)	2
Operations (1Ad, 1Bd & 1Dd)	1
Management (1Ae, 1Be, & 1De)	

3/Do not include here students working as research assistants and receiving course credits.

E. Identify by name and discipline and briefly describe instances, if any, in which the institute program, in the past year, has resulted in individuals, other than students, doing research or teaching in the water resources field, who, previously, were not involved in water work.

Christopher W. Brown, Ph.D.	Chemistry	- University of Rhode Island Kingston, R. I.
Gerard P. O'Leary, Ph.D.	Biology	- Providence College Providence, R.I.
Yuzuru Shimizu, Ph.D.	Pharmacognosy	- University of Rhode Island Kingston, R. I.
Roger I. Tanner, Ph.D.	Mechanical Engineering	- Brown University Providence, R. I.

F. Cite any instances you know of, in which individuals who previously served as student research assistants on P.L. 88-379 projects, are now serving as professional investigators of P.L. 88-379 projects following graduation. Do not include individuals reported in this category last year or before.

NONE

PUBLICATIONS AND THESES

Publications

S.F. Baldwin and C.W. Brown, "Detection of Ionic Water Pollutants by Laser Excited Raman Spectroscopy", Water Research-in press.

F.P.Daly, C.W. Brown and D.R. Kester, "Sodium and Magnesium Sulfate Ion-Pairing: Evidence from Raman Spectroscopy", J. Phys. Chem., submitted for publication.

Theses

Wen-Hsiung Chen, "Finite Element Solutions to Groundwater Flow with Infiltration", M.S. Univ. of Rhode Island.

Roger S. Hoeh, "Impact of Pricing and Administrative Variables in Planning the Use and Development of Water Resources in Rhode Island", M.S. Univ. of Rhode Island.

A. J. Patton, "Turbulent Thermal Diffusion of a Slot Jet Flowing into a Moving Stream", partial fulfillment of the requirements for the degree of Doctor of Philosophy, Univ. of Rhode Island.

TECHNICAL SECTION
OF THE ANNUAL REPORT OF THE
RHODE ISLAND WATER RESOURCES CENTER
FISCAL YEAR 1973

RHODE ISLAND WATER RESOURCES CENTER

DIRECTOR'S REPORT FOR FISCAL YEAR 1973

Current and Anticipated Water Problems

During the year a new state Advisory Board for the Rhode Island Water Resources Center was established which set up a modified list of priorities for water problems in the state as follows:

1. Control of iron and manganese in groundwater supplies.
2. Control of pollution from industrial plants especially in the metal-working and jewelry industries.
3. Legal, social and economic problems of water resources.
4. Study of viruses and pathogenic bacteria in water.
5. Operational modeling of groundwater aquifers.
6. Modeling of fresh water streams and potential reservoir development.

It is likely that these problems will continue to concern the state for some time to come.

Cooperation with State Agencies

For several years now the Rhode Island Water Resources Center, under the supervision of the state Department of Health, has operated a free program of private well testing for the citizens of the state. This effort has expanded so that several samples per day are now tested.

On February 1, 1973 the Director of the Rhode Island Water Resources Center appeared before the Governor's Environmental Task

Force to provide information concerning the current program of the Center, to answer questions on water resources research and to give opinions on such problems as the advisability of combining water supply and sewage disposal in the state under a single authority. The Task Force report recommended, as was also advised by the Rhode Island Director, that the Water Resources Board coordinate water supply and sewage disposal in the State of Rhode Island. The Board is currently investigating out-of-state agencies which have such combined functions.

A study involving four agencies is currently underway to investigate the ultimate effect of multiple use of ponds and lakes in the state. The Department of Natural Resources, the Department of Health, the Water Resources Board and the Rhode Island Water Resources Center are cooperating in a pilot study to thoroughly monitor a pond of approximately 100 acres which previously has had restricted use. The intention is to follow the effect on water quality as recreational use is increased and, if the results prove fruitful, to extend this type of investigation and analysis to larger bodies of water within the state.

Current Research

As indicated by the priority list established by the Advisory Board, contamination of water sources and pollution by industrial plants continue to be of major importance in this state and much of the water resources research falls into these areas.

Development of pollution detection techniques occupied two investigators during the year. Work on project B-036-RI has demonstrated that Raman spectroscopy shows considerable promise for the remote detection of all types of water pollutants. Efforts on Project B-039-RI resulted in the construction of a versatile and sensitive fluorimeter which can be used either as a scanning or filter instrument in the detection of pollutants.

Two projects were concerned with the presence of pesticides in water. Project A-044-RI has been concerned with the extent of pesticide accumulation by aquatic algae which could be very useful to an investigator interested in quantifying certain pesticides in the presence of interfering compounds. Project A-045-RI is studying the biodegradation of halogenated aromatic acids, which are common pesticides, using the co-oxidation approach with a view to speeding up the process.

Three projects were involved in the area of waste water treatment. Project A-040-RI continued work on the design of an electrochemical process for the removal of nitrogen and phosphorus nutrients from water. Information which has been determined in this project should enable industries to develop and build full scale treatment systems with wide applications. Cellulose, the most plentiful of organic compounds, is a major component of municipal and agricultural solid wastes which contribute to the pollution of natural waters. Research in project A-046-RI is developing a high pressure fermentation process for cellulose waste treatment using thermophilic bacteria. Project A-048-RI has been working on the development of an effective and economical process for the treatment of wastewater from fish and shellfish processing plants. This study should prove of value in controlling pollution problems created by the numerous small-scale operations of this type in New England.

The presence of toxic or pathogenic substances in water sources has been the concern of three investigators during the year. The results of the two-year study in Project A-039-RI have shown that if the concentration of Escherichia Coli (probably the most common bacterial pollutant) reaches a high enough level in a fresh water system, sufficient endotoxin may exist in the water to cause the death of fish. Further research on Project A-041-RI has shown that toxic compounds can be formed from the combination of eluted organic substances and chlorine (which is used extensively in water supply treatment). In tests to date it would appear that the concentration of chlorinated phenols in water supplies is likely to be low enough so that acute toxicity would not be encountered, but the effects of long periods of exposure to these compounds is not yet known. Ozonation has some advantages over chlorination in the purification of water but its effect on the destruction of viruses has not been studied extensively. If ozone is to be used on a large scale for water treatment, it is important that the effect of ozonation on all types of human viruses be known. Project B-047-RI has already determined that the use of ozone to replace chlorine should proceed with caution.

When water comes into contact with galvanized metal, traces of cadmium and zinc go into solution, which poses a health hazard to man, animals and fish. Project A-047-RI is determining the mechanism by which water is contaminated by these elements and developing methods for controlling the corrosion rate.

Project B-033-RI continued to extend knowledge of the process of the biological degradation of hydrocarbons in water. Considerable background information of this type is needed in the possible development of methods employing bacteria for the control of oil spills.

A. Ralph Thompson
Director, Rhode
Island Water Resources
Center

OTHER NARRATIVE ITEMS

RHODE ISLAND WATER RESOURCES CENTER

Examples of Research Findings and Their Actual or Potential Application to Water Resource Problems

The development of methods for controlling the copper content in water has been cited before by this center as an example of a local problem solved by its research. Some areas of Rhode Island have groundwater supplies which are so aggressive that sufficient copper is dissolved from piping that it causes a serious health hazard. The research on this problem (Project A-014-RI) showed that neutralization or dimineralization can reduce the copper content to a safe level.

The new Advisory Board to the Rhode Island Water Resources Center has indicated that the control of iron and manganese in groundwater supplies is the Number One priority water resources problem in Rhode Island. Several years ago the Center helped in the initiation of the statewide groundwater iron and manganese survey which was completed during the past year in cooperation with the U.S. Geological Survey. Through several projects (A-003-RI, A-017-RI and A-029-RI) definite progress has been made toward the development of methods and equipment for the continuous filtration of iron and manganese from small groundwater supplies. Although there was no project supported by OWRR during the year concerned with the control of iron and manganese in groundwater, the work begun in earlier projects was continued by a Ph.D. student in Chemical Engineering with the aid of state funds. It is certain that there will be proposals in the near future in this important area so that this research will continue. This research will eventually make it possible for the state to use many water sources which would otherwise be unsatisfactory.

New Developments in Advisory Boards and State Activities

The new Advisory Board for the Rhode Island Water Resources Center is represented by officials from a number of state agencies and has the following members:

Robert B. Russ, General Manager, Water Resources Board

Carleton A. Maine, Chief, Water Supply and Pollution Control Division, Department of Health

Frederick C. Williamson, Director, Department of Community Affairs

Alonzo W. Quinn, Member, Water Resources Board

Daniel W. Varin, Chief, Statewide Planning Program

By virtue of the Water Resources Planning Act, the Water Resources Board received a matching grant for the purpose of preparing a comprehensive plan for water and related land resources in the state. The formulation of the plan was programmed into seventeen separate tasks. To date, the tasks completed are as follows:

Inventory of Water Resources Reports

Municipal Water Supplies and Water Use

Inventory of Industrial Water Supplies and Water Use

Inventory of Municipal Waste Treatment Plants

Rhode Island River Basins

Rhode Island Lakes and Ponds

Legal and Legislative Aspects of Water Resources

A Statewide groundwater iron and manganese content survey, which was initiated with the help of the Rhode Island Water Resources Center, was completed by the Water Resources Board in cooperation with the United States Geological Survey. The Water Resources Board is now in the process of preparing a groundwater management plan for the State of Rhode Island.

Regional Cooperation in Research and Training

The Rhode Island Water Resources Center continues to cooperate fully in all regional projects and is presently involved as financial administrator for one effort of the New England states and another for fifteen Northeastern states. The Title II project (C-2034) entitled "The Feasibility of Optimizing Multi-University Regional Water Resources Research", for which the Rhode Island director was Principal Investigator, officially terminated December 31, 1972. The completion report for this project entitled "Water Resources Research Coordination in New England" was printed (68 pages) and distributed nationally. As recommended by this report, the office of Regional Research Coordinator is being continued by contributions from the six New England water resources centers with Rhode Island serving as financial agent. As indicated, the Rhode Island center is also handling the finances for the project supported by OWRR involving the assessment of regional water resources research needs through a series of workshops being organized by the centers in the Northeast.

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-039-RI

Agreement No. 14-31-0001-3840

FCST-OWRR Research Category: V C

Project Title:

The Effects of Differently Extracted Endotoxins from Escherichia Coli on Rainbow Trout (Salmo Gairdneri)

Name and Location of University Where Project is Being Carried Out:

Providence College, Providence, R. I.

Proj. Began--Month: July ; Year: 1971

To Be Completed--Month: June ; Year: 1973

Principal Investigators	Degree	Discipline
Gerard P. O'Leary	Ph.D.	Microbiology

Student Assistants 1/	Degree Held (if any)	Discipline - Academic Background
Henry R. Vaillancourt	B.S.	Biology
Michael S. Flood	B.S.	Biology
Kenneth Deloge		Biology

OWRR Project No. A-039-RI

Research Project Accomplishments:

The extraction of endotoxins from two strains of *Escherichia coli* by four different procedures has been completed. *E. coli* 0111:B4 and *E. coli* K-12λ has been extracted for endotoxic material by the ethylenediamine-tetraacetic acid method, distilled water method, trichloroacetic acid method and the aqueous ether method. All materials extracted have shown the normal monosaccharide chromatographic profile. The typical monosaccharides detected were glucose, galactose, glucosamine and the seven carbon sugar D glycero L manno-heptose. These results indicated that the material extracted by the four different methods chemically conform to the lipopolysaccharide (endotoxin) material normally obtained from gram-negative bacteria.

Rainbow trout (Salmo gairdeneri) were obtained from the Perryville hatchery (Natural Resources, Rhode Island) and were kindly donated by the State of Rhode Island with the permission of Mr. John Stolgitis. The trout were transported from the hatchery in 50 gal. plastic buckets equipped with continuous airation systems. The fish were then immediately transferred to a 200 gal life Support system kept at a constant temperature of $52^{o}F \pm 2.0^{o}F$. The fish were fed once daily with approximately 12-15g. of Ranger's Quality trout feed (Zeigler Bro. Feed) Mills, Gardners, Pa.). Airation was kept constant by means of two water airation systems at each end of the tank while the pH was controlled at 7.0 ± 0.2 using Calcium carbonate. Since the life support system is a closed system and wastes build up, each week 100 gal. of the total 200 gal. was replaced with fresh water of the same quality as the tank with respect to temperature and pH. On the average twenty-one rainbow trout were introduced into the life support system and monitored daily for one month before experimentation proceeded.

Experimental Procedure For Introduction of Endotoxin

The fish were separated into three compartments containing approximately seven fish each. One compartment housed the control animals which were inoculated with comparable amount of 0.85% Sodium chloride while the other two compartments were used for fish inoculated with different types of Endotoxin. Each compartment contained fish injected with one particular endotoxin preparation. The fish were removed for inoculation and anaesthetized. The fish were tagged for identification by cutting a portion of one of their fins. Each fin which was cut indicated a specific organism. The fish were then weighed and inoculated with a predetermined amount of endotoxin using either a Becton-Dickinson 3cc plastipak disposable syringe with a 27G 1/2 needle or a 1cc disposable tuberculin syringe with a 27G 1/2 needle. The fish were inoculated intraperitoneally, place in fresh water and allow to come to a conscious state. They were then placed in their particular compartment in the Aquatic life support system.

The inoculated fish were fed on their regular schedule and observed twice daily for any effects.

Results

Four experiments were conducted, each taking approximately two months. Of the four the third experiment was disregarded due to the development of a fungal infection in the life support system which eventually effected all fish including the control animals.

The first experiment involved the use of the E. coli K 12 endotoxin extracted by both the water and EDTA methods. In the former case, approximately 143.7 mg/Kg weight of fish of the water extracted endotoxin was inoculated into 6 fishes while the latter, EDTA extracted endotoxin, was administered at a concentration of approximately 162.3 mg/Kg weight of fish. After approximately two weeks visible reaction occurred in both sets of test organisms. Three of the water-endotoxin inoculated fish showed large red hemorrhaging along the lateral line of the body. The onset of the hemorrhagic and necrotic areas began with edema and swelling of the area. The fish were removed and weighed and showed a substantial weight loss of between 16.8% and 7.2% weight loss from time of inoculation. During the same period the control animals gained on the average 14.0% in weight. Two of the EDTA endotoxin fish also showed the same symptoms however their weight loss was less dramatic showing approximately a 3.4% loss in weight from the time of inoculation. The experiment was terminated at this point.

The second experiment was designed to repeat the EDTA-endotoxin preparation while raising the endotoxin concentration to 207.2 mg/Kg wt. of fish. The ether-endotoxin preparation at a concentration of 154.6 mg/Kg. wt. of fish was also added. The experiment consisted of six fish in each section, control, EDTA-endotoxin, and ether-endotoxin. The raised level of EDTA-endotoxin caused death in fish 1, 2, and 3 after seven days while fish 4 and 5 of the series died after 13 days. The sixth animals remained alive but weak at the termination of the experiment. The test organisms inoculated with the ether-endotoxin preparation also showed similar results with fish 1 and 2 expiring after seven days, 3 and 4 after 12 days and the 5th after 13 days.

The final trial was a repeat of the previous using both the EDTA and ether extracted, however the concentration of endotoxin per Killogram of body weight was increased while younger and smaller trout were used. During the first two successive trials the trout average approximately 30 grams. The trout using for this experiment averaged approximately 13 grams. The ether extracted endotoxin was increased to 207.2 mg/Kg. of body weight while the EDTA preparation was increased to an average value of 410.8 mg/Kg of body weight. In this experiment each section, controls, ether, and EDTA, contained seven fish. The first death (fish No. 7) due to the ether-endotoxin occurred two days after inoculation with similar symptons of the previous trials, however this organism showed significant weight loss as did fish number 6 which died three days after inoculation. Fish number 2 and 4 died on the four day both showing weight losses of approximately 30.0% of their initial body weight. The experiment was terminated on the 5th day due to a power failure during the night which caused the main tank containing the test animals to drain causing death of all animals. During this five day period their were also five deaths in the EDTA-endotoxin treated fish. Death occurred to fish numbers one, four and five after two days. Fish number one showed a 10% loss in weight, fish number five approximately 25% loss in weight while fish number four showed no significant weight loss. Two more fish expired on the fourth day both showing a 20% weight loss.

Discussion

We have not been able to gather enough data at this time to make conclusive calculation as to leathal dose, however we do feel that we have shown that the endotoxin from Escherichia coli can be toxic for rainbow trout if the concentration is great enough. It would also seem that certain extractions yield endotoxin preparation with greater or lesser toxicity to rainbow trout.

Our results to date show that the ether extracted endotoxin caused death in the test animals at lower concentrations than the other preparations tested. Approximately 154 mg/Kg weight of animal was capable of causing death in 5 out of 6 animals where for the same result 207 mg/Kg body wt. was needed using the EDTA extracted endotoxin.

Data obtained from the final experiment using an average amount of 207.23 mg ether endotoxin per killogram body weight indicated that the rate of effect of the endotoxin may have some dependence on the age and size of the rainbow trout. Death was seen to occur within 2-3 day in trout having an average weight of only 16.08 g while in a comparable experiment the time for death occurred was lengthened to 9 to 13 days using fish having an average weight of 29.0g. More experimentation with different size trout and exact comparable amounts of endotoxin will be necessary to confirm these initial results.

The results to date have definitely shown that at least for rainbow trout, certain entodoxic preparations from Escherichia coli K12 λ, are toxic and result in death of the organism.

Project Status

According to Water Resources of Rhode Island the grant A-029 R.I. will terminate on June 30, 1973. The final report on research accomplishments will be presented to Water Resources on July 30, 1973.

Due to the time involved in each experimental procedure, approximately two months, the amount of experiments were cut short. The object of the project, that of the effects of differently extracted endotoxins on rainbow trout was accomplished, however much information is still lacking. We therefore plan to continue experimentation for the next year with the equipment supplied by the grant and a small amount of money supplied by the College. We plan to gather data on the smallest dose of Endotoxin necessary to cause death in trout and the correlation between age and size as to death of the animals.

Application of Research Results.

The application of these results cannot be completely determined at this time. However, this is the first report of endotoxins from any bacteria being toxic to fish. These results may have implications as far reaching as to effect the quality of fresh water systems and certain types of fish kills. These results may also be applicable to part of our fresh water pollution problems. If, the concentration of Escherichia coli reaches certain levels in a fresh water system, there are possibilities that enough endotoxin may exist in the waters to cause the death of certain fish. We have shown that at least certain concentration of E. coli K 12 endotoxin will cause death in Rainbow trout (Salmo gairdneri).

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ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-040-RI

Agreement No. 14-31-0001-3840

FCST-COWRR Research Category: V D

Project Title:
Electrochemical Process for Nutrient Removal

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R.I.

Proj. Began--Month: July ; Year: 1971

To Be Completed--Month: June ; Year: 1973

Principal Investigators	Degree	Discipline
Calvin P.C. Poon	Ph.D.	Environmental Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Mung-Shium Shieh	B.S.	Environmental Engineering

OWRR Project No. A-040-RI

Electrochemical Process for the Removal of Nitrogen and Phosphorous from Wastewater

The work in the second year of the project was concerned with the removal of phosphate and nitrogen in various forms in a batch electrochemical cell. Disinfection and BOD as well as suspended solids removals were also evaluated. The last stage of the work was to repeat the experiments in a flow-through model.

Phosphate Removal -- By using 0.33 ampere per each liter of sewage treated and with a sewage to seawater loading ratio of 9 to 1, 98% or more of orthophosphate could be removed in 25 - 35 minutes. Total phosphate removals were greater than 90% with approximately 45 minutes. Voltage requirements varied between 4.5 and 6.0 volts, depending on the degree of stratification. Figure 1 shows the orthophosphate removal under various conditions and Table 1 shows the results of some typical experiments.

Jar tests using solutions of known concentrations of Mg^{++} and $PO_4^{=}$ at pH 11.0 demonstrated the mechanism of phosphate removal as adsorption. The $Mg(OH)_2$ flocs generated at high pH removed phosphate followed closely a Langmuir type isotherm.

Nitrogen Removal -- Experimental results showed superchlorination as a primary mechanism in nitrogen removal. A pattern of gradually increasing free chlorine and rapidly increasing com-

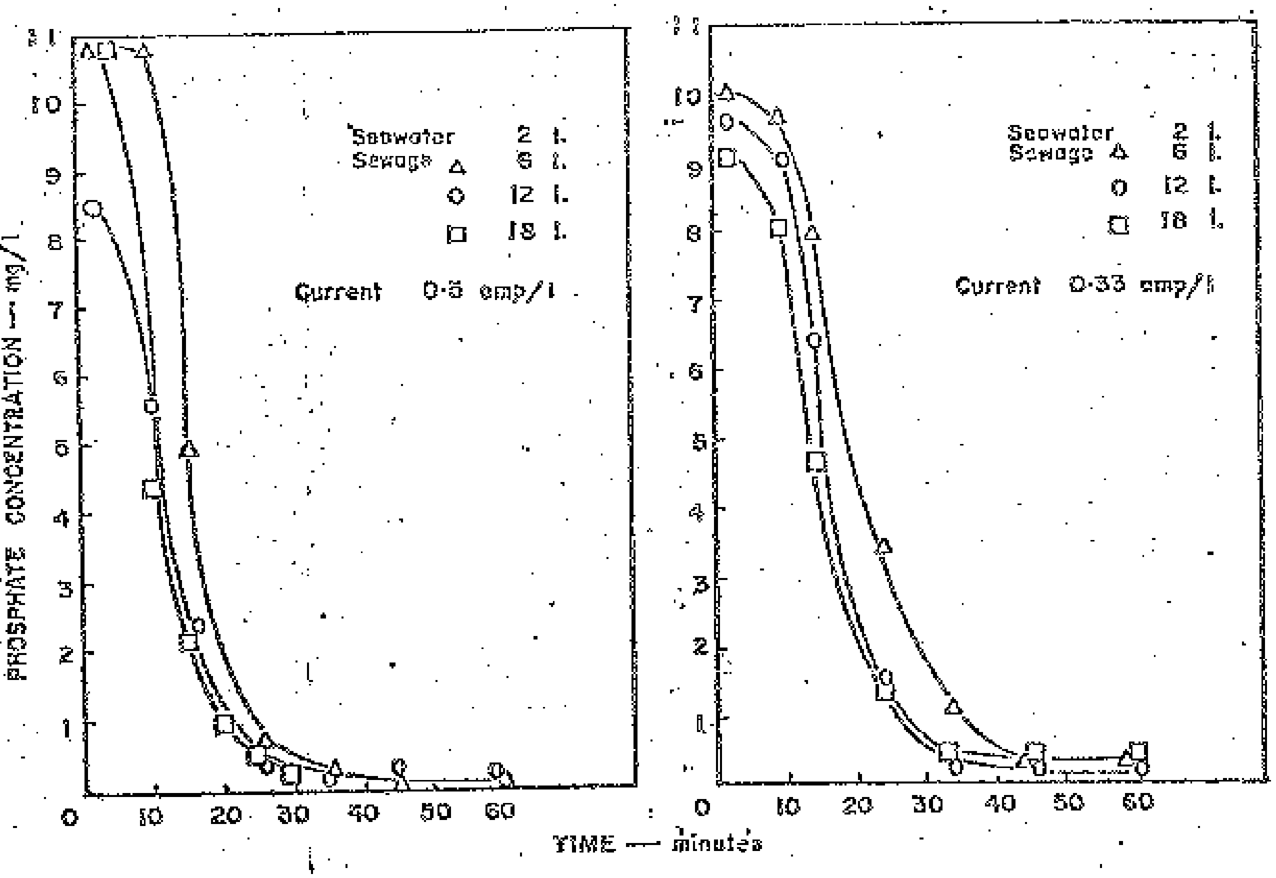

FIGURE 1 — PHOSPHATE REMOVAL WITH TIME AT VARIOUS SEWAGE LOADINGS

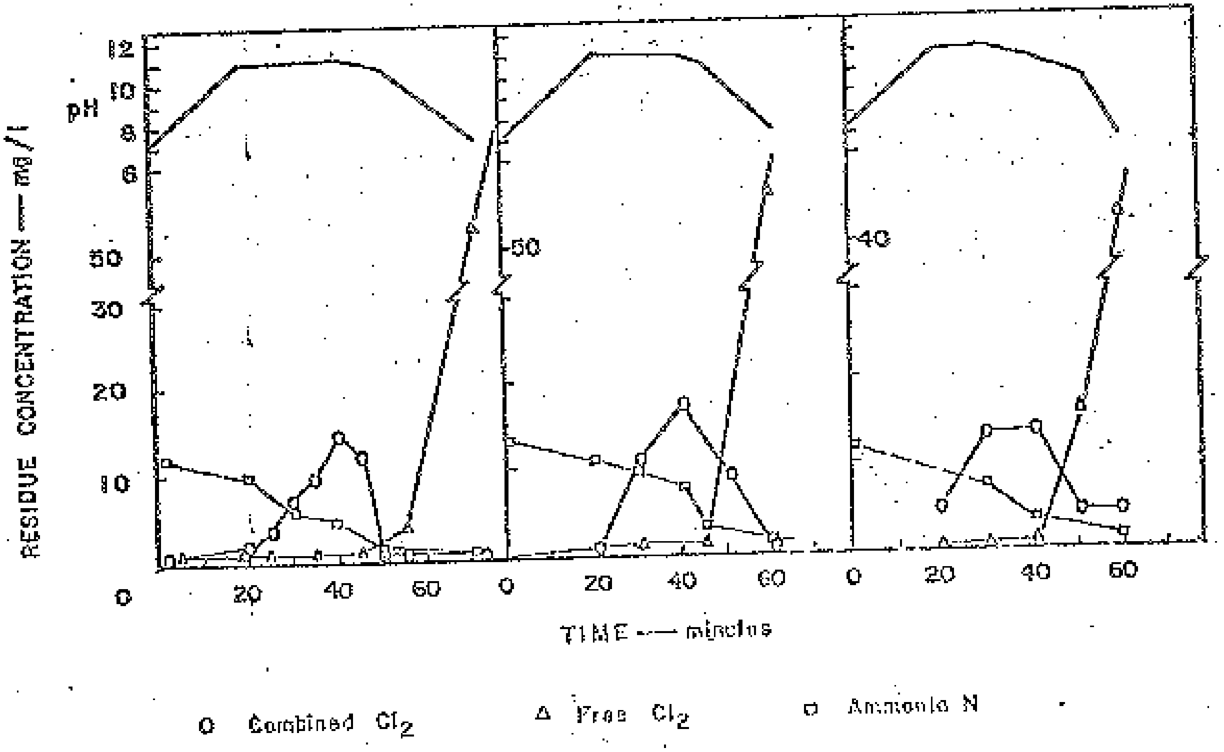

FIGURE 2 — CHANGE OF AMMONIA NITROGEN, COMBINED CHLORINE, FREE RESIDUE CHLORINE CONCENTRATION, AND pH WITH TIME

TABLE I Ammonia Nitrogen, Total Nitrogen, Orthophosphate, and Total Phosphate Removals for 5 amperes and 9 amperes of current*

	Time (min)	pH	** NH_3N	% rem.	** Total N	% rem.	** ortho-PO_4^{-3}	% rem.	Total PO_4^{-3}	% rem.
URI raw sewage	0	7.00	9.2		18.0		3.20		4.20	
	30	10.90	5.8	37.0	15.0	16.7	0.20	94.0	–	–
	45	10.80	3.8	59.0	–	–	0.20	94.0	0.42	90.0
	60	10.10	1.4	85.0	5.2	71.0	0.20	94.0	–	–
URI raw sewage, 5 amps	0	6.85	8.9		17.7		1.85		2.50	
	20	10.60	8.3	0.7	14.6	17.5	0.20	89.5	0.22	87.0
	30	10.70	6.3	29.0	–	–	0.20	89.5	0.20	92.0
	45	10.30	1.0	89.0	6.9	61.0	0.20	89.5	0.20	92.0
	65	7.20	0.8	91.0	5.0	72.0	–	–	–	–
URI raw sewage, 9 amps	0	6.95	11.4		23.0		2.95		5.10	
	15	10.50	10.8	0.5	19.1	17.0	0.25	91.5	0.44	91.5
	25	10.10	4.8	58.0	10.9	53.0	0.20	93.5	0.31	94.0
	30	6.70	0.9	92.0	3.0	87.0	–	–	–	–
Warwick raw sewage, 5 amps	0	6.85	13.2		21.7		4.00		5.30	
	[illegible]	10.65	11.5	13.0	–	–	1.13	72.0	1.92	66.0
	[illegible]	10.90	9.8	26.0	15.2	30.0	0.20	95.0	0.50	89.0
	[illegible]	10.85	7.3	45.0	11.6	47.0	0.20	95.0	0.43	92.0
	[illegible]	6.10	1.9	86.0	3.9	82.0	–	–	–	–

*2liters of seawater and 12 liters of the specified sewage were added slowly through a hose for better stratification in each experiment

**mg/liter

bined chlorine was observed in the first 40 minutes followed by a rapid increase of free chlorine and a subsequent decrease of combined chlorine. The pattern suggested a breakpoint chlorination whereby the chloramines were decomposed by the presence of excess chlorine. Figure 2 shows typical ammonia nitrogen removals with changing pH and chlorine species during the course of 3 experiments.

Ammonia nitrogen removals were consistently greater than 85% (average 90%) and total nitrogen removals were on the average 80%. Tables1 also shows such removals from several typical experiments.

BOD and Suspended Solids Removals -- With good stratification, the average BOD removal at 60 minutes was 85%. The initial rate of removal at the first 30 minutes was faster which suggested that the $Mg(OH)_2$ floc carrying the insoluble form BOD was primarily responsible. The subsequent removal mostly soluble form, was much slower and comparatively inefficient.

Although the original amount of suspended solids was reduced significantly in the process, excess amount of $Mg(OH)_2$ flocs generated may remain in the process effluent. Experiments conducted with good stratification produced a combined process effluent (treated sewage and spent seawater mixture) with an average suspended solid concentration of 25 mg/l. The spent seawater had a low pH which helped to dissolve the excess $Mg(OH)_2$ flocs and consequently yield a sparkling clean effluent. Suspended solid removal was 87% on the average.

Disinfection -- The disinfection of sewage effluent was 100% for total coliform groups with a dentention time of 30 minutes or longer.

In operating the batch process, one has to be careful to terminate the treatment in time to avoid a high chlorine residue in the effluent. This sometimes resulted in a slightly higher nitrogen effluent.

Power consumption in the batch process varied from 3.16 to 6.65 kwh/1000 gallons of sewage treated. Average consumption with good stratification was approximately 4.5 kwh/1000 gallons. This consumption did not include power for seawater pumpage.

The final stage of the work was to conduct similar experiments in a flow-through model. The flow-through model is a cell constructed with 1/4" lucite with an inside dimension of 14" x 6 1/2" x 6" deep. The arrangements for anodes and cathodes were identical to that of the batch study except that the steel cathode was supported on all sides so that no interchange of anolyte and catholyte was possible except through the holes on the steel plate. Separate inlets for seawater and sewage were provided. Also separate outlets for seawater and sewage were provided. These arrangements were made to assure minimal mixing of the colution even when seawater and sewage were introduced into the cell at different flow rates. Multiple outlets were also provided for sewage at various levels to allow different depths of sewage above the cathode. In later experiments, the cathode was lowered to provide an electrodes spacing of 2 cm. in order to reduce power requirement and to reduce the seawater working volume.

Each experiment was started out as a batch process. The flow-through mode of operation was initiated after a period was elapsed which was equivalent to the average detention time the sewage remained in the cell in the continuous flow operation. Samples were then taken to monitor the effluent qualities over a period of time. Measurements include amperage, voltage, pH, suspended solids, BOD, ammonia and total nitrogen, orthophosphate and total phosphates and sometimes the residue chlorine. Methods of sample analysis were the same used in the batch model study. In most cases, the effluent characteristics of the treated sewage and spent seawater mixture were analyzed as the mixture will be the form of the final effluent to be discharged from the process (with the floating solids skimmed off).

Using a sewage-seawater loading ratio of 2 to 1, the flow-through model provided satisfactory performance summarized in the following Table 2.

Table 2: Performance of a Flow-Through Model at Low Sewage-Seawater Loading Ratio

Parameter	Experimental Conditions: Sewage/seawater ratio = 2/1 Detention time: 60 minutes Current: 2 amp Power Consumption: 10.0 kwh/1000 gal.
S.S. Removal	78.5% (68.7 - 85.4)
BOD Removal	65.0% (60.0 - 73.4)
NH_3-N Removal	100.0% ----
Total -N Removal	91.5% (88.3 - 94.5)
Ortho -PO_4 Removal	83.7% (80.9 - 85.6)
Total -PO_4 Removal	85.1% (77.9 - 90.2)

Despite the fact that satisfactory removals of nutrients could be obtained in the process, high residual chlorine was detected in the effluents of all experiments. The high chlorine residue explained the fact that very high nitrogen removal was accomplished. Since high chlorine residualis objectionable in sewage effluents, some control of the concentration is necessary. Also the low sewage to seawater ratio required a higher power consumption for unit sewage volume treated.

Increasing the sewage to seawater loading and reducing the seawater retention time in the electrolytic cell to one-half of the sewage retention time led to the followin results.

Table 3: Performance of a Flow-Through Model with Adjustments in Operation

Parameter	Experimental Conditon: Sewage/Seawater ratio = 3/1 Detention time: 60 min. or 40 min. Current: 2 amp. 3 amp. Power Consumption: 8 kwh/1000 gal.
S.S. Removal	70.1% (66.7 - 73.5)
BOD Removal	63.5% (59.8 - 68.2)
NH_4 -N Removal	68.1% (67.5 - 68.8)
Total -N Removal	64.0% (59.0 - 69.0)
Ortho -PO_4 Removal	80.7% (74.0 - 87.4)
Total -PO_4 Removal	81.7% (78.6 - 84.9)

The residual chlorine was reduced to 69 mg/l as compared to 126 mg/l in previous experiments. The concentration of residual chlorine was still undersirable. In addition, the performance was slightly inferior. The lower power consumption, however, could justify a small sacrifice in performance.

It should be noted that the effluent quality was exceptionally well compared to a conventional secondary treatment process (S.S. 20 mg/l; BOD, 20 mg/l; NH_4-N, 1.4 mg/l; Total -N, 3.0 mg/l; Ortho-PO_4, 1.3 mg/l; Total —PO_4, 2.9 mg/l). This was so because the raw sewage in the flow-through model experiments was rather weak. The same effluent quality cannot be expected if stronger sewage had been used. However the percentages of nutrients removal would be higher for stronger sewage.

The project has been completed and the major objectives of the project has been fulfilled. A completion report of this project is being prepared. The information should allow industries to build prototype treatment units for a development program from which full scale treatment systems could be eventually designed and built for wide applications. Part of the project work was presented at the 28th Purdue Industrial Waste Conference at Purdue University in May 1973.

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ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-041-RI
Agreement No. 14-31-0001-3840
FCST-COWRR Research Category: V A

Project Title:

Plant Phenols and Related Organic Compounds in Public Water Sources, Their Relationship to Chlorination

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R.I.

Proj. Began--Month: July ; Year: 1971
To Be Completed--Month: June ; Year: 1973

Principal Investigators	Degree	Discipline
Yuzuru Shimizu	Ph.D.	Pharmacognosy

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Rong Yew Hsu	M.S.	Pharmacognosy

OWRR Project No. A-041-RI

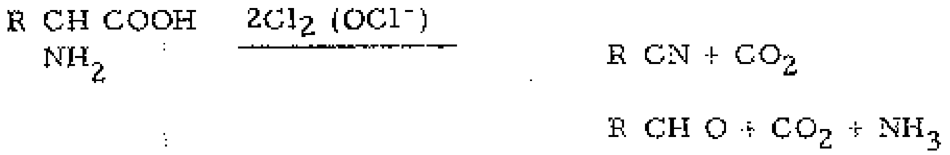
Plant Phenols and Related Organic Compounds in Public Water Sources, Their Relationship to Chlorination

The work conducted in the previous year showed that phenolic compounds afford a variety of chlorinated and degraded products upon contact with chlorine or hypochlorite in aqueous media. In this year, further chemical studies have been carried out to expand the previous findings, and at the same time efforts have been made to evaluate the biological activities of the products.

In the chemical studies, the formation of nitrile derivatives from tyrosine was thoroughly studied, and it was discovered that most α-amino acids give the nitrile derivatives by chlorine oxidation rather than the aldehydes. The reaction was shown to take place at very high dilutions regardless of molar ratio of chlorine present. Consequently, it is now reasonable to assume that free amino acids in chlorinated water are mostly transformed first to the nitriles.

Typically, in experiments using phenylalanine and leucine, phenylacetonitrile and isovaleronitrile were formed in ca. 80% yields respectively.

The reaction can be expressed in the following generalized form.



$$\underset{NH_2}{R\,CH\,COOH} \xrightarrow{2Cl_2\,(OCl^-)} \begin{array}{l} R\,CN + CO_2 \\ R\,CH\,O + CO_2 + NH_3 \end{array}$$

The chlorinated benzoquinones, such as 2,6-dichlorobenzoquinone or chloranil showed microbiological activities at the concentration of 2 ppm, but the compounds, such as 1-(4-hydroxyphenyl)-2,2-dichloroethanol, 1-(3,5-dichloro-4-hydroxyphenyl-2,2 dichloroethanol, 1-(3-chloro-4-hydroxyphenyl)-2,2-dichloroethanol, 3,5-dichloro-4-hydroxybenzyl cyanide, 3-chloro-4-hydroxybenzyl cyanide were shown to have little effect against microorganisms at the same concentration. Similarly, the chlorinated benzoquinones showed more potency in the molluscicidal activity than the other examined chlorined phenols.

EXPERIMENTAL

I. Antimicrobial Test

Five species of bacteria, E. coli, Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus Subtilis, Proteus sp. and three species of fungi Candida albicum, Aspergillus sp., Sacchromyces sp. were obtained from the American Type Culture Collection (ATCC). Ten chlorinated phenols were weighed accurately about 4 mg then dissolved in ethyl acetate to make 1:500 solution (2 ppm). One tenth milliliter of 1:500 dilution of chlorinated phenols was placed on filter paper discs (13 mm in diameter). One tenth milliliter of 24-hour culture of microorganisms was added to the tube of media. Plates were formed and solidified then placed in the refrigerator for one hour. After discs were placed on the plates, the plates were put in the refrigerator for 2 hours then place in the incubator at 37°C, examined the inhibition zone after 24, 48 hours. The results of antimicrobiological test were shown in Table I.

TABLE I

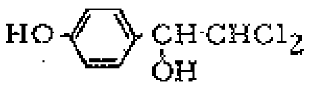
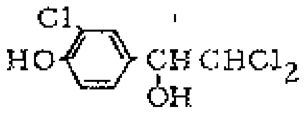
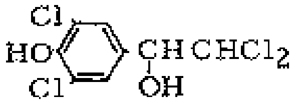
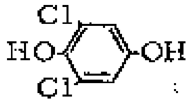
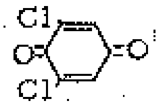
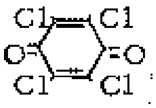
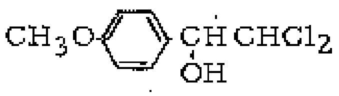
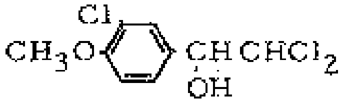
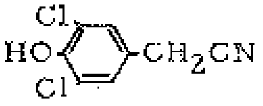
Phenolic Compounds		Hour	Candida albicans		Aspergillus sp.		Sacchromyces sp.	
I		24	-	-	-	-	-	-
		48	-	-*	-	-	-	-*
II		24	-	-	-	-	-	-
		48	-	-	±	±	-	-
III		24	-	-	-	-	-	-
		48	-	-	-	-	-	-
IV		24	15	16	-	-	-	-
		48	15	16	-	-	-	-
V		24	17	17	-	-	-	-
		48	16	16	-	-	-	-
VI		24	15	15	-	-	-	-
		48	15	15	14	14	-	-
VII		24	-	-	-	-	-	-
		48	-	-	-	-	-	-
VIII		24	-	-	-	-	-	-
		48	-	-	-	-	-	-
IX		24	-	-	-	-	-	-
		48	-	-	-	-	-	-
X		24	-	-	-	-	-	-
		48	-	-	-	-	-	-

TABLE 1 (continued)

		S. aureus		*E. coli*		*P. aeruginosa*		*Proteus sp.*		*B. subtilis*	
I	24	-	-	-	-	-	-	-	-	-	-
	48	-	-*	-	-*	-	-	-	-	-	-*
II	24	-	-	-	-	-	-	-	-	-	-
	48	-	-	-	-	-	-	-	-	-	-
III	24	-	-	-	-	-	-	-	-	-	-
	48	-	-	-	-	-	-	-	-	-	-
IV	24	15	16	16	16	36	36	20	20	17	17
	48	14	15	16	15	36	36	20	20	17	17
V	24	16	16	15	15	14	14	15	15	17	17
	48	16	16	15	15	14	14	15	15	17	17
VI	24	16	15	15	15	-	-	15	15	14	14
	48	16	15	14	14	-	-	14	14	15	14
VII	24	-	-	-	-	-	-	20	20	-	-
	48	-	-	-	-	-	-	18	18	-	-
VIII	24	-	-	15	14	-	-	-	-	15	15
	48	-	-	14	-	-	-	-	-	14	14
IX	24	-	-	-	-	-	-	-	-	-	-
	48	-	-	-	-	-	-	-	-	-	-
X	24	-	-	-	-	-	-	-	-	-	-
	48	-	-	-	-	-	-	-	-	-	-

* - to be repeated

II. Laboratory Screening Test for Molluscicidal Activity

The fresh water pulmonate snail Biomphalaria glabrata was employed for the molluscicidal testing. The snails were reared in glass aquaria filled with Arbor Springs spring water about 8-10 gallon capacity. Each aquarium was fitted with a green glass-paper cover and air releasers. The food of the snails was supplied daily including fresh green lettuce leaves or romaine lettuce and a commercial tropical fish food. Snail growth and reproduction were in room temperature.

The chlorinated phenols were weighed accurately and were diluted in a volumetric flask with distilled water to the desired part per million (ppm). All compounds for testing were dissolved in distilled water with the aid of one drop of Tween 80 as co-solvent. Ten snails in a beaker were exposed for twenty-four hours to the test solution. After the exposure period, the snails were rinsed in distilled water and placed in fresh distilled water with food for a recovery period of twenty-four hours. At the end of the recovery period, mortality was determined. Ten control snails were employed in one drop of Tween 80 and distilled water for the same period of time as the test snails. The results of molluscicidal activities were shown in Table II.

TABLE II

	Concentration (ppm)					
	1	10	20	50	75	100
I	-	-	-	0*	0*	0*
II	-	-	-	2	4	8
III	-	-	-	6	10	10
IV	0	4	-	10	-	10
V	0	10	-	10	-	10
VI	0	5	-	10	-	10
VII	-	0	-	0	10	10
VIII	-	0	0	10	10	10
IX	-	-	-	0	0	2
X	-	0	0	6	-	10

* to be repeated

- test did not perform

0 tested snails all alive

10 number of killed snails

III. Mice Test

The chlorinated phenols were ground to fine powder, weighed accurately and diluted with 1% CMC to the desired concentration. The suspension was injected into mice intraperitoneally. Observed the tested mice for 48 hours and recorded the results. 5.0 gm/kg of 1-(3,5-dichloro-4-hydroxyphenol)-2,2-dichloroethanol was injected into mice intraperitoneally showing convulsion then dead. 2.5 gm/kg of this compound was showing convulsion at first thirty minutes and recovering to normal after 48 hours. 1.0 gm/kg of 3,5-dichloro-4-hydroxybenzyl cyanide was injected into mice intraperitoneally showing weakness then the mice were expired within thirty minutes. Injected 0.5 gm/kg of this compound into mice, they recovered to normal after 48 hours.

CONCLUSIONS

It is well known that chlorinated phenols have a high potential as antimicrobiological activities. The presence of a cyanide group does not increase activity. Chlorinated benzoquinones and its reduced form, 1,3-dichloro-2,4-hydroxy benzene, which are the final products of most natural phenols in chlorination, showed greater antimicrobiological activities than the other examined chlorinated phenols. Molluscicidal activity can be denotation of the effects of the chlorinated products to estuaries. The results indicate that most of the compounds have the activity.

Because chlorination of water supplies is a widespread practice, the formation of toxic compounds from a combination of the eluted organic substances and chlorine is very probable. From the mice test, we know there is no acute toxicity shown in the experimental animals, if water contains small amounts of chlorinated phenols. But we still do not know the toxicities caused by long periods of exposure to the chlorinated phenols. The further research of this is still needed.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

CWRR Project No. A-044-R.I.

Agreement No. 14-31-0001-3840

FCST-COWRR Research Category: V C

Project Title:

Interception and Degradation of Pesticides by Aquatic Algae

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 71

To Be Completed--Month: June ; Year: 73

Principal Investigators	Degree	Discipline
Leonard R. Worthen	Ph.D.	Pharmacognosy

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Steven G. Zelenski	Ph. D.	Pharmacognosy

OWRR A-044-RI

Progress Report
June, 1973

A. Research Program Accomplishments

(1) Due to the increasing awareness of the presence of polychlorinated biphenyl contamination (PCB) in natural samples, it was particularly important to determine if quantitations for halogenated pesticide residues reported by us were influenced by PCB's. It was felt that present methods to separate and quantitate PCB's and halogenated pesticides were unnecessarily tedious and time-consuming. A method to quantitate the components of a two-component system which were unresolvable in a given gas chromatography system was developed. The method utilized the p-values of individual components and was extensively tested with mixtures of p, p'-DDT and the hexachlorobiphenyl isomer which overlapped DDT in the SE-30/QF-1 GC system used, and proved to be very useful and accurate to ± 11%.

(2) As a result of our initial survey of streams and ponds in Rhode Island, two streams were chosen for a detailed analysis of their blue-green pesticide residue levels--the Queen's River and the Chipuxet. Eighteen algae samples were taken from the Chipuxet while ten samples were obtained from the Queen's. To determine the extent of sediment contamination in the algae collected, separate sediment samples were taken. Pesticide residues were determined by GLC and confirmed using the p-value method of Beroza and Bowman (1965) and Zelenski et.al. (1973). The Queen's River algae samples exhibited p, p'-DDT

levels in the range of 15-44 ppb dry weight of algae while the sediment values ranged from 0.9-1.1 ppm. The Chipuxet's samples ranged from 1.1-18 ppb p, p'-DDT for the algae and 0.1-0.65 ppm for the sediment with the exception of one sediment value obtained near Rt. 138 which indicated a p, p'-DDT value of 12.1 ppm. These values are consistent with pesticide use on the watersheds of the two streams.

The fresh water and marine blue-green Synechococcus elongatus was carefully studied to determine its ability to intercept, accumulate and metabolize p, p'-DDT.

These experiments indicated that S. elongatus did indeed accumulate virtually all of the pesticide added to the media within 24 hours of addition. Furthermore, the algae was able to metabolize significant amounts--about 4% of the added p, p'-DDT to the metabolite p, p'-DDE. This metabolite was found exclusively on the cell wall, no detectable quantities were detected within the cells as determined by differential solvent extraction. However, about 11% of that found in the cells and in the media was detected in the media itself.

These results indicate that this unicellular algae can be a significant sink for large amounts of p, p'-DDT which may find its way to streams and lakes containing this species. This experiment also indicated that the levels of p, p'-DDT used--.099 ppm--were not toxic to the algae, as there was no change in growth curve characteristics vs. the control, nor in gross morphology vs. the control.

B. Publications

A Gas Chromatographic Method of Quantitating p, p'-DDT in the Presence of Interfering PCB, 1973, Zelenski, S. G., Tashiro, J., Worthen, L. R., and C. Olney. J. Chromat. in press.

C. Project Status

A completion report for this project is in preparation. Of the original objectives outlined in our project proposal, we have been able to (1) determine the levels of pesticides in select local streams, (2) Determine the extent of accumulation of p, p'-DDT by a blue-green algae, Synechococcus elongatus and (3) Determine the extent of metabolism and major metabolite of the p, p'-DDT which was adsorbed by the algae.

Certain questions were raised by this research and only partly answered. These include: (1) The extent of incorporation of p, p'-DDT into the cell constituents, (2) The exact area of localization of p, p'-DDT within the cell, (3) The enzyme responsible for the partial metabolism of p, p'-DDT, (4) The selectivity of uptake of the algae for different pesticides.

D. Application of Research Results

The p-value method of quantitating p, p'-DDT in the presence of PCB may have extensive use when an investigator is interested in quantitating certain pesticides in the presence of interfering compounds. The method should also be applicable to other types of compounds.

Reference

Beroza, M. and M. C. Bowman, 1965. Identification of Pesticides at Nanogram Level by Extraction p-values, Anal. Chem. 37:291-292.

Form OW-1 (1-72)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-045-RI

Agreement No. 14-31-0001-3840

FCST-COWRR Research Category: V G

Project Title:

Microbial Co-Oxidation of Halogenated Aromatic Acids

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 72

To Be Completed--Month: June ; Year: 74

Principal Investigators	Degree	Discipline
Richard W. Traxler	Ph.D.	Plant Pathology-Entomology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
G. H. Traux	BS, PhD	Microbiology/Biochemistry

Microbial Co-oxidation of Halogenated Aromatic Acids

Dr. R.W. Traxler

A. Research Project Accomplishments

A number of different bacteria have been isolated, by the enrichment culture method, which utilize sodium benzoate, indene, phenoxyacetic acid and diphenylethane as a primary growth substrate. Selected isolates have been used to develop analytical methods to demonstrate co-oxidation of halogenated compounds when the isolate is growing or oxidizing at the expense of the primary substrate.

Analytical methods have centered on Warburg respirometry with endogenous rates corrected by radio-chemical methods. Gas Liquid Chromatography of chlorinated hydrocarbon has been used as a supplemental analytical method. Chordane and heptachlor systems have been studied using the OV-17 column and the electron capture detector to determine changes in concentration of the chlorinated compounds in co-oxidation systems. An extraction technique has been devised to quantitatively recover the chlorinated compounds from culture systems prior to analysis by GLC. This extraction system in conjunction with the quantitative GLC determinations is currently being used as a rapid and sensitive method for screening the various isolates for utilization of the different halogenated compound in the presence of a variety of primary growth substrates. Thin Layer Chromatography systems are under study which are to be used for detection of oxidation products of the halogenated compounds.

An example of the Warburg data is shown in Figure 1. The cells of isolate 6-A7-25-1 were grown on sodium benzoate, harvested and oxygen uptake followed with benzoate, heptachlor and a mixture of benzoate and heptachlor. There is not a significant difference in the rate of oxygen uptake by the cells of 6-A7-25-1 on benzoate or the benzoate-heptachlor mixture during the initial oxidation period. The heptachlor rate was the same as the endogenous rate of 6-A7-25-1. The break for oxygen uptake with benzoate occurred between 120-150 minutes at which point the rate returned to the endogenous level indicating maximum utilization of the primary substrate. The oxidation curve with the mixture shows continued oxygen uptake beyond 150 minutes but at a reduced rate. This secondary rate, however, is still above the endogenous rate. In terms of total oxygen uptake the benzoate system consumed a total of 215 µl of oxygen whereas the benzoate-heptachlor system utilized a total of 310 µl of oxygen or 105 µl more than the primary substrate. GLC analysis confirmed loss of the heptachlor peak in the sodium benzoate-heptachlor system.

B. Project Publications

There have been no publications of the preliminary data obtained this year. It is expected that at least one publication will be prepared during the coming year.

C. Project Status

This project will continue in the next fiscal year.

D. Application of Research Results

The personnel involved in USDA regional project NE-53 have expressed an interest in the results of this project. It is planned to present a summary of progress on this project at the annual meeting of NE-53 to be held in October 1973.

E. Work Remaining and Contemplated Progress During Next Fiscal Year

In the next year it is contemplated that the screening studies for co-oxidation now underway will have been completed. Also, the identified co-oxidation systems will be quantitated for extent of co-oxidation and C^{14} isotope experiments will be integrated with Warburg and growth data so that proper stoichiometric data can be generated. Efforts will be placed on the identification of co-oxidation products of the halogenated compounds so that the pathway and extent of halogenated acid degradation can be assessed. Some cell-free systems will be investigated using sonic disrupted cells to determine if a mechanistic model can be developed for the co-oxidaton system.

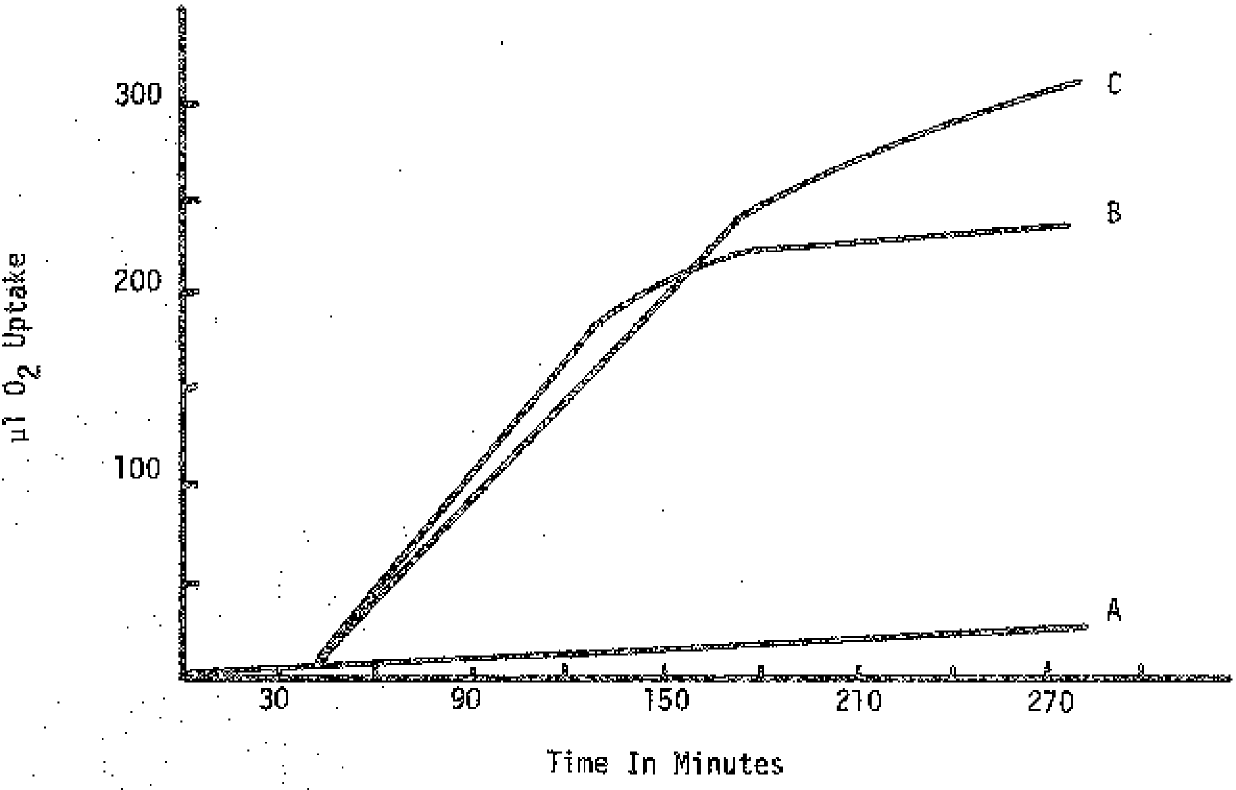


Figure 1. Oxygen uptake by benzoate grown resting cells of isolate 6-A7-25-1

A = Endogenous rate and Heptachlor rate
B = Sodium benzoate 2µM
C = Sodium benzoate 2µMt Heptachlor 10 mg

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ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-046-RI

Agreement No. 14-31-0001-3840

FCST-COWRR Research Category: V D

Project Title:

Thermophilic Hyperbaric Fermentation for Cellulose Waste Treatment

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1972

To Be Completed--Month: June ; Year: 1974

Principal Investigators	Degree	Discipline
Stanley M. Barnett	Ph.D.	Chemical Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Richard Romanelli (Research Assistant)		Chemical Engineering
Duen-gang Mou (Special Assistant)		" "
Nan-shun Shen (Special Assistant)		" "

Accomplishments:

1. Three highly cellulolytic thermophilic fungi have been obtained from the Natick Army Laboratory. The microorganisms are: Chaetomium thermophile vac coprophile
   Sporotrichum thermophile
   Thermoascus aurantiacus

   Previous work has shown that these fungi are 2-3 times as active on cellulose as the most active mesophiles tested.

2. Of the three, Sporotrichum has proven easiest to maintain and culture. Factorial testing has yielded a standard innoculum of 10^4 spores per ml. Each batch culture of 50 ml per 250 ml flask is innoculated with one ml of freshly prepared spore suspension.

3. Preliminary efforts to bracket temperature and pressure ranges have shown that work ought to be done between 40 and 60°C and between one and six atmospheres absolute pressure. Studies have shown little or no growth at temperatures above 60°C. Qualitative estimates of growth show an increase at three and four atmospheres absolute, but a marked decline in growth at pressures above six atmospheres absolute.

4. A nutrient media with cellulose as the sole carbon source has been formulated. The cellulose to be used is Souka Fuoc BW-200. One percent cellulose suspensions are contemplated.

5. Batch cultures of Sporotrichum in 250 ml flasks show increased growth with temperature as shown in Figure 1.

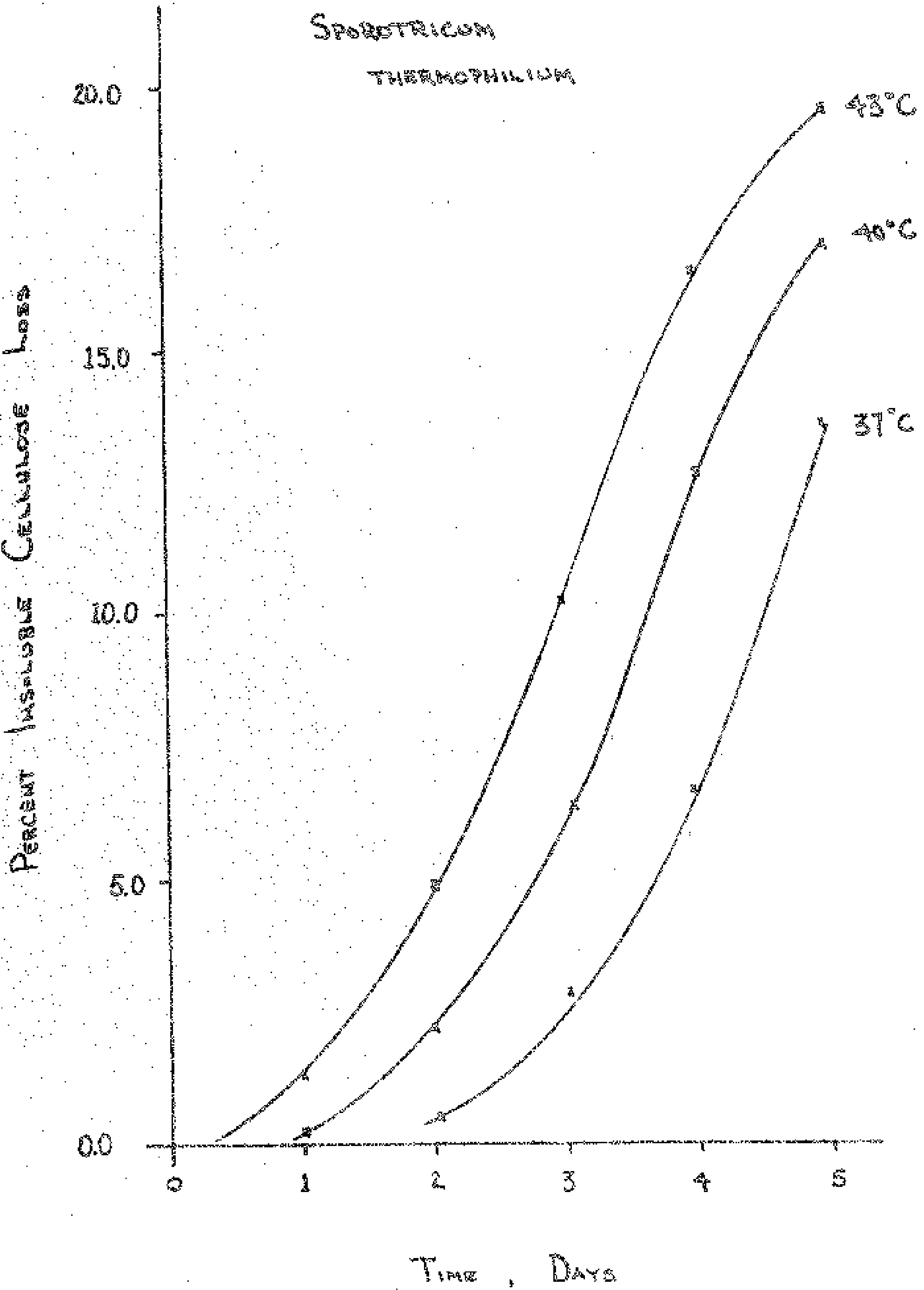
6. Fermentation under pressure will be accomplished in 500 ml stainless steel pressure bombs and in specially designed and constructed stainless steel 'beaker-like' vessels. All vessels have been fitted with a quick-connect for pressurization and a ball valve for nutrient loading, innoculation and sampling. The beakers have also been fitted for dissolved oxygen monitoring.
7. A manifold has been designed and constructed which will allow for the simultaneous pressurization of four (4) bombs or beaker vessels.

Project Status

Project will continue in progress in the next fiscal year.

Work Remaining & Progress Contemplated

1. Completion of batch fermentations in 250 ml flasks to determine cellulose and mineral utilization and optimum growth temperature at atmospheric pressure. Included here is a method for separating cellulose and fungal growth.
2. Fermentation in the bombs and beakers to test for similarity with the flask cultures.
3. Pressure fermentation to obtain the optimum growth temperature at each pressure increment and ultimately the optimum pressure for growth.
4. An analysis of the end products of metabolism to determine any variability produced by pressure. Liquid and gas samples will be taken, under pressure, and analyzed.



Sporotricum
thermophilium
43°C
40°C
37°C
Percent Insoluble Cellulose Loss
20.0
15.0
10.0
5.0
0.0
0
1
2
3
4
5
Time , Days

Form OWRR (1-72)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-047-RI

Agreement No. 14-31-0001-3840

FCST-OOWRR Research Category: V B

Project Title:

Development of Methods for Controlling the Cadmium and Zinc Content in Water

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1972 To Be Completed--Month: June ; Year: 1974

Principal Investigators	Degree	Discipline
Kenneth H. Mairs	Met.E.	Chemical Engineering
Ferdinand Votta, Jr.	D.Eng.	Chemical Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
R.M. Jambekhar	B.S.	Chemical Engineering

Development of Methods for Controlling the Cadmium and Zinc Content in Water

It is our intention to study the presence of zinc and cadmium in drinking water. Since zinc does not cause serious health hazards, its permissible concentration in water is liberal (5.0 mg/l). On the other hand, cadmium is recognized as a highly toxic element and its permissible concentration (0.01 mg/l) is in keeping with its nature.

Zinc and cadmium are members of the same chemical group and, as a consequence, are found closely associated with one another. There are no specific ores of cadmium; all cadmium is produced from high cadmium zinc ores. One can understand, then, that all zinc contains some cadmium as an impurity, with even the so-called HighGrade containing up to 0.07%. The less pure grades can contain as much as 0.75% cadmium or more.

With few exceptions zinc and cadmium are not found in objectionable concentrations in ordinary water sources. To identify exceptions, however, cadmium has been found in ground water as the result of seepage from electroplating facilities and it seems quite possible that water distributed through galvanized pipes, wherein the zinc coating contained cadmium as an impurity, could show the presence of both zinc and cadmium. It is generally acknowledged that "hot dip galvanizing employs chiefly the less pure grades of zinc".*

Another possibility of simultaneous zinc and cadmium contamination could result from the dezincification of high brass pipe. It is known that all grades of zinc, and particularly the less pure and less costly grades, are used in making brass.

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* A.S.M. Handbook (1948 edition) p. 1077

Whether or not there are restrictions on the selection of zinc when making brass water pipe has not been established.

A search of some of the important literature has been mad but little information dealing directly with this problem has been found. Information on the corrosion of brass and galvanized products is very extensive and our review of it is not complete. There appears to be considerable information dealing with zinc in drinking water and very little dealing with cadmium. The extensive OWRR bibliographies on zinc and cadmium in water have been consulted: the information reported therein, however, deals almost exclusively with trace quantities and biological effects.

Experimentally, we have begun a series of tests to explore the influence of various gases dissolved in water on the solution of these metals. Galvanized iron pipe immersed in deionized water through which nitrogen was being bubbled continuously, gave up 4 to 5 ppm. zinc and no detectable cadmium within 72 hours. The same exposures but using instead oxygen and/or carbon dioxide, yielded several hundred ppm. zinc and detectable cadmium in the ration of about 1 cadmium to 10,000 zinc when the zinc exceeded about 100 ppm.

Several exposures using a high brass instead of galvanized iron have yielded very erratic results. It appears at this writing that our initial surface preparations (specimen cleaning and conditioning) are not adequate and may be responsible for some of the apparent solution. Some of our analytical details must be reveiwed and the influence of the initial surface must be determined.

The influence of other ingredients in natural waters, particularly calcium, magnesium, iron, etc., must then be determined as must conditions for limiting or controlling the extent of solution of zinc and cadmium. It is expected that most of this can be done within the coming year.

Kenneth H. Mairs
Principal Investigator
22 June 1973

Form OW-1 (1972)

ANNUAL REPORT — TITLE I PROJECT

OWRR Project No. A-048-RI

Agreement No. 14-31-0001-3840

FCST-COWRR Research Category: II A

Project Title:

Treatment of Wastewater from Fish and Shellfish Processing Plants

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1972

To Be Completed--Month: June ; Year: 1974

Principal Investigators	Degree	Discipline
Harold N. Knickle	Ph.D.	Chemical Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Harold Mantius	M.S.	Chemical Engineering

TREATMENT OF WASTE WATER FROM FISH AND SHELLFISH PROCESSING PLANTS

Dr. Harold Knickle, Principal Investigator
Project No. A-048-RI
June, 1973

A. Research Project Accomplishments

Some of the simpler methods of treating liquid effluent from fish and shellfish processing plants have been reviewed; these include reverse osmosis, activated carbon adsorption, chemical precipitation, settling, filtration, aeration, and flotation. The intent of this research is to determine an effective and economic process to treat waste water of fish, and shellfish processing plants. Included in the scope of the investigation is determination of the potential re-cycle of water, and reduction of the usage of water. These two factors hold the potential for economic operation of the total plants with respect to water.

Initially, the characterization of waste water from a shellfish processing plant was determined. The samples were taken over an extended period of time, and charted. Averages of these parameters were determined. Some of these averages are presented in Table I.

TABLE I: Average Waste Water Characteristics

a) Dissolved Oxygen - 3.3 mg./l

b) Total Hardness - 13 grains/gal.

c) Calcium Hardness - 6 grains/gal. (aCO_3)

d) Sulfate - 0

cont.)

Table I, cont.)

e) Sulfite - less than 10 mg./l

f) Silica - 36 mg./l

g) Alkalinity - 7 grains/gal.

h) BoD - 1180 mg./l

Since it was apparent the solids content of the waste water was high, filtration appeared to be a natural process to remove a portion of the biological oxygen demand, BoD. Generally, waste water from fish and shellfish plants has a high percentage of the BoD tied up in the suspended solids. Bench scale tests have indicated filtration alone can result in a significant reduction of the BoD. The average BOD decreased from 1180 for unfiltered waste to 680 for filtered waste. This is better than a 60% reduction.

Besides the characterization, a study of the water usage indicated peak and average values of the total quantity of water used in processing. The peak rate at the shellfish plant which is cooperating in this research, was found to be approximately 17,000 gal./day. The average rate was found to be approximately 12,000 gal./day.

Reverse osmosis has proven satisfactory in treating many industrial wastes. To determine the feasibility and economic potential of using reverse osmosis, a small scale pilot operation has been constructed. Membranes from Philco-Ford and Gulf have been obtained. The effectiveness of these membrances will be determined by experiment. Calculations will be made to determine economic feasibility of reverse osmosis. It is expected that the use of reverse osmosis will require pre-treatment of the waste water by filtration, to prevent clogging of the membrane.

The BoD of the effluent streams of the reverse osmosis operation will be determined as the pressure is varied.

A number of tests have been made to determine the effectiveness of carbon adsorption in reducing BoD. Again, filtration is most likely a pretreatment before the carbon adsorption process. The data is now being reduced to determine the linear form of the Freundlich isotherm. Standard, commercially available activated carbon has been used. Economic calculations will be made to determine the costs of carbon adsorption. It appears some sizes of activated carbon particles are much more effective than others.

Chemical precipitation appears to be another economic process for treating this waste water. A number of scoping bench studies have been made to determine feasibility of different chemicals. Alum and lime have been tried at different concentrations and different pH values. Work is continuing in this area.

Work is continuing in all of the aforementioned areas. Evaluation of aeration and flotation as potential treatment processes will begin in the coming year. An expanded effort in filtration is foreseen.

B. Publications: None

C. Project Status:

This project will continue in progress during the next fiscal year.

D. Application of Research Results:

The owner of the shellfish plant, Harbor Shell Fish, Paul Jarvis, is keenly interested in the results of this work. Economical results may be applied to his plant. Some other operating fish processing plants have indicated interest.

E. Work Remaining, and Progress Contemplated During Next Year:

Continued effort on the application of reverse osmosis, activated carbon adsorption, chemical adsorption, chemical precipitation, settling, filtration, aeration, and flotation to fish and shellfish processing waste water is contemplated. Final Progress expected is an economical method to treat the waste water of fish and shellfish processing plants. The result is expected to be combination of the unit operations evaluated, and not a single unit operation.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-033-RI

Agreement No. 14-31-0001- 3640

FCST-COWRR Research Category: V D

Project Title:

Biological Degradation of Hydrocarbons in Water

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1971 To Be Completed--Month: June ; Year: 1973

Principal Investigator	Degree	Discipline
Chester W. Houston	Ph.D.	Bacteriology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Satish Velankar	M.S.	Chemical Engineering
Crandall W. Dimock	B.S.	Zoology
Peter Paolella	Ph.D.	Microbiology

1/ List only those serving as research assistants in a professional sense; do not include hourly wage earners such as dishwashers here but include them in Forms OW-2, 3, 7 and 8. Include post-doctoral students if not serving as professional investigators.

Narrative Statements

The growth of Pseudomonas aeruginosa on n-heptane was studied in batch and continuous culture to determine the mass transfer characteristics of the system and to determine the feasibility of using oxygen-enriched air in the biooxidation of this highly reduced substrate. It was found that under the experimental conditions employed, oxygen was not limiting. Figure 1 shows the variation of dissolved oxygen concentration and the oxygen concentration in the exit gas during growth of the batch culture. It is seen that when linear growth begins, both the dissolved oxygen and oxygen in the exit gas increase. This indicates a decrease in the oxygen demand of the culture. The minimum dissolved oxygen concentration is above the critical value of 0.75ppm. The change from exponential to linear growth at high cell concentrations when dissolved oxygen was well above the critical value means that heptane transfer rate is the limiting factor. Figures 2 and 3 show that exponential growth is followed by linear growth in shake flask cultures. It is seen that linear growth occurs first in the cultures containing the lowest amount of hydrocarbon. The data fit the mathematical model for homogeneous kinetics developed by Dunn (1958). They suggest that heptane is used in the dissolved form rather than by direct contact between microorganism and hydrocarbon droplet, as has been suggested for the utilization of such substances.

In an attempt to explain the growth rate of Pseudomonas aeruginosa on a substrate of extremely low solubility (3 ppm), measurements of interfacial tension were made on growing cultures, since it has been reported by LaRiviere (1955) that certain surface active agents increase the solubility of hydrocarbons. The solubilization effect is reported to increase the solubility of some hydrocarbons 2-3000 times. It was found that the interfacial tension does indeed decrease, presumably as a result of the production of a surface tension depressant by the organism. Typical results are shown in Figure 4. The substance(s) responsible was not identified, but it is suggested that increased solubility of the hydrocarbon as a result of its production may account for the high growth rate observed on this substrate of low solubility. A successful search for a non-toxic surface tension depressant which would increase solubility would be a significant contribution and have practical value.

The study suggests that in the design of equipment for the biooxidation of some hydrocarbons, primary consideration should be given to means whereby hydrocarbon transfer rate can be increased, since, at least in the system studied, the increase in oxygen transfer rate with agitation alone, was always greater than the increase in heptane transfer rate. The relative rate of transfer of the particular hydrocarbon under consideration and of oxygen should be determined prior to scale-up.

During these studies of the effects of aeration, agitation, and oxygen supply on the growth of Pseudomonas aeruginosa on n-heptane, a study of end-products of the fermentation was made. Differences in end-products as a result of variation in growth conditions could have considerable practical significance. In this system, the production of by-products is minimal. Only trace amounts of heptanoic, acetic, and valeric acids together with detectable C_{16} and C_{18} fatty acids were found. These were not found to vary appreciably with variations in growth conditions. The utilization of this particular hydrocarbon with the production of small amounts of by-products suggests that studies of biodegradation of other hydrocarbons by Pseudomonas aeruginosa should be pursued. The high growth rate with efficient degradation could mean the development of systems for the effective removal of hydrocarbons. Excessive foaming with high heptane feed rates and high cell concentrations as encountered in this study, however, is a problem. Better foam control than was possible with the agents used would be needed.

This project ends June, 1973, and a completion report will be submitted at that time.

References

Dunn, I. J. 1958. An interfacial kinetic model for hydrocarbon oxidation. Biotech and Bioeng. 10:891-894.

LaRiviere, J. S. M. 1955. The production of surface active compounds by microorganisms and its possible significance in oil recovery. Antonie von Leeuwenhoek 21:1-8.

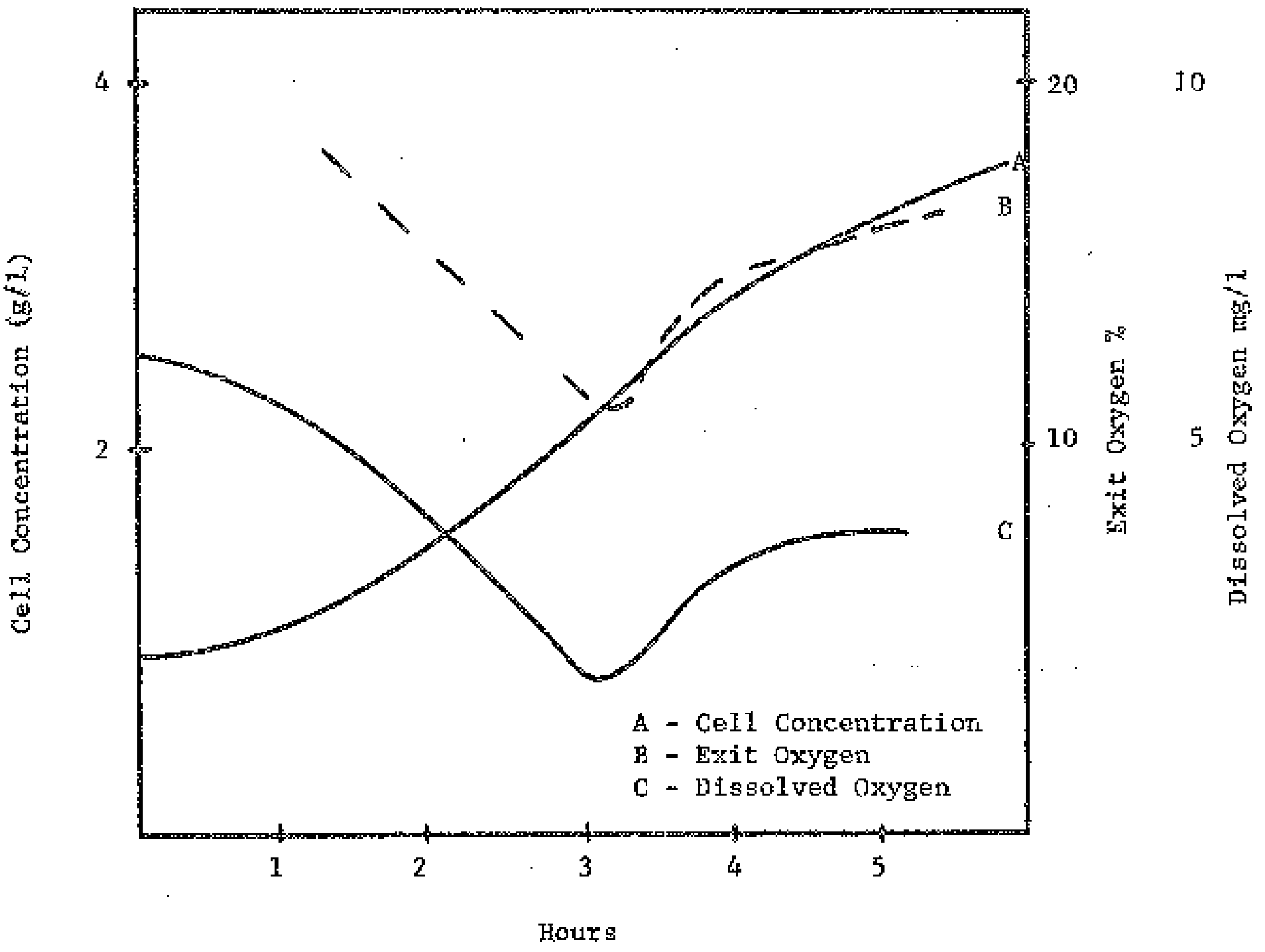


Figure 1. Relationship of Dissolved Oxygen and Exit Oxygen to Cell Concentration of _Pseudomonas aeruginosa_ Growing on n-Heptane in Fermentor. (Operating Conditions: 30C, 1500 RPM, 0.5 VVM)

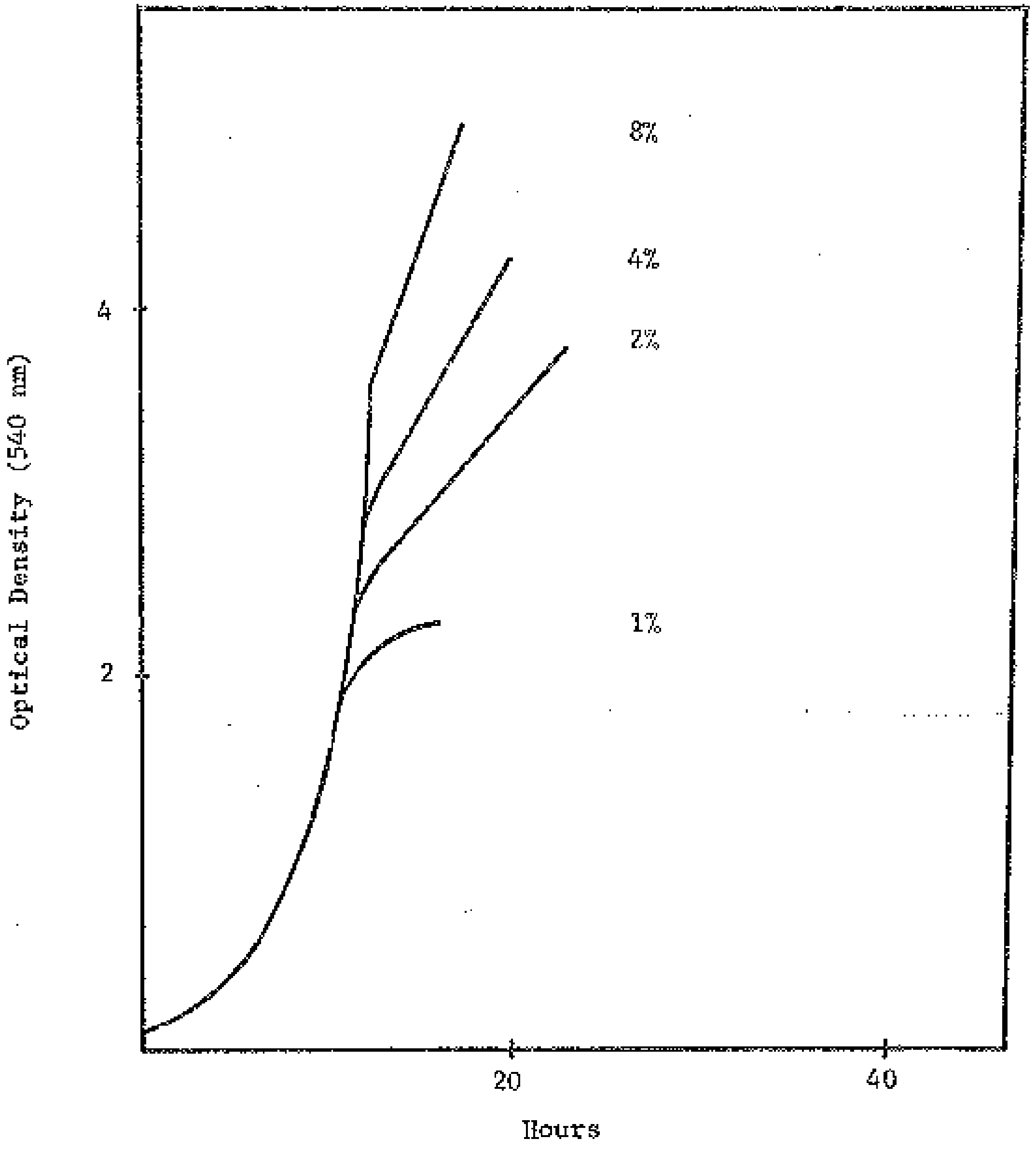


Figure 2. Growth of *Pseudomonas aeruginosa* on Various Concentrations (V/V) of n-Heptane in Shake Flask Cultures at 30° C.

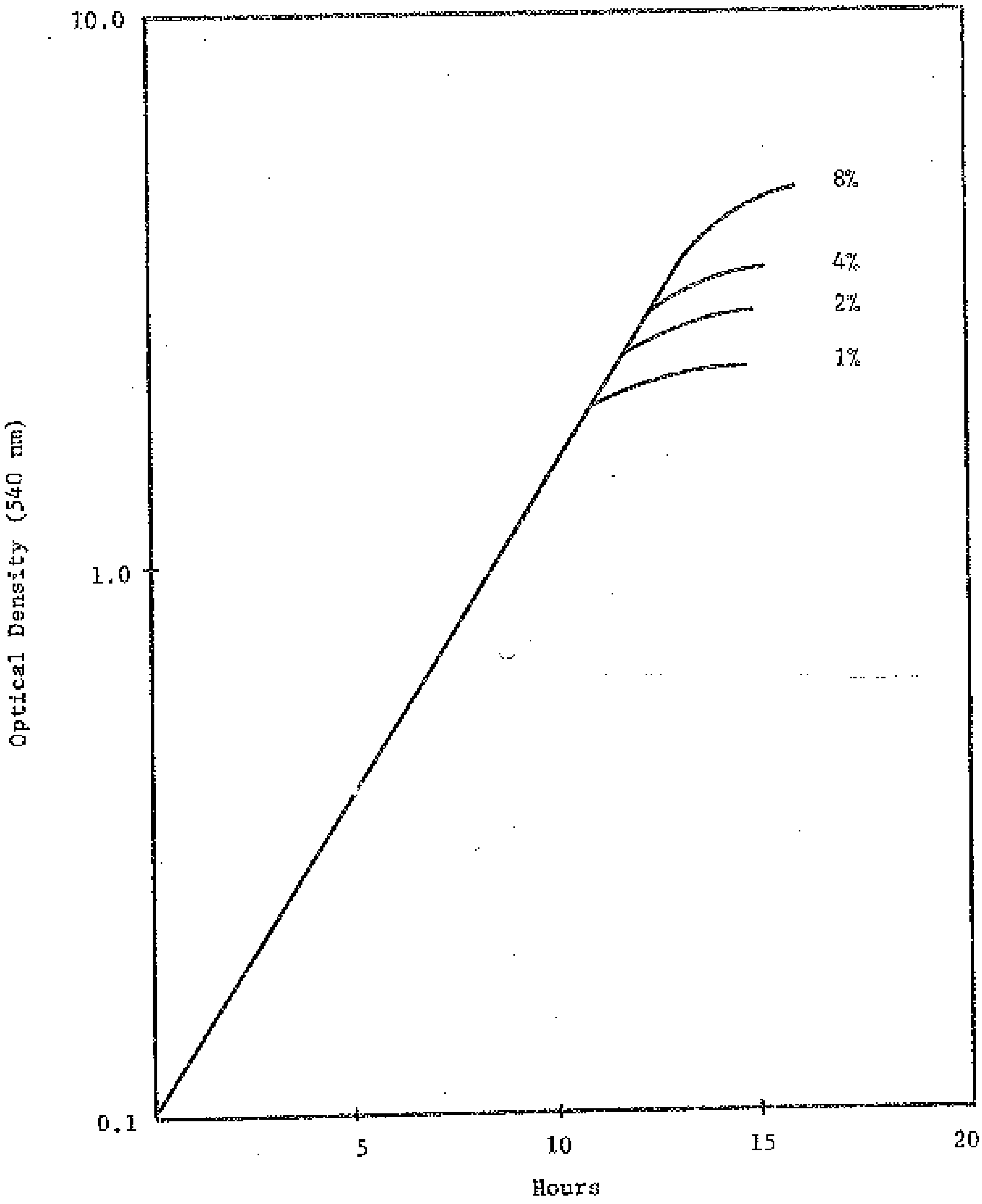


Figure 3. Growth of *Pseudomonas aeruginosa* on Various Concentrations (V/V) of n-Heptane in Shake Flask Cultures at 30° C.

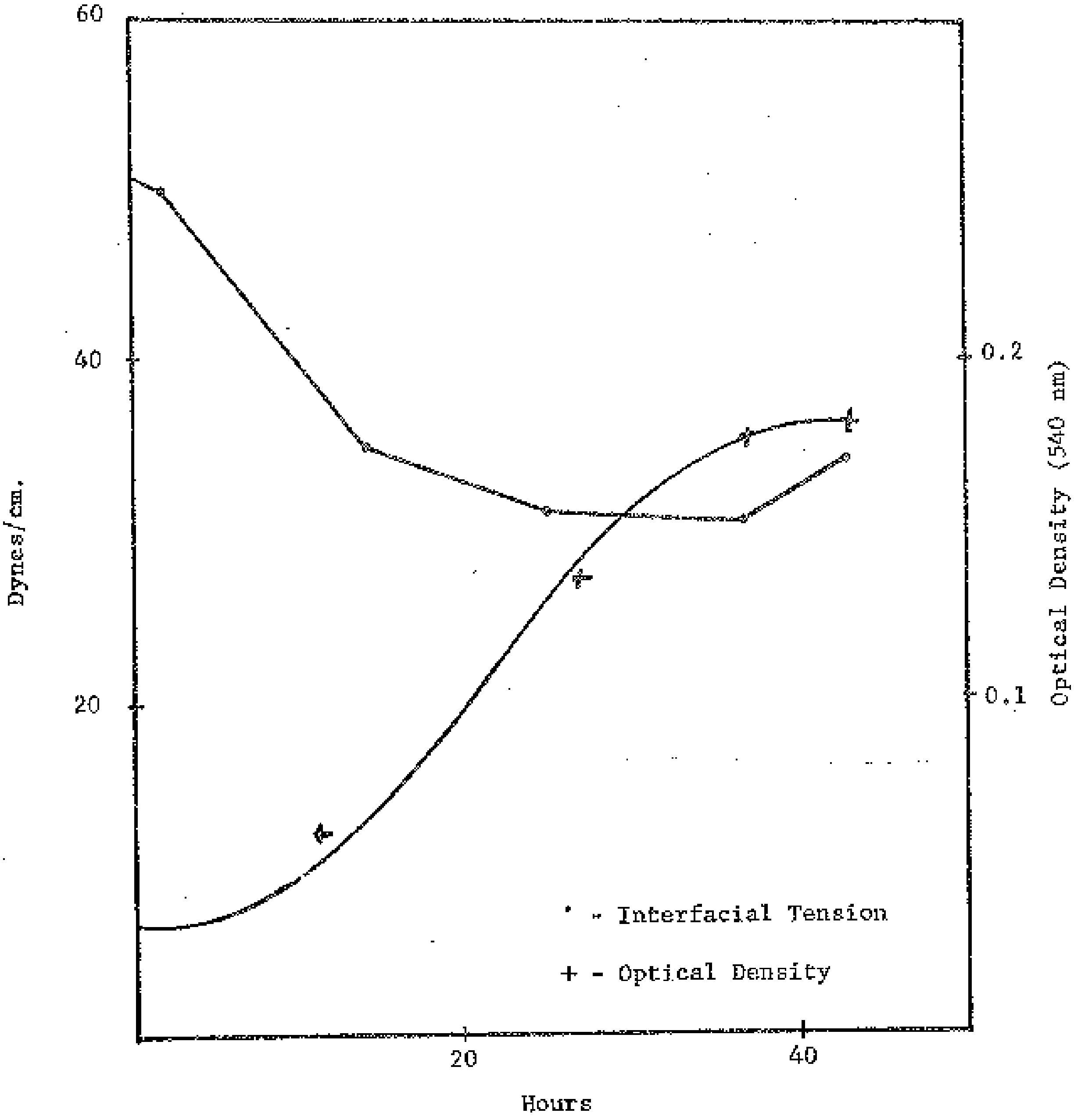


Figure 4. Interfacial Tension during Growth of *Pseudomonas aeruginosa* on n-Heptane in Shake Flask Cultures at 30° C.

Form OW-1 ([illegible])

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-036-RI

Agreement No. 14-31-0001-3541

FCST-COWRR Research Category: V A

Project Title:

Laser Raman Spectroscopy of Solutes Dissolved in Water from a Remote Platform

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1971

To Be Completed--Month: June ; Year: 1973

Principal Investigators	Degree	Discipline
Christopher W. Brown	Ph.D.	Chemistry

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
M. Ahmedjian	B.S.	Chemistry
S. Y. Tang	B.S.	Chemistry
A. G. Hopkins	B.S.	Chemistry
D. T. Moore	B.S.	Chemistry

A. Research Project Accomplishments

The primary goal of this research is to develop an optical system for detecting water pollutants remotely by Raman spectroscopy. During the first year of the project the minimum level of detectivity by Raman spectroscopy was determined and a preliminary optical system for detecting remote Raman scattering was developed. During the present year the optical system was modified and used to detect pollutants at low concentrations.

A schematic of the modified optical system for the remote detection of spectra is shown in Figure 1. The collimated laser beam is reflected by the plane mirrors M_1 (30 mm diam), M_2 (12 mm diam), and M_3 (102 x 127 mm) and is focused by lens L_1 (113 mm diam and 165 mm F.L.) onto the sample. The scattered light is collected by the same lens, over a large angle, and is returned to the monochromator as a large collimated beam. Just prior to the monochromator this large beam is focused by lens L_2 (same dimensions as L_1). The image formed by this lens is then focused onto the entrance slits of the monochromator by a Rexator F:1.7 camera lens L_3 (55 mm F.L.). The latter lens is mounted in a XYZ translator to allow for maximum adjustment. The addition of this camera lens was the only major modification made to the optical system during the present year. To obtain a reasonable distance

(21 ft.) in our laboratory, two mirrors (102 x 127 mm) were placed between M_2 and L_2 to reflect the scattered light into the spectrometer. These are not included in the optical diagram, since they are used only for convenience.

The trick to the optical arrangement is that the laser beam has a very small diameter (~1 mm), whereas the collimated scattered beam has a large diameter (~13 cm). The geometry of the optical system takes advantage of these facts so that both beams traverse the same optical path between the instrument and the sample.

Initially, the remote optical system was aligned and tested using CCl_4 as the sample. After obtaining a good spectrum of CCl_4 we changed the sample to 1 M $NaNO_3$, and we were able to obtain a good spectrum. The concentration of $NaNO_3$ was reduced to one-half and the spectrum recorded again. This process of reducing the concentration and recording the spectrum was continued until the minimum detectable concentration was reached. The spectrum of 300 ppm NO_3^- is shown in Figure 2. The only band observable at this concentration is ν_1, the symmetric stretching vibration, at 1051 cm^{-1}. At present, the minimum detectable level for NO_3^- with the remote optical system is ~150 ppm.

As an additional demonstration of the remote detection system, we have used it to detect #2 grade oil (household heating grade) on the surface of water. The spectrum of the oil in the C-H stretching region is shown in Figure 3. First, we obtained a spectrum of the oil sample contained in a capillary tube in the spectrometer (spectrum a), then on the surface of water with the sample located in the spectrometer (spectrum b), and finally on the surface of water by the remote system (spectrum c). Oils are weak Raman scatterers, they give a high fluorescent background, and they tend to vaporize in the laser beam. Therefore, it is difficult to measure their Raman spectra even under ideal conditions. However, the problem of vaporizing is reduced by having the oil on the surface of water, since the water dissipates the heat. The spectra in Figure 3 clearly demonstrate that the spectrum of oil measured remotely is comparable to those taken in the sample compartment.

There are several advantages to this remote optical system. Since the laser beam and the scattered beam are both collimated over most of the light path, it is possible to extend the light path to almost any realistic distance. Furthermore, by enclosing the optical path in a light-tight pipe, such as 4-inch plastic plumbing pipe, interferences from daylight or other external lights can be avoided. This latter advantage is made possible by the fact that the laser and scattered beams traverse the same path to and from the sample.

Publications

1. "Detection of Ionic Water Pollutants by Laser Excited Raman Spectroscopy," S. F. Baldwin and C. W. Brown, Water Research, 6, 1601 (1972).
2. "Sodium and Magnesium Sulfate Ion Pairing: Evidence from Raman Spectroscopy," F. P. Daly, C. W. Brown and D. R. Kester, J. Phys. Chem., 76, 3664 (1972).
3. "Feasibility of Remote Detection of Water Pollutants and Oil Slicks by Laser-Excited Raman Spectroscopy," M. Ahmadjian and C. W. Brown, Environ. Sci. Technol., 7, 452 (1973).

Project Status

The project has been completed and a completion report will be submitted shortly.

The goal of this research was to demonstrate the power of Raman spectroscopy to detect water pollutants from a remote location. During the time of this project we developed a simple optical system for detecting both water pollutants and oil slicks remotely. We have shown that ionic pollutants in concentrations of ~150 ppm can be detected and identified by this system.

We conclude from our work that Raman spectroscopy shows considerable promise for remote detection of all types of water pollutants. The next step in developing this method is to lower the level of detectivity. We propose that this can be done by computerizing the spectral data. Techniques and instrumentation for computer analysis of Raman spectra are now well established, and are capable of lowering the detectivity of <10 ppm.

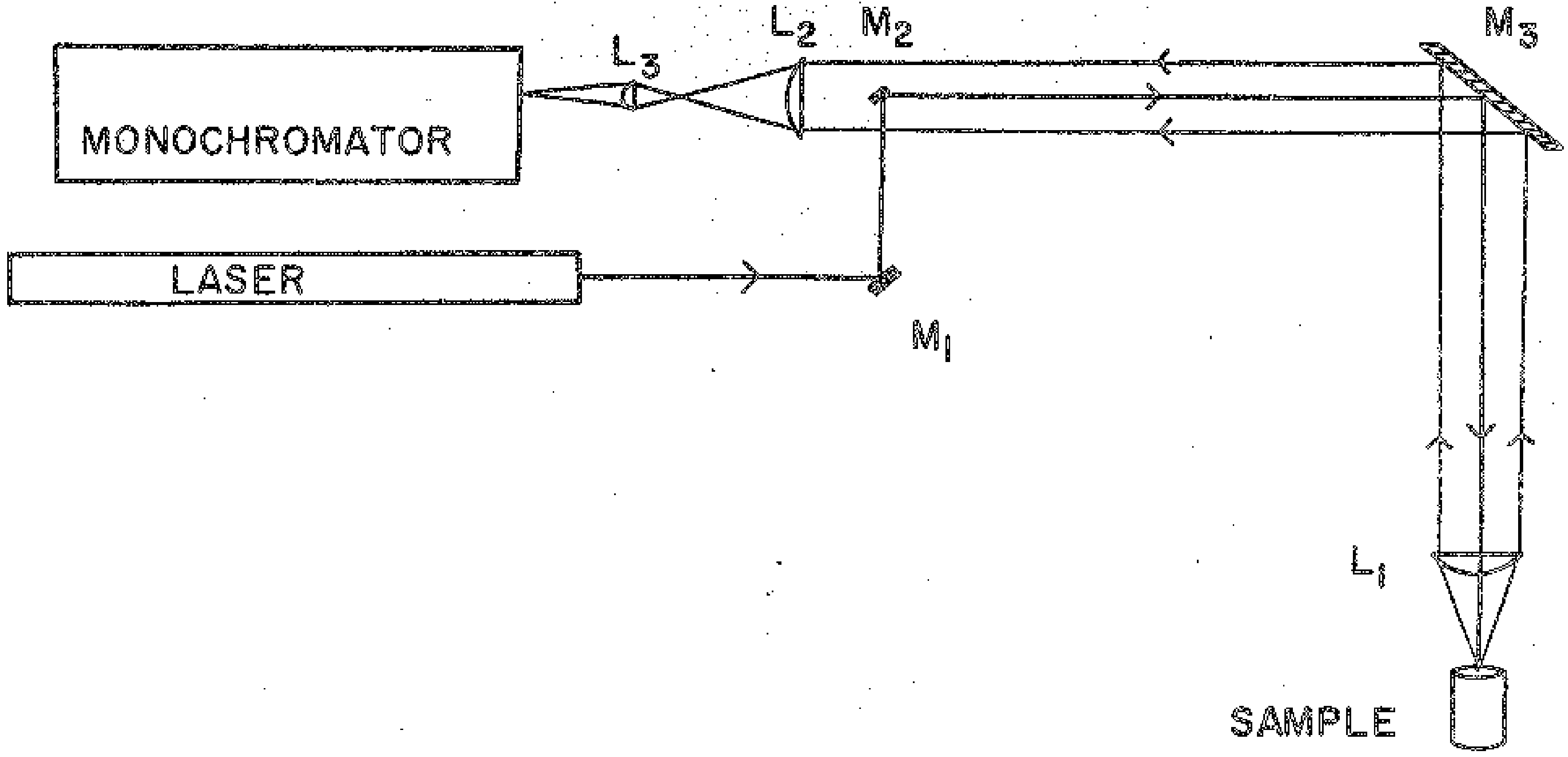


Figure 1. Schematic of the optical system used for obtaining Raman spectra of samples located 21 ft from the instrument.

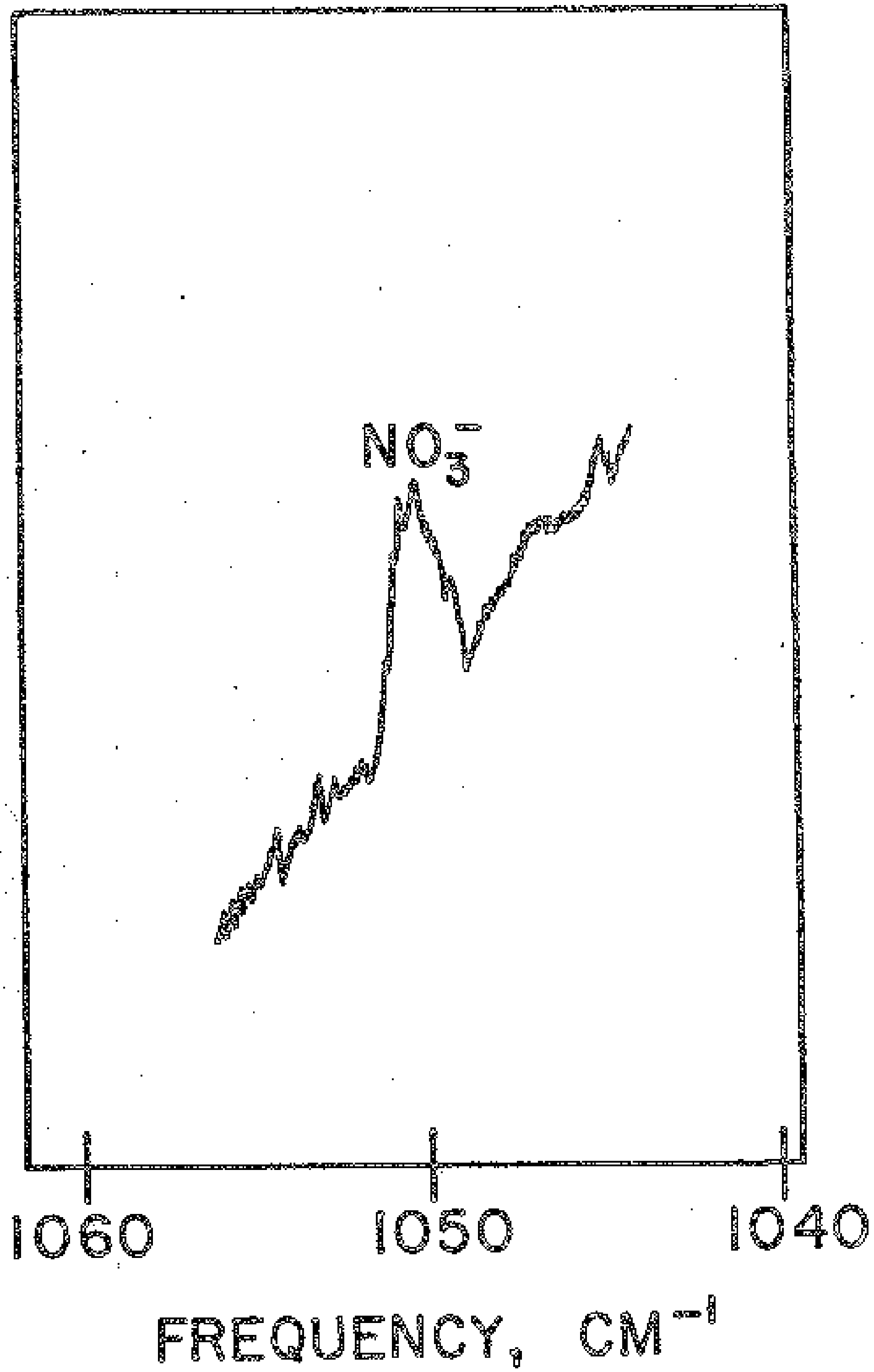


Figure 2. Raman band of 300 ppm of NO_3^- in water obtained with the remote system.

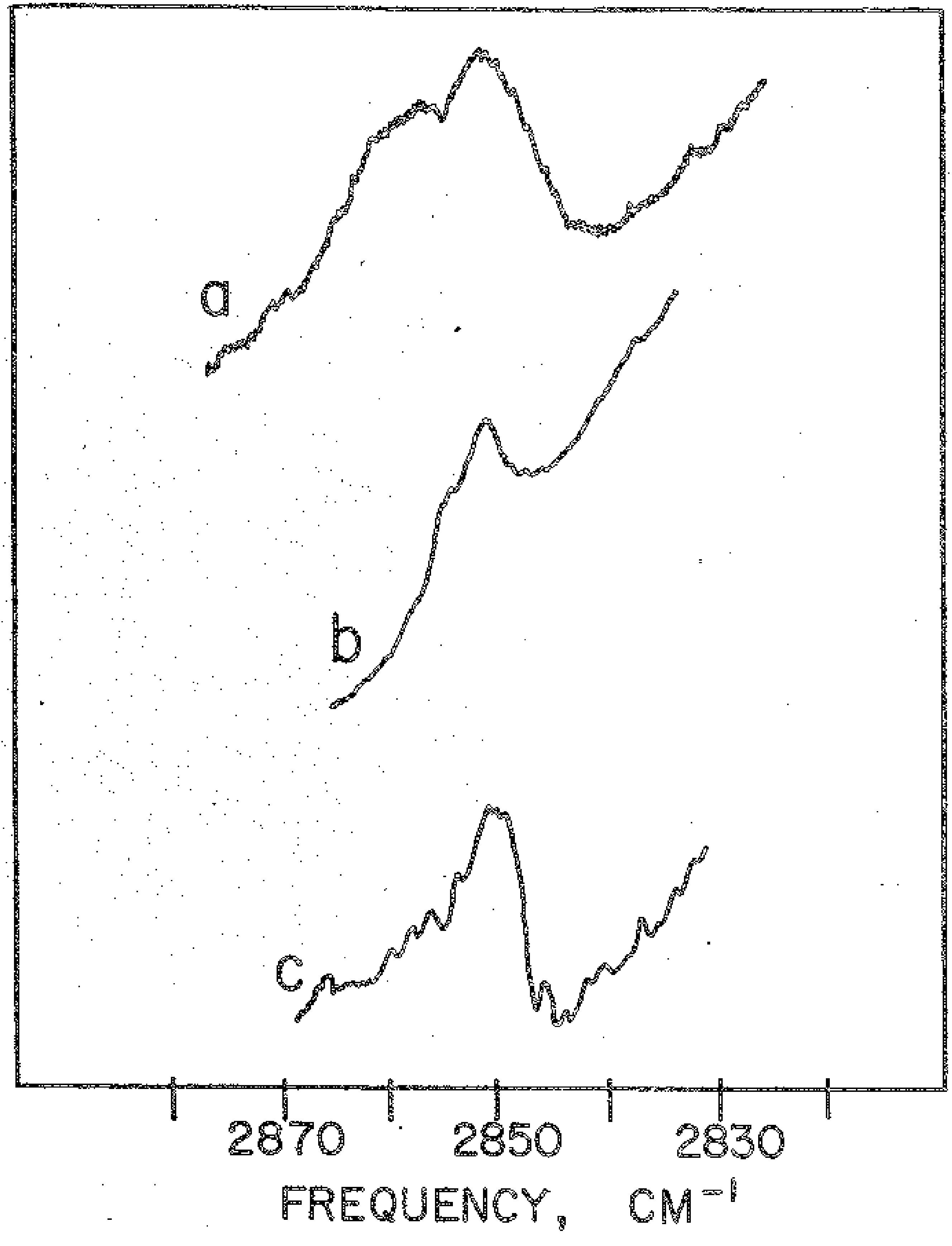


Figure 3. Raman spectra of oil in the C-H stretching region: a, oil contained in a capillary tube (conventional sampling); b, oil on the surface of water in sampling compartment; c, oil on the surface of water obtained with the remote detection system.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-039-RI	**Project Title:** "New Fluorescent Tracer Detection Techniques for Use in Polluted Environments"
Agreement No. 14-31-0001-3643	
FCST-COWRR Research Category: VII B	

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: July **; Year:** 1971 **To Be Completed--Month:** June **; Year:** 73

Principal Investigators	Degree	Discipline
Dr. J. A. Northby	Ph.D.	Physics
Dr. W. Nelson (Assoc. Investigator)	Ph.D.	Chemistry

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
M. Sarkes (July - Sept. '71)	B.S.	Ocean Engineering
R. Sierra (Sept. '71 to date)	B.S.	Physics

Fluorescent dyes are extremely valuable as tracers for determining the motion of natural waters because of their high detectability by simple methods. However, detection sensitivity is usually limited by variability of the background fluorescence (BF), particularly in polluted water, which means that high tracer concentrations are required in such environments. The present research was based on the speculation that while the unpolarized BF might be quite variable, certain of its polarization properties might prove to be much more constant. In particular, if the molecules responsible for the BF proved to be in solution and not in suspended solids, it seemed reasonable to hope that the BF would be nearly unpolarized.(1) In such a case, the detection of a polarized tracer could easily be made independent of the variable amount of BF present.

Our research efforts can be broken down into three main areas: (A) Development of instrumentation suitable for studying the polarization of very low level fluorescence; (B) A study of the fluorescent properties of natural water samples; and (C) Development of a highly polarized tracer dye. We will discuss each of these below.

A: INSTRUMENTATION

We have constructed a versatile and sensitive fluorimeter which can be used either as a scanning instrument, with which the wavelength dependence of fluorescent intensity may be determined, or as a filter instrument, which measures integrated intensity and is inherently more sensitive. Both of these configurations can be used with or without polarizers to study either ordinary or polarized spectra. The instrument is shown schematically in figure 1. Extreme care was used to shield against scattered light, and to insure purity of the incident beam, as otherwise low level polarization measurements would be badly distorted. Incident mercury lines (primarily 546 nm, 440 nm, and 365 nm) were isolated with a thin film filter/didymimum glass combination. When used as a filter instrument specific for Rhodamine B output light was isolated with a combination of three or more filters: a Corning CS4-97, a Corning CS3-66, and one or more Wrattan #21 filters. This combination has a peak transmission near 590 nm, and removes essentially all the scattered light at 546 nm. Polarizers were cut from HNP'B polaroid sheets. The instrument was used to measure polarization of solutions of Rhodamine B and Rhodamine 6G in both glycerol and water, with results in good agreement with previous measurements.(1)

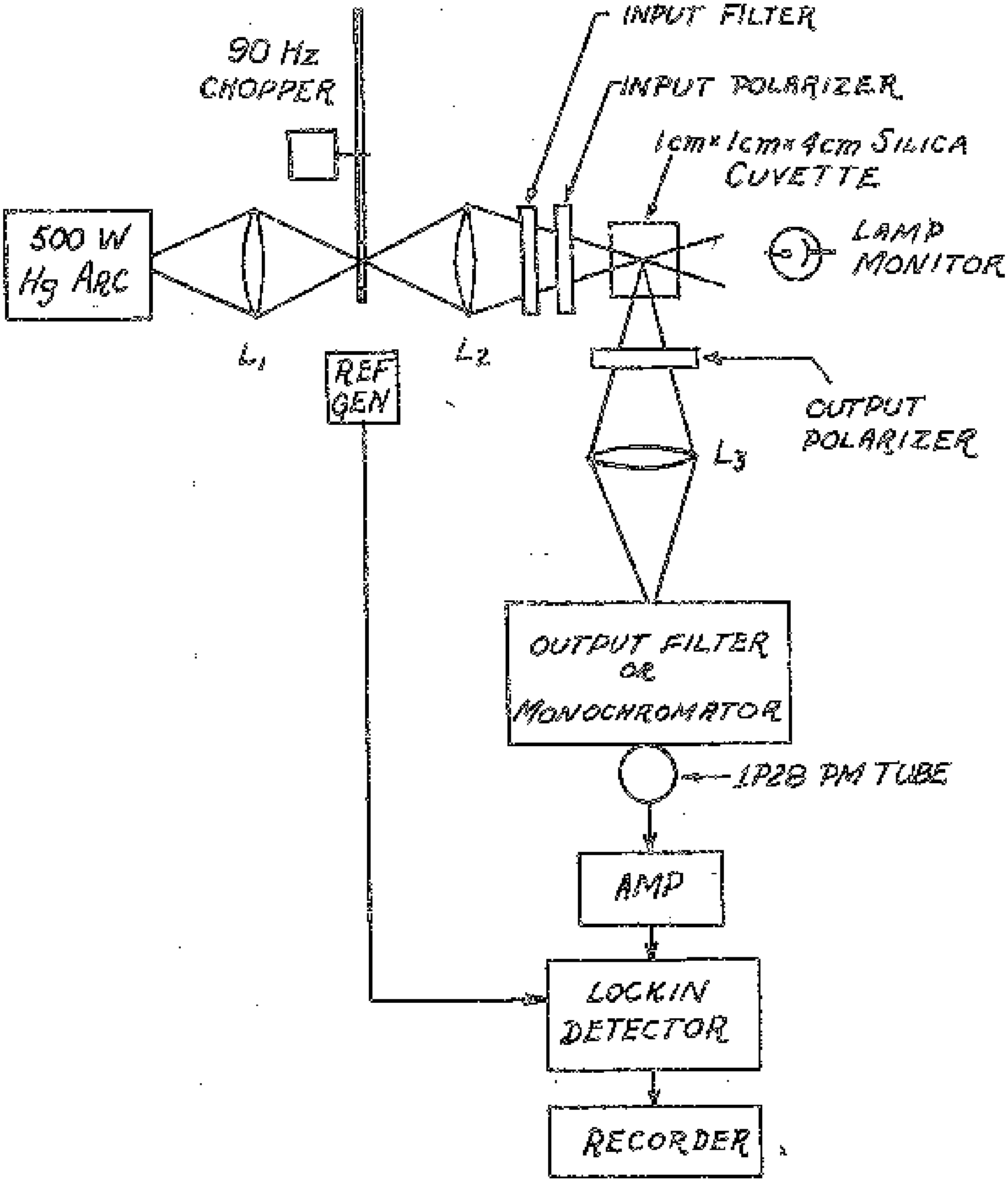
B: FLUORESCENCE OF NATURAL WATER SAMPLES

Our early work confirmed the observation of others(2) that the wavelengths of minimum BF lie near the wavelength of maximum Rhodamine B fluorescence. Consequently, most or our data on BF were taken with the filter instrument optimized for detection of Rhodamine B. Samples were excited with vertically polarized 546 nm light, and the vertical ($I_{\parallel}$) and the horizontal ($I_{\perp}$) components of the fluorescence near 590 nm were determined. Results for one set of samples are given in table 1. These samples were taken within a five hour period at stations ranging from outside of Narragansett Bay to the upper Providence River. They were filtered through 8 micron millipore filters when taken, and stored near freezing temperatures until shortly before the measurements were made. As can be seen, the BF is quite polarized (∿ 10%) and none of the quantities measured shows appreciably less variability than the others. Some of the samples were also studied with 365 nm exciting light, and the magnitude and sign of the polarization were comparable. Distilled water blank corrections were made individually for each sample, and were less affected by filtration through millipore filters. If another dye or better filter can be found, or some other modification of Rhodamine made (as in C above) which prevents it from staining the filter, then perhaps significant improvements in sensitivity could be achieved.

e) The variability of the BF which limits detectability of tracer dyes may prove an interesting effect in its own right. We have observed the BF to be higher where one would expect the water "quality" to be poorer. Consequently, BF could prove useful as a simple monitor of water quality. Note that we have concerned ourselves primarily with a small wavelength region where BF is a minimum. Total BF is orders of magnitude greater, and is easily detectable by simple techniques.

(1) G. Weber, JOSA 46, 962 (1956)

(2) D. W. Pritchard & J. H. Carpenter, Bull. Int. Assoc. Sci. Hydrol. 20, 37 (1960)


90 Hz
CHOPPER
INPUT FILTER
INPUT POLARIZER
1cm× 1cm× 4cm SILICA
CUVETTE
500 W
Hg ARC
LAMP
MONITOR
L_1
REF
GEN
L_2
OUTPUT
POLARIZER
L_3
OUTPUT FILTER
OR
MONOCHROMATOR
1P28 PM TUBE
AMP
LOCKIN
DETECTOR
RECORDER

- FIGURE 1 -

Station	Distance from Fox Point (miles)	$I_{\parallel} + I_{\perp}$ (arbitrary) units	$I_{\parallel} - I_{\perp}$ (arbitrary) units	Polarization (%)	Equivalent Rhodamine B Conc. (mg/lts)
Wickford Harbor	17.1	129.0	9.6	7.4	8.53×10^{-5}
Bay Campus	22.6	42.6	4.0	9.5	2.81×10^{-5}
Beavertail	26.7	26.5	3.7	8.8	1.75×10^{-5}
Dumplings	23.3	20.3	1.7	8.6	1.34×10^{-5}
Newport Harbor	23.6	20.1	2.1	10.2	1.33×10^{-5}
Melville	17.4	27.5	2.9	10.7	1.82×10^{-5}
Mt. Hope Bridge	14.3	34.6	2.6	7.5	2.29×10^{-5}
Rumstick Point	9.52	39.8	3.6	9.0	2.63×10^{-5}
Pawtuxet Neck	4.2	70.3	6.1	8.3	4.64×10^{-5}
Pomham Rocks	3.32	75.2	7.2	9.6	4.97×10^{-5}
Fox Point	0.0	144.9	11.7	8.0	9.57×10^{-5}

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-047-RI

Agreement No. 14-31-0001- 3933

FCST-COWRR Research Category: V F

Project Title:

Effect of Ozonation on Human Enteric Viruses in Water from Rhode Island Rivers

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1972

To Be Completed--Month: June ; Year: 1974

Principal Investigators	Degree	Discipline
Pei W. Chang	Ph.D.	Animal Pathology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
John Snyder	B.A.	Medical Technology

A) RESEARCH PROJECT ACCOMPLISHMENTS

1. Design of ozone production and monitorizing equipment

a. An ozonating water chamber was designed to achieve increased pressure and maximum contact of the water with ozone. The chamber can be placed in various temperature baths and an electronic device monitors the temperature of the water at any given time. The chamber also serves as a cuvette for the monitor.

b. A monitor utilizing ultraviolet light to measure the amount of residual ozone in water was constructed. Each component of the monitor was placed in a spectrograph and absorbance curves were run in order to determine the efficiency of each. At this time the sensitivity of the monitor is below that required to detect low ozone residuals. Further improvements are being made.

c. The orthotolidine-manganese sulfate method was used to chemically detect residual ozone in water.

2. Collection and chemical analysis of river water

a. A five-gallon carboy was cleaned and sterilized. The carboy was filled with water from the Saugatucket River. The water was filtered through 16 layers of gauze to remove macroscopic debris. Then the water was treated with aluminum sulfate at 100 mg per liter. The treatment continued for 24 hours, after which the supernatant fluid was filtered through a Whatman paper filter. The clear water was dispensed in 20 ml aliquots and frozen at -20° for future use.

b. Chemical analysis of post-floculated and filtered river water was made. Results are shown in Table 1.

3. Production of ozone demand free distilled water and river water

Water was prepared by bubbling ozone in it for 20 hours at 38 mg of ozone per hour. The residual ozone was allowed to drop to zero mg/liter. All studies were determined using ozone demand free water.

4. Sterility of the test systems

It was necessary to determine if the routine proceedure of ozonating contaminated river or distilled water would be sufficient to kill consequential bacterial. It was shown that the residual ozone levels and contact times used for our experiments were sufficient to sterilize the water samples, making virus assays in tissue culture methods possible.

5. Stopping the action of ozone

a. Experiments were carried out to determine the minimum concentration of sodium thiosulfate required to combine all the free residual ozone. For the ranges of residual ozone used in this project, one drop of 0.01 M sodium thiosulfate was sufficient.

b. It was also demonstrated that the action of ozone could be stopped when a sample was taken from the chamber and pipetted into the nutrient broth, which is used in the virus assays.

6. The kinetics of residual ozone at 0°C, 25°C and 37°C

The kinetics of residual ozone were determined at three temperatures (Figure 1). Results showed that at 0°C it requires approximately 20 minutes to achieve a 0.2 mg/liter residual ozone concentration and the half-life is approximately 150 minutes. At 25°C less than 0.05 mg/liter could be achieved in the same amount of time with a half-life of less than 5 minutes. At 37°C an almost instantaneous decomposition occurrs.

7. Collection and preparation of stock virus

a. The following viruses were obtained, propagated and virus titers determined. The results are shown below.

Virus	Cell Cultures	Titer
Poliovirus type 1	Rhesus monkey kidney	$3x10^6$
Poliovirus type 3	Rhesus monkey kidney	$1x10^3$
Echovirus type 12	Rhesus monkey kidney	$4x10^6$
Echovirus type 29	Rhesus monkey kidney	$2x10^3$
Coxsackie virus type B3	Rhesus monkey kidney	$3x10^3$

b. Preliminary inactivation of Echovirus type 12 and Poliovirus type 1 by residual ozone in water.

A 9.5 ml sample of ozone-demand free distilled water was placed in the chamber and ozonated at 0°C. After 40 minutes the water contained an ozone residual of 0.5 mg/liter. To 4.5 ml of ozone-containing water was added 0.5 ml of Echovirus type 12, making a 1:10 dilution. At various time intervals ranging from 1 to 30 minutes post ozonation, samples were taken from the chamber and assayed for the virus titer. The same procedure was followed for poliovirus type 1. The results show that there were incomplete inactivation of Echovirus type 12 and Poliovirus type 1 at 30 minutes.

Table 1. CHEMICAL ASSAY OF RIVER WATER POST FLOCCULATION AND FILTRATION

CHEMICALS	PPM
Chlorine	0
Chloride	6
Sulfide	0
Phosphate	0
Nitrate	0
Alkalinity	0
Total Hardness	20 (very soft)
Calcium	0
Magnesium	20
Total dissolved solids	77 (very good)

Table 2. INACTIVATION OF ECHOVIRUS TYPE 12 AND POLIOVIRUS TYPE 1 BY RESIDUAL OZONE**

TIME POST-OZONATION (in min.)	ECHOVIRUS 12 PFU*/ml	POLIOVIRUS 1 PFU/ml
0	$1x10^7$	$1x10^6$
1	$6x10^6$	$4x10^3$
2	$4x10^6$	$4x10^3$
3	$4x10^6$	$4x10^3$
4	$4x10^6$	$4x10^3$
5	$4x10^6$	$4x10^3$
10	$4x10^6$	$4x10^3$
15	$4x10^6$	$4x10^3$
30	$4x10^6$	$4x10^3$

* PFU = Plaque-forming units

** 0.5 mg/liter of residual ozone in water

B) PUBLICATION

None.

C) PROJECT STATUS

The project will continue in the next fiscal year.

D) APPLICATION OF RESEARCH RESULTS

In our preliminary studies, ozone used in water purification seems to be ineffective when depending on free residual ozone. Further work should be conducted using continously bubbling ozone in water as a mean of purification.

E) WORK REMAINING AND PROGRESS CONTEMPLATED DURING NEXT YEAR

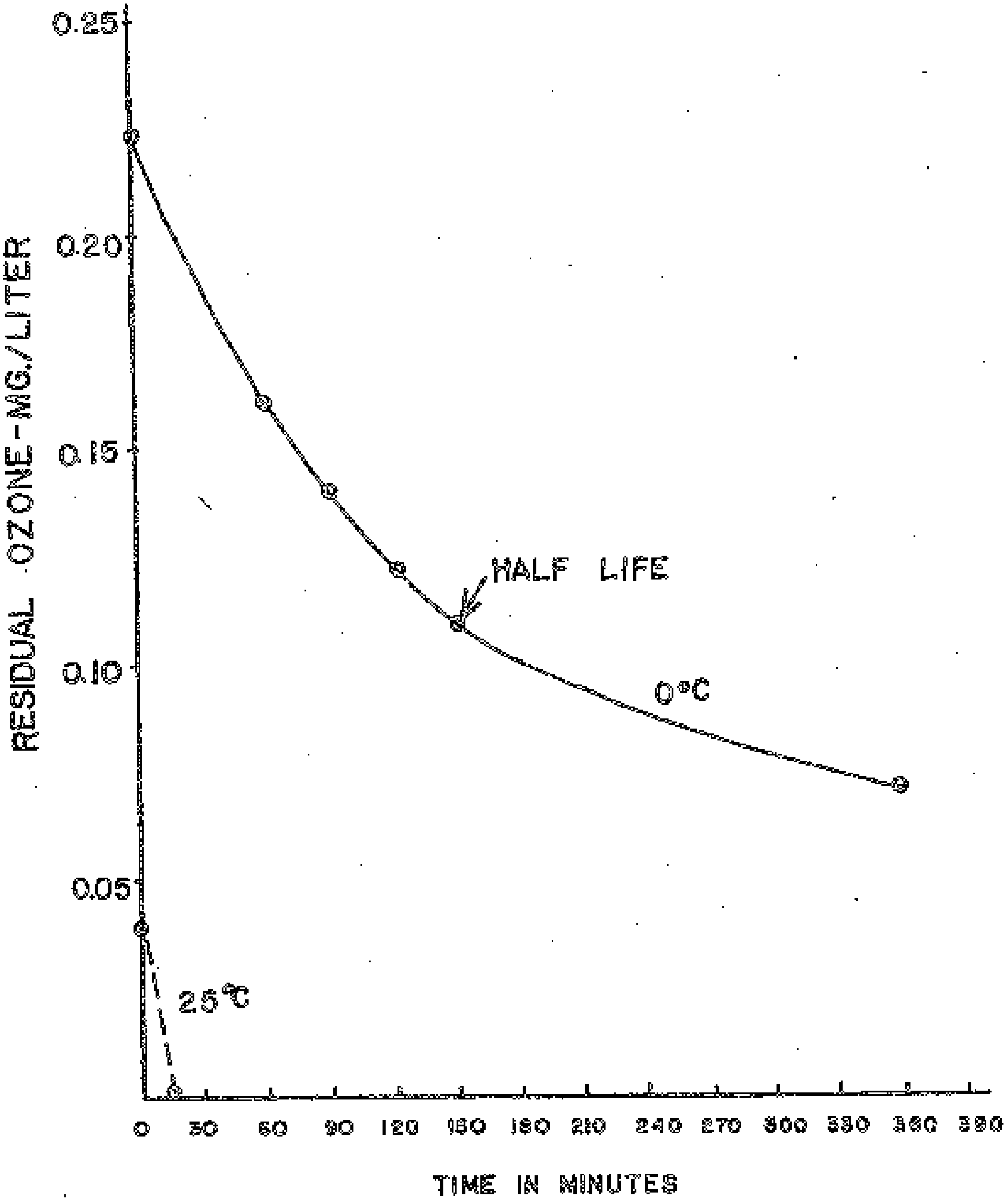
1. Purification of human enteric viruses

In our present studies, virus was not purified. It was suspended in tissue culture medium which contain 2-5% calf serum. The presence of calf serum was shown to inactivate residual ozone in water. Steps will be taken to purify the tissue culture propagated enteric viruses by low and high speed centrifugation and by passage through Sephadex column (G-200) thus eliminating calf serum and other low molecular weight contaminants, which interfers with the viricidal action of ozone.

2. As indicated in (D) water purification will also be carried out using continuously bubbling ozone in water instead of depending on residual ozone alone. The units of ozone generated by continuously bubbling method will be dependent upon the total time of treatment and rate of generation.

3. The viricidal efficiency of ozone on 14 viruses will be completed. These viruses will be Poliovirus type 1, 2, 3, Coxsackievirus type B1, B3 and B5, Echovirus type 12 and 29, Adenovirus type 3, 7a and 12 and Reovirus type 1, 2 and 3.

FIGURE I. DECOMPOSITION OF RESIDUAL OZONE AT VARIOUS TEMPERATURES



NO RESIDUAL OZONE WAS DETECTABLE AT 37°C.

ANNUAL REPORT - TRAINING AND EDUCATION ASPECTS OF THE WATER RESEARCH PROGRAM UNDER P.L. 88-379

Name of University:
(or College) University of Rhode Island

SUBMIT THE INFORMATION SPECIFIED BELOW FOR THE UNIVERSITY AT WHICH THE WATER RESOURCES RESEARCH INSTITUTE OR CENTER APPROVED UNDER P.L. 88-379 IS LOCATED, AND FOR OTHER UNIVERSITIES WITH WHICH THE INSTITUTE OR CENTER IS COOPERATING. KEEP THE STATISTICS ON ENROLLMENTS, NUMBER OF STUDENTS GRADUATING, EMPLOYMENT STATUS OF GRADUTES, NEW COURCES, ETC., SEPARATE FOR EACH UNIVERSITY. IT IS RECOGNIZED CERTAIN OF THE REQUESTED DATA ON STUDENTS MAY NOT BE READILY AVAILABLE. IF SO, PROVIDE BEST ESTIMATE FIGURES. IN OW-9, DATA ON STUDENTS ARE REQUESTED ONLY FOR THOSE STUDENTS WHO RECEIVED EMPLOYMENT AS RESEARCH PROJECT OR PROGRAM ASSISTANTS THROUGH THE P.L. 88-379 PROGRAM. IF EXTRA SPACE IS NEEDED, ADD PAGES AND NUMBER EACH CONTINUATION ITEM IN THE ORDER SHOWN BELOW.

A. During period since last annual report was submitted provide information on: (See footnote 1/ below.)

(1) New water resources related courses developed. (Give title, state whether interdisciplinary, and give brief description of course. Please indicate if any of these were outgrowths of P.L. 88-379 program activities.)

SEE ATTACHED SHEET

(2) Water resources related staff members added to fill new positions. (List highest degree obtained and scientific discipline. Indicate which ones received any salary from P.L. 88-379 funds. Do not list staff replacements.)

NONE

1/ Our intent here is to obtain information on improved academic capability for water resources research and training. Indicate for each position, research facility or other item, whether support was provided in whole or in part through P.L. 88-379 funds, or from other sources; however, also list improvements supported by State or other funds.

(1) New water resources related courses developed.

Botany 417 - Methods in Aquatic Plant Ecology

Field and laboratory work in marine and freshwater ecology. Designed to provide practical experience in aquatic biology.

Instructor's P.L. 88-379 projects certainly had an influence in the development of this course.

Botany 419 - Freshwater Botany

Field and laboratory study of freshwater algae and certain other plants, with emphasis on classification and use of keys, and with consideration of their morphology, ecology and physiology.

Instructor's P.L. 88-379 projects certainly had an influence in the development of this course.

Botany 421 - Advanced Practicum in Aquatic Plant Ecology

Experience in team research involving group selection of field project, preparation of proposal, design of experiment, investigation and final report.

Instructor's P.L. 88-379 projects certainly had an influence in the development of this course.

Forestry 421 - The Wetland Environment

Characteristics and values of freshwater and saltwater wetlands. Man's use of wetlands; review of wetland legislation, evaluation of wetlands as wildlife habitat.

The presence of the Water Resources Center on the campus may have influenced the development of this course.

Plant and Soil Science 450 - Soil Conservation and Land Use

The application of soil survey interpretation as a tool in soil and water conservation and land use planning.

A. (Continued)

(3) Water resources related staff members employed to replace those who retired, died, or moved. (List highest degree obtained and scientific discipline. Indicate which ones received any salary from P.L. 88-379 funds.)

NONE

(4) New water resources research and training facilities other than research equipment items. (Include only major facilities such as new laboratories, buildings, etc.)

NONE

(5) Interdepartmental interuniversity or regional agreements consummated with respect to improved research and training capabilities. (To be answered only by institutes under P.L. 88-379. If copies of such institute-related agreements have not been provided OWRR, please provide.) With the Rhode Island Director as principal investigator, the six New England centers completed the regional project (C-2034) as of December 31, 1972 entitled "The Feasibility of Optimizing Multi-University Regional Water Resources Research". The completion report entitled "Water Resources Research Coordination in New England" was printed (68 pages) and distributed nationally.

The Rhode Island Director is also serving as the principal investigator on behalf of the Northeast Water Institute Directors (NEWID) on the project "Analysis of Critical Water Problems in the Northeastern United States to Determine Essential Research Requirements".

B. Number of students receiving employment as research project or program assistants through the P.L. 88-379 program. (Include only those students, both continuing and graduating, paid wholly or in part with P.L. 88-379 funds during the past fiscal year.)

Category of Students	No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc. 2/	
	Scientific Discipline of Student	Number
(1) Undergraduates	Animal Pathology	1
	Chemistry	3
	Civil & Environmental Engr.	1
	Pharmacognosy	1
		6
(2) Master's Students	Animal Pathology	2
	Bacteriology & Biophysics	2
	Chemical Engineering	4
	Chemistry	2
	Civil & Environmental Engr.	4
	Pharmacognosy	1
	Physics	1
		16

2/ This refers to educational background prior to employment as research assistant on P.L. 88-379 projects--not to departments in which projects are being conducted.

B. (Continued)

Category of Students	Scientific Discipline of Student	Number
(3) Doctoral Students	Chemical Engineering	
	Chemical Engineering	3
	Pharmacognosy	1
		4
(4) Postdoctoral Students		
	Plant Pathology-Entomology	1

No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc.

C. Employment status of majors in water-related fields who graduated during the school year ending about June and who receive P.L. 88-379 support.

EMPLOYMENT STATUS	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1. No. employed in water-related positions in: Total----	1	1		2
Federal Agencies----------	( )	( )	( )	( )
State & Local Agencies--------	( )	( )	( )	( )
University or College--------	( )	( )	( )	( )
Other - Including private enterprise-------------	(1)	(1)	(0)	(2)
2. No. graduates returning to school for advanced degree------------				
3. No. going into military service--------------				
4. No. unemployed or working in other fields-------------			1	1
5. No. status unknown-------------				
6. Totals-------------------	2	2	1	5

D. Type of employment of those school year graduates who received P.L. 88-379 support and who are known to have gone into water-related positions. (Number should agree with total listed under Item 1 of the preceding paragraph "C". Graduates enrolled for further course work or training should not be listed here as employed.)

Number of Graduates Engaged in Water-Related Work In:	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1A. Federal Agencies:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1B. State & Local Agencies:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1C. University or College: 3/				
a. Primarily Teaching				
b. Primarily Research				
c. Primarily Research & Teaching				
d. Other or not known				
1D. Other - Including Private Enterprise:	1			1
a. Primarily Research				
b. Primarily Planning		1		1
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
Totals	1	1		2

Selected summary of above data -- from the "Total" column: 1

Research (1Aa, 1Ba, 1Cb, 1Cc& 1Da) ____

Planning (1Ab, 1Bb & 1Db) 1

Development (1Ac, 1Bc & 1Dc) ____

Operations (1Ad, 1Bd & 1Dd) ____

Management (1Ae, 1Be, & 1De) ____

3/ Do not include here students working as research assistants and receiving course credits.

E. Identify by name and discipline and briefly describe instances, if any, in which the institute program, in the past year, has resulted in individuals, other than students, doing research or teaching in the water resources field, who, previously, were not involved in water work.

Stanley M. Barnett, Ph.D.	Chemical Engineering-Univ. of Rhode Island Kingston, R.I.
Harold N. Knickle, Ph.D.	" " "
Richard W. Traxler, Ph.D.	Plant Pathology-Entomology "

F. Cite any instances you know of, in which individuals who previously served as student research assistants on P.L. 88-379 projects, are now serving as professional investigators of P.L. 88-379 projects following graduation. Do not include individuals reported in this category last year or before.

NONE

PUBLICATIONS AND THESES

Publications

1. C.W. Brown and S.F. Baldwin, "Detection of Ionic Water Pollutants by Laser Excited Raman Spectroscopy". Water Resources Research, 6, 1601 (1972).

2. C.W. Brown, F.P. Daly and D.R. Kester, "Sodium and Magnesium Sulfate Ion Pairing: Evidence from Raman Spectroscopy",-Phys. Chem., 76, 3664 (1972).

3. C.W. Brown and M. Ahmadjian, "Feasibility of Remote Detection of Water Pollutants and Oil Slicks by Laser-Excited Raman Spectroscopy," Environ. Sci. Technol., 7, 452 (1973).

L.R. Worthen, S.G. Zelenski and J. Tashiro, "A Gas Chromatograph Method of Quantitating p,p'-DDT in the Presence of Interfacing PCB," (1973). Water Resources Research-in press.

Theses

Thomas Brueckner, "Electrochemical Process for the Removal of Nitrogen and Phosphorous from Wastewater," M.S. Univ. of Rhode Island.

TECHNICAL SECTION
OF THE ANNUAL REPORT OF THE
RHODE ISLAND WATER RESOURCES CENTER
FISCAL YEAR 1974

RHODE ISLAND WATER RESOURCES CENTER

DIRECTOR'S REPORT FOR FISCAL YEAR 1974

Water Problem Priorities in the State

The state Advisory Board for the Rhode Island Water Resources Center during the year decided that the list of priorities for state water problems should be retained as established last year. This leaves the control of iron and manganese in groundwater supplies and the control of pollution from industrial plants as the two most important problems. The operational modeling of groundwater aquifers is receiving increasing attention as indicated by the cooperation in this area of the state Water Resources Board and the Water Resources Center.

Cooperation with State Agencies

To quote from a statement issued recently by Robert B. Russ, the General Manager of the state Water Resources Board: "The Rhode Island Water Resources Board is working in close cooperation and coordination with the Water Resources Research Center at the University of Rhode Island to encourage and support research effort in various water related endeavors to the net effect that research results will be of immediate and general benefit to the public. Toward this objective the Water Resources Board serves as a member of the State Advisory Board for the Water Resources Research Center to assist in formulating and guiding research efforts into areas of immediate concern to operating state and local water agencies. To this end, the Advisory Board established a list of priorities for water problems in the State of Rhode Island."

Throughout the year, in cooperation with the Department of Natural Resources, the Department of Health and the Water Resources Board, the Water Resources Center continued to monitor a 100-acre pond which now has restricted use. It was hoped that the pond could be opened for public recreational use and that a satisfactory road to the site could be constructed but the Water Resources Board has not yet granted its approval. At present the pond is of drinking water quality and it was expected that the direct effect on water quality of limited recreation could be determined through analysis of the water before and after the removal of restrictions. Monitoring will be continued.

The Water Resources Center cooperated in two projects which were supported financially by the Water Resources Board. These involved a resistivity study of the area between a landfill site and One Hundred Acre pond in South Kingstown and construction of an analog computer model of the Chipuxet groundwater reservoir.

Current Research

As has been stressed by the Center's Advisory Board pollution of its waters continues to be one of the major problems in the state of Rhode Island and it has been in this area that much of the research has been conducted during the past year.

Three projects were concerned with wastewater treatment. Project A-046-RI continued work on increasing the rate of biological decomposition of cellulose which is a major component of municipal and agricultural wastes contributing to the pollution of water. It has been shown that by using high pressure fermentation the oxygen limitation at elevated temperatures can be overcome. The effectiveness of methods of treating wastewater from fish and shellfish processing plants has been studied in the continuation of Project A-048-RI. These have included reverse osmosis, activated carbon adsorption, filtration, aeration and chemical treatment (which appears to be the most promising). An interesting procedure for concentrating industrial wastes was proposed in Project A-049-RI. The idea was to study the feasibility of using direct osmosis in conjunction with sea water to concentrate the solutions of such wastes. Using existing commercially available reverse osmosis membranes the method did not appear to be promising due to low water permeation rates and high salt flux through the membranes. It is still believed that the method might be practical if a membrane having suitable properties can be found or developed.

This year three projects were involved with aquatic pesticidal pollutants. The research of two of these was concerned with the biodegradation of the pollutants while the third was interested in determination of actual molecular structures. Project A-045-RI has demonstrated clearly that microbial co-oxidation of halogenated aromatic compounds (pesticides) does occur and this fact will be of interest to scientists in assessing the fate of such pesticidal pollutants in water. During the first year of Project A-050-RI a number of organisms capable of growing on common pesticides have been isolated using enrichment cultures prepared from the effluent of a nearby chemical plant and from soil samples from turf plots where various pesticides have been in use for several years. Both biological activity and persistence of pesticides in the ecosystem have been found to depend directly on molecular structure. It is therefore crucial to an understanding of the behavior of these materials that the exact molecular structure be known. Project A-051-RI is making such valuable determinations.

Two projects have been interested in the effects of two important chemical treatment processes which are employed in water supply namely chlorination and ozonation. Project B-051-RI has shown during it first year that unexpectedly large amounts of chlorine are incorporated into the nucleic acids, both RNA and DNA, which are the most essential constituents of all organisms. So far it has not been possible to pinpoint the exact locations of chlorine substitutions nor their effects but it is believed that chlorine attacks the nucleic acids destructively to form smaller chain compounds. Project B-047-RI has demonstrated that ozone is viricidal but its efficiency depends upon the strain of viruses and on the presence of impurities in the water. Pending more thorough studies, caution should be used in the replacement of chlorine with ozone in water treatment.

Movement of chemical constituents of water through soils or sediments was the concern of two projects during this year.

In Project A-052-RI, after construction of the test apparatus for infiltration tests, studies were made of the effect of several variables on the adsorption and movement of cupric ions through a number of Rhode Island soils. In the first year's work on Project B-052-RI, sediment sampling stations were established at seven points along Narragansett Bay and samples were taken for physical and chemical analyses. Sampling and analysis will continue during the next year to permit an accurate assessment of sediment pollution in the Bay.

Continuation of research on Project A-047-RI has indicated that there is little likelihood that drinking water will be seriously contaminated with zinc or cadmium as a result of distribution through galvanized or yellow brass piping.

Regional Cooperation

The Rhode Island Water Resources Center is an active partner among the six states in the regional research project undertaken during the year by the New England Council of Water Center Directors entitled, "The Impact of Urbanization on New England Lakes: An Assessment of Lake Quality Control Methods" (C-5342).

The Rhode Island Center is continuing to serve as fiscal administrator for the fifteen Northeastern institutes in the project to identify water resources research needs through a series of workshops involving federal, state and local water agency representatives as well as the public, decision makers and researchers. (Project B-061-RI).

A. Ralph Thompson, Director
Rhode Island Water Resources
Center

OTHER NARRATIVE ITEMS

RHODE ISLAND WATER RESOURCES CENTER

Examples of Research Findings and Their Actual or Potential Application to Water Resources Problems

During the year the Rhode Island Water Resources Board called upon the Water Resources Center to make use of its research ability to assist in the solution of two problems.

Techniques developed through OWRR Project A-008-RI were used to make resistivity measurements which were extremely helpful to the Board in making decisions regarding proposed land use.

Also, the Board is making valuable use of an analog model of the Chipuxet groundwater aquifer in the Lower Pawcatuck River Basin which was based on research begun before and now continuing on OWRR Project A-056-RI.

Water Resources Developments within the State during F/Y 1974

The Water Resources Board continued to license well drillers operating in Rhode Island. During the year more than 600 well drillers reports were supplied to the Board. These reports are furnishing very useful information concerning groundwater.

During the year considerable work was done on the Chipuxet groundwater reservoir. A number of test wells were drilled and pumping tests made as well as seismic investigations to show the extent of underground reservoirs. The statewide manganese study initiated in depth last year was continued with emphasis on the Chipuxet Reservoir.

The Governor's Environmental Task Force recommended the creation of a Solid Waste Management Corporation which will, in conjunction with the Department of Health, serve as the basic mechanism for carrying out the state's future solid waste management activities and programs. Previously, the Task Force had recommended that the Water Resources Board coordinate both water supply and sewage disposal in the State of Rhode Island. To date, no action has been taken on this recommendation.

The Water Resources Board is initiating feasibility studies regarding two cross bay water connectors. One of these is to serve Bristol, Barrington and Warren through the Bristol County Water Company and the other to serve Aquidneck Island.

Through the Water Resources Planning Act, the Water Resources Board received a matching grant of $37,600 from the federal government for the purpose of preparing a comprehensive plan for water and related land resources in the state. The formulation of the plan was programmed into seventeen separate tasks of which nine have been completed. The first seven of these were listed in last year's report.

Those completed during this fiscal year were:

Inventory of Solid Waste Disposal

Character and Analysis of Rhode Island's Groundwater Resources

Another, Inventory and Analysis of the Fish and Wildlife Inhabiting Rhode Island's Fresh Water Areas, will be completed in the latter part of this year.

It was decided that a bond issue of three million dollars will be floated in November of 1974 for the design of the Big River Reservoir for the State of Rhode Island.

RHODE ISLAND WATER RESOURCES CENTER

INDIVIDUAL PROJECT ANNUAL REPORTS

FISCAL YEAR 1974

A-045-RI	Microbial Co-oxidation of Halogenated Aromatic Acids	Traxler
A-046-RI	Thermophilic Hyperbaric Fermentation for Cellulose Waste Treatment	Barnett
A-047-RI	Development of Methods for Controlling the Cadmium and Zinc Content in Water	Mairs
A-048-RI	Treatment of Wastewater from Fish and Shellfish Processing Plants	Knickle
A-049-RI	Concentration of Industrial Wastes by Direct Osmosis	Votta
A-050-RI	Biodegradation of Aquatic Pollutants	Houston
A-051-RI	Crystal and Molecular Structure of Selected Pesticidal Water Pollutants	Cheer
A-052-RI	Movement of Trace Metals with Percolating Water	Wang
B-047-RI	Effect on Ozonation on Human Enteric Viruses in Water from Rhode Island Rivers	Chang
B-052-RI	Nutrient Exchange in Water-Sediment Interface and its Effects on Water Quality	Poon
B-057-RI	Further Studies of the Interaction of Chlorine and Organic Molecular in Water	Shimizu
B-061-RI	Analysis of Critical Water Problems in the Northeastern United States to Determine Essential Research Requirements	Thompson

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-045-RI

Agreement No. 14-31-0001-4040

FCST-COWRR Research Category: VG

Project Title:

Microbial Co-oxidation of Halogenated Aromatic Acids

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1972

To Be Completed--Month: June ; Year: 1974

Principal Investigators	Degree	Discipline
Richard W. Traxler	Ph.D.	Microbiology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Richard H. Pierce, Jr.	BS,MS,Ph.D.	Chemistry

Microbial Co-oxidation of Halogenated Aromatic Acids

Dr. R. W. Traxler

A. Research Project Accomplishments.

This year a series of isolates were examined by the techniques developed last year for co-oxidative action on DDT-Benzoate, DDT-Indene, Heptachlor-Benzoate, Heptachlor-Indene and Cyclopentene systems. The only systems showing co-oxidation with the isolates examined were the Heptachlor-Benzoate and Heptachlor-Indene systems.

The organism providing the best response was obtained from brackish sediment exposed for many years to a variety of organic pesticides. This isolate is a Gram negative rod producing a smooth pink to orange pigmented colony identified as Isolate #2.

Warburg respiration studies (Table 1) showed that the metabolism of Isolate #2 was different on each substrate but that the mixture was much closer to the indene system than to the heptachlor system.

Table 1. Respiratory Quotients of Isolate #2

Substrate	Q_{O_2}	Q_{CO_2}	RQ
Indene	19	10	0.53
Heptachlor	28	17	0.61
Indene-Heptachlor	28	15	0.54

Gas chromatographic analyses were performed on the reaction products from the Warburg study and demonstrated a 25% reduction in Heptachlor concentration in the Indene-Heptachlor system. Calculation showed that 0.25 μM of heptachlor had been used in the co-oxidation system and that 0.3 μM of oxygen were required in the reaction. This means that two atoms of oxygen were taken up for each molecule of heptachlor oxidized.

This data is indicative of microbial co-oxidation of heptachlor via one or two oxidation steps when Isolate #2 is growing at the expense of indene.

B. Project Publications.

None.

C. Project Status.

This project will not be funded for next fiscal year. A completion report will be submitted to OWRR.

D. Application of Research Results.

The results of this project have been described to the personnel involved in USDA regional project NE-53. This project has shown that microbial co-oxidation of halogenated aromatic compounds does occur. The project has been difficult because locating such microbial systems is a chance phenomenon. It is significant however that co-oxidation of such molecules does occur and will be of interest to the scientific community in assessing the fate of such recalcitrant molecules as heptachlor as pollutants in aquatic environments.

Form OW-1 (1972)

ANNUAL REPORT — TITLE I PROJECT

OWRR Project No. A-046-RI

Agreement No. 14-31-0001-4040

FCST-COWRR Research Category: 1 VD

Project Title:

Thermophilic Hyperbaric Fermentation For Cellulose Waste Treatment

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, RI 02881

Proj. Began—Month: July ; Year: 1972

To Be Completed—Month: June ; Year: 1974

Principal Investigators	Degree	Discipline
Stanley M. Barnett	Ph.D.	Chemical Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
R. A. Romanelli	B.S.	Chemical Engineering

A. Project Accomplishments

Cellulose, the most plentiful of organic compounds, is also the major component of municipal and agricultural solid waste. Any practical method of increasing the rate of decomposition of cellulose in wastes would have important economic and environmental implications.

The effect of pressure on the grwoth of the cellulolytic fungi *Sporotrichum thermophile*, *Thermascus aurantiacus* and *Chaetomium thermophile* var. *coprophile* was studied. The organisms were first grown in conventional stainless steel gas sample cylinders to obtain maximum and limiting growth pressures. Especially designed pressure vessels were then used to determine the effect of pressure on growth rate, cell yield, cellulose decomposition and optimum growth temperature. Dissolved oxygen and pH were also followed. Fermentation gas was sampled from the confined pressure vessels and analyzed by gas chromatography to monitor oxygen utilization and carbon dioxide production. The effect of pressure *per se* on the degree of polymerization of cellulose was determined in uninoculated medium. Pressure above 90 psig air were inhibitory to all three fungi. *Sporotrichum thermophile* displayed the best growth rate on cellulose at 40 psig.

The results of the effect of pressure and temperature on optimum growth are shown in Figure 1. The optimum growth temperature of *S. thermophile* was previously determined in shake flask studies to be 40°C, in a series of tests at 37, 40 and 43°C. Pressure appeared to have no effect on the optimum growth temperature of *S. thermophile*. The optimum remained at 40°C.

As shown in Figure 1, pressure does improve utilization of cellulose by a thermophillic organism. We have accomplished our original goal, showing that we can overcome the oxygen limitation in fermentations at elevated temperatures.

B. Publications. None yet.

C. Project Status. Although project funds will run out in June 1974, we plan to continue our work. We are developing data on saccharification of cellulose, an intermediate step on the way to producing useful products from cellulose laden wastes. Our kinetic data which will appear in the final report, should prove useful for process design of waste treatment systems.

D. Application of Research Results. L. Spano, J. Nystrom, and M. Mandels, Pollution Abatement Program, U.S. Army Natick Laboratories, Natick, MA. We have developed process design data with their organisms. They are planning a pilot waste treatment unit. They were very much interested in the effect of elevated oxygen partial pressures on microorganisms since increased oxygen is a variable which they can easily provide and control.

E. Work Remaining, and Progress Contemplated During Next Year. The work called for in our original proposal is now complete except for a final report. We would like to continue pressure studies in a large fermentor, if available and continue work started on saccharification of cellulose. Several publications should be available by the end of August 1974.

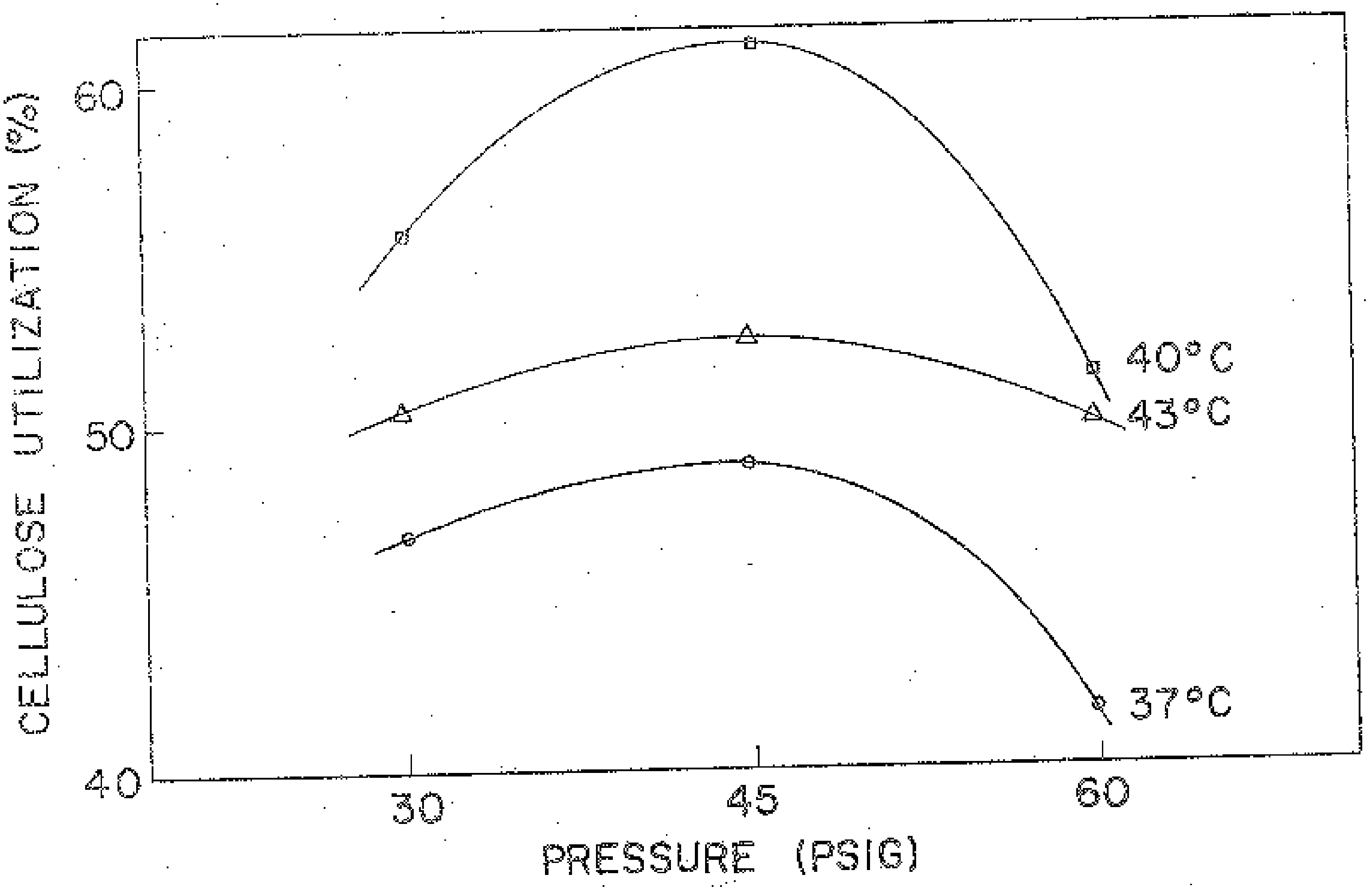


Fig. 1 Effect of Pressure and Temperature on Cellulose Utilization

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-047-R.I. Agreement No. 14-31-0001-4040 FCST-COWRR Research Category: VB	Project Title: Development of Methods for controlling the Cadmium and Zinc Content of Water.

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island

Proj. Began--Month: July ; Year: 1972 | To Be Completed--Month: Sept. ; Year: 1974

Principal Investigators	Degree	Discipline
Kenneth H. Mairs	Met. E.	Metallurgy

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Chung Chih Hsu	B.S.	Chemical Engineering
R.M. Jambekhar	M.S.	Chemical Engineering

Previous studies have shown that gases dissolved in water have a marked influence on the corrosion of metals and on the solubility of the corrosion products. This project, then, was designed to study the attack of galvanized iron and yellow brass pipe by (drinking) water, and in particular, to determine if cadmium, as an impurity in zinc, could be detected as a soluble substance in objectionable concentrations.

Our annual report for 1973 indicated we had studied the influence of various gases in deionized water upon the corrosion of galvanized pipe. These initial test conditions were much too severe; zinc concentrations many times that permissible in drinking water were observed. These tests, however, did suggest that attack was uniform without preference for either zinc or cadmium.

The erratic results first reported for brass pipe exposed to similar test conditions have been re-examined and found related to initial surface preparation. It has been demonstrated that solvent cleaning alone is quite unsatisfactory, that mechanical cleaning is an improvment but still unsatisfactory and that chemical cleaning in strong acids is necessary for reproducible results.

During recent months we have turned our attention to the attack of these materials by tap or drinking water with its natural mineral composition rather that the "simple" systems involving deionized water. The tap water chosen was that available on the V.P.I. campus, a relatively soft and neutral water with dissolved air and some free carbon dioxide.

One exasperating aspect of our studies is that we have been unable to find a yellow brass with an appreciable initial cadmium content. While this places some limit upon experimentation, it is a happy circumstance from the practical side of the picture: no cadmium in brass is a desirable condition from the viewpoint of public health. In order to retain a focus upon cadmium in copper base alloys, corrosion exposures were made using a 1% Cd-Cu alloy. This is not a pipe or tubing material and was exposed as coupons of relatively thick strip.

A similar situation presented itself with the commercially available galvanized pipe: the cadmium contamination of the galvanized surface was generally so low that at permissible levels of zinc, cadmium usually could not be detected. To provide experimental materials, we regalvanized several test coupons producing cadmium concentrations of approximately ¼ and ½%. These were then tested in a similar manner.

Many of our observations are essentially negative indicating there is little likelihood that drinking water will be contaminated with cadmium as the result of distribution through galvanized or yellow brass piping. The aspect of control has not yet been investigated adequately for we have not observed naturally occurring conditions requiring control. We have, therefore, requested an extension on this project through September 1974 to complete this facet.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-048-RI Agreement No. 14-31-0001-4040 FCST-COWRR Research Category: IIA	Project Title: Treatment of Wastewater from Fish and Shellfish Processing Plants

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, RI 02881

Proj. Began--Month: July 1 ; Year: 1972	To Be Completed--Month: June30 ; Year: 1974

Principal Investigators	Degree	Discipline
Harold N. Knickle	Ph.D.	Chemical Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Gary Flynn	BS	Chemical Engineering

Harold N. Knickle

Research Project Accomplishments

The effectiveness of some of the simpler methods of treating wastewater from fish and shellfish processing plants have been reviewed; these include reverse osmosis, activated carbon adsorption, chemical treatment, filtration, and aeration.

Since the majority of the pollutant in the wastewater consists of soluble and suspended proteins and organic matter, the biological oxygen demand, BOD, was chosen as the key variable to be monitored. The BOD can be easily reduced by 30% in some of the simpler operations such as aeration and filtration to about 90% in the more complicated operations such as reverse osmosis and chemical treatment. Two or more of these processes can easily be combined to meet requirements of water quality standards.

The intent of this study includes not only finding an effective method for treatment of the wastewater but also to find a process or combination which would be economic and feasible for fish and shellfish processing plants. Estimation of treatment costs are being made and will be presented in the final report. A small processing plant operating 200 days per year and discharging on the average 12,000 gallons per day of wastewater has been chosen as the basis for the economic calculations. The potential for recycle has not been evaluated but if utilized could reduce the annual costs of operation.

One of the difficulties in treating the wastewater from these processing plants is the variability of the wastewater itself. Average parameters for the wastewater were presented in the last annual report. The average BOD was reported as 1180 mg/l but the values over 2000 mg/l and under 300 mg/l have been encountered. The pH has ranged between 6.0 and 12.0. The variability results from startup and shotdown during a single day of operation and over a period of months due to seasonal factors.

Filtration was investigated by simple bench scale vacuum filtration using Whatman #1 and #40 filter paper. The surface of the papers were quickly coated with slime which drastically impeded the filtration rate. The addition of filter aids slightly improved the rate of filtration. The reduction of BOD from these simple tests was highly variable and ranged between 30% and 60%. The use of a GAF bag filter with a five micron rating was evaluated. The BOD reduction was less than 10%, probably because of the bag stretching. A five micron sedimentation filter was evaluated resulting in about a 30% reduction in BOD. A charcoal filter was placed in series with the sedimentation filter resulting in a 35% reduction in BOD. The flow rates were excellent using these cartridge filters, and work on finer filters is indicated.

Reverse osmosis was studied using commercially available units; one from Philco-Ford and the other from Desalination Incorporated (DSI). The Philco-Ford unit ruptured because of operating difficulties and no useful BOD removal values were obtained. The DSI unit was run at 200 psi and approximately 75% recovery. The BOD reduction with one unit was approximately 80%. Thus with more than one of these units in series a satisfactory BOD reduction could be obtained.

Simple bench scale tests were run using activated carbon to adsorb the BOD causing impurities. Many different carbon samples were used at five concentrations of activated carbon. The BOD reductions varied from a low of 13% using powdered carbon to 51% using a coarse carbon. These samples were not filtered and further experiments should be performed using activated carbon with filtered waste. Aeration treatment is installed in the operating plant from which the raw waste was obtained. The actual BOD reduction for this operational process was as low as 30%.

Chemical treatment studies were not complete. Initial tests with lime and alum show a variable BOD reduction for the unfiltered waste. However, experiments should be pursued on filtered waste. An alternative chemical treatment was tested called the Organiform Process (Orgonics Inc.). In this process urea and formaldehyde are reacted and this reactive mixture is then reacted with the pollutants in the waste stream. Initial tests showed about a 90% BOD reduction. Further development of this process seems fruitful.

Application of Research Results

The owner, Paul Jarvis, of the shellfish plant, Harbon Shell Fish, has indicated keen interest in these results. Economical results may be applied to his plant. Some other operating fish processing plants have indicated interest. Robert Ernst of the National Marine Fisheries Service has also indicated an interest in the results of the project.

(1572)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-049-RI

Agreement No. 14-31-0001-4040

FCST-COWRR Research Category: VD

Project Title:
Concentration of Industrial Waste by Direct Osmosis

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, RI

Proj. Began--Month: July 1, Year: 1973 | To Be Completed--Month: June 30 Year: 1974

Principal Investigators	Degree	Discipline
Ferdinand Votta, Jr.	D. ENG	Chemical Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Anderson, Dana K.	B.S.	Chemical Engineering

Concentration of Industrial Waste by Direct Osmosis

Research Project Accomplishments

The purpose of this investigation is to study the feasibility of using direct osmosis in conjunction with sea water to concentrate industrial waste.

Several continuous flow laboratory size osmosis units were designed and constructed. Continuous flow was possible on each side of the membrane. Several different types were built:

1. Type I units were constructed of 1/4 inch sections of 1 1/2 inch brass pipe. These were for small pieces of flat membranes and the exposed membrane area was 13.135 sq. cm.

2. Type II units were constructed from 5 x 5 sections of 3/4 inch plexiglas. These were also for flat membranes and the exposed area was 58.06 sq. cm.

3. Type III units were for testing tubular membranes and were constructed of 1 inch copper tubing.

4. A small pilot plant was constructed of 4 x 4 inch sections of 3/8 inch plexiglas. It was designed for counter current flow and its area could be increased by adding sections. The pilot plant resembled a filter press.

About 10 commercially available reverse osmosis membranes and a cellulose acetate membrane made by Dr. Barnett at URI were tested under various conditions. Most tests were made using simulated sea water on one side of the membrane and distilled water on the other. Simulated waste copper and chromium solutions and an actual sample of waste water from a fish and shellfish processing plant were concentrated. Two tests were carried out using a concentrated sugar solution in place of the sea water. The concentration was such that osmotic pressure was approximately the same as the sea water.

In all cases the observed permeation rate by direct osmosis was much lower than expected. The maximum average osmosis rate obtained was for Eastman KP-98 membrane. The average rate for this membrane was only 2.67 gallons/day/sq. ft. However, the manufacturer rated it as a reverse osmosis membrane at rates of 9-14 gallons/day/sq. ft. when used with 0.5% NaCl and 600 psi pressure. Correcting for the difference in driving force, the water flux should have been between 6 and 10 GPD/sq.ft. The difference between the observed and expected permeation rates in all other cases were greater. For example, Fluid Science #420 membrane only gave a flux of .025 GPD/sq.ft. but as a reverse osmosis membrane was rated at 15 GPD/sq. ft. (corrected to the same driving force).

Replacing the simulated sea water by a concentrated sucrose solution of essentially the same osmotic pressure did not seem to change the water permeation rate.

In those cases in which simulated sea water was used, the sodium chloride flux through the membrane was found to be high. With distilled water as the "waste solution", the exit water stream was found to contain several hundred mg/liter, equivalent sodium chloride. It had been expected that since the salt permeation would be against the flow of the diffusing water, the salt flux would be minimal.

Copper and chromium ions from the simulated waste solutions were also found to permeate through the membrane at a significant rate. The dilute waste solutions were concentrated but a relatively high proportion of the metallic ions were lost in the diluted sea water.

Typical results obtained when using simulated sea water as the concentrated solution are given in Table I. In most cases these are averages of a large number of tests. Listed are the water permeation rates, the equivalent NaCl concentration of the exit water, and the relative water to NaCl fluxes.

TABLE I

TYPICAL RESULTS OF OSMOSIS TESTS

Membrane	Permeation Rate gal/day/sq. ft.	Exit Water Conc. ppm	Relative Flux $gmH_2O/gmNaCl$
Eastman KP-98	2.67	1355	390
Eastman KP-90	2.47	1771	74
Keating Dry	1.90	351	668
Osmotic Sepa-97	.79	417	299
Osmotic Sepa-89	.83	285	439
"Barnett" Membrane	.65	—	—
Fluid Science Flat#NS1	.3	20	—
Fluid Science Tubular #420	.025	—	—
Fluid Science Tubular #NS1	.012	—	—
Polypropylene 2400W #469	.12	>1200	<11.5

Attempts were made to improve the performance of membranes by treatment processes.

Several samples of Eastman KP-98 membranes were treated with 10 PPM and 6 PPM polyvinyl methyl ether in an attempt to improve the salt rejection. No significant change in either the permeation rate or salt rejections were noted.

Reverse osmosis cellulose acetate membranes are normally tempered by immersion in hot water. This forms a dense surface layer and improves the salt rejection properties of the membrane. Samples of Eastman KP-00(untempered) membrane were each tempered by immersion in water for 4 minutes at different temperatures. Other samples were tempered at 93°C for different times. The results of osmosis test on these membranes are given in Table II.

TABLE II
EFFECT OF TEMPERING EASTMAN KP-00 MEMBRANE

Temp. °C	Tempering Time, Min.	Permeation Rate gal/day/sq. ft.	NaCl Permeation Rate mg/hr/ft^2	Equiv. NaCl out PPM	Relative Rate gm/H$_2$O/gm NaCl
60	4.0	0.65	4170	3600	24.4
70	4.0	.79	3050	2640	40.8
80	4.0	1.97	995	1033	315
85	4.0	1.93	638	745	481
90	4.0	1.09	215	204	777
93	4.0	.57	99	89	934
96	4.0	.41	51	46	1240
93	0.5	.91	2750	2533	58
93	1.0	.86	230	213	608
93	2.0	.66	139	129	767
93	4.0	.57	99	89	934
untempered	—	0	—	—	—

CONCLUSIONS

Concentration of industrial wastes by direct osmosis using existing commercially available reverse osmosis membranes does not appear promising on the basis of the reverse osmosis membranes tested. The low water permeation rates and the high salt fluxes through the membrane would probably make the method impractical.. If valuable materials were being concentrated, their further use or recovery would be complicated by the addition to the waste solution of a high concentration of sodium chloride. Also in concentrating dilute metal solutions, a high proportion of metallic ions would be lost in the sea water. It is possible that it might be practical to use the proposed method with an existing membrane to concentrate a waste which would not be affected by addition of NaCl and where the only desired effect is to reduce the total volume of waste to be handled. The waste water from a fish and shellfish plant is such an example. This waste water already contains a high concentration of NaCl and the addition of a little more will not hurt it. It is expected that the organic material will not pass through the membrane to the sea water.

It is believed that concentration of waste by direct osmosis might be practical if a suitable membrane were available. The membrane should permit a high water permeation rate under direct osmosis and should have a much lower salt flux than existing membranes. Membrane development was not within the scope of this current investigation.

The project ended June 30, 1974 and a completion report is being prepared.

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-050-RI

Agreement No. 14-31-0001- 4040

FCST-COWRR Research Category: VB

Project Title:

Biodegradation of Aquatic Pollutants

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R. I. 02881

Proj. Began--Month: July ; Year: 1973

To Be Completed--Month: June ; Year: 1975

Principal Investigators	Degree	Discipline
Chester W. Houston	Ph.D.	Microbiology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Crandall W. Dimock	B. S.	Zoology

Narrative Statement

This project is concerned with microbial interaction in the degradation of commonly used pesticides. Work during the first year of the project has been largely of a preparatory nature to the study of interacting cultures in commercially available equipment in which pure cultures of microorganisms share a common metabolic pool. The preliminary work has involved the isolation of cultures, the determination of growth kinetics on selected pesticides, and an assessment of analytical methods which may be of value in later work. A number of organisms capable of growing on such pesticides as 2,4-D, 2,4,5-T, and chlordane have been isolated using enrichment cultures prepared from the effluent of a nearby chemical plant and from soil samples from commercial turf farms and turf plots at the University of Rhode Island where various pesticides have been in use for several years. Additional cultures which utilize intermediates and/or end products of growth of these organisms are currently being sought for use in interacting cultures.

The possibility of using surfactants to enhance the availability of some of the compounds which have low solubility has been investigated. It has been found that the addition of surfactants to the mineral solution medium has a marked effect on solubility and that the increase in solubility, as suspected, results in a much better growth of organisms on the substrate and thus has a marked effect on the degradation of the compound.

Non-biodegradable surfactants such as Dow-192 have also been incorporated into an agar medium for the isolation and maintenance of cultures. It was found in early work that a mineral solution-agar medium contains sufficient impurities to support the growth of heterotrophic organisms. It is also true of a medium prepared with commercially available "purified agar." Since the impurities can be removed by washing, a medium has been prepared with washed agar, minerals, and pesticide which will support the growth only of an organism capable of utilizing the pesticide added. With these compounds of low solubility, however, the growth is scant. The non-biodegradable surfactant has been added to enhance solubility in the solid medium. Colony size is markedly increased. The medium has been of value in isolation procedures. It appears to be a good maintenance medium and it should keep the organism "adapted" to the compound in question.

The equipment to be used for the study of interacting cultures was withheld from the market by the manufacturer for design changes and has only recently been received. Most of the work of the second year of this project will be directed toward determining symbiotic and/or synergistic effects of interacting cultures of the isolates in the degradation of pesticides using this equipment.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-051-RI Agreement No. 14-31-0001-4040 FCST-COWRR Research Category: V A	Project Title: Crystal and Molecular Structure of Selected Pesticidal Water Pollutants

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island

Proj. Began--Month: July ; Year: 1973 | To Be Completed--Month: June ; Year: 1975

Principal Investigators	Degree	Discipline
Clair J. Cheer	Ph.D.	Chemistry

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Francis Pickles	B.S.	Chemistry

A. Research Project Accomplishments

1. Preliminary data collection

The list of compounds under study has been expanded to five with the availability of both isomers of endosulfan (thiodan I and thiodan II). Of these five only one (carbaryl, sevin) has thus far resisted all efforts to obtain suitable single crystals of diffraction quality. The material crystallizes in very thin plates from all solvent systems thus far explored. Efforts to obtain suitable crystals from other solvent systems, from melts, and from sublimation are continuing.

Pertinent preliminary crystallographic data obtained on the remaining materials is listed in the following table (page 3).

2. Intensity data collection

The advertised availability of an automated GE XRD6 X-ray diffractometer at MIT has never achieved fruition. After numerous visits to Cambridge to make preliminary arrangements culminated in initiation of data collection on a crystal of Paden, the process was prematurely halted when the operator of the diffractometer abruptly severed her relationship with MIT to assume a teaching position at another institution.

The recent discovery of severe contamination (tungsten?) of a copper target X-ray tube precluded its use and a replacement is presently on order.

	Methoxychlor	Padan	Thiodan I	Thiodan II
solvent	methanol	-	acetone	hexane
crystal system	triclinic	orthorhombic	orthorhombic	hexagonal
lattice parameters				
a	10.768	9.82	15.82	*
b	6.32	12.87	9.61	*
c	12.39	10.02	9.47	11.42
α	99°50'	90	90	90
β	97°30'	90	90	90
γ	92°7'	90	90	120
density (obs)	1.401	1.469	1.874	1.841
density (calc)	1.447	1.438	1.875	*
z	2	4	4	*
space group	$P\bar{1}$	$P2_12_12_1$	$P222_1$	*

*these parameters have not been unambiguously determined.

B. Publications

None.

C. Project Status

Incomplete, will continue into next fiscal year.

D. Application of Research Results

The potential application of the research results has already been dramatically demonstrated for a series of diaryl insecticides related to DDT by Holan. From accurate steric models a theoretical model was formulated which allowed the prediction of activity for new compounds. In all cases the predictions have been substantiated by the demonstrated increased activity of the new insecticides. In order to develop further theoretical models for other types of insecticides accurate molecular dimensions are required. This research is aimed at fulfilling this goal.

E. Work Remaining, and Progress Contemplated During Next Year

Future work will involve intensity data collection utilizing the Picker diffractometer at Brown University. Continuing efforts to obtain suitable crystals of carbaryl will be intensified.

A variety of programs dealing with the solution of the phase problem for centric space groups are presently available at URI. However, since only methoxychlor crystallizes in a centric space group, a new system of programs (the MULTAN system) which deal specifically with acentric phasing methods has been solicited and is expected in the near future. It is anticipated that this system will be operational by the end of the current fiscal year.

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ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-052-RI

Agreement No. 14-31-0001-4040

FCST-COWRR Research Category: VB

Project Title:

Movement of Trace Metals with Percolating Water

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R.I. 02881

Proj. Began--Month: July ; Year: 1973

To Be Completed--Month: June ; Year: 1975

Principal Investigators	Degree	Discipline
Mian C. Wang	Ph.D.	Civil & Environmental Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
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OWRR Project No. A-052-RI

Movement of Trace Metals with Percolating Water

Progress Report

(July 1, 1973 - June 30, 1974)

Work completed in this first year of study includes (1) design and construction of infiltration test apparatus, (2) selection of test soils and determination of soil properties, (3) study of metal ion adsorption capacity of test soils, and (4) infiltration test.

(1) Design and Construction of Test Apparatus

The apparatus for infiltration test was designed to meet the following requirements: (i) test soil column must be sufficiently large to minimize any possible edge effect, (ii) cost must be as low as possible, (iii) it must possess high mobility so that the hydraulic boundary condition can be easily varied, and (iv) percolated solution must be easily collected from various depths of the test soil column. Based upon these criteria, five sets of test apparatus were constructed by the Engineering Machine Shop. Each setup is composed of a reservoir for supplying infiltration solution, a constant head control chamber, and a lysimeter having 6-in. diameter by 39-in. height. Along the wall of the lysimeter were installed six ¼-in. diameter porous cups, 6 in. apart vertically and staggered around the periphery, for collecting percolated solution. In addition, two 24-gallon tanks on the floor refilled infiltration solution to the reservoir. A pump, manually controlled and inert to chemical solution, connected the tank to the reservoir.

(2) Test Soils

Using the available Rhode Island state soil map, some soils commonly encountered throughout the state are selected for study. They are a brown sandy soil, a grey silty soil, a brown sandy silt, a gravelly sandy soil, and Providence silt. Also studied are some commercial clays. Physical properties including specific gravity and gradation and chemical properties such as cation exchange capacity, and organic content of the test soils have been determined.

(3) Study of Cupric ion Adsorption Capacity

The rate and amount of cupric ion adsorption of the test soils has been studied under various solution concentrations and durations of interaction. Figs. 1 thru 3 summarize the study results. The effect of organic content on the adsorption capacity has also been investigated.

(4) Infiltration Test

Infiltration tests for cupric solution through some of the test soils have been conducted for various hydraulic boundary conditions. The test soil columns were prepared to a height of 39 in. with a density of 89 lb/ft^3, approximately equal to the field density. Percolated solution was collected from various depths at different times. Each test lasted for 10 days to 14 days depending upon the soil texture, hydraulic head, and concentration of solution. Figure 4 shows a typical lysimeter test result.

Test results to date show that cupric ion adsorption capacity of soils depends largely upon two factors: cation exchange capacity, duration of percolation, organic matter content and grain size of test soils. In general, increasing cation exchange capacity, concentration of solution, and organic content individually increase cupric ion adsorption. Meanwhile, the smaller the soil particle size, the greater the adsorption capacity. With other factors being constant, increasing concentration of solution increased the rate of adsorption.

Infiltration test on cupric solution indicates that hydraulic head, soil type, and soil density are among the important factors governing the rate and distance of movement of cupric ion through the test soil.

Work remaining to be accomplished are: (1) quantitative analysis of clay mineral content in the test soils by using the differential thermal analysis and x-ray diffraction methods, (2) adsorption and infiltration tests for other proposed trace metals, and (3) a model test for axisymmetrical infiltration to be conducted in an 8-ft. diameter test tank.

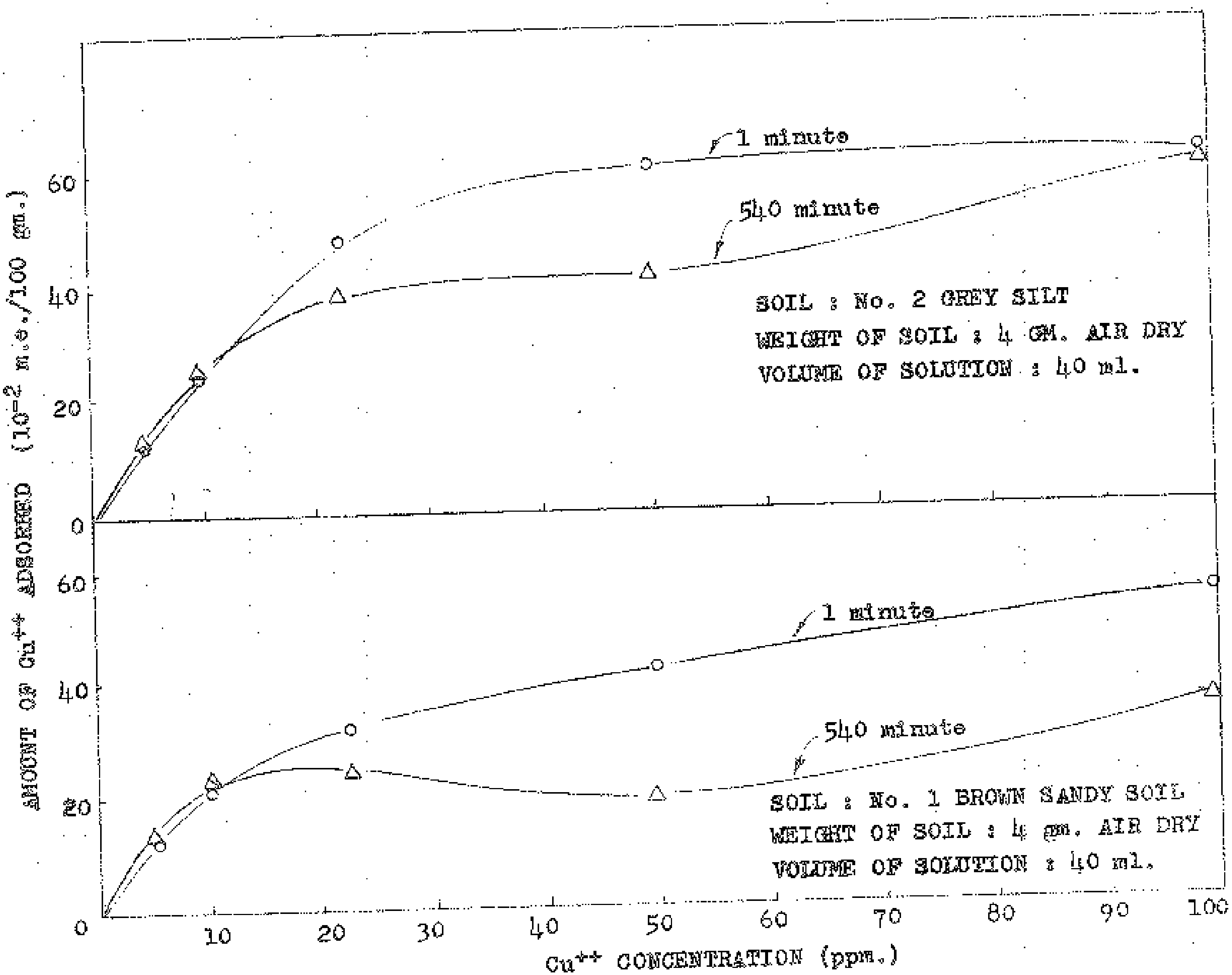


FIGURE 1 ADSORPTION CAPACITY OF TEST SOILS

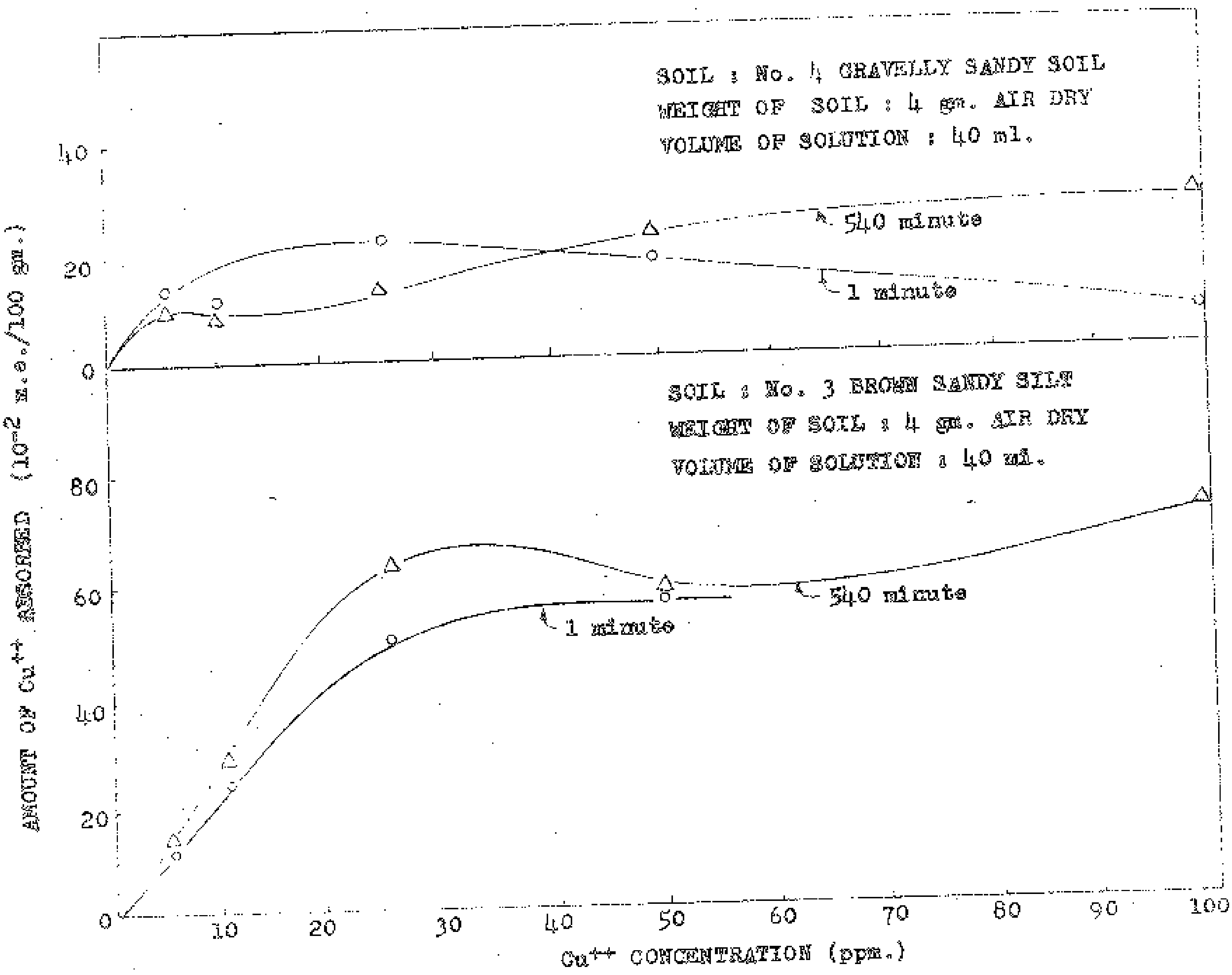


FIGURE 2 ADSORPTION CAPACITY OF TEST SOILS

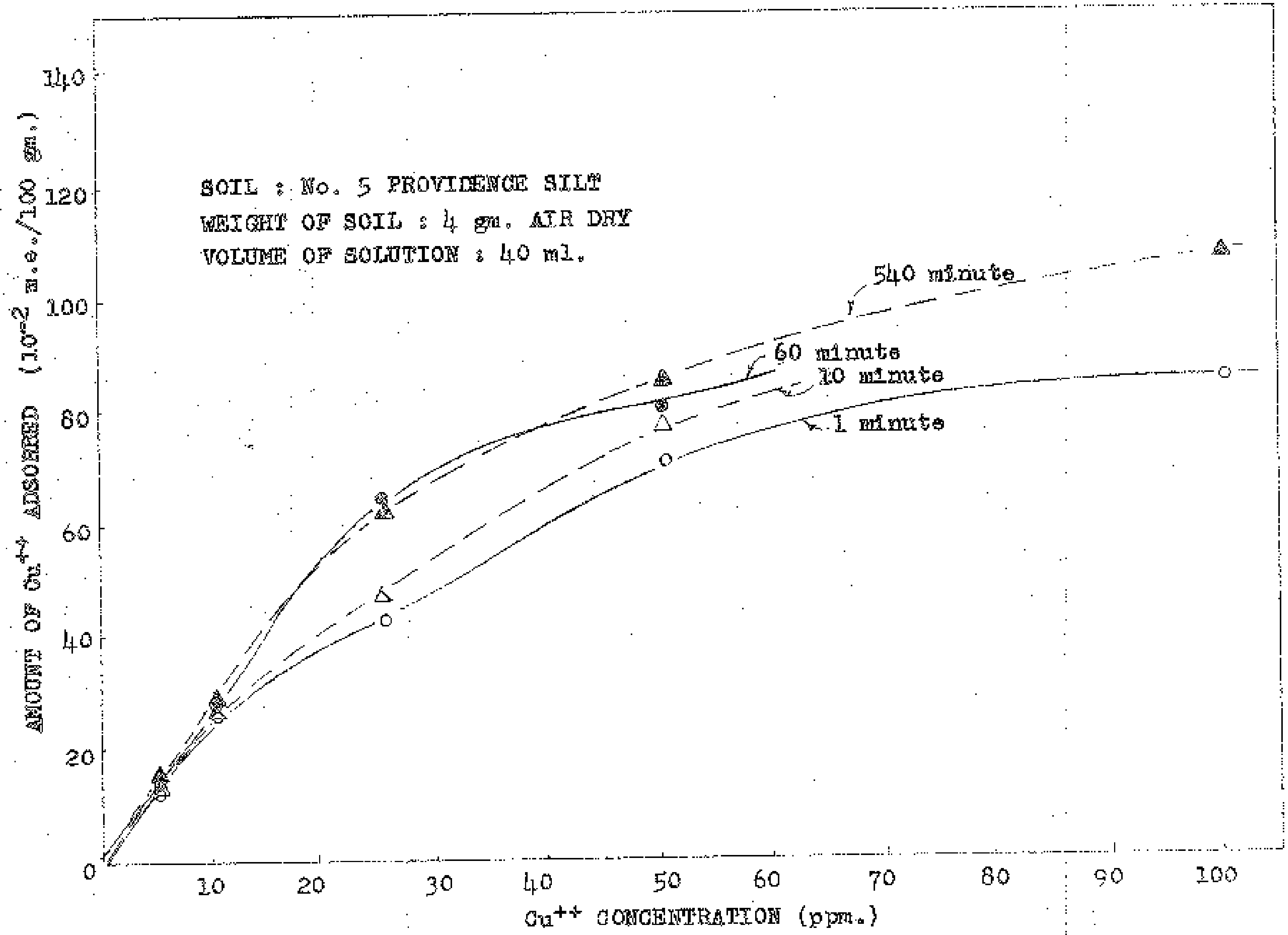


FIGURE 3 ADSORPTION CAPACITY OF TEST SOIL

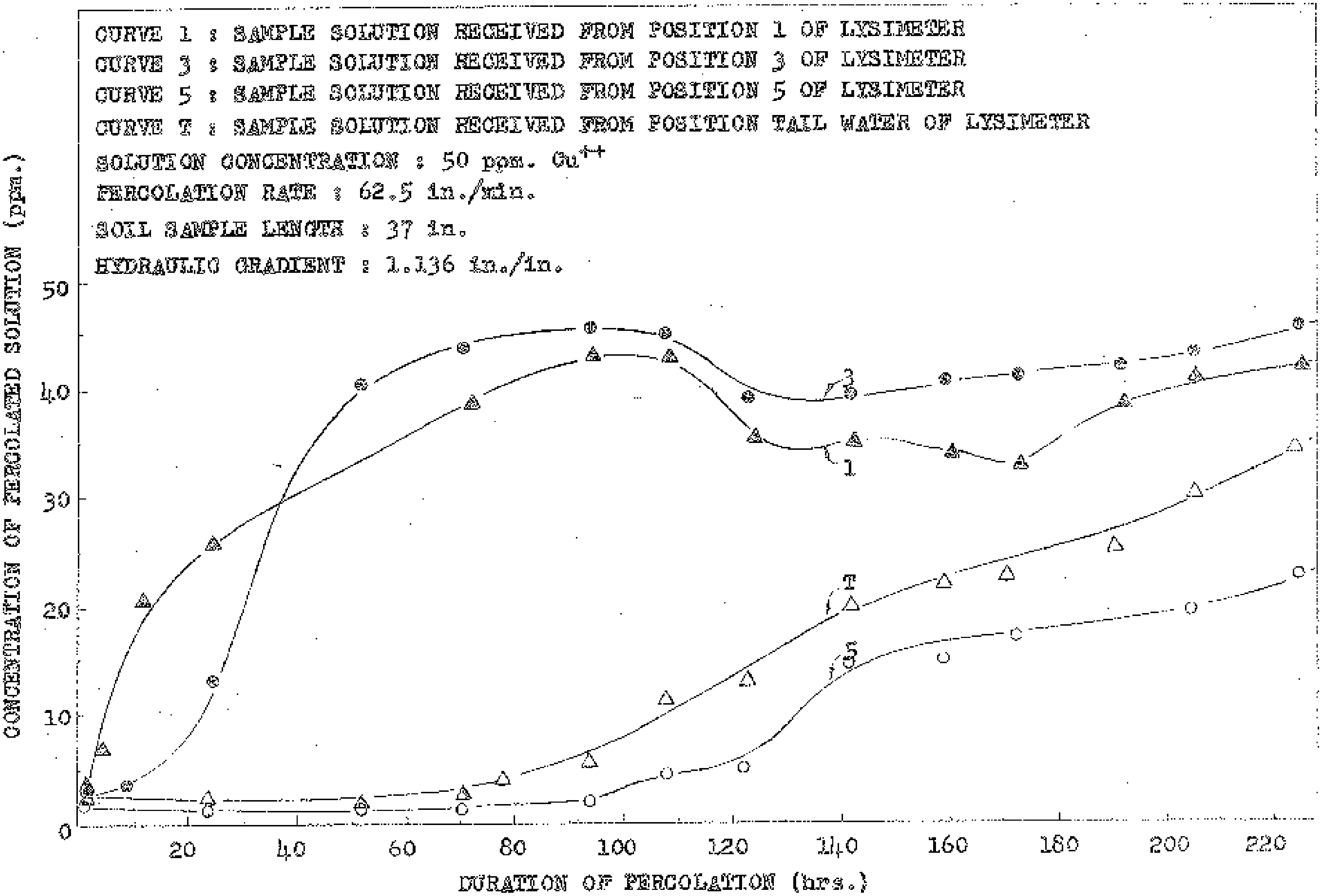


FIGURE 4 VARIATION OF Cu^{++}-ION CONCENTRATION AT VARIOUS DEPTHS WITH TIME FOR No. 3 TEST SOIL

Form OW-1 (1972)

ANNUAL REPORT — TITLE I PROJECT

OWRR Project No. B-047-RI Agreement No. 14-31-0001- 3933 FCST-COWRR Research Category: V F	Project Title: Effect of Ozonation on Human Enteric Viruses in Water from Rhode Island Rivers

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: July ; Year: 1972 | To Be Completed--Month: June ; Year: 1974

Principal Investigators	Degree	Discipline
Pei W. Chang	Ph.D.	Animal Pathology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
John Snyder	B.A.	Medical Technology
Cheng-Mo Chen	B.Sc.	Biology
Edward Balkovic	B.Sc.	Animal Science
Mei Shin Yuan	B.Sc.	Microbiology

A) RESEARCH PROJECT ACCOMPLISHMENTS

1. Construction of a new ozone generator.

Due to the poor yield of ozone from our old ozone generator, which is 0.25 mg of ozone per hour, a new more powerful ozone generator was constructed. The new one generated ozone at the maximum rate of 7.0 grams per hour. The output rate of ozone as determined by the potassium iodide method is presented in Table 1.

2. The kinetics of residual ozone at 2° and 24°C.

The kinetics of residual ozone were determined at 2 ozone concentrations and 2 temperatures (Table 2). Results indicate that at 2°C loss of residual ozone was none or slight at the end of 60 minutes.

However at 24°C, the residual ozone was greatly reduced; at 1 mg per liter of residual ozone, 50% was lost at the end of 60 minutes. At 0.5 mg per liter of residual ozone, all was lost at 14 minutes.

3. Inactivation dynamics of enteric viruses.

Viruses were purified by ultracentrifugation. Pelleted virus particles were resuspended in ozone demand free water. A known quantity of purified virus was added to a reaction chamber. The chamber consisted of a 100 ml graduated cylinder with a sparger at the bottom. Ozone was sparged into the chamber at a rate of 1 gram per hour. Samples of virus were removed from the reaction chamber at various intervals during ozonation. The virus samples were immediately diluted ten-fold in nutrient broth, which inactivated the residual ozone. The virus was then assayed in rhesus monkey kidney cell (RMKC) cultures by the plaque forming technique.

The inactivation dynamics of poliovirus, type 1, 2 and 3 in ozone demand free water are presented in Table 3. Six logs of poliovirus type 1 were inactivated at the end of 3 minutes, whereas Poliovirus type 2 was inactivated at the end of 8 minutes. Poliovirus type 3 was inactivated at the end of 4 minutes. In Saugatucket river water, a much longer period of time was required to inactivate the same viruses (Table 4). These were 10 minutes for poliovirus type 1 and 3, and 12 minutes for type 2.

The inactivation dynamics for Echoviruses are presented in Tables 5 and 6. Echovirus type 12 and 29 in ozone demand free water were inactivated in 10 and 1 minutes respectively (Table 5). In Saugatucket river water the same viruses required 14 and 4 minutes respectively (Table 6).

The inactivation dynamics for Coxsackie virus type B3 and B5 are presented in Table 7 and 8.

Coxsackie virus type B3 and B5 were both inactivated in 6 minutes in ozone demand free water. Coxsackie virus type B3 and B5 required 12 minutes for inactivation in Saugatucket river water (Table 8). It took twice the time to inactivate Coxsackie virus type B3 and B5 in Saugatucket River water than in ozone demand free water.

The inactivation dynamics for adenovirus type 7A are presented in Tables 9 and 10. In ozone demand free water, the virus was inactivated in 4 minutes (Table 9). In Saugatucket river water, the virus was inactivated in 8 minutes (Table 10), which was twice the time required in the ozone demand free water.

A comparison of the inactivation dynamics for Echovirus type 12 and 29, adenovirus type 7a, Coxsackie virus type B3 and B5, and poliovirus type 1, 2 and 3 is shown in Figures 1 and 2. Echovirus type 29 required the shortest time for inactivation whereas Echovirus type 12 required the longest time for inactivation. Poliovirus type 1, 2 and 3 adenovirus type 7a and Coxsackie virus type B3 and B5 fall in the intermediate range of time for inactivation.

B) PUBLICATION

None.

C) PROJECT STATUS

The project has been completed. A termination report will be submitted in July, 1974.

D) APPLICATION OF RESEARCH RESULTS

1. The present studies demonstrated that ozone is viricidal.
2. The viricidal efficiency of ozone depended upon the strain of virus and the presence of impurities in the water. Echovirus type 29 was inactivated by ozone, which was generated at the rate of 1 gram per hour in 1-3 mintues, whereas Echovirus type 12 was inactivated by ozone in approximately 10-14 minutes. A greater demand of ozone was required to inactivate the same amount and kind of virus in Saugatucket river water than ozone demand free water.

TABLE 1

Rate of Ozone Production as it is Related

to AC Voltage

Voltage AC	Ozone Production (Grams per hour)			
	Trials			
	1	2	3	4
2000	0.02	0.019	0.02	0.02
3000	0.36	0.36	0.36	0.36
4000	2.59	2.57	2.58	2.59
5000	4.90	4.90	4.90	4.89
6000	7.10	7.11	7.10	7.11

TABLE 2

Effect of Temperature on Residual Ozone

	Ozone Demand Free Water				Saugatucket River Water			
	Initial Residual 1.0 mg/liter		Initial Residual 0.5 mg/liter		Initial Residual 1.0 mg/liter		Initial Residual 0.5 mg/liter	
	Temperature							
*Time	2°C	24°C	2°C	24°C	2°C	24°C	2°C	24°C
0	1.0	1.0	0.50	0.50	1.0	1.0	0.50	0.50
5	1.0	0.93	0.48	0.28	0.98	0.35	0.29	0
15	1.0	0.81	0.43	0	0.94	0	0	0
30	1.0	0.63	0.36	0	0.90	0	0	0
45	1.0	0.45	0.28	0	0.84	0	0	0
60	1.0	0.27	0.21	0	0.80	0	0	0

* Time in minutes

TABLE 3

Rate of Inactivation of Poliovirus Type 1, 2 and 3 by Ozone[a,b]

as a Function of Time in Ozone-Demand Free Water

Time of Ozonation (min)	Virus titers in $Logs^{c}_{10}$								
	Poliovirus 1			Poliovirus 2			Poliovirus 3		
	Control[d]	Trial 1	Trial 2	Control[d]	Trial 1	Trial 2	Control[d]	Trial 1	Trial 2
0	$3.3x10^6$	$3.3x10^6$	$4.0x10^6$	$2.3x10^5$	$3x10^5$	$5x10^5$	$4.6x10^5$	$4.3x10^5$	$5.6x10^5$
1		$3.6x10^5$	$3.6x10^4$					$3.3x10^4$	$2.6x10^5$
2		$4.6x10^2$	0					$4.6x10^2$	$2.3x10^3$
3		0	0						
4		0	0		$4x10^3$	$2.6x10^4$		0	0
6					$2x10^1$	0		0	0
8					0	0			
10	$3.3x10^6$			$4.6x10^5$	0	0	$3.6x10^5$		

a. Ozone produced at a rate of 1 gram per hour.

b. Temperature at 2°C

c. Virus titer is the average of 3 replicates.

d. Control consist of viruses not treated with ozone.

TABLE 4

Rate of Inactivation of Poliovirus type 1, 2 and 3 by Ozone[a,b]

as a Function of Time in Saugatucket River Water

Time of Ozonation (min)	Virus titers in $\log_{10}^{c}$								
	Poliovirus 1			Poliovirus 2			Poliovirus 3		
	Control[d]	Trial 1	Trial 2	Control[d]	Trial 1	Trial 2	Control[d]	Trial 1	Trial 2
0	5.2×10^{6}	4.2×10^{6}	3.1×10^{6}	4.2×10^{5}	6.1×10^{5}	6.1×10^{5}	6.1×10^{5}	4.9×10^{5}	4.3×10^{5}
1		3.2×10^{6}	2.9×10^{6}		2.1×10^{5}	4.2×10^{5}		4.2×10^{5}	3.1×10^{5}
2		3.9×10^{6}	3.3×10^{6}		4.8×10^{5}	5.5×10^{5}		2.8×10^{5}	3.3×10^{5}
4	5.0×10^{6}	4.1×10^{5}	4.1×10^{6}	3.9×10^{5}	2.4×10^{5}	4.6×10^{5}	5.3×10^{5}	4.7×10^{5}	6.2×10^{4}
6		3.3×10^{3}	2.6×10^{4}		3.0×10^{5}	2.9×10^{4}		4.2×10^{3}	2.7×10^{3}
8		2.0×10^{2}	0		6.2×10^{4}	2.1×10^{4}		2.6×10^{2}	6.0×10^{1}
10	5.2×10^{6}	0	0	5.1×10^{5}	4.2×10^{2}	2.0×10^{2}	5.0×10^{5}	0	0
12		0	0		0	0		0	0

a. Ozone produced at a rate of 1 gram per hour.

b. Temperature at 2°C.

c. Virus titer is the average of 3 replicates.

d. Control consist of viruses not treated with ozone.

TABLE 5

Rate of Inactivation of Echovirus Type 12 and 29 by Ozone[a,b] as a Function of Time in Ozone Demand Free Water

Time of Ozonation (min)	Virus titers in log$_{10}$[c]					
	Echovirus 12			Echovirus 29		
	Control[d]	Trial 1	Trial 2	Control[d]	Trial 1	Trial 2
0	$4.7x10^5$	$4.4x10^5$	$3.3x10^5$	$5x10^5$	$4.2x10^5$	$3.1x10^5$
½					$2.0x10^4$	$1.8x10^2$
1		$3.1x10^5$	$3.7x10^5$		0	0
2		$4.8x10^4$	$2.1x10^5$		0	0
4		$5.7x10^4$	$6.2x10^3$			
5	$4.0x10^5$			$4.6x10^5$	0	0
6		$5.1x10^2$	$4.7x10^3$			
8		$3.1x10^1$	$3.8x10^1$			
10	$3.9x10^5$	0	0	$3.1x10^5$		

a. Ozone produced at a rate of 1 gram per hour.

b. Temperature at 2°C.

c. Virus titer is the average of 3 replicates.

d. Control consist of viruses not treated with ozone.

TABLE 6

Rate of Inactivation of Echovirus Type 12 and 29 by Ozone[a,b]

as a Function of Time in Saugatucket River Water

Time of Ozonation (min)	Virus titer in $\log_{10}^{c}$					
	Echovirus 12			Echovirus 29		
0	Control[d]	Trial 1	Trial 2	Control[d]	Trial 1	Trial 2
0	$2.8\text{x}10^5$	$2.0\text{x}10^5$	$2.5\text{x}10^5$	$3.1\text{x}10^5$	$2.3\text{x}10^5$	$3.0\text{x}10^5$
½						
1		$2.5\text{x}10^5$	$1.3\text{x}10^5$		$6.1\text{x}10^4$	$2.3\text{x}10^5$
2		$2.1\text{x}10^5$	$1.0\text{x}10^5$		$3.1\text{x}10^3$	$6.3\text{x}10^2$
4		$1.2\text{x}10^5$	$2.1\text{x}10^5$	$2.1\text{x}10^5$	0	0
5	$1.9\text{x}10^5$					
6		$1.0\text{x}10^5$	$4.0\text{x}10^4$		0	0
8		$4.2\text{x}10^3$	$1.3\text{x}10^3$		0	0
10		$1.0\text{x}10^2$	$2.6\text{x}10^1$			
12		$3.1\text{x}10^1$	$2.6\text{x}10^1$			
14	$2.3\text{x}10^5$	0	0			

a. Ozone produced at a rate of 1 gram per hour.
b. Temperature at 2°C.
c. Virus titer is the average of 3 replicates.
d. Control consist of virus not treated with ozone.

TABLE 7

Rate of Inactivation of Coxsackie Virus Type B3 and B5 by Ozone[a,b] as a Function of Time in Ozone Demand Free Water

Time of Ozonation (min)	Virus titer in log$_{10}^{c}$					
	Coxsackie virus B3			Coxsackie virus B5		
	Control[d]	Trial 1	Trial 2	Control[d]	Trial 1	Trial 2
0	$4.8\text{x}10^5$	$3.7\text{x}10^5$	$4.2\text{x}10^5$	$4.0\text{x}10^5$	$3.6\text{x}10^5$	$4.4\text{x}10^4$
1		$2.6\text{x}10^5$	$3.1\text{x}10^5$		$2.8\text{x}10^5$	$3.0\text{x}10^5$
2		$4.3\text{x}10^4$	$6.1\text{x}10^4$		$4.2\text{x}10^4$	$3.6\text{x}10^5$
4		$3.1\text{x}10^2$	$2.3\text{x}10^1$		$3.1\text{x}10^2$	$2.7\text{x}10^3$
5	$3.2\text{x}10^5$	$3.2\text{x}10^5$		$3.7\text{x}10^5$		
6		0	0		0	0
8		0	0		0	0
10	$3.6\text{x}10^5$			$3.0\text{x}10^5$		

a. Ozone produced at a rate of 1gram per hour.

b. Temperature at 2°C.

c. Virus titer is the average of 3 replicates.

d. Control consist of virus not treated with ozone.

TABLE 8

Rate of Inactivation of Coxsackie Virus Type B3 and B5 by Ozone[a,b] as a Fucntion of Time in Saugatucket River Water

Time of Ozonation (min)	Virus titer in $\log_{10}^{c}$					
	Coxsackie virus B3			Coxsackie virus B5		
	Control[d]	Trial 1	Trial 2	Control[d]	Trial 1	Trial 2
0	$4.7x10^5$	$3.8x10^5$	$4.1x10^5$	$5.1x10^5$	$4.8x10^5$	$4.0x10^5$
1		$2.6x10^5$	$4.0x10^5$		$3.2x10^5$	$3.0x10^5$
2		$4.0x10^5$	$2.9x10^5$		$4.1x10^5$	$4.4x10^5$
4		$4.4x10^5$	$3.1x10^5$		$4.0x10^5$	$4.1x10^5$
5	$2.6x10^5$			$4.9x10^5$		
6		$3.6x10^5$	$4.0x10^5$		$3.3x10^4$	$2.0x10^4$
8		$2.4x10^3$	$5.0x10^2$		$2.1x10^3$	$6.1x10^2$
10	$3.3x10^5$	$1.2x10^1$	$3.2x10^1$	$4.1x10^5$	$1.6x10^2$	$3.3x10^1$
12		0	0		0	0

a. Ozone produced at a rate of 1 gram per hour.

b. Temperature at 2^oC.

c. Virus titer is the average of 3 replicates.

d. Control consist of virus not treated with ozone.

TABLE 9

Rate of Inactivation of Adneovirus Type 7A by Ozone[a,b] as a Function of Time in Ozone Demand Free Water

Time of Ozonation (min)	Virus titer in $\log_{10}$[c]		
	Control[d]	Trial 1	Trial 2
0	3.0×10^{5}	2.3×10^{5}	3.3×10^{5}
1		4.5×10^{4}	2.0×10^{4}
2		1.3×10^{1}	0
4		0	0
5	2.1×10^{5}		
6		0	0
10	2.6×10^{5}		

[a] Ozone produced at a rate of 1 gram per hour.

[b] Temperature at 2°C.

[c] Virus titer is the average of 3 replicates.

TABLE 10

Rate of Inactivation of Adenovirus Type 7A by Ozone[a,b] as a Function of Time in Saugatucket River Water

Time of Ozonation (min)	Virus titer in $\log_{10}^{c}$		
	Control[d]	Trial 1	Trial 2
0	3.1×10^{5}	2.8×10^{5}	2.2×10^{5}
1		1.5×10^{5}	2.0×10^{5}
2		1.0×10^{5}	2.6×10^{5}
4		2.1×10^{5}	1.8×10^{4}
5	2.0×10^{5}		
6		3.6×10^{2}	4.5×10^{3}
8		0	0
10	3.5×10^{5}	0	0

a. Ozone produced at a rate of 1 gram per hour.

b. Temperature at 2°C.

c. Virus titer is the average of 3 replicates.

d. Control consist of virus not treated with ozone.

FIGURE I

INACTIVATION OF VIRUSES BY OZONATION IN OZONE DEMAND - FREE WATER

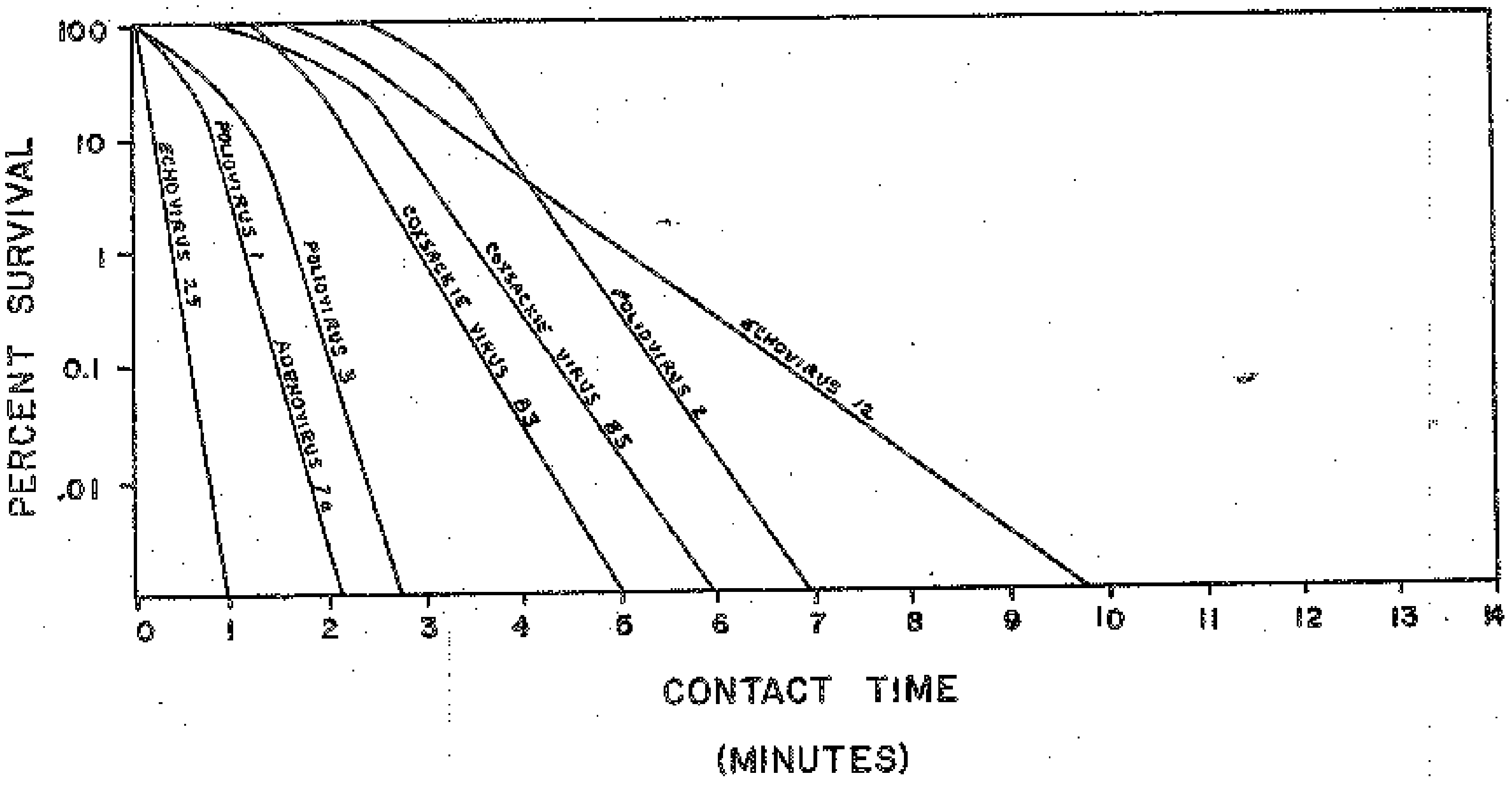
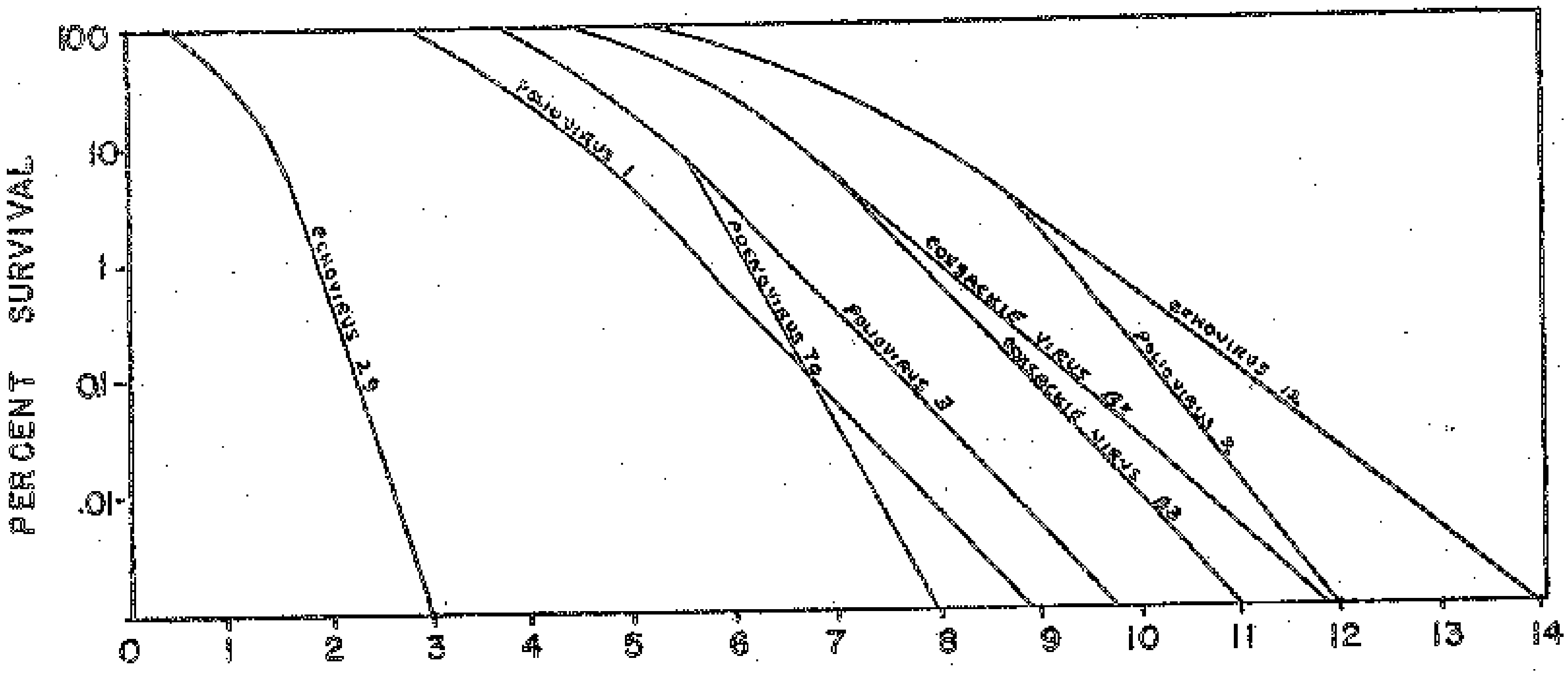


FIGURE 2

INACTIVATION OF VIRUSES BY OZONATION IN SAUGATUCKET RIVER WATER



Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-052-RI Agreement No. 14-31-0001-4123 FCST-COWRR Research Category: V C	Project Title: NUTRIENT EXCHANGE IN WATER-SEDIMENT INTERFACE AND ITS EFFECTS ON WATER QUALITY

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island
Kingston, Rhode Island 02881

Proj. Began--Month: July ; Year: 1973 | To Be Completed--Month: June 30; Year: 1975

Principal Investigators	Degree	Discipline
Calvin P.C. Poon	Ph.D.	Environmental Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Mung Shium Sheih	B.S.	Civil Engineering

Research Project Accomplishments

Stations were selected to take sediment samples in Narragansett Bay as follows (Figure 1):

Y. Fields Point -- 500 yards southeast off Fields Point Sewage Treatment Plant at a water depth of 10' - 12'.

YY. Pomham Rocks -- 500 yards southwest off Pomham Rocks at a water depth of 12' - 15'.

Z. Mouth of Pawtuxet River -- 600 yards SSE off Pawtuxet River Mouth at a water depth of 15'.

L. Providence Point -- 5,000 feet NNE off the tip of Prudence Island or Providence Point.

H. Conanicut Point -- 3,000 feet SSE off Conanicut Point.

G. Dutch Island -- 1,000 feet West of Dutch Island

B. Whales Rock -- Its vacinity.

Three sediment columns were taken at each of these stations with a 3-ft. Kullenberg cover. All cores had plastic core liners. They were sectioned at 2-inch and 4-inch intervals and put in polyethylene bags for refrigeration at 5°C prior to preparation for analyses. Analyses included soil fractionation (size and size distribution of sand, silt and clay); total organic and inorganic carbon; total nitrogen; fixed ammonium nitrogen; exchangeable ammonium nitrogen; water soluble ammonium nitrogen; calcium carbonate; total phosphorus; available phosphorus; and iron. Profiles of nutrients (N and P in various forms) are constructed to show the pollution history in the Bay and the potential of nutrient and/or organic pollution of the Bay sediment.

In general, the bay sediment has very little or no sand in the upper bay. Distribution of silt and clay are approximately 3 to 2. Starting from Providence Point and further south, more sand is found in the sediment. Sand fraction increases from 20% to 46% in the vicinity of the Wale's Rock while the silt fraction drops significantly from 65% to 40%. The specific gravity of the sediment, however, remains fairly constant to be 2.6 to 2.7.

Both Stations Y (Field Point) and YY (Pomham Rocks) are selected because they are only a few hundred yards away from sewage treatment plants outfalls which represent major sources of continuous pollution of the bay. Figure 2 shows the distribution of carbon, nitrogen and phosphorus of the sediment at Station Y. As is expected, the carbon content and particularly the organic carbon content is high at Station Y. On the top layer, the total carbon and organic carbon contents are respectively 36.5% and 31.0% of the sediment day weight. The organic content of the total is therefore 84.7%. The distribution profile indicates that both total carbon, and (Organic-C/Total-C) ratio decrease with sediment depth. The decreasing Org-C/Total-C ratio is partially accounted for by the fact that anaerobic digestion that has taken place in the past years has degraded part of the organic sediment. The significant difference of organic and total carbon at different sediment depths does indicate a heavier carbon pollution load in recent years than in the past. The profile also shows that, if the top six inches of sediment were removed, a significant amount of organic carbon could be eliminated representing approximately 33% of Organic-C reduction.

The nitrogen profile of Station Y shows approximately 510 ug/g and 377 ug/g respectively of total and organic nitrogen on the top layer of sediment. The nitrogen content decreases with depth similar to the carbon profile. This result reinforces the belief that pollution in the bay in recent years is more severe than it was years ago. Nevertheless, the ratio of Org-C/N is high at all sediment depths (52.5 ~ 62.6). This ratio is much higher than that found in other studies of polluted lakes, indicating that nitrogen occumulation in the sediment is not yet serious. Furthermore, Figure 2 shows relatively very little soluble NH_3-N and exchangeable NH_3-N. The amount of NH_3-N that could be released from the sediment to the overlying water is perhaps insignificant. The exact amount has to be determined in the 2nd pahse of the study.

More phosphorus is found in the sediment than nitrogen at Station Y. Total-P content again decreases with depth. It is interesting to note that available phosphorus content increases with depth. The major mechanism of phosphorus precipitation is adsorption-coagulation with ferric hydroxides in the water. When anaerobic condition occurs in the bottom layers of the sediment, ferric ions are reduced and the precipitated phosphorus would be transformed to available-P. However unlike CO_2 or nitrogen gas there is very little or no access for the available-P to move up the sediment column, resulting in greater occumulation in the bottom layers. In terms of phosphorus pollution, the fact that more available-P exists in the bottom layers of sediment has a great impact on sludge dredging in the bay. More available-P would be exposed to the overlying water as a result and consequently sludge dredging is not desirable.

Analyses of sediments at Station YY and Station Z show similare results. Contents and distribution profiles of carbon, nitrogen and phosphorus are all comparable.

Less sediment pollutant is found at Station L. Further down the bay there is a drastic decrease of the sediment pollutants accumulation. For example, Station B (also shown in Figure 2) in the vicinity of the Whale's Rock shows very little pollutant accumulation. Comparing with Station Y, the ratios of soluble NH_3-N, exchangeable NH_3-N, organic-N, Total-N, Organic-C, Total-C, and available-P are respectively 1 to 8, 1 to 7, 1 to 2.5, 1 to 3, 1 to 6, 1 to 2.5 and 1 to 2.5.

Project Status

Mineral contents of the sediment samples are being analyzed. The project will continue in the next fiscal year.

Application of Research Results

The sediment in the upper Narragansett Bay is demonstrated to be a potential source of organic carbon, nitrogen and phosphorus. Dredging of sludge in the upper bay can eliminate much of the pollutants. The dredging is deemed undesirable however, if phosphorus pollution is critical in the Bay because more available-P exists in bottom layers of the sediment than in the top layer.

Work and Progress Contemplated Next Year

Starting June 15, 1974, microcosms will be employed to evaluate the possible exchange rate and amounts of N and P across the sediment-water interface. The ability of the sediment nutrients to support algal growth will also be studied. The true potential of sediment pollution in Narragansett Bay can therefore be accurately assessed.

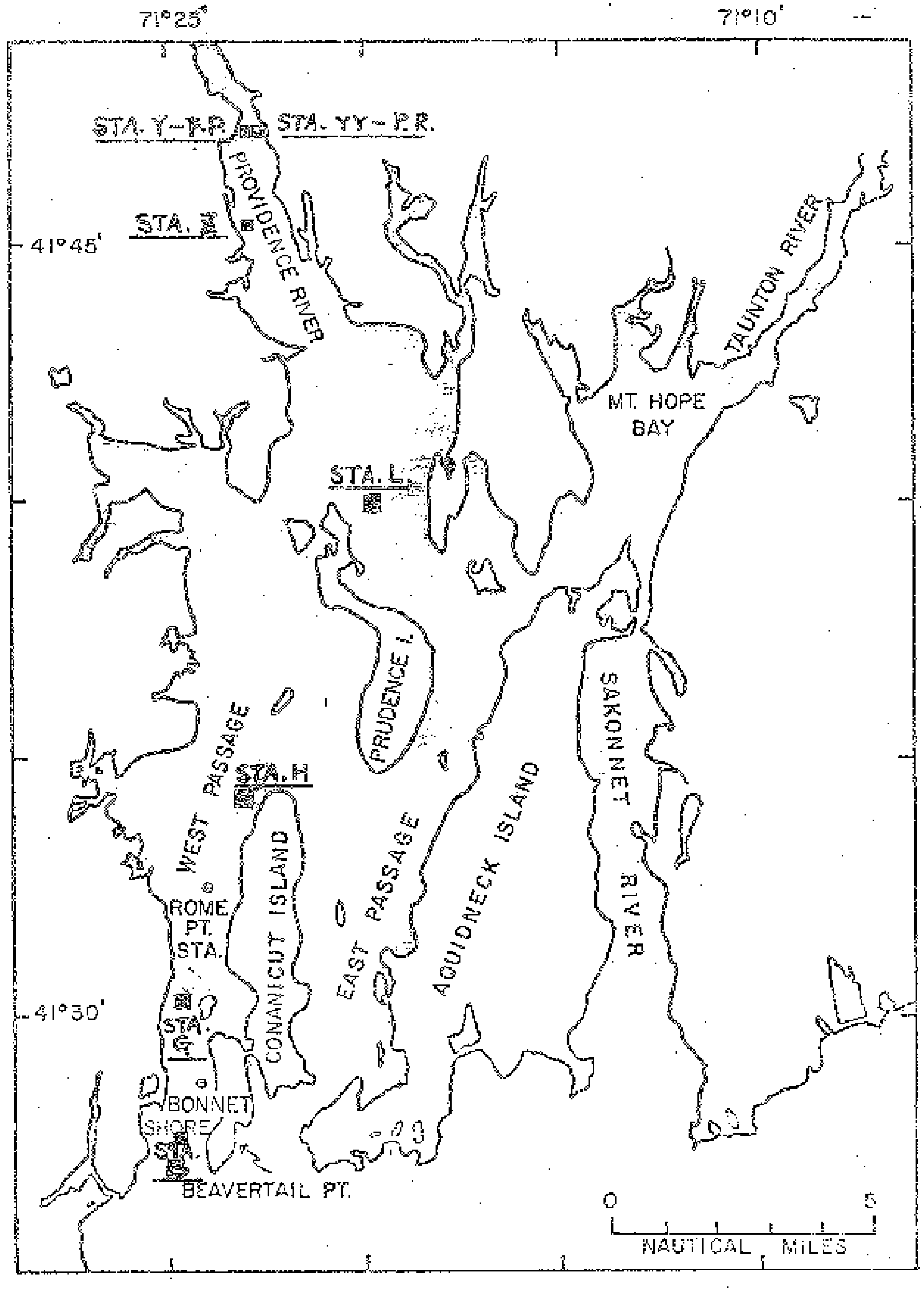
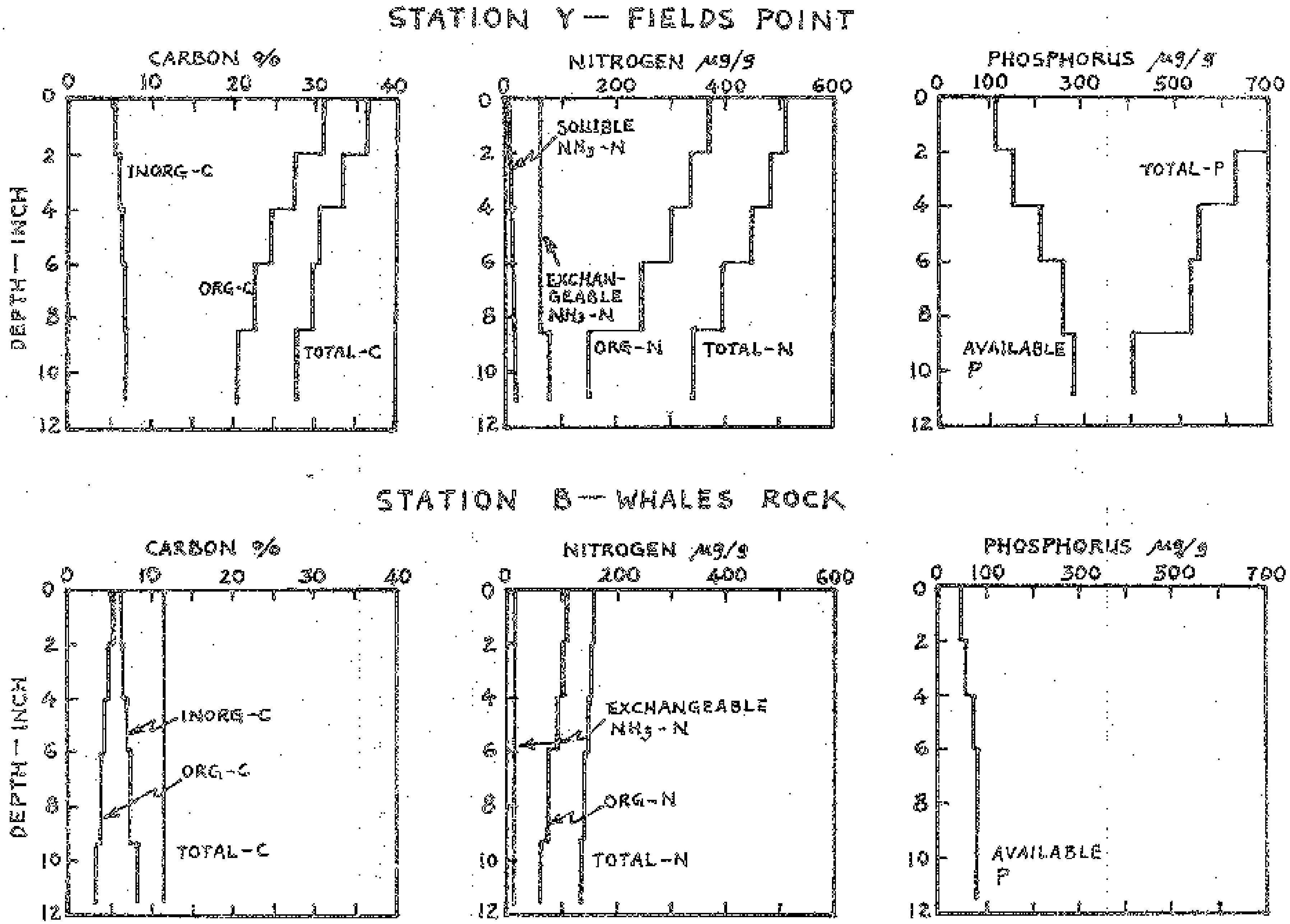


Figure 1. Map of Narragansett Bay showing locations of sampling stations in West Passage.



STATION Y — FIELDS POINT

STATION B — WHALES ROCK

FIGURE 2

ANNUAL REPORT -- TITLE X PROJECT

OWRR Project No. B-057-RI Agreement No. 14-31-0001-4124 FCST-COWRR Research Category: V-A, G	Project Title: Further Studies of the Interaction of Chlorine and Organic Molecules in Water.

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: July ; Year: 1973	To Be Completed--Month: June ; Year: 1975

Principal Investigators	Degree	Discipline
Yuzuru Shimizu	Ph. D.	Natural Product Chemistry Pharmacognosy

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Rong Yew Hsu	M. S.	Pharmacognosy

Research Project Accomplishments. 1) Chlorination of amino acids. It was discovered in the previous study[1] that upon treatment with chlorine or hypochlorite, amino acids afford predominantly nitrile compounds and lesser amounts of aldehydes. As an extension of the research, detailed stoichiometrical investigation of the reaction was carried out. Amino acids were treated with chlorine under various conditions, and the products were analyzed. The results are summarized in Table 1.

Table 1. Products of Chlorination of α-Amino acid.

Amino Acids	Chlorine (moles)		Products
Phenylalanine	NaOCl	4	Benzylcyanide
Leucine	NaOCl	4	Isovaleronitrile
Isoleucine	NaOCl	3	2-Cyanobutane
Tyrosine	Chlorine Water	4	3-Chloro-4-hydroxybenzylcyanide 3, 5-Dichloro-4-hydroxbenzyl cyanide
Tyrosine	NaOCl	3	3, 5-Dichloro-4-hydroxybenzyl cyanide
Histidine HCl	NaOCl	1	Cyanomethylimidazole*
Tryptophan	NaOCl	5	I.R. showed CN group

* Biochem. preparations 5:97-100 (1957).

2) Chlorine treatment of nucleic acids.

a. Chlorination of RNA

RNA [ribonucleic acid (yeast)] was treated with chlorine water (3 mg/ml) at 4-6°C. The pH of the yellow colored mixture was 2.0. After ten minutes, it was adjusted to pH 7 with ammonia and dialyzed for 72 hrs in cold distilled water. At the end of dialysis the pH rose to 4.8. Lyophilization of the resulting mixture gave a slightly yellow colored cotton-like chlorinated RNA. The yield was 67% in weight indicating the possibility that chlorine breaks down the RNA chain to the fragments which are dialyzable. Significant changes are also expected from the UV spectrum which shows no definite absorption peaks. The IR spectrum showed absorptions at 3300, 1700, 1640, 1400, 1230, 1010 and 540 cm^{-1}.

Elemental analyses of this chlorinated RNA gave the chlorine content 7.50 and 7.60%.

b. Hydrolysis of chlorinated RNA and analysis of the hydrolysate. In order to locate the chlorine atoms in chlorinated RNA, it was hydrolyzed with 2.5 N NaOH and $HClO_4$ successively. The hydrolysate was examined by paper chromatograph using separately prepared chlorinated nucleic acid bases as standards. The results are shown in Table 2.

c. Chlorination of DNA

DNA (desoxyribonucleic acid, salmon sperm) was treated with chlorine in a similar manner as RNA. After work-up, yellowish cotton-like chlorinated DNA was obtained (yield 60.1% in weight). The chlorine content of this substance was 8.92 to 9.20%.

d. Hydrolysis of Chlorinated DNA

The following experiment was done to determine the locations of the chlorine attachment.

Chlorinated DNA was hydrolyzed with 90% formic acid in a sealed tube at 175 °C and the hydrolysate was analyzed by paper chromatography. Perchloric acid hydrolysis was also attempted. The results were summarized in Table 2.

Table II. Analysis of Chlorinated RNA and DNA Bases.

Products	Rf Values*	UV [H_2O] max nm
Cl-RNA Hydrolysate ($HClO_4$)	0.27	no max.
	0.33	no max.
Cl-DNA Hydrolysate ($HClO_4$)	0.31	271
Cl-DNA Hydrolysate (formic acid)	0.21	249
	0.31	270
	0.49	270
Cytosine	0.20	267
Thymine	0.47	265
Uracil	0.33	258
Adenine	0.32	270

Whatman No. 1, n-BuOH:H_2O 86:14 (v/v)

Discussion. Needless to say, nucleic acids, both RNA and DNA, are the most essential constituents of organisms. It is expected that, in contact with active chlorine, these important biopolymers are affected in some forms. Also nucleic acids or degraded nucleic acids in effluent can be chlorinated and re-incorporated in living organisms. Slight changes in nucleic acids composition are expected to bring about serious problems such as hereditary damages, carcinogenicity or teratogenicity. In that respect, recent report on the isolation of chlorocytosine of unknown origin from salmon sperm DNA needs a special attention.

Chlorination of nucleic acids have not been studied well, although halogenation of individual bases in general were reported by a number of people. In our experiment, unexpectedly large amounts of chlorine were incorporated into DNA and RNA. This indicates chlorine atoms substituted not only nuclei of known chlorine susceptible bases such as cytosine but also chlorinated other moieties such as amino or methyl groups. Undoubtedly chlorine also worked on nucleic acids destructively making smaller chains. So far we are unable to pin point the exact locations of chlorine substitutions, but efforts are being made to isolate chlorinated bases and nucleosides by enzymatic hydrolysis.

B. Publications. No publications.

C. Project Status. The project will be continued through next year.

D. Application of Research Results. This research will lead to the re-evaluation or reassurance of chlorination for the treatment of drinking water, sewage, bleaching or sterilization. In view of the fact that a large portion of the world production of chlorine is being used for the above mentioned purposes, this problem seems to be no less important than widely advocated chlorinated pesticides hazards.

E. Plans for Next Year. Further studies of chlorination of biopolymers such as nucleic acids, protein and lignin are planned. Specifically, isolation and identification of chlorinated products and examination of their biological activities to lower experimental organisms (microorganisms and snails) are intended.

ANNUAL REPORT — TITLE I PROJECT

OWRR Project No. B-061-RI

Agreement No. 14-31-0001-3953

FCST-COWRR Research Category:

Project Title:
Analysis of Critical Water Problems in the Northeastern United States to Determine Essential Research Requirement

Name and Location of University Where Project is Being Carried Out:
Various locations in Northeastern United States. Designated fiscal agent: University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: March ; Year: 1973

To Be Completed--Month: Feb. ; Year: 1975

Principal Investigators	Degree	Discipline
A. Ralph Thompson	Ph.D.	Chemical Engineering

Co-Principal Investigators: Directors of 14 other Northeastern Water Resources Centers or Institutes

During the year one workshop supported by this project was held in Harrisburg, Pennsylvania, June 19-21, 1974 on the topic "Research Needs Related to Recycling Urban Wastewater on Land".

The General Chairman of the Workshop was Archie J. McDonnell, of the Pennsylvania State University. He was assisted by the following state institute directors: Gordon L. Byers (New Hampshire), Chester L. Dodson (West Virginia), John C. Frey (Pennsylvania), R.L.Green (Maryland), Robert C. Stiefel (Ohio), A. Ralph Thompson (Rhode Island) and Robert D. Varrin (Delaware).

First, the entire invited assembly was addressed by selected experts in the following seven aspects related to the general problem:

Social:
Dr. Madge Ertel
Institute for Man and His Environment
University of Massachusetts

Political-Legal-Institutional:
Dr. Frederic O. Sargent
Department of Resource Economics
University of Vermont

Economic:
Dr. Donald J. Epp
Department of Agricultural Economics and Rural Sociology
The Pennsylvania State University

Biological and Chemical:
Dr. Lowell Douglas
Department of Soils and Crops
Cook College, Rutgers University

Hydrological and Physical:
Dr. Richard R. Parizek
Department of Geology and Geophysics
The Pennsylvania State University

Engineering and Management:
Mr. D. Russel Tatman
Edward H. Richardson Associates, Inc.
Newark, Delaware

Environmental and Public Health:
Major Charles Sorber
U.S. Army Medical Bio-Engineering
Research and Development Laboratory
Aberdeen Proving Ground

Participants were divided into groups of about a dozen each covering these various aspects of the problem. For over six hours, each group made an in-depth dissection of its particular aspect in order to identify research needs in that phase of the overall problem. Finally, the chairmen of the groups reported to all participants what they considered to be their most important findings. Proceedings of this workshop will be published in the near future and it is planned that a combined report from this effort, along with those from similar workshops held in the South Atlantic-Gulf and Ohio-Great Lakes regions, will be prepared as soon as possible.

The initial planning for a workshop to identify water resources research needs on "Acid Mine Drainage" is underway under the direction of Chester L. Dodson.

Approval was given during the year to add the topic "Residuals in Water" to the list of those requiring identification of research needs in the Northeastern United States. No workshop is planned in this area for the immediate future nor on any of the other topics included in the initial proposal.

ANNUAL REPORT - TRAINING AND EDUCATION ASPECTS OF THE WATER RESEARCH PROGRAM UNDER P.L. 88-379

Name of University:
(or College) University of Rhode Island

SUBMIT THE INFORMATION SPECIFIED BELOW FOR THE UNIVERSITY AT WHICH THE WATER RESOURCES RESEARCH INSTITUTE OR CENTER APPROVED UNDER P.L. 88-379 IS LOCATED, AND FOR OTHER UNIVERSITIES WITH WHICH THE INSTITUTE OR CENTER IS COOPERATING. KEEP THE STATISTICS ON ENROLLMENTS, NUMBER OF STUDENTS GRADUATING, EMPLOYMENT STATUS OF GRADUTES, NEW COURCES, ETC., SEPARATE FOR EACH UNIVERSITY. IT IS RECOGNIZED CERTAIN OF THE REQUESTED DATA ON STUDENTS MAY NOT BE READILY AVAILABLE. IF SO, PROVIDE BEST ESTIMATE FIGURES. IN OW-9, DATA ON STUDENTS ARE REQUESTED ONLY FOR THOSE STUDENTS WHO RECEIVED EMPLOYMENT AS RESEARCH PROJECT OR PROGRAM ASSISTANTS THROUGH THE P.L. 88-379 PROGRAM. IF EXTRA SPACE IS NEEDED, ADD PAGES AND NUMBER EACH CONTINUATION ITEM IN THE ORDER SHOWN BELOW.

A. During period since last annual report was submitted provide information on: (See footnote 1/ below.)

(1) New water resources related courses developed. (Give title, state whether interdisciplinary, and give brief description of course. Please indicate if any of these were outgrowths of P.L. 88-379 program activities.)

See accompanying sheet - next page

(2) Water resources related staff members added to fill new positions. (List highest degree obtained and scientific discipline. Indicate which ones received any salary from P.L. 88-379 funds. Do not list staff replacements.)

None

1/ Our intent here is to obtain information on improved academic capability for water resources research and training. Indicate for each position, research facility or other item, whether support was provided in whole or in part through P.L. 88-379 funds, or from other sources; however, also list improvements supported by State or other funds.

(1) New water Resources related courses developed.

Botany 651 - Seminar in Aquatic Botany

Readings and discussion on current research involving algae and other aquatic plants.

This course is definitely related to instructor's P.L. 88-379 projects involving algae.

Botany 659 - Seminar in Physiological Ecology of Macro-algae II

Readings and discussion of specialized and advanced research, stressing mechanism of environmental adaption.

This course, too, is related to P.L. 88-379 research involving algae.

Civil Engineering 495 - Civil and Environmental Engineering Systems

Practical Civil and Environmental Engineering projects which are broad in scope from the areas of water resources, structures, pollution control and transportation.

Community Planning 634 - Environmental Law

Legal precedents, developments and alternative policy approaches to protection, control and development of the environment.

Certainly of value in many disciplines concerned with water resources.

Mechanical Engineering 651 - Turbulent Flows

A study of turbulent flows from both the phenomenological and statistical points of view. Applications to meteorology, boundary layers and turbulent diffusion.

Mechanical Engineering 652 - Experimental Methods in Fluid Mechanics.

An over-view of measurement techniques and instrumentation used in the current practice of experimental fluid mechanics.

A. (Continued)

(3) Water resources related staff members employed to replace those who retired, died, or moved. (List highest degree obtained and scientific discipline. Indicate which ones received any salary from P.L. 88-379 funds.)

None

(4) New water resources research and training facilities other than research equipment items. (Include only major facilities such as new laboratories, buildings, etc.)

None

(5) Interdepartmental interuniversity or regional agreements consummated with respect to improved research and training capabilities. (To be answered only by institutes under P.L. 88-379. If copies of such institute-related agreements have not been provided OWRR, please provide.)

The Rhode Island Water Resources Center is one of the six partners in the New England regional research project "The Impact of Urbanization on New England Lakes" (C-5342). A Memorandum of Understanding has been signed with the University of Vermont which is acting as the fiscal agent for the New England Council of Water Center Directors.

B. Number of students receiving employment as research project or program assistants through the P.L. 88-379 program. (Include only those students, both continuing and graduating, paid wholly or in part with P.L. 88-379 funds during the past fiscal year.)

Category of Students	No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc. 2/	
	Scientific Discipline of Student	Number
(1) Undergraduates		
	Bacteriology	1
	Chemical & Ocean Engrg.	1
	Pharmacognosy	1
		3
(2) Master's Students	Animal Pathology	3
	Bacteriology & Biophysics	1
	Chemical Engineering	4
	Chemistry	2
	Civil & Environmental Engr.	5
	Mechanical Engrg.	1
	Pharmacognosy	2
		18

2/ This refers to educational background prior to employment as research assistant on P.L. 88-379 projects--not to departments in which projects are being conducted.

B. (Continued)

Category of Students	No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc.) Scientific Discipline of Student	Number
(3) Doctoral Students	Animal Pathology	1
	Chemical Engineering	4
		5
(4) Postdoctoral Students		
	Plant Pathology-Entomology	1
	Pharmacognosy	1
		2

C. Employment status of majors in water-related fields who graduated during the school year ending about June and who receive P.L. 88-379 support.

EMPLOYMENT STATUS	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1. No. employed in water-related positions in: Total----	1			1
Federal Agencies---------------	( )	( )	( )	( )
State & Local Agencies---------	( )	( )	( )	( )
University or College----------	( )	( )	( )	( )
Other - Including private enterprise------------------	( )	( )	( )	( )
2. No. graduates returning to school for advanced degree----------------				
3. No. going into military service---------------------------				
4. No. unemployed or working in other fields---------------------				
5. No. status unknown-------------				
6. Totals-------------------------	1			1

D. Type of employment of those school year graduates who received P.L. 88-379 support and who are known to have gone into water-related positions. (Number should agree with total listed under item 1 of the preceding paragraph "C". Graduates enrolled for further course work or training should not be listed here as employed.)

Number of Graduates Engaged in Water-Related Work In:	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1A. Federal Agencies:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1B. State & Local Agencies:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1C. University or College: 3/				
a. Primarily Teaching				
b. Primarily Research				
c. Primarily Research & Teaching				
d. Other or not known				
1D. Other - Including Private Enterprise:				
a. Primarily Research				
B. Primarily Planning				
c. Primarily Development	1			1
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
Totals	1			1

Selected summary of above data -- from the "Total" column:

Research (1Aa, 1Ba, 1Cb, 1Cc& 1Da)	0
Planning (1Ab, 1Bb & 1Db)	0
Development (1Ac, 1Bc & 1Dc)	1
Operations (1Ad, 1Bd & 1Dd)	0
Management (1Ae, 1Be, & 1De)	0

3/Do not include here students working as research assistants and receiving course credits.

E. Identify by name and discipline and briefly describe instances, if any, in which the institute program, in the past year, has resulted in individuals, other than students, doing research or teaching in the water resources field, who, previously, were not involved in water work.

Ferdinand Votta, D.Eng., Chemical Engineering-University of Rhode Island, Kingston, R.I.

Clair J. Cheer, Ph.D., Chemistry-University of Rhode Island, Kingston, R. I.

F. Cite any instances you know of, in which individuals who previously served as student research assistants on P.L. 88-379 projects, are now serving as professional investigators of P.L. 88-379 projects following graduation. Do not include individuals reported in this category last year or before.

None

PUBLICATIONS AND THESES

Publications

S.M.Barnett, C. Houston, and S. Velankar, "Mechanism of Hydrocarbon Uptake by Microorganisms". Biotech and Bioeng, 16, 863 (1974).

Theses

John Snyder, "The Effect of Ozonation on Human Enteric Viruses in Saugatucket River Water," M.S., University of Rhode Island

Richard Romanelli, "Thermophilic Fermentation of Cellulose Under Pressure" Ph.D., University of Rhode Island

TECHNICAL & FINANCIAL SECTIONS
OF THE ANNUAL REPORT OF THE
RHODE ISLAND WATER RESOURCES CENTER
FISCAL YEAR 1976

RHODE ISLAND WATER RESOURCES CENTER
DIRECTOR'S REPORT FOR FISCAL YEAR 1976

Current and Anticipated Water Problems

As was pointed out in last year's report, leading water officials in the state have certainly become more concerned about the condition of Rhode Island's groundwater. The Water Resources Board, in its desire to determine the effect of external changes on groundwater aquifers, has enrolled the aid of the Water Resources Center to construct analog and digital models to predict the effects of such changes. The presence of iron and manganese in many of the state's groundwater supplies continues to present a problem. Some progress has been made through the efforts supported by a number of OWRT projects but a satisfactory economical solution is extremely difficult to attain. It is anticipated that work will be pursued in this direction for some time. Pollution of fresh water by industrial plants, municipalities and non-point sources has been, and will continue to be, a major problem for a number of years.

Cooperation with State Agencies

The Rhode Island Water Resources Center has always worked closely with state agencies which are concerned with water and with the Water Resources Board in particular. Members of the Center's Advisory Board,which sets priorities for water resources research problems and reviews project proposals, have been chosen from state agencies. These include: the Water Resources Board, the Water Supply and Pollution Control Division of the Department of Health, the Department of Community Affairs and the Statewide Planning Program. In cooperation with the Department of Health, the Center continues to administer a program of free bacteriological examination of well water for Rhode Island residents.

During the year, as part of its Comprehensive Planning Program, the Water Resources Board published Report Number One of its Water Information Series entitled, "West Kingston Landfill, An Evaluation of its Effects on Groundwater Quality". The work for this report was carried out in cooperation with the Department of Civil and Environmental Engineering at the University of Rhode Island and the Water Resources Center.

The three groups named above have been cooperating, along with the U.S. Geological Survey, in a broad groundwater program for the state. State-wide monitoring of groundwater has been continued. In fiscal year 1976, was included determination of water levels, streamflow and stream quality in the Beaver, Queen-Usquepaug, and Chipuxet aquifers. During the year field work was concentrated in the Beaver River reservoir. This involved drilling about 30 test wells and pumping tests at 7 proposed pumping centers. Digital and analog models were prepared to assist in future development and operation of the aquifer.

Current Research

Increasing interest in groundwater in Rhode Island is reflected in the number of research projects devoted to this source of supply. Two projects during the year were concerned with the development of models for the purpose of predicting the effect of changes on the quantity and quality of groundwater aquifers. Project A-056-RI continued the development of analog and digital models for the Chipuxet Aquifer primarily to study proposed development schemes with a secondary goal of better understanding aquifer mechanics particularly stream-aquifer interaction. The Rhode Island Water Resources Board is using results from this study and has continued their interest by supporting the development of two additional aquifer models for the ultimate purpose of evaluating various management alternatives. Project A-061-RI has concentrated on the water quality of an aquifer as indicated by chemical and physical properties and has related these to a computer model. To date, specific conductance appears to be the most appropriate parameter for computer modeling. Work continued in efforts to determine an economical process for the removal of iron and manganese from groundwater. This is still indicated by the Center's Advisory Board as the top priority research problem and this year Project A-053-RI further studied adsorption of these elements by diatomaceous earth.

Pollution of its streams and estuaries continues to be one of Rhode Island's most serious problems. For this reason, detection of pollutants is very important and during the year three projects were devoted to this objective. Project A-054-RI further refined the technique for the remote detection of water pollutants using computerized Laser-Raman spectroscopy. Project A-058-RI has demonstrated that, in principle, laser methods may be used for the rapid detection of viruses in aqueous solution. Also, on the basis of present results it is asserted that Polio I virus has a messurable Raman spectrum and that its spectrum is different from the few other viruses studied. The results of the research on Project A-055-RI indicate that the electrical conductivity instrument which has been developed provides an effective method for sediment pollution study. The in-situ conductivity device allows rapid and economical monitoring of pollution in marine sediment.

The fate of the organophosphate insecticide Parathion in two freshwater invertebrates (crayfish and snails) has been studied on Project A-060-RI with some interesting results. In addition to the knowledge gained of the relationship between metabolism of Parathion by freshwater invertebrates and its toxicity to them, information has been obtained which will allow evaluation of these species as environmental monitors. This aspect of the project has gained increased significance by the fact that the lethal range for Parathion to crayfish is very close to the concentration that can be obtained via ordinary farm spraying.

Two projects were involved with methods for the removal of pollutants. Project B-062-RI has demonstrated clearly that nutrient flux through salt marsh sediment occurs rapidly and vegetation growing in these sediments does absorb appreciable nutrient. Project A-070-RI began an intensive study of the biological degradation of cellulose and lignin waste.

Project A-050-RI has developed numerical models for estimating various water quality properties of Rhode Island river basins for application to water resources planning and management problems.

Regional Cooperation

The Rhode Island Water Resources Center considers cooperation with other centers in the northeast to be a very important phase of its operations.

The Rhode Island center continues to handle fiscal responsibility for the two regional projects:

"The Impact of Urbanization on New England Lakes:
An Assessment of Lake Quality Control Methods"(C-5342)
for the New England Council of Water Center Directors (NECWCD).

"Analysis of Critical Water Problems in the Northeastern
United States to Determine Essential Research Requirements"
(B-061-RI) for the Northeast Water Institute Directors (NEWID).

A. Ralph Thompson, Director
Rhode Island Water Resources Center

RHODE ISLAND WATER RESOURCES CENTER
OTHER NARRATIVE ITEMS

Water Resources Developments within the State During F/Y 1976

The Water Resources Board working within a cooperative agreement with the United States Geological Survey published Hydrologic Bulletin Number Seven, "Geologic and Hydrologic Data for the Blackstone River Area, Rhode Island".

Effort continued by the Water Resources Board on the seventeen separate tasks indicated in the program to develop a comprehensive plan for water and related land resources in the state with assistance from a matching grant under the Water Resources Planning Act. Tasks studied during the year included: Character and Analysis of Fish and Wildlife inhabiting Rhode Island's Fresh Water Areas, Inventory and Characteristics of Rhode Island Groundwater Reservoirs, and Rhode Island Water Use Analysis.

Early in fiscal year 1976, Governor Philip Noel of Rhode Island and Mayor Vincent Cianci of Providence pledged their cooperation in the development of the Big and Wood River reservoirs. Two engineering firms, Fenton Keyes and Associates and Metcalf and Eddy were designated by the Water Resources Board as joint venture engineering firms. They are proceeding with studies for preliminary engineering work on the Big River reservoirs. It was agreed that in the election of November 1976 a bond issue of 3.8 million dollars will be sought for the design and engineering of this reservoir.

A Public Utility Commission on Hydroelectric Power Potential for Rhode Island was established during the year.

Rhode Island Water Resources Center
Individual Project Annual Reports
Fiscal Year 1976

A-053-RI	Manganese and Iron Removal from Water by Adsorption on Diatomaceous Earth	DeLuise
A-054-RI	Remote Detection of Water Pollutants by Computerized Laser-Raman Spectroscopy	Brown
A-055-RI	Development of a System to Detect and Monitor Sediment Pollution	Nacci
A-056-RI	An Analog Model of the Chipuxet Aquifer, Rhode Island	Kelly
A-057-RI	A Comprehensive Systems Engineering Study of the True Economic Value of Unpolluted Water Versus Varying Degrees of Polluted Water	Nash
A-058-RI	Laser Methods of Rapid Detection and Quantitation of Human Viruses in Sewage and Rivers	Nelson
A-059-RI	Numerical Estuarine Models for Water Quality Management in the Blackstone-Providence River Complex and the Taunton River-Mount Hope Bay Complex	White
A-060-RI	Fate of the Organophosphate Insecticide Parathion in Freshwater Invertebrates	Carlson - Fuller
A-061-RI	Ground Water Quality Model of the Chipuxet Aquifer in the Upper Pawcatuck River Basin	Marcus
B-061-RI	Analysis of Critical Water Problems in the Northeastern United States to Determine Essential Research Requirements	Thompson
B-062-RI	The Capacity of Salt Marsh Vegetation to Modify the Quality of Estuarine Waters	Hull
B-070-RI	Fermentation and Enzymatic Saccharification of Cellulose and Lignin Wastes	Barnett

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-053-RI

Agreement No. 14-34-0001- 6041

FCST-COWRR Research Category: VF

Project Title:

Manganese and Iron Removal From Water by Adsorption on Diatomaceous Earth

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R. I. 02882

Proj. Began--Month: July ; Year: 1974 To Be Completed--Month: June ; Year: 1976

Principal Investigators	Degree	Discipline
Frank J. DeLuise	M.S.	Mechanical Engineering and Applied Mechanics

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Anthony Deruosi	B.S.	Chemical Engineering
Otto Gregory	B.S.	Chemical Engineering

ANNUAL REPORT

A-053-RI

Manganese and Iron Removal From Water by Adsorption on Diatomaceous Earth

July 1974 - June 1976

Frank J. DeLuise
Mechanical Engineering and Applied Mechanics
University of Rhode Island
Kingston, R. I.

Research Project Accomplishments

The aim of this project was to determine the possibility of adsorbing manganese and iron in water on diatomaceous earth to improve the filtering characteristics of the oxidized particles. Improved filtering characteristics would be indicated by a less rapid increase in pressure drop across the filter and therefore longer run times than are currently attainable.

Experimentation during the first year of the project indicated that adsorption of hydroxo complexes of iron and manganese on diatomaceous earth followed by flocculation takes place in a reasonably short time (less than 5 minutes) when the proper pH (between 6 and 7) is maintained. This information was used during this second year of the project to conduct a series of tests to determine the effectiveness of removal of oxidized manganese from water by adsorption on diatomaceous earth, flocculation, and subsequent filtration. The tests were conducted in the following manner:

Water containing a known concentration of manganese (manganese salts were added to tap water) was placed in a large mixing tank and diatomaceous earth was added. After a short mixing time, sodium hypochlorite was added to oxidize the manganese, and the mixing was continued to effect the adsorption and flocculation of the oxidized particles. The water was then pumped at a constant rate from the mixing tank through a pressure filter which had previously been precoated with diatomaceous earth. The change in the pressure drop across the filter as a function of operating time (total water throughput) was observed. Samples of the water before and after filtration were analyzed for manganese concentration using atomic absorption spectrophotometry.

With this system various grades and concentrations of diatomaceous earth were used to obtain relative performance data (pressure drops) while maintaining effective removal of the manganese. Removal of the manganese was considered effective when the effluent contained less than the minimum detectable quantity (0.02 mg/l) for the analytical equipment which was used.

Some general results of these tests are shown in the accompanying figure. In all cases shown, effective removal of manganese was accomplished. In each case the water was filtered at a constant rate of one gallon per minute per square foot of filter area. This is a normal filtration rate. The length of the runs was limited by the time the available personnel could work. The diatomaceous earth was obtained from the Johns-Manville Corporation and the various grades used are indicated in order of decreasing particle size as Celite 545, Celite 503, and Hyflo Super-Cel. With equal concentrations of different particle sizes of diatomaceous earth it can be seen that as particle size increases, the total water throughput (operating time) increases substantially for the same pressure drop across the filter. Likewise for the same particle size but increasing concentration of diatomaceous earth the total throughput increases for the same pressure drop. This suggests using as large a particle size and as high a concentration of diatomaceous earth as possible. The 100 mg/l concentration of diatomaceous earth was considered the maximum allowable because on a practical scale, operating costs above this concentration would be too high.

These results suggest an improvement over current methods for the removal of manganese. However, since these tests were run with a synthetic water (manganese salts added to tap water), it now would be desireable to try this procedure on a larger scale at a location where actual manganese bearing ground water could be used.

Project Status

The project has been completed and a completion report is in preparation.

Application of Research Results

The Water Resources Board of the State of Rhode Island is vitally interested in the results of this research since many potential water supplies in the state have a relatively hign concentration of manganese. In addition, the BIF and Johns-Manville Corporations have expressed an interest in the work and have provided equipment, supplies, and information for the project.

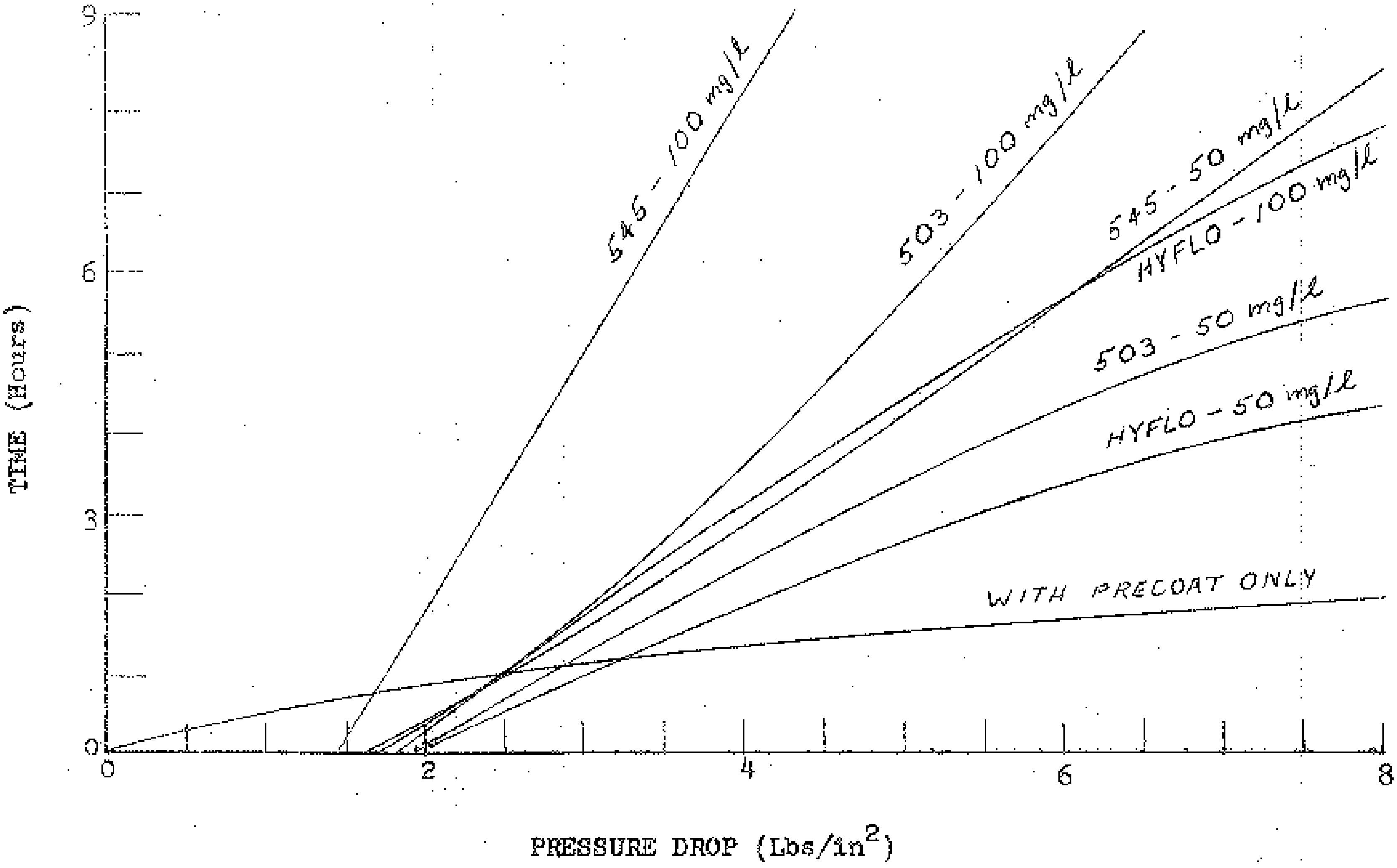


Figure 1 - Run Time versus Pressure Drop for Various Grades and Concentrations of Diatomaceous Earth

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-054-R.I. Agreement No. 14-34-0001-6041 FCST-OWRR Research Category: V-A	Project Title: Remote Detection of Water Pollutants by Computerized Laser-Raman Spectroscopy

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, RI 02881

Proj. Began--Month: July ; Year: 1974 | To Be Completed--Month: June ; Year: 1976

Principal Investigators	Degree	Discipline
Chris W. Brown	Ph.D.	Chemistry

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Richard J. Thibeau	B.S.	Chemistry

ANNUAL REPORT

A-054

REMOTE DETECTION OF WATER POLLUTANTS BY COMPUTERIZED LASER-RAMAN SPECTROSCOPY

July 1, 1975 to June 30, 1976

Chris W. Brown
Arts and Sciences
Department of Chemistry
University of Rhode Island
Kingston, Rhode Island 02881

The objective of this research was to investigate methods to lower the level of detectability of water pollutants by Raman spectroscopy. Previously, we (1,2) explored the feasibility of using laser-Raman spectroscopy for detecting pollutants, and we remotely detected nitrates at <150 ppm and petroleum on the surface of water. During the first year of the present project we tested computer methods for lowering the level of detectability, and we were able to detect nitrate at 5 ppm, phosphate at 25 ppm, and sulfate at 10 ppm.

During the present year we have concentrated on the following objectives:

1) measurement of Raman spectra of various hazardous chemicals in aqueous solution and the determination of minimum detectability limits of each

2) measurement of resonance Raman spectra of industrial dyes, food and drug dyes, and hazardous chemicals in both standard aqueous solutions and commercial products. Minimum detectability limits were also determined for these substances

3) measurement of remote resonance Raman spectra of selected dyes

4) methods for measuring the complete Raman "fingerprints" of petroleum products.

Raman Spectra of Hazardous Chemicals in Water

There are presently over 900 compounds on the hazardous chemical lists compiled by both the EPA and the U. S. Coast Guard. Using these tables, we have compiled a list of hazardous chemicals for which Raman spectra may be obtained and have classified each substance as to its ability to scatter light. The list includes 290 hazardous chemicals and over 1/3 of these are considered as at least "good" Raman scatterers.

We have measured Raman spectra of a limited number of standard aqueous solutions of hazardous pollutants from this list by means of direct scan (conventional Raman) and have determined the minimum limits of detectability for each. Table I lists the results we have obtained thus far. No sample treatment was necessary prior to measurement of the spectra.

Measurements of Resonance Raman Spectra of Hazardous Substances

Resonance Raman spectra are obtained when a molecule is excited by a laser frequency which falls within or close to the visible absorption envelope of that molecule. The resultant Raman signal is enhanced up to 10^6 times over the Raman signal normally observed.

Most industrial dyes are polynuclear aromatics and, as such, can be considered hazardous chemicals. Because of their visible absorption, dyes lend themselves ideally to analysis by resonance Raman spectroscopy. We have been able to obtain a very well defined spectral fingerprint for aqueous solutions of food and fabric dyes at concentrations as low as 2 ppm. The Raman spectra of an aqueous solution of crystal violet at a concentration of 2 ppm is shown in Figure 1. Only subtle differences between the spectra of the violet form and the blue form are seen in the region below 800 cm^{-1}. Raman spectra of two different aqueous solutions of the fabric dye, superlitefast grey, are shown in Figure 2. In the top spectrum, the solution was prepared using deionized distilled water and the dye at a concentration of 10 ppm. To test the ability of Raman spectroscopy to detect the dye at the same concentrations under more realistic conditions, another solution was prepared using creek water and the dye at 10 ppm. Little difference is seen between these two spectra. The bottom spectrum is that of the creek water used in preparing the second dye solution; the only prominent band is that of water at 1630 cm^{-1}. The industrial and food dyes we have analyzed are listed in Table II.

In addition to dyes, we have analyzed phenols, anilines and pesticides by resonance Raman spectroscopy; the compounds and their concentrations are listed in Table III. The spectrum of 3,4-dinitrophenol at 14 ppm is shown in Figure 3 and that of the pesticide DNOC at 7.6 ppm in Figure 4. One of the more interesting hazardous chemicals that we investigated was o-nitrophenol, whose spectrum is shown in Figure 5. By simply adding this compound to water ($pH \approx 5$) we could detect it only at 308 ppm. However, by increasing the pH we could easily detect it in the ppm range as is shown in Figure 5.

In Situ Analysis of Hazardous Substances by Remote Resonance Raman

Previously, we explored the feasibility of using Raman spectroscopy for the remote detection of water pollutants (2). After being successful measuring resonance Raman of dyes and certain other hazardous substances by conventional techniques we explored the feasibility of measuring resonance Raman spectra of aqueous solutions of these substances placed in a beaker located 20 feet from the instrument. The optical system was the same as the one used previously (2). With these inexpensive optics, we were able to detect the presence of selected dyes at very low levels. Remote resonance Raman spectra of an aqueous solution of Congo Red at 10 ppm is seen in Figure 6. As can be seen, a well defined fingerprint can be obtained for both the neutral and the acidified forms of Congo Red dye.

Judging from the results we have obtained to date with this system, we estimate that by upgrading the optics and by applying digital processing methods, we should improve these results by a factor of 10. This technique, with further testing and refinements, would be an invaluable tool for in situ monitoring of plant effluent streams.

Petroleum Identification (3)

In addition to developing laser-Raman spectroscopy as a method to detect hazardous chemicals in water, we discovered a method for measuring the complete Raman spectrum of petroleum. Fluorescing compounds present in petroleum obscure the Raman spectrum. Previously, we have shown that two very weak Raman bands can be observed when oils are present on the surface of water (2); however, these two bands due to the C-H stretching vibration are very nearly the same for all oils.

During the present project we found that the fluorescing compounds can be removed from light petroleum products by the following procedure: 2 ml of oil is diluted with 4 ml of pentane, 4 grams of coconut charcoal is added, the solution is stirred for 2 minutes, filtered through Celulite Filter Aid to remove the charcoal, and the pentane allowed to evaporate at room temperature in an exhaust hood. This process removes most or all of the color from the oil, and completely removes the fluorescing components; however, both the infrared spectrum and the gas chromatogram show very little change indicating that the fluorescing compounds account for only a small percentage of the oil's total composition.

An example of the Raman "fingerprint" of a No. 2 fuel oil is shown in Figure 7. An oil involved in an actual spill is shown at the top and oils from two suspect tankers are shown below; all oils were treated in the manner described above. Comparison of the three spectra, especially in the 700-1100 cm^{-1} and 1300-1400 cm^{-1} regions, strongly indicates that suspect A is the source of the spill and, indeed, this was the source.

The chemical treatment described here works for any light fuel or lubricating oil, and it provides an entirely new method for identifying petroleum.

REFERENCES

1. S. F. Baldwin and C. W. Brown, Water Research 6, 1601 (1972).
2. M. Ahmadjian and C. W. Brown, Environ. Sci. Technol. 7, 452 (1973).
3. M. Ahmadjian and C. W. Brown, Anal. Chem., July (1976).

TABLE I

Raman Spectra of Hazardous Chemicals

(Direct scan, conventional Raman)

Pollutant	Level, ppm
NO_3^-	25
SO_4^{-2}	50
PO_4^{-3}	50
$CHCl_3$	100
CCl_4	100
HOCl	100
Cl_2	100
phenol	200
acrylonitrile	200

TABLE II

Resonance Raman Spectra of Industrial and Food Dyes

(Direct Scan)

Pollutant	Level, ppm
Congo Red (neutral)	1
Congo Red (acidified)	1
Crystal Violet	2
Superlitefast Grey	10
Procion Yellow	10
Superlitefast Rubine	10
Nylomine Yellow	10
Nylomine Red	10
FD&C Red No. 2	5
FD&C Red No. 4	5
FD&C Red No. 40	5
FD&C Yellow No. 5	5
FD&C Yellow No. 6	5

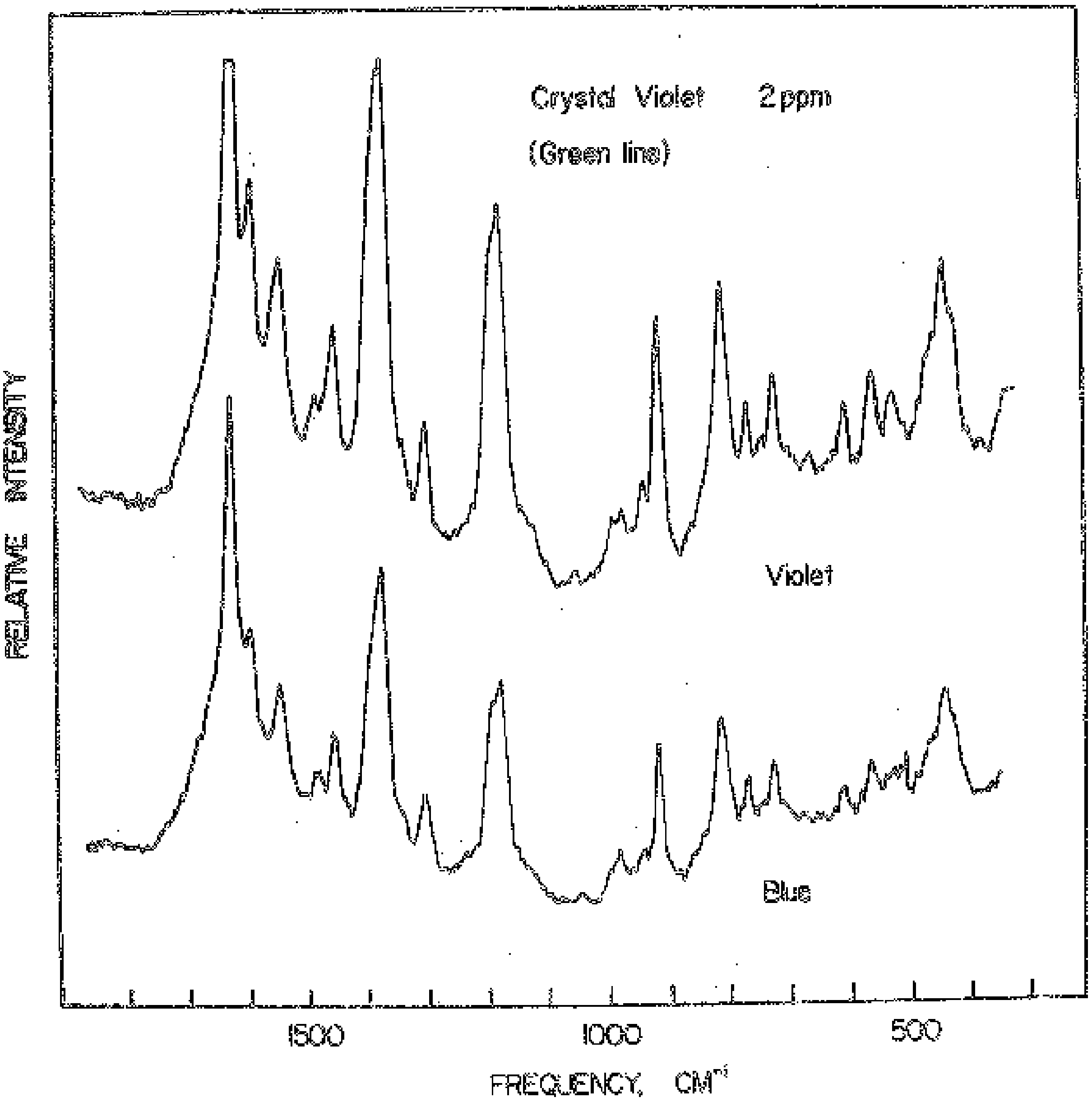
TABLE III

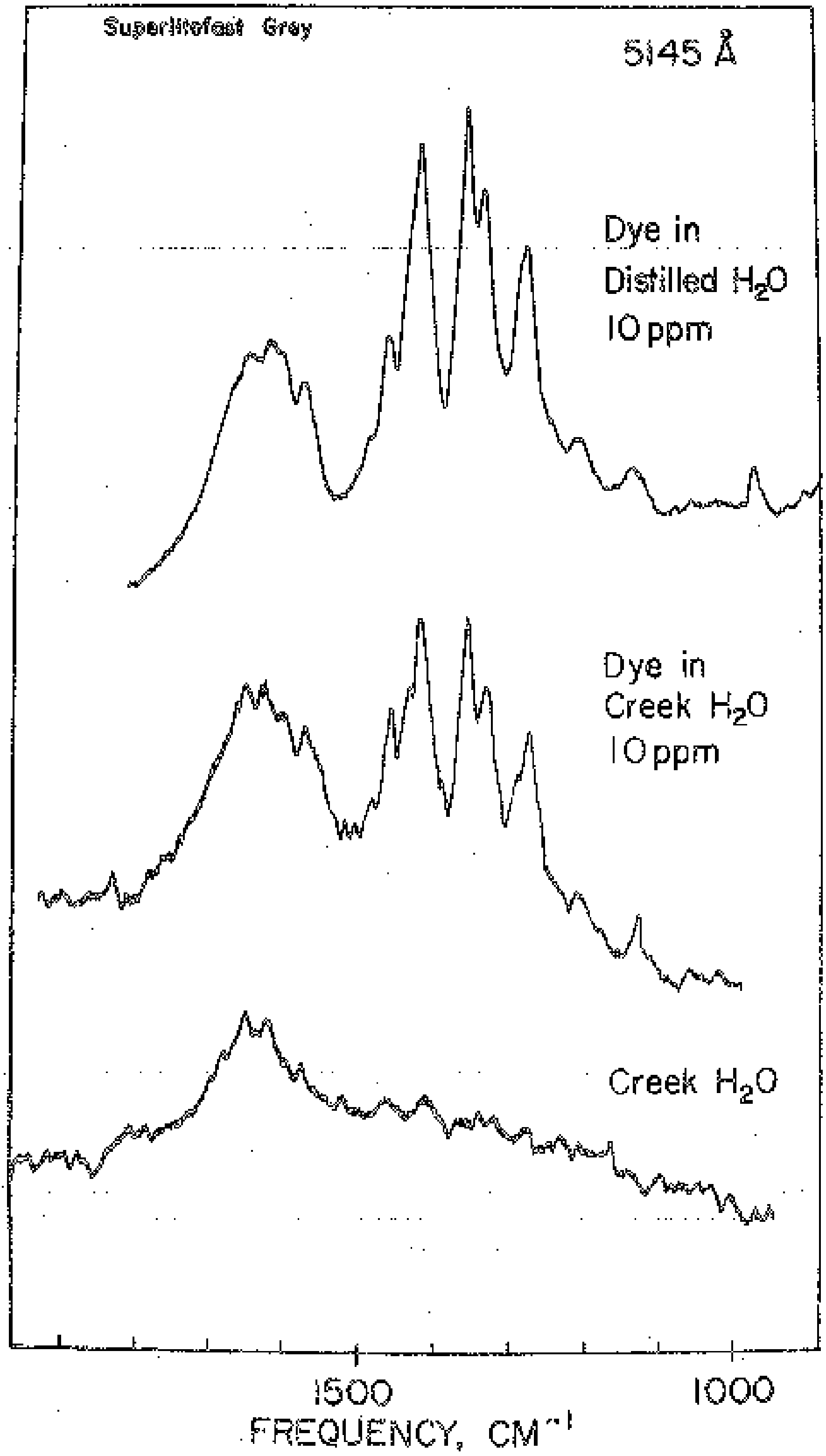
Resonance Raman Spectra of Hazardous Chemicals

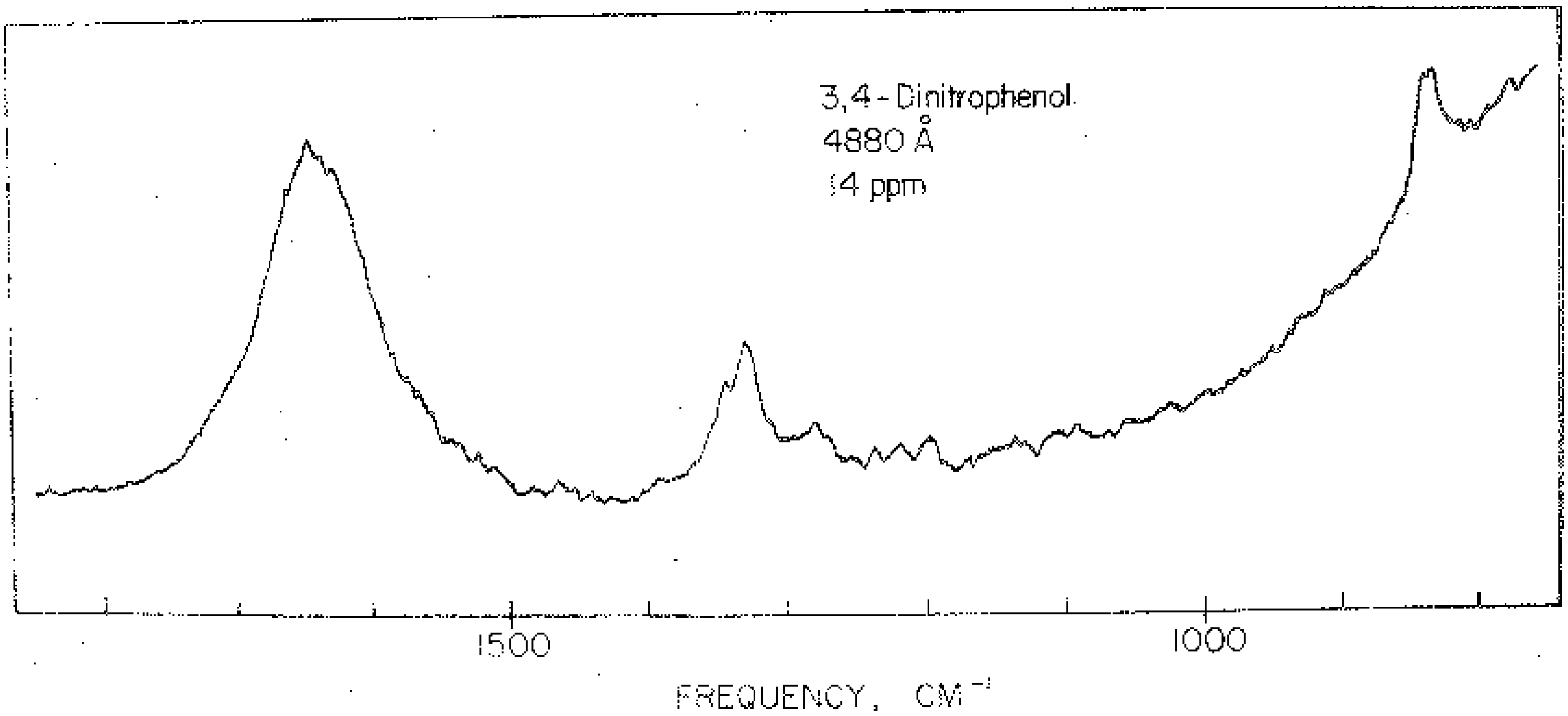
Pollutant	Level, ppm
potassium permanganate	3.2
2,4 dinitrophenol	2.8
o-nitrophenol	3.1
m-nitrophenol	9
p-nitrophenol	3.4
2,4 dinitroaniline	3.4
m-nitroaniline	14.9
p-nitroaniline	3.6
Pesticides	
DNOC (2-methyl-4,6-dinitrophenol)	3.8
methyl parathion	27
Dichloran (2,6-dichloro-4-nitroaniline)	1.4
Dinoseb (4,6-dinitro-2-sec-butylphenol)	1.8

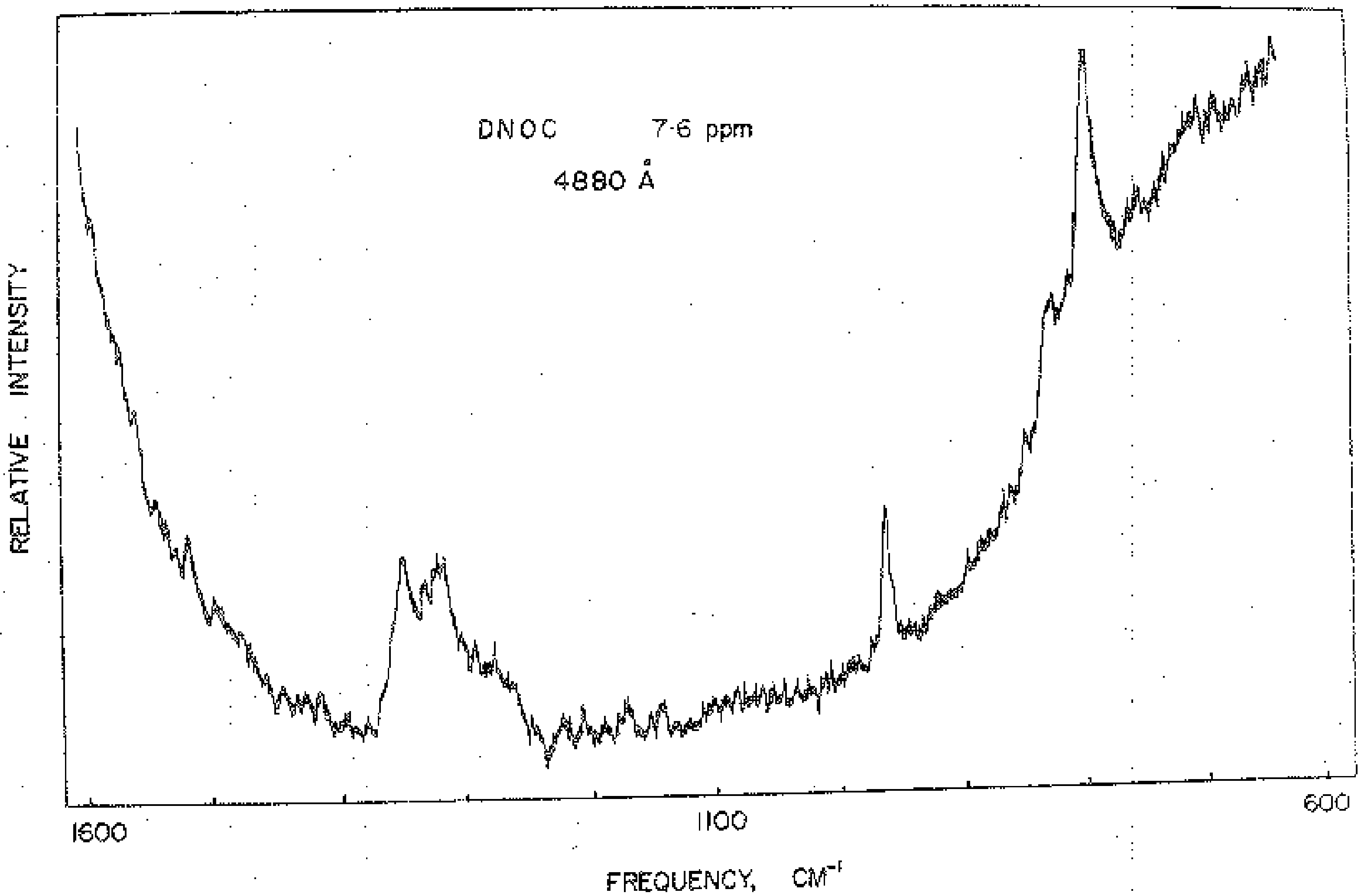
LEGEND FOR FIGURES

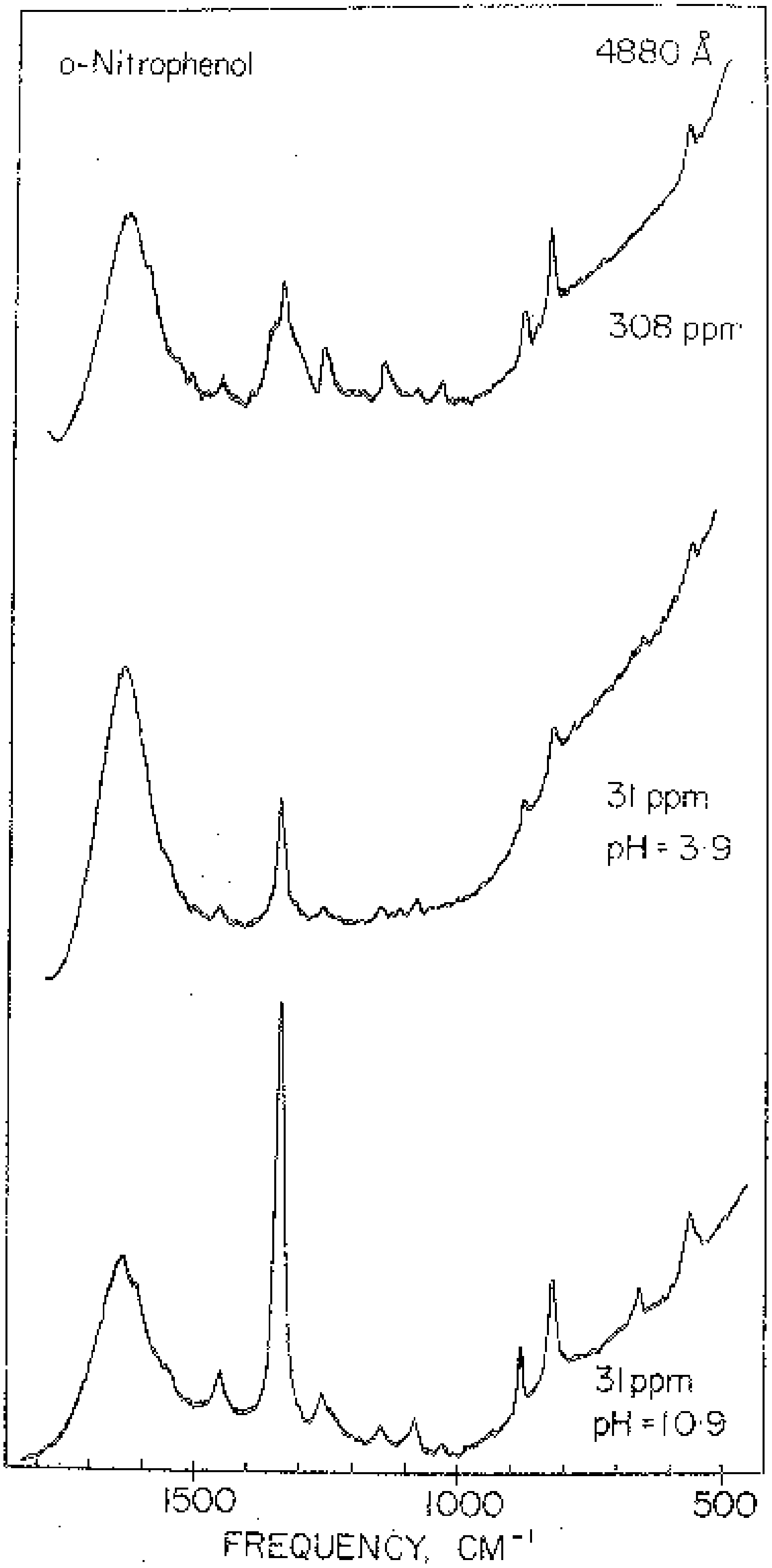
Figure 1.	Raman spectral fingerprint of 2 ppm of the industrial dye crystal violet before and after adding acid.
Figure 2.	Raman spectral fingerprint of 10 ppm of the industrial dye superlitefast grey in distilled and creek water.
Figure 3.	Raman spectral fingerprint of 14 ppm of 3,4-dinotrophenol in distilled water.
Figure 4.	Raman spectral fingerprint of 7.6 ppm of the pesticide DNOC.
Figure 5.	Raman spectrum of o-nitrophenol in water at three different pH values.
Figure 6.	Remote (20 ft.) resonance Raman spectrum of the industrial dye Congo Red (10 ppm) in neutral (a) and acid solutions (b).
Figure 7.	Raman spectral fingerprints of three No. 2 fuel oils.

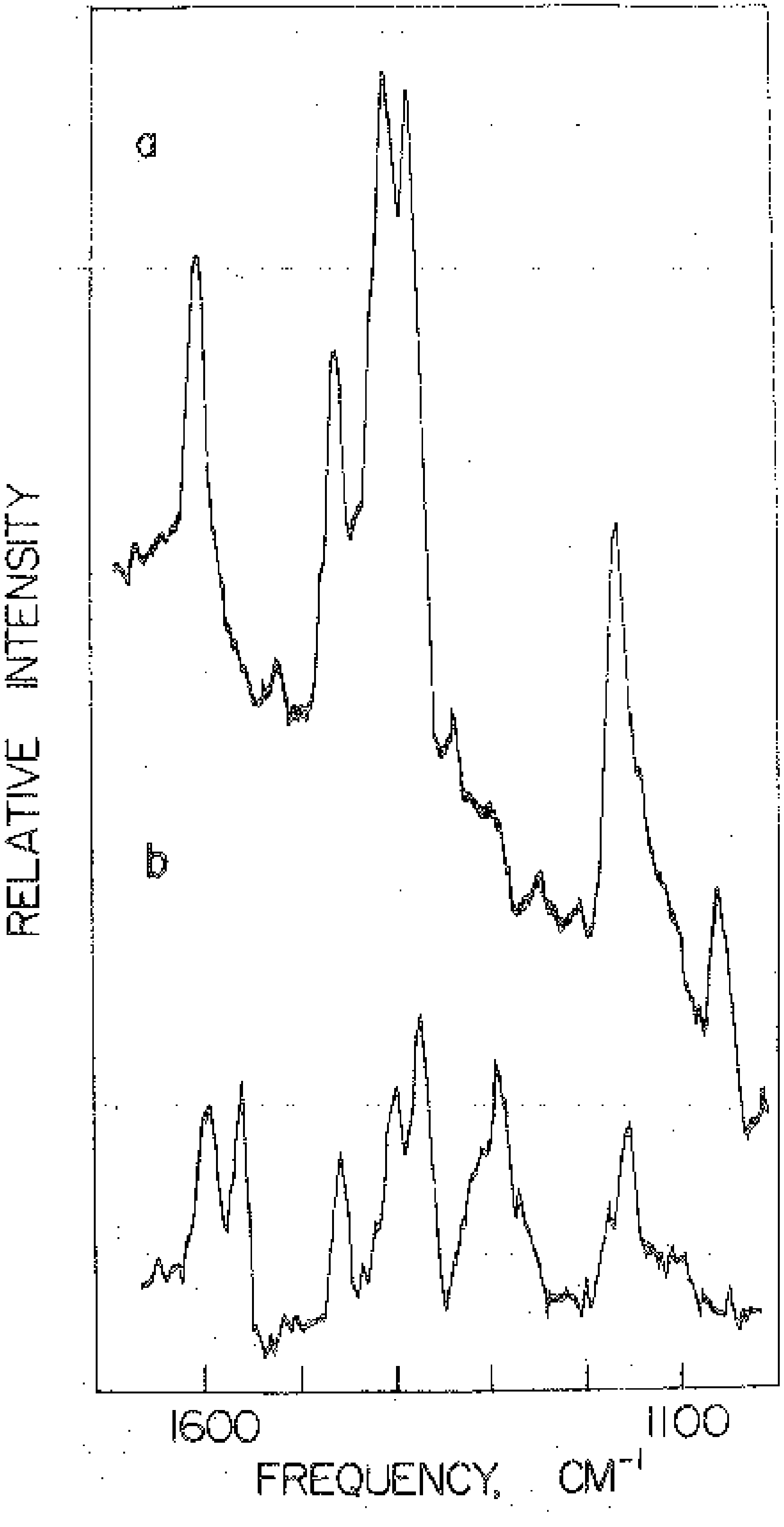

Crystal Violet 2 ppm
(Green line)
RELATIVE INTENSITY
Violet
Blue
1500
1000
500
FREQUENCY, CM^{-1}

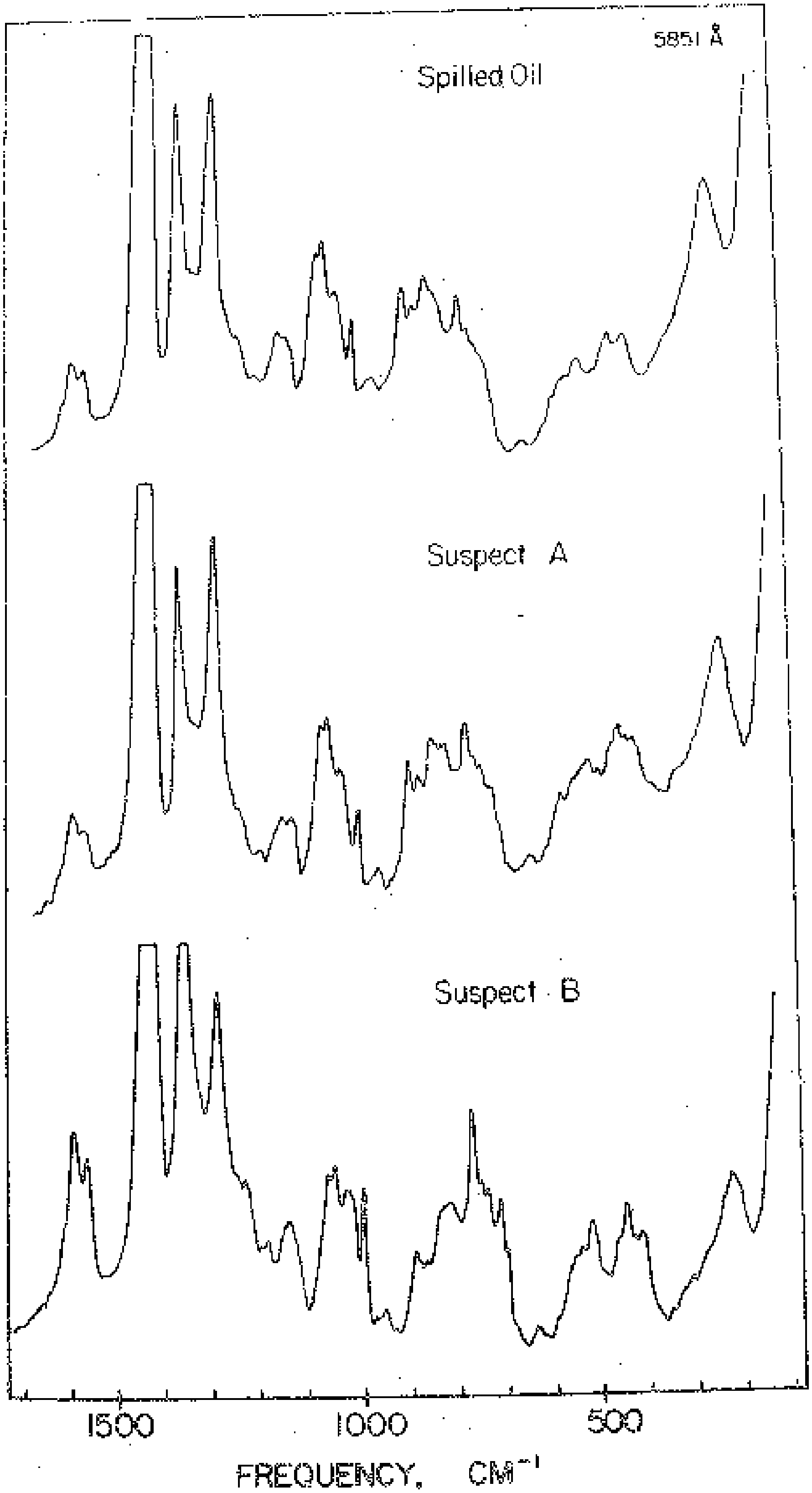

Superlitofast Grey
5145 Å
Dye in Distilled H_2O 10 ppm
Dye in Creek H_2O 10 ppm
Creek H_2O
1500
1000
FREQUENCY, CM^{-1}


3,4 - Dinitrophenol
4880 Å
14 ppm
1500
1000
FREQUENCY, CM⁻¹


DNOC 7·6 ppm
4880 Å
RELATIVE INTENSITY
1600
1100
600
FREQUENCY, CM⁻¹


o-Nitrophenol
4880 Å
308 ppm
31 ppm
pH = 3·9
31 ppm
pH = 10·9
1500
1000
500
FREQUENCY, CM⁻¹


a
b
RELATIVE INTENSITY
1600
1100
FREQUENCY, CM⁻¹


5851 Å
Spilled Oil
Suspect A
Suspect B
1500
1000
500
FREQUENCY, CM⁻¹

PUBLICATIONS

1) "Fingerprinting Petroleum by Raman Spectroscopy", M. Ahmadjian and C. W. Brown, Anal Chem., July, 1976.

2) "Detection and Identification of Pesticides in Water by Resonance - Raman Spectroscopy", R. J. Thibeau and C. W. Brown, Anal. Chem., to be submitted.

3) "Analysis of Industrial Dyes in Water by Resonance - Raman Spectroscopy", P. F. Lynch and C. W. Brown, Applied Spectroscopy, submitted for publication.

PROJECT STATUS

Completed June 30, 1976

APPLICATION OF RESEARCH RESULTS

We have had many inquires about this research from industrial and government laboratories including NASA (Langley Research Center), Battelle N.W., U.S. Coast Guard and Monsanto Chemical.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-055-RI

Agreement No. 14-34-0001-6041

FCST-COWRR Research Category: II, L, VE VG

Project Title: Development of a System to Detect and Monitor Sediment Pollution

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R. I. 02881

Proj. Began--Month: July 1, Year: 1974

To Be Completed--Month: June 30 Year: 1976

Principal Investigators	Degree	Discipline
Vito A. Nacci	M.S.	Civil Engineering/Ocean Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Jerold Baird	M.S.	Ocean Engineering

ANNUAL REPORT

A-055

Development of a System to Detect and Monitor Sediment Pollution

July 1, 1974 - June 30, 1976

Vito A. Nacci
Civil and Environmental Engineering
University of Rhode Island
Kingston, R. I. 02881

OWRR Project No. A-055-RI
Agreement No. 14-34-0001- 6042 Prof. Vito A. Nacci

Development of a System to Detect and Monitor Sediment Pollution

A study on monitoring sediment pollution by measuring electrical conductivity of the sediment has been completed. The study was conducted first in the laboratory and later in the field. The laboratory study included (1) the design and construction of an electrical resistivity measuring apparatus, (2) an investigation of the relationship between sediment porosity and soil resistivity, and (3) the effects of pollutant addition on soil resistivity.

The instrument developed was composed of a conductivity signal conditioner, a digital voltmeter, a thermistor, and a microlateralog sensing device. The signal conditioner supplied the current to drive the conductivity sensor and compared the resultant output of the sensor with a stable reference voltage. The microlateralog consists of four concentric electrodes located on the inside diameter of a plastic cylinder with the outside two acting as current electrodes and the inner two being the potential measuring electrodes.

The initial phase of the laboratory research was to investigate the relationship between sediment porosity, n, and soil resistivity (expressed as the relationship between saturated sediment resistivity and interstitial water resistivity, called formation factor, F.F.). Porosity predictions yielded accuracies of ± 5%. The prediction equations are as follows:

Sands $FF = 1.6/n$

Silts $FF = 1.1/n$

Clays $FF = 1/n^3$ or $FF = 1/n^4$

In the second phase of the laboratory study, the effects of added pollutants on soil resistivity were analyzed. Test soils were sedimented in simulated sea water and common pollutants were added to the water column. Conductivity tests were made after diffusion of the pollutants took place. Pollutants studied included fuel oil, gasoline, cold water All, zinc chloride, dextrose, nitrogen fertilizer "Otho-Gro Liquid Plant Food," "Otho Sevin Garden Dust," iron sulfate, "Devoe Vinyl Latex House Paint," and Isopropyl alcohol.

Test results for three of the added pollutants are tabulated in Table 1. Test results show that for sand and silt, the presence of the pollutants shown, decreases the formation factor while for illite clay it increases slightly for gasoline and oil but decreases considerably with soap.

The difference in formation factor readings between each pollutant could be attributed, among others, to their different rates of diffusion from the overlying solution to the sediment. When the pollutants were added to the water, all three pollutants first formed a thin film on the surface of the overlying water. The soap film broke up within minutes, the gasoline film diminished over several days, and the oil film was still substantial after a month. The small changes in sand and silt would indicate that little penetration of pollutant into the soil occurred. The larger soil voltage changes with illite clay, except for soap, could be due to its greater adsorption of the pollutant, because many organic compounds containing polar groups are strongly adsorbed on the clay particle surface; oil and gasoline are such organic compounds.

Phase II of the project concentrated on field application of the resistivity device. The field device was similar to the laboratory model. The planned study area is in Narragansett Bay, Rhode Island, immediately south of Quonset Point.

Field testing was accomplished from a 15-ft. open boat. At each site the boat was anchored and the conductivity device lowered to the bottom. Conductivity readings were made of the bottom sediment and then of the overlying water - from the ratio, formation factors of the sediment were obtained. In addition to the formation factor survey, core samples were taken for laboratory analyses. Laboratory tests included water content, gradation, organic content, hydrocarbon content, and heavy metal content.

Results of the field formation factor survey are shown in Fig. 1. Table 2 summarizes results of laboratory analyses from core samples taken from the field test area.

A comparison of in-situ conductivity with laboratory analyses of core samples showed good agreement. The results of this investigation indicate that the electrical conductivity method is effective for sediment pollution study. The in-situ conductivity device provides a quick and economic way of monitoring pollution in the marine sediment.

Table 1. Laboratory Test Results

Test Soil	Pollutant	Pore Water Voltage	
		Value	% Change
Glacial Sand	None	3.91	-
	Fuel Oil	3.55	-9.2
	Gasoline	3.46	-11.5
	Soap	3.45	-11.8
Providence Silt	None	3.54	-
	Fuel Oil	3.35	-5.4
	Gasoline	3.29	-7.1
	Soap	3.15	-11.0
Illite Clay	None	2.53	-
	Fuel Oil	2.59	+2.4
	Gasoline	2.65	+4.7
	Soap	2.01	-20.6

Sample Number	Water Content (%)	Specific Gravity	Gradation (% by Wt.)			Organic Content (%)	Hydrocarbon Content (%)	Heavy Metal Content (ppm)					
			Sand	Silt	Clay			Cd	Cr	Cu	Ni	Zn	Pb
1	33.1	2.65	100	0	0	1.4	3.6	28	100	21	43	118	23
2T	60.5	2.68	57	40	3	4.8	3.1	17	100	28	35	174	7
2B	77.8	2.65	52	48	0	6.1	1.3	9	50	18	37	135	5
3T	18.8	2.65	93	7	0	0.9	1.1	12	10	18	35	40	10
3M	18.7	2.65	92	8	0	1.4	0.9	15	10	20	33	60	30
3B	18.2	2.65	92	8	0	1.2	0.9	25	10	18	38	50	26
4	68.1	2.61	83	17	0	4.1	10.5	28	20	31	40	150	6
5	32.6	2.66	28	68	4	3.8	1.9	22	20	15	34	118	8
6T	52.5	2.69	50	43	7	4.9	1.8	28	10	23	38	118	6
6B	62.7	2.66	54	40	6	6.1	2.8	12	30	24	37	118	5
7T	24.5	2.66	88	12	0	2.2	1.5	35	20	18	44	81	15
7B	23.8	2.69	93	7	0	1.2	1.0	20	20	17	34	90	6
8T	72.7	2.69	37	56	7	6.0	2.4	9	60	36	38	162	7
8B	60.1	2.72	36	57	7	4.4	2.6	31	10	21	38	120	6
9	37.3	2.72	51	44	5	2.6	2.0	17	50	19	39	60	19
10	44.4	2.67	67	28	5	3.1	1.4	4	10	12	37	70	7
11T	29.6	2.67	49	50	1	1.5	0.9	12	10	15	35	40	10
11M	20.0	2.67	75	24	1	2.0	1.1	-	-	-	-	-	-
11B	21.7	2.68	78	22	0	1.5	0.9	-	-	-	-	-	-

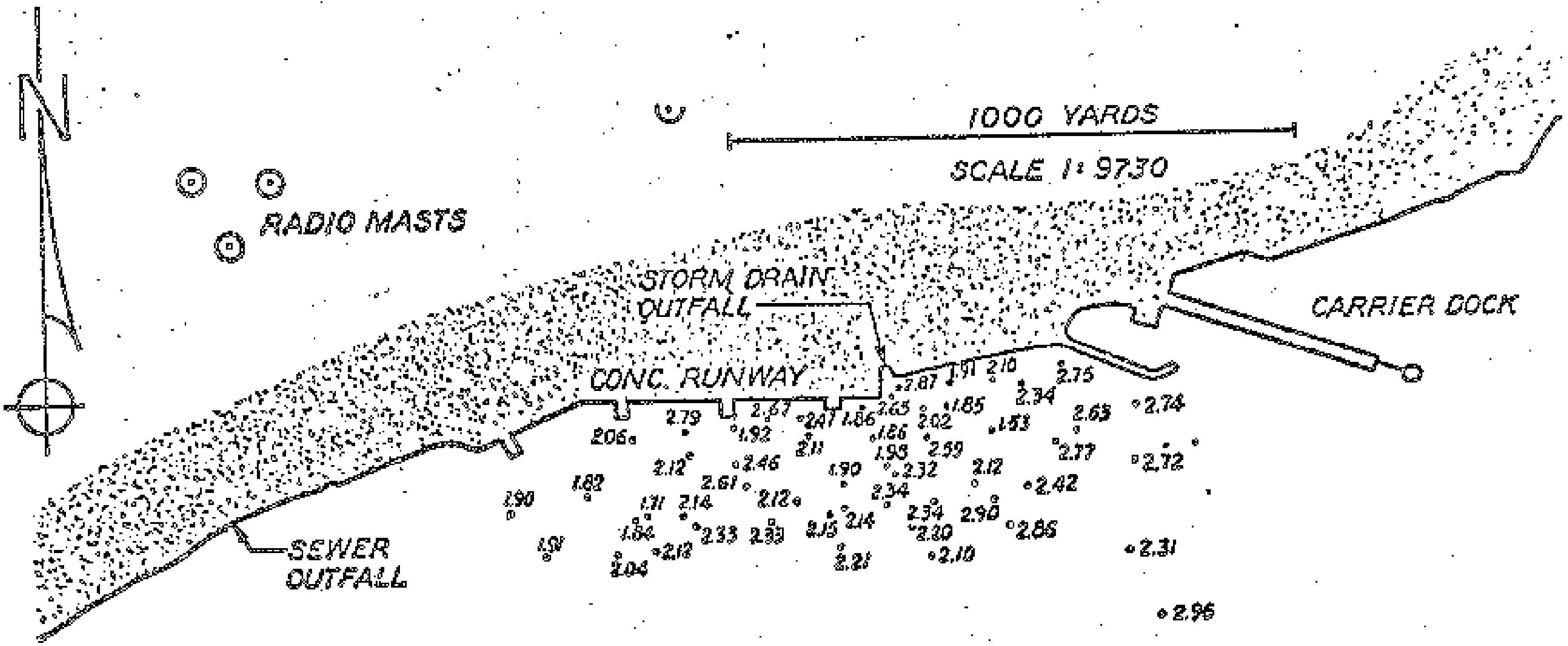


FIGURE 1 FIELD TEST SITES AND FORMATION FACTOR AT EACH SITE

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-056-RI	Project Title:
Agreement No. 14-34-0001-6041	An Analog Model of the Chipuxet Aquifer, Rhode Island
FCST-COWRR Research Category: II A	

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R.I. 02881

Proj. Began--Month: July ; Year: 1975	To Be Completed--Month: June ; Year: 1976

Principal Investigators	Degree	Discipline
William E. Kelly	Ph.D.	Civil Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Kwo-Jen Liaw	M.S.	Civil Engineering
Harry A. Niles, Jr.	B.S.	Civil Engineering

ANNUAL REPORT

A-056

An Analog Model of the Chipuxet Aquifer
Rhode Island

July 1, 1975 - June 30, 1977

William E. Kelly
Civil and Environmental Engineering
University of Rhode Island
Kingston, R. I. 02881

OWRR Project No. A-056-RI
Agreement No. 14-31-001-6041

Dr. William E. Kelly

An Analog Model of the Chipuxet Aquifer, Rhode Island

RESEARCH PROJECT ACCOMPLISHMENTS

The second year of this project was spent operating the previously developed analog and digital aquifer models to determine sensitivity to various input parameters, and to study stream-aquifer interaction. The analog and digital models developed are for all practical purposes equivalent and in the following discussion, no distinction between the two models will be made.

Steady-state model response was verified using water table maps and available streamflow measurements. The contour interval for the water table map used in verification was five feet and is a constraint on the accuracy of the verification. A water table map with a one or two foot contour interval would be more appropriate.

Various steady-state conditions were simulated and predictions were found to be in good agreement with the observed average monthly response; the average monthly aquifer response was computed from stream flow records and water levels measured at SOK6 - a monitoring well maintained by the U.S. Geological Survey for recording natural aquifer conditions. Figure 1 shows the steady-state model response and the observed behavior. Differences at the higher baseflows (recharges) may reflect the effect of a stream near SOK6 which flows at the higher rates and was not considered in the model, or the effects of evapotransporation which were not accounted for either. Steady-state response is in good agreement at the lower rates - the range of most interest.

Initial estimates of transmissivity were not modified significantly during verification, since it was observed that steady-state response was not sensitive to minor changes in transmissivity. Adjustments to the model during verification consisted almost entirely of changes in stream bed leakances, since leakances were poorly defined (as is often the case) in contrast to transmissivities which were reasonably well known. The model is sensitive to the ratio of stream bed leakance to aquifer transmissivity or when transmissivity is known to stream bed leakance. Leakances were in fact estimated using the model and a trial and error approach; the final values were found to be in good agreement with leakances determined from a leaky artesian analysis of results from a test near Thirty Acre Pond. Initial estimates of stream bed leakances accurate to the right order of magnitude would greatly facilitate model verification.

Stream-aquifer interaction was studied using both the analog and digital models and various theoretical solutions. Estimating stream flow depletion is a reasonable first step towards evaluating the effect of pumping on streamflow; however, it is exceedingly time consuming process with an analog model and efforts were made to develop techniques for simplifying and improving these estimates.

Similarites in theoretical solutions of aquifer response to stream stage fluctuations and stream depletion due to pumping in infinite, homogeneous aquifers were tested for application to finite nonhomogeneous aquifers by a series of experiments with the analog and digital models of the Chipuxet Aquifer. Initial results indicate that the response of the aquifer at any point due to a step change in stream stage is equivalent to the response of the stream (depletion) due to a step change in pumping rate at the same point. Since the response (head change with time) at any point in the analog model due to a step change in stream level is accurately and easily measured this offers an important simplification of modeling techniques. This aspect of model behavior is being further studied. Typical results are shown in Figure 2 which shows the response due to stream stage change and pumping at a model located about 800 feet west of SOK6. S/S_s is the ratio of head change to stream stage change and q/Q is the fraction of stream depletion.

While there may be deviations at larger times the agreement during the 180 day period is excellent.

PUBLICATIONS

Papers:

Kelly, W.E., 1976. "Modeling The Chipuxet Ground Water Aquifer," Proceedings of the Second International Conference on Numerical Methods in Geomechanics, Blacksburg, VA, pp 1188-1193.

Kelly, W.E., and Niles, H., Jr., 1976. "Digital and Analog Models of Southern Rhode Island Ground Water Aquifers," Abstracts, ASCE 24th Annual Specialty Conference Applications of Mathematical and Physical Modeling in Hydraulic Engineering, Purdue University, August 1976.

Kelly, W.E., 1976. "Representing Stream Aquifer Inter-Action," to be presented at Annual Meeting of American Water Resources Association, Chicago, September 1976.

M.S. Thesis:

Geisser, D.F. "An Electric Analog and Digital Computer Model of the Chipuxet Ground Water Aquifer, Kingston, R.I.," 1975.

PROJECT STATUS

The project has been completed and a completion report is being prepared for submission to OWRT.

APPLICATION OF RESEARCH RESULTS

The Rhode Island Water Resources Board is using results from this study and an indication of their continuing interest is their support of the development of two additional analog models - one of the Beaver River aquifer and one of the lower Wood River aquifer. All of the analog models are currently being used primarily to study proposed development schemes with a secondary goal of better understanding aquifer mechanics particularly stream-aquifer interaction. As the aquifers are developed the intention is for the Water Resources Board to operate models themselves for the purpose of studying various management alternatives.

Model sensitivity has been studied with the goal of identifying for the Water Resources Board any special modeling data requirements. The importance of measurements of baseflow and related water levels for steady-state verification has already been discussed and partly in recognition of this result the Water Resources Board has installed two stream gage stations and a water level recorder in the Beaver River aquifer. The continuous record being collected will allow development of improved water level recharge relations as well as better estimates of stream flow pickup.

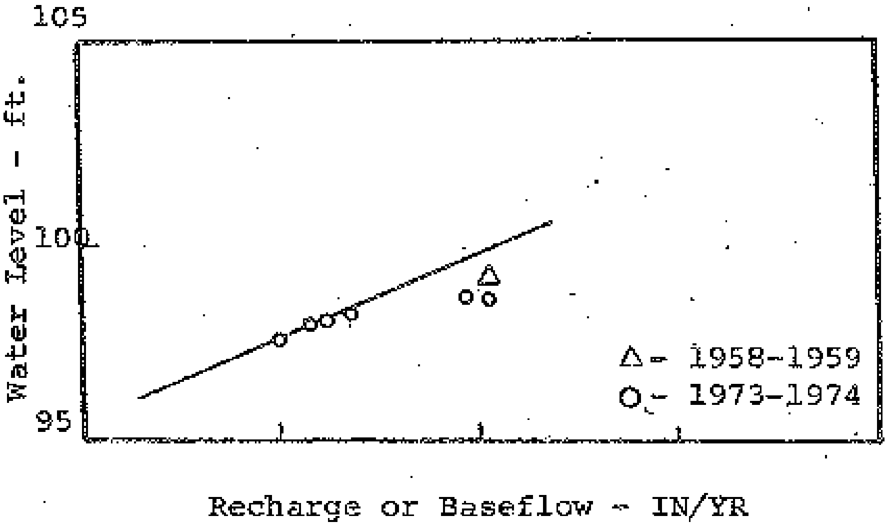


FIG. 1 Variation of Ground Water Runoff with Ground Water Level at SOK6

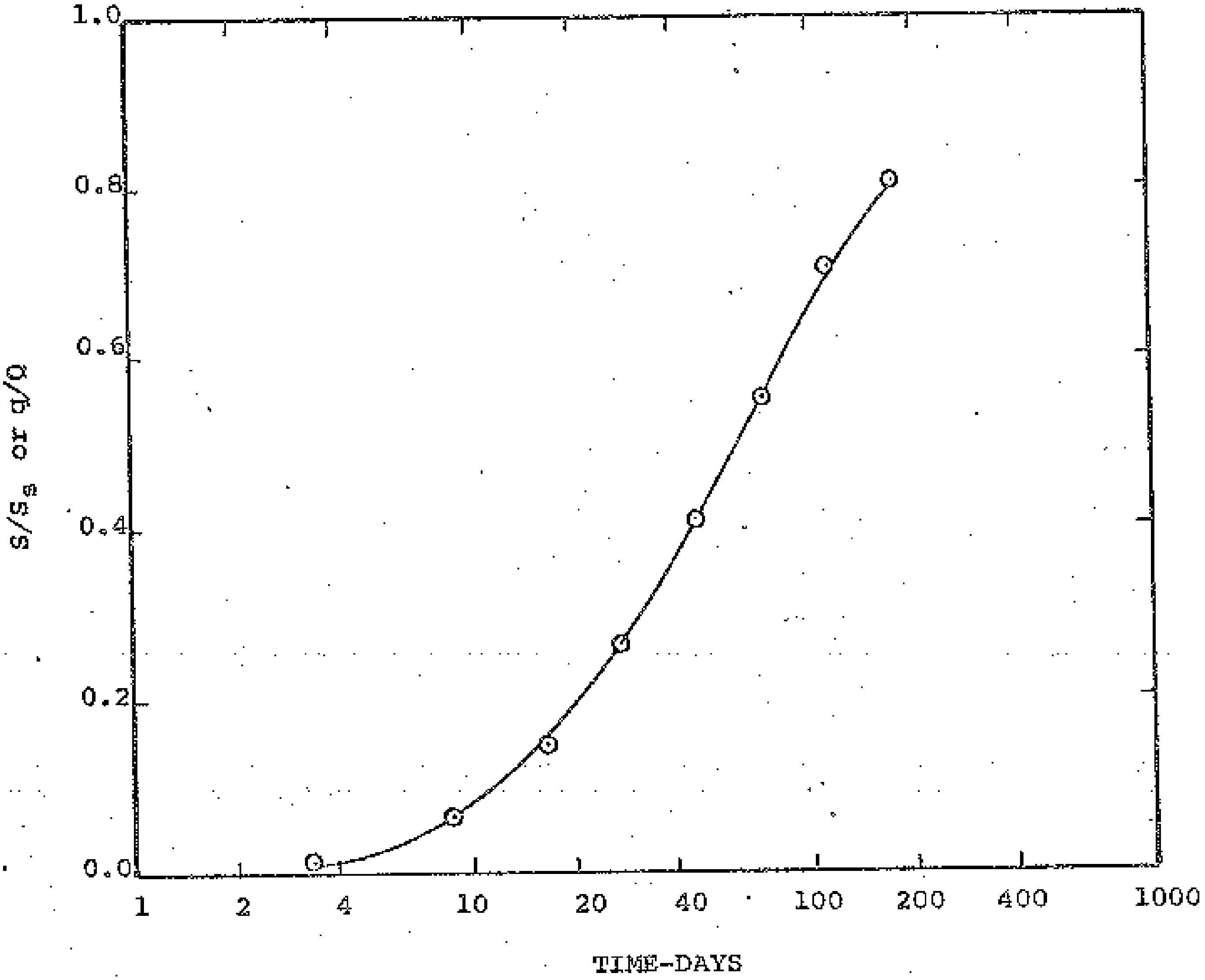


FIG. 2 Response to a Step Change in Pumping Rate or a Step Change in Stream Stage

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ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-058-RI

Agreement No. 14-34-0001- 6041

FCST-COWRR Research Category: V A

Project Title:
Laser Methods of Rapid Detection Identification and Quantitation of Human Enteric Viruses in Sewage and Rivers

Name and Location of University Where Project is Being Carried Out:

UNIVERSITY OF RHODE ISLAND, KINGSTON, R. I. 02881

Proj. Began--Month: Jan ; Year: 75 | To Be Completed--Month: Aug ; Year: 76

Principal Investigators	Degree	Discipline
Wilfred H. Nelson	Ph.D.	Chemistry
Pei W. Chang	Ph.D.	Animal Pathology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Allan D. Pronovost	B.S.	Microbiology
Shama M. Kajiji	B.S.	Microbiology
Elinor M. Yuan	M.S.	Microbiology
Part-time Laboratory Technician:		
Helen Seraichekas	M.S.	Microbiology

Period Covered: July 1, 1975 - June 30, 1976

ANNUAL REPORT

A-058

Laser Methods of Rapid Detection Identification and Quantitation of Human Enteric Viruses in Sewage and Rivers

January 1, 1975 - August 31, 1976

Wilfred H. Nelson
Department of Chemistry
University of Rhode Island
Kingston, R. I. 02881

A. RESEARCH PROJECT ACCOMPLISHMENTS:

Preparation of Type I Polioviruses

Polioviruses type 1, strain LSc2ab was supplied through the courtesy of the E.P.A. Laboratory, Narragansett, R.I. Mass production of the virus was accomplished by propagating it in monolayers of HeLa cell cultures. In a representative preparation, a total volume of 7 liters of virus with a titer of 10^{10} $TCID_{50}$ per ml was produced. That amount corresponds to about 0.6 mg of virus.

Purification of Concentration

Since Raman spectra are sensitive to chemical as well as biological contamination it was necessary to devise a purification procedure which eliminated all Raman-active impurities. Phosphate, for example, could not be used. The procedure finally settled upon consisted of five steps: cell debris removal; virus precipitation with polyethylene glycol 6000; ultrasedimentation into a discontinuous CsCl step gradient; chloroform extraction in the hypertonic state; and isopycnic density gradient centrifugation.

Cellular debris was removed by 2 cycles of low speed centrifugation at 12,000xg for 10 minutes at 4°C. After the clarified tissue culture fluid was pooled, the virus was precipitated by addition of NaCl at a final concentration of 0.5M. Solid polyethylene glycol 6000 was added at a concentration of 10 per cent. After 24 hours the precipitate containing the virus was sedimented by centrifugation at 8,000xg for 10 minutes at 1°C. The pellet was resuspended at 15°C in a vortex for 7 minutes. The residual polyethylene glycol was removed by four or more cycles of resuspension and low-speed centrifugation.

Discontinuous CsCl step gradients were prepared in large nitrocellulose rotor tubes (see Fig.1). Densities of stock solutions ranged from 1.18 to 1.70 g/ml. The concentrated virus and the viral capside were separated at their respective bouyant densities, 1.34 and 1.29 g/ml. Virus was removed through the side of the tube with a needle and syringe.

Next, the virus was chloroform extracted twice in the hypertonic state to remove extraneous glycoprotein. Five ml of cold chloroform was added to 2 ml of virus suspension. This was shaken vigorously at 4°C for 5 minutes. Slow speed centrifugation at 4°C separated the chloroform and the aqueous phase, which contained the virus.

In the final step isopycnic density gradient centrifugation was performed at 110,000xg for 48 hours at 4°C. Two visible bands were formed as shown in Fig. 2. The top band had a bouyant density of 1.29g/ml and contained empty capsids. The bottom band had a density of 1.34 g/ml and contained complete virus. Electron micrographs and UV spectra confirmed the assignments as did infectivity data. An electron micrograph is shown in Fig. 3. The average 260/280 UV absorption ratio was 1.67 (Fig. 4) for purified samples. End-tail absorption at 233.5 nm has been observed whenever substantial amounts of capsid or chemical contaminations such as ethanol have been present.

A procedure involving precipitation with methanol; extraction with n-butanol; reprecitation, and extraction with saline at pH 9 followed by pelletization and resuspension in 0.14 M NaCl has been attempted also. That work has been discontinued due to the suspected contamination of virus by cellular nucleic acid.

Virus samples were removed at various stages of the purification process and examined for infectivity. Large numbers of capsids are produced in the cell along with the virus and these must be separated from the complete virus. It is fortunate, therefore, that the capsid absorbs strongly below 240 nm and that it can be detected under the electron miscrope as well.

Concentration of the virus was accomplished in several steps. Volume reduction from 7 liters to 15 ml was accomplished through polyethylene glycol precipitation followed by resuspension. Volume was reduced to 2 ml in the discontinuous CsCl step gradient, and the final isopycnic density gradient centrifugation reduced volumes by another factor of ten. The size of the sample placed in the laser beam was about 20 microliters. Infectivity data indicated that virus loses were relatively low, 10 to 20 per cent. Infectivity and UV data are in basic agreement regarding virus concentration which ranged between 1.5 to 3.0 mg/ml. in Raman samples.

Raman Spectra

Figure 5 shows the first spectrum obtained using a methanol precipitation technique. Sensitivity was rather low, but characteristic identifiable peaks appear at 1485. 1460, 1390, 1350, 1100, 1015, and 955cm^{-1} and in the 850-790 cm^{-1} region. Sample preparation by the pelletization method had the advantage of superior sensitivity in the region 600-900 cm^{-1}, since CsCl did not have to be used. But, the process failed to exclude substantial amounts of cellular nucleic acid. Hence, the more elaborate process involving precipitation with polyethylene glycol was used in all later work.

Solid poliovirus obtained by evaporative removal of water in a capillary tube shows many of the same peaks, (Fig. 6). Peaks at 1270 and 1460 cm^{-1} are easily observed, and, as expected, pronounced activity in the Amide I region is observed unobstructed in the portion of the spectrum normally obscured by the 1625 cm^{-1} water peak.

Figure 7 shows a spectrum obtained from a sample contaminated by ethyl alcohol. The 1485 and 1460 cm^{-1} peaks of the virus are substantially enhanced by superposition of alcohol peaks. Figures 8 and 9 show spectra of virus solutions at maximum instrument sensitivity. Characteristic alcohol peaks at 1050, 1090, 1280 and 880cm are still present, but at reduced intensity. Peaks probably attributable to the virus appear at 670, 685, 755, 790, 815, 840, 980, 1005, 1100, 1130, 1170, 1210, 1240, 1320, 1350, 1390, 1460, and 1485cm^{-1}.

At present the assignments of many of the lines are uncertain. At best there are many overlapping lines due to the protein and RNA components and our spectral resolution of about 10 cm^{-1} makes the spectra appear less-well-defined than need be the case in the near future. Even so, the basic features of the spectra do make sense. As expected the most intense line due to peptide groups is at 1665 cm^{-1} in the Amide I region. Similar activity is observed near 1270 cm^{-1} in the Amide III region. Unfortunately, in aqueous solutions the 1665 cm^{-1} peak is hidden beneath a water peak. The line at 1485 cm^{-1} is due to C-H deformations and is not specific to virus components. The 1100 and 815 cm^{-1} lines due to PO_2 stretching vibrations also have been observed. Likewise frequencies at 770, 1015, and 1005 cm^{-1} can be assigned to tryptophan and phenylalanine residues.

It is asserted that on the basis of present results that polio I virus has a measurable Raman spectrum and that its spectrum is different from the few other viruses studied. Thus, we have demonstrated that, in principle, Raman spectroscopy can be used for the rapid detection of viruses in aqueous solution.

B. PUBLICATIONS:

None.

C. PROJECT STATUS:

The project will be completed September 1, 1976. Mr. Alan Pronovost who is finishing a Master's thesis involving this work plans to complete all work by that date.

D. APPLICATION OF RESEARCH RESULTS:

Keen interest in our progress has been expressed by several research groups. Dr. Carol Burke, a member of the UConn Pathobiology Department has cooperated on a regular basis. She and her colleagues wish to develop a method for monitoring viruses on a real time basis.

The Carborundum Corporation has also expressed interest in developing a virus analysis machine, although their interest has flagged since the recession hit them hard.

Several medical doctors have indicated that a virus analysis machine would be invaluable to them in their clinical work. The spectroscopic research personnel at Spex, Inc., of Metuchen, N.J. have shown strong interest in our work and have offered use of their facilities on a limited basis.

The most useful application of our work would be toward the development of a virus analysis machine.

E. WORK REMAINING, AND PROGRESS CONTEMPLATED DURING THE NEXT YEAR:

In the immediate future one final attempt will be made to prepare chemically-pure poliovirus. It is believed that such an effort will succeed within a month. Once these samples are prepared their spectra will be studied as a function of temperature. Such an effort will help in the analysis of the spectra and should speed the publication of our results. It should be emphasized that ours will be the first reported Raman spectrum of a human virus.

In the more distant future, if a virus analysis machine is to be developed several hurdles must be overcome. In principle, on the basis of present technology it is possible to detect femptogram amounts of material using the Raman technique. In terms of viruses this translates to a minimum of 18 polioviruses need for detection. A limit of 18 vuruses may be far too low, however. Sample preparation is difficult since such small samples are very hard to manipulate.

The problem of real time measurement is quite solvable. Electronic detection systems presently available allow many scans to be made in one minute. Data averaging techniques can be fully employed and spectra displayed on a cathode ray tube. We have done this already with concentrated samples with the cooperation of the people at Spex, Inc. Thus, in principle, one can take 18 viruses and one minute later see the spectrum displayed. Realistically, at present there is no rapid way of obtaining a few virus in pure form suitable for application of this technique.

Cost is a serious problem. The apparatus need for the analysis in real time would cost at least $50,000. Our laboratory would need $25,000 for a second generation of equipment to proceed. This is not a huge amount, but it presents a real obstacle at the moment.

The prospect of being able to display a Raman spectrum of a virus on a cathode ray tube minutes after sample preparation is an exciting one. Now that we know that human virus spectra can be obtained it is hoped that sufficient interest will be stimulated to allow the funding of the sample preparation work.

Our results show most definately for the first time that human viruses can be studied by Raman spectroscopy. It is expected that our results will encourage study of human and animal virus structure in addition to contributing to progress in the detection and identification of viruses.

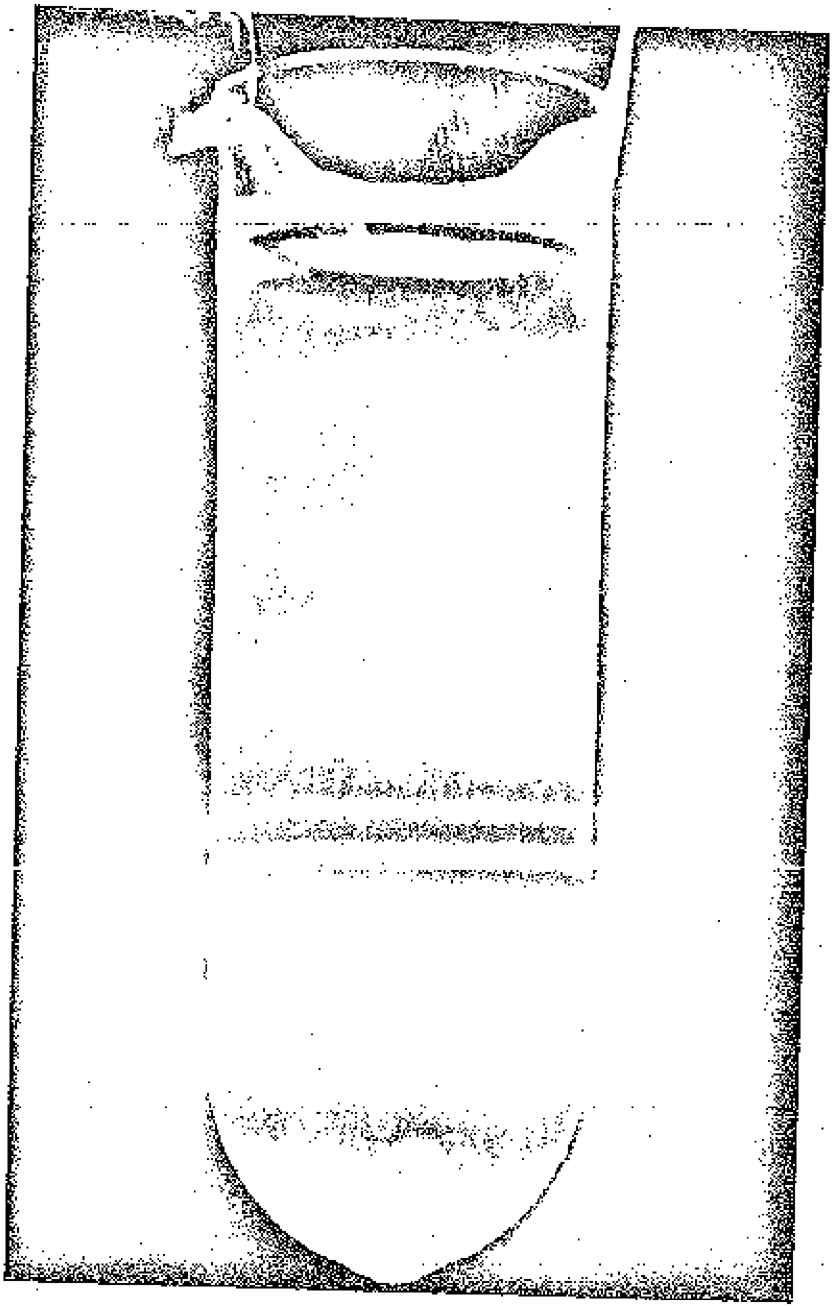


Fig. 1. Discontinuous CsCl step gradient of poliovirus. Viral capsids (upper band) and mature viruses (lower band) are separated.

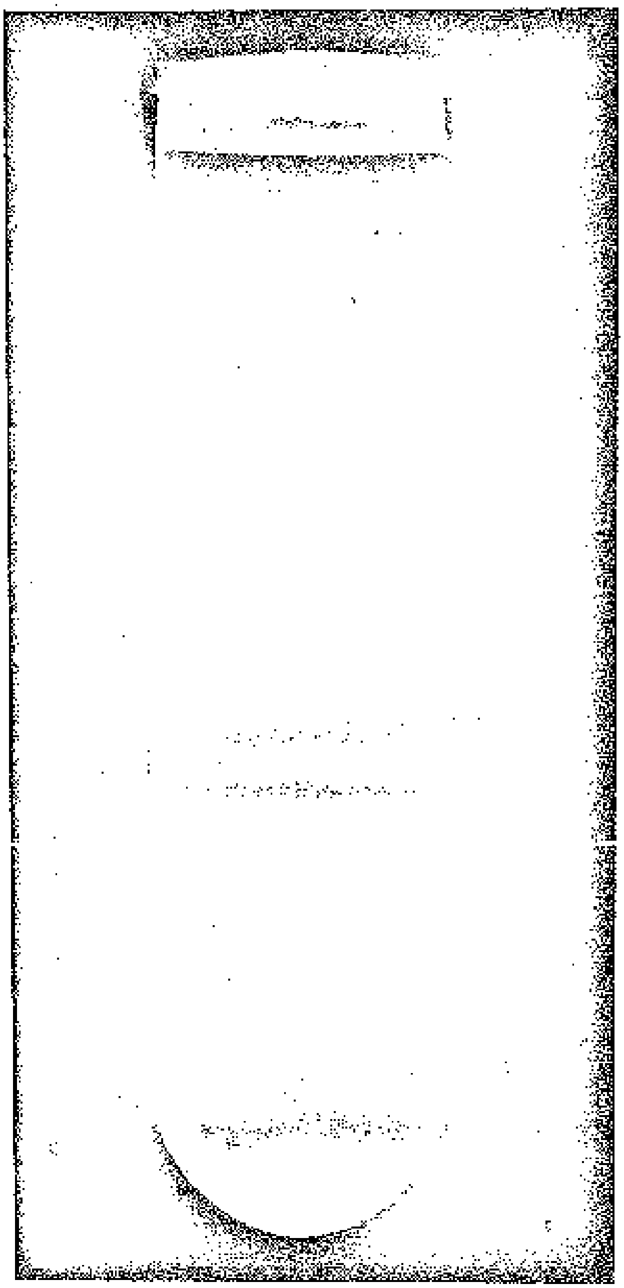


Fig. 2. Isopycnic density gradient of poliovirus. Lower band is mature virus, upper band contains capsids.

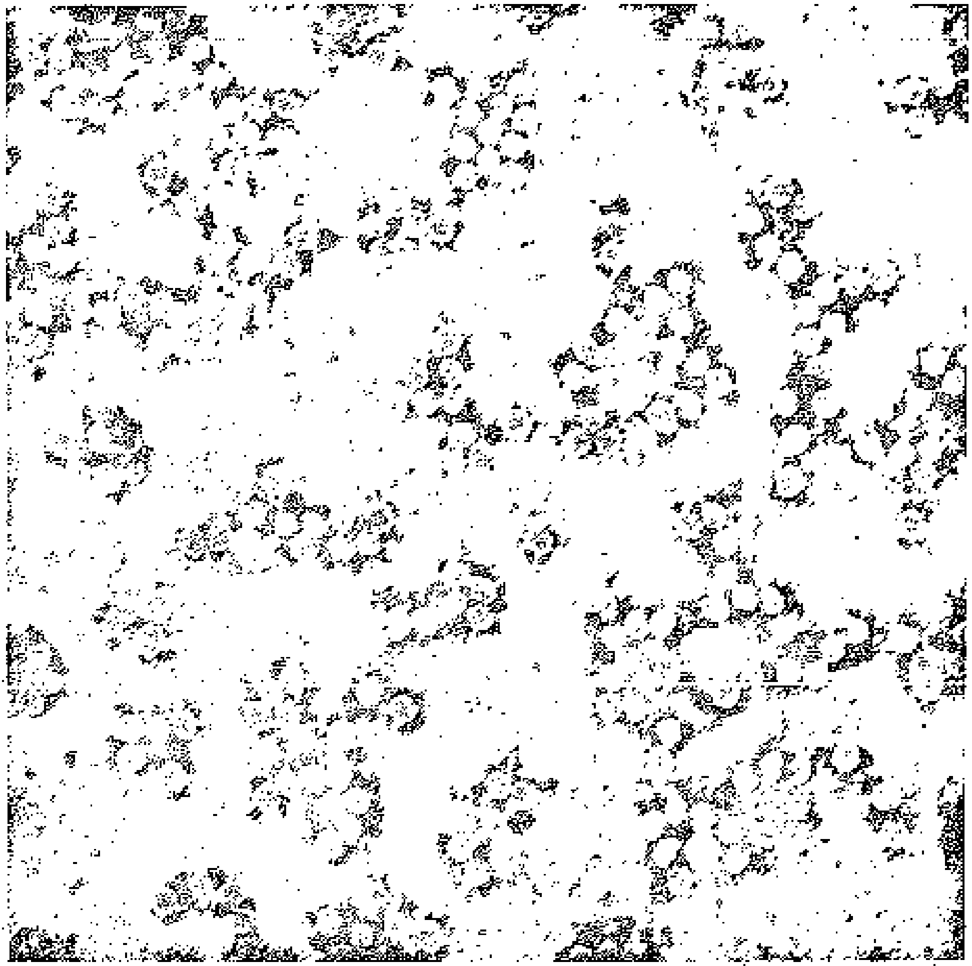


Fig. 3. Electron micrograph of pure poliovirus negatively stained with 1% phosphotungstic acid by pseudoreplication (approx. 150,000 X).

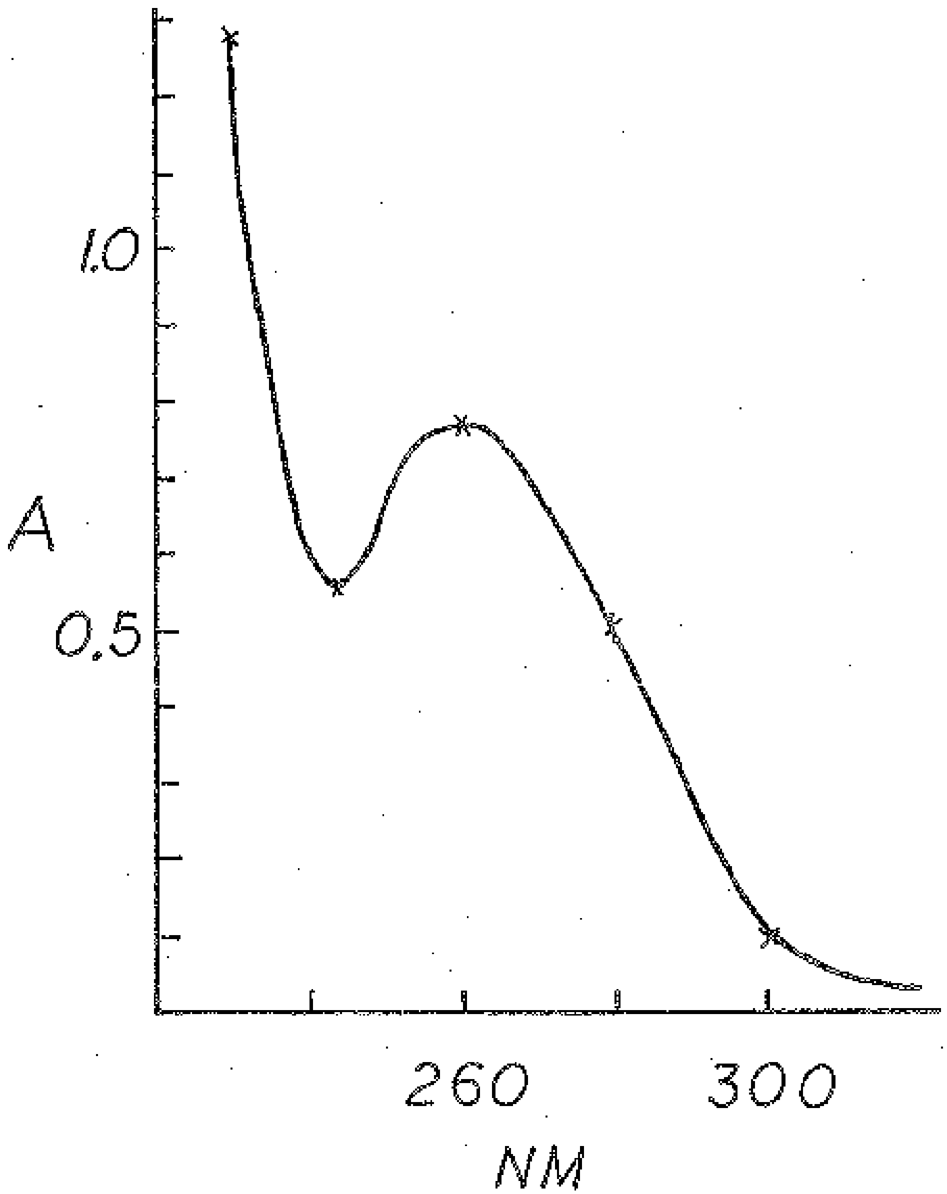


Figure 4. Ultraviolet Spectra of Poliovirus Type I

Figure 5. Raman Spectra of Poliovirus Prepared by the Methanol Precipitation Method in .2M NaCl.

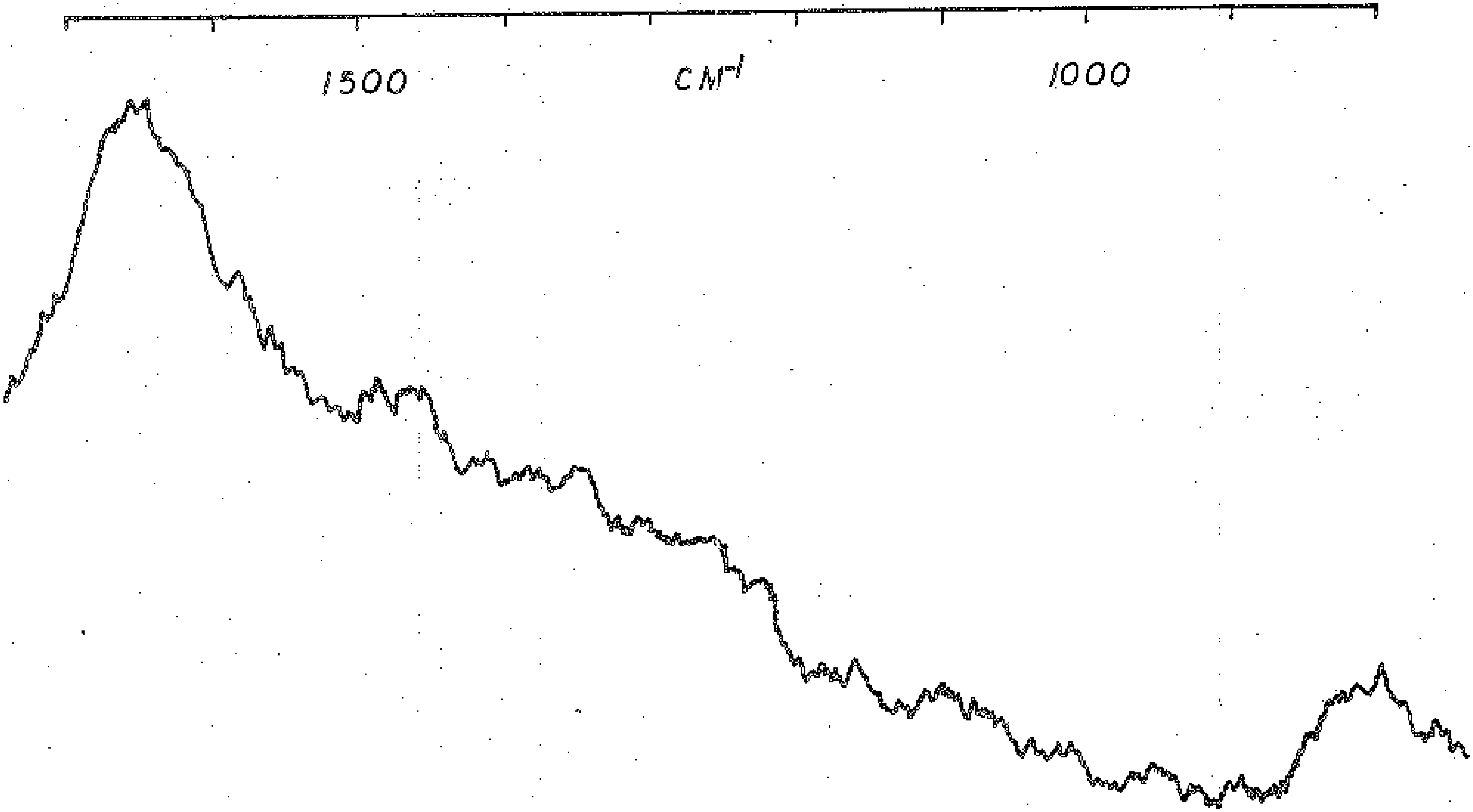


Figure 6. Raman Spectra of Solid Poliovirus.

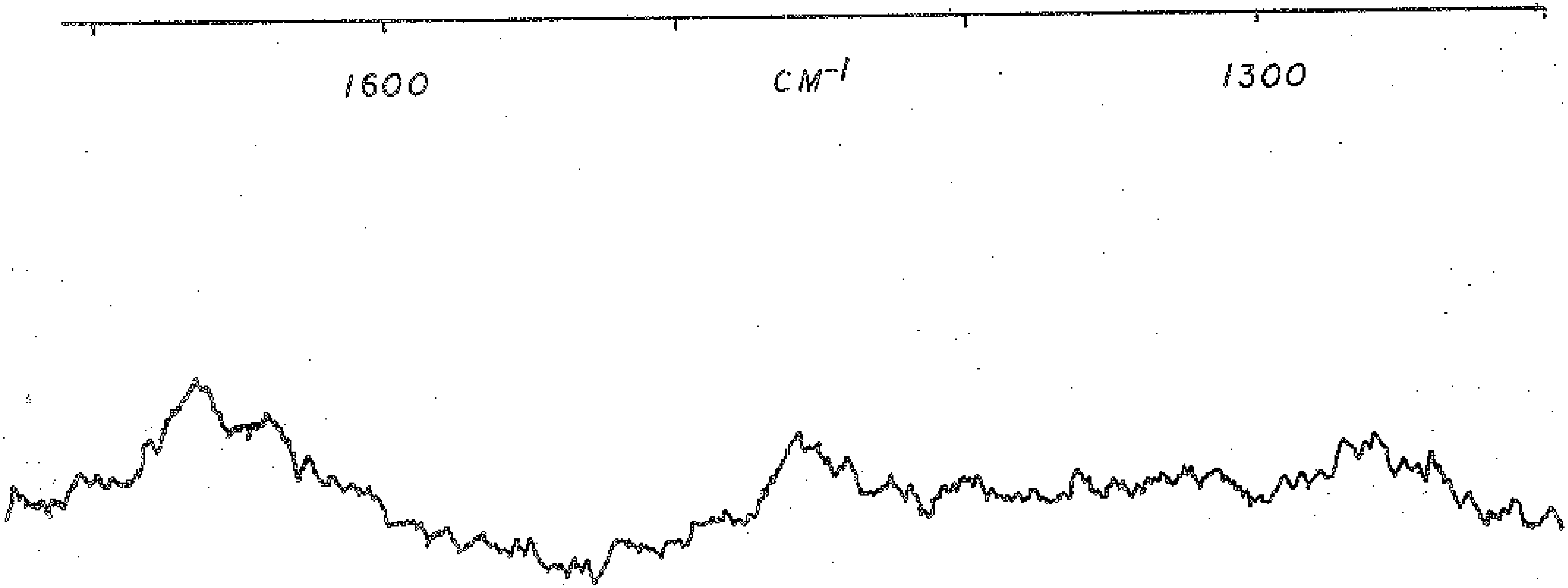
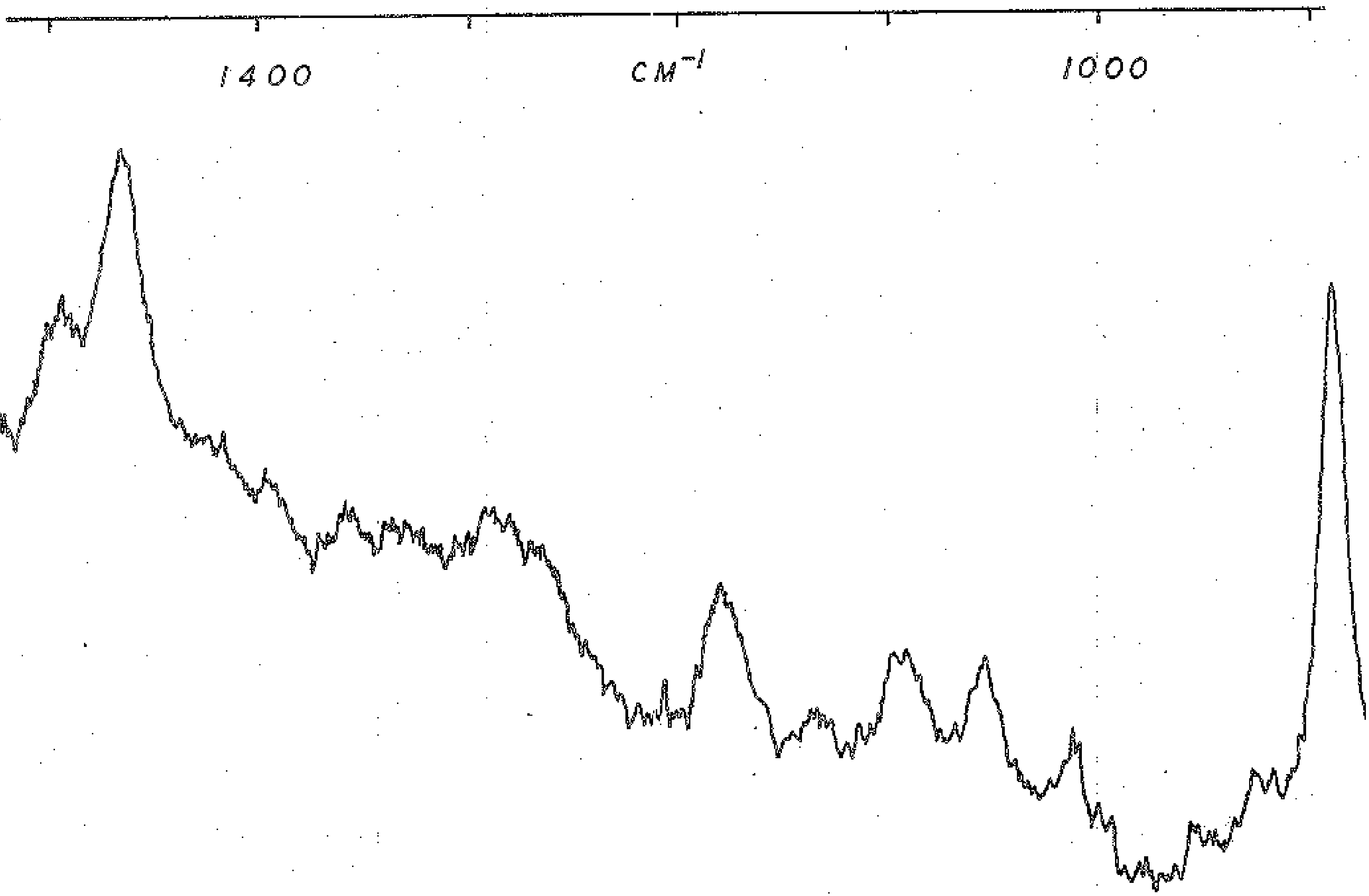


Figure 7. Raman Spectra of Poliovirus in 33% CsCl (Ethanol Contaminated)



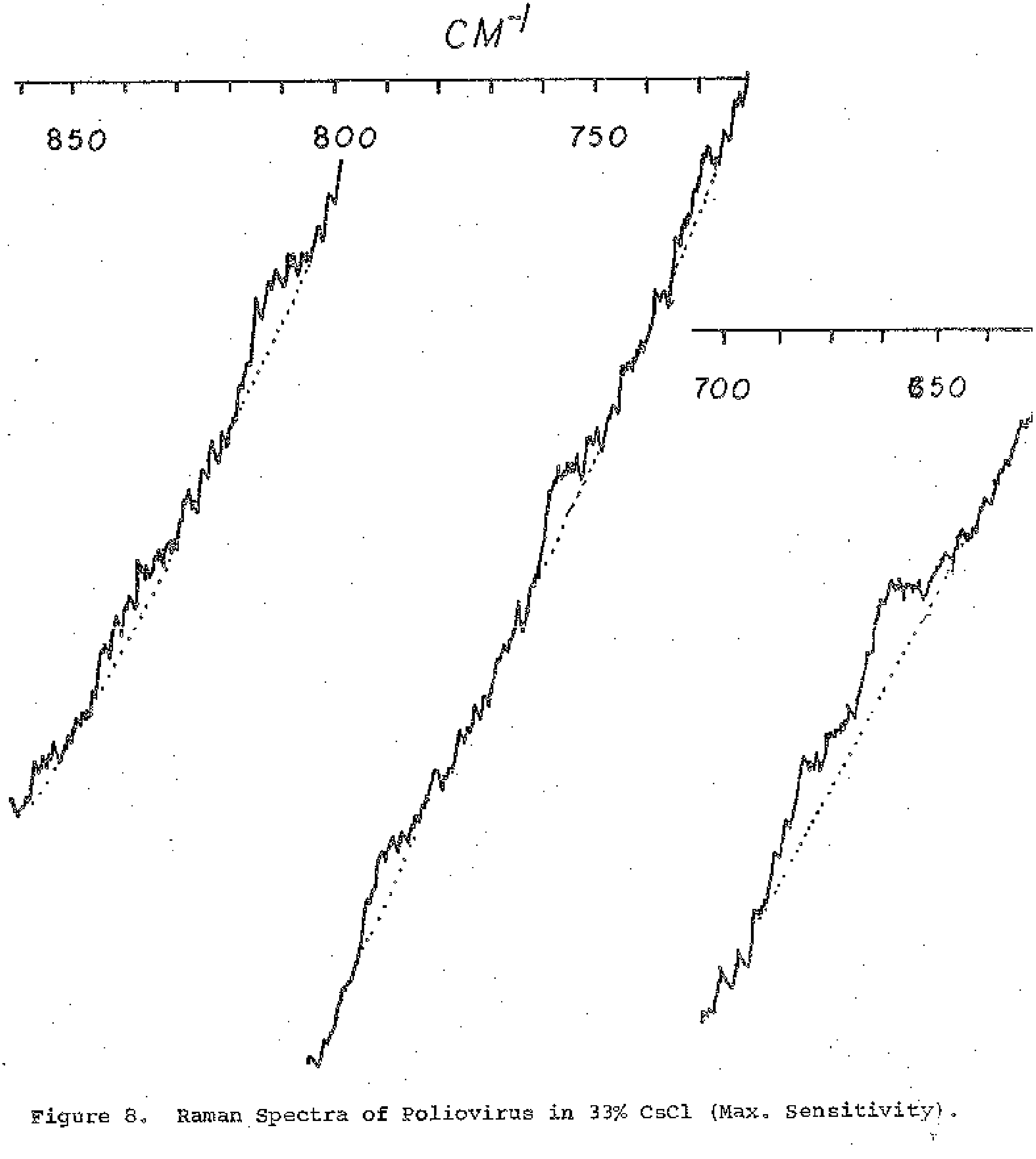


Figure 8. Raman Spectra of Poliovirus in 33% CsCl (Max. Sensitivity).

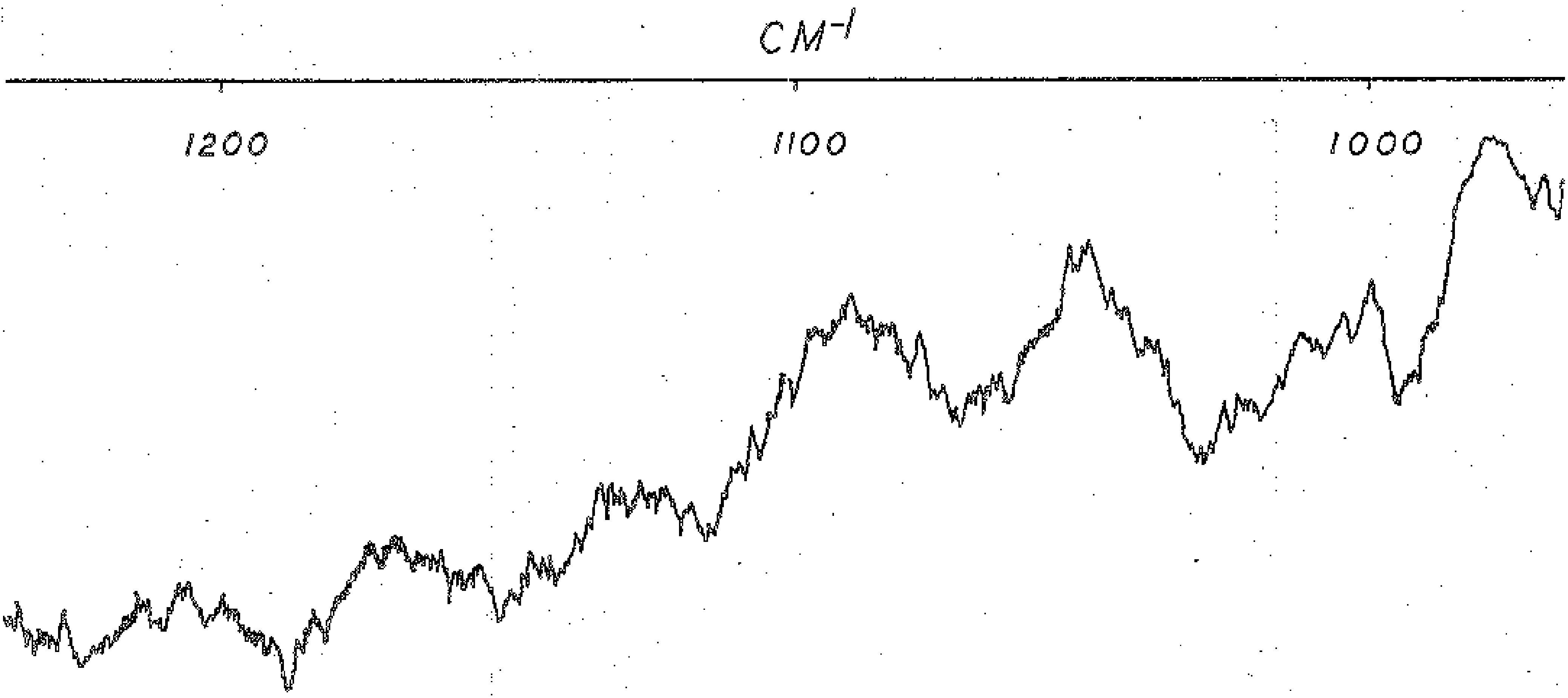


Figure 9. Raman Spectra of Poliovirus in 33% CsCl (Max. Sensitivity).

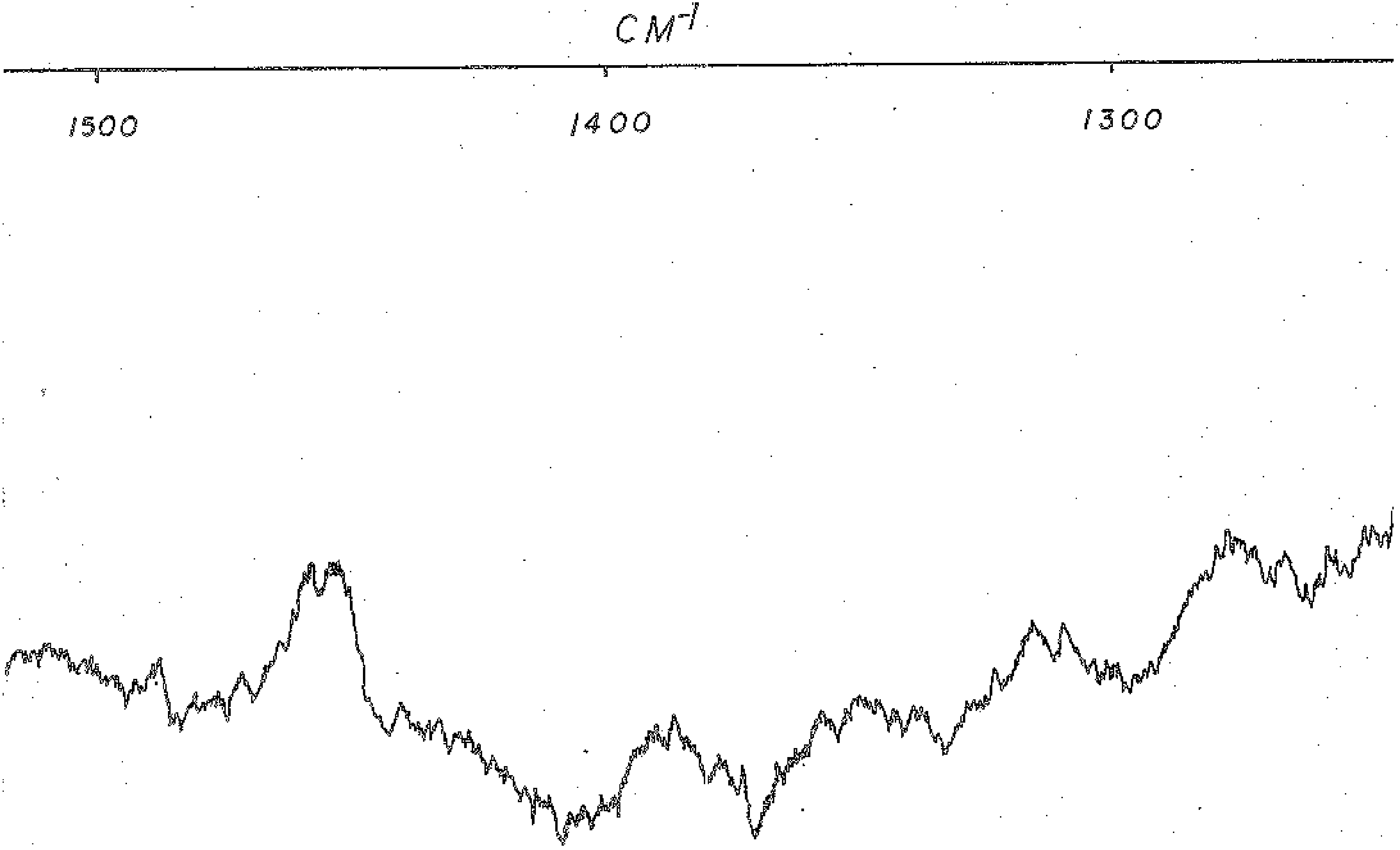


Figure 10. Raman Spectra of Poliovirus in 33% CsCl (Max. Sensitivity).

Form CW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

CWRR Project No. A-059- RI	Project Title:
Agreement No. 14-34-0001- 6041	NUMERICAL ESTUARINE MODELS FOR WATER QUALITY MANAGEMENT IN THE BLACKSTONE-PROVIDENCE RIVER COMPLEX AND THE TAUNTON RIVER-MT. HOPE BAY COMPLEX
FCST-COWRR Research Category: VI A I	

Name and Location of University Where Project is Being Carried Out:

UNIVERSITY OF RHODE ISLAND, KINGSTOWN, R.I. 02881

Proj. Began--Month: Feb. ; Year: 1975 | To Be Completed--Month: June ; Year: 1976

Principal Investigators	Degree	Discipline
1. Frank M. White	PhD	Mechanical & Ocean Engineering
Co-Investigators:		
2. Richard C. Lessmann	PhD	Mechanical Engineering
3. Malcolm L. Spaulding	PhD	Ocean Engineering

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
1. Eva Griffeths	BS	Computer Science
2. Christopher Noll	BS	Ocean Engineering
3. Toyoki Nakamura	BS	Ocean Engineering

ANNUAL REPORT

A-059

Numerical Estuarine Models for Water Quality Management In the Blackstone-Providence River Complex and the Taunton River-Mt. Hope Bay Complex

February 1975 - June 1976

Frank M. White
Mechanical Engineering & Ocean Engineering
University of Rhode Island
Kingston, R. I. 02881

PROJECT ACCOMPLISHMENTS

The overall goal of this research is to develop numerical models for estimating various water quality properties in Rhode Island river basins, especially the Blackstone River. The numerical results can then be compared with existing data and, once verified, applied to management problems by making parametric studies to determine the overall dynamics of the basin.

The type of numerical model chosen was a one-dimensional unsteady system with variable cross-sectional area, volume flow rate, and longitudinal diffusion rate. If C is the concentration of the given water quality variable - for example, phosphorus - the basic partial differential equation was taken to be

$$\frac{\partial}{\partial t}(AC) + \frac{\partial}{\partial x}(UAC) = \frac{\partial}{\partial x}\left(EA\frac{\partial C}{\partial x}\right) - KAC + AS \qquad (1)$$

where:
A = cross-sectional area
U = flow velocity
E = longitudinal diffusion coefficient
K = first order decay coefficient
S = source for the variable C

The primary dependent variable is the concentration C. The area variations A(x,t) are taken from known river bathymetry plus tidal variations, if any. The coefficients E and K may be approximated from known engineering correlations or may be estimated from data for the specific river. The source distribution S(x,t) is taken from known point discharges along the river.

As mentioned in the 1975 Annual Report, our initial attempts were adapted from an existing water quality model developed by C. H. Lee and D. R. F. Harleman at M.I.T. For the particular geometry and sources extant in the Blackstone River Basin, these calculations exhibited some pathology and instability, and it was decided to develop another model. An implicit finite-difference technique published by H. L. Stone and P. L. T. Brian [A.I.Ch.E. JOURNAL, Vol. 9, No. 5, Sept. 1963, pp 681-688] was used in the new model. This technique provides satisfactory numerical stability even in the absence of diffusive smoothing terms.

A map of the Blackstone River Basin is shown in Figure 1. It has a length of approximately 53 miles from Auburn, Massachusetts to where it enters the Seekonk River in Central Falls, Rhode Island. There are numerous tributaries, of which the five most important are shown: the Quinsigamond, Mumford, West, Branch, and Mill Rivers. These tributaries add considerable discharge so that the river flow rate increases by about a factor of five from Worcester to Central

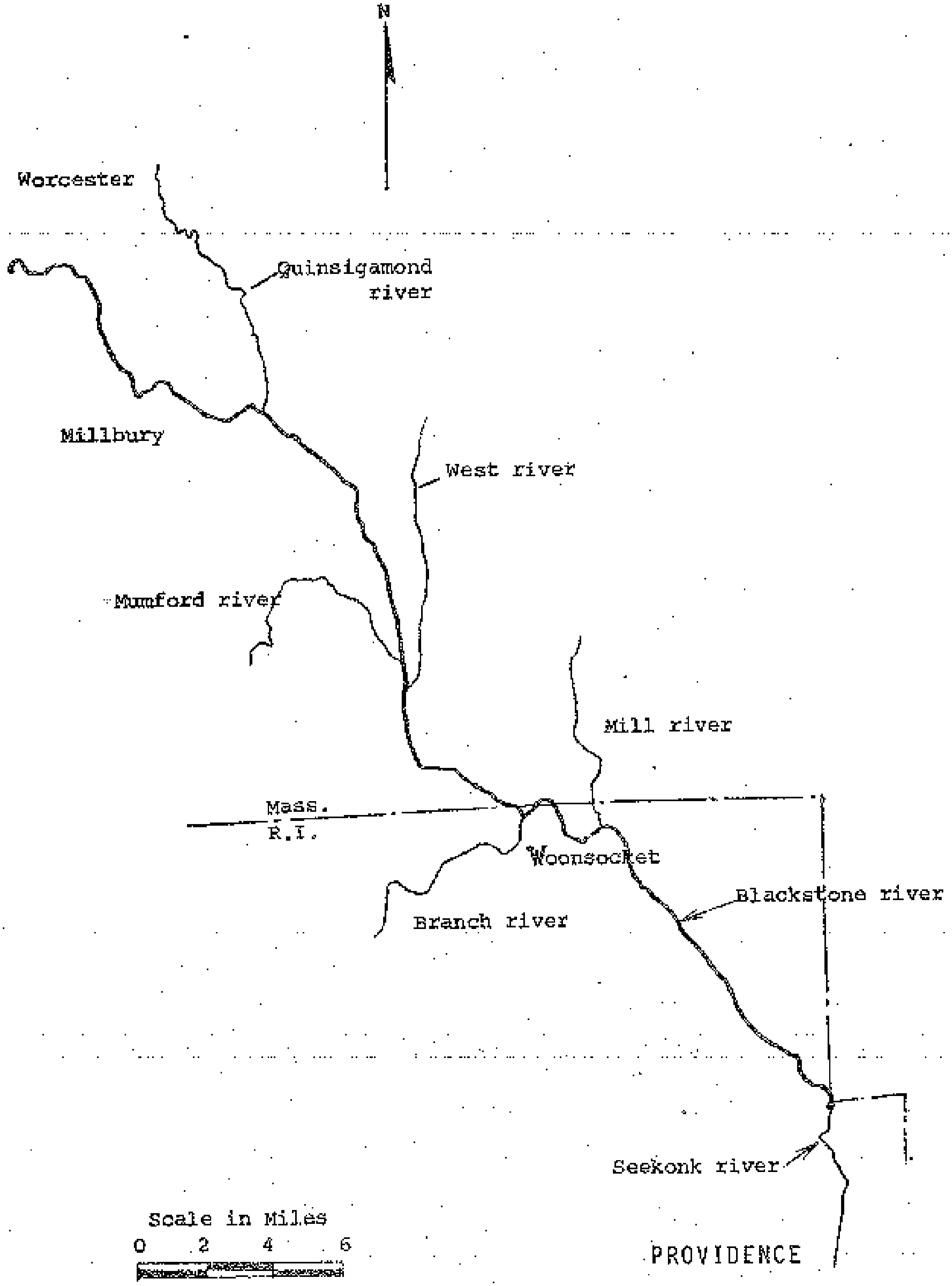


Figure 1. THE BLACKSTONE RIVER BASIN.

Falls. There are also five major sewage plants discharging into the river: Worcester, Millbury, Grafton, Northbridge, and Woonsocket. Various industries along the river contribute smaller discharges, the four most important being the Quincy Dye Works, the Enterprise Dye Works, the Rochambeau Worsted Company, and the Owens-Corning Fiberglas Company.

For the purposes of this annual report, the results of the model computations will be given for only a single water quality parameter: phosphate concentration. Computations for many other parameters, e.g. dissolved oxygen and coliform bacteria, are given in the 1976 Completion Report. The design values for principal points of water and phosphate discharge are given in Table 1. There are twelve important source points with an accumulated water discharge of 300 cubic feet per second and accumulated phosphate discharge of 1936 pounds per day. These values were entered as data in the computer model and the resulting phosphate concentrations computed along the river.

The river was divided into 57 segments of approximately 5000 ft length each. From examination of various water quality data in the river, the following coefficient values were chosen:

Decay Coefficient: $K = 0.4$ per day
Turbulent Diffusion: $E = 1600\ \text{ft}^2/\text{sec}$

TABLE 1

PHOSPHATE DISCHARGE DESIGN DATA FOR THE BLACKSTONE RIVER BASIN

FINITE DIFFERENCE SEGMENT NUMBER	X = DOWNSTREAM DISTANCE IN FEET	WATER DISCHARGE, C.F.S.	PHOSPHATE DISCHARGE, LBS/DAY
3 (Kettle Brook)	12,300	54	73
8 (Worcester STP)	39,300	5	447
12 (Millbury STP)	62,300	3	244
16 (Quinsigamond R.)	81,800	44	28
18 (Grafton STP)	90,300	4	287
24 (Northbridge STP)	121,800	3	204
28 (Mumford River)	144,300	54	35
30 (West River)	153,300	51	14
37 (Branch River)	184,300	55	42
41 (Mill River)	204,300	16	6
43 (Woonsocket STP)	213,300	10	468
45 (Roch. Worsted Co.)	226,300	1	88
	TOTALS:	300 CFS	1936 LB/DAY

The upstream boundary condition was taken as a phosphate concentration of 0.01 mg/l as measured near segment No. 1 just north of Auburn, Massachusetts. The cross-sectional area variation for the 57 segments are shown in Figure 3. Figure 2 shows the monthly average water flow rates at Woonsocket, R.I. as measured during 1973-74. It is seen that the design flow rates correspond to the summer or low-flow condition for which the constituent concentrations are highest. There are no tidal flow variations in the Blackstone River because of the dam in Central Falls, R.I. which separates the river from Narragansett Bay tides.

Figure 4 shows the computed variation of phosphate concentration in the Blackstone River as compared to measured data obtained from the Rhode Island Department of Health and the U. S. Army Corps of Engineers. The agreement is satisfactory but there are deviations near segment 10, indicating some uncertainty in the design discharge data near Worcester. The generally high phosphate concentrations in the upper river are basically due to the low flow rates, which provide inadequate dilution. The five-fold increase in flow rate is the primary cause of the decreased concentrations toward Woonsocket, which has comparable phosphate discharges but more dilution. This is a general conclusion which can be applied to other water quality parameters, as discussed in the project Completion Report.

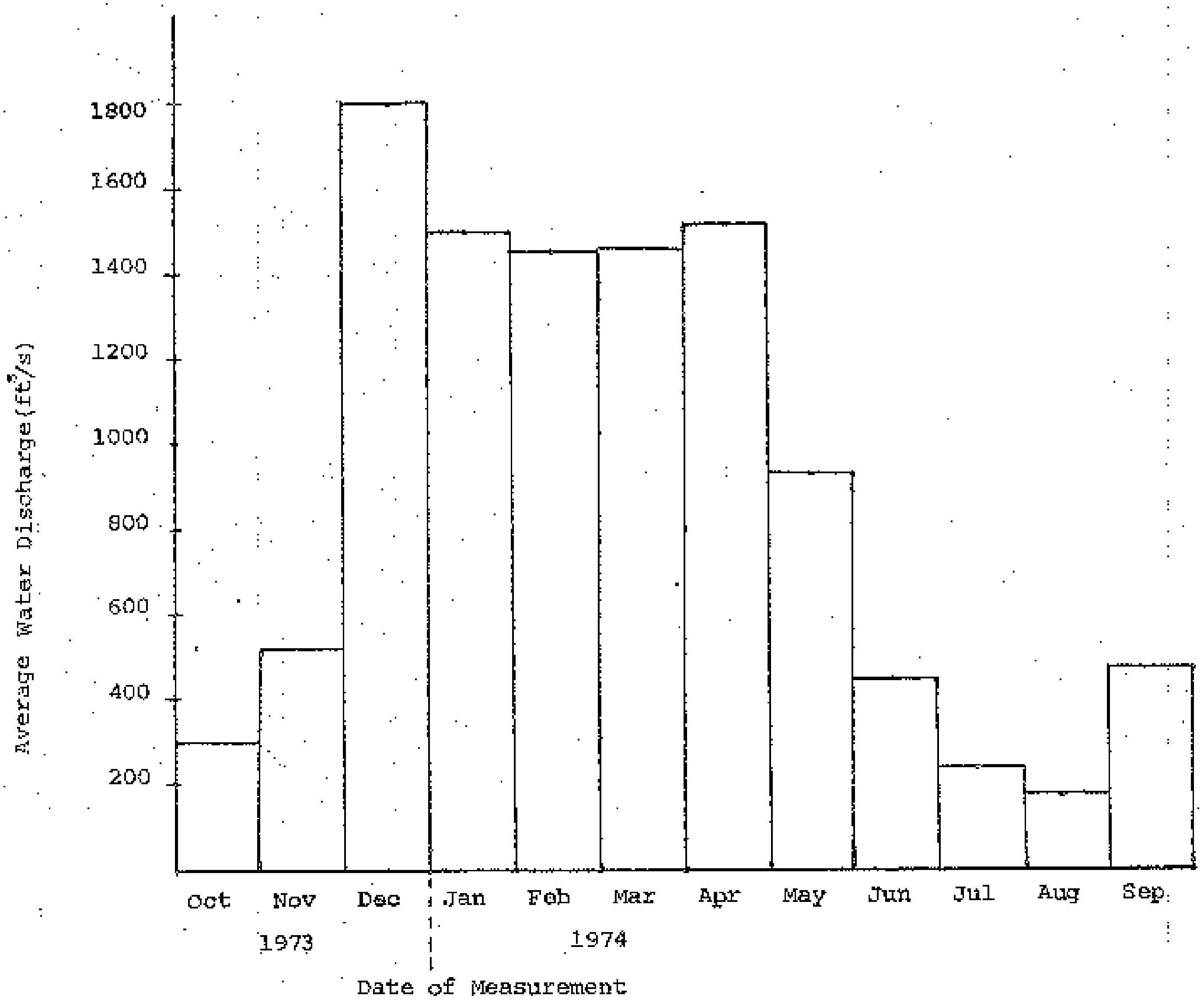


Figure 2. BLACKSTONE RIVER AVERAGE WATER DISCHARGE AT WOONSOCKET, R.I.

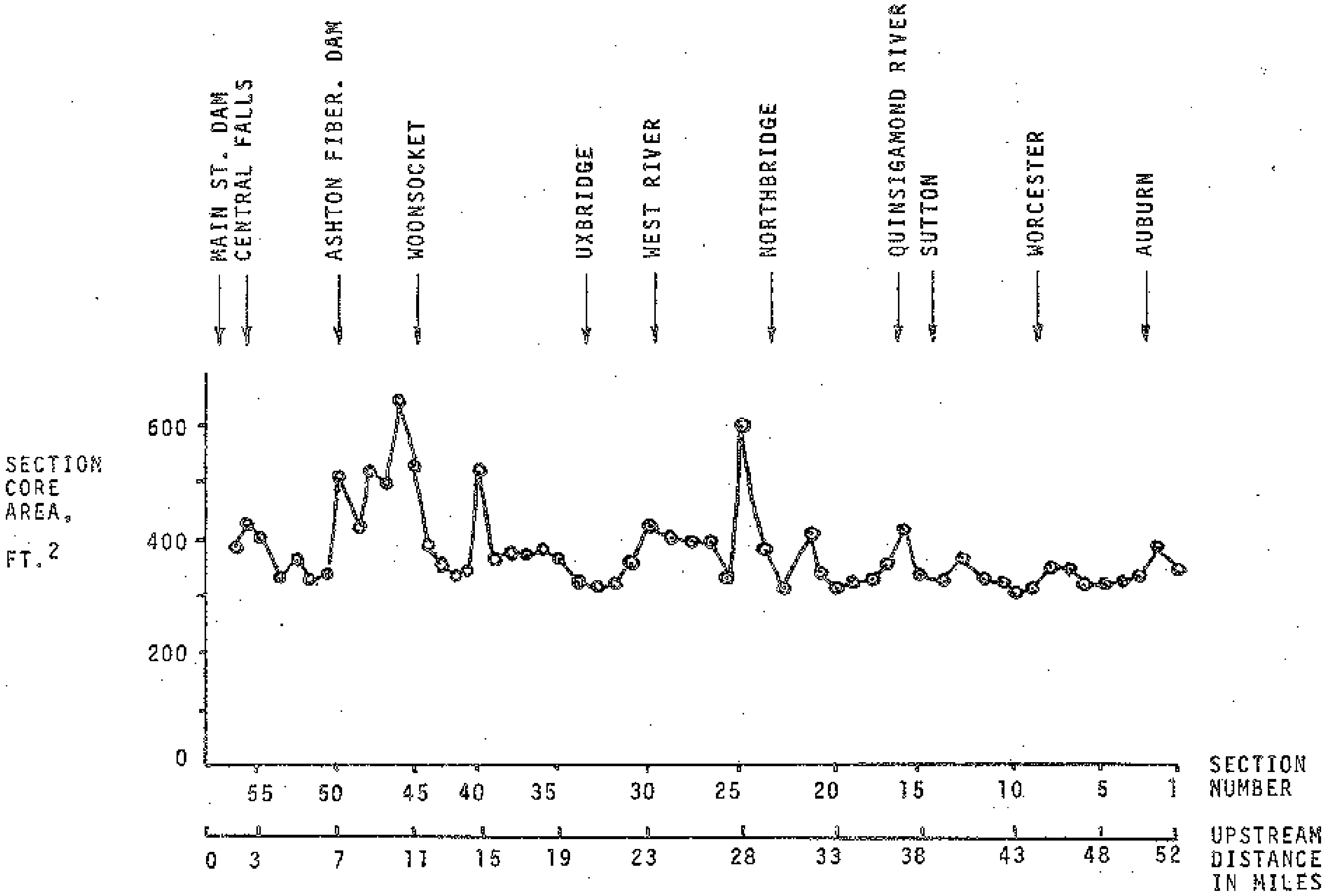


Figure 3. CORE CROSS-SECTIONAL AREAS OF THE BLACKSTONE MODEL SEGMENTS.

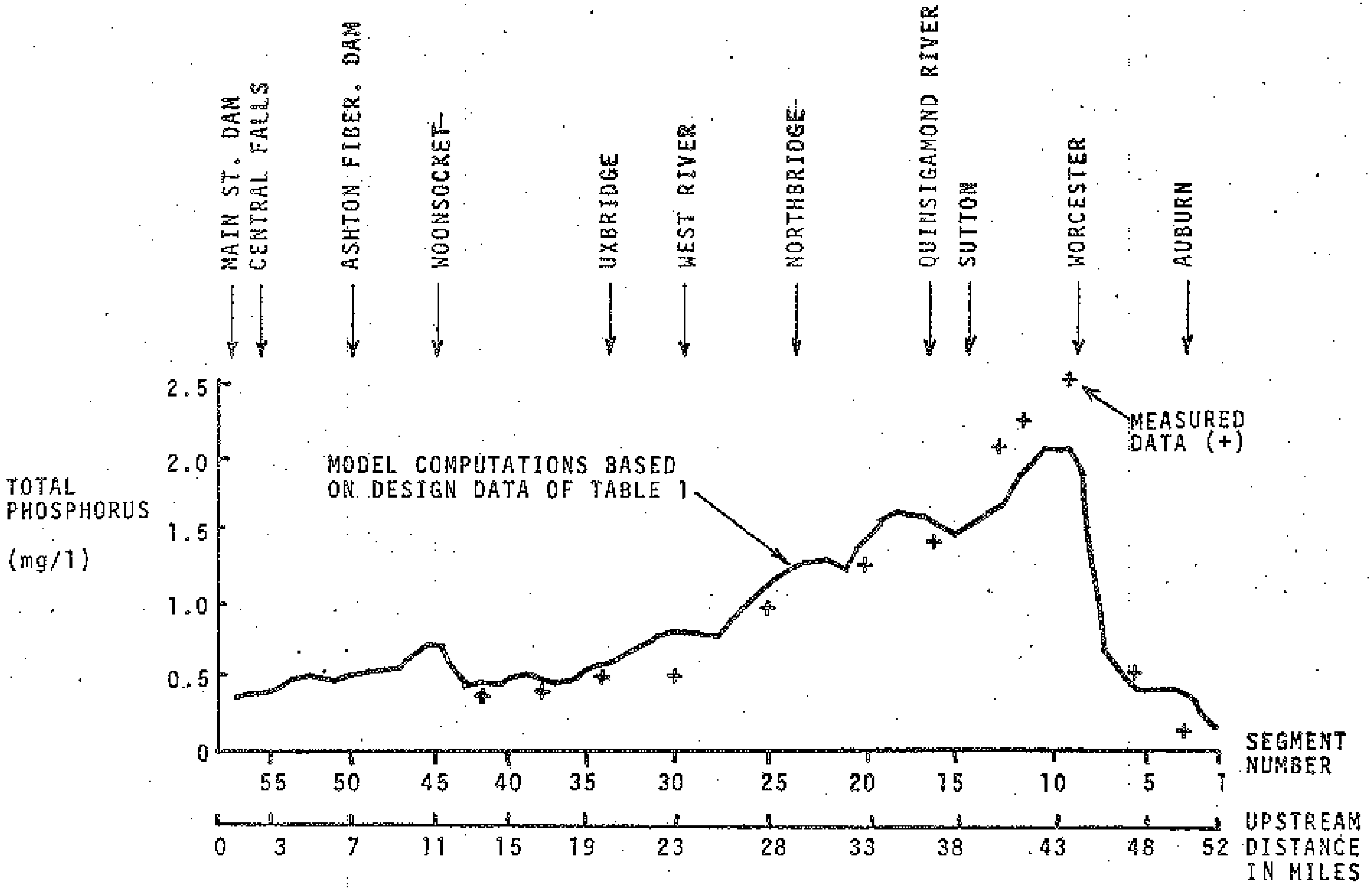


Figure 4. COMPARISON OF THEORY AND EXPERIMENT FOR PHOSPHATE CONCENTRATIONS IN THE BLACKSTONE RIVER BASIN.

The computer model has a short run time of the order of seconds and the cost of a given parameter computation is approximately $ 1.00 on the IBM 370/155 computer at the University of Rhode Island. Thus a variety of parametric computations can be made economically for management purposes. It is hoped that the model will be of use to agencies in the region concerned with water resource planning.

WORK REMAINING

None. The project has terminated and a Completion Report has been prepared.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-060-RI

Agreement No. 14-34-0001- 6041

FCST-COWRR Research Category: VC, IV

Project Title: Fate of the Organophosphate Insecticide Parathion in Freshwater Invertebrates

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, R. I. 02881

Proj. Began--Month: Jan. 1, ; Year: 1975

To Be Completed--Month: Oct. 1, ; Year: 1976

Principal Investigators	Degree	Discipline
Gary P. Carlson	B.S. Ph.D.	Chemistry Pharmacology
George C. Fuller	Ph.D.	Pharmacology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Leslie A. Goldsmith	B.S. M.S.	Biology Pharmacology & Toxicology

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. A-060 RI Agreement No. 14-34-0001-6041 FCST-COWRR Research Category: VC, IV	Project Title: Fate of the Organophosphate Insecticide Parathion in Freshwater Invertebrates

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: Jan. 1; Year: 1975 To Be Completed--Month: Oct. 1; Year: 1976

Principal Investigators	Degree	Discipline
Gary P. Carlson	B.S. Ph.D.	Chemistry Pharmacology
George C. Fuller	Ph.D.	Pharmacology

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Leslie A. Goldsmith	B.S.	Biology
	M.S.	Pharmacology & Toxicology

A. Research Project Accomplishments

This project is concerned with the uptake, metabolism and excretion of the organophosphate insecticide parathion by two freshwater species, the crayfish, Cambarus and the snail, Viviparus. It is designed to measure the toxicity of this particular pesticide to these species in relation to their ability to take it upp metabolize it to the active metabolite paraoxon and inactive metabolites, principly p-nitrophenol, and finally excrete the pesticide. All three processes are important, not only in relation to the toxicity of this pesticide to the species studied, but also to other species which may use these as a source of food.

The previous annual report established that there was indeed a great disparity in the susceptibility of the two species to parathion toxicity. That report noted that a preliminary toxicity determination indicated that the snails were able to tolerate 12mg/l while crayfish succumbed at a concentration in water of 2 μg/l in 18 hrs. Expansion of that investigation this last year has established that the snail is not only insensitive to very high concentrations of parathion but that the toxic metabolite of parathion, paraoxon did not produce toxic effects on the gastropods. This was tested using the method of the American Public Health Assoc. Astonishingly even concentrations as high as 200 mg/l of paraoxon were ineffective in causing toxicity to snails. These data support the findings associated with the in vitro data acquired by incubation of various snail tissues with parathion. Consistanly there was no metabolism of the parathion detected via the presence of p-nitrophenol, the common metabolic by-product of parathion metabolism with the in vitro technique. The in vitro data did indicate that the snails were resistant to parathion toxicity through a lack of metabolic enzymes to convert the parathion to paraoxon, however this paraoxon resistant data shows that even if paraoxon was formed by the snail the compound would not cause toxicity.

The toxicity of parathion to the crayfish was thoroughly investigated in this last year in order to expand the initial data of the year before. The data clearly shows that extremely low concentrations of parathion cause acute toxicity. Using the American Public Health Assoc. procedures for lethal concentrations and time determination values 3.15 µg/liter was able to kill 50% of a group of animals in 24 hrs. (TL_m 3.15 µg/l/24hr)

Thin Layer Chromatography

Thin layer chromatography was investigated as a possible technique for identifying the metabolites of parathion, and the compound itself after extraction and concentration from either water or tissue samples. This technique was important as it would be possible to extract the compound off the TLC plate for gas chromatographic analysis. Using silical gel G plates 250 microns thick and a solvent mixture of hexane chloroform methanol in ratios of 7:2:1 it was established that concentrations as low as 1.0 µg could be identified with the aid of Rhodamine B spray, and that the spot could indeed be eluted off the plate for gas chromatographic analysis or scintilation counting in the event of radioactive samples. The Rf values for the metabolites with this system were determined as follows: Parathion 63, Paraoxon 32, p-nitrophenol 18, Diethylthiophosphate 74, Diethylphosphate 9.

Extraction

The extraction of parathion and its metabolites from water and tissue samples is central to this project. Using radioactive parathion to monitor the percent recovery of parathion from the water samples tested the procedure of using 3 hexane extractions followed by sodium sulfate drying and rotary evaporator concentration consistantly produced between 85 and 95 percent recovery. Unfortunately the hexane extraction did not contain the p-nitrophenol and paraoxon metabolites so chloroform and ether are now used.

Gas Chromatography

The gas chromatographic analysis of small amounts of parathion and metabolites that could be extracted and concentrated from water or tissue with or with out the aid of initial TLC preparation has been worked on this year. Using a 6' glass column with Chromasorb WAW 80-100 packing with DC 200 as the stationary phase aided by carbowax treatment consistant peaks and retention volumes have been recorded for parathion, paraoxon and p-nitrophenol. This is important as the amounts of parathion used in the crayfish experiments are so small and the technique can be used to verify the TLC determinations.

B. Publications

Toxicity and Identification of Parathion Metabolites in Freshwater Crayfish (Cambarus) and Snail (Viviparus) Les A. Goldsmith, Gary P. Carlson, and George C. Fuller, Volume 18 1976 The Pharmacologist.

C. Project Status

Project is being continued until October 1, 1976.

D. Application of Research Results

The final results will be useful in gaining a better knowledge of the relationship between metabolism of parathion by freshwater invertebrates and its toxicity to them. This is especially important in view of the fact that such species are often important members of food chains. In addition, the information obtained will allow evaluation of these species as environmental monitors.

The monitor aspect of the project has gained increased significance by the fact that the lethal range for parathion to crayfish is very close to the concentration that can be attained via ordinary farm spraying.

E. Work Remaining, and Progress Contemplated During Next Year

The application of the techniques perfected to determine the metabolites formed by the species still needs to be completed. The perfection of extraction and clean up procedures for the tissue samples also need to be done. These two areas plus an organization of the pertinant data in a report will be completed in the summer of 1976.

Form OW-1 (1972)

ANNUAL REPORT — TITLE I PROJECT

OWRR Project No. A-061-RI

Agreement No. 14-31-0001- 6041

FCST-OWRR Research Category: IIA.V

Project Title: Ground Water Computer Model of the Chipuxet Aquifer in the Upper Pawcatuck River Basin

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, RI 02881

Proj. Began—Month: 7/1 ; Year: 75

To Be Completed—Month: 6/30 ; Year: 77

Principal Investigators	Degree	Discipline
Alan S. Marcus	Ph.D.	Civil Engineering
William E. Kelly	Ph.D.	Civil Engineering
Louis J. Kirschenbaum	Ph.D.	Chemistry

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Daniel Urish	M.S.	Civil Engineering
Philip Sirios	B.S.	Civil Engineering
Cheryl Babcock	B.S.	Civil Engineering
John Spirito	B.S.	Civil Engineering
David Sexton	B.S.	Chemistry
Ricci Siciliano	-	Chemistry
David Dickinson	B.S.	Chemistry

ANNUAL REPORT

A-061

Ground Water Computer Model of the Chipuxet Aquifer in the Upper Pawcatuck River Basin

July 1, 1975 - June 30, 1977

Alan S. Marcus
Civil and Environmental Engineering
University of Rhode Island
Kingston, R. I. 02881

OWRR Project No. A-061-RI

Ground Water Computer Model of the Chipuxet Aquifer in the Upper Pawcatuck River Basin

Dr. William E. Kelly
Dr. Louis J. Kirschenbaum
Dr. Alan S. Marcus

Research Project Accomplishments

During the first year water samples have been taken and analyzed on a regular basis. Well points of polypropylene have been driven to approximately ten foot depths at various locations along the Chipuxet River. The plastic sampling system was introduced both to increase the reliability of the chemical analysis, especially for trace metal ions, and to give a better idea of the effect of galvanized iron wells on the actual chemical analysis. Galvanized wells already in place were also used for sampling stations.

Routine Chemical Analysis

Procedures have been devised or extracted from the literature for the rapid analysis (same day as sampling) of most of the ionic components found in ground water. Routine analyses include anions (e.g. Cl^-, NO_3^-) alkali and akaline earth metal cations, iron, manganese, alkalinity and total hardness. Other data necessary for the model such as temperature, pH, conductivity of samples, rainfall, water table, stream level and stream flow are also being recorded.

Trace Metals

Detection of metals such as Hg, Cd, Zn, Mn, Cu, Pb, etc., at the parts per billion level have traditionally been achieved by uv-visible or atomic absorption spectrophotometry following some extraction or concentration process. We have performed some of these analyses after concentration by evaporation, ion exchange and solvent extraction have concluded that these are too time consuming for our limited personnel. We have therefore purchased the necessary instrumentation for electrochemical quantitation (by polarography and anodic stripping voltammetry) of these elements. Analysis for Zinc, Cadmium, Lead and Copper are now routine.

Project Status

Based on the first year's measurements, specific conductance seems to be the most appropriate parameter for computer modeling. It is hoped that continued study of chemical water quality will yield data consistent with this model. Work will continue in the second year with emphasis in these two areas.

Application of Research Results

It is expected that the water quality data and computer model can be a basis for better management of the Chipuxet Aquifer and as a basis for managing other aquifers. The Rhode Island Water Resources Board plans to model additional aquifers in southern Rhode Island.

Work Remaining and Progress Contemplated During Next Year

Water sampling will continue while a major emphasis is placed on the development of one or more mathematical models to correlate our observations with water flow through the aquifer.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-061-RI

Agreement No. 14-31-0001- 3953

FCST-COWRR Research Category: VI B

Project Title:
Analysis of Critical Water Problems in th
Northeastern United States to Determine
Essential Research Requirements

Name and Location of University Where Project is Being Carried Out:
Various locations in Northeastern United States. Designated fiscal agent
University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: March ; Year: 1973

To Be Completed--Month: Feb. 28; Year: 1977

Principal Investigators	Degree	Discipline
A. Ralph Thompson	Ph.D.	Chemical Engineering

Co-Principal Investigators: Directors of other Northeastern Water Resources Centers or Institutes

ANNUAL REPORT

B-061

ANALYSIS OF CRITICAL WATER PROBLEMS IN THE NORTHEASTERN UNITED STATES TO DETERMINE ESSENTIAL RESEARCH REQUIREMENTS

March 1973 to February 28, 1977

A. Ralph Thompson
R.I. Water Resources Center
University of Rhode Island
Kingston, Rhode Island 02881

On March 11-12, 1976 a workshop supported by this project was held at the University of Connecticut, Storrs, Conn. The regional workshop considered "River Management Research Needs" and was attended by over 50 individuals vitally interested in the problem.

The first day was aimed at past experience with a variety of approaches to river modeling and related studies while the second day considered recommendations for the future. Specific topics studied in the workshops included:

Case Studies in River Modeling
Distinction Between Research and Management
Effectiveness of Regional Collaboration
Transferability of Research Data

A second workshop conference was supported during the year by this project on May 24-25, 1976 at the New England Center for Continuing Education, Durham, New Hampshire. The general topic for the conference was "Implementation of Non-Structural Alternatives in Flood Damage Abatement".

The program began with a plenary session on the first morning which reflected on the state of non-structural implementation and on assessments of informational and research needs to facilitate implementation. The afternoon session consisted of three concurrent workshops considering informational needs specific to:

(1) insurance and rehabilitation programs
(2) local implementation
(3) land management alternatives

The second plenary session on the next morning consisted of workshop reports plus an open discussion of informational needs for an integrated approach with consideration of all non-structural alternatives.

Also during fiscal year 1976 the project gave financial support to the publication of a compendium of summaries of water resources research, active during the year, in the north-eastern United States and Puerto Rico. This compilation was carried out by the Water Resources Center at the University of Delaware on behalf of the Northeast Water Institute Directors (NEWID).

Limited numbers of copies of the Proceedings of the two workshop conferences and of the Compendium of water resources research will be available upon request.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-062-RI

Agreement No. 14-31-0001-5110

FCST-COWRR Research Category: ____

Project Title:

The Capacity of Salt Marsh Vegetation to Modify the Quality of Estuarine Waters.

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Kingston, Rhode Island 02881

Proj. Began--Month: June 1 ; Year: 1974 To Be Completed--Month: Sept. 30 Year: 1976

Principal Investigators	Degree	Discipline
Richard J. Hull	Ph.D.	Plant Physiology

Student Assistants	Degree Held	Discipline or Academic Background
Carl D. Sawyer	B.S.	Plant and Soil Science and Geography
Anne F. Wrona	B.S.	Botany

ANNUAL REPORT

B-062

The Capacity of Salt Marsh Vegetation to Modify the Quality of Estuarine Waters

June 1, 1974 - September 30, 1976

Richard J. Hull
Plant Physiology
University of Rhode Island
Kingston, R. I. 02881

THE CAPACITY OF SALT MARSH VEGETATION TO MODIFY THE QUALITY OF ESTUARINE WATERS

(A) RESEARCH PROJECT ACCOMPLISHMENTS

The efficiency of nutrient removal from estuarine waters by tidal marsh vegetation depends upon nutrient penetration of marsh sediments and the capacity of marsh plants to abosrb nutrients from these sediments. The high salinities, 25-30 ppt, of tidal marsh sediment water and the water-logged condition of the sediment present environmental factors which probably influence nutrient uptake by plant roots growing on tidal marshes. This study has demonstrated that nutrient flux through marsh sediment occurs with rapidity and plants growing in these sediments absorb nutrients. The environmental conditions characteristic of tidal marsh sediments do not appear to inhibit nutrient absorption by roots growing in them.

Methods

A set of 18 plots, 3m square, were established adjacent to a tidal stream on the Succotash Salt Marsh at Jerusalem, Rhode Island. The principal vegetation on these plots was salt water cordgrass, Spartina alterniflora. This is a fairly new marsh having a substrate composed of a surface layer of partially decomposed plant debris mixed with fine sand and silt to a depth of 10-15 cm over a meter or more of fine to course sand. Most living roots were in the upper 30 cm of sediment.

Half of the plots were edged with plastic "weedguard" dug into the sediment to form a 5 cm rim around the plot. This rim restricted the flow of tidal water off the marsh and may promote penetration of the sediment by flood water. Three wells were established in each plot at 15, 30, and 60 cm into the sediment. The wells, consisting of 5 cm diameter ABS pipe, extended

45 cm above the sediment surface and were capped by a coupling and clean out to exclude rain and surface tidal water. A pinhole drilled just below the coupling permitted the water level within the pipes to rise and fall.

On July 2, 1975 plots were fertilized with two rates of N and P; 5-2.5 and 10-5 gN-P/m^2. An identical application was made on July 31. N was applied as urea (45%N) and P as superphosphate (8.8%P). Materials were mixed with quartz sand and applied by hand during low tide. Fertilizer rates and water flow restrictions were set out as a factorial experiment in a randomized complete block design. There were three replications.

At weekly intervals following fertilizer application, water samples were collected from the wells. Samples were filtered, acidified to pH 3-4 with HCl, and aerated to remove H_2S. Ammonium was measured by the phenol-hypochlorite method of Solorzano (1969) and PO_4^{-3} was measured using the Fiske Subbarow (1925) method.

On July 31 and again on September 15, a 0.25 m^2 area of each plot was harvested of all S. alterniflora. On September 30, a 316 cm^2 block of sediment was lifted from each plot and all rhizomes washed free of sediment and roots removed. All samples were oven dried, weighed, ground to pass a 40 mesh screen, and analyzed for Kjeldahl N and P using standard methods (Horwitz 1970).

Ammonium and phosphate uptake by Spartina patens as influenced by salinity and oxygen content of the nutrient solution was measured by determining nutrient depletion from solutions in which plants were growing. Salinity was measured over the range of 0 to 25 ppt NaCl and solution oxygen over a range of 5.5 to <1 ml O_2/l.

Results and Discussion

Nutrient Mobility Within Sediment:

The concentration of N and P in marsh sediment water following surface applications of N and P in soluble form are presented in Figure 1. Results from the 30 cm wells are presented but similar observations were obtained from the 15 and 60 cm wells. Within a few days of surface application, significant increases in NH_4^+ and PO_4^{-3} were detected in sediment water samples taken from all well depths. Within two weeks of the time of application, sediment water samples returned to background levels of NH_4^+ and PO_4^{-3}. The rapid loss of soluble nutrients from sediment water results from absorption by plant roots, flushing by tidal flooding, or binding within the sediment solid phase. The following section indicates that plant uptake accounts for some of the nutrient loss. Restricted drainage of tidal water off the marsh surface slightly increased nutrient penetration into the sediment as was stated in our report of last year (Hull 1975). Drainage effects were small however so only fertilizer rate effects are reported here.

Nutrient Uptake by Marsh Plants:

Surface applied nutrients stimulated top growth of S. alterniflora although variation within the plot area prevented the yield differences from being statistically significant (Table 1). September harvests were no larger than those of late July due to loss of lower leaves and the fact that flower initiation occurs in mid-summer after which there is little further shoot growth. Only S. alterniflora was harvested from the plots and any growth of companion species principally Salicornia europaea was not recorded. Heavy growth of Salicornia was noted on some plots during the late summer. Rhizome growth did not respond to fertilization possibly

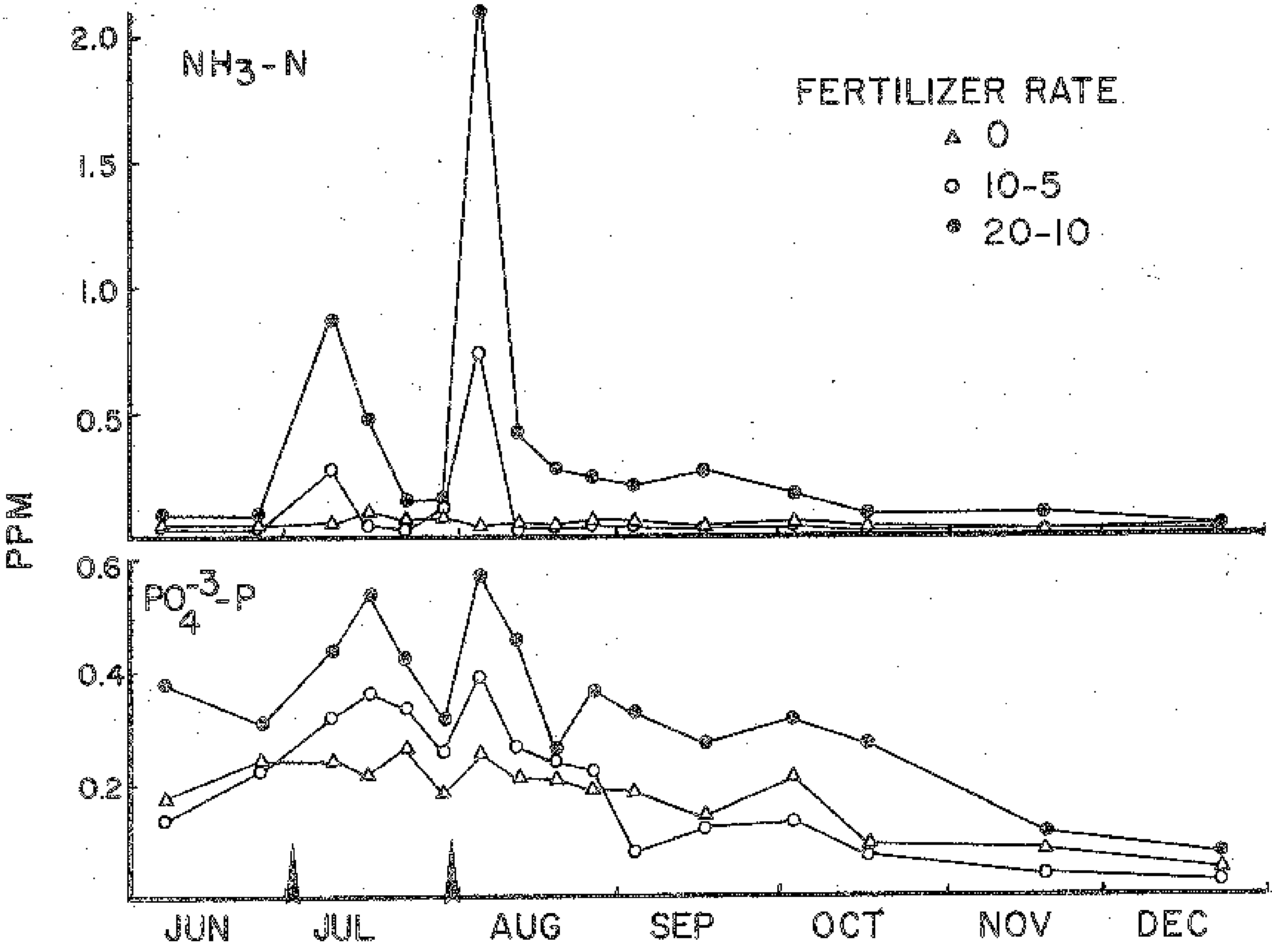


Figure 1. Ammonium and phosphate content of marsh sediment water sampled at 30 cm depth. Fertilizer applications were made on 7-2-75 and 7/31/75.

Table 1. Dry Weight Yields of S. alterniflora harvested from plots receiving 3 rates of N and P

Fertilizer rate	Yields – Dry Weight		
	Shoots		Rhizomes
	7-31-75	9-15-75	9-30-75
g N-P/m^2		g/m^2	
0	354	336	211
10-5	439	432	286
20-10	491	456	249

due to the perennial character of these organs and the short duration of increased fertility.

The N and P content of S. alterniflora shoots and rhizomes was increased by nutrient application (Table 2). Fertilizer rate differences were not reflected in nutrient content of plants but nonfertilized plots yielded grass with significantly lower N and P levels. These data suggest that under the conditions of the Succotash Salt Marsh the growth rate of S. alterniflora may be limited by N or P or both.

Greater amounts of N and P were removed from nutrient enriched plots than from nonfertilized plots (Table 3). A rate response was noted with N but less so with P. Again yield variability of rhizomes prevented nutrient removal by these organs from showing a significant response to fertilization. Considering the July 31 harvest when the plots had received half of their fertilizer rate and assuming half of the rhizome nutrient increase was obtained from the initial fertilizer increment, the N recovery for the low and high fertilizer rates was 42 and 37% respectively. The recovery of low and high P applications was 21 and 11% respectively. These values must be highly conservative because they do not reflect leaf loss during the four weeks from fertilizer application to harvest, nutritents contained in roots which were not harvested, and nutrients absorbed by plants including microflora other than S. alterniflora. Taking these sources of error into account we conclude that nutrient recovery by S. alterniflora is reasonably efficient.

Nutrient Uptake as Influenced by Salinity and Aeration:

The impact of salinity and reduced oxygen levels on nutrient uptake by tidal marsh grasses was studied under greenhouse conditions using salt meadow cordgrass, Spartina patens. The results of several experiments

Table 2. N and P content of S. alterniflora plants harvested following application of N and P fertilizer

Fertilizer Rate	Shoots				Rhizomes	
	7-31-75		9-15-75		9-30-75	
	N	P	N	P	N	P
g N-P/m^2	% Dry Weight					
0	1.68 a*	0.19 a	1.61 a	0.16 a	0.72 a	0.12 a
10-5	1.72 a	0.23 b	1.73 b	0.19 b	0.89 b	0.16 b
20-10	1.78 a	0.22 b	1.74 b	0.19 b	0.94 b	0.16 b

* Means in a column followed by the same letter are not significantly different at the 5% level.

Table 3. N and P recovered in *S. alterniflora* harvested from marsh plots fertilized with N and P

Fertilizer Rate	Shoots				Rhizomes	
	7-31-75		9-15-75		9-30-73	
	N	P	N	P	N	P
g N-P/m^2			g/m^2			
0	5.99 a*	0.69 a	5.47 a	0.53 a	1.51 a	0.26 a
10-5	7.54 ab	1.02 b	7.47 ab	0.82 b	2.60 a	0.45 a
20-10	8.86 b	1.11 b	7.99 b	0.88 b	2.32 a	0.39 a

* Means in a column followed by the same letter are not significantly different at the 5% level.

measuring PO_4^{-3} and NH_4^+ uptake are summarized in Table 4. Optimal salinity for NH_4^+ absorption was about 12 ppt, however, respectible absorption rates were obtained over the range of 6 to 15 ppt. These salinities are less than tidal marsh sediment water which normally is greater than 20 ppt. Nevertheless, a definite adaptation to high salinity by this grass is indicated.

Uptake of PO_4^{-3} was slow and showed no clear salinity optimum. The nutrient solutions used were not buffered and the pH of high salt solutions tended to increase as plants grew in them. The pka of 7.2 for

$$H_2PO_4^- \rightleftharpoons H\ PO_4^{-2}$$

was approached in some cases which would have the effect of exposing the roots to a mixture of the mono- and divalent forms of PO_4^{-3}. This could explain the low uptake rates at higher salinities.

Nutrient uptake as a function of solution aeration is graphed in Figure 2. Solution oxygen levels were establsihed as follows: A, solution aerated with compressed air; C, solution non-aerated; N, nitrogen bubbled through solution; O, solution purged with N_2 and layered with mineral oil during uptake. Oxygen levels of the nutrient solution had no effect on rates of NH_4^+ uptake. Only the mineral oil layered solution depressed ion uptake. Histological observation revealed that the mineral oil had penetrated the grass stem and filled the internal aerenchyma presumably blocking the free exchange of gas between roots and atmosphere. This internal gas exchange within tidal marsh grasses apparently is the mechanism by which low sediment oxygen levels are tolerated. These data indicate that Spartina grasses are uniquely adapted to optimum nutrient absorption under tidal marsh conditions.

Table 4. Effect of salinity on NH_4^+ and PO_4^{-3} uptake by S. patens grown in nutrient solution under greenhouse conditions. Average of two experiments.

Salinity	Uptake Rate	
	NH_4^+	PO_4^{-3}
ppt	µM/g/hr	
0	0.12 a*	0.12 a
3	0.48 ab	0.08 a
6	0.83 bc	0.03 a
9	0.65 ab	0.10 a
12	1.41 c	0.12 a
15	0.68 ab	0.07 a

* Means in a column followed by the same letter are not significantly different at the 5% level.

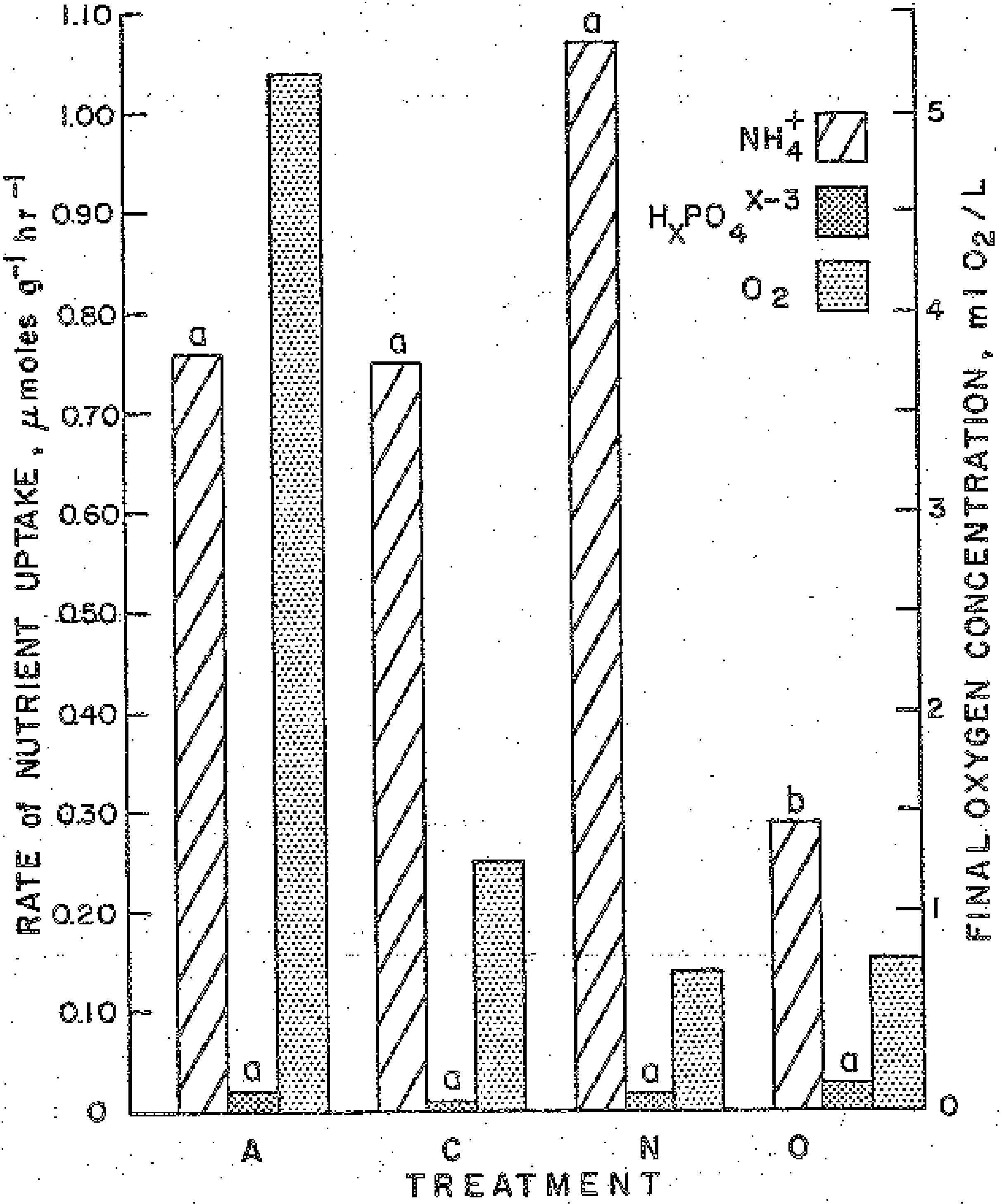


Figure 2. Ammonium and phosphate uptake by S. patens as affected by solution oxygen content. A = aerated, C = non-aerated, N = nitrogen purged, O = nitrogen purged followed by layering with mineral oil. Like bars surmounted by the same letter are not significantly different at the 5% level.

Conclusions

Surface applied water soluble nutrients effectively penetrate tidal marsh sediments and are efficiently absorbed by tidal marsh grasses. The halophytic cord grasses are well adapted for efficient nutrient retrieval from marsh sediments. These findings support the concept that tidal marsh vegetation exerts an ameliorating effect on estuarine water quality by removing dissolved nutrients and possibly other elements before they enter the marine environment.

Literature Cited

Fiske, C. H. and Y. Subbarow. 1925. The colorimetric determination of phosphorus. J. Biol. Chem. 66: 375-400.

Horwitz, W. 1970. Official methods of analysis of the Association of Official Analytical Chemists (Ed. 11). Assoc. Off. Anal. Chem., Washington, D.C.

Hull, R. J. 1975. The capacity of salt marsh vegetation to modify the quality of estuarine waters. Ann. Rept., R. I. Water Res. Center. 11:57-60.

Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnol. Oceanogr. 14: 799-801.

(B) PUBLICATIONS

Wrona, Anne. 1976. Nutrient uptake and growth of Spartina patens as a function of salinity and oxygen concentration. M.S. Thesis, University of Rhode Island.

(C) PROJECT STATUS

This project is scheduled for completion on September 30. 1976. The work is progressing on schedule.

(D) APPLICATION OF RESEARCH RESULTS

Our findings, that tidal marsh vegetation represents a rather efficient sink for nutrients contained in estuarine waters, offer evidence for an important natural function of tidal marshes. Management programs for tidal marsh areas should be designed so as to maximize the nutrient absorption process. Systematic removal of marsh grass hay may provide an effective means of reducing the nutrient and heavy metal load of estuarine waters.

(E) WORK REMAINING, AND PROGRESS CONTEMPLATED DURING NEXT YEAR

During the three remaining months the following objectives should be accomplished. Some of these are already underway.

Nutrient uptake of *S. alterniflora* as influenced by salinity and oxygen levels similar to that reported for *S. patens* will be completed.

The comparative utilization of NH_4^+ and NO_3^- by *S. alterniflora* under both field and laboratory conditions is underway, and should be completed soon after this project expires.

The flux of surface applied Cd and Zn within tidal marsh sediments will be investigated during this growing season.

Uptake rates of Cd and Zn by *S. alterniflora* roots under controlled conditions will be studied.

The completion of these tasks should fill in many of the gaps in the story of nutrient utilization by tidal marsh grasses outlined in this report.

Form OW-1 (1972)

ANNUAL REPORT -- TITLE I PROJECT

OWRR Project No. B-070-RI

Agreement No. 14-34-0001- 6115

FCST-COWRR Research Category: VD

Project Title:

Fermentation and Enzymatic Saccharification of Cellulose and Lignin Waste.

Name and Location of University Where Project is Being Carried Out:

University of Rhode Island, Bioengineering and Food Laboratory
Kingston, Rhode Island 02881

Proj. Began--Month: July ; Year: 75

To Be Completed--Month: June ; Year: 77

Principal Investigators	Degree	Discipline
Stanley M. Barnett	Assoc. Prof.	Chemical Engineering
C. W. Houston	Professor	Microbiology
A. G. Rand, Jr.	Assoc. Prof.	Food and Resource Chemistry

Student Assistants 1/	Degree Held (if any)	Discipline or Academic Background
Donald Aidala	B.S.	Chemistry
Dana Anderson	B.S.	Chemical Engineering

ANNUAL REPORT

B070 RI

Fermentation and Enzymatic Saccharification of Cellulose and Lignin Wastes

July 1, 1975-June 30, 1977

Stanley M. Barnett
Departments of Chemical Engineering
and Food Science and Technology

University of Rhode Island
Kingston, R.I. 02881

A. Research Project Accomplishments.

This project has observed the effects of different parameters upon the cellulose fermentation process. Experimental runs have been conducted at the shaker flask level with the utilization of T. viride QM9123. Variables considered for the optimization of cellulase yield were pH of the medium, temperature, concentration of the substrate, peptone concentration, urea concentration, and concentration of surfactant.

The organism together with nutrient salts in solution in shaker flasks yielded cellulase; however the quantities of enzyme were enhanced with the addition of a soluble nitrogen source, in this instance peptone and urea. Peptone and urea produced enzyme solutions of higher filter paper activity, however, while peptone concentrations much above .5% were inhibitory to cellulase generation. Cellulose substrate concentration appeared most effective ranging from .5-1.0%, depending upon the peptone concentration. In addition, surfactants were employed in attempts to further enhance cellulase quantities.

Much of the above study has confirmed prior experimental results, and consequently we have scaled up.

Cellulose is accompanied by ligneous material. We feel that it is equally important to investigate possible means of lignin biodegradation. On a shaker flask level we have had some success in generating lignase, and thus further attempts on a large scale set-up, similar to that for cellulose, appear warranted.

B. Publications. None

C. Project Status. Will continue in progress in the next fiscal year.

D. Application of Research Results. Many organizations and companies have expressed interest in this work. Each is interested in a different facet of the study.

E. Work Remaining, and Progress Contemplated During Next Year.

We plan to continue the investigation of fermentation and enzymatic breakdown of cellulose and lignin on a larger scale during the coming year.

Form OW-9 (1972)
Page 1 of 7

ANNUAL REPORT - TRAINING AND EDUCATION ASPECTS OF THE WATER RESEARCH PROGRAM UNDER P.L. 88-379

Name of University:
(or College) UNIVERSITY OF RHODE ISLAND

SUBMIT THE INFORMATION SPECIFIED BELOW FOR THE UNIVERSITY AT WHICH THE WATER RESOURCES RESEARCH INSTITUTE OR CENTER APPROVED UNDER P.L. 88-379 IS LOCATED, AND FOR OTHER UNIVERSITIES WITH WHICH THE INSTITUTE OR CENTER IS COOPERATING. KEEP THE STATISTICS ON ENROLLMENTS, NUMBER OF STUDENTS GRADUATING, EMPLOYMENT STATUS OF GRADUATES, NEW COURSES, ETC., SEPARATE FOR EACH UNIVERSITY. IT IS RECOGNIZED CERTAIN OF THE REQUESTED DATA ON STUDENTS MAY NOT BE READILY AVAILABLE. IF SO, PROVIDE BEST ESTIMATE FIGURES. IN OW-9, DATA ON STUDENTS ARE REQUESTED ONLY FOR THOSE STUDENTS WHO RECEIVED EMPLOYMENT AS RESEARCH PROJECT OR PROGRAM ASSISTANTS THROUGH THE P.L. 88-379 PROGRAM. IF EXTRA SPACE IS NEEDED, ADD PAGES AND NUMBER EACH CONTINUATION ITEM IN THE ORDER SHOWN BELOW.

A. During period since last annual report was submitted provide information on: (See footnote 1/ below.)

(1) New water resources related courses developed. (Give title, state whether interdisciplinary, and give brief description of course. Please indicate if any of these were outgrowths of P.L. 88-379 program activities.)

See accompanying sheet - next page

(2) Water resources related staff members added to fill new positions. (List highest degree obtained and scientific discipline. Indicate which ones received any salary from P.L. 88-379 funds. Do not list staff replacements.)

None

1/ Our intent here is to obtain information on improved academic capability for water resources research and training. Indicate for each position, research facility or other item, whether support was provided in whole or in part through P.L. 88-379 funds, or from other sources; however, also list improvements supported by State or other funds.

(1) New Water Resources related courses developed

ASC 281 - Introduction to Aquaculture

Aquaculture, its contribution to world fuel supply, methods of production, environmental and ecological considerations.

OCE 611 X - Coastal Zone Processes

Near shore coastal circulation and dispersion processes.

OCE 612 X - Numerical Modeling of Coastal Processes

Numerical modeling of coastal circulation, temperature water quality and mass transport.

GEL 100 X (or ESC 100 X) - Environmental Geology

Relationships of geologic processes and physiography to such mass related land-use topics as: geologic hazards, earthquake impact, offshore oil shoreline development, waste disposal and water resources.

A. (Continued)

(3) Water resources related staff members employed to replace those who retired, died, or moved. (List highest degree obtained and scientific discipline. Indicate which ones received any salary from P.L. 88-379 funds.)

NONE

(4) New water resources research and training facilities other than research equipment items. (Include only major facilities such as new laboratories, buildings, etc.)

NONE

(5) Interdepartmental interuniversity or regional agreements consummated with respect to improved research and training capabilities. (To be answered only by institutes under P.L. 88-379. If copies of such institute-related agreements have not been provided OWRR, please provide.)

The Rhode Island Water Resources Center is one of the six partners in the New England regional research project "The Impact of Urbanization on New England Lakes" (C-5342). A Memorandum of Understanding has been signed with the University of Rhode Island which is acting as the fiscal agent for the New England Council of Water Center Directors.

B. Number of students receiving employment as research project or program assistants through the P.L. 88-379 program. (Include only those students, both continuing and graduating, paid wholly or in part with P.L. 88-379 funds during the past fiscal year.)

Category of Students	No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc. 2/ Scientific Discipline of Student	Number
(1) Undergraduates	Chemical Engineering	2
	Chemistry	2
	Civil & Environmental Engrg.	2
(2) Master's Students	Chemical Engineering	4
	Civil & Environmental Engrg.	4
	Geography	1
	Microbiology	2
	Ocean Engineering	1

2/ This refers to educational background prior to employment as research assistant on P.L. 88-379 projects--not to departments in which projects are being conducted.

B. (Continued)

Category of Students	No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc. Scientific Discipline of Student	Number
(3) Doctoral Students		
	Chemistry	1
	Ocean Engineering	1
	Pharmacology	1
(4) Postdoctoral Students		
	Microbiology	1

C. Employment status of majors in water-related fields who graduated during the school year ending about June and who receive P.L. 88-379 support.

EMPLOYMENT STATUS	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1. No. employed in water-related positions in: Total----	2	1		3
Federal Agencies-------------	( )	( )	( )	( )
State & Local Agencies--------	( )	( )	( )	( )
University or College---------	( )	( )	( )	( )
Other - including private enterprise----------------	(2)	(1)	( )	(3)
2. No. graduates returning to school for advanced degree------------	1	3	3	7
3. No. going into military service--------------------------				
4. No. unemployed or working in other fields-------------------				
5. No. status unknown---------------		1		1
6. Totals-----------------------	3	5	3	11

D. Type of employment of those school year graduates who received P.L. 88-379 support and who are known to have gone into water-related positions. (Number should agree with total listed under item 1 of the preceding paragraph "C". Graduates enrolled for further course work or training should not be listed here as employed.)

Number of Graduates Engaged in Water-Related Work In:	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1A. Federal Agencies:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1B. State & Local Agencies:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1C. University or College: 3/				
a. Primarily Teaching				
b. Primarily Research				
c. Primarily Research & Teaching				
d. Other or not known				
1D. Other - Including Private Enterprise:				
a. Primarily Research				
b. Primarily Planning		1		1
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
Totals		1		1

Selected summary of above data -- from the "Total" column:

Research (1Aa, 1Ba, 1Cb, 1Cc& 1Da) ______
Planning (1Ab, 1Bb & 1Db) 1
Development (1Ac, 1Bc & 1Dc) ______
Operations (1Ad, 1Bd & 1Dd) ______
Management (1Ae, 1Be, & 1De) ______

3/ Do not include here students working as research assistants and receiving course credits.

E. Identify by name and discipline and briefly describe instances, if any, in which the institute program, in the past year, has resulted in individuals, other than students, doing research or teaching in the water resources field, who, previously, were not involved in water work.

Geoge C. Fuller, Ph.D., Pharmacology

Louis C. Kirschenbaum, Ph.D., Chemistry

Allan S. Marcus, Ph.D., Civil & Environmental Engineering

F. Cite any instances you know of, in which individuals who previously served as student research assistants on P.L. 88-379 projects, are now serving as professional investigators of P.L. 88-379 projects following graduation. Do not include individuals reported in this category last year or before.

NONE

PUBLICATIONS AND THESES

Publications:

Romanelli, R.A., Houston, C.W., and Barnett, S.M., "Studies on Thermophilic Cellulolytic Fungi", Applied Microbiology, 30, 2, 276-281 (August 1975).

M. Ahmadjian and C.W. Brown, "Fingerprinting Petroleum by Raman Spectroscopy", Anal. Chem., July (1976).

P.F. Lynch and C.W. Brown, "Analysis of Fabric Dyes in Water by Resonance Raman Spectroscopy", Appl. Spectroscopy, submitted for publication.

R. Thibeau and C.W. Brown, "Analysis of Pesticides in Water by Resonance Raman Spectroscopy", Anal Chem., submitted for publication.

Kelly, W.E. & Geisser, D., "An Electric Analog Model of the Chipuxet Ground Water Aquifer, Upper Pawcatuck River Basin, Rhode Island, Geol Soc. America, ABS with Programs (N.E. Sect.) V.7 n.1, p 84.

Kelly, W.E., "Modeling the Chipuxet Ground Water Aquifer", Proceedings of the Second International Conference on Numerical Methods in biomechanics, June, 1976 (in press).

Kelly, W.E. and Harry A. Niles, Jr., "Digital and Analog Models of Southern Rhode Island Ground Water Aquifers" (ABSTRACT) to be presented at 1976 ASCE Hydraulics Division Specialty Conference, Purdue University, August 1976.

Goldsmith, Les.A., Carlson, Gary P., Fuller, George C., "Toxicity and Identification of Parathion Metabolites in Freshwater Crayfish (Cambarus) and Snail (Viviparus)", (Bull. Environ. Contam. and Toxicol, 9, 296, 1973).

M.S. THESES:

Anne Wrona, "Nutrient Uptake and Growth of Spartina Patens as a Function of Salinity and Oxygen Concentration" (Project B-062-RI)

Crandall W. Dimock, "The Effects of Soluble Organic Matter on the Utilization of Phenoxy Herbicides by Pseudomonas sp." (Project A-050-RI).

FORM GW-2
(1973)

FY 1977 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

Prepare separate form for each Sec. 100 project in progress in Fiscal Year)

State where institute is located: Rhode Island

Report as of June 30, 1976

OWRR Project No. A-053-RI

Annual Allotment Agreement No. 14-34-0001- 6041

Principal Investigator(s):

Frank DeLuise

Project Title:

Manganese and Iron Removal from Water by Adsorption in Diatomaceous Earth

roject Began-- Month: July 1; Yr: 1974

Scheduled Completion--Month: June 30 Yr: 19 76

Cost Categories to Which FY1976 Federal Sec. 100 Funds Applied	Amount Budgeted For FY 1976	Actual Expenditures For FY 1976
A. SALARIES & WAGES: TOTAL	9068.	9015.94
Prin. Investigators: No: 1 - Man-yrs: 0.26	(4168.)	(4289.54)
Other Prof. Staff: No: 1 - Man-yrs: ___	( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS) No: 1 - Man-yrs: 0.625	(4900.)	(3100.00)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS) No: 1 - Man-yrs: 0.30	( )	(1626.40)
Technicians & Others: (NON-STUDENTS) No: ___ - Man-yrs: ___	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL	500.	235.77
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL	500.	489.76
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL		
	( )	( )
	( )	( )
	( )	( )
	( )	( )
E. TOTALS:	10068.	9741.47

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Research and Technology. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted," an explanation of such variance should be provided on an attachment to this sheet.

FORM OW-2
(1973)

FY 1977 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

Prepare separate form for each Sec. 100 project in progress in Fiscal Year)

State where institute is located: Rhode Island

Report as of June 30, 1976

OWRR Project No. A- 054-RI

Annual Allotment Agreement No. 14-31-0001- 6041

Principal Investigator(s):

Chris Brown

Project Title:
Remote Detection of Water Pollutants by Computerized Laser-Raman Spectroscopy

roject Began-- Month: July 1; Yr: 1974

Scheduled Completion--Month: June 30, Yr: 1976

Cost Categories to Which FY19 76 Federal Sec. 100 Funds Applied	No:	Man-yrs:	Amount Budgeted For FY 1976	Actual Expenditures For FY 19 76
A. SALARIES & WAGES: TOTAL			4800.00	4800.00
Prin. Investigators:	1	0.28	( )	( )
Other Prof. Staff:	1	0.625	(4800.00)	(4800.00)
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)			( )	( )
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)			( )	( )
Technicians & Others: (NON-STUDENTS)			( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL				
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			500.00	673.73
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			400.00	184.74
Travel			(200.00)	(184.74)
Publication			(200.00)	( )
			( )	( )
			( )	( )
E. TOTALS:			5700.00	5658.47

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Research and Technology. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

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If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted," an explanation of such variance should be provided on an attachment to this sheet.

FORM OW-2
(1973)

FY 1976 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

Prepare separate form for each Sec. 100 project in progress in Fiscal Year)

State where institute is located: Rhode Island

Report as of June 30, 1976

OWRR Project No. A-055-RI

Annual Allotment Agreement No. 14-34-0001- 6041

Principal Investigator(s):

Vito A. Nacci

Project Title:

Development of a System to Detect and Monitor Sediment Pollution

roject Began-- Month: July 1 Yr: 1974

Scheduled Completion--Month: June 30 Yr: 1976

Cost Categories to Which FY19 76 Federal Sec. 100 Funds Applied	Amount Budgeted For FY 1976	Actual Expenditures For FY 19 76
A. SALARIES & WAGES: TOTAL	10,000.	10,299.32
Prin. Investigators: No: 1 - Man-yrs: 0.26	(5,100.)	(4,999.32)
Other Prof. Staff: No: ___ - Man-yrs: ___	( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS) No: 1 - Man-yrs: 0.625	(4,900.)	(5,300.00)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS) No: ___ - Man-yrs: ___	( )	( )
Technicians & Others: (NON-STUDENTS) No: ___ - Man-yrs: ___	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL		
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL	300.	290.41
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL	100.	
Publication	(100.)	( )
	( )	( )
	( )	( )
	( )	( )
E. TOTALS:	10,400.	10,589.73

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Research and Technology. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted " an explanation of such variance should be provided on an attachment to this sheet.

FORM OR-2
(1973)

FY 1976 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

Prepare separate form for each Sec. 100 project in progress in Fiscal Year)

State where institute is located: Rhode Island

Report as of June 30, 1976

OWRR Project No. A-056-RI

Annual Allotment Agreement No. 14-34-0001-6041

Principal Investigator(s):

William C. Kelly

Project Title:

An Analog Model of the Chipuxet Aquifer, Rhode Island

roject Began-- Month: July 1, Yr: 1974

Scheduled Completion--Month: June 30 Yr: 1976

Cost Categories to Which FY1976 Federal Sec. 100 Funds Applied	No:	Man-yrs:	Amount Budgeted For FY 1976	Actual Expenditures For FY 1976
A. SALARIES & WAGES: TOTAL			6400.00	6549.29
Prin. Investigators	1	0.16	(1600.00)	(1650.89)
Other Prof. Staff			( )	( )
Graduate Student Assistants (INCLUDES STUDENT TECHNICIANS)	2	0.625	(4800.00)	(4898.40)
Undergrad. Student Assistants (INCLUDES STUDENT TECHNICIANS)			( )	( )
Technicians & Others (NON-STUDENTS)			( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL				
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			200.00	220.14
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			500.00	412.00
Travel			(500.00)	(412.00)
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			7100.00	7181.43

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Research and Technology. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted," an explanation of such variance should be provided on an attachment to this sheet.

FORM OW-2
(1973)

FY 1976 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepare separate form for each Sec. 100 project in progress in Fiscal Year)

State where institute is located: Rhode Island

Report as of June 30, 1976

OWRR Project No. A- 058-RI

Annual Allotment Agreement No. 14-34-0001- 6041

Principal Investigator(s):

Wilfred H. Nelson

Project Title:

Laser Methods of Rapid Detection, Identification and Quantitation of Human Viruses in Sewage and Rivers

roject Began-- Month: Jan 1 ; Yr: 1975

Scheduled Completion--Month: June 30 Yr: 1976

Cost Categories to Which FY1976 Federal Sec. 100 Funds Applied			Amount Budgeted For FY 1976	Actual Expenditures For FY 1976
A. SALARIES & WAGES: TOTAL			6640.	6177.75
Prin. Investigators:	No: 2	Man-yrs: 0.67	(2140.)	(2001.55)
Other Prof. Staff:	No:	Man-yrs:	( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No: 3	Man-yrs: 0.625	(4500.)	(4176.20)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No:	Man-yrs:	( )	( )
Technicians & Others: (NON-STUDENTS)	No:	Man-yrs:	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL			800.	
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			3500.	4360.86
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL				59.00
Travel			( )	(59.00)
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			10940.	10597.61

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Research and Technology. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted," an explanation of such variance should be provided on an attachment to this sheet.

FORM OW-2
(1973)

FY 1976 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

repare separate form for each Sec. 100 project in progress in Fiscal Year)

State where institute is located: Rhode Island | Report as of June 30, 1976

WRR Project No. A- 059-RI

Annual Allotment Agreement No. 14-34-0001- 6041

rincipal Investigator(s):

Frank White

Project Title:
Numerical Estuarine Models for Water Quality Management in the Blackstone-Providence River Complex and the Taunton River-Mount Hope Bay Complex

oject Began-- Month: Jan 1 ; Yr: 1975 | Scheduled Completion--Month: June 30 Yr: 1976

Cost Categories to Which FY19 76 Federal Sec. 100 Funds Applied	No	Man-yrs	Amount Budgeted For FY 1976	Actual Expenditures For FY 19 76
A. SALARIES & WAGES: TOTAL			6432.	5459.85
Prin. Investigators	1	0.12	(1632.)	(1476.83)
Other Prof. Staff	1	0.02	( )	(983.00)
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	2	0.625	(4800.)	(3000.02)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)			( )	( )
Technicians & Others: (NON-STUDENTS)			( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL				
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL				
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			700.	601.13
Computer			(500.)	(556.69)
Publications			(200.)	(12.84)
Travel			( )	(31.60)
			( )	( )
E. TOTALS:			7132.	6060.98

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Research and Technology. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted," an explanation of such variance should be provided on an attachment to this sheet.

FORM OW-2
(1973)

FY 1976 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepare separate form for each Sec. 100 project in progress in Fiscal Year)

State where institute is located: Rhode Island | Report as of June 30, 1976

OWRR Project No. A-060-RI

Annual Allotment Agreement No. 14-31-0001-6041

Principal Investigator(s):
Gary Carlson
George Fuller

Project Title:
Fate of the Organophosphate Insecticide Parathion in Freshwater Invertebrates

Project Began-- Month: Jan 1 ; Yr: 1975 | Scheduled Completion--Month: June 30 Yr: 1976

Cost Categories to Which FY19 76 Federal Sec. 100 Funds Applied			Amount Budgeted For FY 19 76	Actual Expenditures For FY 19 76
A. SALARIES & WAGES: TOTAL			4700.	6901.00
Prin. Investigators:	No: 1	Man-yrs 0.25	( )	( )
Other Prof. Staff:	No: __	Man-yrs: __	( )	( )
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No: 1	Man-yrs 0.625	(4700.)	(6901.00)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No: __	Man-yrs: __	( )	( )
Technicians & Others: (NON-STUDENTS)	No: __	Man-yrs: __	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL			400.	
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			2500.	327.06
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			350.	117.37
Travel			(150.)	(117.37)
Publications			(200.)	( )
			( )	( )
			( )	( )
E. TOTALS:			7950.	7345.43

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Research and Technology. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments (or obligations) including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the Amount [illegible] should be provided [illegible] attachment to

FORM OW-2
(1975)

FY 19 76 ANNUAL REPORT--ANNUAL ALLOTMENT (Sec. 100) PROJECT

(Prepare separate form for each Sec. 100 project in progress in Fiscal Year)

State where institute is located: Rhode Island

Report as of June 30, 1976

OWRR Project No. A-061-RI

Annual Allotment Agreement No. 14-31-0001- 6041

Principal Investigator(s):

Alan S. Marcus

Project Title:

Ground Water Quality Model of the Chipuxet Aquifer in the Upper Pawcatuck River Basin

Project Began-- Month: July 1; Yr: 1975

Scheduled Completion--Month: June 30 Yr: 1977

Cost Categories to Which FY19 76 Federal Sec. 100 Funds Applied			Amount Budgeted For FY 1976	Actual Expenditures For FY 19 76
A. SALARIES & WAGES: TOTAL			7711.	8714.95
Prin. Investigators:	No: 1	Man-yrs: 0.04	(2911.)	(900.00)
Other Prof. Staff:	No: 1	Man-yrs: 0.35	( )	(2411.00)
Graduate Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No: 1	Man-yrs: 0.625	(4800.)	(3300.00)
Undergrad. Student Assistants: (INCLUDES STUDENT TECHNICIANS)	No: 5	Man-yrs: 0.30	( )	(2016.75)
Technicians & Others: (NON-STUDENTS)	No: 1	Man-yrs:	( )	(87.20)
B. NON-EXPENDABLE PROPERTY: TOTAL			1000.	448.45
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL			1000.	841.24
D. OTHER COSTS (SPECIFY): (Travel, ADP Svcs., etc.) TOTAL			500.	
Computer			(500.)	( )
			( )	( )
			( )	( )
			( )	( )
E. TOTALS:			10211.	10,004.64

Notes: Amount Budgeted is as set forth in project budgets (and revisions) submitted to and accepted by the Office of Water Research and Technology. Dollars shown are Federal funds.

Actual Expenditures includes firm outstanding commitments for obligations including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the Amount [illegible]

FORM OW-3
(1973)

FY 1976 ANNUAL REPORT -- FOR THE INSTITUTE DIRECTOR'S OFFICE

State Where Institute is Located: Rhode Island
Report as of June 30, 1976

Director's Name: A. Ralph Thompson
Annual Allotment Agreement No. 14-34-0001-6041

Cost Categories to Which FY1976 Federal Sec. 100 Funds Applied	Amount Budgeted FY1976	Actual Expenditures FY1976
A. SALARIES & WAGES: TOTAL	36317.	35272.07
Institute Director: Man-yrs: 0.6	(20076.)	(19218.50)
Other Prof. Staff: No. 3 - Man-yrs: 2	(16241.)	(16053.57)
Graduate Student Assistants: No. ___ - Man-yrs: ___ (Includes Student Technicians)	( )	( )
Undergrad. Student Assistants: No. ___ - Man-yrs: ___ (Includes Student Technicians)	( )	( )
Technicians & Others: No. ___ - Man-yrs: ___ (Non-Students)	( )	( )
B. NON-EXPENDABLE PROPERTY: TOTAL		239.80
C. EXPENDABLE PROPERTY: (Supplies, Materials, etc.) TOTAL	882.	1281.04
D. OTHER COSTS (SPECIFY): (Travel; ADP Svcs., etc.) TOTAL	3300.	3707.21
Travel	(2000.)	(2207.21)
Publications	(1300.)	(1500.00)
	( )	( )
	( )	( )
	( )	( )
	( )	( )
E. TOTALS:	40499.	40500.12

Notes: Amount Budgeted is as set forth in the allotment program budget (and revisions) submitted to the Office of Water

Actual Expenditures includes firm outstanding commitments including, for example, unliquidated orders for equipment.

Man-years relate to time paid for by Federal funds only.

Non-expendable property is defined as property which has continuing use as a self contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine, plant, etc.

If the "Total" of "Actual Expenditures" varies more than 10% from the "Amount Budgeted," an explanation of such variance should be provided on an attachment to this sheet.

TECHNICAL & FINANCIAL SECTIONS
OF THE ANNUAL REPORT OF THE
RHODE ISLAND WATER RESOURCES CENTER
FISCAL YEAR 1977

RHODE ISLAND WATER RESOURCES CENTER
DIRECTOR'S REPORT FOR FISCAL YEAR 1977

Current and Anticipated Water Problems

Improving the quantity and quality of available groundwater is definitely the number one water research problem in the State of Rhode Island at the present time. Attention continues to be given to the economic removal of iron and manganese from groundwater sources containing relatively high concentrations of these elements. Priorities for other water problems, as established by the state Advisory Board, remain the same as determined four years ago. The other problems in order are: control of pollution from industrial plants especially in the metal-working and jewelry industries; legal, social and economic problems of water resources; study of viruses and pathogenic bacteria in water; operational modeling of groundwater aquifers; modeling of fresh water streams and potential reservoir development.

Cooperation with State Agencies

The groundwater program, directed by the Water Resources Board, continued with work in Southern Rhode Island in cooperation with the U.S. Geological Survey and the Department of Civil and Environmental Engineering at the University of Rhode Island through the Water Resources Center. Field work involved drilling about 85 test wells and pumping tests at 7 proposed pumping centers in the lower Wood River reservoir. Digital and analog models were prepared to assist in future development and operation of the groundwater reservoir. State-wide monitoring of groundwater was continued and the Water Resources Board acquired the Wolf Rock pumping center in Exeter for future water supply.

Free bacteriological examination of well water continued to be provided by the Water Resources Center to residents of the state. This service has been particularly valuable to southern Rhode Islanders and close to 1500 samples per year are now analyzed in our laboratory.

Current Research

Effects and control of pollution in streams, estuaries and wetlands occupied much of the water researchers' time during the year. Also, in line with the state's interest in improving the groundwater supply, work on modeling of aquifers was continued.

Control of pollution in wastewater from the metal finishing industry is an extremely difficult problem as the water may contain compounds of several heavy metals, cyanide, oil, grease and phosphate. Project A-062-RI (Calvin P.C. Poon) has developed an electrochemical treatment system which should prove to be very valuable to this specific industry which is very important in the State of Rhode Island.

Hydrocarbons are a major component of the pollutants in municipal waste streams and of leaks and spills. One approach to the tertiary treatment of wastewater containing hydrocarbons has been the use of activated carbon. A definite drawback to the widespread use of this procedure is the high expenditure of energy needed for regeneration of the carbon. Project A-063-RI (Chester W. Houston) has completed preliminary work for studying the biological regeneration of activated carbon which has been exhausted with hydrocarbons. The effort this year has been concerned with analytical procedures, the isolation of microorganisms, and an investigation of adsorption characteristics of activated carbon samples. The research on Project B-073-RI (Stanley M. Barnett) is concentrating on what is believed to be the rate controlling factor in the biodegradation of hydrocarbons - the transport of hydrocarbons through aqueous media.

In the New England area, small streams, lakes and reservoirs which comprise the major sources of public water are affected by organic materials (including phenolic compounds) eluted into the water from fallen leaves, pollen, etc. and their secondary products formed by biodegradation. On chlorination, compounds can be produced which are potentially very toxic. Project B-076-RI (Yuzuru Shimizu) is completing the analysis and identification of chlorinated organic compounds in the water of several cities in Rhode Island. This project is also studying how inorganic ions such as ammonium, iron and manganese affect the interaction between chlorine and organic molecules in water.

Ozonation has been gaining wider acceptance in wastewater treatment because ozone has unique properties that offer possible advantages over chlorination. Project A-064-RI (Pei Wen Chang) is determining guidelines for dosage and contact time of ozonation with respect to virus inactivation in various types of secondary sewage effluents.

Many of the inland wetlands of southern New England are in reality artificial, as many of these have resulted from the breakdown of dams in mill operations which began 150 or more years ago. Project A-066-RI (John E. Lukens and J. Michael Everett) has been investigating the possibility of intentionally creating artificial wetlands and of assessing the value of these wetlands. One of the practical results of this study might be to indicate whether or not inland wetland acts should be amended to consider the construction of artificial wetlands. Setting out beds for growing and harvesting useful marine algae in the region of sewage outfall may, in some estuarine and coastal areas, serve as a simple and feasible alternative to advanced treatment. Project A-065-RI (Nelson Marshall, Paul E. Hargraves, and Marilyn M. Harlin) is thoroughly investigating this possibility.

The major source of water in southern Rhode Island is groundwater. It is important to have information regarding the quality of this water and its possible pollution. Project A-061-RI (Alan S. Marcus, Louis J. Kirschenbaum and William E. Kelly) has been developing models which will make it possible to predict the fate of existing aquifers and to identify sources of contamination.

Cellulose is known to be a major component of municipal, agricultural and some industrial wastes. All of these sources contribute to the pollution of natural waters because of runoff and incomplete treatment. The research underway on Project B-070-RI (Stanley M. Barnett) is concerned with the fermentation and saccharification of cellulose. The results from this study should provide a method of increasing the rate of decomposition of cellulose in wastes and thus have beneficial economic and environmental effects.

Regional Cooperation

The Rhode Island Water Resources Center devotes much of its time to cooperation on regional projects with other centers in the northeast.

Two regional projects, which will be completed December 31, 1977, have had financial administration by the Rhode Island center:

> "The Impact of Urbanization on New England Lakes: An Assessment of Lake Quality Control Methods" (C-5342) for the New England Council of Water Center Directors (NECWCD) 1974 - 1977.
>
> "Analysis of Critical Water Problems in the Northeastern United States to Determine Essential Research Requirements". (B-061-RI) for the Northeast Water Institute Directors (NEWID) 1973 - 1977.

During the year the Rhode Island Center has worked actively with the other New England centers in the development of two new regional projects for which Rhode Island will have some fiscal responsibility. These projects are:

"Evaluating Proximity and Personal Access to the Water Resources Scientific Information Center (WRSIC) System"

"The Impact of Water Availability on Electric Energy Production in New England: Implications for Economic Development"

A. Ralph Thompson, Director
Rhode Island Water Resources Center

RHODE ISLAND WATER RESOURCES CENTER
OTHER NARRATIVE ITEMS

Information Dissemination Activities

During the year a major effort was made by the Director and the office staff, with the expert aid of a student from the Graduate School of Library Science, to study the Center's library.

The purpose of this project is to develop the optimum type of library to serve water resources research in the State of Rhode Island with given constraints of space, finances and personnel. A study was made of what publications should be retained in the library and what specific directions should be on file for obtaining rapidly information not in books, journals or reports stored in the library. Current holdings in the library were critically examined and recommendations were made for cataloging, those to be retained, in the most efficient manner possible. A file giving the locations throughout the state, region and country of information available to water researchers is to be developed.

A summary of what is to be contained in the Completion Report for the project entitled "Development of Water Resources Research Library" was prepared by the library science specialist, Mr. Richard J. Burtt, and is presented on the following pages.

DEVELOPMENT OF WATER RESOURCES RESEARCH LIBRARY

by

Richard J. Burtt

The first section of the final project report concerns itself with the history and nature of information resources in water resource research. Among other things, it notes its interdisciplinary character (scientific-technical, economic, legal, political, etc.). The recent shift in water resource research to environmental, problem solving, and technological transfer concerns is discussed as well as the increasing importance of the work of social scientists in the repertoire of the water resource literature.

Noted here are the various known uses of the water resource literature according to various user groups. It summarizes the research that has investigated how various user groups use the literature, what types of library services are preferred by each group, and what type of research reporting genres are best suited for each user group. Three major user groups are evaluated: (1) researchers and water information creators; (2) water information technological consumers (e.g., engineers); and (3) water information administrative consumers (e.g., community planners). The general public is also considered.

Previous research regarding the use by these different consumers of the bibliographic access system for the water literature is outlined. Deterrents to effective use of the literature are noted and suggestions are recorded for attempting to overcome them (i.e., language discrepancy between producers and users of water information, information and data explosion, dual publishing, physical and bibliographic access failure, etc.).

The problem of the lack of bibliographic familiarity among applied scientists and technologists in the field of water resources is examined in the light of citation and literature awareness studies. How these studies can suggest methods of increasing familiarity are also noted.

Also within this first section an analysis of what sources of information in water resources are available today appears. Included here are automated and conventional abstracting and indexing devices, citation bulletins, technical journals, trade magazines, directories, bibliographies, patents, etc. Specific retrieval systems or services that are critically examined are the WRSIC data base (GIPSY system), National Technical Information Service (NTIS), Science Information Exchange, National Referral Center of the Library of Congress, Northeast Water Resources Information Terminal (NEWRIT), National Water Data Exchange (NAWDEX), and the various data bases from the Northeast Academic Science Information Center (NASIC). The role of the Water Resources Scientific Information Center (WRSIC) in relation to the research community is discussed.

The second major section of the report is a discussion of Rhode Island's Institute and how it ought to serve its constituents' informational needs. Two major user groups are delineated which provides the major division of the section: (1) servicing principal investigators and other grantees for research, and (2) servicing the local water resources information user community. Emphasis for the whole section are in the provision of information service rather than information resources as well as the need for regionalization and cooperation.

Servicing Grantees: A description of the present library's collection, services, and patron use is offered and an attempt is made to show the propriety of limiting its growth and in servicing its patrons through extramural resources. In addition, suggestions are proferred as to the necessity to specialize its own resources in regional materials. All of this is articulated with an understanding of Rhode Island's user groups physical locales as well as alternative sources of bibliographic service.

For those library materials in which it is recommeded that the Institute continue to maintain and acquisition, various methods of organization and retirement are suggested. Three methods of cataloging and/or indexing the materials are developed: (1) maintaining a card catalog using the Committee on Scientific and Technical Information (COSATI) standard; (2) uniterm coordinate indexing; and (3) computerized Key-Word-Out-of-Context (KWOC) book catalog (modified FAMULUS documentation system). Advantages and disadvantages are given for each method including economic considerations. The relevant literature regarding weeding library stock is discussed in its relation to the initiation of a retirement program at the Institute's library.

Various ideas are suggested on how to bibliographically assist the grantees including building an extramural resource file, writing guides for water resource bibliographic research, instituting a current awareness bulletin, providing Selective Dissemination of Information (SDI) contracts for grantees, utilizing computerized retrospective literature searching services in Rhode Island, and introducing professional services through information service personnel. The emphasis here is the tapping of general information sources and services already available in the Institute's jurisdiction toward the end of specialized bibliographic service to its clientele.

Suggestions for future empirical research are made through the use of (1) questionnaires to present and past grantees regarding informational needs and how they were/were not met; (2) questionnaires to other institutes regarding the offering of resources and services; and (3) the maintaining of records of future resources used and services offered.

An overture is made towards the feasibility of enlisting the aid of other institutes in the region (i.e., New England) in the fulfilling of Rhode Island's responsibility in bibliographically servicing its grantees by the initiation of a compact for regionalized servicing. Several ideas are offered as to what types of resources and services are feasible in a cooperative program.

Servicing Water Research Information Users: Citing a wealth of literature it is concluded here that there is substantial evidence that (nationwide) a large majority of potential users are unaware of research findings of projects sponsored by the Office of Water Resources and Technology (OWRT). With the need to improve dissemination of research that is carried out by the Rhode Island Water Resource Center as well as other institutes, many suggestions are made toward the end of using the Institute's library and proposed library (and library-like) services in relating the results of specific research to specific user groups (e.g., state water agencies, policy makers, water technology engineers). With Rhode Island research in particular, it is realized that written project reports do not always in and of themselves present themselves as the best medium to making potential users aware to the significance of new information. Suggestions for using a variety of communication methods to improve the climate among users that is conducive to change are made. Recent advances in communication research are used to suggest means in which greater and better dissemination of research findings could be instituted (e.g., personalized dissemination services, maintaining a clientele file, increasing environmental concern of other professions, etc.).

Two final chapters, one on conclusions drawn, and the other on recommendations made will conclude the report.

RHODE ISLAND WATER RESOURCES CENTER
Individual Project Annual Reports
Fiscal Year 1977

A-061-RI	Ground Water Quality Model of the Chipuxet Aquifer in the Upper Pawcatuck River Basin	Marcus
A-062-RI	Water Pollution Control in Metal Finishing Industry	Poon
A-063-RI	Bio-regeneration of Hydrocarbon Exhausted Activated Carbon	Houston
A-064-RI	Ozonation for Control of Human Enteric Viruses in Secondary Sewage Effluent	Chang
A-065-RI	Cultivating and Harvesting Algae to Forestall Accelerated Eutrophication	Marshall
A-066-RI	Artificial Wetlands: Values, Regulatory and Developmental Issues	Lukens
B-061-RI	Analysis of Critical Water Problems in the Northeastern United States to Determine Essential Research Requirements	Thompson
B-070-RI	Fermentation and Enzymatic Saccharification of Cellulose and Lignin Wastes	Barnett
B-073-RI	Solubilization and Biodegradation of Hydrocarbons	Barnett
B-076-RI	Interaction of Chlorine and Organic Molecules--Effects of Inorganic Ions	Shimizu

FORM OW-1
(Rev. 6-77)

ANNUAL REPORT -- TITLE I PROJECT

OWRT PROJECT NO. A-061-RI

AGREEMENT NO. 14-34-0001-7084

FCCSET (COWRR) RESEARCH CATEGORY: II A V

PROJECT TITLE:
Ground Water Quality Model of the Chipuxet Aquifer in the Upper Pawcatuck River Basin

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT:
University of Rhode Island
Kingston, RI 02881

PROJECT BEGAN -- MONTH: July, YEAR: 1975 TO BE COMPLETED -- MONTH: June, YEAR: 1977

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
Alan S. Marcus	Ph.D.	Civil Engineering
William E. Kelly	Ph.D.	Civil Engineering
Louis J. Kirschenbaum	Ph.D.	Chemistry

STUDENT ASSISTANTS 1/	DEGREES HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND
Daniel W. Urish	M.S.	Civil Engineering

OWRT A-061-RI

SUMMARY

Ground Water Quality Model of the Chipuxet Aquifer in the Upper Pawcatuck River Basin

The Chipuxet ground water aquifer is located primarily in Kingston, Rhode Island. Within the aquifer (approximately 3 miles by 2 miles) are suspected pollution sources. The apparent pollution sources are a landfill, highways, agriculture and farming areas, and housing septic systems.

Both well and surface water quality measurements were made in an attempt to trace the pollution sources into, through, and out of the aquifer. While many chemical measurements were made over a two year period the major part of the report deals with specific conductivity measurements as these are the only measurements which appear to be extensive enough to yield potential modelling data.

There were three basic types of conductivity monitoring stations. Firstly, there were the stations where anticipated pollution input to the aquifer could be monitored. Secondly, there were stations where outputs from these inputs and other inputs were attempted to be monitored. Thirdly, there were "state of the aquifer" monitoring stations where it was anticipated some useful ground water information could be obtained. These latter well locations were chosen because either a well already existed or the location was very accessible and seemed reasonably likely to yield "state of the aquifer" information.

Ground water levels and stream measurements were also made. A sketch of the "best estimate" of the ground water levels and the resulting ground water flow estimates was made from these measurements.

The conclusions indicate that some of the suspected pollution sources were successfully monitored while others yielded unsuspected results. The interaction between a landfill, and agricultural area, and a pond was also studied.

Form CW-1
(Rev. 5-77)

ANNUAL REPORT — TITLE I PROJECT

OWRT PROJECT NO. A-062-RI

AGREEMENT NO. 14-34-0001-7084

FCCSET (COWRR) RESEARCH CATEGORY: VD

PROJECT TITLE:

Water Pollution Control in Metal Finishing Industry

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT:

University of Rhode Island
Kingston, R.I. 02881

PROJECT BEGAN—MONTH: July ; YEAR: 1976

TO BE COMPLETED—MONTH: June ; YEAR: 1978

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
Calvin P.C. Poon	Ph.D.	Environmental Engineering

STUDENT ASSISTANTS 1/	DEGREE HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND
Kenneth P. Soscia(76-77)	B.S.	- Civil & Environmental Engineering
Steven Feng(77 Summer)	B.S.	- Chemical Engineering
Cheng-Fa Lu(77-78)	B.S.	- Chemical Engineering

Project Accomplishments

The objective of this research work is to use an electrochemical process in treating metal plating and finishing wastewater. In the past 15 months, an electrochemical cell has been constructed and modified for numerous experiments. Metal wastes containing zinc, nickel, copper and cadmium were collected from the plating industry in Providence, Rhode Island. They were successfully treated to yield effluent qualities conforming to the National Pollution Discharge Elimination System (NPDES) permit requirements for heavy metals. Important system and control variables were identified. Models are being developed using package computer programs to relate treatment efficiency or fractional metal removal with the system and control variables.

1. Construction of electrochemical cell

The plexiglass cell, as shown in Figure 1, has a maximum working volume (wastewater volume) of 14.5 liters up to the top of the overflow weir. Originally the anode consisted of graphite rods. The experience of excessive graphite erosion led to the replacement of the graphite rods with a platinum plated columbium metal later. Although the platinum plated anode is approximately 15 times more expensive, its life span is more than 15 times longer than the graphite rods. In addition, a great saving in maintenance costs can be realized since the platinum plated anode can last several years without replacement. The position of the anode can be adjusted to give different electrod spacing (between the anode and the cathode) which was found to be an important system variable affecting the system performance.

2. Removal of zinc, nickel, and copper in a batch process

Seawater was introduced into the cell to a level slightly above the cathode. Wastewater depth above the cathode and power used were operational variables. Both alkalides and chlorine

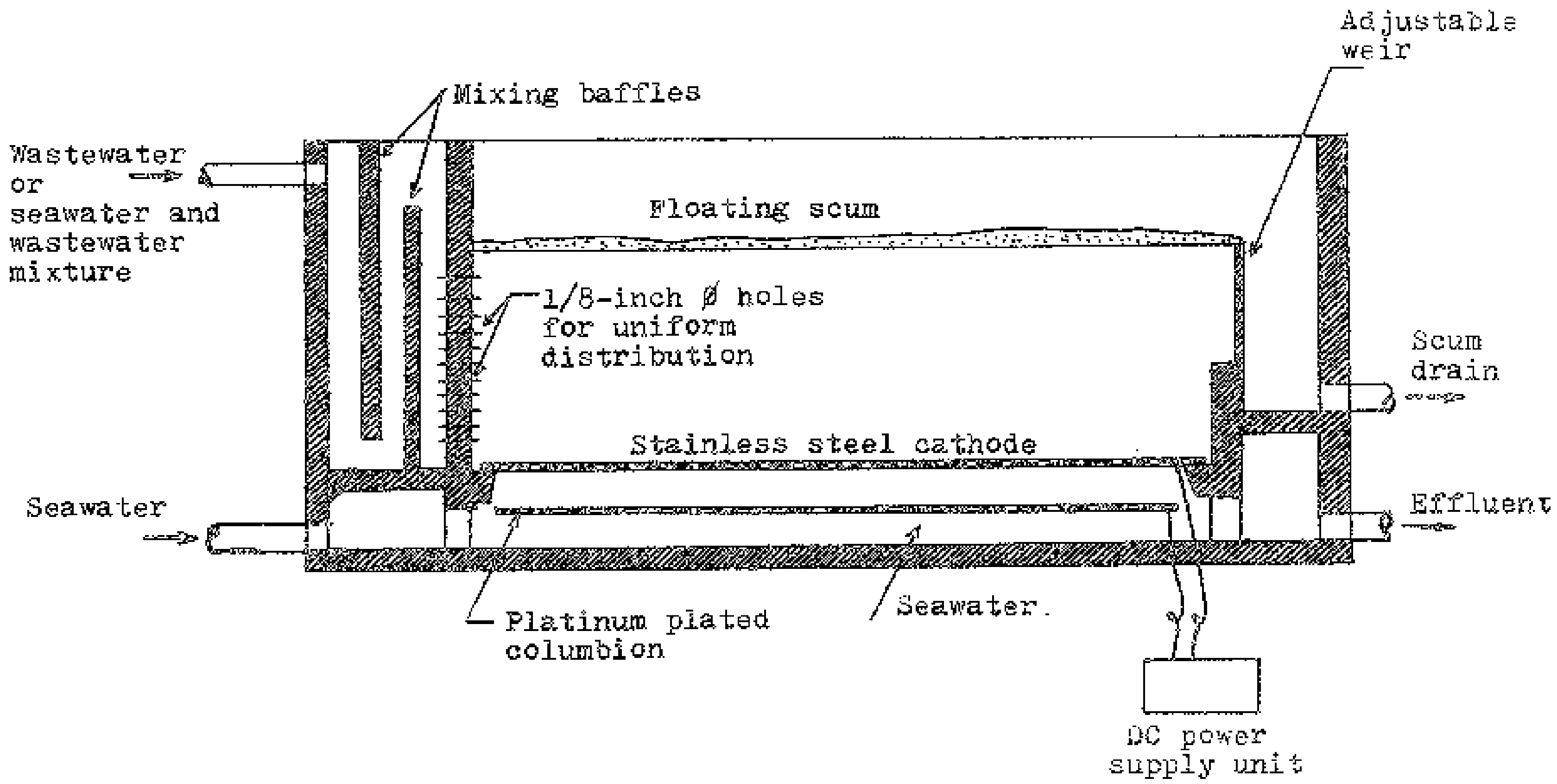

FIGURE 1 - ELECTROCHEMICAL CELL (not to scale)

were generated in the process. The increase of alkalides changed the pH and consequently decreased the solubility of the metal to a point when effective precipitation occurred. The precipitated metal flocs were carried up to the surface by the rising hydrogen bubbles, metal hydroxide flocs (primarily magnesium hydroxides) and bubbles of other gases. Chlorine accumulation should be minimized because it inhibited the pH from rising. A high residual chlorine in the treated effluent was also deemed undesirable.

Experiments were designed to investigate the system and control variables one at a time. Each experiment was conducted long enough to ensure that the NPDES permit requirement for the effluent containing a specific heavy metal had been satisfied. Table 1 shows the acceptable limits for the metals studied and Tables 2 to 4 show the summarized experimental results. Specific removal here is defined as the weight of a metal removed (milligram) per kilowatt-hour of electricity used or $\frac{mg}{kwh}$. It serves as a common basis for comparing the efficiency of removal for all metals. The results that were marked "fail" in these tables indicate that acceptable effluent metal concentration could not be reached in these experiments. The cause for the failure was the excessive buildup of chlorine in the wastewater which prevented the pH from rising to the point where effective metal precipitation occurred.

Conclusions can be drawn by examining Tables 2 to 4 as in the following:

a. Electrode spacing at 1.0 cm was too close which caused excessive chlorine buildup, preventing the metal precipitation. Low initial pH enhanced the failure since a longer reaction time was required to raise the pH, but the opportunity of chlorine buildup was also greater.

b. Although zinc removal was successful using the 1.0 cm electrode spacing, the high residual chlorine in the effluent (see Table 2) would be unacceptable to sewer discharge or discharge to natural waters.

c. Zinc removal from rinse water obtained from the plating industrial was successful in the electrochemical process using 3.0 or 5.0-cm electrode spacing. In general an electrochemical cell with 3.0 cm electrode space was a more efficient unit and a 15-watt power supply was better than the 25-watt or 35-watt power supply. The highest specific removal, 129,730 mg/kwh, was obtained in a cell with 3-cm electrode spacing at 10-cm wastewater depth and 15-watt power supply (3 cm-10 cm depth-15w).

d. Nickel removal was also successful with 3-cm and 5-cm electrode spacing. However a power supply of 35 watts usually resulted in unacceptably high residual chlorine. Again the 3 cm-10 cm depth-15w condition was most efficient in that the specific removal was 156,384 mg/kwh, the highest in all nickel experiments.

e. The nickel finishing wastewater had a very low pH. As a result, time of treatment required to produce an acceptable effluent quality was longer. Nevertheless specific removal was higher for nickel when compared to zinc in every identical experimental condition (electrode spacing-wastewater depth-power supply). The high initial metal concentration, in the case of nickel, was responsible for this higher specific removal. More evidence will be presented later to verify this fact.

f. Experiments of copper removal were divided into two parts. The initial pH of the copper wastewater per se was very low from 2.25 to 2.45. The initial copper concentration was medium in relation to zinc (low) and nickel (high). This combination of very low pH and medium but not high initial metal concentration resulted in the lowest specific removal. Experiments were repeated with the initial pH raised to 4.65 to 5.5. With the exception of only one experiment, specific removal was significantly increased with a higher initial pH. The highest specific removal was found for the 5cm-25cm depth-15w condition at 95,464 mg/kwh (initial pH 2.35) and at 162,948 mg/kwh (initial pH 5.1). A cost analysis later in the project will determine if the tradeoff is economically acceptable.

3. Effects of initial metal concentration on zinc, nickel and copper removal

The concentration of metal in each finishing wastewater was adjusted by adding the concentrated dragout solution or by tap water dilution so that high and low metal solutions were made available for the study. The pH of each of these solutions was adjusted back to the same level as the finishing wastewater. Table 5 shows that the effect of initial metal concentration on specific removal is highly significant. The electrochemical process is more efficient in treating higher metal concentration solutions. Plant engineers should take advantage of this unique characteristic for cost-effective operation of the system.

4. Removal of cadmium and cyanide in a batch process

The finishing wastewater contained both cadmium and cyanide which presented a unique opportunity to test the versatility of the electrochemical process to treat different metal wastewaters. The chlorine generated from the seawater oxidized the cyanide to CO_2 and nitrogen gases. The precipitation of cadmium required a very high pH, between 11.0 and 12.0. A long reaction time was required in order to fulfill the objectives of complete oxidation of cyanide and raising the solution to a very high pH. Experiments with 1-cm electrode spacing all failed, as in the case of treating nickel and copper, because excessive buildup of chlorine which prevented the pH rise. Lower power supply, 15w, could not be used for successful treatment at any wastewater depth investigated. The results of the sucessful experiments are presented in Table 6. It is obvious that the electrochemical process was successful in the removal of Cd and CN, but with a lower specific removal compared to that of Zn, Ni, and Cu. It is also apparent that the initial metal concentration had the same effect on the specific removal as in the case of Zn, Ni and Cu.

5. Practical highest metal concentration which can be successfully treated in the electrochemical cell

Since the electrochemical process was found more efficient in treating higher metal concentration solutions, experiments were conducted to establish the practical highest concentration for each metal. Above this concentration, a longer reaction time would be required. But the accumulation of chlorine would have inhibited the pH from rising to a level required for the precipitation of the metal. These highest concentrations are listed in Table 7 together with a summary of the experimental conditions. The information is useful to plant engineers who would like to combine some drag-out solution with the finishing wastewater for treatment.

Project Status

The project will be continued in progress in the next fiscal year.

Application of Research Results

Results obtained thus far can be used by plant engineers in charge of metal plating and finishing wastewater treatment in the following manner:

1. Design of electrochemical cell

The plant engineer can determine the size of the cell required for his wastewater flow based on the detention time requirement and electrode spacing recommendation specified for each metal. Electrode spacing should be adjustable so that the cell is versatile for the treatment of wastewaters containing different metals.

2. Using the electrochemical cell in a batch operation, the choice of values for the system and operational variables have been identified for each metal for achieving the highest specific removal. This information should serve as a valuable guideline for a plant engineer to follow in order to be cost-effective in his pollution control program.

3. Sometimes it is advantageous to combine the drag-out wastewater and the finishing wastewater for treatment in order to save capital as well as operational cost. This study has established the highest metal concentration allowable in a batch operation (for zinc, nickel, copper and cadmium) which is an important parameter within which a plant engineer can determine the size of the cell and estimate the fractions of dragout and finishing wastewater to be combined for treatment.

Work Remaining

1. Mathematical models are being developed to relate the specific removal to system and operational variables.
2. Chromium removal in the electrochemical process is being investigated. Since hexavalent chromium needs reduction prior to precipitation, the operation is different from other metal treatment. The two methods of Cr removal are:
    - (a) chemical reduction prior to electrochemical reaction
    - (b) replace the platinum anode with iron electrode; the sacrificing iron is used to reduce as well as to coagulate-precipitate the chromium out of the solution.

3. After the completion of all batch process treatment, the electrochemical process will be operated on a continuous flow basis. System and operational parameters will be established again for each metal and the most cost-effective conditions will be determined.
4. Capital and operational costs will be estimated for full scale systems of various sizes.

The experimental program is expected to terminate in late April, 1978. A final report with all the findings and data analyses will be prepared immediately following.

TABLE 1. Acceptable Limits of Effluent Metal and Cyanide Concentrations, mg/1

	Zinc	Nickel	Copper	Cadmium	Cyanide
NPDES requirement 1977	0.50	2.0	0.5	0.2	0.08 (amenable) 0.24 (total)
State of Connecticut Effluent limitations	2.0	2.0	1.5	1.0	0.1 (amenable)

TABLE 2. Zinc Removal (Starting Condition: pH = 5.75 to 6.90, Zn Conc. = 49 to 64 mg/1)

Electrode Spacing	Power	15 Watts		25 Watts		35 Watts	
	Wastewater Depth	10 cm	25 cm	10 cm	25 cm	10 cm	25 cm
1 cm	Effluent conc., mg/1	0.50	0.50	0.50	0.50		
	Time req'd, min.	13.50	27.00	7.00	16.50	fail	fail
	Residue, Cl_2, mg/1 conc.	40.00	10.00	20.00	25.00		
	Effluent, pH	10.25	9.95	10.50	9.65		
	Specific removal, $\frac{mg}{KWh}$	99,440	139.700	121,176	128,520		
3 cm	Effluent conc., mg/1	0.40	0.51	0.50	0.50	0.50	0.50
	Time req'd, min.	10.0	30.00	9.50	15.00	27.00	26.00
	Residue, Cl_2, mg/1 conc.	0.30	0.20	0.40	2.50	0.60	2.50
	Effluent pH	10.15	10.30	10.55	11.00	11.05	11.15
	Specific removal $\frac{mg}{kwh}$	129,730	109,870	92,289	68,904	28,776	52,611
5 cm	Effluent conc., mg/1	0.50	0.50	0.44	0.50		0.50
	Time req'd, min.	30.00	31.00	10.00	18.00	fail	26.50
	Residue, Cl_2, mg/1 conc.	3.00	0.40	0.60	0.80		0.80
	Effluent pH	11.35	11.05	10.70	9.80		11.10
	Specific conc. $\frac{mg}{kwh}$	47,132	92,932	67,802	98,010		46,591

TABLE 3. Nickel Removal (Starting Condition: pH = 2.8 to 3.1, Ni Conc. = 180 to 210 mg/1)

Electrode Spacing	Power	15 Watts		25 Watts		35 Watts	
	Wastewater Depth	10 cm	25 cm	10 cm	25 cm	10 cm	25 cm
3 cm	Effluent conc., mg/1	2.00		2.00	2.00	2.00	2.00
	Time req'd, min.	27.50		19.50	53.00	27.50	47.00
	Residue Cl_2 conc. mg/1	2.00	fail	2.50	5.00	50.00	35.00
	Effluent pH	10.60		9.65	10.30	10.65	10.05
	Specific removal, $\frac{mg}{kwh}$	156,384		152,064	121,714	67,022	112,661
5 cm	Effluent conc., mg/1	2.00	2.00	2.00	2.00	2.00	2.00
	Time req'd., min.	37.50	67.00	21.50	59.00	24.50	57.50
	Residue Cl_2 conc., mg/1	4.00	0.60	1.20	10.00	16.00	7.20
	Effluent pH	10.80	8.90	9.40	9.45	11.05	10.15
	Specific removal $\frac{mg}{kwh}$	112,781	157,809	118,026	107,524	73,982	78,807

ABLE 4. Copper Removal (Starting Cu Concentration: 87 to 125 mg/l)

lectrode pacing	Power	15 Watts				25 Watts				35 Watts			
	Wastewater Depth	10 cm		25 cm		10 cm		25 cm		10 cm		25 cm	
3 cm	Effluent conc., mg/l	0.50	0.45		0.50	0.50	0.50	0.50	0.50	0.50		0.50	0.50
	Time req'd min.	45.00	30.00		59.00	39.00	19.50	80.00	36.00	32.00	fail	54.00	50.00
	Residue Cl_2 conc. mg/l	10.00	2.00	fail	2.00	7.50	2.00	7.50	2.00	50.00		30.00	25.00
	Influent pH	2.35	5.20		4.80	2.45	5.30	2.35	5.40	2.40		2.25	4.65
	Effluent pH	9.05	9.80		7.85	9.75	10.75	6.90	7.45	10.90		7.80	11.10
	Specific removal mg/kwh	50,952	68,548		95,141	34,543	66,894	42,991	88,605	39,617		45,493	49,641
5 cm	Effluent conc., mg/l	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
	Time req'd min.	30.00	25.00	70.00	37.00	44.00	15.00	74.00	42.50	22.50	32.50	59.00	54.00
	Residue Cl_2 conc. mg/l	4.00	0	0.10	0	20.00	0	13.00	0.20	8.00	8.00	10.00	15.00
	Influent pH	2.35	5.50	2.35	5.10	2.40	4.75	2.40	5.05	2.35	5.10	2.40	5.20
	Effluent pH	7.15	7.50	6.90	6.75	11.55	8.25	11.45	7.00	7.40	10.85	7.65	11.00
	Specific removal mg/kwh	70,884	87,912	95,464	162,948	34,506	97,416	46,477	94,341	50,914	31,175	45,089	50,207

TABLE 5. Effect of Initial Metal Concentration on the Specific Removal, mg/kwh

Metal	Experiments and Results				
	Parameter	3cm-10cm-15w depth	3cm-10cm-15w depth	3cm-25cm-15w depth	3cm-25cm-15w depth
Zn	Initial conc.	166.0 mg/1 (high conc.)	20.0 mg/1 (low conc.)	166.0 mg/1 (high conc.)	16.0 mg/1 (low conc.)
	Effluent conc.	0.5 mg/1	0.5 mg/1	0.5 mg/1	0.5 mg/1
	Time required	23.5 min.	8.5 min.	49.5 min.	24.5 min.
	Residual Cl_2	1.5 mg/1	0	0	0.5
	Initial→final pH	5.85→10.20	6.0→10.2	6.25→9.50	5.95→10.40
	Specific removal	167,331 mg/kwh	54,508 mg/kwh	198,600 mg/kwh	37,580 mg/kwh
	*Net change and Percentage	+37,601 mg/kwh +29%	-75,220 mg/kwh -58%	+88,730 mg/kwh +80.8%	-72,290 mg/kwh -62.8%
	Parameter	5cm-25cm-15w depth	5cm-25cm-15w depth		
Ni	Initial conc.	530.0 mg/1 (high conc.)	65.0 mg/1 (low conc.)		
	Effluent conc.	2.0 mg/1	2.0 mg/1		
	Time required	115.0 min.	29.0 min.		
	Residual Cl_2	7.0 mg/1	0.1 mg/1		
	Initial→final pH	3.0→7.9	2.9→9.0		
	Specific removal	273,000 mg/kwh	129,041 mg/kwh		
	*Net change and percentage	+115,191 mg/kwh +73%	-28,768 mg/kwh -18.2%		
	Parameter	5cm-25cm-15w depth	5cm-25cm-15w depth		
Cu	Initial conc.	290.0 mg/1 (high conc.)	31.6 mg/1 (low conc.)		
	Effluent conc.	0.5 mg/1	0.5 mg/1		
	Time required	-	36.0 min.		
	Residual Cl	3.0 mg/1	0 mg/1		
	Initial→final pH	2.45→7.35	2.4→6.7		
	Specific Removal	110,951 mg/kwh	51,315 mg/kwh		
	*Net change and percentage	+15,487 mg/kwh +16.2%	-44,149 mg/kwh 46.2%		

*Positive net change and percentage indicate increase of specific removal, and negative sign indicates decrease due to the change of (high or low) initial metal concentration in relation to an identical experiment with the finishing wastewater without metal concentration adjustment.

TABLE 6. Cadmium and Cyanide Removal (Except as noted, all experiments were carried out using the finishing wastewater per se without adjusting the metal and cyanide concentrations.)

Electrode Spacing		25 W	35 W				
	Wastewater Depth	10 cm	10 cm			25 cm	
3 cm	Initial Cd conc.	14.1 mg/l	14.1 mg/l	17.4 mg/l	7.5 mg/l	7.25 mg/l	–
	Effluent Cd conc.	0.2 mg/l	0.2 mg/l	0.2 mg/l	0.18 mg/l	0.20 mg/l	
	Initial CN conc.	42.5 mg/l	42.5 mg/l	60.0 mg/l	35.0 mg/l	35.0 mg/l	
	Effluent CN conc.	0.1 mg/l	0 mg/l	0 mg/l	0 mg/l	0 mg/l	
	Residual Cl_2 conc.	0 mg/l	7.0 mg/l	1.0 mg/l	0 mg/l	4.0 mg/l	
	Initial→final pH	9.70→12.45	9.75→12.45	9.25→11.55	10.05→11.95	9.9→11.7	
	Time required	72.0 min.	90.0 min.	75.0 min.	50.0 min.	83.5 min.	
	Specific removal	2752 mg/kwh	2247 mg/kwh	2335 mg/kwh	1491 mg/kwh	2028 mg/kwh	
	Net change and percentage				-756 mg/kwh -33.6%		
5 cm	Initial Cd conc.	12.0 mg/l	–	–	8.4 mg/l	5.1 mg/l	42.0 mg/l
	Effluent Cd conc.	0.5 mg/l			0.2 mg/l	0.2 mg/l	0.2 mg/l
	Initial CN conc.	32.5 mg/l			35.0 mg/l	not determined	not determined
	Effluent CN conc.	0 mg/l			0 mg/l		
	Residual Cl_2 conc.	15.0 mg/l			20.0 mg/l	1.5 mg/l	0.4 mg/l
	Initial→final pH	9.15→12.35			8.7→12.1	6.85→11.35	10.3→11.35
	Time required	90.0 min.			70.0 min.	53.0 min.	181.0 min.
	Specific removal	1818 mg/kwh			1740 mg/kwh	2354 mg/kwh	6310mg/kwh
	Net change and percentage						

TABLE 7. Practical Highest Metal Concentration Successfully Treated by the Electrochemical Process

Metal	Practical Highest Concentration in the Beginning of Experiment mg/1	Final Concentration mg/1	Time Required min.	System and Operation Variables
Zn	500	0.22	100	5cm-25cm-35W - depth
Ni	493 493	0.10 0.72	80 100	5cm-10cm-35W - depth 5cm-10cm-15W - depth
Cu	510 (starting pH = 5.4) 560 (starting pH = 2.35)	0.54 0.12	160 100	5cm-25cm-35W - depth 5cm-10cm-35W - depth
Cd	50 mg/1 - cadmium 160 mg/1 - cyanide	0.15 0.10	240	5cm-25cm-35W - depth

FORM CW-1
(REV. 6-77)

ANNUAL REPORT — TITLE I PROJECT

OWRT PROJECT NO. A-063-RI

AGREEMENT NO. 14-34-0001-7084

FCCSET (COWRR) RESEARCH CATEGORY: V D

PROJECT TITLE: Bio-regeneration of Hydrocarbon-exhausted Activated Carbon

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT:

University of Rhode Island, Kingston, Rhode Island

PROJECT BEGAN — MONTH: Oct. ; YEAR: 1976

TO BE COMPLETED — MONTH: Sept. ; YEAR: 1978

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
Chester W. Houston	Ph.D.	Bacteriology
Stanley M. Barnett (Consultant)	Ph.D.	Chemical Engineering

STUDENT ASSISTANTS 1/	DEGREE HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND
Gilbert Houston, IV	B.S.	Biology

Narrative Statement

During the first year of this project concerned with the bio-regeneration of hydrocarbon-exhausted activated carbon, much of the work was of a preliminary nature concerned with analytical procedures which would be used later, isolating microorganisms, and in studying adsorption characteristics of samples of activated carbon which were obtained for the study. Microorganisms capable of growth on hydrocarbons as sole carbon and energy sources were obtained by the enrichment culture technique. Soil samples from areas of oil pollution were used. Several bacteria have been isolated and identified as members of the genus, Pseudomonas. In addition, cultures of Candida lipolytica and Cladosporium resinae have been secured and their growth characteristics studied since they may prove of value in the regeneration studies.

Samples of activated carbon in various grades for both vapor phase and aqueous phase applications were obtained from two commercial sources. Preliminary work involved a study of the adsorption of moisture by the activated carbon and the effect of its adsorption on the removal of organics. The results of this work suggested that the gravimetric approach which we had planned to use in some phases of the work, while perhaps workable after modification and further study, be abandoned and that studies be limited to the aqueous phase.

Some parameters of adsorption by the carbon to be used were determined in flasks to expedite work with the adsorption columns. Quantity and rate of adsorption were determined so that the carbon in columns could be charged readily and rinsed free of unbound organic. Glucose was used in this work since it could be easily quantitated and because it is oxidized readily by many microorganisms. For regeneration, Escherichia coli has been used in this study of bound glucose. Since it is a non-exacting heterotroph, a mineral solution medium can be used, and the system is therefore comparable to that which will constitute the main work of the project - the oxidation of bound hydrocarbon by adapted microorganisms.

Growth of E. coli on the bound glucose has been found to take place readily. Since quantitation procedures are simpler than those to be used in the planned work with hydrocarbons, it was decided to use the glucose-exhausted carbon for further study of the adsorption and regeneration processes. The effect of metabolic end products of microbial growth on the efficiency of the spent and regenerated carbon is currently being studied. Problems associated with the removal of microbial cells and the effects of incomplete removal are also being investigated.

Gas chromatographic procedures for the determination of hydrocarbons have been studied so that the methodology will be available for the project work involving the oxidation of adsorbed hydrocarbons and the regeneration of activated carbon which will constitute most of the work of the second year.

FORM OWR-1
(REV. 6-77)

ANNUAL REPORT -- TITLE I PROJECT

OWRT PROJECT NO. A-064-RI

AGREEMENT NO. 14-34-0001-7084

FCCSET (COWRR) RESEARCH CATEGORY: VD

PROJECT TITLE:
Ozonation for control of Enteric Viruses in Sewage Effluent.

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT:
Room 1, Woodward Hall, Univ. of Rhode Island, Kingston, RI 02881

PROJECT BEGAN--MONTH: Oct. 1 ; YEAR: 1976

TO BE COMPLETED--MONTH: Oct. 1 ; YEAR: 1978

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
Pei Wen Chang	DVM, Ph.D.	Microbiology

STUDENT ASSISTANTS 1/	DEGREE HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND
Kerry A. M. Georgitis	B.S.	Microbiology

Annual Report
Dr. P. W. Chang

A. RESEARCH PROJECT ACCOMPLISHMENTS

1) Preparation of tissue culture.

Because of the difficulties encountered in the purchasing of Rhesus monkeys, human and monkey cell lines were used in the preparation and assaying of virus stocks.

The two cell lines used were Hep-2 and Vero green monkey kidney cell lines. Technical difficulties were encountered in the growing of the cell lines. This was later found to be caused by the contamination of the commercially obtained serum with mycoplasma. With a change of serum the problem was eliminated. However, upon the continuous passage of the cells, a spontaneous degeneration of the cells occurred. New sources of cell lines were obtained. Again at the start the cell grew successfully, but as the cells were passed, they showed vacuolation, detachment from the glass surface and death. The reason for this was never found out, inspite of changing of medium and glassware.

Primary monkey kidney cells were then used. Since Rhesus monkeys from India were not available, Cynomolgus monkeys were used instead. Four monkeys were purchased and sacrificed at different times. One monkey had gross lesions on its spleen and its tissues were discarded. The other three monkeys appeared healthy and their kidneys were trypsinized and grown into monolayer of cell cultures. Difficulties were again encountered and an endogenous virus was isolated from the cell cultures. The virus was tentatively identified as SV40.

Another attempt was made in growing primary green monkey kidney cells. These were purchased as cell suspensions. The results were good and we have been able to, at last, maintain the cell cultures.

2) Preparation of stock viruses.

Poliovirus type 1, 2 and 3 and Coxsackie virus type B5 and ECHO virus type 12 and 29 were propagated either in Hep-2 cell line or green monkey kidney cell cultures in large quantities. The titer of the stock viruses were as follows: Polio 1, 2.4×10^7 $TCID_{50}$; Polio 2, 5.6×10^5 $TCID_{50}$; Polio 3, 1.65×10^6 $TCID_{50}$; Coxsackie B5, 1.5×10^6 $TCID_{50}$; ECHO 12, 5.9×10^6 $TCID_{50}$ and ECHO 29, 2.5×10^5 $TCID_{50}$. The viruses were then distributed in small aliquots and frozen at -70 C for future use.

3) Ozone production.

To obtain a sufficient amount of ozone production, trials were made at various flow rates of oxygen supply and at various voltages. It was determined that to obtain a consistent ozone concentration of 1 gm per hour in 50 ml samples, oxygen must be at a flow rate of 3 liters per minute and generator operated at 2300 volts. The method for assaying ozone is the potassium iodate procedure as described in the Standard Methods for Wastewater and Water Treatment.

4) Sewage collection and assaying for BOD.

Secondary sewage effluents were collected at the University of Rhode Island, Cranston and Warwick sewage plants. The effluents were tested for BOD, COD, nitrate, chloride, suspended solids, pH, and temperature. The effluent samples were then frozen at -20 C for future use.

B. PUBLICATION

None

C. PROJECT STATUS

The project will continue until September 30, 1978.

D. APPLICATION OF RESEARCH RESULT

None

E. WORK REMAINING AND PROGRESS CONTEMPLATED DURING NEXT YEAR

The object of the project is to determine guidelines for dosage and contact time of ozonation with respect to virus inactivation in various types of secondary sewage effluents.

Work yet to be done is to determine the inactivation dynamics of different viruses in the sewage effluents. The inactivation of the virus as a function of time will be compared with sewage effluent from different sewage plants, collected at different times of the year. The inactivation dynamics will also be compared with the controls not treated with ozone.

With the problem of growing cell culture for the assay of virus behind us, we expect that the remainder of the project should follow without difficulties.

FORM OW-1
(REV. 6-77)

ANNUAL REPORT — TITLE I PROJECT

OWRT PROJECT NO. A-065-RI AGREEMENT NO. 14-34-0001-7084 FCCSET (COWRR) RESEARCH CATEGORY: III C	PROJECT TITLE: CULTIVATING AND HARVESTING ALGAE TO FORESTALL EUTROPHICATION

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT:

Graduate School of Oceanography
University of Rhode Island, Kingston, R.I. 02881

PROJECT BEGAN—MONTH: October ; YEAR: 1976 | TO BE COMPLETED—MONTH: Sept ; YEAR: 78

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
Professor Nelson Marshall	Ph.D.	Oceanography
Cooperating Investigators		
Marilyn Harlin	Ph.D.	Botany
Paul Hargraves	Ph.D.	Oceanography

STUDENT ASSISTANTS 1/	DEGREE HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND
Henry S. Parker	B.A.; M.M.A.	Ph.D. candidate in Oceanography

1/ LIST ONLY THOSE STUDENTS SERVING AS RESEARCH ASSISTANTS IN A PROFESSIONAL SENSE. DO NOT INCLUDE HOURLY WAGE EARNERS SUCH AS DISHWASHERS HERE BUT INCLUDE THEM IN FORMS OW-2, 3, 7, AND 8. INCLUI POST-DOCTORAL STUDENTS IF NOT SERVING AS PROFESSIONAL INVESTIGATORS.

NARRATIVE STATEMENTS

ON A SEPARATE SHEET OR SHEETS TO BE ATTACHED HERETO, PROVIDE THE FOLLOWING INFORMATION USING THE SECTION OR PARAGRAPH HEADINGS SET FORTH BELOW WHEREVER POSSIBLE:

(A) RESEARCH PROJECT ACCOMPLISHMENTS. A DESCRIPTION OF RESEARCH PERFORMED AND FINDINGS, RESULTS, OR CONCLUSIONS RELATING THERETO.

(B) PUBLICATIONS. A LISTING BY TITLE, AUTHOR, VOLUME, PAGE NUMBER, ETC., OF PROJECT RELATED PUB-
LICATIONS OR REPORTS ISSUED AND PAPERS PREPARED. (ONE COPY OF EACH SUCH PUBLICATION, REPORT OR
PAPER SHOULD BE TRANSMITTED TO OWRT BY THE INSTITUTE DIRECTOR EXCEPT IN THOSE INSTANCES WHERE
ONE COPY HAS ALREADY BEEN PROVIDED TO OWRT IN ACCORDANCE WITH OWRT'S PROJECT REPORTING GUIDELI

(C) PROJECT STATUS. INDICATE WHETHER THE PROJECT HAS BEEN COMPLETED OR WILL CONTINUE IN PROGRESS IN
THE NEXT FISCAL YEAR. IF A PROJECT WAS COMPLETED DURING THE FISCAL YEAR ENDING SEPTEMBER 30 AN
A COMPLETION REPORT HAS BEEN SUBMITTED TO OWRT, PLEASE SO INDICATE BUT RECORD AS PART OF THIS
FORM THE PERTINENT FINDINGS, RESULTS, OR CONCLUSIONS (SEE "A" ABOVE), AND A LIST OF PUBLICATION
AND PAGES (SEE "B" ABOVE).

(D) APPLICATION OF RESEARCH RESULTS. WHEN POSSIBLE, IDENTIFY PERSONS OR ORGANIZATIONS THAT HAVE
USED RESULTS STEMMING FROM THIS PROJECT OR HAVE INDICATED KEEN INTEREST IN KNOWING OF SUCH
RESULTS AS SOON AS THEY BECOME AVAILABLE. IF POSSIBLE, DESCRIBE HOW RESULTS WILL BE OR ARE
EXPECTED TO BE USED.

(E) WORK REMAINING, AND PROGRESS CONTEMPLATED DURING NEXT YEAR. FOR AN UNCOMPLETED PROJECT, INCLUC
WORK REMAINING TO BE COMPLETED AND AN INDICATION OF WHAT PROJECT PROGRESS

NARRATIVE STATEMENT

A. RESEARCH PROJECT ACCOMPLISHMENTS

The objective of the research is to assess physiological/ecological responses of selected marine macroalgae under a variety of light, NH_4-N, and water motion regimes in order to investigate the feasibility of using these algae to effect advanced sewage treatment under field conditions. A series of laboratory and field experiments have been conducted to date:

Laboratory Experiments:

An apparatus was constructed which allows the simultaneous testing of algal plants in several combinations of light and nutrient (NH_4-N) regimes at different current speeds. Seven experiments (3 day growth periods) were conducted in a greenhouse using Gracilaria verrucosa, a commercially valuable red alga. Results suggested that current speed was a significantly more important factor than light or NH_4-N levels in controlling algal growth despite wide light level ranges (18.5 to 131.3 Ly day^{-1}) and varied initial NH_4-N concentrations (3 to 121 ug-At l^{-1}).

In order to verify greenhouse experimental results for Gracilaria, 7 subsequent experiments have been conducted under fluorescent lights in a laboratory, after modifying the apparatus so that four current speeds could be run simultaneously, rather than sequentially, as in previous experiments. Light levels tested were 40, 120, and 200 uE m^{-2} sec^{-1}, initial NH_4-N levels were 3, 20, 40, and 120 ug-AT l^{-1}, and current speeds were 0, 7.5, 15, 22.5, and 30 cm sec^{-1}. Preliminary results indicate the following:

1. At all water motion and NH_4-N levels tested, Gracilaria growth rates show a positive response to increased light levels from 40 to 200 uE m^{-2} sec^{-1}.

2. At relatively high light intensities (200 uE m^{-2} sec^{-1}), current increases up to 15 cm sec^{-1} enhance Gracilaria growth rates at all NH_4-N levels tested.

3. At all light levels tested, current increases up to 15 cm sec^{-1} enhance growth rates at low NH_4-N levels (0-3 ug-AT l^{-1}), but little or no enhancement of growth results at higher NH_4-N concentrations.

4. There is some evidence that optimal current velocities are between 10 and 20 cm sec^{-1} under all conditions but that the effects of current are most apparent at relatively low NH_4-N levels and relatively high light intensity.

Field Experiments:

Field experiments have been conducted since July, 1975. These provide for simultaneous analysis of growth rates of G. verrucosa and Ulva lactuca, a green alga, exposed in adjacent tubes to two different water motion levels at several sites representing a range of nutrient conditions from high NH_4-N levels (adjacent to a sewage outfall) to NH_4-N limited control sites. Again, preliminary analysis indicates that water motion may be an important factor positively affecting algal growth rates. At stations where NH_4-N levels are comparatively low (generally less than 6 ug-At l^{-1}) Ulva appears to grow 10%-40% faster in tubes experiencing 35-45% greater water motion; no such growth enhancement appears at stations exposed to comparatively high NH_4-N levels (generally 10 - 250 ug-At l^{-1}). Gracilaria shows more variable field responses to increasing water motion, but generally there is some enhancement of growth (10-20%) in more exposed tubes at all stations irrespective of NH_4-N levels.

B. PUBLICATIONS

Parker, H.S. 1977. Seaweed- An important resource with a promising future. Maritimes 21(3):1-3.

C. PROJECT STATUS

Estimated Date of Completion: 30 September 1978.

D. APPLICATION OF RESEARCH RESULTS

There are three potential applications for this research:

1. As a further insight into the potential role of Gracilaria and Ulva in advanced sewage treatment under field conditions: Dr. John Ryther of Woods Hole Oceanographic Institution has conducted considerable research on the ability of these plants to take up waste sewage nutrients with the objective of evaluating the feasibility of using them to provide tertiary sewage treatment in land-based ponds and raceways. He has recently expressed interest in a similar scheme under in-situ field conditions. Dr. Marilyn Harlin of the Botany Department, University of Rhode Island, has conducted research into the ability of these plants to take up NH_4-N excreted in a closed-system salmon farming operation.

2. As a contribution to the understanding of the physiological ecology of Gracilaria verrucosa, a commercially valuable red alga, and Ulva lactuca, variously described as a nuisance alga, a potential source

of feed, fertilizer, energy or carbohydrates, or as an organism potentially useful in advanced sewage treatment applications. Researchers from the University of Hawaii, the University of California, the University of South Florida, the University of New Hampshire, the University of Rhode Island, Dalhousie University in Halifax, N.S., the Catholic University of Santiago, Chile, the University of Concepcion, Chile, Woods Hole Oceanographic Institution, the Asian Institute of Technology, Bangkok, Thailand, the Canadian Government, and several private companies are just some of the institutions currently studying *Gracilaria* and *Ulva*.

3. As a contribution to the understanding of the role of water motion in aquatic plant physiological ecology: Largely neglected or taken for granted in the past, water motion is beginning to be considered as an important parameter in the biology of marine ecosystems, and generally deserving of considerably more study.

E. WORK REMAINING AND PROGRESS CONTEMPLATED DURING NEXT YEAR

Future plans include the repetition of all *Gracilaria* laboratory experiments at initial NH_4-N concentrations of 1-3, 40, and 120 ug-At l^{-1}, at current speeds of 0, 7.5, 15, and 22.5 cm sec^{-1} and at the light levels described in section A, above. In addition, a similar series of experiments will be conducted with the green alga, *Ulva lactuca*. Initial and final algal tissue samples will be analyzed for total nitrogen content for both species in order to detect possible differences in N incorporation corresponding to the various treatments. Finally, efforts will be made to analyze NH_4-N uptake rates under the various growth treatments, and to compare results with tissue N composition. As in the past, growth rates of all algal test plants will be determined and compared for each separate treatment.

9/27/77

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Graduate School of Oceanography

Mary Matzinger, Editor
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Cover: The seaweed *Gracilaria verrucosa* (see story page 1).

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SEAWEED: An Important Resource with a Promising Future

Henry S. Parker,
Ph.D. candidate in oceanography

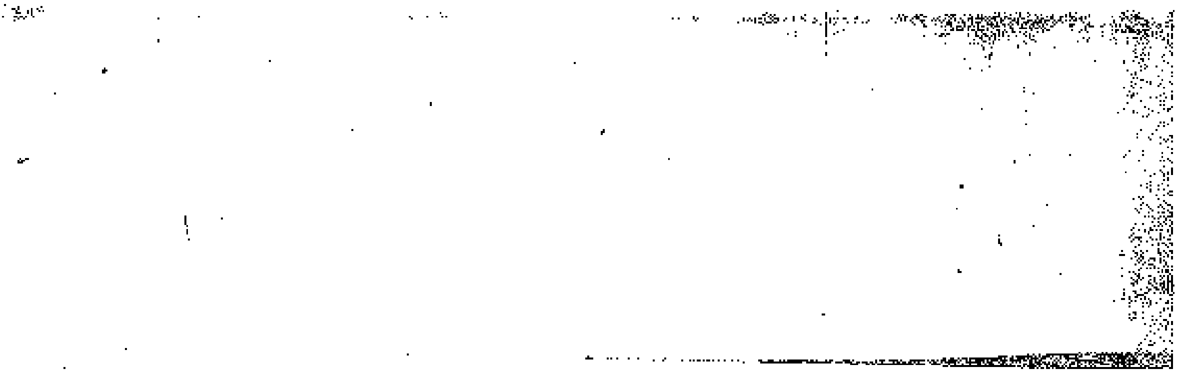
Ask the average New Englander what he thinks about seaweed, and the answer will most likely be ambivalent or downright derogatory. Tell him he probably brushed his teeth with seaweed that morning or that there's a good chance he had it for dinner the night before and he'll probably look at you strangely and find a sudden excuse to move on.

But you would be right. Seaweed has so many applications right now that it's a rare day when most of us don't use it, however unwittingly, in one form or another. And new uses are being found all the time. So much seaweed is used, in fact, that the market value of the world's production approaches a half billion dollars annually, representing a harvest of over 1.7 million metric tons.

What happens to all this seaweed? Though many of us may recoil at the thought, most of it is eaten. Seventy-five percent of the world's seaweed is harvested in Japan, China, and Korea for direct human consumption. As recently as 1955, it was estimated that seaweeds still comprised 25 percent of the daily Japanese diet. It is true that seaweeds contain important trace elements, vitamins, and minerals, but many of the world's people eat seaweed simply because they think it tastes good. Furthermore, though seaweed would cause some distress to the uninitiated human digestive system many Asians have apparently adapted to a diet of marine algae.

Most of the rest of the world's seaweed harvest is processed into a bewildering and fascinating variety of products. The use of seaweed as animal feed and crop fertilizer is familiar to almost everyone, but how many people know that in parts of the British Isles some sheep thrive on nothing but seaweed for most of the year or that seaweed comprised some 25 percent of the fertilizer used on Rhode Island farms at the turn of this century? Seaweed's potential as a fertilizer may be stronger today than ever because of its demonstrated effectiveness in promoting crop growth and hardiness, and because of the rising price of petroleum-based chemical fertilizers.

Outside of Asia, seaweed is primarily processed for the polysaccharides extracted from it. There are three major classes of seaweeds: The Reds (Rhodophyceae), the Browns (Phaeophyceae), and the Greens (Chlorophyceae). Certain Reds contain vegetable gums or the polysaccharides, agar and carrageenan, while some Browns contain the polysaccharide, algin. Agar, algin and carrageenan have unique suspending, stabilizing, thickening and gelling properties and act as colloids or emulsifiers in solution. They are so effective in this that they are used extensively in the food,



chemical, and pharmaceutical industries. Not only toothpaste, but milk, ice cream, puddings, soap, hand lotions, paint, polishes, and insecticides, to name just a few products, benefit by the addition of algin or carrageenan as a thickener, binder, or suspending agent.

Agar is used extensively as a bacterial culture medium, in the preservation of canned foods, in the waterproofing of paper and cloth, and in the preparation of some breads. Algal polysaccharides find their way into pharmaceutical products including pill coverings, deworming agents, laxatives, and, occasionally, ulcer therapy agents. Even the clothes we wear may contain a seaweed extract used in the preparation of sizing. In fact, so valuable and unique are seaweed polysaccharides that they form the basis of a 120-million-dollar-per-year industry worldwide and demand for them has now exceeded the available raw material supply.

The problem of limited supplies of important species is further aggravated by the extreme variability in seaweed quality, the vagaries of climate and politics in many of the harvesting areas, and changes in living standards which make it no longer economical or desirable for seaweed harvesters to ply their trade. Several researchers have suggested that only through cultivation can industry be assured of a sufficient reliable supply of high quality raw material at a stable competitive price.

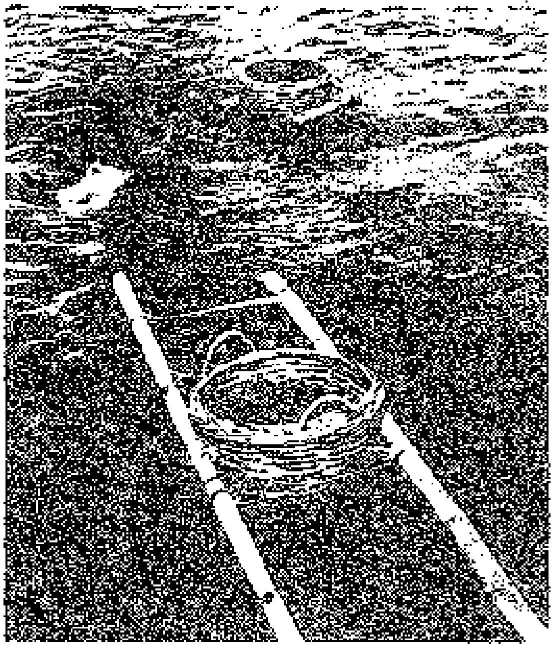
There is nothing new about seaweed cultivation. The Japanese first cultivated the Red alga, *Porphyra*, in 1736 and the farming of that genus alone is now a 150-million-dollar-a-year industry. Seaweed lends itself rather easily to cultivation. Growth rates are frequently remarkable with plants often doubling in size in as little as three days. Most plants may be sectioned anywhere and regrowth will occur in all sections, a characteristic helpful in seaweed culture. Nutrients are generally abundant in coastal waters and, when excessive, they may actually enhance the growth of some species suggesting a possible role for seaweed in sewage treatment. Finally, the technology for growing seaweed as a crop is already established in many parts of the world. A recent FAO report estimated that one sixth of the world's present aquaculture production consists of seaweeds.

U.S. involvement in seaweed cultivation has been slow, but is now accelerating rapidly. Most efforts have remained experimental with industry and government-financed research being carried out at a number of universities. Initial results have been sufficiently encouraging to justify several small-scale pilot projects and, in one case, a full cultivation program. There have been two general approaches to date. The first is labor-intensive, with projects located in tropical underdeveloped countries using local materials, labor, and technology and oriented toward developing a family-based cottage industry. Examples are Marine Colloids Inc.'s projects in Mexico, Indonesia, and the Philippines (see photo). In the latter country, a full-scale family-based cultivation program was developed which, within a short period of time, was able to supply the company's requirements for an important species.

Cultivation projects within the United States and Canada have, in contrast, been capital-intensive. In these experimental projects, seaweed is characteristically grown in large tanks or raceways in high density with aeration, circulation, and water renewal provided mechanically. The increased algal growth rates, ease of maintenance and harvesting, and degree of control which is possible does much to recommend such artificial cultivation techniques in countries where labor costs are high. Researchers at the University of South Florida, experimenting with the culture of a valuable Red alga, calculated that their tank culture approach would yield 60 times the revenue of a natural seaweed bed of comparable size.

The problems of scaling-up, scarcity of coastal land, and high energy, maintenance, and materials costs of capital-intensive projects may raise questions about their practicality. One way to offset these costs is to make use of waste energy. John Ryther of Woods Hole Oceanographic Institution has devised a scheme whereby waste heat from a power plant and waste nutri-

Seaweed culture in the Philippines. *Above:* Plants are grown by suspending them from homemade nets strung between mangrove slats visible in the background. The harvesters in the foreground display one plant grown in this fashion. *At right:* Collecting seaweed from natural beds in baskets floated on bamboo poles.



ents from a sewage treatment plant are used to stimulate the growth of a number of coexisting valuable marine species, including seaweeds. Degradation of water quality is forestalled while a revenue-producing crop is produced.

Whatever the approach, demand for seaweed products and the vulnerability of natural supplies suggest strongly that seaweed farming will become an increasingly attractive proposition in the future. A prerequisite to any successful farming operation is a detailed, fundamental knowledge of the biological requirements and tolerances of the species in question. Research conducted here and elsewhere is directed toward determining these requirements.

FORM OW-1
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ANNUAL REPORT — TITLE I PROJECT

OWRT PROJECT NO. A-066 R.I.

AGREEMENT NO. 14-34-0001-7084

FOCSET (COWRR) RESEARCH CATEGORY: ________

PROJECT TITLE:

Artificial Wetlands: Values, Regulatory and Developmental Issues

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT:

Rhode Island School of Design
55 Canal Street
Providence, R.I. 02903

PROJECT BEGAN—MONTH: Oct. 1 ; YEAR: 1976

TO BE COMPLETED—MONTH: Feb. 1 ; YEAR: 1978

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
John E. Lukens	Ph.D.	Civil Engineering
J. Michael Everett	M.A.	Architecture & Landscape Architecture

STUDENT ASSISTANTS 1/	DEGREE HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND
Raymond Short	B.A.	Landscape Architecture
Christopher	B.A.	Biology*

*currently pre-law at Harvard

A. Research Project Accomplishments

The project's primary purpose is to assess the various types of artificial wetlands for their value as wildlife habitats, for water supply, flood control, sediment control, recreation, and as open space, and to compare them to natural wetlands in these respects. We are working from the premise the the current wetlands acts may be overly restrictive, with two results:

1. they are ignored whenever possible because enforcement is difficult and spotty in individual cases, and
2. when observed by developers and town agencies, unfavorable patterns of community development may result.

One solution to this problem is to permit the filling of a natural wetland if the value lost in the process can be recreated elsewhere in an artificial wetland.

Thus, two questions must be answered:

1. How have wetlands affected patterns of community development in the past, and will the process be appreciably and unfavorably altered in the future by the wetlands acts?
2. Can artificial wetlands reproduce the important values of natural wetlands, and is it practical to create them?

Research has concentrated in these two separate but related questions, with Everett primarily responsible for the answer to the first question and Lukens primarily responsible for the answer to the second.

To date, the following tasks have been accomplished toward these ends:

I. Preparation

We have notified all relevant federal, state, local, university and private groups of this project. Part D of this report is a list of those persons or agencies that have expressed an interest in our work and results. Many of them have provided us with useful information and data, including maps, reports, research results, other publications and references and helpful critical comments.

These reference materials, plus other reports, books, wetlands acts and amendments, etc., discovered through library computer searches or in annotated wetland bibliographies, have been assembled into a small research library.

From this material we devised a classification for wetland types, a hybrid system incorporating: 1.) elements of the systems in the in the state wetlands acts 2.)the new Federal Fish and Wildlife Service system, and 3) hydrogeologic characteristics.

Our next step was to select the main types of wetland physical characteristics that need to be inventoried in order to be able to describe the various wetland values. As it turned out, relatively few characteristics, (topography, vegetation type, etc.) are necessary to describe these values. With the exception of visual character, these characteristics can be taken from commonly available data sources (topographic maps, airphotos, etc.).

II. Inventory

Early in the research, it became apparent that much of the necessary had already been mapped and inventoried by public agencies in four towns: Concord, Burlington, and Dracut, Mass. and South Kingstown, R.I. These towns also ranged in community development patterns from rural to highly-developed. Complete sets of reports and maps were purchased for these towns from the contractors that did the work, along with additional maps and reports on land use, geology, vegetation, and flood control. Field work was still needed for visual analysis and dating the creation of artificial wetlands. Approximately 120 artificial wetlands were identified in these towns. Twenty-five additional artificial wetlands from New York will be used for the assessment of wildlife value.

Initially, we intended to evaluate artificial wetlands by a one-to-one pairing of an artificial vs. a similar nearby natural wetland. It soon became apparent that a more valid approach would be to establish a norm for each value for each wetland type within an area (town), and then compare the values of artificial wetlands to these norms.

The inventory is complete with the exception of the visual characteristics during the fall and winter seasons, and the dating of 23 artificial wetlands in Burlington and Dracut.

III. Evaluation

During and after the remaining inventory work, the data will be evaluated, comparing artificial vs natural wetlands for the following values:

1. wildlife habitat(for hunting, birdwatching, and other educational and recreational uses)
2. water supply
3. flood control
4. visual and open space

The value of wetlands for sediment control is not being assessed because that function is damaging to a wetland and is incompatible with some other values. In fact, most of the values are not independent, but related to each other - often incompatible relationships. As one example, high wildlife values are incompatible with high values for flood control (and often incompatible with high surface water quality.)

Initially, it was our intent not only to compare values of artificial to natural wetlands, but also to correlate these values to the age of the artificial wetland. However, research indicates that the only values that change appreciably over a reasonable period of time are the wildlife and scenic values. Furthermore, both of these values are influenced as much, if not more, by surrounding land uses and vegetation than by intrinsic factors. The external and internal factors affecting wildlife and visual values may vary independently with time, making it meaningless to compare changes in these values with time. Thus, dating the artificial wetlands serves only to show how certain internal factors vary with time, but does not provide information on changes in values with time.

B. Publication

None

C. Project Status

Incomplete

D. Application of Results

See attached list of interested persons and organizations

E. Work Remaining, and Progress Contemplated During Next Year

We are requesting a four-month extension to allow the collection of visual data during fall and winter conditions, and to analyze the other data we have collected during the past twelve months. We did not collect fall and winter data last year because we were awaiting the completion of wetland projects by contractors in Burlington and Dracut, Mass., and South Kingstown, Rhode Island, from which we selected the artificial wetlands to study. We would like to be allowed February 1, 1978 as a completion date.

D. List of Interested Persons and Agencies

Mr. Charles H. Collison, Vice-President
National Audubon Society
950 Third Avenue
New York, N.Y. 10022

Mr. John H. Montanari, Project Leader
National Wetlands Inventory
Office of Biological Services
U.S. Fish and Wildlife Service
Washington, D.C. 20240

Mr. Bruce Lund, Director
Broadmoor Sanctuary
Massachusetts Audubon Society
79 South Street
South Natick, Mass. 01766

Mr. James Coleman
Miss Elizabeth Kline
The Wetlands Project
Massachusetts Audubon Society
Lincoln, Mass. 01773

Mr. Albert Bromberg
Division of Pure Waters, Room 306
New York State
Dept. of Environmental Conservation
50 Wolf Road
Albany, N.Y. 12233

Mr. Arthur Doyle
U.S. Army Corps of Engineers
New England Division
424 Tropelo Road
Waltham, Mass. 02154

Miss Ruth L. Hine
Water Planning
Wisconsin Dept. of Natural Resources
P.O. Box 7921
Madison, Wisconsin 53707

Mr. John V. Krutilla
Resources for the Future, Inc.
1755 Massachusetts Ave., N.W.
Washington, D.C. 20036

Mr. Eric Fried
Mr. David O'Dell
Wildlife Resources Center
New York State
Dept. of Environmental Conservation
Delmar, New York 12054

Mr. David Lavine
The Connecticut Inland Wetlands Project
P.O. Box 326
Durham, Conn. 06422

Dr. Francis Hall
I.N.E.R.
James Hall
University of New Hampshire
Durham, N.H. 03824

Mr. Kenneth H. Anderson, Director
Planning & Coordination
Maine Dept. of Inland Fisheries & Wildlife
284 State St.
Augusta, Maine 04333

Professor John H. Peverly
Dept. of Agronomy, Bradfield and Emerson Halls
N.Y. State College of Agriculture & Life Sciences
Cornell University
Ithaca, N.Y. 14853

Dr. Francis Golet
Dept. of Forestry and Wildlife Management
University of Rhode Island
Kingston, R.I. 02881

Professor Joseph S. Larson
Dept. of Forestry and Wildlife Management
Holdsworth Hall
University of Massachusetts
Amherst, Mass. 01002

Mr. J. Alfred Hawkes
R.I. Audubon Society
40 Bowen St.
Providence, R.I. 02903

Mr. Bruce Goodwin
Mr. Michael Pickering
R.I. Dept. of Natural Resources
40 Park St.
Providence, R.I. 02903

Mr. Michael Lapisky
R.I. Dept. of Natural Resources
P.O. Box 37
West Kingston, R.I. 02893

In addition, the directors of the State Water Resources Institutes of the New England States and New York are included, as are the Directors of Planning and Conservation in the Towns of Burlington, Concord, and Dracut, Mass., and South Kingstown, R.I.

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ANNUAL REPORT — TITLE I PROJECT

OWRT PROJECT NO. B-061-RI

AGREEMENT NO. 14-34-0001-3953

FCCSET (COWRR) RESEARCH CATEGORY: VI B

PROJECT TITLE: Analysis of Critical Water Problems in the Northeastern United States to Determine Essential Research Requirements

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT: Various locations in Northeastern United States. Designated fiscal agent: University of Rhode Island, Kingston, Rhode Island 02881

PROJECT BEGAN—MONTH: March ; YEAR: 73

TO BE COMPLETED—MONTH: Dec. ; YEAR: 77

PRINCIPAL INVESTIGATORS	DEGREES	DISCIPLINE
A. Ralph Thompson	Ph.D.	Chemical Engineering

Co-Principal Investigators: Directors of other Northeastern Water Resources Centers or Institutes

STUDENT ASSISTANTS 1/	DEGREE HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND

A workshop supported by this project was held November 10-12, 1976 at the Ramada Inn, Morgantown, West Virginia. This regional workship was entitled "Research Needs Related to Acid Mine Water" and was attended by over 60 people from various state and federal agencies, consulting firms, private industry and research organizations.

Topics considered during the two half-day and one full day periods were:

Overview: Research Needs Related to Acid Mine Water

Research Needs Related to:

Planning and Management Aspects
Mining Methodology for Prevention or
 Reduction of Acid Mine Water
Chemical and Physical Aspects
Biological Aspects
Treatment of Acid Mine Water
Social, Political and Institutional Aspects

Another workshop, supported by the project, was held on August 10 and 11 at the University of Maine, Orono, Maine. This workshop studied research needs related to "On-Site Disposal of Domestic Wastes". Approximately 40 people were in attendance representing a cross-section of state regulatory agencies and health departments as well as legal, social and physical research workers. The relatively small group, which was planned by invitation, made it possible to discuss many of the important problems in reasonable depth. There were numerous lively discussions during the course of the meeting. Participants responded to a request for written comments regarding their thoughts on research needs in this area. The compilation and consolidation of this information should provide an interesting report.

The workshop just mentioned will be the last in the series supported by this project. In all there were six workshops which attempted to analyze the critical water problems in the Northeast and determine research needs.

Also, a compendium of active water resources research in the region during Fiscal Year 1976 was published using project funds.

A completion report which will discuss the findings of the workships will be prepared at the conclusion of the project December 31, 1977.

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ANNUAL REPORT — TITLE I PROJECT

OWRT PROJECT NO. B070

AGREEMENT NO. 14-34-0001-6115

FCCSET (COWRR) RESEARCH CATEGORY: VD

PROJECT TITLE: Fermentation and Enzymatic Saccharification of Cellulose and Lignin Wastes

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT:

University of Rhode Island, Kingston, RI 02881

PROJECT BEGAN—MONTH: July ; YEAR: 1975

TO BE COMPLETED—MONTH: Sept. ; YEAR: 1977

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
Stanley M. Barnett	PhD	Chemical Engineering
C. W. Houston	PhD	Microbiology
A. G. Rand, Jr.	PhD	Food Science

STUDENT ASSISTANTS 1/	DEGREE HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND
Donald Aidala	BS	Chemical Engineering

Research Project Accomplishments

Cellulose is a major component of municipal, agricultural, and some industrial wastes. All sources contribute to polluting of natural waters because of runoff and incomplete treatment. This study has concentrated on developing a dual enzyme reactor system for breaking down both the cellulose and the lignin usually inhibiting easy utilization of cellulosic wastes

We have found that using pure oxygen rather than air increases cellulase enzyme activity levels during production of cellulase by T. viride, even though soluble oxygen levels remain the same. We have also shown that cellulase, the enzyme system responsible for breakdown of cellulose, is not foam fractionated as previously believed.

Also, we have isolated extra-cellular laccases from several organisms. The concentrated laccase has been found to degrade a purified lignin as well as guaiacol and hydroquinone.

Publications

J. Montecalvo, Jr. and S. M. Barnett, "An Extracellular Laccase: A Key To Enhanced Cellulose Utilization," in Proceedings of the 2nd Pacific Annual Chemical Engineering Congress, Denver, Aug. 1977.

Project Status

The project is now complete.

Application of Research Results

Dr. A. Allen, Pollution Abatement Division, US Army Natick Research and Development Command, Natick, MA, is particularly interested in our results. We have had requests for information from Dow Chemical and Union Carbide Corporation as well.

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ANNUAL REPORT — TITLE I PROJECT

OWRT PROJECT NO. B-073-RI

AGREEMENT NO. 14-34-0001-7130

FOCUS (OWRT) RESEARCH CATEGORY: VD

PROJECT TITLE:
Solubilization and Biodegradation
of Hydrocarbons

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT:

University of Rhode Island, Kingston, R. I. 02881

PROJECT BEGAN—MONTH: July; YEAR: 1976

TO BE COMPLETED—MONTH: Sept.; YEAR: 1978

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
Stanley M. Barnett	Ph.D.	Chemical Engineering
Chester W. Houston	Ph.D.	Microbiology
A. Ralph Thompson	Ph.D.	Chemical Engineering

STUDENT ASSISTANTS 1/	DEGREE HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND
K. Kulkarni	M.S.	Chemical Engineering

Research Accomplishments

Hydrocarbons are a major component of industrial and energy related leaks and spills and of municipal and industrial waste streams. This study has concentrated on what is believed to be the rate controlling factor in the biological treatment of hydrocarbon-the transport of hydrocarbons through an aqueous media.

Kinetics and mass transfer for the fermentation of hydrocarbons by Candida lipolytica and Pseudomonas aeruginosa was studied. Hexadecane and heptane were used as representative substrates. Addition of commercial surfactants showed that some surfactants can reduce the lag phase required for growth of the hydrocarbon degrading organism. However, if the organism is allowed to produce its own surfactant, its growth rate will eventually surpass that of an organism utilizing a commercial surfactant.

Project Status

The project is schedule to continue until September, 1978.

Work Remaining

We are now isolating the surfactant which the organism itself produces to increase hydrocarbon utilization. We are also preparing to study the role of the surfactant as a promoter of enzymatic breakdown of the hydrocarbon as well as that of a transport agent.

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ANNUAL REPORT — TITLE I PROJECT

OWRT PROJECT NO. B-076-RI

AGREEMENT NO. 14-34-0001-7134

OCSET (COWRR) RESEARCH CATEGORY: V B

PROJECT TITLE:

Interaction of Chlorine and Organic Molecules - Effects of Inorganics

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CARRIED OUT:

University of Rhode Island, Kingston, Rhode Island

ROJECT BEGAN—MONTH: 10 ; YEAR: 76

TO BE COMPLETED—MONTH: 12 ; YEAR: 77

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
Yuzuru Shimizu	Ph.D.	Natural Product Chemistry

STUDENT ASSISTANTS 1/	DEGREE HELD (IF ANY)	DISCIPLINE OR ACADEMIC BACKGROUND
Fujio Shimamura	M.S.	Marine Chemistry

INTERACTION OF CHLORINE & ORGANIC MOLECULES - EFFECTS OF INORGANICS

14-34-0001-7184 (B-076-RI) Dr. Yuzuru Shimizu

Chlorination is a common practice for the treatment of drinking, cooling and waste water. It is a very efficient and inexpensive method and is considered indispensable in most cases. However, recent changes in the concept of toxicology, especially as concerns carcinogenesis, teratogenesis, and potential harm to delicately balanced ecosystems, cast some questions on this widely used practice. The amount of active chlorine used in drinking water, waste water, power plant cooling water (antifouling) and in bleaching is enormous and its final destination in the natural system has not been fully elucidated.

Since 1970, we have been studying the interaction of active halogen atoms with organic molecules in water. We have proven that certain organic molecules in fact "fix" chlorine atoms to form chlorinated organic compounds (1)(2). The potential toxicity of such compounds in view of modern molecular toxicology is unpredictable, as is well exemplified by the reputed high toxicity of the fairly simple chloro phenol derivatives, dioxin. In fact, some deformations among children have been linked to a water system which depended on a river having a high content of phenylpropanoids and other organic compounds (3). Motivated by this report, we have studied the chlorination of various phenylpropanoids and amino acids, and have demonstrated the formation of a number of potentially harmful products, e.g. chlorinated styrenes from phenylpropanoids and nitrite (cyano-) compounds from amino acids.

However in naturally existing conditions, the reactions are expected to be more complicated. For example, in Rhode Island where manganese and iron ions are abundant in water, amino acids and various phenolic acids exist in chelate forms. Being in different entities and with the catalytic action of metal ions, these organic compounds may take unexpected reaction pathways. In this report we wish to describe a work on phenylalanine, a common amino acid, as a model compound in regards to the effects of heavy metal ions and chlorine (hypochlorite) concentrations.

EXPERIMENTAL

1. Chlorination of Phenylalanine

Ten ml of an aqueous solution of sodium hypochlorite at various concentrations was added to 10 ml of a 0.5 x 10^{-2}M aqueous phenylalanine solution. One ml of each reaction mixture was extracted with 1 ml of ether after 1 min to 24 hrs, and the ethereal extracts were immediately injected into the GLC (GLC parameters: column 1% OV17 6 ft, column temp: 90°C, injection temp: 120°C, detected temp: 140°C). Under the conditions chosen, four peaks: I, II, III, and IV were detected at retention times I: 1.4 min; II: 2.5 min; III: 5.6 min; IV: 8.2 min.

In order to identify these four compounds, a large scale experiment was done and the four compounds were separated by thin-layer chromatography (TLC) on plates using benzene as the solvent. Rechromatography on TLC was repeated until each compound appeared as one peak on GLC. The identification of these compounds was confirmed by comparing their retention times on GLC;

their co-chromatography on TLC and GLC; and their IR, UV and mass spectra to those of authentic compounds. Consequently the four isolates were identified as I: benzaldehyde, II: phenylacetoalde, III: phenylacetonitrile, IV: 2,2-dichlorophenylacetoaldehyde.

2. Effect of the Concentration of NaClO

The relationship between the concentration of sodium hypochlorite and the amount of product isolated was studied. Different concentrations of sodium hypochlorite were added to a phenylalanine solution (0.5×10^{-2}M).

Benzaldehyde (I) began to form after several hours except at a concentration of 5×10^{-2}M. The maximum yield of phenylacetoaldehyde (II) was obtained when an equimolar amount of hypochlorite was added to the phenylalanine. The higher the concentration of NaClO, the lesser the amount of II was formed, suggesting that an excess amount of NaClO can alter the reaction mode or further react with phenylacetoaldehyde. Phenylacetonitrile (III) was produced at rather high concentrations of NaClO.

2,2-Dichlorophenylacetoaldehyde (IV) at a conc. of 5×10^{-2}M the amount of IV initially formed was very high but it rapidly decreased.

3. Effect of Fe^{+++}

Three different concentrations (0.5×10^{-2}M, 0.5×10^{-3}M, 0.5×10^{-4}M) of ferric sulfate were added to the reaction solution at several concentrations of sodium hypochlorite (0.5×10^{-2}M, 1.0×10^{-2}M, 1.5×10^{-2}M, 5.0×10^{-2}M).

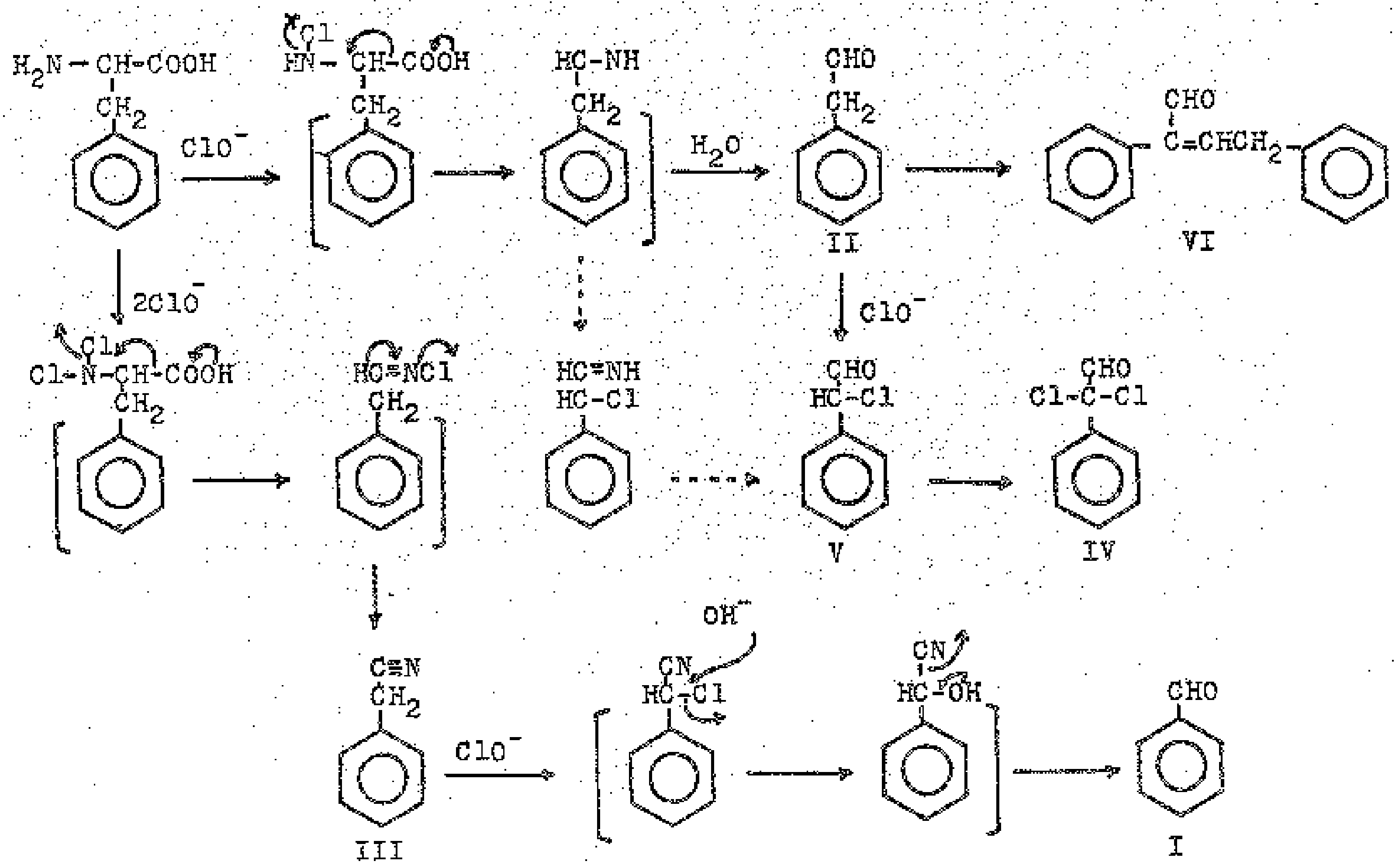
4. Effect of Mn^{++}

We also studied the effect of manganese ion concentrations. Two different concentrations ($0.5 \times 10^{-2}M$ and $0.5 \times 10^{-3}M$) of manganese (M^{++}) sulfate were added to the amino acid solution at sodium hypochlorite concentrations of: $0.5 \times 10^{-2}M$, $1 \times 10^{-2}M$, $1.5 \times 10^{-3}M$, and $5 \times 10^{-2}M$.

RESULTS AND DISCUSSION

Under the employed conditions, when the sodium hypochlorite concentration is below or equal to that of phenylalanine, phenylacetoaldehyde appears to be the only product. Above that concentration phenylacetonitrile became the major product together with 2,2-dichlorophenylacetoaldehyde. This process can be explained by monochlorination of an amino group as a first step and subsequent hydrolysis to the aldehyde. K. L. Murphy, et al (4) investigated how far amino acids could be oxidized by measuring the amount of organic carbon of glycine and chlorine that remained after 2 hours of reaction. They observed at molar ratios less than 2.0 a chloramine residue and no loss of carbon, which indicates that only chlorination of amino groups had occurred. A molar ratio of 2.0 would be required to form dichloramine. At higher molar ratios, a sharp decrease in both residual chlorine and organic carbon took place. Our results agree with their observations.

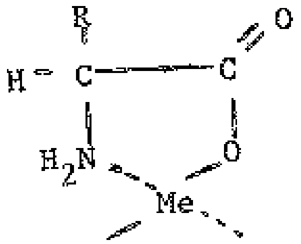
Other than the four compounds previously mentioned, 2-chlorophenylacetoaldehyde (V) and the dimeric aldehyde (VI) were also isolated from the large scale reaction products. The former is



Scheme 1. Degradation of Phenylalanine by Hypochlorite.

considered to be an intermediate formed one step before 2,2-dichlorophenylacetoaldehyde and the latter a secondary product due to an aldol condensation between two molecules of phenylacetoaldehyde. The entire proposed mechanism is shown on Scheme 1.

The effects of heavy metals on the reaction was obvious at the concentration of 0.5×10^{-2}M, with both Mn^{++} and Fe^{+++}. At this concentration phenylalanine is likely to exist in the chelated form, which



undoubtedly effects the initial process of N-chlorination and the subsequent decarboxylation process. The results indicate that the metal ions enhance remarkably (2-3 times) the initial formation of such compounds as phenylacetaldehyde and phenylacetonitrile but at the same time seem to catalyze further oxidation of the formed products. It implies that in the case of chlorination of iron or manganese rich organic material containing water, a rapid consumption of active chlorine is expected.

CONCLUSION

An amino acid (phenylalanine) was found to be oxidized with excess hypochlorite more rapidly in the presence of Fe^{+++} and Mn^{++}.

Benzaldehyde (I), phenylacetoaldehyde (II), phenylacetonitrile (III), and 2,2-dichlorophenylacetoaldehyde (IV) were identified as reaction products and a reaction mechanism is speculated.

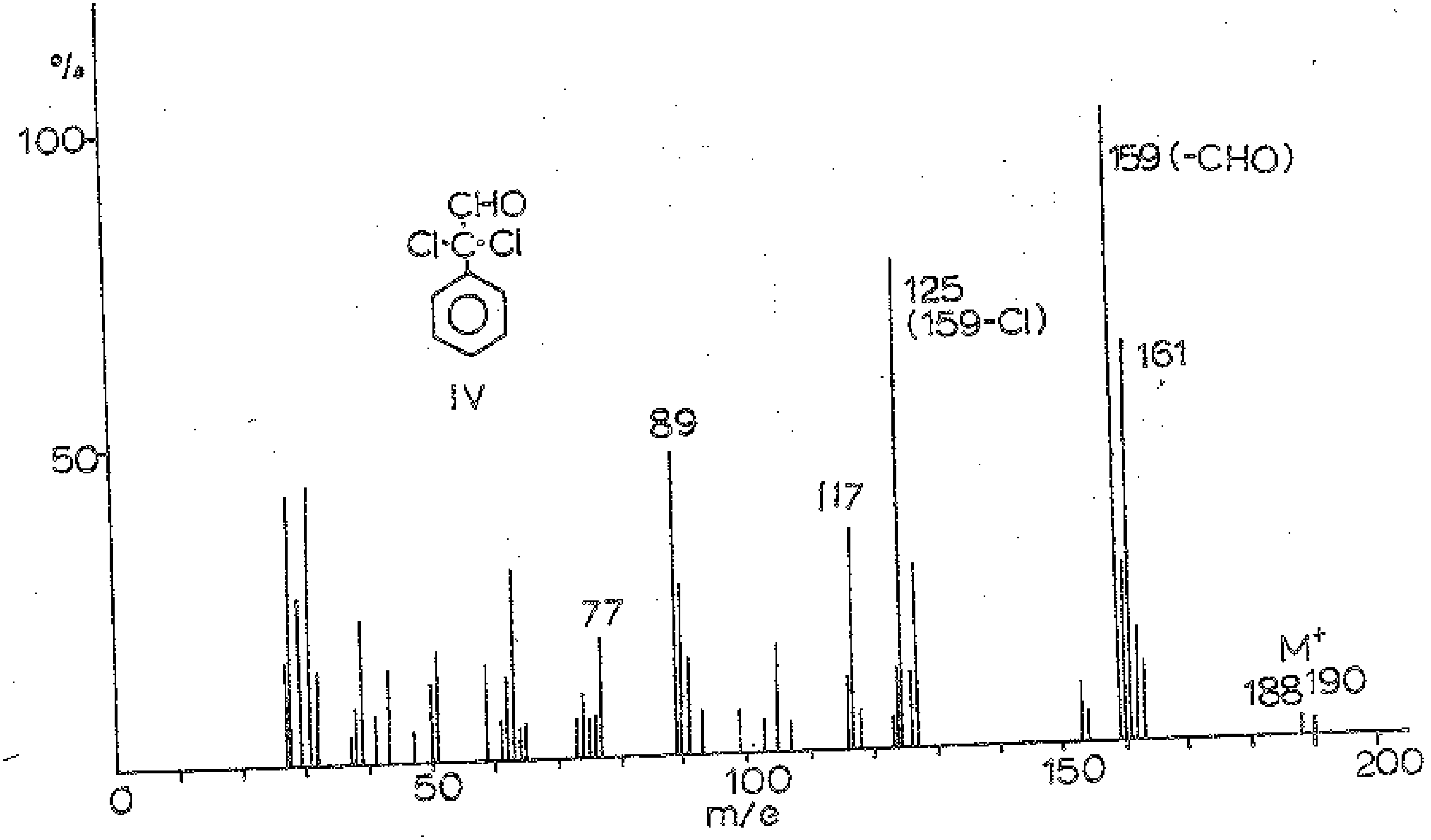


Fig. 1. Mass Spectrum of 2,2-Dichlorophenylacetoaldehyde (IV) Isolated from Phenylalanine Chlorination Products.

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2) Shimizu, Y., and Hsu, R. Y., Phenylpropanoids in chlorination, EPA Chlorination Workshop, Chesapeake Sciences 18 (1), 129 (1977).

3) Takizawa, E., "Study on Kaschin-Beck Disease in Japan" Ogata-Shoten, Tokyo 1970.

4) Murphy, K. L., Zalsum, R. and Fulford, D., Effect of Chlorination Practice on Soluble Organics, Water Res. 9, 389-396 (1975).

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Parker, Henry S., "Seaweed - An Important Resource with a Promising Future" Maritimes, Volume 21, Number 3, p. 1, August 1977.

J. Montecalvo, Jr., and S.M. Barnett, "An Extracellular Laccase: A Key to Enhanced Cellulose Utilization", Proceedings of the 2nd Pacific Annual Chemical Engineering Congress, Denver, Colorado, August 1977.

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ANNUAL REPORT - TRAINING AND EDUCATION ASPECTS OF THE WATER RESEARCH PROGRAM UNDER P.L. 88-379

Name of University: (or College) University of Rhode Island

SUBMIT THE INFORMATION SPECIFIED BELOW FOR THE UNIVERSITY AT WHICH THE WATER RESOURCES RESEARCH INSTITUTE OR CENTER APPROVED UNDER P.L. 88-379 IS LOCATED, AND FOR OTHER UNIVERSITIES WITH WHICH THE INSTITUTE OR CENTER IS COOPERATING. KEEP THE STATISTICS ON ENROLLMENTS, NUMBER OF STUDENTS GRADUATING, EMPLOYMENT STATUS OF GRADUATES, NEW COURSES, ETC., SEPARATE FOR EACH UNIVERSITY. IT IS RECOGNIZED CERTAIN OF THE REQUESTED DATA ON STUDENTS MAY NOT BE READILY AVAILABLE. IF SO, PROVIDE BEST ESTIMATE FIGURES. IN OW-9, DATA ON STUDENTS ARE REQUESTED ONLY FOR THOSE STUDENTS WHO RECEIVED EMPLOYMENT AS RESEARCH PROJECT OR PROGRAM ASSISTANTS THROUGH THE P.L. 88-379 PROGRAM. IF EXTRA SPACE IS NEEDED, ADD PAGES AND NUMBER EACH CONTINUATION ITEM IN THE ORDER SHOWN BELOW.

A. Number of students receiving employment as research project or program assistants through the P.L. 88-379 program. (Include only those students, both continuing and graduating, paid wholly or in part with P.L. 88-379 funds during the past fiscal year.)

Category of Students	No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc. 2/ Scientific Discipline of Student	Number
(1) Undergraduates	Biology	1
	Landscape Architecture	1

2/ This refers to educational background prior to employment as research assistant on P.L. 88-379 projects--not to departments in which projects are being conducted.

A. (Continued)

Category of Students	No. by Scientific Discipline or Major Field of Study (Engineering, Biology, Economics, etc.	
	Scientific Discipline of Student	Number
(2) Master's Students	Biology	1
	Chemical Engineering	1
	Civil & Environmental Engrg.	3
(3) Doctoral Students	Chemical Engineering	1
	Civil & Environmental Engrg.	1
	Oceanography	1
	Pharmacognosy	1
(4) Postdoctoral Students		

B. Employment status of majors in water-related fields who graduated during the school year ending about June and who receive P.L. 88-379 support.

EMPLOYMENT STATUS	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1. No. employed in water-related positions in: Total----				
Federal Agencies---------------	( )	( )	( )	( )
State & Local Agencies---------	( )	( )	( )	( )
University or College----------	( )	( )	( )	( )
Other - Including private enterprise------------------	( )	( )	( )	( )
2. No. graduates returning to school for advanced degree--------------				
3. No. going into military service------------------------				
4. No. unemployed or working in other fields------------------				
5. No. status unknown-------------				
6. Totals---------------------------	None	None	None	None

C. Type of employment of those school year graduates who received P.L. 88-379 support and who are known to have gone into water-related positions. (Number should agree with total listed under item 1 of the preceding paragraph "-". Graduates enrolled for further course work or training should not be listed here as employed.)

Number of Graduates Engaged in Water-Related Work In:	CATEGORY OF SCHOOL YEAR GRADUATE BY DEGREE OBTAINED			
	Bachelor's Degree	Master's Degree	Doctoral Degree	Total
1A. Federal Agencies:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1B. State & Local Agencies:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
1C. University or College: 3/				
a. Primarily Teaching				
b. Primarily Research				
c. Primarily Research & Teaching				
d. Other or not known				
1D. Other - Including Private Enterprise:				
a. Primarily Research				
b. Primarily Planning				
c. Primarily Development				
d. Primarily Operations				
e. Primarily Management				
f. Other or not known				
Totals	None	None	None	None

Selected summary of above data -- from the "Total" column:

Research (1Aa, 1Ba, 1Cb, 1Cc& 1Da) ____

Planning (1Ab, 1Bb & 1Db) ____

Development (1Ac, 1Bc & 1Dc) ____

Operations (1Ad, 1Bd & 1Dd) ____

Management (1Ae, 1Be, & 1De) ____

3/Do not include here students working as research assistants and receiving course credits.

FY 1977 ANNUAL REPORT--ANNUAL ALLOTMENT (SEC. 100) [illegible]

State Water Resources Research Institute: Rhode Island | Report [illegible]

OWRT Project No. A-062-RI

Annual Allotment Agreement No. 14-34-0001-7084

Principal Investigator(s):

Alan S. Marcus

Project Title: Ground W[illegible] of the Stratified Aquifer in the Upper [illegible] River Basin

Project Began-- Month: July , Yr: [illegible] Scheduled Completion--Month: June , 1977

Cost Categories to Which FY19 77 Federal Sec. 100 Funds Applied	Annual 1/ Budgeted For FY 1977	Actual 2/ Expenditures For FY 19 77
A. SALARIES AND WAGES .. TOTAL	4801.	4801.00
PRINCIPAL INVESTIGATOR(S) 3/ No. 1 MAN-MONTHS 0.9	(355.)	(481.00)
OTHER PROFESSIONAL STAFF: No. 2 MAN-MONTHS	(470.)	( )
GRADUATE STUDENT ASSTS & [illegible] No. 1 MAN-MONTHS 4.5	(3976.)	(4320.00)
UNDERGRADUATE STUDENT ASSTS & [illegible] No. MAN-MONTHS	( )	( )
NON-STUDENT TECHNICIANS & OTHERS No. MAN-MONTHS	( )	( )
B. EMPLOYEE BENEFITS TOTAL		
C. NON-EXPENDABLE PROPERTY 4/ TOTAL	500.	357.23
D. EXPENDABLE PROPERTY TOTAL	353.	259.89
E. OTHER DIRECT COSTS TOTAL	200.	135.94
Travel	(200.)	(135.94)
	( )	( )
	( )	( )
F. GRAND TOTAL FY 77 COSTS 5/	5654.	5554.06

1/ AMOUNT BUDGETED IS AS SET FORTH IN PROJECT BUDGETS (AND REVISIONS) SUBMITTED TO AND ACCEPTED BY OWRT. DOLLARS SHOWN ARE FEDERAL FUNDS.

2/ ACTUAL EXPENDITURES INCLUDES FIRM OUTSTANDING COMMITMENTS (OR OBLIGATIONS) INCLUDING, FOR EXAMPLE, UNLIQUIDATED ORDERS FOR EQUIPMENT.

3/ MAN-MONTHS RELATE TO TIME PAID FOR BY FEDERAL FUNDS ONLY.

4/ NON-EXPENDABLE PROPERTY IS DEFINED AS PROPERTY WHICH HAS CONTINUING USE AS A SELF-CONTAINED UNIT; IS NOT CONSUMED IN USE; DOES NOT ORDINARILY BECOME A FIXTURE OR LOSE ITS IDENTITY, OR FORM A COMPONENT OF EQUIPMENT, MACHINE, PLANT, ETC.

5/ IF THE "TOTAL" OF "ACTUAL EXPENDITURES" VARIES MORE THAN 10% FROM THE "AMOUNT BUDGETED," AN EXPLANATION OF SUCH VARIANCE SHOULD BE PROVIDED AS AN ATTACHMENT TO THIS SHEET.

State where Institute is located: Rhode Island

Report as of [illegible]

OWRT Project No. A-0[illegible]-RI

Annual Allotment Agreement No. 14-34-0001-7069

Principal Investigator(s)

Calvin P.C. Poon

Project Title:

Water Pollution Con[illegible]

Industry

Project Began-- Month: July ; Yr: 1976

Scheduled Completion--Month: [illegible] , 19 78

Cost Categories to Which FY1977 Federal Sec. 100 Funds Applied		Amount 1/ Budgeted For FY 19 77	Actual 2/ Expenditures For FY 197
A. SALARIES AND WAGES	TOTAL:	12125.	12899.68
PRINCIPAL INVESTIGATOR(S) 3/ NO: 1 MAN-MONTHS:	2.0	(5324.)	(4776.88)
OTHER PROFESSIONAL STAFF NO: MAN-MONTHS:		( )	( )
GRADUATE STUDENT ASSTS & TECH. NO: 3 MAN-MONTHS:	7.5	(6801.)	(8122.80)
UNDERGRADUATE STUDENT ASSTS & TECH. NO: MAN-MONTHS:		( )	( )
NON-STUDENT TECHNICIANS & OTHERS NO: MAN-MONTHS:		( )	( )
B. EMPLOYEE BENEFITS	TOTAL:		
C. NON-EXPENDABLE PROPERTY 4/	TOTAL:	1000.	168.50
D. EXPENDABLE PROPERTY	TOTAL:	600.	1367.52
E. OTHER DIRECT COSTS	TOTAL:	400.	
Travel		(300.)	( )
Publication		(100.)	( )
		( )	( )
F. GRAND TOTAL FY 77 COSTS 5/		14125.	14435.70

1/ AMOUNT BUDGETED IS AS SET FORTH IN PROJECT BUDGETS (AND REVISIONS) SUBMITTED TO AND ACCEPTED BY OWRT. DOLLARS SHOWN ARE FEDERAL FUNDS.

2/ ACTUAL EXPENDITURES INCLUDES FIRM OUTSTANDING COMMITMENTS (OR OBLIGATIONS) INCLUDING, FOR EXAMPLE, UNLIQUIDATED ORDERS FOR EQUIPMENT.

3/ MAN-MONTHS RELATE TO TIME PAID FOR BY FEDERAL FUNDS ONLY.

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FY 19__ ACTUAL BUDGET--ANNUAL ALLOTMENT (Sec. 100) Funds

State where Institute is located: Rhode Island | Report

OWRT Project No. A-069-RI

Annual Allotment Agreement No. 14-34-0001-7081

Project Title

Bio-regeneration of Hy[illegible] [illegible] Activated Carbon

Principal Investigator(s)

Chester W. Houston

Project Began-- Month: Oct. ; Yr: 1976 | Scheduled Completion--Month: Sept. , 1978

Cost Categories to Which FY1977 Federal Sec. 100 Funds Applied		Amount Budgeted 1/ For FY 1977	Actual Expenditures 2/ For FY 1977
A. SALARIES AND WAGES	TOTALS	8644.	6004.00
PRINCIPAL INVESTIGATOR(S) 3/ NO: 1 MAN-MONTHS:		( )	( )
OTHER PROFESSIONAL STAFF. NO: 1 MAN-MONTHS:		(2000.)	( )
GRADUATE STUDENT ASSTS & TECH. NO: MAN-MONTHS: 7.5		(6644.)	(6004.00)
UNDERGRADUATE STUDENT ASSTS & TECH. NO: MAN-MONTHS:		( )	( )
NON-STUDENT TECHNICIANS & OTHERS NO: MAN-MONTHS:		( )	( )
B. EMPLOYEE BENEFITS	TOTALS		
C. NON-EXPENDABLE PROPERTY 4/	TOTALS	1500.	1061.33
D. EXPENDABLE PROPERTY	TOTALS	600.	1765.80
E. OTHER DIRECT COSTS	TOTALS	100.	
Travel		(100.)	( )
		( )	( )
		( )	( )
F. GRAND TOTAL FY 77 COSTS 5/		10844.	8831.13 ✓

1/ AMOUNT BUDGETED IS AS SET FORTH IN PROJECT BUDGETS (AND REVISIONS) SUBMITTED TO AND ACCEPTED BY OWRT. DOLLARS SHOWN ARE FEDERAL FUNDS.

2/ ACTUAL EXPENDITURES INCLUDES FIRM OUTSTANDING COMMITMENTS (OR OBLIGATIONS) INCLUDING, FOR EXAMPLE, UNLIQUIDATED ORDERS FOR EQUIPMENT.

3/ MAN-MONTHS RELATE TO TIME PAID FOR BY FEDERAL FUNDS ONLY.

4/ NON-EXPENDABLE PROPERTY IS DEFINED AS PROPERTY WHICH HAS CONTINUING USE AS A SELF-CONTAINED UNIT; IS NOT CONSUMED IN USE; DOES NOT ORDINARILY BECOME A FIXTURE OR LOSE ITS IDENTITY, OR FORM A COMPONENT OF EQUIPMENT, MACHINE, PLANT, ETC.

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Project A-063-RI

Anticipated professional staff was not available and far more supplies than estimated for project were required.

[illegible]

[illegible] Institute [illegible] | [illegible]

[illegible] | Project Title:
[illegible] Agreement | [illegible] for [illegible]
No. 14-[illegible]-0001-701 | [illegible] in [illegible]

Principal Investigator(s)

[illegible] Chang

Project Began - Month: Oct. ; Year: 1975 | Scheduled Completion - Month: Sept. , 1978

Cost Categories to Which FY19 77 Federal Sec. 100 Funds Applied	Amount Budgeted For FY 1977 1/	Actual Expenditures For FY 1977 2/
TOTALS	6644.	5561.15
A. SALARIES AND WAGES 3/	( )	( )
PRINCIPAL INVESTIGATOR(S) NO: 1 MAN-MONTHS:	( )	(5561.15)
OTHER PROFESSIONAL STAFF NO: 1 MAN-MONTHS: 11.0	( )	( )
GRADUATE STUDENT ASSTS & TECH. NO: 1 MAN-MONTHS:	(6644.)	( )
UNDERGRADUATE STUDENT ASSTS & TECH. NO: MAN-MONTHS:	( )	( )
NON-STUDENT TECHNICIANS & OTHERS NO: MAN-MONTHS:	(	
TOTALS		
B. EMPLOYEE BENEFITS 4/ TOTALS		
C. NON-EXPENDABLE PROPERTY TOTALS	3200.	4341.07
D. EXPENDABLE PROPERTY TOTALS	90.	42.92
E. OTHER DIRECT COSTS	(90.)	(42.92)
Travel	( )	( )
	( )	( )
	(	
F. GRAND TOTAL FY 77 COSTS 5/	9934.	9945.14

1/ AMOUNT BUDGETED IS AS SET FORTH IN PROJECT BUDGETS (AND REVISIONS) SUBMITTED TO AND ACCEPTED BY OWRT. DOLLARS SHOWN ARE FEDERAL FUNDS.

2/ ACTUAL EXPENDITURES INCLUDES FIRM OUTSTANDING COMMITMENTS (OR OBLIGATIONS) INCLUDING, FOR EXAMPLE, UNLIQUIDATED ORDERS FOR EQUIPMENT.

3/ MAN-MONTHS RELATE TO TIME PAID FOR BY FEDERAL FUNDS ONLY.

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[illegible]

Project Title:

Cultivating and Harv[illegible]
Forestall Accelerat[illegible]

Principal Investigator(s)

Nelson Marshall

Project Began-- Month: Oct. ; Yr: 1976 | Scheduled Completion--Month: [illegible], 19 78

Cost Categories to Which FY1977 Federal Sec. 100 Funds Applied	Amount Budgeted For FY 19 77 1/	Actual Expenditures For FY 19 __ 2/
A. SALARIES AND WAGES TOTALS	7145.	7145.00
PRINCIPAL INVESTIGATOR(S) 3/ No. 1 MAN-MONTHS	( )	( )
OTHER PROFESSIONAL STAFF No. 2 MAN-MONTHS	( )	( )
GRADUATE STUDENT ASSTS & TECH. No. 1 MAN-MONTHS 7.5	(7145.)	(7145.00)
UNDERGRADUATE STUDENT ASSTS & TECH. No. MAN-MONTHS	( )	( )
NON-STUDENT TECHNICIANS & OTHERS No. MAN-MONTHS	( )	( )
B. EMPLOYEE BENEFITS TOTALS	3200.	1475.58
C. NON-EXPENDABLE PROPERTY 4/ TOTALS	239.	1324.52
D. EXPENDABLE PROPERTY TOTALS	500.	1106.69
E. OTHER DIRECT COSTS TOTALS	500.	1106.69
Travel	(500.)	(1106.69)
	( )	( )
	( )	( )
F. GRAND TOTAL FY 77 COSTS 5/	11084.	11051.79

1/ AMOUNT BUDGETED IS AS SET FORTH IN PROJECT BUDGETS (AND REVISIONS) SUBMITTED TO AND ACCEPTED BY OMRT. DOLLARS SHOWN ARE FEDERAL FUNDS.

2/ ACTUAL EXPENDITURES INCLUDES FIRM OUTSTANDING COMMITMENTS (OR OBLIGATIONS) INCLUDING, FOR EXAMPLE, UNLIQUIDATED ORDERS FOR EQUIPMENT.

3/ MAN-MONTHS RELATE TO TIME PAID FOR BY FEDERAL FUNDS ONLY.

4/ NON-EXPENDABLE PROPERTY IS DEFINED AS PROPERTY WHICH HAS CONTINUING USE AS A SELF-CONTAINED UNIT; IS NOT CONSUMED IN USE; DOES NOT ORDINARILY BECOME A FIXTURE OR LOSE ITS IDENTITY, OR FORM A COMPONENT OF EQUIPMENT, MACHINE, PLANT, ETC.

5/ IF THE "TOTAL" OF "ACTUAL EXPENDITURES" VARIES MORE THAN 10% FROM THE "AMOUNT BUDGETED," AN EXPLANATION OF SUCH VARIANCE SHOULD BE PROVIDED ON AN ATTACHMENT TO THIS SHEET.

Project A-065-RI

Balance of equipment will be
constructed during second year
of project.

[illegible]

[illegible]

OWRT [illegible] Project Title:

Annual Allotment Agreement No. [illegible]

Principal Investigator(s)

[illegible]

Artificial [illegible] and Development [illegible]

Project Began - Month: Oct. ; Yr: 1976 | Scheduled Completion - Month: [illegible], 1977

Cost Categories to Which FY1977 Federal Sec. 100 Funds Applied		Amount 1/ Budgeted For FY 1977	Actual 2/ Expenditures For FY 1977
A. SALARIES AND WAGES	TOTAL:	11500.	7783.35
PRINCIPAL INVESTIGATOR(S) 3/ NO: 1 MAN-MONTHS:	1.5	(3500.)	(4228.35)
OTHER PROFESSIONAL STAFF. NO: 2 MAN-MONTHS:	2.0	(4000.)	(1910.00)
GRADUATE STUDENT ASSTS & TECH. NO: MAN-MONTHS:		(4000.)	( )
UNDERGRADUATE STUDENT ASSTS & TECH. NO: 2 MAN-MONTHS:	2.0	( )	(1645.00)
NON-STUDENT TECHNICIANS & OTHERS NO: 1 MAN-MONTHS:		( )	( )
B. EMPLOYEE BENEFITS	TOTAL:		
C. NON-EXPENDABLE PROPERTY 4/	TOTAL:		
D. EXPENDABLE PROPERTY	TOTAL:	200.	809.40
E. OTHER DIRECT COSTS	TOTAL:	700.	357.09
Travel		(700.)	(357.09)
		( )	( )
		( )	( )
F. GRAND TOTAL FY 77 COSTS 5/		12400.	8949.84

1/ AMOUNT BUDGETED IS AS SET FORTH IN PROJECT BUDGETS (AND REVISIONS) SUBMITTED TO AND ACCEPTED BY OWRT. DOLLARS SHOWN ARE FEDERAL FUNDS.

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3/ MAN-MONTHS RELATE TO TIME PAID FOR BY FEDERAL FUNDS ONLY.

4/ NON-EXPENDABLE PROPERTY IS DEFINED AS PROPERTY WHICH HAS CONTINUING USE AS A SELF-CONTAINED UNIT; IS NOT CONSUMED IN USE; DOES NOT ORDINARILY BECOME A FIXTURE OR LOSE ITS IDENTITY, OR FORM A COMPONENT OF EQUIPMENT, MACHINE, PLANT, ETC.

5/ IF THE "TOTAL" OF "ACTUAL EXPENDITURES" VARIES MORE THAN 10% FROM THE "AMOUNT BUDGETED," AN EXPLANATION OF SUCH VARIANCE SHOULD BE PROVIDED ON AN ATTACHMENT TO THIS SHEET.

FY 19 77 -- ANNUAL REPORT -- FOR THE [illegible]

[illegible] IS LOCATED: Rhode Island | REPORT AS OF [illegible]

[illegible] Ralph Thompson | ANNUAL ALLOTMENT [illegible]

COST CATEGORIES TO WHICH FY 19 77 FEDERAL SEC. 100 FUNDS APPLIED		AMOUNT BUDGETED 1/	ACTUAL EXPENDITURES 2/
A. SALARIES AND WAGES	TOTAL:	38959.	40979.45
INSTITUTE DIRECTOR 1	MAN-MONTHS: 3/ 6.0	(21174.)	(21798.17)
OTHER PROFESSIONAL STAFF NO:	MAN-MONTHS:	( )	( )
GRADUATE STUDENT ASSTS & TECH. NO:	MAN-MONTHS:	( )	( )
UNDERGRADUATE STUDENT ASSTS & TECH. NO:	MAN-MONTHS:	( )	( )
NON-STUDENT TECHNICIANS & OTHERS NO: 2	MAN-MONTHS: 24.0	(17785.)	(19181.28)
B. EMPLOYEE BENEFITS	TOTAL:		
C. NON-EXPENDABLE PROPERTY 4/	TOTAL:		
D. EXPENDABLE PROPERTY	TOTAL:	500.	1415.56
E. OTHER DIRECT COSTS	TOTAL:	4500.	8837.33
Travel		(2000.)	(1671.33)
Publications		(3000.)	(1754.00)
Partial support Regional Coordinator		(1500.)	(5412.00)
		( )	( )
	TOTAL DIRECT COSTS	45959.	51232.34 5/

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2/ ACTUAL EXPENDITURES INCLUDES FIRM OUTSTANDING COMMITMENTS (OR OBLIGATIONS) INCLUDING, FOR EXAMPLE, UNLIQUIDATED ORDERS FOR EQUIPMENT.

3/ MAN-MONTHS RELATE TO TIME PAID FOR BY FEDERAL FUNDS ONLY.

4/ NON-EXPENDABLE PROPERTY IS DEFINED AS PROPERTY WHICH HAS CONTINUING USE AS A SELF-CONTAINED UNIT; IS NOT CONSUMED IN USE; DOES NOT ORDINARILY BECOME A FIXTURE OR LOSE ITS IDENTITY, OR FORM A COMPONENT OF EQUIPMENT, MACHINE, PLANT, ETC.

5/ IF THE "TOTAL" OF "ACTUAL EXPENDITURES" VARIES MORE THAN 20% FROM THE "AMOUNT BUDGETED," AN EXPLANATION OF SUCH VARIANCE SHOULD BE PROVIDED ON AN ATTACHMENT TO THIS SHEET.

[illegible]

Table [illegible] [illegible] Distribution of FY 197_ Allotment (Sec. 10)
Expenditures of the Office of the Institute Director

1	Research program (P.L. 88-379) planning and development, including review and analysis of research project proposals - - - - - - - - - - - - - -	$ [illegible]
2	Coordinating the approved Institute P.L. 88-379 research and related training activities, including evaluation of progress, coordination with State agencies, etc. -	$ 8531.00
3	Water research and training program symposia relating to current or projected P.L. 88-379 activity but not directly associated with (or included in) the budgets of specific projects - - - - - - - - -	$ 2000.00
4.	Information Dissemination Activities	10800.00
5.	Supplies, postage, stationary, telephone	1415.34
6.	Printing and Publications	1754.00
7.	Partial support Regional Coordinator	5412.00
8.	Administrative expenses, including such housekeeping activities as the preparation of Institute time and attendance reports, requisitioning miscellaneous office supplies and equipment, operating Institute mails and files systems, general Institute record keeping, etc. -	$ 15161.00
	TOTAL Expenses for the Institute Director's Office - - - - - - -	$ 51232.34

1/ If a cost of the Institute Director's Office can be attributed to a research program activity, such as described in items 1, 2, and 3 above, then that cost should be included in that program activity and not as "administrative expenses." For example, that portion of the Institute Director's salary cost, as well as related stenographic-clerical costs, that are attributable to program planning and development activity of the Office of the Institute Director should be included in item 1 above rather than in item 8 above.

2/ This dollar figure should be equal to the total "actual expenditures FY19__" as shown on line "K" of Form OW-3, FY 19__ Annual Report--For the Institute Director's Office.

SUMMARY SHEET FOR FY 1977 ANNUAL ALLOTMENT PROGRAM (SEC. 100, [illegible]

Summary of information from forms OW-2 and OW-3 covering Institute Direct [illegible] program projects utilizing FY 19__ allotment program [illegible]

State Rhode Island | Total no. of allotment projects [illegible] Of these, indicate no. completed [illegible]

Annual Allotment Agreement No. (FY1977): 14-34-0001-7082.

Cost Categories to Which FY1977 Federal Sec. 100 Funds Applied	Amount 1/ Budgeted For FY 1977	Actual Expenditures For FY 1977
A. SALARIES AND WAGES TOTALS	89618.	85173.63
PRINCIPAL INVESTIGATOR(S) + Director NO. MAN-MONTHS 3/ 10.0	(30153.)	(31284.40)
OTHER PROFESSIONAL STAFF NO. 8 MAN-MONTHS 13.0	(6470.)	(7471.15)
GRADUATE STUDENT ASSTS & TECH. NO. 6 MAN-MONTHS 27.0	(35210.)	(25591.80)
UNDERGRADUATE STUDENT ASSTS & TECH. NO. 2 MAN-MONTHS 3.0	( )	(1645.00)
NON-STUDENT TECHNICIANS & OTHERS NO. 2 MAN-MONTHS 24.0	(17785.)	(19181.28)
B. EMPLOYEE BENEFITS TOTALS		
C. NON-EXPENDABLE PROPERTY 4/ TOTALS	6200.	3062.64
D. EXPENDABLE PROPERTY TOTALS	5692.	11283.76
E. OTHER DIRECT COSTS TOTALS	8490.	10479.97
Travel	(3890.)	(3313.97)
Publication	(3100.)	(1754.00)
Partial Support Regional Coordinator	(1500.)	(5412.00)
F. GRAND TOTAL FY 77 COSTS 5/	110000.	110000.00

OWRT PROJECT NUMBERS FOR ANNUAL ALLOTMENT PROJECTS COMPLETED DURING THE FISCAL YEAR TO WHICH THIS REPORT RELATES ARE AS FOLLOWS:

A-061, A-062 & A-066 RI

1/ AMOUNT BUDGETED IS AS SET FORTH IN PROJECT BUDGETS (AND REVISIONS) SUBMITTED TO AND ACCEPTED BY OWRT. DOLLARS SHOWN ARE FEDERAL FUNDS.

2/ ACTUAL EXPENDITURES INCLUDES FIRM OUTSTANDING COMMITMENTS (OR OBLIGATIONS) INCLUDING, FOR EXAMPLE, UNLIQUIDATED ORDERS FOR EQUIPMENT.

3/ MAN-MONTHS RELATE TO TIME PAID FOR BY FEDERAL FUNDS ONLY.

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5/ IF THE "TOTAL" OF "ACTUAL EXPENDITURES" VARIES MORE THAN 10% FROM THE "AMOUNT BUDGETED," AN EXPLANATION OF SUCH VARIANCE SHOULD BE PROVIDED ON AN ATTACHMENT TO THIS SHEET.

Form OW-6
(Rev. 6-77)

FY 1977 ANNUAL REPORT -- ESTIMATE OF NON-FEDERAL CONTRIBUTIONS
(Relating to Annual Allotment Program)

State: Rhode Island

Report covering FY 1977

The legislative history leading to passage of the Water Resources Research Act of 1964 emphasizes the importance of State-Federal cooperation in the conduct of the program and indicates that there will be substantial amounts of non-Federal cost participation. Pursuant thereto, please provide an estimate of non-Federal cost participation in the FY 1977 research and training activities carried out pursuant to your institute's FY 1977 annual allotment, Sec. 100, program.

The following types of non-Federal cost participation items are suggested for your consideration. Use these, or others, as you deem appropriate.

1. Estimated non-Federal contributions to salaries and wages of professional staff who participated in the FY annual allotment, Sec. 100, program:- -$ 50376.

2. Estimated non-Federal contribution to indirect costs and employee fringe benefits relating to the FY annual allotment, Sec. 100, program:- -$ 74898.

3. Estimated FY 77 fair-use-value non-Federal contribution relating to equipment, facilities, etc., used in the FY 77 annual allotment, Sec. 100, program:- $ 37000.

4. Salary for graduate assistant-Water Testing 5577.

5. Supplies, subscriptions and membership dues 2200.

6.

7.

TOTAL - - - - - - - - - - - - - - - - - - - 170,071.

FORM OW-7
(Rev. 5/77)

FY 19 77 ANNUAL REPORT —MATCHING GRANT (SEC. 101) PROJECT

(PREPARE A SEPARATE FORM FOR EACH SEC. 101 PROJECT IN PROGRESS DURING FY 19___)

STATE WHERE INSTITUTE LOCATED: Rhode Island

REPORT AS OF SEPT. 30, 19 77

GRANT PROJECT NO. B-061-RI
MATCHING GRANT AGREEMENT NUMBER: 14-31-0001-3958
TOTAL FEDERAL AMOUNT OF THE M.G.A. – $ 25,000.

PROJECT TITLE: Analysis of Critical Water Problems in the Northeastern United States to Determine Essential Research Requirements

PRINCIPAL INVESTIGATOR(S): A. Ralph Thompson

PROJ. BEGAN—MO: March ; YR: 1973

ACTUAL OR SCHEDULED COMPLETION—MO: Dec. ; YR: 19 77

COST CATEGORIES AND MAN-MONTHS 1/	EXPENDITURES IN FY 19 3/		
	FEDERAL $	NON-FEDERAL $	TOTAL $
A. SALARIES AND WAGES TOTAL:		600.00	600.00
PRINCIPAL INVESTIGATOR(S) NO: MAN-MONTHS:	( )	(600.00)	(600.00)
OTHER PROFESSIONAL STAFF NO: MAN-MONTHS:	( )	( )	( )
GRADUATE STUDENT ASSTS & TECH. NO: MAN-MONTHS:	( )	( )	( )
UNDERGRADUATE STUDENT ASSTS & TECH. NO: MAN-MONTHS:	( )	( )	( )
NON-STUDENT TECHNICIANS & OTHERS NO: MAN-MONTHS:	( )	( )	( )
B. EMPLOYEE BENEFITS 11.4% salaries TOTAL:		68.40	68.40
C. NON-EXPENDABLE PROPERTY 2/ TOTAL:			
D. EXPENDABLE PROPERTY TOTAL:			
E. OTHER COSTS (SPECIFY) TOTAL:	9018.73	235.20	9253.93
Workships: Durham, N.H. Harrisburg, Pa.	882.77 (775.85)	( )	882.77 (775.85)
Storrs, Conn. Morgantown, W.Va.	640.18 (3312.26)	( )	640.18 (3312.26)
Orono, Maine Compendium: Univ. of Delaware	1587.96 (1819.71)	( )	1587.96 (1819.71)
I.C. 39.2% of salaries TOTAL EXPENDITURES FY 77	9018.73	235.20 903.60	235.20 9922.33
CUMULATIVE EXPENDITURES SINCE START OF PROJECT March , 19 73	23690.43	29,510.50	53,200.93

1) Man-months relate to time paid from Federal Funds only.
2) Non-expendable property is property having a continuing use as a self-contained unit; is not consumed in use; does not ordinarily become a fixture or lose its identity, or form a component of equipment, machine parts, etc.
3) Firm outstanding commitments or obligations are considered as expenditures. (For example, unliquidated orders for equipment.)

FORM OW-7
(REV. 5/77)

FY 19 77 ANNUAL REPORT —MATCHING GRANT (SEC. 101) PROJECT

(PREPARE A SEPARATE FORM FOR EACH SEC. 101 PROJECT IN PROGRESS DURING FY 19 77)

STATE WHERE INSTITUTE LOCATED: Rhode Island

REPORT AS OF SEPT. 30, 19 77

OWRT PROJECT NO. A-070-RI
MATCHING GRANT AGREEMENT NUMBER: 14-34-0001-6115
TOTAL FEDERAL AMOUNT OF THE M.G.A. - $ 18110.

PROJECT TITLE: Fermentation and Enzymatic Saccharification of Cellulose and Lignin Wastes

PRINCIPAL INVESTIGATOR(S): Stanley Barnett

PROJ. BEGAN—MO: July; YR: 19 75

ACTUAL OR SCHEDULED COMPLETION—MO: June ; YR: 19 77

COST CATEGORIES AND MAN-MONTHS 1/	EXPENDITURES IN FY 19 77 3/ FEDERAL $	NON-FEDERAL $	TOTAL $
A. SALARIES AND WAGES TOTALS	3200.00	4099.00	7299.00
PRINCIPAL INVESTIGATOR(S) NO: 1 MAN-MONTHS:	( )	(4099.00)	(4099.00)
OTHER PROFESSIONAL STAFF NO: 2 MAN-MONTHS:	( )	( )	( )
GRADUATE STUDENT ASSTS & TECH. NO: 1 MAN-MONTHS: 4.5	(3200.00)	( )	(3200.00)
UNDERGRADUATE STUDENT ASSTS & TECH. NO: MAN-MONTHS:	( )	( )	( )
NON-STUDENT TECHNICIANS & OTHERS NO: MAN-MONTHS:	( )	( )	( )
B. EMPLOYEE BENEFITS 8.5% salaries TOTAL:		620.41	620.41
C. NON-EXPENDABLE PROPERTY 2/ TOTAL:			
D. EXPENDABLE PROPERTY TOTAL:	824.62		824.62
E. OTHER COSTS (Specify) TOTAL:		3590.11	3590.11
Fees	( )	(780.00)	(780.00)
	( )	( )	( )
Indirect Costs 38.5% salaries	( )	(2810.11)	(2810.11)
TOTAL EXPENDITURES FY 77	4024.62	8309.52	12334.14
CUMULATIVE EXPENDITURES SINCE START OF PROJECT July , 19 75	18100.07	20183.36	38283.43

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FORM OW-7
(Rev. 5/77)

FY 19 77 ANNUAL REPORT —MATCHING GRANT (SEC. 101) PROJECT

(PREPARE A SEPARATE FORM FOR EACH SEC. 101 PROJECT IN PROGRESS DURING FY 19 77)

STATE WHERE INSTITUTE LOCATED: Rhode Island

REPORT AS OF SEPT. 30, 19 77

GRANT PROJECT NO. B- 073-RI

MATCHING GRANT AGREEMENT NUMBER: 14-34-0001- 7130

TOTAL FEDERAL AMOUNT OF THE M.G.A. - $ 21086.

PROJECT TITLE: Solubilization and Biodegradation of Hydrocarbons

PRINCIPAL INVESTIGATOR(S): Stanley Barnett

PROJ. BEGAN—MO: July ; YR: 1976

ACTUAL OR SCHEDULED COMPLETION—MO: Sept. ; YR: 1978

COST CATEGORIES AND MAN-MONTHS 1/	EXPENDITURES IN FY 1977 3/		
	FEDERAL $	NON-FEDERAL $	TOTAL $
A. SALARIES AND WAGES TOTAL:	5501.00	2057.00	7558.00
PRINCIPAL INVESTIGATOR(S) NO: 1 MAN-MONTHS:	( )	(2057.00)	(2057.00)
OTHER PROFESSIONAL STAFF NO: MAN-MONTHS:	( )	( )	( )
GRADUATE STUDENT ASSTS & TECH. NO: 1 MAN-MONTHS: 7.5	(5501.00)	( )	(5501.00)
UNDERGRADUATE STUDENT ASSTS & TECH. NO: MAN-MONTHS:	( )	( )	( )
NON-STUDENT TECHNICIANS & OTHERS NO: MAN-MONTHS:	( )	( )	( )
B. EMPLOYEE BENEFITS TOTAL:		755.80	755.80
C. NON-EXPENDABLE PROPERTY 2/ TOTAL:			
D. EXPENDABLE PROPERTY TOTAL:	199.26	1578.71	1777.97
E. OTHER COSTS (SPECIFY) TOTAL:		4711.10	4711.10
Fees	( )	(1310.00)	(1310.00)
	( )	( )	( )
I.C. 45% of salaries	( )	(3401.10)	(3401.10)
TOTAL EXPENDITURES FY 77	5700.26	9102.61	14802.87
CUMULATIVE EXPENDITURES SINCE START OF PROJECT July 19 76	10213.26	11644.10	21857.36

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FORM OWRT
(REV. 8/77)

FY 1977 ANNUAL REPORT --MATCHING GRANT (SEC. 101) PROJECT

(PREPARE A SEPARATE FORM FOR EACH SEC. 101 PROJECT IN PROGRESS DURING FY 1977)

STATE WATER INSTITUTE LOCATED: Rhode Island

REPORT AS OF SEPT. 30, 1977

OWRT PROJECT NO. B-076-RI

MATCHING GRANT AGREEMENT NUMBER: 14-34-0001-7184

TOTAL FEDERAL AMOUNT OF THE M.G.A. - $11984.

PROJECT TITLE: Interaction of Chlorine and Organic Molecules--Effects of Inorganic Ions

PRINCIPAL INVESTIGATOR(S): Yuzuru Shimizu

PROJ. BEGAN--MO: Oct ; YR: 1976

ACTUAL OR SCHEDULED COMPLETION--MO: June ; YR: 1978

COST CATEGORIES AND MAN-MONTHS 1/	EXPENDITURES IN FY 1977 3/		
	FEDERAL $	NON-FEDERAL $	TOTAL $
A. SALARIES AND WAGES TOTAL:	3787.75	4276.00	8063.75
PRINCIPAL INVESTIGATOR(S) NO: 1 MAN-MONTHS:	( )	(2075.00)	(2075.00)
OTHER PROFESSIONAL STAFF NO: MAN-MONTHS:	( )	( )	( )
GRADUATE STUDENT ASSTS & TECH. NO: 1 MAN-MONTHS:	(3300.00)	(2201.00)	(5501.00)
UNDERGRADUATE STUDENT ASSTS & TECH. NO: 2 MAN-MONTHS: 2.0	(487.75)	( )	(487.75)
NON-STUDENT TECHNICIANS & OTHERS NO: MAN-MONTHS:	( )	( )	( )
B. EMPLOYEE BENEFITS 10% salaries TOTAL:		806.40	806.40
C. NON-EXPENDABLE PROPERTY 2/ TOTAL:			
D. EXPENDABLE PROPERTY TOTAL:	2345.89		2345.89
E. OTHER COSTS (SPECIFY) TOTAL:	239.02	4283.89	4522.82
Fees	( )	(655.00)	(655.00)
Travel	(239.02)	( )	(239.02)
I.C. 45% of salaries	( )	(3628.80)	(3628.80)
TOTAL EXPENDITURES FY 77	6372.66	9366.20	15738.86
CUMULATIVE EXPENDITURES SINCE START OF PROJECT Oct. 19 76	6372.66	9366.20	15738.86

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Form OW-8
(Rev. 6-77)

SUMMARY SHEET FOR MATCHING GRANT (SEC. 101) PROGRAM ACTIVITIES - FY 19 77

This sheet provides summary information covering all Sec. 101 projects in progress during FY 19 77 using FY 19 77 or prior years Sec. 101 funds. Hence, it is a summarization of information set forth on the separate project report forms OW-7.

State: Rhode Island Total No. of Sec. 101 Projects in Progress During FY 19 77 4

COST CATEGORIES AND MAN-MONTHS 1/	EXPENDITURES IN FY 77		
	FEDERAL $	NON-FEDERAL $	TOTAL $
A. SALARIES AND WAGES TOTALS	12488.75	11032.00	23520.75
PRINCIPAL INVESTIGATOR(S) NOS 4 MAN-MONTHS:	( )	(8831.00)	(8831.00)
OTHER PROFESSIONAL STAFF NOS 2 MAN-MONTHS:	( )	( )	( )
GRADUATE STUDENT ASSTS & TECH. NOS 3 MAN-MONTHS: 19.5	(12001.00)	(2201.00)	(14202.00)
UNDERGRADUATE STUDENT ASSTS & TECH. NOS 2 MAN-MONTHS: 2.0	(487.75)	( )	(487.75)
NON-STUDENT TECHNICIANS & OTHERS NOS MAN-MONTHS:	( )	( )	( )
B. EMPLOYEE BENEFITS TOTALS		2251.01	2251.01
C. NON-EXPENDABLE PROPERTY 2/ TOTALS			
D. EXPENDABLE PROPERTY TOTALS	3369.77	1578.71	4948.48
E. OTHER COSTS (SPECIFY) TOTALS	9257.75	12820.21	22077.96
Workships	(7199.02)	( )	(7199.02)
Compendium	(1819.71)	( )	(1819.71)
Travel	(239.02)	( )	(239.02)
Fees	( )	(2745.09	(2745.00)
Indirect Costs	( )	(10075.21)	(10075.21)
TOTAL EXPENDITURES FY 77 3/	25116.27	27681.93	52798.20
CUMULATIVE EXPENDITURES SINCE START OF PROJECT March, 19 73	58376.42	70704.16	129080.58

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USER'S MANUAL

DIGITAL MODEL
for
CONTINUOUS AQUIFER SIMULATION

UNIVERSITY OF RHODE ISLAND

HOPE

1892

RHODE ISLAND
WATER RESOURCES CENTER

RHODE ISLAND WATER RESOURCES CENTER

Digital Model
for
Continuous Aquifer Simulation

by: William E. Kelly
Melih Ozbilgin
Rhode Island Water Resources Center
University of Rhode Island

Prepared by the Rhode Island
Water Resources Center, University
of Rhode Island in Cooperation with the
Rhode Island Water Resources Board

The programs and activities described herein are supported in part by funds provided by the Office of Water Research and Technology, U.S. Department of the Interior, Washington, D.C. as authorized by P.L. 95-467, the Water Research and Development Act of 1978.

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INTRODUCTION

The two dimensional aquifer finite difference program, developed by Pinder (1970) and modified by Trescott (1972), was further modified by Beckman (1978) to allow for convenient continuous aquifer simulations. The objective was to be able to simulate several seasons which would then allow simulation of aquifer performance during critical periods of record. The method of data input and output in the 1972 version of the program was modified but the computational scheme was not changed. The sole purpose of this report is to provide a user's manual for the program in the version modified by Beckman.

Although the modified program has been applied in several studies, users should be aware that undiscovered errors in logic could still exist and model results should always be evaluated carefully by a trained hydrologist. Furthermore, as for the original program, this version may require additional programming modifications for some applications; for example, the user might want more detail on the time-history of stream infiltration.

Most of the information presented in this report is taken directly from Trescott (1972) and Beckman (1978). For detailed information on theory and model development the user is referred to the report by Trescott, Pinder and Larson (1976) and the text by Rushton and Redshaw (1979).

PROGRAM MODIFICATIONS AND TESTING

The method of data input and output in the 1972 version of the two dimensional, finite difference aquifer program (Trescott, 1972) was modified to allow for convenient multi-year aquifer simulations. A generalized flow chart for the modified program is shown in Figure 1.

The major modifications in the program were made in subroutines DATAIN, COMPUT and CHECK. A new entry DATVAR was added to subroutine DATAIN to handle the variable data input and a new entry SET was added in subroutine COMPUT to set the output options for the end-of-simulation printout. The entire entry OUTPUT in this subroutine was rewritten to allow the flexibility required for the various output options. The entry RPICK was added to subroutine CHECK to calculate leakage rates and cumulative leakage at the individual nodes designated as river and/or lake nodes. Also a new entry in this subroutine, RWRITE prints results obtained in entry RPICK.

The rest of the program has been modified only to the extent necessary to handle the modifications listed above with format statements changed throughout the program as needed.

The modified program was tested to insure that the computational scheme had remained intact. For this purpose, two steady state problems were run; one for idealized conditions and one for an actual field situation. The two steady-state problems were run with both the original and the modified program. Except for variations in format, results from the two programs were identical. For both cases, nodal spacings and time steps were varied to test the integrity of the computational scheme.

To test continuous simulation capabilities, the idealized aquifer problem shown in Figure 2, was simulated and tested against results given by Oakes and Wilkinson (1972). For the idealized

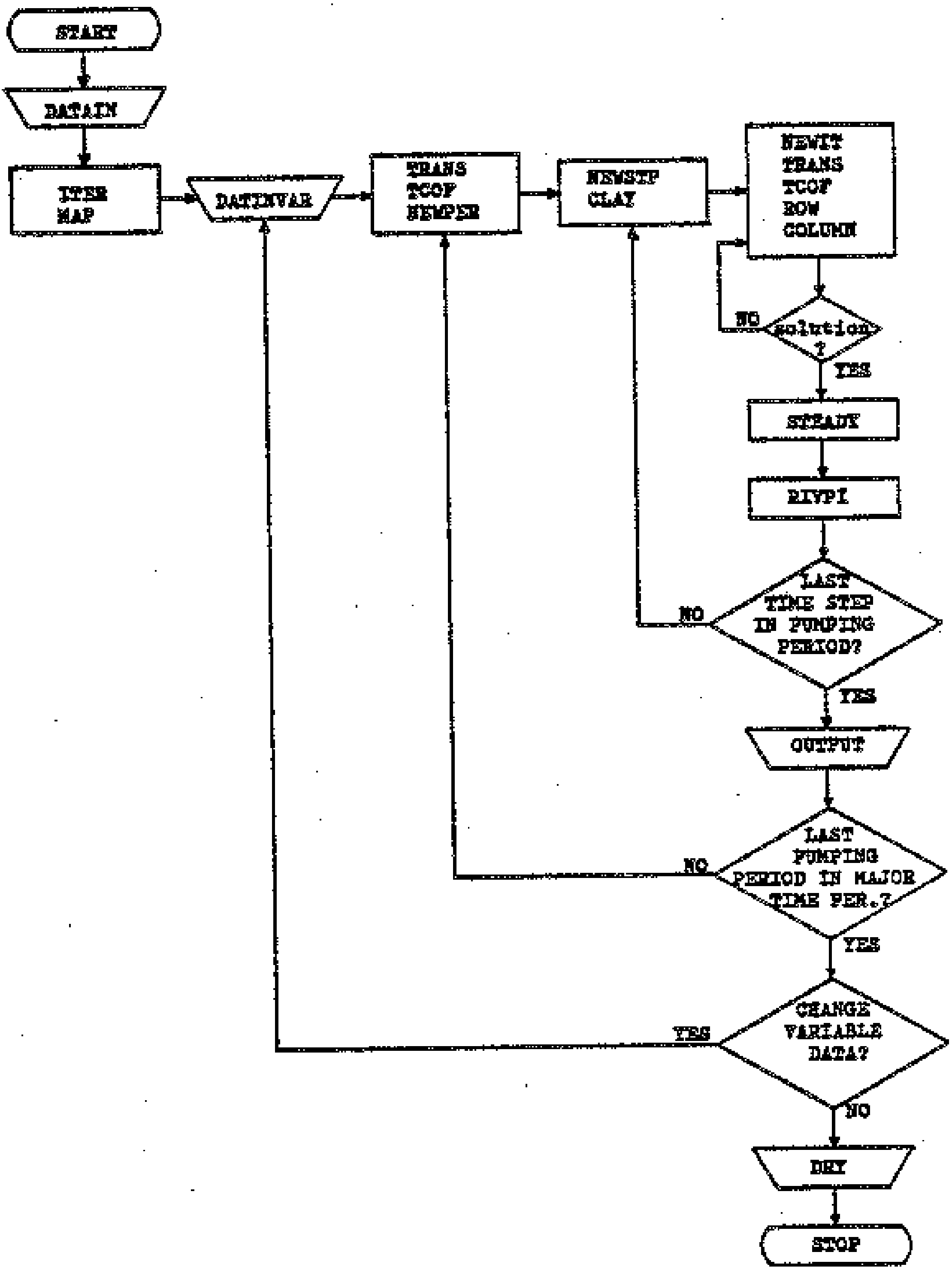
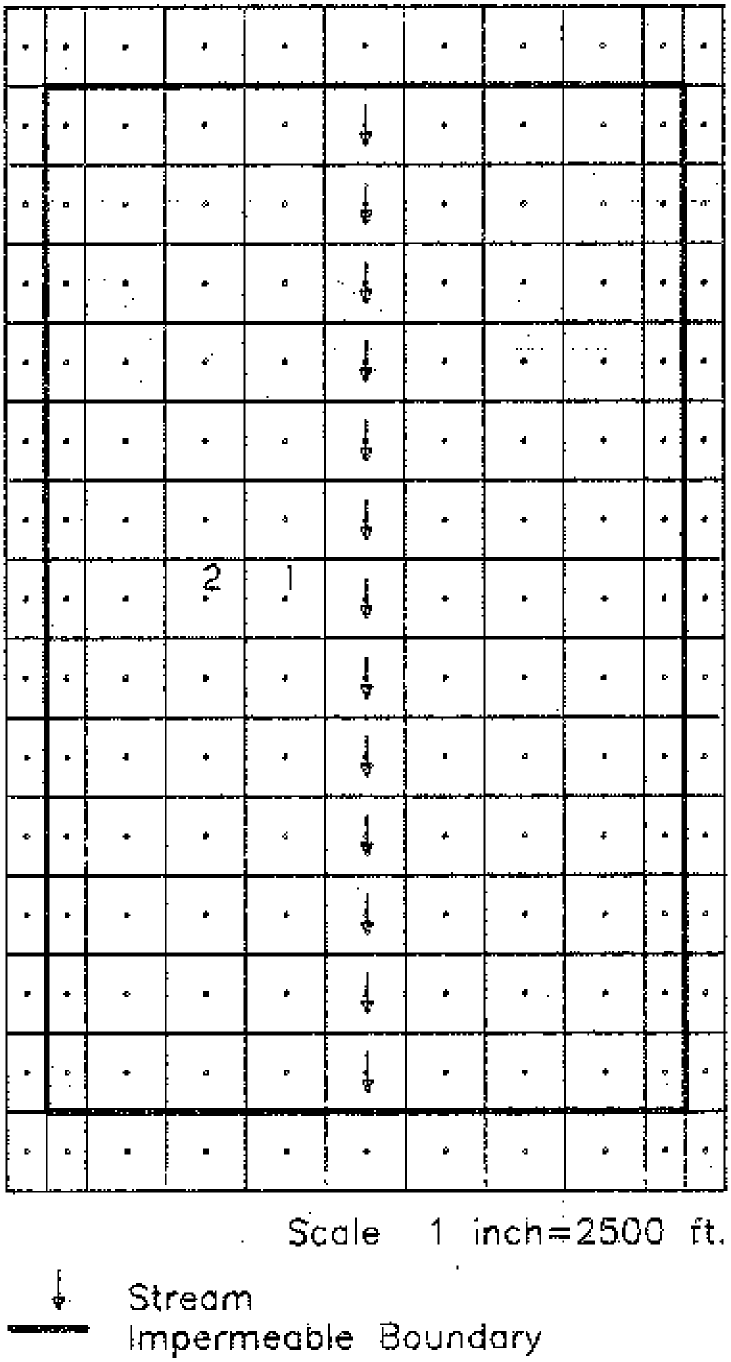


FIGURE 1. GENERALIZED FLOW DIAGRAM



Streambed Permeability =1 ft./day
Transmissivity =3200 ft.**2/day
Storage Coefficient =0.2

FIGURE 2. IDEALIZED AQUIFER

aquifer, water levels and base flows for a given recharge distribution (Figure 3) were examined. The computer simulations were continued for several seasons to obtain equilibrium seasonal variations. The equilibrium cyclic results for water-table elevations (Figure 4) and base flows (Figure 5) were compared directly to the results given by Oakes and Wilkinson.

The modified program was also checked against a one-dimensional transient model. In this case the idealized aquifer's (Figure 2) response to a given river stage fluctuation was examined. For simplicity, the river head was varied sinusoidally and aquifer response was examined for an observation well 1000 ft. from the river. Figure 6 shows results for the one-dimensional and two-dimensional modified program.

PROGRAM OPTIONS

ARTESIAN AQUIFER: The artesian aquifer is the easiest to model since the problem is linear. Water may be derived from storage, uniform areal recharge, recharge wells, constant head boundaries, and leakage from confining beds in which the effects of storage may be considered. Discharge may be to wells and constant head boundaries. Steady state can be simulated by setting the storage coefficient of the aquifer and the specific storage of the confining bed to zero, computing one time step of any length and iterating to a solution.

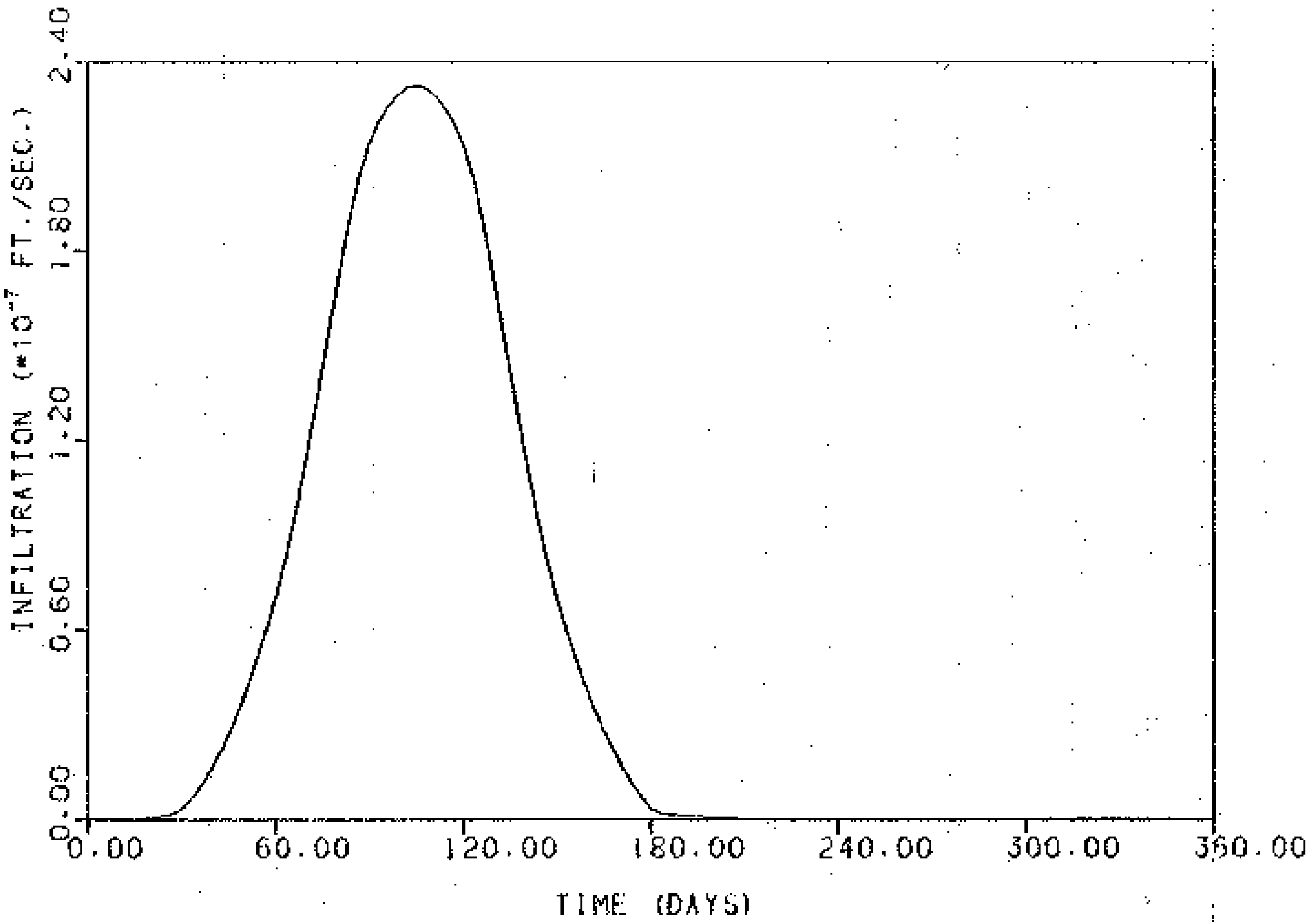


FIGURE 3. RECHARGE DISTRIBUTION APPLIED TO IDEALIZED AQUIFER

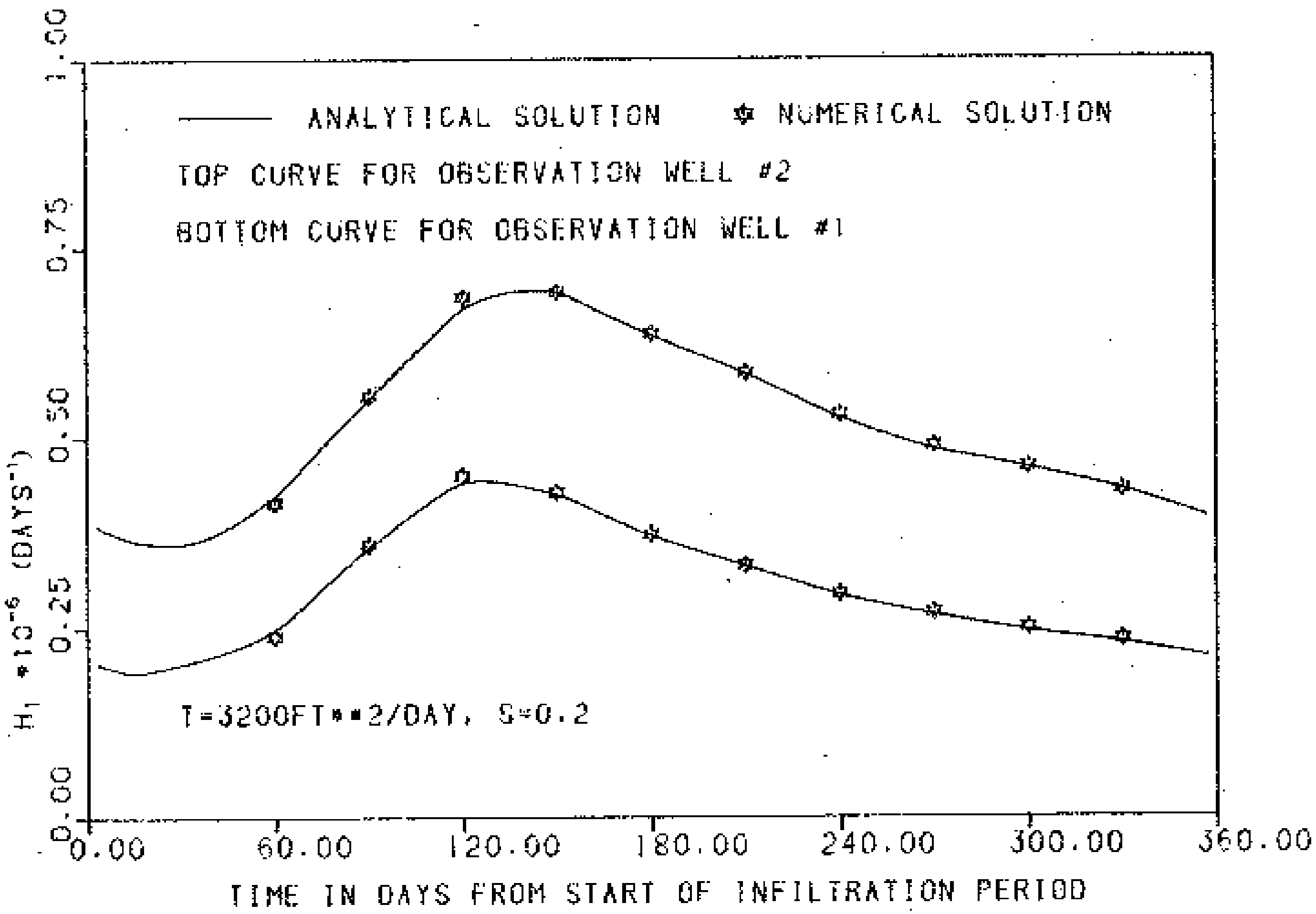


FIGURE 4. COMPARISON OF HEADS FOR NUMERICAL AND ANALYTIC SOLUTIONS

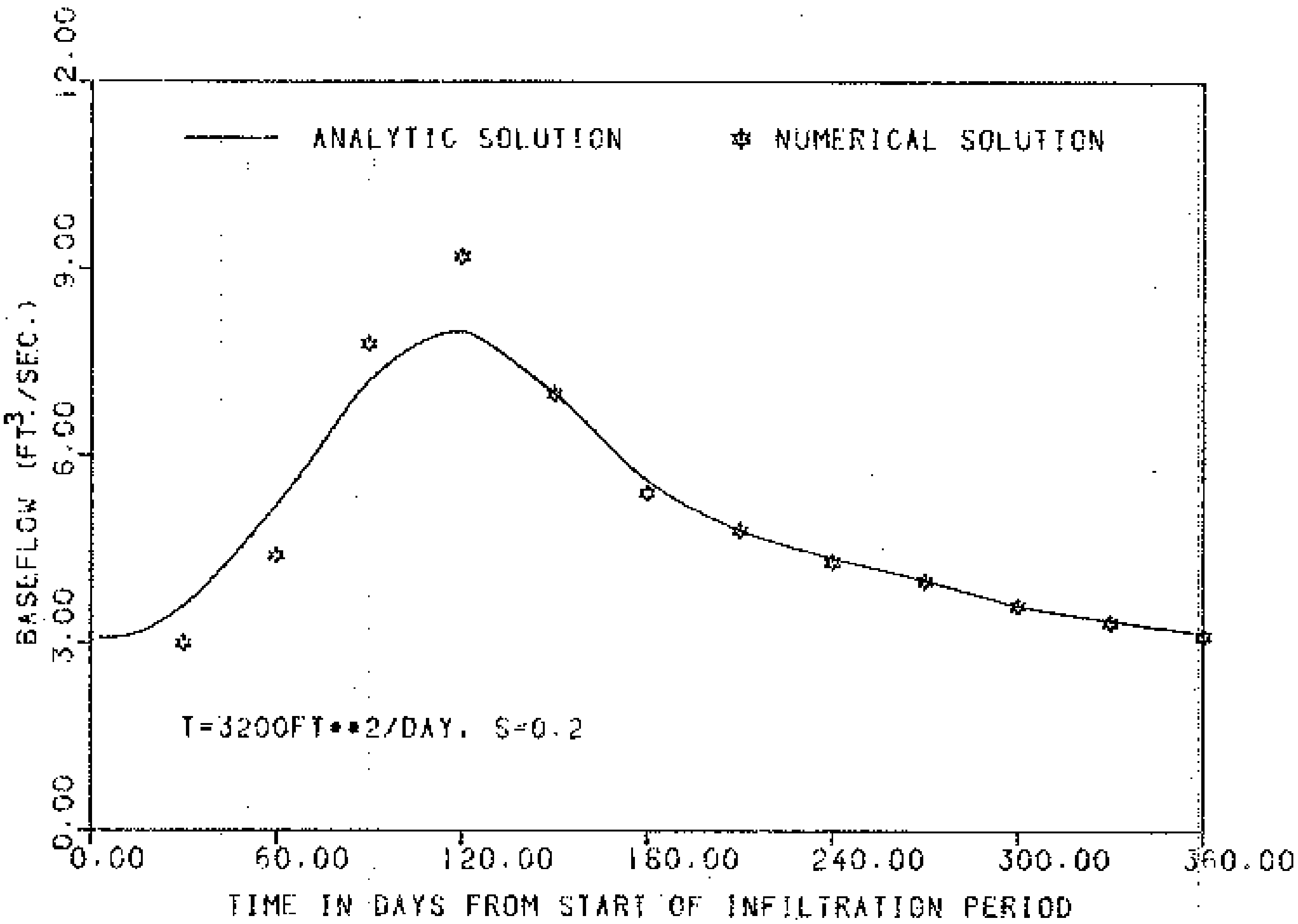


FIGURE 5. COMPARISON OF FLOWS FOR NUMERICAL AND ANALYTIC SOLUTIONS

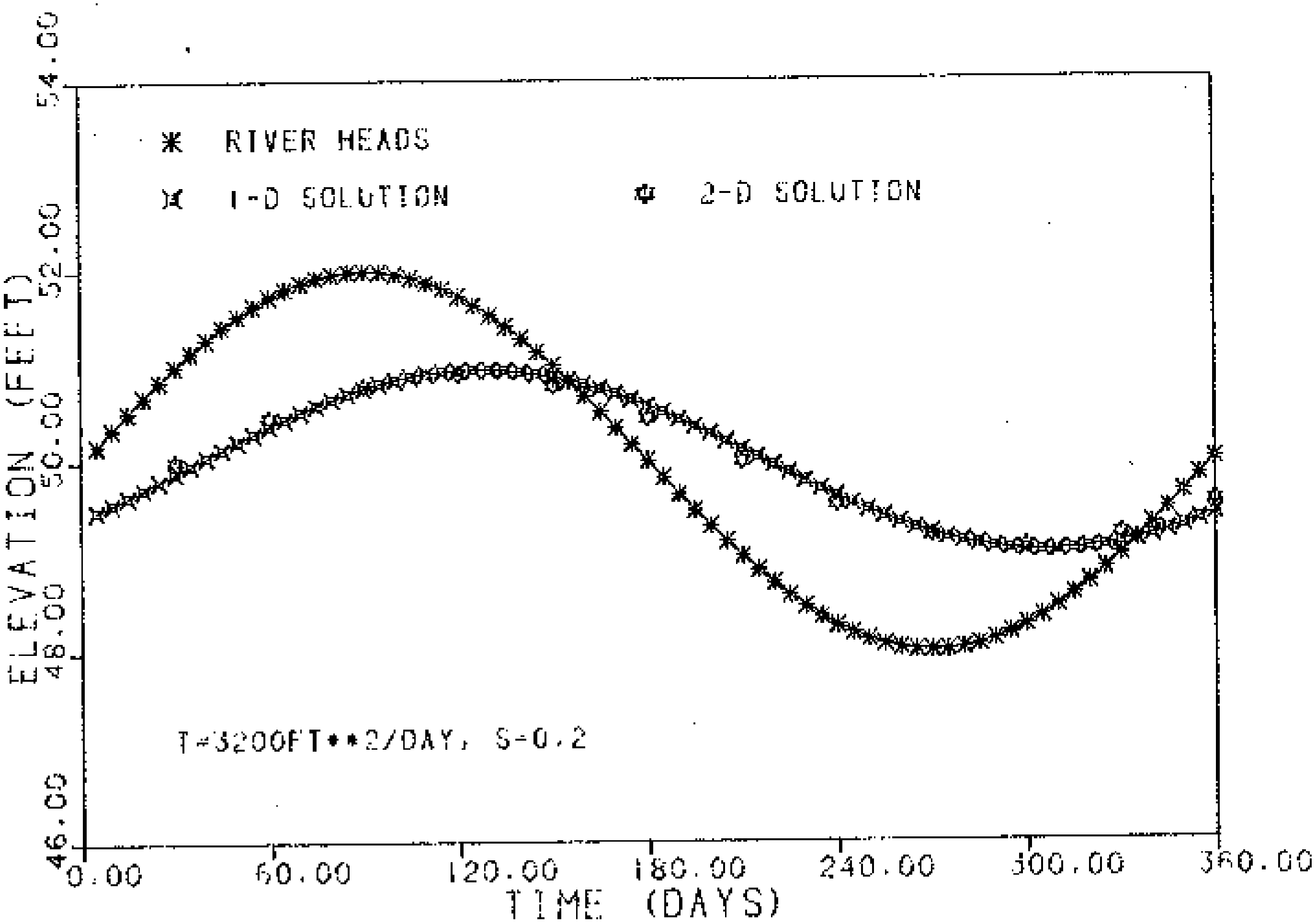


FIGURE 6. COMPARISON OF ANALYTIC AND NUMERICAL SOLUTIONS FOR A SINUSOIDAL FLUCTUATION OF RIVER HEADS

WATER TABLE AQUIFER: The transmissivity in the water table problem is computed each iteration as the product of saturated thickness and hydraulic conductivity at each node. The program is set up to terminate computation for a given problem if the "well goes dry". Punched output consisting of the head matrix and mass balance parameters is produced so the user can decide whether to continue the run. For nodes that go "dry" other than pumping nodes, a saturated thickness of one foot is maintained so that water levels at these nodes can recover during the next pumping period.

In addition to the types of recharge and discharge available in the artesian aquifer option, evapotranspiration can be included as a discharge. This assumes a linear decrease in evapotranspiration rate from the land surface to a given depth where evapotranspiration ceases. Steady state can be simulated in the same manner as in the artesian problem.

COMBINED WATER TABLE-ARTESIAN AQUIFER: This option can simulate an aquifer that is part artesian and part water table or an artesian aquifer converting to a water table aquifer and vice versa. As in the water table option the hydraulic conductivity of the aquifer and its bottom elevation must be specified. In addition, the elevation of the top of the aquifer is needed to compute transmissivity when the aquifer is artesian, to determine when the storage coefficient changes from its artesian value to specific yield, and to limit the leakage when the head falls below the top of the aquifer.

Other Program Features

VARIABLE DATA OPTION: Input data such as recharge, river stage, evapotranspiration and transmissivity may be changed at specified time periods. The time simulated by one time period is specified by the total length of the pumping period(s) from which it is composed. The total number of time periods (NMON) to be simulated is initially read in along with the time period unit (day, week, month, etc.).

MULTIPLE PUMPING PERIODS: There may be more than one pumping period within any time period. A new pumping period is started by reading in the length of the new period, the approximate DELT, and well locations and pumping rates. A major assumption is made in treating leakage for multiple pumping periods; dimensionless time for the previous pumping period is assumed to be large so that storage in the confining bed has a negligible effect on leakage from this period. For many real problems in which pumping periods are months to years in length, this is a reasonable assumption. Problems involving short pumping periods may require reprogramming in order to treat leakage more realistically.

SOLUTIONS APPROACHING STEADY STATE: In simulations for which a steady state is possible, the solution may approach a steady state long before the designated pumping period is completed. To reduce unnecessary computation time and output, the program checks the magnitude of changes in water level from one time step to the next, if the change at all nodes is less than some previously assigned difference (ie. 0.1 foot) the pumping period is terminated with all desired printed and punched output. The program proceeds to read the data for the next pumping period and/or time period, if any.

BOUNDARY CONDITIONS: To treat an impermeable boundary specify zero hydraulic conductivity or transmissivity for the impermeable material. Referring to Figure 7, if $T(i-1, j) = T(i-1,j-1) = T(i,j-1) = 0$, the impermeable boundary is located $-\Delta x/2$ and $-\Delta y/2$ from the node i,j. In Figure 7 Δx and Δy are constant. To simulate a constant head boundary, place a negative number (ie. -1) in the storage coefficient matrix at the constant head nodes which must have a finite transmissivity. The boundary is at the constant head nodes. The head entered at the start of the simulation is maintained as a constant head. To simulate a constant flux boundary with a value other than zero, a recharging well is placed at the appropriate node. Referring to Figure 8, if a recharging well is placed at node i,j, along the edge of a model the recharge boundary is located as shown in Figure 8.

DRAWDOWN AT A PUMPING WELL NODE: Withdrawal from a well is assumed to occur over the area of influence of the well node. Drawdown at a pumping node in the model is therefore considerably less than would be observed in a real well. The real well drawdown

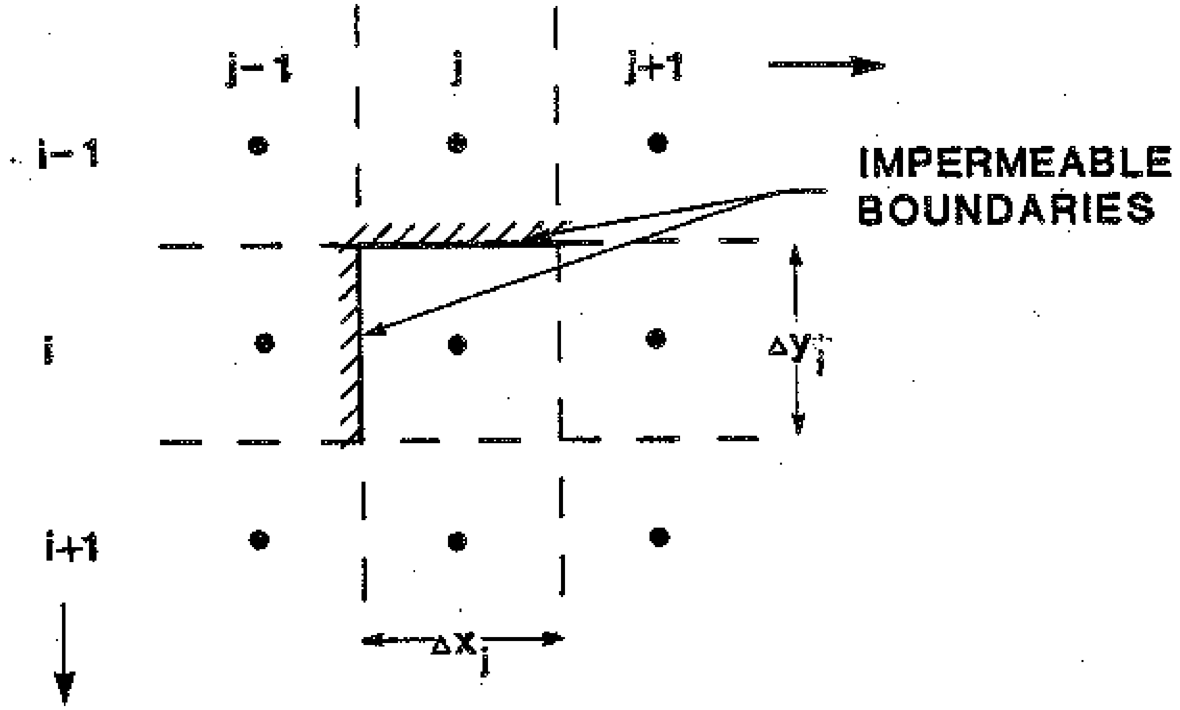


FIGURE 7. IMPERMEABLE BOUNDARY

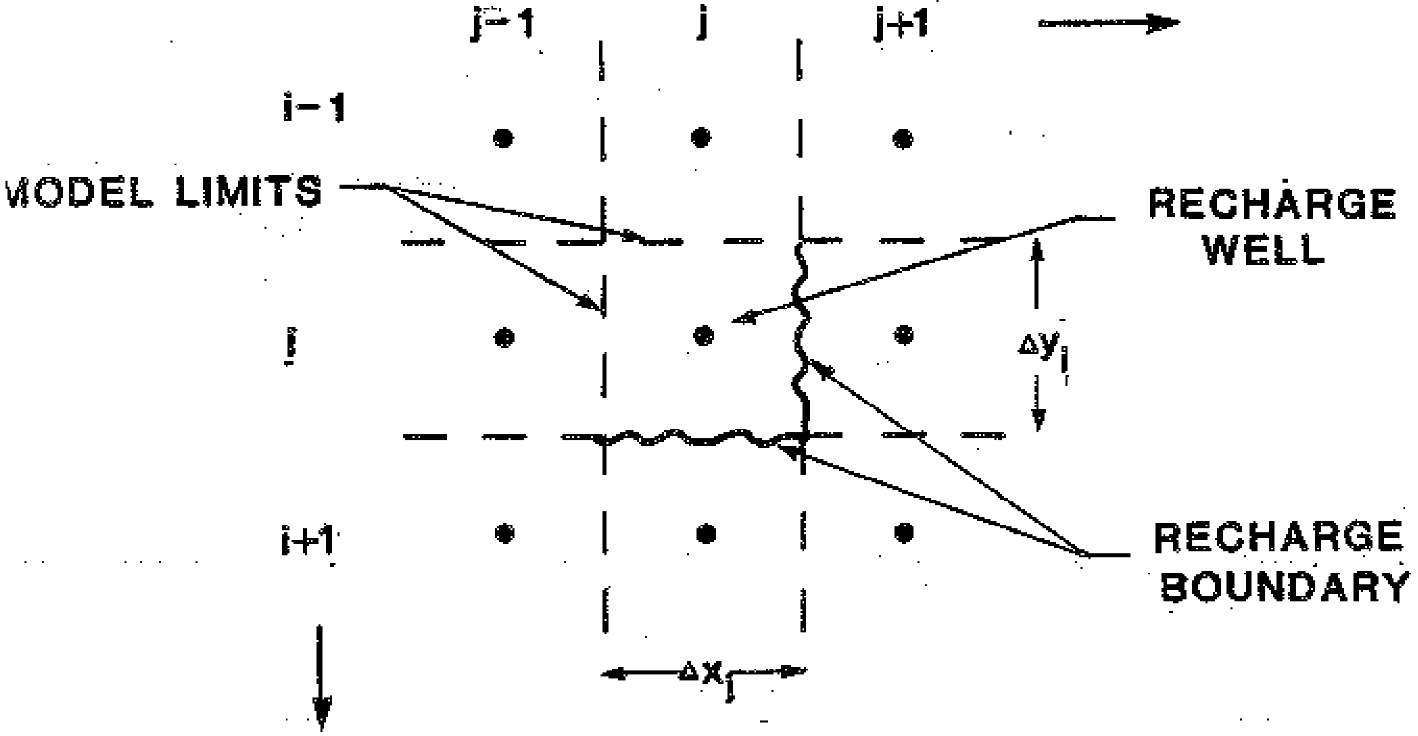


FIGURE 8. RECHARGE BOUNDARY

can be predicted by plotting drawdown versus the log of distance for nodes near the pumping node (excluding those directions in which other wells are within two nodes) and extrapolating to the radius of the real well. Alternatively, these data can be used in the Theim equation to calculate the additional drawdown in a real, fully penetrating well.

PROBLEM SIZE: Computer storage requirements and computation time are directly proportional to the number of nodes in a problem. The dimensions of the arrays in the source listing and card deck may need to be changed to suit a given problem and minimize computer storage requirements. Transient analysis requires more computation time than does steady state analysis.

The source program and scalar parameters will require about 57,000 bytes of storage. For a 20x20 or 400 node problem, the arrays require about 26,000 bytes of storage; for a 50x50 or 2,500 node problem, the arrays require about 163,000 bytes of storage. If computer storage is at a premium, 5 more arrays (WELL, RATE, M, S, SY) can be made half-word integers (INTEGER *2). This will require some program modifications and additional computation time because of the number of times multiplication factors must be used.

LOGICAL UNIT NUMBERS: The unit numbers for card reader, line printer, and card punch are commonly 5, 6, and 7, respectively. At computer installations where other numbers are used, change the initializations of P, R, and PU in the BLOCK DATA subroutine.

Application

FORMATS: The format for each parameter is given along with the description of that parameter. The G format is conveniently used to read data normally read under I, F, and E formats. Mistakes on data input can be minimized by always right justifying the data in each field. The only exceptions are the character strings on cards 3-15 which are left justified.

Except for the M matrix and the matrices specified as INTEGER *2, assume that the FORTRAN default typing of integer and real variables applies. The M matrix is explicitly made REAL *4. The INTEGER *2 matrices are made real variables by multiplication factors where needed. Except for the PHI and STRT matrices, leave decimal points off the input card sets; matrices are converted to their proper decimal values using the multiplication factors specified on cards 17, 18, and 19.

OUTPUT: Cards 7-14 allow te user needed flexibility in obtaining the type of output desired. The various options are described in the following section. The PUNCH option results in punched cards of the head matrix and mass balance parameters.

Data Deck Preparation

CARD	COLUMNS	FORMAT	VARIABLE	DEFINITION
CD1	1-80	10A8	HEADNG	Any title the user wishes to print on one line at the start of output.
CD2	1-48	10A8	HEADNG	
CD3	1-8	A8	WATER	Punch WATERTABLE for a water table or combined water table-artesian aquifer.[1]
CD4	1-8	A8	LEAK	Punch LEAKAGE for a problem including leakage from a stream, confining bed, etc.[1]
CD5	1-8	A8	CONVRT	Punch CONVERT for combined artesian/water table aquifer.[1]
CD6	1-8	A8	EVAP	Punch EVAPOTRANSPIRATION for a problem including evapotranspiration.[1]
CD7	1-8	A8	PNCH	Punch PUNCH for punched output at termination of simulation.[1]
CD8	1-20	A8,11X,I1	CHCK,ICH[2]	Punch CHECK for a problem in which a mass balance is to be computed.[1]
CD9	1-20	A8,11X,I1	RIVPI,IRP[2]	Punch RIVERPICKUP for output of leakage rates and amounts at surface water nodes.[1]
CD10	1-20	A8,11X,I1	HEAD,IHM[2]	Punch HEAD to print the head matrix.[1]
CD11	1-20	A8,11X,I1	HEADV,IHV[2]	Punch HEADVALUES to print head values at specified nodes.[1]
CD12	1-20	A8,11X,I1	NUM,IDM[2]	Punch NUMERIC to print drawdown in numeric form.[1,3]
CD13	1-20	A8,11X,I1	NUMV,IDV[2]	Punch NUMERICVALUES to

				print drawdown at specified nodes.[4,3]
CD14	1-20	A8,11X,I1	CONTR,ICO[2]	Punch CONTOUR to generate alphameric map.[4]
	21-30	G10.0	SCALE	Multiplication factor to convert model length unit to unit used on alphameric map.[4]
	31-40	G10.0	DINCH	Number of map units per inch.
	41-50	G10.0	SPACNG	Contour interval (L)
	51-58	A8	MESUR	Name of map length unit.
CD15	1-8	A8	PERIOD	Name of time period at which data is periodically changed (day, week, etc.).
CD16	1-8	G8.0	NMON	Number of time periods to simulated.
	9-16	G8.0	DIML	Number of rows.
	17-24	G8.0	DIMW	Number of columns.
	25-32	G8.0	LENGTH	Number of iteration parameters.[5]
	33-40	G8.0	ERR	Error criteria for closure, ie. the head change between row and column computations for every node must be less than or equal to this value to terminate iteration for a time step. (L)
	41-48	G8.0	SS	Specific storage of confining bed. (1/L)
	49-56	G8.0	ITMAX	Maximum number of iterations per time step (if exceeded, printed output is produced and the run is terminated.[6]
	57-64	G8.0	EROR	Change-in-head criteria for steady state (if the

				change in head at every node is less than this amount, the pumping period is terminated). (L)
	65-72	G8.0	ETDIST	Depth below land surface at which evapotranspiration ceases. (L)
	73-80	G8.0	NNODE	Number of nodes specified for output.
CD17	1-4	I4	IHED	Initial head[7]
	5-8	I4	ISTO	Storage coefficient[7]
	9-12	I4	ISYI	Specific yield[7]
	13-16	I4	IRAT	Hydraulic conductivity of confining bed[7]
	17-20	I4	IRIV	Head in sub- or superadjacent aquifer[7]
	21-24	I4	ITHK	Thickness of confining bed[7]
	25-28	I4	IPER	Aquifer hydraulic conductivity[7]
	29-32	I4	IBOT	Elevation of bottom of aquifer[7]
	33-36	I4	ITRA	Transmissivity of aquifer[7]
	37-40	I4	IDLX	Space increment in x-direction[7]
	41-44	I4	IDLY	Space increment in y-direction[7]
	45-48	I4	ITOP	Elevation of top of aquifer[7]
	49-52	I4	ILND	Elevation of land surface[7]
CD18	1-10	G10.0	FACH	Initial head (L)*
	11-20	G10.0	FACS	Storage coefficient*
	21-30	G10.0	FACY	Specific yield*

	31-40	G10.0	FACK	Hydraulic conductivity (permeability) of confining bed (L/T)[*,9]
	41-50	G10.0	FACM	Thickness of confining bed (L)[*]
	51-60	G10.0	FACP	Aquifer hydraulic conductivity (L/T)[*]
	61-70	G10.0	FACB	Elevation of bottom of aquifer (L)[*]
	71-80	G10.0	FACX	Space increments in x-direction (L)[*]
CD19	1-10	G10.0	FACZ	Space increments in y-direction (L)[*]
	11-20	G10.0	FACO	Elevation of top of the confined aquifer (L)[*]
	21-30	G10.0	FACL	Elevation of land surface (L)[*]
	31-40	G10.0	FACTY	Ratio of transmissivity in y-direction to transmissivity in x-direction.
	41-50	G10.0	RECOVR	Can not equal zero for recovery of a water table aquifer.
CARD SET				
CS1[10]	1-5	I5	I	Y-coordinate of specified node for output
	6-10	I5	J	X-coordinate of specified node for output
CS2	1-80	8F10.4	STRT(I,J)	Starting head matrix (do not set equal to zero)[11]
CS3	1-80	20F4.0	S(I,J)	Storage coefficient matrix. Let S(I,J) = -1 for constant head boundary. Use for artesian option.[11]
CS4	1-80	20F4.0	SY(I,J)	Specific yield matrix.

				Use for water table option.[1]
CS5	1-80	20F4.0	RATE(I,J)	Hydraulic conductivity matrix of confining bed.[1]
CS6	1-80	20F4.0	M(I,J)	Thickness matrix of confining bed.[1]
CS7	1-80	20I4	PERM(I,J)	Hydraulic conductivity for water table or combined water table-artesian problem; otherwise omit.[1,2]
CS8	1-80	20I4	BOTTOM(I,J)	Elevation of bottom of aquifer for water table or combined water table-artesian problem; otherwise omit.[1]
CS9	1-80	20I4	TOP(I,J)	Elevation of top of confined aquifer (bottom of confining layer) in combined water table-artesian problem; otherwise omit.[1]
CS10	1-80	20I4	LAND(I,J)	Elevation of land surface for problem including evapotranspiration; otherwise omit.[1]
CS11	1-80	8G10.0	DELX(J)	Spacing in x-direction represented by each node.[1]
CS12	1-80	8G10.0	DELY(I)	Spacing in y-direction represented by each node.[1]
CD20	1-10	G10.0	NPER	Number of pumping periods in present time period.
	11-20	G10.0	KTH	Number of time steps between printouts (assign interval between printouts larger than number required for printout of results at the final time step).

	21-30	G10.0	QRE	Uniform recharge rate (L/T)
	31-40	G10.0	QET	Maximum evapotranspiration rate (L/T)
	41-50	G10.0	FACR	Head in rivers and lakes (L)[13]
	51-60	G10.0	FACT	Transmissivity of aquifer (L /T)[13]
CS13	1-80	20I4	RIVER(I,J)	Head matrix of rivers and lakes[14]
CS14	1-80	20F4.0	TM(I,J)	Transmissivity matrix for artesian problem; otherwise omit.[14,12]
CD21	1-10	G10.0	KP	Number of present pumping period
	11-20	G10.0	KPM1	Number of previous pumping period (ie. KPM1 = 0 if KP = 1; but for a continuation of a previous pumping period KPM1 = KP).
	21-30	G10.0	NWEL	Number of wells for this pumping period.
	31-40	G10.0	TMAX	Number of DAYS in this pumping period.[14]
	41-50	G10.0	NUMT	Number of time steps in this pumping period.[14]
	51-60	G10.0	CDLT	Multiplying factor for DELT (commonly set at 1.5).[14]
	61-70	G10.0	DELT	Initial time step in HOURS.[14]
CS15	1-10	G10.0	I	Row location of well.
	11-20	G10.0	J	Column location of well.

21-30	G10.0	WELL(I,J)	Pumping rate (L /T). Positive for recharge, negative for pumping; one well on each card. (if NWEL = 0, omit CS15)

Submit CD20, CD21, and CS15 for each time period to be simulated.

Submit CD21 and CS15 for each pumping period within a time period.

Footnotes

1. For any option not used, insert a blank card or a card with some other characters in columns 1-8 keeping in mind that these characters will be printed beneath the title in the output.

2. Set variables ICH, IRP, IHM, IHV, IDM, IDV, and ICO equal to ZERO (0) to have the corresponding output option printed at the end of each time period. Otherwise set equal to ONE (1) for output at the end of simulation. Note that these variables will not be in effect unless the corresponding option is specified. Also, a blank field will be read as zero.

3. Drawdown for each node is referenced from the intial value in the starting head matrix.

4. The program is operating in units, length (L) and time (T), of feet and seconds, respectively. All input data should comply to these conditions unless otherwise specified.

5. Fewer iteration parameters are needed for transient analysis than for steady state. Commonly used values are 5 and 9, respectively.

6. Fewer iterations are needed for transient analysis than for steady state. commonly used values are 20 and 100, respectively.

7. Insert 1 if a uniform value for the matrix is to be used; insert -1 if the data matrix is to be read in and printed out; insert -2 if the data matrix is to be read in but not printed out.

8. This is the uniform value for this matrix where the corresponding parameter on CD17 is assigned the value of 1; this is the multiplication factor for the input data matrix where the corresponding parameter on CD17 is assigned the value of -1 or -2.

9. Once a value has been chosen, the actual area of the stream represented by a particular node may be taken into account for by adjusting this value.

10. There should be one set of coordinates on each card; the total number of cards in CS1 should equal NNODE.

11. This matrix is required if the corresponding parameter on CD17 has been assigned -1 or -2; otherwise omit. The corresponding parameter on CD18 will be used as a multiplier for this matrix to obtain values actually used by the program. Start data for each row on a new card.

12. Zero values must be placed around the perimeter of the PERM or TM array for reasons inherent in the computational scheme. If 1 is specified on CD17 for IPER or ITRA, PERM = 0 or TM = 0 is automatically inserted around the border of the model.

13. This parameter is used as described in Footnote #7. At the end of each time period, it may be changed to provide a new uniform value for the matrix or used as a multiplier on the data matrix INITIALLY read in.

14. The program has two options for the simulation period:
    a) To simulate a given pumping period (which make up time periods), set NUMT larger than the number required for the simulation period (ie. 100). The program will compute the exact DELT (which will be less than or equal to the DELT specified) and NUMT to arrive exactly at TMAX on the last time step.
    (method used for transient analysis)

    b) To simulate a given number of time steps, set TMAX to a value larger than the expected simulation period. The program will use NUMT, CDLT, and DELT as specified.
    (method used for steady state analysis)

INPUT DATA FOR IDEALIZED AQUIFER SHOWN IN FIGURE 2.

```
00 12345678901234567890123456789012345678901234567890123456789012345678901234567890
01 MODIFIED 2-D AQUIFER EVALUATION PROGRAM
02                  TEST PROBLEM FOR MODELLING AN IDEALIZED AQUIFER
03
04 LEAKAGE
05
06
07
08
09 RIVERPICKUP        0
10 HEAD               0
11 HEADVALUES         0
12
13
14
15 MONTHS
16       12      11      15       5    .001      .2     100    .001     1.0       5
17    1   1   1  -1  -1   1   1   1   1   1   1   1   1
18       50.0       0.2       0.0 .1157E-04       1.0       0.0       0.0     800.0
19      800.0      50.0      50.0       1.0       0.0
20     2    7
21     3    7
22     4    7
23     5    7
24     6    7
25   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
26   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
27   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
28   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
29   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
30   1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.
31   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
32   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
33   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
34   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
35   0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
36          1       100       0.0       0.0      50.0 .3704E-01
37    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
38    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
39    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
40    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
41    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
42    1   1   1   1   1   1   1   1   1   1   1   1   1   1   1
43    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
44    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
45    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
46    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
47    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
48          1         0         0        30         4       1.5      72.0
49          1       100 .3344E-08       0.0      50.0 .3704E-01
50          1         0         0        30         4       1.5      72.0
51          1       100 .7031E-07       0.0      50.0 .3704E-01
52          1         0         0        30         4       1.5      72.0
53          1       100 .2143E-06       0.0      50.0 .3704E-01
54          1         0         0        30         4       1.5      72.0
55          1       100 .2646E-06       0.0      50.0 .3704E-01
56          1         0         0        30         4       1.5      72.0
57          1       100 .2143E-06       0.0      50.0 .3704E-01
58          1         0         0        30         4       1.5      72.0
59          1       100 .7031E-07       0.0      50.0 .3704E-01
60          1         0         0        30         4       1.5      72.0
61          1       100 .3344E-08       0.0      50.0 .3704E-01
62          1         0         0        30         4       1.5      72.0
63          1       100       0.0       0.0      50.0 .3704E-01
64          1         0         0        30         4       1.5      72.0
65          1       100       0.0       0.0      50.0 .3704E-01
66          1         0         0        30         4       1.5      72.0
67          1       100       0.0       0.0      50.0 .3704E-01
68          1         0         0        30         4       1.5      72.0
69          1       100       0.0       0.0      50.0 .3704E-01
70          1         0         0        30         4       1.5      72.0
71 /*
72 //
```

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TABLE 1

```
                                                                              MAIN0010
                 /
                 C    ************************************************************MAIN0020
                 C    AN ITERATIVE DIGITAL MODEL FOR AQUIFER EVALUATION           MAIN0030
                 C        UPDATED DECEMBER,1972 BY P.C. TRESCOTT                  MAIN0040
                 C
                 C        MODIFIED DECEMBER, 1977 BY W. K. BECKMAN
                 C    ************************************************************MAIN0050
                 C    SUBPROGRAMS AND ENTRIES                                     MAIN0060
                 C                                                                MAIN0070
                 C    1. DATAIN                         3. COEF                   MAIN0080
                 C          ITER                              CLAY                MAIN0090
                 C          MAP                               TRANS (IERR)
                 C          NEWPER                            TCOF                MAIN0110
                 C          DATVAR                            ETRATE(I,J)
                 C                                            STORAGE
                 C    2. COMPUT                               LEAKAGE(I,J)
                 C          NEWSTP
                 C          NEWIT1                      4. CHECK
                 C          NEWITO                            RPICK
                 C          ROW                               CWRITE              MAIN0170
                 C          COLUMN                            RWRITE
                 C          STEADY
                 C          SET                         5. PRNTA                  MAIN0200
                 C          OUTPUT                                                MAIN0210
                 C          DRY                         6. BLOCK DATA
                 C    ************************************************************MAIN0220
                 C    MAIN PROGRAM                                                MAIN0230
                 C    SPECIFICATIONS:                                             MAIN0240
 0001                 COMMON /DARRAY/ PHI(33,62),RHOP(20),CHK(13)
 0002                 COMMON /SARRAY/ KEEP(33,62),T(33,62),Q(33,62),STRT(33,62),RATE(33,MAIN0260
                     162),H(33,62),WELL(33,62),S(33,62),SY(33,62),TR(33,62),TC(33,62),DEMAIN0270
                     2LX(62),DELY(33)                                             MAIN0280
                     3,PHE(33,62)                                                 MAIN0290
 0003                 COMMON /TARRAY/ TH(33,62),RH(33,62),PICK(33,62),PICKUP(33,62)
 0004                 COMMON /HARRAY/ TOP(33,62),ISUR(33,62),LAND(33,62),RIVER(33,62),PEMAIN0300
                     1RM(33,62),BOTTOM(33,62)                                     MAIN0310
 0005                 COMMON /GARRAY/ NODE(33,62)
 0006                 COMMON /DPARAM/ WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTR,EROR,LEMAI50320
                     1AK,RIVPI,HEADV,NUMV
 0007                 COMMON /SPARAM/ FACS,FACY,FACK,FACR,FACM,FACP,FACH,FACB,FACL,FACW,MAIN0340
                     1SLEAK,U,SS,TT,TMIN,ETDIST,QET,IFINAL,TMAX,CDLT,DELT,SUM,SUMP,NUMT,MAIN0350
                     2KT,KP,NPER,KTH,ITMAX,LENGTH,NWEL,QRE,ERR,DIML,DIMW,JNO1,INO1,R,P,PMAIN0360
                     3U,SUBS,STORE,TEST,ETQB,ETQD                                 MAIN0370
 0008                 COMMON /TPARAM/ ICH,IRP,IHM,IHV,IDM,IDV,ICD,KH,NMON,NNODE   MAIN0380
                 C                                                                MAIN0390
 0009                 REAL KEEP,M
 0010                 REAL*8 PHI,DBLE,RHOP,CHK,WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTMAIN0400
                     1R,EROR,LEAK,RIVPI,HEADV,NUMV
```

```
 FORTRAN IV G LEVEL  21                 MAIN                DATE = 78096         09/24/29            PAGE 0002

    0011                 INTEGER DIML,DIMW,R,P,PU                                         MAIN0420
    0012                 INTEGER*2 TOP,ISUR,LAND,RIVER,PERM,BOTTOM                        MAIN0430
    0013                 INTEGER*2 NODE
                  C                                                                       MAIN0440
                  C      ---READ AND WRITE CONSTANT DATA FOR THE PROBLEM---
    0014              10 CALL DATAIN                                                      MAIN0460
                  C                                                                       MAIN0470
                  C      ---COMPUTE ITERATION PARAMETERS---                               MAIN0510
    0015                 CALL ITER                                                        MAIN0520
                  C                                                                       MAIN0500
                  C      ---INITIALIZE PARAMETERS FOR ALPHAMERIC MAP---                   MAIN0540
    0016                 IF (CONTR.EQ.CHK(3)) CALL MAP                                    MAIN0550
                  C                                                                       MAIN0560
    0017                 KM=0
    0018              15 KT=0
    0019                 IFINAL=0                                                         MAIN0640
    0020                 IERR=0                                                           MAINC650
                  C                                                                       MAIN0620
                  C      ---READ AND WRITE VARIABLE DATA FOR THE PROGRAM---
    0021                 CALL DATVAR
                  C
                  C      ---INITIALIZE TRANSMISSIVITY VALUES IN WATER TABLE PROBLEM---    MAIN0480
    0022                 IF (WATER.EQ.CHK(2)) CALL TRANS (IERR)                           MAIN0490
                  C                                                                       MAIN0590
                  C      ---COMPUTE T COEFFICIENTS FOR ARTESIAN PROBLEM---                MAIN0570
    0023                 IF (WATER.NE.CHK(2)) CALL TCOF                                   MAIN0580
                  C                                                                       MAIN0690
                  C      ---READ TIME PARAMETERS AND PUMPING DATA FOR NEW PUMPING PERIOD---
    0024              20 CALL NEWPER                                                      MAIN0610
                  C                                                                       MAIN0530
                  C      ---START NEW TIME STEP COMPUTATIONS---                           MAIN0700
    0025              30 CALL NEWSTP                                                      MAIN0710
                  C                                                                       MAIN0720
                  C      ---COMPUTE LEAKAGE COEFFICIENTS---                               MAIN0730
    0026                 IF (LEAK.EQ.CHK(9)) CALL CLAY                                    MAIN0740
                  C                                                                       MAIN0750
                  C      ---PREPARE FOR ANOTHER ITERATION---
    0027                 CALL NEWIT0                                                      MAIN0770
    0028                 GO TO 50                                                         MAIN0780
    0029              40 CALL NEWIT1                                                      MAIN0790
                  C                                                                       MAIN0800
                  C      ---COMPUTE TRANSMISSIVITY IN WT OR WT-ARTESIAN CONVERSION PROBLEM-MAIN0810
    0030              50 IF (WATER.NE.CHK(2)) GO TO 70                                    MAIN0820
    0031                 CALL TRANS (IERR)                                                MAIN0830
    0032                 IF (IERR.EQ.0) GO TO 60                                          MAIN0840
    0033                 IF (KT.NE.0) CALL DRY                                            MAIN0850
    0034                 GO TO 100                                                        MAIN0880
                  C                                                                       MAIN0900
```

```
FORTRAN IV G LEVEL  21                 MAIN            DATE = 79086        09/24/29              PAGE 0003
                C     ---COMPUTE T COEFFICIENTS IN WATER TABLE PROBLEM---                 MAIN0910
      0035        60 CALL TCOF                                                             MAIN0920
                C                                                                          MAIN0930
                C     ---COMPUTE IMPLICITLY ALONG ROWS---                                  MAIN0940
      0036        70 CALL ROW                                                              MAIN0950
                C                                                                          MAIN0960
                C     ---COMPUTE IMPLICITLY ALONG COLUMNS---                               MAIN0970
      0037           CALL COLUMN                                                           MAIN0980
                C                                                                          MAIN0990
                C     ---IF SOLUTION NOT OBTAINED START NEW ITERATION---                   MAIN1000
      0038           IF (TEST.EQ.1.) GO TO 40                                              MAIN1010
                C                                                                          MAIN1020
                C     ---CHECK FOR STEADY STATE---                                         MAIN1030
      0039           CALL STEADY                                                           MAIN1040
                C                                                                          MAIN1050
                C     ---PRINT OUTPUT AT DESIGNATED TIME STEPS---                          MAIN1060
      0040           IF (MOD(KT,KTH).NE.0.AND.IFINAL.NE.1) GO TO 30                        MAIN1070
      0041           IF (KP.LT.NPER) GO TO 20
      0042           IF (KM.EQ.NMON) CALL SET
      0043           CALL OUTPUT                                                           MAIN1080
                C
                C     ---CHECK FOR START OF NEW TIME STEP OR PUMPING PERIOD OR MONTH---
      0044           IF (IFINAL.NE.1) GO TO 30                                             MAIN1090
      0045        80 IF (KP.LT.NPER) GO TO 20                                              MAIN1140
      0046           IF (KM.LT.NMON) GO TO 15
                C                                                                          MAIN1200
                C                                                                          MAIN1120
      0047       100 STOP                                                                  MAIN1170
      0048           END                                                                   MAIN1220
```

```
FORTRAN IV G LEVEL  21              MAIN              DATE = 78086          09/05/14            PAGE 0001

              C/                                                                        DATA0010
    0001             SUBROUTINE DATAIN                                                  DATA0020
              C      ----------------                                                   DATA0030
              C                                                                         DATA0040
              C      SPECIFICATIONS:                                                    DATA0050
    0002             COMMON /DARRAY/ PHI(33,62),RHOP(20),CHK(13)
    0003             COMMON /SARRAY/ KEEP(33,62),T(33,62),Q(33,62),STRT(33,62),RATE(33,DATA0070
                    162),H(33,62),WELL(33,62),S(33,62),SY(33,62),TR(33,62),TC(33,62),DEDATA0080
                    2LX(62),DELY(33)                                                    DATA0090
                    3,PHE(33,62)                                                        DATA0100
    0004             COMMON /TARRAY/ TM(33,62),RH(33,62),PICK(33,62),PICKUP(33,62)
    0005             COMMON /HARRAY/ TOP(33,62),ISUR(33,62),LAND(33,62),RIVER(33,62),PEDATA0110
                    1RM(33,62),BOTTOM(33,62)                                            DATA0120
    0006             COMMON /GARRAY/ NODE(33,62)
    0007             COMMON /DPARAM/ WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTR,EROR,LEDATA0130
                    1AK,RIVPI,HEADV,NUMV,PERIOD
    0008             COMMON /SPARAM/ FACS,FACY,FACK,FACR,FACM,FACP,FACB,FACO,FACL,FACW,DATA0150
                    1SLEAK,U,SS,TT,TMIN,ETDIST,QET,IFINAL,TMAX,CDLT,DELT,SUM,SUMP,NUMT,DATA0160
                    2KT,KP,NPER,KTH,ITMAX,LENGTH,NWEL,QRE,ERR,DIML,DIMW,JND1,IND1,R,P,PDATA0170
                    3U,SUBS,STORE,TEST,ETQB,ETQD                                        DATA0180
    0009             COMMON /TPARAM/ ICH,IRP,IHM,IHV,IDM,IDV,ICO,KM,NMON,NNODE
    0010             COMMON /CK/ ETFLXT,STORT,QRET,CHST,CHDT,FLUXT,PUMPT,CFLUXT         DATA0190
    0011             COMMON /PR/ XLABEL(3),YLABEL(6),TITLE(4),XN1,SYM(28),PRNT(122),BLADATA0200
                    1NK(60),DIGIT(122),VF1(6),VF2(6),VF3(7),NA(4),XN(100),YN(13),XSF,NXDATA0210
                    2D,WIDTH,SPACNG,N1,N2,N3,N4,N6,N8,NC                                DATA0220
    0012             COMMON /ANI/ FACTY,RECOVR                                          DATA0230
              C                                                                         DATA0240
    0013             REAL*4 O(100),KEEP,M                                               DATA0250
    0014             REAL*8 PHI,DBLE,RHOP,CHK,WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTDATA0260
                    1R,EROR,LEAK,RIVPI,HEADV,NUMV,XLABEL,YLABEL,TITLE,XN1,HEADNG(16),ME
                    2SUR,LEAK,PERIOD
    0015             INTEGER DIML,DIMW,R,P,PU                                           DATA0280
    0016             INTEGER*2 TOP,ISUR,LAND,RIVER,PERM,BOTTOM                          DATA0290
    0017             INTEGER*2 NODE
              C                                                                         DATA0310
              C     ....................................................................DATA0300
              C     ---READ AND WRITE CONSTANT DATA---
    0018             READ (R,390) HEADNG
    0019             WRITE (P,395) HEADNG
    0020             READ (R,400) WATER,LEAK,CONVRT,EVAP,PNCH
    0021             READ (R,405) CHCK,ICH,RIVPI,IRP,HEAD,IHM,HEADV,IHV,NUM,IDM,NUMV,ID
                    1V
    0022             READ (R,410) CONTR,ICO,SCALE,DINCH,SPACNG,MESUR
    0023             READ (R,400) PERIOD
    0024             WRITE (P,415) WATER,LEAK,CONVRT,EVAP,PNCH
    0025             WRITE (P,420) CHCK,ICH,RIVPI,IRP,HEAD,IHM,HEADV,IHV,NUM,IDM,NUMV,I
                    1DV,CONTR,ICO
    0026             IF (CONTR.EQ.CHK(3)) WRITE (P,425) SCALE,MESUR,DINCH,SPACNG
```

```
 0027                READ (R,430) NMON,DIML,DIMW,LENGTH,ERR,SS,ITMAX,EROR,ETDIST,NNODE
 0028                WRITE (P,435) PERIOD,NMON,DIML,DIMW,ERR,SS,ITMAX,EROR,ETDIST,NNODE
 0029                READ (R,440) IHED,ISTO,ISYI,IRAT,IRIV,ITHK,IPER,IBOT,ITRA,IDLX,IDL
                    1Y,ITOP,ILND                                                        DATA0440
 0030                READ (R,445) FACH,FACS,FACY,FACK,FACM,FACP,FACB,FACX,FACZ,FACQ,FAC
                    1L,FACTY,RECOVR
            C        .................................................................DATA0470
            C        ---READ NODES SPECIFIED FOR OUTPUT---
 0031                IF (NNODE.EQ.0) GO TO 15
 0032                DO 5 I=1,DIML
 0033                DO 5 J=1,DIMW
 0034              5 NODE(I,J)=0
 0035                DO 10 II=1,NNODE
 0036                READ (R,450) I,J
 0037             10 NODE(I,J)=1
            C        .................................................................DATA0790
            C        ---INITIALIZE MATRICES TO CONSTANT VALUES----                    DATA0490
 0038             15 DO 20 I=1,DIML
 0039                DELY(I)=FACZ                                                     DATA0510
 0040                DO 20 J=1,DIMW
 0041                STRT(I,J)=FACH                                                   DATA0530
 0042                PHI(I,J)=FACH                                                    DATA0540
 0043                S(I,J)=FACS                                                      DATA0550
 0044                SY(I,J)=FACY                                                     DATA0560
 0045                RATE(I,J)=FACK                                                   DATA0570
 0046                H(I,J)=FACM                                                      DATA0590
 0047                PERM(I,J)=IPER                                                   DATA0600
 0048                IF (I.EQ.1.OR.I.EQ.DIML.OR.J.EQ.1.OR.J.EQ.DIMW) PERM(I,J)=0      DATA0610
 0049                BOTTOM(I,J)=IBOT                                                 DATA0620
 0050                ISUR(I,J)=STRT(I,J)*10.                                          DATA0630
 0051                TOP(I,J)=ITOP                                                    DATA0640
 0052                LAND(I,J)=ILND                                                   DATA0650
 0053                DELX(J)=FACX                                                     DATA0680
 0054                Q(I,J)=0.0                                                       DATA0690
 0055                PICK(I,J)=0.0
 0056                PICKUP(I,J)=0.0
 0057             20 CONTINUE
 0058                PER=PERM(2,2)*FACP                                               DATA0720
 0059                BOT=BOTTOM(1,1)*FACB                                             DATA0730
 0060                TOPP=TOP(1,1)*FACO                                               DATA0740
 0061                GRO=LAND(1,1)*FACL                                               DATA0750
 0062                WRITE (P,455)
 0063                WRITE (P,460) STRT(1,1),S(1,1),SY(1,1),RATE(1,1),H(1,1),PER,BOT,TO
                    1PP,GRO,DELX(1),DELY(1)
            C        .................................................................
            C        ---READ DATA MATRICES---
 0064                IF (IHED.GT.-1) GO TO 55
 0065                IF (IHED.EQ.-2) GO TO 25
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```
 0066                WRITE (P,465)
 0067             25 CONTINUE
 0068                DO 50 I=1,DIML                                             DATA0920
 0069                READ (R,470) (STRT(I,J),J=1,DIMW)
 0070                DO 30 J=1,DIMW
 0071                STRT(I,J) = STRT(I,J)*FACH                                 DATA0950
 0072             30 ISUR(I,J)=STRT(I,J)*10.
 0073                DO 35 J=1,DIMW
 0074             35 PHI(I,J)=STRT(I,J)
 0075                IF (IHED.EQ.-2) GO TO 50
 0076                WRITE (P,475) I,(STRT(I,J),J=1,DIMW)
 0077             50 CONTINUE
               C     ...........................................................DATA1030
 0078             55 IF (ISTO.GT.-1) GO TO 75
 0079                IF (ISTO.EQ.-2) GO TO 60
 0080                WRITE (P,480)
 0081             60 CONTINUE
 0082                DO 70 I=1,DIML
 0083                READ (R,485) (S(I,J),J=1,DIMW)
 0084                DO 65 J=1,DIMW
 0085             65 S(I,J)=S(I,J)*FACS
 0086                IF (ISTO.EQ.-2) GO TO 70
 0087                WRITE (P,490) I,(S(I,J),J=1,DIMW)
 0088             70 CONTINUE
               C     ...........................................................DATA1150
 0089             75 IF (ISYI.GT.-1) GO TO 95
 0090                IF (ISYI.EQ.-2) GO TO 80
 0091                WRITE (P,495)
 0092             80 CONTINUE
 0093                DO 90 I=1,DIML
 0094                READ (R,485) (SY(I,J),J=1,DIMW)
 0095                DO 85 J=1,DIMW
 0096             85 SY(I,J)=SY(I,J)*FACY
 0097                IF (ISYI.EQ.-2) GO TO 90
 0098                WRITE (P,490) I,(SY(I,J),J=1,DIMW)
 0099             90 CONTINUE
               C     ...........................................................DATA1270
 0100             95 IF (IRAT.GT.-1) GO TO 115
 0101                IF (IRAT.EQ.-2) GO TO 100
 0102                WRITE (P,500)
 0103            100 CONTINUE
 0104                DO 110 I=1,DIML
 0105                READ (R,485) (RATE(I,J),J=1,DIMW)
 0106                DO 105 J=1,DIMW
 0107            105 RATE(I,J)=RATE(I,J)*FACK
 0108                IF (IRAT.EQ.-2) GO TO 110
 0109                WRITE (P,505) I,(RATE(I,J),J=1,DIMW)
 0110            110 CONTINUE
```

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C     ..................................................................DATA1390
  115 IF (ITHK.GT.-1) GO TO 135
      IF (ITHK.EQ.-2) GO TO 120
      WRITE (P,510)
  120 CONTINUE
      DO 130 I=1,DIML
      READ (R,485) (M(I,J),J=1,DIMW)
      DO 125 J=1,DIMW
  125 M(I,J)=M(I,J)*FACM
      IF (ITHK.EQ.-2) GO TO 130
      WRITE (P,475) I,(M(I,J),J=1,DIMW)
  130 CONTINUE
C     ..................................................................DATA1630
  135 IF (WATER.NE.CHK(2)) GO TO 180
  140 IF (IPER.GT.-1) GO TO 160
      IF (IPER.EQ.-2) GO TO 145
      WRITE (P,515)
  145 CONTINUE
      DO 155 I=1,DIML
      READ (R,440) (PERM(I,J),J=1,DIMW)
      DO 150 J=1,DIMW
  150 O(J)=PERM(I,J)*FACP
      IF (IPER.EQ.-2) GO TO 155
      WRITE (P,505) I,(O(J),J=1,DIMW)
  155 CONTINUE
C     ..................................................................DATA1920
  160 IF (IBOT.GT.-1) GO TO 180
      IF (IBOT.EQ.-2) GO TO 165
      WRITE (P,520)
  165 CONTINUE
      DO 175 I=1,DIML
      READ (R,440) (BOTTOM(I,J),J=1,DIMW)
      DO 170 J=1,DIMW
  170 O(J)=BOTTOM(I,J)*FACB
      IF (IBOT.EQ.-2) GO TO 175
      WRITE (P,475) I,(O(J),J=1,DIMW)
  175 CONTINUE
C     ..................................................................DATA2040
  180 IF (ITOP.GT.-1) GO TO 200
      IF (ITOP.EQ.-2) GO TO 185
      WRITE (P,525)
  185 CONTINUE
      DO 195 I=1,DIML
      READ (R,440) (TOP(I,J),J=1,DIMW)
      DO 190 J=1,DIMW
  190 O(J)=TOP(I,J)*FACO
      IF (ITOP.EQ.-2) GO TO 195
      WRITE (P,475) I,(O(J),J=1,DIMW)
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 0155          195 CONTINUE
             C     ...........................................................................DATA2160
 0156          200 IF (ILND.GT.-1) GO TO 220
 0157              IF (ILND.EQ.-2) GO TO 205
 0158              WRITE (P,530)
 0159          205 CONTINUE
 0160              DO 215 I=1,DIML
 0161              READ (R,440) (LAND(I,J),J=1,DIMW)
 0162              DO 210 J=1,DIMW
 0163          210 D(J)=LAND(I,J)*FACL
 0164              IF (ILND.EQ.-2) GO TO 215
 0165              WRITE (P,475) I,(D(J),J=1,DIMW)
 0166          215 CONTINUE
             C     ...........................................................................DATA2260
 0167          220 IF (IDLX.GT.-1) GO TO 230
 0168              READ (R,445) (DELX(J),J=1,DIMW)
 0169              DO 225 J=1,DIMW
 0170          225 DELX(J)=DELX(J)*FACX
 0171              IF (IDLX.EQ.-2) GO TO 230
 0172              WRITE (P,535) (DELX(J),J=1,DIMW)
 0173          230 IF (IDLY.GT.-1) GO TO 240
 0174              READ (R,445) (DELY(I),I=1,DIML)
 0175              DO 235 I=1,DIML
 0176          235 DELY(I)=DELY(I)*FACZ
 0177              IF (IDLY.EQ.-2) GO TO 240
 0178              WRITE (P,540) (DELY(I),I=1,DIML)
 0179          240 JND1=DIMW-1
 0180              IND1=DIML-1                                                                DATA2400
 0181              ETQB=0.0                                                                   DATA2410
 0182              ETQD=0.0                                                                   DATA2420
 0183              SLEAK=0.0                                                                  DATA2430
 0184              SUBS = 0.0                                                                 DATA2440
 0185              SUM=0.0
 0186              U = 0.0                                                                    DATA2450
 0187              TT = 0.0                                                                   DATA2460
 0188              RETURN                                                                     DATA2470
             C     ...........................................................................DATA2480
             C                                                                                DATA2490
             C     ********************                                                       DATA2510
 0189              ENTRY ITER                                                                 DATA2520
             C     ********************                                                       DATA2530
             C     ---COMPUTE AND PRINT ITERATION PARAMETERS---                               DATA2500
 0190              HMIN=2.                                                                    DATA2540
 0191              XVAL=3.1415**2/(2.*DIMW**2)                                                DATA2550
 0192              YVAL=3.1415**2/(2.*DIML**2)                                                DATA2560
 0193              DO 245 I=1,DIML
 0194              DO 245 J=1,DIMW
 0195              T(I,J)=1.0
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  0196            245 IF (I.EQ.1.OR.I.EQ.DIML.OR.J.EQ.1.OR.J.EQ.DIMW) T(I,J)=0.0
  0197                DO 250 I=2,DIML
  0198                DO 250 J=2,DIMW
  0199                IF (T(I,J).EQ.0.) GO TO 250
  0200                XPART=XVAL*(1/(1+DELX(J)**2/DELY(I)**2))                           DATA2600
  0201                YPART=YVAL*(1/(1+DELY(I)**2/DELX(J)**2))                           DATA2610
  0202                HMIN=AMIN1(HMIN,XPART,YPART)                                       DATA2620
  0203            250 CONTINUE
  0204                ALPHA=EXP(ALOG(1/HMIN)/(LENGTH-1))                                 DATA2640
  0205                RHOP(1)=HMIN                                                       DATA2650
  0206                DO 255 NTIME=2,LENGTH
  0207            255 RHOP(NTIME)=RHOP(NTIME-1)*ALPHA
  0208                WRITE (P,545) LENGTH,(RHOP(J),J=1,LENGTH)                          DATA2690
  0209                RETURN                                                             DATA2700
              C       ....................................................................DATA2710
              C                                                                          DATA2730
              C       ********************                                               DATA2740
  0210                ENTRY MAP                                                          DATA2750
              C       ********************                                               DATA2720
              C       ---INITIALIZE DATA FOR ALPHAMERIC PLOT---                          DATA2760
  0211                WIDTH=0.
  0212                DO 260 J=2,JND1
  0213            260 WIDTH=WIDTH+DELX(J)                                                DATA2790
  0214                YDIM=0.
  0215                DO 265 I=2,IND1
  0216            265 YDIM=YDIM+DELY(I)
  0217            270 XSF=DINCH*SCALE                                                    DATA2830
  0218                NYD=YDIM/XSF                                                       DATA2840
  0219                IF (NYD*XSF.LE.YDIM-DELY(IND1)/2.) NYD=NYD+1
  0220                IF (NYD.LE.12) GO TO 275
  0221                DINCH=YDIM/12.                                                     DATA2860
  0222                GO TO 270
  0223            275 NXD=WIDTH/XSF                                                      DATA2890
  0224                IF (NXD*XSF.LE.WIDTH-DELX(JND1)/2.) NXD=NXD+1                      DATA2900
  0225                N4=NXD*N1+1                                                        DATA2910
  0226                N5=NXD+1                                                           DATA2920
  0227                N6=NYD+1                                                           DATA2930
  0228                N8=N3*NYD+1                                                        DATA2940
  0229                NA(1)=N4/2-1                                                       DATA2950
  0230                NA(2)=N4/2                                                         DATA2960
  0231                NA(3)=N4/2+3                                                       DATA2970
  0232                NC=(N3-N8-10)/2                                                    DATA2980
  0233                ND=NC+N8                                                           DATA2990
  0234                NE=MAX0(N5,N6)                                                     DATA3000
  0235                VF1(3)=DIGIT(ND)                                                   DATA3010
  0236                VF2(3)=DIGIT(N8)                                                   DATA3020
  0237                VF3(3)=DIGIT(NC)                                                   DATA3030
  0238                XLABEL(3)=MESUR
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  0239                YLABEL(6)=MESUR                                            DATA3040
  0240                DO 285 I=1,NE
  0241                NNX=N5-I                                                   DATA3060
  0242                NNY=I-1                                                    DATA3070
  0243                IF (NNY.GE.N4) GO TO 280
  0244                YN(I)=XSF*NNY/SCALE                                        DATA3090
  0245           280  IF (NNX.LT.0) GO TO 285
  0246                XN(I)=XSF*NNX/SCALE                                        DATA3110
  0247           285  CONTINUE
  0248                RETURN                                                     DATA3130
             C        ..........................................................DATA3140
             C                                                                   DATA3150
             C        ************************                                   DATA3170
  0249                ENTRY NEWPER                                               DATA3180
             C        ************************                                   DATA3190
             C        ---READ TINE PARAMETERS AND PUMPING DATA FOR A NEW PUMPING PERIOD-DATA3160
  0250                READ (R,445) KP,KPM1,NWEL,TMAX,NUMT,CDLT,DELT
             C                                                                   DATA3220
             C        ---COMPUTE ACTUAL DELT AND NUMT---                         DATA3230
  0251                DT=DELT/24.                                                DATA3240
  0252                TZ=0.0
  0253                DO 290 I=1,NUMT
  0254                DT=CDLT*DT                                                 DATA3270
  0255                TZ=TZ+DT
  0256                IF (TZ.GE.TMAX) GO TO 295
  0257           290  CONTINUE
  0258                GO TO 300
  0259           295  DELT=TMAX/TZ*DELT
  0260                NUMT=I                                                     DATA3330
  0261           300  WRITE (P,550) KP,TMAX,DELT,NUMT,CDLT
  0262                DELT=DELT*3600.                                            DATA3350
  0263                TMAX=TMAX*86400.                                           DATA3360
             C                                                                   DATA3200
             C        ---READ AND WRITE WELL PUMPING RATES---                    DATA3370
  0264                WRITE (P,555) NWEL
  0265                IF (KP.GT.KPM1) SUMP=0.                                    DATA3390
  0266                DO 305 I=1,DIML
  0267                DO 305 J=1,DIMW
  0268                IF (KP.EQ.KPM1) GO TO 305
  0269                STRT(I,J)=PHI(I,J)                                         DATA3430
  0270           305  WELL(I,J)=0.
  0271                IF (NWEL.EQ.0) GO TO 315
  0272                DO 310 II=1,NWEL
  0273                READ (R,445) I,J,QW
  0274                WELL(I,J)=QW                                               DATA3480
  0275           310  WRITE (P,560) I,J,WELL(I,J)
  0276           315  RETURN
             C        ..........................................................DATA3510
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              C                                                            DATA3520
              C       **************************
0277                  ENTRY DATVAR
              C       **************************
              C       ---READ AND WRITE VARIABLE DATA---
0278                  KM=KM+1
0279                  READ (R,445) NPER,KTH,QRE,QET,FACR,FACT
0280                  IF (KM.GT.1) GO TO 380
0281                  WRITE (P,565) PERIOD,KM,NPER,QRE,QET,KTH
              C
              C       ---INITIALIZE MATRICES TO CONSTANT VALUES---
0282                  DO 320 I=1,DIML
0283                  DO 320 J=1,DIMW
0284                  RH(I,J)=FACR
0285                  RIVER(I,J)=IRIV
0286                  T(I,J)=FACT
0287                  TM(I,J)=ITRA
0288                  IF (I.EQ.1.OR.I.EQ.DIML.OR.J.EQ.1.OR.J.EQ.DIMW) T(I,J)=0.0
0289                  IF (I.EQ.1.OR.I.EQ.DIML.OR.J.EQ.1.OR.J.EQ.DIMW) TM(I,J)=0.0
0290              320 CONTINUE
0291                  IF (IRIV.LT.1) GO TO 325
0292                  WRITE (P,570) FACR
0293              325 IF (ITRA.LT.1) GO TO 330
0294                  WRITE (P,575) FACT
0295              330 IF (IRIV.GT.-1) GO TO 335
0296                  WRITE (P,580) FACR
0297              335 IF (ITRA.GT.-1) GO TO 340
0298                  WRITE (P,585) FACT
0299              340 IF (IRIV.GT.-1) GO TO 360
0300                  IF (IRIV.EQ.-2) GO TO 345
0301                  WRITE (P,590)
0302              345 CONTINUE
0303                  DO 355 I=1,DIML
0304                  READ (R,440) (RIVER(I,J),J=1,DIMW)
0305                  DO 350 J=1,DIMW
0306              350 RH(I,J)=RIVER(I,J)*FACR
0307                  IF (IRIV.EQ.-2) GO TO 355
0308                  WRITE (P,475) I,(RH(I,J),J=1,DIMW)
0309              355 CONTINUE
              C       ................................................................
0310              360 IF (WATER.EQ.CHK(2)) GO TO 375
0311                  IF (ITRA.GT.-1) GO TO 375
0312                  IF (ITRA.EQ.-2) GO TO 365
0313                  WRITE (P,595)
0314              365 CONTINUE
0315                  DO 375 I=1,DIML
0316                  READ (R,485) (TM(I,J),J=1,DIMW)
0317                  DO 370 J=1,DIMW
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 0318          370 T(I,J)=TM(I,J)*FACT
 0319              IF (ITRA.EQ.-2) GO TO 375
 0320              WRITE (P,490) I,(T(I,J),J=1,DIMW)
 0321          375 CONTINUE
 0322              RETURN
             C
             C     ---MODIFY VARIABLE DATA FOR A NEW MONTH---
 0323          380 WRITE (P,565) PERIOD,KM,NPER,QRE,QET,KTH
 0324              WRITE (P,580) FACR
 0325              WRITE (P,585) FACT
 0326              DO 385 I=1,DIML
 0327              DO 385 J=1,DIMW
 0328              RH(I,J)=RIVER(I,J)*FACR
 0329              T(I,J)=TM(I,J)*FACT
 0330          385 CONTINUE
 0331              RETURN
             C     ***********************************************************************
             C
             C     FORMATS:
             C
 0332          390 FORMAT (10A8)
 0333          395 FORMAT (1H1,16A8)
 0334          400 FORMAT (A8)
 0335          405 FORMAT (A8,11X,I1)
 0336          410 FORMAT (A8,11X,I1,3G10.0,A8)
 0337          415 FORMAT ('-PROBLEM OPTIONS:  ',5(A8,7X))
 0338          420 FORMAT ('0OUTPUT OPTIONS:   ',7(A8,1X,I1,5X))
 0339          425 FORMAT ('-ON ALPHAMERIC MAP:'/'   BASIC LENGTH UNIT IS MULTIPLIED
              1BY',F10.2,' TO GET ',A8/'   NUMBER OF MAP UNITS PER INCH =',F10.2/
              2'   CONTOUR INTERVAL =',F10.2)
 0340          430 FORMAT (10G8.0)
 0341          435 FORMAT ('-NUMBER OF ',A8,'SIMULATED =',I4///' NUMBER OF ROWS =',I9
              1//' NUMBER OF COLUMNS =',I5//' ERROR CRITERIA FOR CLOSURE =',G15.7
              2//' SPECIFIC STORAGE OF CONFINING BED =',G15.7//' MAXIMUM PERMITTE
              3D NUMBER OF ITERATIONS =',I10//' MAXIMUM CHANGE IN HEAD ALLOWED FO
              4R STEADY STATE =',G15.7//' EFFECTIVE DEPTH OF EVAPOTRANSPIRATION =
              5',G15.7//' NUMBER OF NODES SPECIFIED FOR OUTPUT =',I5/)
 0342          440 FORMAT (20I4)
 0343          445 FORMAT (8G10.0)
 0344          450 FORMAT (2I5)
 0345          455 FORMAT ('-PARAMETER MATRICES WERE ASSIGNED THE FOLLOWING INITIAL V
              1ALUES *'//)
 0346          460 FORMAT (' ','STARTING HEAD VALUE (STRT) =',F21.2/' STORAGE COEFFIC
              1IENT (S) =',F25.6/' SPECIFIC YIELD (SY) =',F29.6/' PERMEABILITY OF
              2 CONFINING BED (RATE) =',G12.7/' THICKNESS OF CONFINING BED (M) ='
              3,F18.2/' PERMEABILITY OF AQUIFER (PERM) =',G18.7/' ELEVATION OF BO
              4TTOM OF AQUIFER (BOTTOM) =',F9.2/' ELEVATION OF TOP OF AQUIFER (TO
              5P) =',F15.2/' ELEVATION OF LAND SURFACE (LAND) =',F16.2/' GRID SPA
```

```
                    6CING IN X DIRECTION (DELX) =',F14.2/' GRID SPACING IN Y DIRECTION
                    7(DELY) =',F14.2//' * THE RESULTING MATRIX IS PRINTED OUT IN FULL B
                    BELOW IF ANY ABOVE VALUE IS USED AS A MULTIPLIER')
  0347          465 FORMAT ('1',60X,'STARTING HEAD MATRIX')
  0348          470 FORMAT (8F10.4)
  0349          475 FORMAT ('0',I2,2X,20F6.1/(5X,20F6.1))
  0350          480 FORMAT (1H1,54X,26HSTORAGE COEFFICIENT MATRIX)
  0351          485 FORMAT (20F4.0)
  0352          490 FORMAT (1H0,I5,14F9.5/(1H,5X,14F9.5))
  0353          495 FORMAT (1H1,56X,21HSPECIFIC YIELD MATRIX)
  0354          500 FORMAT (1H1,61X,11HRATE MATRIX)
  0355          505 FORMAT (1H0,I5,10E11.3/(1H ,5X,10E11.3))
  0356          510 FORMAT ('1',55X,'CONFINING BED THICKNESS')
  0357          515 FORMAT (1H1,52X,29HHYDRAULIC CONDUCTIVITY MATRIX)
  0358          520 FORMAT (1H1,46X,40HELEVATION OF IMPERMEABLE BASE OF AQUIFER)
  0359          525 FORMAT ('1',53X,'ELEVATION OF TOP OF AQUIFER')
  0360          530 FORMAT ('1',54X,'ELEVATION OF LAND SURFACE')
  0361          535 FORMAT (1H1,40X,40HGRID SPACING IN PROTOTYPE IN X DIRECTION//(1H0,
                    112F10.0))
  0362          540 FORMAT (1H0,40X,40HGRID SPACING IN PROTOTYPE IN Y DIRECTION//(1H0,
                    112F10.0))
  0363          545 FORMAT (///1H0,I5,22H ITERATION PARAMETERS:,8D12.3//28X,8D12.3)
  0364          550 FORMAT ('-PUMPING PERIOD NO.',I4 ,':',F10.2,' DAYS'/' -----------
                    1-------------------------'//' DELT IN HOURS =',F12.3//' NUMBER OF
                    2TIME STEPS =',I5//' MULTIPLIER FOR THIS TIME STEP =',F5.2)
  0365          555 FORMAT ('-',10X,I4,' WELLS'/10X,'-------------'//10X,'I',9X'J    PU
                    1MPING RATE'/)
  0366          560 FORMAT (' ',2I10,F13.2)
  0367          565 FORMAT (1H1,A8,'=     ',I37//' PUMPING PERIODS =',I33/' RECHARGE RA
                    1TE =',20X,G15.6/' EVAPOTRANSPIRATION RATE =',10X,G15.6/' TIME STEP
                    2S PER PRINT-OUT =',I24)
  0368          570 FORMAT (' RIVER HEAD =',F30.2)
  0369          575 FORMAT (' TRANSMISSIVITY =',19X,G15.6)
  0370          580 FORMAT (' MULTIPLIER FOR RIVER HEAD MATRIX =',F16.6)
  0371          585 FORMAT (' MULTIPLIER FOR TRANSMISSIVITY MATRIX =',G12.6)
  0372          590 FORMAT (1H1,60X,17HRIVER HEAD MATRIX)
  0373          595 FORMAT (1H1,64X,23HTRANSMISSIVITY MATRIX  )
  0374              END                                                           DATA4100
```

```
          C/                                                                      CPT00010
  0001          SUBROUTINE COMPUT                                                 CPT00020
          C     -----------------                                                 CPT00030
          C                                                                       CPT00040
          C     SPECIFICATIONS:                                                   CPT00050
  0002          COMMON /DARRAY/ PHI(33,62),RHOP(20),CHK(13)
  0003          COMMON /SARRAY/ KEEP(33,62),T(33,62),Q(33,62),STRT(33,62),RATE(33,CPT00070
               162),M(33,62),WELL(33,62),S(33,62),SY(33,62),TR(33,62),TC(33,62),DECPT00080
               2LX(62),DELY(33)                                                   CPT00090
               3,PHE(33,62)                                                       CPT00100
  0004          COMMON /TARRAY/ TM(33,62),RH(33,62),PICK(33,62),PICKUP(33,62)
  0005          COMMON /HARRAY/ TOP(33,62),ISUR(33,62),LAND(33,62),RIVER(33,62),PECPT00110
               1RM(33,62),BOTTOM(33,62)                                           CPT00120
  0006          COMMON /GARRAY/ NODE(33,62)
  0007          COMMON /DPARAM/ WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTR,EROR,LECPT00130
               1AK,RIVPI,HEADV,NUMV
  0008          COMMON /SPARAM/ FACS,FACY,FACK,FACR,FACM,FACP,FACB,FACO,FACL,FACW,CPT00150
               1SLEAK,U,SS,TT,TMIN,ETDIST,QET,IFINAL,TMAX,CDLT,DELT,SUM,SUMP,NUMT,CPT00160
               2KT,KP,NPER,KTH,ITMAX,LENGTH,NWEL,QRE,ERR,DIML,DIMW,JNO1,INO1,R,P,PCPT00170
               3U,SUBS,STORE,TEST,ETQB,ETQD                                       CPT00180
  0009          COMMON /TPARAM/ ICH,IRP,IHM,IHV,IDM,IDV,ICO,KM,NMON,NNODE
  0010          COMMON /CK/ ETFLXT,STORT,QRET,CHST,CHDT,FLUXT,PUMPT,CFLUXT        CPT00190
          C                                                                       CPT00200
  0011          REAL*4 MINS,TEST3(102),DDN(100),KEEP,M                            CPT00210
  0012          REAL*8 PHI,DBLE,RHOP,CHK,WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTCPT00220
               1R,EROR,LEAK,RIVPI,HEADV,NUMV,XLABEL,YLABEL,TITLE,B(99),BE(99),TEMP
               2(99),IMK,K,DABS,D,W,T1,T2,T3,T4,RHO,A,B,C,PARAM,TEST2,DMAX1
  0013          INTEGER DIML,DIMW,R,P,PU                                          CPT00260
  0014          INTEGER*2 TOP,ISUR,LAND,RIVER,PERM,BOTTOM                         CPT00270
  0015          INTEGER*2 NODE
          C                                                                       CPT00280
          C     ********************                                              CPT00300
  0016          ENTRY NEWSTP                                                      CPT00310
          C     ********************                                              CPT00320
          C     ---START A NEW TIME STEP---                                       CPT00290
  0017          KT=KT+1                                                           CPT00330
  0018          KOUNT=0                                                           CPT00340
  0019          DO 5 I=1,DIML
  0020          DO 5 J=1,DIMW
  0021        5 KEEP(I,J)=PHI(I,J)
  0022          DELT=CDLT*DELT                                                    CPT00380
  0023          SUM=SUM+DELT                                                      CPT00390
  0024          SUMP=SUMP+DELT                                                    CPT00400
  0025          DAYSP=SUMP/86400.                                                 CPT00410
  0026          YRSP=DAYSP/365.                                                   CPT00420
  0027          HRS=SUM/3600.                                                     CPT00430
  0028          MINS=HRS*60.                                                      CPT00440
  0029          DAYS=HRS/24.                                                      CPT00450
```

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  0030                 YRS=DAYS/365.                                               CPT00460
  0031                 RETURN                                                      CPT00470
             C                                                                     CPT00480
             C         ************************                                    CPT00500
  0032                 ENTRY NEWIT1                                                CPT00510
             C         ************************                                    CPT00520
             C         ---INITIALIZE DATA FOR A NEW ITERATION---                   CPT00490
  0033                 IF (KOUNT.LT.ITMAX) GO TO 20
  0034                 KOUNT=KOUNT+1                                               CPT00540
  0035                 GO TO 140
  0036              10 WRITE (6,230)
  0037                 STOP                                                        CPT00570
  0038              15 IF (PNCH.EQ.CHK(1)) GO TO 222
  0039                 WRITE (P,235)
  0040                 STOP
  0041              20 KOUNT=KOUNT+1
  0042                 IF (MOD(KOUNT,LENGTH)) 25,25,30
             C         ************************                                    CPT00600
  0043                 ENTRY NEWIT0                                                CPT00610
             C         ************************                                    CPT00620
  0044              25 NTH=0
  0045              30 NTH=NTH+1
  0046                 PARAM=RHOP(NTH)                                             CPT00650
  0047                 TEST3(KOUNT+1)=0.                                           CPT00660
  0048                 TEST=0.                                                     CPT00670
  0049                 DO 35 I=2,IND1
  0050                 DO 35 J=2,JND1
  0051              35 PHE(I,J)=PHI(I,J)                                           CPT00710
  0052                 RETURN                                                      CPT00720
             C         ****************************************************************CPT00740
             C                                                                     CPT00750
  0053                 ENTRY ROW                                                   CPT00760
             C         ************************                                    CPT00730
             C         ---COMPUTE IMPLICITLY ALONG ROWS---
  0054                 DO 40 J=1,DIMW                                              CPT00780
  0055                 BE(J)=0.0                                                   CPT00790
  0056                 G(J)=0.0
  0057              40 TEMP(J)=PHI(I,J)
  0058                 DO 80 I=2,DIML
  0059                 DO 60 J=2,JND1                                              CPT00830
             C                                                                     CPT00840
             C         ---SKIP COMPUTATIONS IF NODE IS OUTSIDE AQUIFER BOUNDARY---
  0060                 IF (T(I,J)) 45,60,45
  0061              45 T1=TR(I,J-1)/DELX(J)                                        CPT00870
  0062                 T2=TR(I,J)/DELX(J)                                          CPT00880
  0063                 T3=TC(I-1,J)/DELY(I)                                        CPT00890
  0064                 T4=TC(I,J)/DELY(I)
  0065                 IF (S(I,J).LT.0.) GO TO 50
```

```
              C                                                                            CPT00910
              C      ---COMPUTE ET RATE (ETQ), STEADY AND TRANSIENT LEAKAGE FACTOR         CPT00920
              C      (SLEAK), AND STORAGE COEFFICIENT---                                   CPT00930
 0066                IF (EVAP.EQ.CHK(6)) CALL ETRATE (I,J)                                 CPT00940
 0067                IF (LEAK.EQ.CHK(9)) CALL LEAKAG (I,J)                                 CPT00950
 0068                CALL STORAG (I,J)                                                     CPT00960
              C                                                                            CPT00970
 0069                RHO=STORE/DELT                                                        CPT00980
 0070                GO TO 55
 0071             50 RHO=1.0E40
              C      ---CALCULATE VALUES FOR PARAMETERS USED IN THOMAS ALGORITHM---        CPT01010
 0072             55 IMK=PARAM*(T1+T2+T3+T4)
 0073                A=T1                                                                  CPT01030
 0074                B=-T1-T2-RHO-IMK-Q(I,J)*U-ETQB                                        CPT01040
 0075                C=T2                                                                  CPT01050
 0076                W=B-A*BE(J-1)                                                         CPT01060
 0077                BE(J)=C/W                                                             CPT01070
 0078                RW=-WELL(I,J)/(DELX(J)*DELY(I))                                       CPT01080
 0079                D=-T3*PHI(I-1,J)+(T4+T3-IMK)*PHI(I,J)-T4*PHI(I+1,J)-RHO*KEEP(I,J)-CPT01090
                    $SLEAK-QRE+RW+ETQD-SUBS                                                CPT01100
 0080                G(J)=(D-A*G(J-1))/W                                                   CPT01110
 0081             60 CONTINUE
              C                                                                            CPT01130
              C      ---CALCULATE HEAD VALUES FOR ROWS OF MATRIX AND PLACE THEM IN         CPT01140
              C      TEMPORARY LOCATION TEMP;IF(I.GT.2) FIRST MAKE PHI(I-1,NO4)=           CPT01150
              C      TEMP(NO4)---                                                          CPT01160
 0082                NO3=DIMW-2                                                            CPT01170
 0083                DO 75 KNO4=1,NO3
 0084                NO4=DIMW-KNO4                                                         CPT01190
 0085                PHI(I-1,NO4)=TEMP(NO4)                                                CPT01200
 0086                IF (T(I,NO4)) 70,65,70
 0087             65 TEMP(NO4)=PHI(I,NO4)
 0088                GO TO 75
 0089             70 TEMP(NO4)=G(NO4)-BE(NO4)*TEMP(NO4+1)
 0090             75 CONTINUE
 0091             80 CONTINUE
 0092                RETURN                                                                CPT01270
              C                                                                            CPT01280
              C      ***********************************************************************
 0093                ENTRY COLUMN                                                          CPT01310
              C      ************************                                              CPT01320
              C      ---COMPUTE IMPLICITLY ALONG COLUMNS---
 0094                DO 85 I=1,DIML
 0095                BE(I)=0.0                                                             CPT01340
 0096                G(I)=0.0                                                              CPT01350
 0097             85 TEMP(I)=PHI(I,1)
 0098                DO 125 J=2,DIMW
 0099                DO 105 I=2,INO1
```

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                C                                                                         CPT01390
                C     ---SKIP COMPUTATIONS IF NODE IS OUTSIDE AQUIFER BOUNDARY---         CPT01400
 0100                 IF (T(I,J)) 90,105,90
 0101              90 T1=TR(I,J-1)/DELX(J)
 0102                 T2=TR(I,J)/DELX(J)                                                  CPT01430
 0103                 T3=TC(I-1,J)/DELY(I)                                                CPT01440
 0104                 T4=TC(I,J)/DELY(I)                                                  CPT01450
 0105                 IF (S(I,J).LT.0.) GO TO 95
                C                                                                         CPT01470
                C     ---COMPUTE ET RATE (ETQ), STEADY AND TRANSIENT LEAKAGE FACTOR       CPT01480
                C     (SLEAK), AND STORAGE COEFFICIENT---                                 CPT01490
 0106                 IF (EVAP.EQ.CHK(6)) CALL ETRATE (I,J)                               CPT01500
 0107                 IF (LEAK.EQ.CHK(9)) CALL LEAKAG (I,J)                               CPT01510
 0108                 CALL STORAG (I,J)                                                   CPT01520
                C                                                                         CPT01530
 0109                 RHO=STORE/DELT                                                      CPT01540
 0110                 GO TO 100
 0111              95 RHO=1.0E40
                C     ---CALCULATE VALUES FOR PARAMETERS USED IN THOMAS ALGORITHM---      CPT01570
 0112             100 IMK=PARAM*(T1+T2+T3+T4)
 0113                 A=T3                                                                CPT01590
 0114                 B=-T3-T4-RHO-IMK-Q(I,J)*U-ETQB                                      CPT01600
 0115                 C=T4                                                                CPT01610
 0116                 W=B-A*BE(I-1)                                                       CPT01620
 0117                 BE(I)=C/W                                                           CPT01630
 0118                 RW=-WELL(I,J)/(DELX(J)*DELY(I))                                     CPT01640
 0119                 D=-T1*PHI(I,J-1)+(T1+T2-IMK)*PHI(I,J)-T2*PHI(I,J+1)-RHO*KEEP(I,J)-CPT01650
                     1SLEAK-QRE+RW+ETQD-SUBS                                              CPT01660
 0120                 G(I)=(D-A*G(I-1))/W                                                 CPT01670
 0121             105 CONTINUE
                C                                                                         CPT01690
                C     ---CALCULATE HEAD VALUES FOR COLUMNS OF MATRIX AND PLACE IN TEMP-   CPT01700
                C     ORARY LOCATION TEMP;IF(J.GT.2) FIRST MAKE PHI(NO4,J-1)=TEMP(NO4)--CPT01710
 0122                 NO3=DIML-2                                                          CPT01720
 0123                 DO 120 KNO4=1,NO3
 0124                 NO4=DIML-KNO4                                                       CPT01740
 0125                 PHI(NO4,J-1)=TEMP(NO4)                                              CPT01750
 0126                 IF (T(NO4,J)) 115,110,115
 0127             110 TEMP(NO4)=PHI(NO4,J)
 0128                 GO TO 120
 0129             115 TEMP(NO4)=G(NO4)-BE(NO4)*TEMP(NO4+1)
 0130                 TCHK = ABS(SNGL(TEMP(NO4)) - PHE(NO4,J))                            CPT01810
 0131                 IF (TCHK .GT. ERR) TEST = 1.                                        CPT01830
 0132                 TEST3(KOUNT+1)=TEST3(KOUNT+1)+TCHK                                  CPT01840
 0133             120 CONTINUE
 0134             125 CONTINUE
 0135                 RETURN                                                              CPT01870
                C     ******************************************************************CPT01890
```

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                 C                                                                      CPT01880
                 C                                                                      CPT01900
                 C       ************************                                       CPT01920
  0136                   ENTRY STEADY                                                   CPT01930
                 C       ************************                                       CPT01940
                 C       ---CHECK FOR STEADY STATE---                                   CPT01910
  0137                   TEST2=0.                                                       CPT01950
  0138                   DO 130 I=2,IN01
  0139                   DO 130 J=2,JN01
  0140               130 TEST2=DMAX1(TEST2,DABS(DBLE(KEEP(I,J))-PHI(I,J)))
  0141                   IF (TEST2.GE.EROR) GO TO 135
  0142                   WRITE (P,240) KT
  0143                   IFINAL=1                                                       CPT02010
  0144                   GO TO 140
  0145               135 IF (KT.EQ.NUNT) IFINAL=1
  0146               140 IF (CHCK.EQ.CHK(5)) CALL CHECK
  0147                   IF (RIVPI.EQ.CHK(12)) CALL RPICK
  0148                   IF (KOUNT.GT.ITMAX) GO TO 145
  0149                   RETURN                                                         CPT02060
                 C
                 C       ************************
  0150                   ENTRY SET
                 C       ************************
                 C       ---SET OUTPUT OPTIONS FOR END-OF-SIMULATION PRINTOUT---
  0151               145 ICH=0
  0152                   IRP=0
  0153                   ICO=0
  0154                   IHM=0
  0155                   IHV=0
  0156                   IDM=0
  0157                   IDV=0
  0158                   GO TO 150
                 C
                 C       ************************
  0159                   ENTRY OUTPUT
                 C       ************************
                 C       ---PRINT OUTPUT AT DESIGNATED TIME STEPS---                    CPT02080
  0160               150 WRITE (P,245) KT,DELT,SUM,MINS,HRS,DAYS,YRS,DAYSP,YRSP,KOUNT
  0161                   IF (CHCK.NE.CHK(5)) GO TO 155
  0162                   IF (ICH.EQ.0) CALL CWRITE
  0163               155 IF (TT.NE.0.) WRITE (P,250) TMIN,TT
  0164                   WRITE (P,255) TEST2
  0165                   KOUNT=KOUNT+1
  0166                   WRITE (P,260) (TEST3(J),J=1,KOUNT)
  0167                   IF (RIVPI.NE.CHK(12)) GO TO 160
  0168                   IF (IRP.EQ.0) CALL RWRITE
  0169               160 IF (CONTR.NE.CHK(3)) GO TO 165
  0170                   IF (ICO.EQ.0) CALL PRNTA
```

```
  165 IF (HEAD.NE.CHK(8).OR.IHM.NE.0) GO TO 175
      WRITE (P,265)
      DO 170 I=1,DIML
  170 WRITE (P,270) I,(PHI(I,J),J=1,DIMW)
  175 IF (HEADV.NE.CHK(10).OR.IHV.NE.0) GO TO 195
      IF (NUMV.NE.CHK(11).OR.IDV.NE.0) GO TO 185
      WRITE (P,275)
      DO 180 I=1,DIML
      DO 180 J=1,DIMW
      IF (NODE(I,J).EQ.0) GO TO 180
      DDN(J)=ISUR(I,J)*0.1-PHI(I,J)
      WRITE (P,280) I,J,PHI(I,J),DDN(J)
  180 CONTINUE
      GO TO 195
  185 WRITE (P,285)
      DO 190 I=1,DIML
      DO 190 J=1,DIMW
      IF (NODE(I,J).EQ.0) GO TO 190
      WRITE (P,290) I,J,PHI(I,J)
  190 CONTINUE
  195 IF (NUM.NE.CHK(4).OR.IDM.NE.0) GO TO 210
      WRITE (P,295)
      DO 205 I=1,DIML
      DO 200 J=1,DIMW
  200 DDN(J)=ISUR(I,J)*0.1-PHI(I,J)
  205 WRITE (P,270) I,(DDN(J),J=1,DIMW)
  210 IF (NUMV.NE.CHK(11).OR.IDV.NE.0) GO TO 220
      IF (HEADV.EQ.CHK(10).AND.IHV.EQ.0) GO TO 220
      WRITE (P,300)
      DO 215 I=1,DIML
      DO 215 J=1,DIMW
      IF (NODE(I,J).EQ.0) GO TO 215
      DDN(J)=ISUR(I,J)*0.1-PHI(I,J)
      WRITE (P,290) I,J,DDN(J)
  215 CONTINUE
  220 IF (KOUNT.GT.ITMAX) GO TO 10
      IF (KM.EQ.NMON) GO TO 15
      RETURN
C                                                                    CPT02330
C     ********************                                           CPT02350
      ENTRY DRY                                                      CPT02360
C     ********************                                           CPT02370
C     ---PUNCHED OUTPUT---                                           CPT02340
  222 WRITE (PU,310) SUM,SUMP,PUMPT,CFLUXT
      WRITE (PU,310) QRET,CHST,CHDT,FLUXT,STORT,ETFLXT
      DO 225 I=1,DIML
  225 WRITE (PU,315) (PHI(I,J),J=1,DIMW)
      WRITE (P,235)
```

```
  0215              STOP
                C                                                                     CPT02430
                C     ..................................................................CPT02440
                C                                                                     CPT02450
                C     FORMATS:                                                        CPT02460
                C                                                                     CPT02470
  0216            230 FORMAT(1H0,39HEXCEEDED PERMITTED NUMBER OF ITERATIONS/40H ********
                     1********************************)
  0217            235 FORMAT(1H0,17HEND OF SIMULATION/18H *****************)
  0218            240 FORMAT ('-*****STEADY STATE AT TIME STEP',I4,'*****')
  0219            245 FORMAT (1H1,'TIME STEP NUMBER = ',I41/' SIZE OF TIME STEP IN SECON
                     1DS =',F30.2//' TOTAL SIMULATION TIME IN SECONDS =',F26.2/26X,'MINU
                     2TES =',F26.2/28X,'HOURS =',F26.2/29X,'DAYS =',F26.2/28X,'YEARS =',
                     3F26.2//' DURATION OF CURRENT PUMPING PERIOD IN DAYS =',F16.2/38X,'
                     4YEARS =',F16.2///' ITERATION NUMBER =',I10/)
  0220            250 FORMAT ('0DIMENSIONLESS TIME FOR THIS TIME STEP RANGES FROM',G15.7
                     1,'  TO',G15.7)
  0221            255 FORMAT ('0MAXIMUM CHANGE IN HEAD FOR THIS TIME STEP =',F10.3)
  0222            260 FORMAT ('0SUM OF THE ABSOLUTE VALUE OF HEAD CHANGES FOR EACH ITERA
                     1TION: '/('0',10G12.4))
  0223            265 FORMAT ('1',60X,'HEAD MATRIX')
  0224            270 FORMAT ('0',I2,2X,10F12.3,/,(5X,10F12.3))
  0225            275 FORMAT ('1','RESULTS AT SPECIFIED NODES ',///,4X,'I',6X,'J',6X,'HE
                     1AD VALUES',4X,'DRAWDOWN VALUES',/2X,'-----',2X,'-----',2X,'------
                     2--------',2X,'---------------',//)
  0226            280 FORMAT (2X,I4,3X,I4,4X,F12.3,5X,F12.3)
  0227            285 FORMAT ('1','RESULTS AT SPECIFIED NODES ',///,4X,'I',6X,'J',6X,'HE
                     1AD VALUES',/2X,'-----',2X,'-----',2X,'---------------')
  0228            290 FORMAT (2X,I4,3X,I4,4X,F12.3)
  0229            295 FORMAT (1H1,60X,'DRAWDOWN')
  0230            300 FORMAT ('1','RESULTS AT SPECIFIED NODES ',///,4X,'I',6X,'J',4X,'DR
                     1AWDOWN VALUES',/2X,'-----',2X,'-----',2X,'---------------')
  0231            310 FORMAT (4G20.10)
  0232            315 FORMAT (8F10.4)
  0233                END                                                             CPT02670
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              C/                                                                     COEF0010
     0001           SUBROUTINE COEF                                                  COEF0020
              C     ----------------                                                 COEF0030
              C                                                                      COEF0040
              C     SPECIFICATIONS:                                                  COEF0050
     0002           COMMON /DARRAY/ PHI(33,62),RHOP(20),CHK(13)
     0003           COMMON /SARRAY/ KEEP(33,62),T(33,62),Q(33,62),STRT(33,62),RATE(33,CDE40070
                   1(62),M(33,62),WELL(33,62),S(33,62),SY(33,62),TR(33,62),TC(33,62),DECOEF0080
                   2LX(62),DELY(33)                                                  COEF0090
                   3,PHE(33,62)                                                      COEF0100
     0004           COMMON /TARRAY/ TM(33,62),RH(33,62),PICK(33,62),PICKUP(33,62)
     0005           COMMON /HARRAY/ TOP(33,62),ISUR(33,62),LAND(33,62),RIVER(33,62),PECOEF0110
                   1RM(33,62),BOTTOM(33,62)                                          COEF0120
     0006           COMMON /GARRAY/ NODE(33,62)
     0007           COMMON /DPARAM/ WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTR,EROR,LECOEF0130
                   1AK,RIVPI,HEADV,NUMV
     0008           COMMON /SPARAM/ FACS,FACY,FACK,FACR,FACM,FACP,FACB,FACD,FACL,FACW,COEF0150
                   1SLEAK,U,SS,TT,TMIN,ETDIST,QET,IFINAL,TMAX,COLT,DELT,SUM,SUMP,NUMT,COEF0160
                   2KT,KP,NPER,KTH,ITMAX,LENGTH,NWEL,QRE,ERR,DIML,DIMW,JNO1,INO1,R,P,PCOEF0170
                   3U,SUDS,STORE,TEST,ETQB,ETQD                                      COEF0180
     0009           COMMON /TPARAM/ ICH,IRP,IHM,IHV,IDM,IDV,ICO,KM,NMON,NNODE
     0010           COMMON /ANI/ FACTY,RECOVR                                        COEF0190
              C                                                                      COEF0200
     0011           REAL KEEP,M                                                      COEF0210
     0012           REAL*8 PHI,DBLE,RHOP,CHK,WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTCOEF0220
                   1R,EROR,LEAK,RIVPI,HEADV,NUMV
     0013           INTEGER DIML,DIMW,R,P,PU                                         COEF0240
     0014           INTEGER*2 TOP,ISUR,LAND,RIVER,PERM,BOTTOM                        COEF0250
     0015           INTEGER*2 NODE
     0016           DATA PIE/3.141593/                                               COEF0260
              C                                                                      COEF0270
              C     ********************                                             COEF0290
     0017           ENTRY CLAY                                                       COEF0300
              C     ********************                                             COEF0310
              C     ---COMPUTE Q COEFFICIENTS---                                     COEF0280
     0018           TMIN=1.E40                                                       COEF0320
     0019           TT=0.0                                                           COEF0330
     0020           PRATE=0.                                                         COEF0340
     0021           DO 60 I=1,DIML                                                   COEF0350
     0022           DO 60 J=1,DIMW                                                   COEF0360
              C                                                                      COEF0370
              C     ---SKIP COMPUTATIONS IF T, RATE OR M = 0, OR IF CONSTANT         COEF0380
              C        HEAD BOUNDARY---                                              COEF0390
     0023           IF (RATE(I,J).LE.0..OR.T(I,J).EQ.0..OR.M(I,J).EQ.0..OR.S(I,J).LT.0COEF0400
                   1.) GO TO 60                                                      COEF0410
              C                                                                      COEF0420
              C     ---CHECK FOR SS = 0---                                           COEF0430
     0024           IF (SS.NE.0.) GO TO 10                                           COEF0440
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 0025                  SUMN=0.0                                                          COEF0450
 0026                  DENOM=1.0                                                         COEF0460
 0027                  GO TO 50                                                          COEF0470
             C         ---CHECK WHETHER VALUE FOR Q(I,J) WILL EQUAL VALUE FOR PREVIOUS   COEF0480
             C            NODE---                                                        COEF0490
 0028             10   IF (RATE(I,J)*M(I,J).EQ.PRATE) GO TO 50                           COEF0500
 0029                  DIMT=RATE(I,J)*SUMP/(H(I,J)*M(I,J)*SS*3)                          COEF0510
 0030                  IF (DIMT.GT.TT) TT=DIMT                                           COEF0520
 0031                  IF (DIMT.LT.TMIN) TMIN=DIMT                                       COEF0530
 0032                  PPT=PIE*PIE*DIMT                                                  COEF0540
             C                                                                           COEF0550
             C         ---RECOMPUTE PPT IF DIMT WITHIN RANGE FOR SHORT TIME COMPUTATION--COEF0560
 0033                  IF (DIMT.LT.1.0E-03) PPT=1.0/DIMT                                 COEF0570
 0034                  CK=(2.3-PPT)/(2.*PPT)                                             COEF0580
 0035                  SUMN=0.0                                                          COEF0590
 0036                  DO 30 K=1,200                                                     COEF0600
 0037                  POWER=K*K*PPT                                                     COEF0610
 0038                  IF (POWER.LE.150.) GO TO 20                                       COEF0620
 0039                  POWER=150                                                         COEF0630
 0040             20   PEX=EXP(-POWER)                                                   COEF0640
 0041                  SUMN=SUMN+PEX                                                     COEF0650
 0042                  IF (PEX.GT.0.00009) GO TO 30                                      COEF0660
 0043                  IF (K.GT.CK) GO TO 40                                             COEF0670
 0044             30   CONTINUE                                                          COEF0680
             C                                                                           COEF0690
             C         ---COMPUTE DENOMINATER DEPENDING ON VALUE OF DIMT---              COEF0700
 0045             40   DENOM=1.0                                                         COEF0710
 0046                  IF (DIMT.LT.1.0E-03) DENOM=SQRT(PIE*DIMT)                         COEF0720
             C                                                                           COEF0730
             C         ---HEAD VALUES ARE NOT INCLUDED IN COMPUTATION OF Q FACTOR SINCE  COEF0740
             C            LEAKAGE IS CONSIDERED IMPLICITLY---                            COEF0750
 0047             50   Q1=RATE(I,J)/(M(I,J)*DENOM)                                       COEF0760
 0048                  Q(I,J)=Q1+2.0*Q1*SUMN                                             COEF0770
 0049                  PRATE=RATE(I,J)*M(I,J)                                            COEF0780
 0050             60   CONTINUE                                                          COEF0790
 0051                  TMIN = TMIN*3.0                                                   COEF0800
 0052                  TT = TT *  3.0                                                    COEF0810
 0053                  RETURN                                                            COEF0820
             C                                                                           COEF0830
             C         *********************                                             COEF0850
 0054                  ENTRY TRANS(IERR)                                                 COEF0860
             C         *********************                                             COEF0870
             C         ---COMPUTE TRANSMISSIVITY IN WT OR WT-ARTESIAN CONVERSION PROBLEM-COEF0840
 0055                  DO 70 I=2,IND1                                                    COEF0880
 0056                  DO 70 J=2,JND1                                                    COEF0890
 0057                  HED=PHI(I,J)                                                      COEF0900
 0058                  IF (CONVRT.EQ.CHK(7)) HED=AMIN1(SNGL(PHI(I,J)),TOP(I,J)*FACD)     COEF0910
 0059                  T(I,J)=PERM(I,J)*FACP*(HED-BOTTOM(I,J)*FACB)                      COEF0920
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  0060                      IF (T(I,J).GE.0.) GO TO 70                                         COEF0930
  0061                      IF (WELL(I,J).LT.0.) GO TO 80                                      COEF0940
  0062                      IF (RECOVR.NE.0.) GO TO 65                                         COEF0950
  0063                      T(I,J) =0.                                                         COEF0960
  0064                      PERM(I,J) = 0.                                                     COEF0970
  0065                      GO TO 70                                                           COEF0980
  0066                   65 T(I,J)=PERM(I,J)*FACP * 0.01                                       COEF0990
  0067                      PHI(I,J)=BOTTOM(I,J)*FACB+0.01                                     COEF1000
  0068                   70 CONTINUE                                                           COEF1010
  0069                      RETURN                                                             COEF1020
  0070                   80 WRITE (P,260) I,J                                                  COEF1030
  0071                      DO 90 I=2,INO1                                                     COEF1040
  0072                      DO 90 J=2,JNO1                                                     COEF1050
  0073                   90 PHI(I,J)=KEEP(I,J)                                                 COEF1060
  0074                      SUM=SUM-DELT                                                       COEF1070
  0075                      SUMP=SUMP-DELT                                                     COEF1080
  0076                      IERR=1                                                             COEF1090
  0077                      RETURN                                                             COEF1100
                 C                                                                             COEF1110
                 C          ********************                                               COEF1130
  0078                      ENTRY TCOF                                                         COEF1140
                 C          *********************                                              COEF1150
                 C          ---COMPUTE T COEFFICIENTS---                                       COEF1120
  0079                      DO 130 I=1,INO1                                                    COEF1160
  0080                      DO 130 J=1,JNO1                                                    COEF1170
  0081                      DENOM=(T(I,J)*DELX(J+1)+T(I,J+1)*DELX(J))                          COEF1180
  0082                      IF (DENOM.NE.0.) GO TO 100                                         COEF1190
  0083                      TR(I,J)=0.                                                         COEF1200
  0084                      GO TO 110                                                          COEF1210
  0085                  100 TR(I,J)=(2.*T(I,J+1)*T(I,J))/DENOM                                 COEF1220
  0086                  110 DENOM=(T(I,J)*DELY(I+1)+T(I+1,J)*DELY(I))                          COEF1230
  0087                      IF (DENOM.NE.0.) GO TO 120                                         COEF1240
  0088                      TC(I,J)=0.                                                         COEF1250
  0089                      GO TO 130                                                          COEF1260
  0090                  120 TC(I,J)=(2.*T(I+1,J)*T(I,J)*FACTY)/DENOM                           COEF1270
  0091                  130 CONTINUE                                                           COEF1280
  0092                      RETURN                                                             COEF1290
                 C                                                                             COEF1300
                 C          ********************                                               COEF1320
  0093                      ENTRY ETRATE(I,J)                                                  COEF1330
                 C          ********************                                               COEF1340
                 C          ---COMPUTE ET RATE---                                              COEF1310
  0094                      ETQB=0.0                                                           COEF1350
  0095                      ETQD=0.0                                                           COEF1360
                 CC         IF (PHI(I,J).LE.LAND(I,J)*FACL-ETDIST) GO TO 140                   COEF1370
  0096                      IF (PHE(I,J).LE.LAND(I,J)*FACL-ETDIST) GO TO 140                   COEF1380
  0097                      ETQB=QET/ETDIST                                                    COEF1390
  0098                      ETQD=ETQB*(ETDIST-LAND(I,J)*FACL)                                  COEF1400
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 0099            140 RETURN                                                            COEF1410
               C                                                                       COEF1420
               C     ********************                                              COEF1440
 0100                ENTRY STORAG(I,J)                                                 COEF1450
               C     ********************                                              COEF1460
               C     ---COMPUTE STORAGE COEFFICIENT---                                 COEF1430
 0101                SUBS=0.0                                                          COEF1470
 0102                IF (WATER.NE.CHK(2)) GO TO 200                                    COEF1480
 0103                IF (CONVRT.NE.CHK(7)) GO TO 180                                   COEF1490
               CC    X=KEEP(I,J)-PHI(I,J)                                              COEF1500
 0104                X=KEEP(I,J)-PHE(I,J)                                              COEF1510
 0105                IF (X) 150,160,160                                                COEF1520
               CC150 HED1=PH-(I,J)                                                     COEF1530
 0106            150 HED1=PHE(I,J)                                                     COEF1540
 0107                HED2=KEEP(I,J)                                                    COEF1550
 0108                GO TO 170                                                         COEF1560
 0109            160 HED1=KEEP(I,J)                                                    COEF1570
               CC    HED2=PHI(I,J)                                                     COEF1580
 0110                HED2=PHE(I,J)                                                     COEF1590
 0111            170 IF (HED1-TOP(I,J)*FACO) 180,180,190                               COEF1600
 0112            180 STORE=SY(I,J)                                                     COEF1610
 0113                GO TO 220                                                         COEF1620
 0114            190 IF (TOP(I,J)*FACO-HED2) 200,200,210                               COEF1630
 0115            200 STORE=S(I,J)                                                      COEF1640
 0116                GO TO 220                                                         COEF1650
 0117            210 STORE=SY(I,J)                                                     COEF1660
 0118                SUBS=(HED1-TOP(I,J)*FACO)*(S(I,J)-SY(I,J))/DELT                   COEF1670
 0119                IF (X.LT.0.) SUBS=-SUBS                                           COEF1680
 0120            220 RETURN                                                            COEF1690
               C                                                                       COEF1700
               C     ********************                                              COEF1720
 0121                ENTRY LEAKAG(I,J)                                                 COEF1730
               C     ********************                                              COEF1740
               C     ---COMPUTE STEADY AND TRANSIENT LEAKAGE FACTOR---                 COEF1710
 0122                HED1=STRT(I,J)                                                    COEF1750
 0123                IF (CONVRT.EQ.CHK(7)) HED1=AMAX1(STRT(I,J),TOP(I,J)*FACO)         COEF1760
 0124                U=1.                                                              COEF1770
 0125                HED2=0.                                                           COEF1780
               CC    IF (CONVRT.NE.CHK(7).OR.PHI(I,J).GE.TOP(I,J)*FACO) GO TO 230      COEF1790
 0126                IF (CONVRT.NE.CHK(7).OR.PHE(I,J).GE.TOP(I,J)*FACO) GO TO 230      COEF1800
 0127                HED2=TOP(I,J)*FACO                                                COEF1810
 0128                U=0.                                                              COEF1820
 0129            230 X=0.                                                              COEF1830
 0130                IF (M(I,J)) 250,250,240                                           COEF1840
 0131            240 X=RATE(I,J)/M(I,J)                                                COEF1850
 0132            250 SLEAK=X*(RIVER(I,J)*FACR-HED1)+Q(I,J)*(HED1-HED2)                 COEF1860
 0133                RETURN                                                            COEF1870
               C                                                                       COEF1880
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                                                                                               COEF1890
                    C     ---FORMATS---                                                        COEF1900
                    C                                                                          COEF1910
      0134            260 FORMAT ('-********************WELL AT ',I3,',',I3,' GOES DRY***')    COEF1920
      0135                END
```

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                   C/                                                                      CHEK0010
      0001                  SUBROUTINE CHECK                                               CHEK0020
                   C        ----------------                                               CHEK0030
                   C        ---THIS SUBROUTINE COMPUTES A MASS BALANCE---                  CHEK0040
                   C                                                                       CHEK0050
                   C        SPECIFICATIONS:                                                CHEK0060
      0002                  COMMON /DARRAY/ PHI(33,62),RHOP(20),CHK(13)
      0003                  COMMON /SARRAY/ KEEP(33,62),T(33,62),Q(33,62),STRT(33,62),RATE(33,CHEK0080
                           1(62),H(33,62),WELL(33,62),S(33,62),SY(33,62),TR(33,62),TC(33,62),DECHEK0090
                           2LX(62),DELY(33)                                                CHEK0100
                           3,PHE(33,62)                                                    CHEK0110
      0004                  COMMON /TARRAY/ TM(33,62),RH(33,62),PICK(33,62),PICKUP(33,62)
      0005                  COMMON /HARRAY/ TOP(33,62),ISUR(33,62),LAND(33,62),RIVER(33,62),PECHEK0120
                           1RM(33,62),BOTTOM(33,62)                                        CHEK0130
      0006                  COMMON /BARRAY/ NODE(33,62)
      0007                  COMMON /DPARAM/ WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTR,ERDR,LECHEK0140
                           1AK,RIVPI,HEADV,NUMV
      0008                  COMMON /SPARAM/ FACS,FACY,FACK,FACR,FACM,FACP,FACB,FACD,FACL,FACW,CHEK0160
                           1SLEAK,U,SS,TT,THIN,ETDIST,QET,IFINAL,TMAX,CDLT,DELT,SUM,SUMP,NUMT,CHEK0170
                           2KT,KP,NPER,KTH,ITMAX,LENGTH,NWEL,QRE,ERR,DIML,DIMW,JNO1,INO1,R,P,PCHEK0180
                           3U,SUBS,STORE,TEST,ETQB,ETQD                                    CHEK0190
      0009                  COMMON /TPARAM/ ICH,IRP,IHM,IHV,IDM,IDV,ICO,KM,NHON,NNODE
      0010                  COMMON /CK/ ETFLXT,STORT,QRET,CHST,CHDT,FLUXT,PUMPT,CFLUXT     CHEK0200
                   C                                                                       CHEK0210
      0011                  REAL KEEP,M                                                    CHEK0220
      0012                  REAL*8 PHI,DDLE,RHOP,CHK,WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTCHEK0230
                           1R,ERDR,LEAK,RIVPI,HEADV,NUMV
      0013                  INTEGER DIML,DIMW,R,P,PU                                       CHEK0250
      0014                  INTEGER*2 TOP,ISUR,LAND,RIVER,PERM,BOTTOM                      CHEK0260
      0015                  INTEGER*2 NODE
                   C                                                                       CHEK0270
                   C        ---INITIALIZE VARIABLES---                                     CHEK0280
      0016                  PUMP=0.                                                        CHEK0290
      0017                  STOR=0.                                                        CHEK0300
      0018                  FLUXS=0.0                                                      CHEK0310
      0019                  CHD1=0.0                                                       CHEK0320
      0020                  CHD2=0.0                                                       CHEK0330
      0021                  QREFLX=0.                                                      CHEK0340
      0022                  CFLUX=0.                                                       CHEK0350
      0023                  FLUX=0.                                                        CHEK0360
      0024                  ETFLUX=0.                                                      CHEK0370
                   C        ...............................................................CHEK0380
                   C                                                                       CHEK0390
                   C        ---COMPUTE RATES,STORAGE AND PUMPAGE FOR THIS STEP---          CHEK0400
      0025                  DO 230 I=2,DIML                                                CHEK0410
      0026                  DO 230 J=2,DIMW                                                CHEK0420
      0027                  IF (T(I,J).EQ.0..OR.S(I,J).LT.0.) GO TO 230                    CHEK0430
      0028                  IF (WELL(I,J)) 10,30,20                                        CHEK0440
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 0029             10 PUMP=PUMP-WELL(I,J)                                                        CHEK0450
 0030                GO TO 30                                                                   CHEK0460
 0031             20 CFLUX=CFLUX+WELL(I,J)                                                      CHEK0470
            C        ---COMPUTE FLOW RATES TO AND FROM CONSTANT HEAD BOUNDARIES---              CHEK0480
 0032             30 IF (S(I,J-1).GE.0.) GO TO 60                                               CHEK0490
 0033                X=DBLE(TR(I,J-1))*(DBLE(STRT(I,J-1))-PHI(I,J))*DBLE(DELY(I))              CHEK0500
 0034                IF (X) 40,60,50                                                            CHEK0510
 0035             40 CHD1=CHD1+X                                                                CHEK0520
 0036                GO TO 60                                                                   CHEK0530
 0037             50 CHD2=CHD2+X                                                                CHEK0540
 0038             60 IF (S(I,J+1).GE.0.) GO TO 90                                               CHEK0550
 0039                X=DBLE(TR(I,J))*(DBLE(STRT(I,J+1))-PHI(I,J))*DBLE(DELY(I))                CHEK0560
 0040                IF (X) 70,90,80                                                            CHEK0570
 0041             70 CHD1=CHD1+X                                                                CHEK0580
 0042                GO TO 90                                                                   CHEK0590
 0043             80 CHD2=CHD2+X                                                                CHEK0600
 0044             90 IF (S(I-1,J).GE.0.) GO TO 120                                              CHEK0610
 0045                X=DBLE(TC(I-1,J))*(DBLE(STRT(I-1,J))-PHI(I,J))*DBLE(DELX(J))              CHEK0620
 0046                IF (X) 100,120,110                                                         CHEK0630
 0047            100 CHD1=CHD1+X                                                                CHEK0640
 0048                GO TO 120                                                                  CHEK0650
 0049            110 CHD2=CHD2+X                                                                CHEK0660
 0050            120 IF (S(I+1,J).GE.0.) GO TO 150                                              CHEK0670
 0051                X=DBLE(TC(I,J))*(DBLE(STRT(I+1,J))-PHI(I,J))*DBLE(DELX(J))                CHEK0680
 0052                IF (X) 130,150,140                                                         CHEK0690
 0053            130 CHD1=CHD1+X                                                                CHEK0700
 0054                GO TO 150                                                                  CHEK0710
 0055            140 CHD2=CHD2+X                                                                CHEK0720
 0056            150 QREFLX=QREFLX+QRE*DELX(J)*DELY(I)                                          CHEK0730
            C        ---COMPUTE ET RATE---                                                      CHEK0740
 0057                IF (EVAP.NE.CHK(6)) GO TO 180                                              CHEK0750
 0058                IF (PHI(I,J).GE.LAND(I,J)*FACL-ETDIST) GO TO 160                           CHEK0760
 0059                ETQ=0.0                                                                    CHEK0770
 0060                GO TO 170                                                                  CHEK0780
 0061            160 ETQ=QET/ETDIST*(PHI(I,J)+ETDIST-LAND(I,J)*FACL)                            CHEK0790
 0062            170 ETFLUX=ETFLUX+ETQ*DELX(J)*DELY(I)                                          CHEK0800
            C        ---COMPUTE VOLUME FROM STORAGE---                                          CHEK0810
 0063            180 STORE=S(I,J)                                                               CHEK0820
 0064                IF (WATER.EQ.CHK(2)) STORE=SY(I,J)                                         CHEK0830
 0065                IF (CONVRT.NE.CHK(7)) GO TO 220                                            CHEK0840
 0066                X=KEEP(I,J)-PHI(I,J)                                                       CHEK0850
 0067                IF (X) 190,200,200                                                         CHEK0860
 0068            190 HED1=PHI(I,J)                                                              CHEK0870
 0069                HED2=KEEP(I,J)                                                             CHEK0880
 0070                X=ABS(X)                                                                   CHEK0890
 0071                GO TO 210                                                                  CHEK0900
 0072            200 HED1=KEEP(I,J)                                                             CHEK0910
 0073                HED2=PHI(I,J)                                                              CHEK0920
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 0074         210 STORE=S(I,J)                                                          CHEK0930
 0075             IF (HED1-TOP(I,J)*FACO.LE.0.) STORE=SY(I,J)                           CHEK0940
 0076             IF ((HED1-TOP(I,J)*FACO)*(HED2-TOP(I,J)*FACO).LT.0.0) STORE=(HED1-CHEK0950
                (TOP(I,J)*FACO)/X*S(I,J)+(TOP(I,J)*FACO-HED2)/X*SY(I,J)                 CHEK0960
 0077         220 STOR=STOR+STORE*DELX(J)*DELY(I)*(KEEP(I,J)-PHI(I,J))                  CHEK0970
            C     ---COMPUTE LEAKAGE RATE---                                            CHEK0980
            CC    IF (M(I,J).EQ.0.) GO TO 230                                           CHEK0990
 0078             IF(LEAK.NE.CHK(9).OR.M(I,J).EQ.0.) GO TO 230                          CHEK1000
 0079             HED1=STRT(I,J)                                                        CHEK1010
 0080             IF (CONVRT.EQ.CHK(7)) HED1=AMAX1(STRT(I,J),TOP(I,J)*FACO)             CHEK1020
 0081             HED2=PHI(I,J)                                                         CHEK1030
 0082             IF (CONVRT.EQ.CHK(7)) HED2=AMAX1(SNGL(PHI(I,J)),TOP(I,J)*FACO)        CHEK1040
 0083             XX=RATE(I,J)*(RIVER(I,J)*FACR-HED1)*DELX(J)*DELY(I)/M(I,J)            CHEK1050
 0084             FLUX=FLUX+XX                                                          CHEK1060
 0085             FLUXS=FLUXS+Q(I,J)*(HED1-HED2)*DELX(J)*DELY(I)+XX                     CHEK1070
 0086         230 CONTINUE                                                              CHEK1080
            C     ..................................................................... CHEK1090
            C                                                                           CHEK1100
            C     ---COMPUTE CUMULATIVE VOLUMES, TOTALS, AND DIFFERENCES---             CHEK1110
 0087             STORT=STORT+STOR                                                      CHEK1120
 0088             ETFLXT=ETFLXT+ETFLUX*DELT                                             CHEK1130
 0089             FLUXT=FLUXT+FLUXS*DELT                                                CHEK1140
 0090             QRET=QRET+QREFLX*DELT                                                 CHEK1150
 0091             CHDT=CHDT-CHD1*DELT                                                   CHEK1160
 0092             CHST=CHST+CHD2*DELT                                                   CHEK1170
 0093             PUMPT=PUMPT+PUMP*DELT                                                 CHEK1180
 0094             CFLUXT=CFLUXT+CFLUX*DELT                                              CHEK1190
 0095             TOTL1=STORT+QRET+CFLUXT+CHST+FLUXT                                    CHEK1200
 0096             TOTL2=CHDT+PUMPT+ETFLXT                                               CHEK1210
 0097             DIFF=TOTL2-TOTL1                                                      CHEK1220
 0098             PERCNT=DIFF/TOTL2*100.                                                CHEK1230
 0099             RETURN                                                                CHEK1240
            C     ..................................................................... CHEK1250
            C
            C     ************************
 0100             ENTRY RPICK
            C     ************************
            C     ---COMPUTE RIVER PICK-UP---
 0101             DO 232 I=1,DIML
 0102             DO 232 J=1,DIMW
 0103             IF (RIVER(I,J).EQ.0) GO TO 232
 0104             PICK(I,J)=RATE(I,J)*(PHI(I,J)-RIVER(I,J)*FACR)*DELX(J)*DELY(I)/M(I
                1,J)
 0105             PICKUP(I,J)=PICKUP(I,J)+PICK(I,J)*DELT
 0106         232 CONTINUE
 0107             RETURN                                                                CHEK1260
            C                                                                           CHEK1280
            C     ************************
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 0108              ENTRY CWRITE                                                 CHEK1290
             C     ************************                                     CHEK1300
             C     ---PRINT RESULTS---                                          CHEK1270
 0109              WRITE (P,240) STORT,QRET,CFLUXT,CHST,FLUXT,TOTL1             CHEK1320
 0110              WRITE (P,250) ETFLXT,CHDT,PUMPT,TOTL2,DIFF,PERCNT            CHEK1330
 0111              WRITE (P,260) QREFLX,CFLUX,CHD2,CHD1,PUMP,ETFLUX,FLUXS,FLUX,STOR CHEK1340
 0112              RETURN                                                       CHEK1370
             C
             C     ************************
 0113              ENTRY RWRITE
             C     ************************
             C     ---PRINT RIVER PICK-UP---
 0114              WRITE (P,270)
 0115              DO 236 I=1,DIML
 0116              DO 236 J=1,DIMW
 0117              IF (RIVER(I,J).EQ.0) GO TO 236
 0118              WRITE (P,280) I,J,PICK(I,J),PICKUP(I,J)
 0119          236 CONTINUE
 0120              RETURN                                                       CHEK1350
             C                                                                  CHEK1360
             C     FORMATS:                                                     CHEK1380
             C
 0121          240 FORMAT ('0MASS BALANCE:'//4X,' CUMULATIVE',25X,'L**3'//7X,' SOURCECHEK1390
                  1S: '/7X,' -------'/14X,' STORAGE =',F20.2/13X,' RECHARGE =',F20.2/CHEK1400
                  28X,' CONSTANT FLUX =',F20.2/8X,' CONSTANT HEAD =',F20.2/14X,' LEAKCHEK1410
                  3AGE =',F20.2/8X,' TOTAL SOURCES =',F20.2)                    CHEK1420
 0122          250 FORMAT ('0',6X,' DISCHARGES:'/7X,' ----------'/3X,' EVAPOTRANSPIRACHEK1430
                  1TION =',F20.2/8X,' CONSTANT HEAD =',F20.2/6X,' QUANTITY PUMPED =',CHEK1440
                  2F20.2/12X,' TOTAL OUT =',F20.2//4X,' TOTAL OUT-SOURCES =',F20.2/3XCHEK1450
                  3,' PERCENT DIFFERENCE =',F20.2)                              CHEK1460
 0123          260 FORMAT ('-',3X,' RATES FOR THIS TIME STEP',9X,'L**3/T'//13X,' RECHCHEK1470
                  1ARGE =',F20.2/8X,' CONSTANT FLUX =',F20.2/5X,' CONSTANT HEAD IN ='CHEK1480
                  2,F20.2/4X,' CONSTANT HEAD OUT =',F20.2/14X,' PUMPING =',F20.2/19X,CHEK1490
                  3' ET =',F20.2/14X,' LEAKAGE:'/16X,' TOTAL =',F20.2/15X,' STEADY ='CHEK1500
                  4,F20.2//' FOR THIS TIME STEP, STORAGE =',F14.2)              CHEK1510
 0124          270 FORMAT (1H1,'RESULTS OF RIVER PICK-UP COMPUTATIONS: ',/5X,'POSITIV
                  1E - SEEPAGE INTO RIVER',/5X,'NEGATIVE - SEEPAGE OUT OF RIVER',//26
                  2X,'PRESENT',12X,'CUMULATIVE',/26X,'SEEPAGE',13X,'AMOUNT OF',/28X,'
                  3RATE',15X,'SEEPAGE',/5X,'I',9X,'J',11X,'(CFS)',16X,'(CF)',/3X,'---
                  4--',5X,'-----',5X,'-------------',6X,'---------------')
 0125          280 FORMAT (4X,I3,7X,I3,6X,F10.5,12X,F10.0)                      CHEK1520
 0126              END
```

```
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                  C/                                                                        PRNT0010
  0001                  SUBROUTINE PRNTA                                                    PRNT0020
                  C     -----------------                                                   PRNT0030
                  C                                                                         PRNT0040
                  C     SPECIFICATIONS:                                                     PRNT0050
  0002                  COMMON /DARRAY/ PHI(33,62),RHOP(20),CHK(13)
  0003                  COMMON /SARRAY/ KEEP(33,62),T(33,62),Q(33,62),STRT(33,62),RATE(33,PRNT0070
                       162),H(33,62),WELL(33,62),S(33,62),SY(33,62),TR(33,62),TC(33,62),DEPRNT0080
                       2LX(62),DELY(33)                                                     PRNT0090
                       3,PHE(33,62)                                                         PRNT0100
  0004                  COMMON /TARRAY/ TM(33,62),RH(33,62),PICK(33,62),PICKUP(33,62)
  0005                  COMMON /HARRAY/ TOP(33,62),ISUR(33,62),LAND(33,62),RIVER(33,62),PEPRNT0110
                       1RM(33,62),BOTTOM(33,62)                                             PRNT0120
  0006                  COMMON /GARRAY/ NODE(33,62)
  0007                  COMMON /DPARAM/ WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTR,EROR,LEPRNT0130
                       1AK,RIVPI,HEADV,NUMV
  0008                  COMMON /SPARAM/ FACS,FACY,FACK,FACR,FACH,FACP,FACB,FACO,FACL,FACW,PRNT0150
                       1SLEAK,U,SS,TT,TMIN,ETDIST,QET,IFINAL,TMAX,CDLT,DELT,SUM,SUMP,NUMT,PRNT0160
                       2KT,KP,NPER,KTH,ITMAX,LENGTH,NWEL,QRE,ERR,DIML,DIMW,JNO1,INO1,R,P,PPRNT0170
                       3U,SUBS,STORE,TEST,ETQB,ETQD                                         PRNT0180
  0009                  COMMON /TPARAM/ ICH,IRP,IHM,IHV,IDM,IDV,ICD,KM,NMON,NNODE
  0010                  COMMON /PR/ XLABEL(3),YLABEL(6),TITLE(4),XN1,SYM(28),PRNT(122),BLAPRNT0190
                       1NK(60),DIGIT(122),VF1(6),VF2(6),VF3(7),NA(4),XN(100),YN(13),XSF,NXPRNT0200
                       2D,WIDTH,SPACNG,N1,N2,N3,N4,N6,N8,NC                                 PRNT0210
                  C                                                                         PRNT0220
  0011                  REAL K,KEEP,H                                                       PRNT0230
  0012                  REAL*8 PHI,DBLE,RHOP,CHK,WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTPRNT0240
                       1R,EROR,LEAK,RIVPI,HEADV,NUMV,XLABEL,YLABEL,TITLE,XN1,Z
  0013                  INTEGER DIML,DIMW,R,P,PU                                            PRNT0260
  0014                  INTEGER*2 TOP,ISUR,LAND,RIVER,PERM,BOTTOM                           PRNT0270
  0015                  INTEGER*2 NODE
                  C                                                                         PRNT0280
                  C     ---INITIALIZE VARIABLES---                                          PRNT0290
  0016                  DIST=WIDTH-DELX(JNO1)/2.                                            PRNT0300
  0017                  JJ=JNO1                                                             PRNT0310
  0018                  LL=1                                                                PRNT0320
  0019                  Z=NXD*XSF                                                           PRNT0330
  0020                  WRITE (P,150) (TITLE(I),I=1,4)                                      PRNT0340
  0021                  DO 140 I=1,N4                                                       PRNT0350
                  C                                                                         PRNT0360
                  C     ---LOCATE X AXES---                                                 PRNT0370
  0022                  IF (I.EQ.1.OR.I.EQ.N4) GO TO 10                                     PRNT0380
  0023                  PRNT(1)=SYM(23)                                                     PRNT0390
  0024                  PRNT(N8)=SYM(23)                                                    PRNT0400
  0025                  IF ((I-1)/N1*N1.NE.I-1) GO TO 30                                    PRNT0410
  0026                  PRNT(1)=SYM(25)                                                     PRNT0420
  0027                  PRNT(N8)=SYM(25)                                                    PRNT0430
  0028                  GO TO 30                                                            PRNT0440
```

```
                 C                                                                      PRNT0450
                 C      ---LOCATE Y AXES---                                             PRNT0460
      0029           10 DO 20 J=1,N8                                                    PRNT0470
      0030              IF ((J-1)/N2*N2.EQ.J-1) PRNT(J)=SYM(25)                         PRNT0480
      0031           20 IF ((J-1)/N2*N2.NE.J-1) PRNT(J)=SYM(24)                         PRNT0490
                 C                                                                      PRNT0500
                 C      ---COMPUTE LOCATION OF NODES AND DETERMINE APPROPRIATE SYMBOL---PRNT0510
      0032           30 IF (DIST.LT.0..OR.DIST.LT.Z-XN1*XSF) GO TO 90                   PRNT0520
      0033              YLEN=DELY(2)/2.                                                 PRNT0530
      0034              DO 80 L=2,IN01                                                  PRNT0540
      0035              J=YLEN*N2/XSF+1.5                                               PRNT0550
      0036              K=(ISUR(L,JJ)*.1-PHI(L,JJ))/SPACNG                              PRNT0560
      0037              IF (K) 60,50,40                                                 PRNT0570
      0038           40 K=AMOD(K,20.)                                                   PRNT0580
      0039              N=K                                                             PRNT0590
      0040              PRNT(J)=SYM(N+1)                                                PRNT0600
      0041              GO TO 70                                                        PRNT0610
      0042           50 PRNT(J)=SYM(26)                                                 PRNT0620
      0043              GO TO 70                                                        PRNT0630
      0044           60 PRNT(J)=SYM(22)                                                 PRNT0640
      0045           70 IF (S(L,JJ).LT.0.) PRNT(J)=SYM(27)                              PRNT0650
      0046              IF (WELL(L,JJ).NE.0.) PRNT(J)=SYM(28)                           PRNT0660
      0047           80 YLEN=YLEN+(DELY(L)+DELY(L+1))/2.                                PRNT0670
      0048              DIST=DIST-(DELX(JJ)+DELX(JJ-1))/2.                              PRNT0680
      0049              JJ=JJ-1                                                         PRNT0690
      0050           90 CONTINUE                                                        PRNT0700
                 C                                                                      PRNT0710
                 C      ---PRINT AXES,LABELS, AND SYMBOLS---                            PRNT0720
      0051              IF (I-NA(LL).EQ.0) GO TO 110                                    PRNT0730
      0052              IF ((I-1)/N1*N1-(I-1)) 120,100,120                              PRNT0740
      0053          100 WRITE (P,VF1) (BLANK(J),J=1,NC),(PRNT(J),J=1,N8),XN(1+(I-1)/6)  PRNT0750
      0054              GO TO 130                                                       PRNT0760
      0055          110 WRITE (P,VF2) (BLANK(J),J=1,NC),(PRNT(J),J=1,N8),XLABEL(LL)     PRNT0770
      0056              LL=LL+1                                                         PRNT0780
      0057              GO TO 130                                                       PRNT0790
      0058          120 WRITE (P,VF2) (BLANK(J),J=1,NC),(PRNT(J),J=1,N8)                PRNT0800
                 C                                                                      PRNT0810
                 C      ---COMPUTE NEW VALUE FOR Z AND INITIALIZE PRNT---               PRNT0820
      0059          130 Z=Z-2.*XN1*XSF                                                  PRNT0830
      0060              DO 140 J=1,N8                                                   PRNT0840
      0061          140 PRNT(J)=SYM(11)                                                 PRNT0850
                 C                                                                      PRNT0860
                 C      ---NUMBER AND LABEL Y AXIS AND PRINT LEGEND---                  PRNT0870
      0062              WRITE (P,VF3) (BLANK(J),J=1,NC),(YN(I),I=1,N6)                  PRNT0880
      0063              WRITE (P,170) (YLABEL(I),I=1,6)                                 PRNT0890
      0064              WRITE (P,160) SPACNG                                            PRNT0900
      0065              RETURN                                                          PRNT0910
                 C                                                                      PRNT0920
```

```
                    C     ---FORMATS---                                                              PRNT0930
                    C                                                                                PRNT0940
                                                                                                     PRNT0950
      0066            150 FORMAT ('1',46X,4A8//)
      0067            160 FORMAT ('-LEGEND'/' -------'//' R = CONSTANT HEAD BOUNDARY'/' W = WPRNT0960
                         1ELL LOCATION'/' 0 = NO-FLOW BOUNDARY'/' * = CONE OF IMPRESSION'//'PRNT0970
                         2 CONTOUR INTERVAL =',F10.2//' THE FOLLOWING 20 SYMBOLS, STARTING WPRNT0980
                         3ITH BLANK, ARE CYCLED:   1 2 3 4 5 6 7 8 9   1 B 3 D 5 F 7 H 9')  PRNT0990
      0068            170 FORMAT ('0',39X,6A8)                                                       PRNT1000
      0069                END                                                                        PRNT1010
```

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                C/                                                                          BLD10010
0001                 BLOCK DATA                                                             BLDA0020
                C    ----------                                                             BLDA0030
0002                 COMMON /DARRAY/ PHI(33,62),RHOP(20),CHK(13)
0003                 COMMON /SARRAY/ KEEP(33,62),T(33,62),Q(33,62),STRT(33,62),RATE(33,BLDA0050
                    162),M(33,62),WELL(33,62),S(33,62),SY(33,62),TR(33,62),TC(33,62),DEBLDA0060
                    2LX(62),DELY(33)                                                        BLDA0070
                    3,PHE(33,62)                                                            BLDA0080
0004                 COMMON /TARRAY/ TM(33,62),RH(33,62),PICK(33,62),PICKUP(33,62)
0005                 COMMON /HARRAY/ TOP(33,62),ISUR(33,62),LAND(33,62),RIVER(33,62),PE2LD10090
                    1RM(33,62),BOTTOM(33,62)                                                BLDA0100
0006                 COMMON /GARRAY/ NODE(33,62)
0007                 COMMON /DPARAM/ WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTR,EROR,LEBLD10110
                    1AK,RIVPI,HEADV,NUMV,PERIOD
0008                 COMMON /SPARAM/ FACS,FACY,FACK,FACR,FACM,FACP,FACB,FACO,FACL,FACW,BLDA0130
                    1SLEAK,U,SS,TT,TMIN,ETDIST,QET,IFINAL,TMAX,CDLT,DELT,SUM,SUMP,NUMT,BLDA0140
                    2KT,KP,NPER,KTH,ITMAX,LENGTH,NWEL,QRE,ERR,DIML,DIMW,JNO1,INO1,R,P,PBLDA0150
                    3U,SUBS,STORE,TEST,ETQB,ETQD                                            BLDA0160
0009                 COMMON /TPARAM/ ICH,IRP,IHM,IHV,IDM,IDV,ICO,KM,NMON,NNODE
0010                 COMMON /PR/ XLABEL(3),YLABEL(6),TITLE(4),XN1,SYM(28),PRNT(122),BLABLDA0170
                    1NK(60),DIGIT(122),VF1(6),VF2(6),VF3(7),NA(4),XN(100),YN(13),XSF,NXBLDA0180
                    2D,WIDTH,SPACNG,N1,N2,N3,N4,N6,N8,NC                                    BLD10190
                                                                                            BLDA0200
                C                                                                           BLDA0210
0011                 REAL KEEP,M
0012                 REAL*8 PHI,DBLE,RHOP,CHK,WATER,CONVRT,EVAP,CHCK,PNCH,NUM,HEAD,CONTBLDA0220
                    1R,EROR,LEAK,RIVPI,HEADV,NUMV,PERIOD,XLABEL,YLABEL,TITLE,XN1
0013                 INTEGER DIML,DIMW,R,P,PU                                               BLDA0240
0014                 INTEGER*2 TOP,ISUR,LAND,RIVER,PERM,BOTTOM                              BLDA0250
0015                 INTEGER*2 NODE
                C    *****************************************************************BLDA0260
0016                 DATA CHK/'PUNCH','WATERTAB','CONTOUR','NUMERIC','CHECK','EVAPOTRA'BLDA0270
                    1,'CONVERT','HEAD','LEAKAGE','HEADVALU','NUMERICV','RIVERPIC',0.D0/
                    2,R,P,PU/5,6,7/,SUBS,U/2*0.0/
0017                 DATA SYM/1H ,1H1,1H2,1H3,1H4,1H5,1H6,1H7,1H8,1H9,1H ,1H1,1HB,1H3,1BLD10290
                    1HD,1H5,1HF,1H7,1HH,1H9,1H ,1H*,1HI,1H-,1H+,1H0,1HR,1HW/                BLD10300
0018                 DATA PRNT/122*' '/,N1,N2,N3,XN1/6,10,133,.0833333333D0/,BLANK/60*'BLDA0310
                    1 '/,NA(4)/1000/                                                        BLDA0320
0019                 DATA XLABEL/' X DIS- ','TANCE IN',' MILES '/,YLABEL/'DISTANCE',' BLDA0330
                    1FROM OR','IGIN IN ','Y DIRECT','ION, IN ','MILES   '/,TITLE/'ALPHABLDA0340
                    2MER','IC CONTO','URS OF D','RAWDOWN '/                                 BLDA0350
0020                 DATA DIGIT/'1','2','3','4','5','6','7','8','9','10','11','12','13'BLDA0360
                    1,'14','15','16','17','18','19','20','21','22','23','24','25','26',BLDA0370
                    2'27','28','29','30','31','32','33','34','35','36','37','38','39','BLDA0380
                    340','41','42','43','44','45','46','47','48','49','50','51','52','5BLDA0390
                    43','54','55','56','57','58','59','60','61','62','63','64','65','66BLDA0400
                    5','67','68','69','70','71','72','73','74','75','76','77','78',' 79BLDA0410
                    6','80','81','82','83','84','85','86','87','88','89','90','91','92'BLD10420
                    7,'93','94','95','96','97','98','99','100','101','102','103',' 104'BLDA0430
```

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                        8,'105','106','107','108','109','110','111','112','113','114','115'BLDA0440
                        9,'116','117','118','119','120','121','122'/                       BLDA0450
    0021                 DATA VF1/'(1H ',',',','      ','A1,F','10.2',')'/                 BLDA0460
    0022                 DATA VF2/'(1H ',',',','      ','A1,1','X,A8',')'/                 BLDA0470
    0023                 DATA VF3/'(1H0',',',','      ','A1,F','3.1,',','12F1','0.2)'/     BLDA0480
                C        *****************************************************************BLDA0490
    0024                 END                                                               BLDA0500
```

"AN ANALYSIS of the CHIPUXET GROUND - WATER RESERVOIR by DIGITAL and ELECTRICAL MODELS"

UNIVERSITY OF RHODE ISLAND
1892

RHODE ISLAND
WATER RESOURCES CENTER

RHODE ISLAND WATER RESOURCES CENTER

CHIPUXET GROUND-WATER RESERVOIR

An analysis of the Chipuxet Ground-Water Reservoir by digital and electrical models

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Prepared by the Rhode Island Water Resources Center,
University of Rhode Island in cooperation with
the Rhode Island Water Resources Board

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LIST OF SYMBOLS USED IN THIS REPORT

A - coefficient matrix

A_s - area of streambed

C - capacitance

K_s - streambed hydraulic conductivity

K_x, K_y, K_z - hydraulic conductivity

M_s - thickness of streambed

Q - discharge per unit area

Q_s - streambed leakage

R - resistance

S - storage coefficient

S_s - specific storage

S_y - specific yield

T - transmissivity

T_x, T_y - transmissivity in the x and y direction respectively

V - voltage

W - recharge per unit area

W_o - recharge at node zero

b - variable matrix

h - total head

h_i - total head at node i

h_a - aquifer head beneath stream

h_s - stream head

i - gradient

m - aquifer thickness

t - time

x,y,z - space variables

INTRODUCTION

In 1973 the Rhode Island Water Resources Board began a cooperative study with the Department of Civil and Environmental Engineering to develop analog and digital models of the Chipuxet ground-water reservoir. From 1974 through 1976 the Office of Water Resources Research supported design, construction and testing of an analog model of the Chipuxet ground-water reservoir through a grant under the Allotment Program of the Rhode Island Water Resources Center. This two year grant (A-056-RI) provided funds for the purchase of specialized equipment for operating resistance capacitance analog models.

On October 30, 1974 a public demonstration of the Chipuxet analog model was made at a meeting organized by the Rhode Island Water Resources Board and held at the University of Rhode Island's Memorial Student Union. On May 12, 1975 results of simulations of the actual pumping schemes proposed for the Chipuxet ground-water reservoir by the RI Water Resources Board were presented at a regular meeting of the Board.

Since the beginning of the cooperative program in 1973, there have been significant advances in ground water modeling techniques. Resistance-capacitance analog models which were common then (Walton, 1970) are now rare in practice. Part of the reason, is the increasing accessibility of large digital computers, and the associated graphical output devices. Coupled with this, are generally lower computing costs, faster execution times, and increased storage capacities. Increased storage capacity means that problems that could not be readily run nine years ago, are now run routinely.

This report is based largely on theses by D. Geisser (1975) and W. Beckman (1978). Geisser developed both an analog and a digital model of the Chipuxet ground-water reservoir. Geisser tested the five pumping schemes proposed by the RI Water Resource Board assuming steady-state equilibrium. Beckman modified the digital computer program used by Geisser so that aquifer behavior on a monthly or even weekly basis could be simulated. Beckman simulated proposed pumping schemes I and II on a monthly basis and compared these results with Geisser's. In the remainder of this report we will discuss the development and application of ground-water models to be used for predicting the effects of proposed future pumping patterns on water levels and streamflows in the Chipuxet ground-water reservoir.

THEORETICAL BACKGROUND

The brief introduction to modeling which follows is intended only to demonstrate that there is nothing mysterious about computer models; they must be completely described by the modeler using data which best represents actual field conditions.

The equation describing ground-water flow can be written

$$K_x \frac{\partial^2 h}{\partial x^2} + K_y \frac{\partial^2 h}{\partial y^2} + K_z \frac{\partial^2 h}{\partial z^2} = S_s \frac{\partial h}{\partial t} \qquad (1)$$

where: K_x, K_y, K_z are hydraulic conductivities; h, is total head; t is time; x, y, and z are space variables; and S_s, is specific storage. In aquifer solutions the assumption is generally made that head does not vary with depth (z) so that equation 1 becomes,

$$K_x \frac{\partial^2 h}{\partial x^2} + K_y \frac{\partial^2 h}{\partial y^2} = S_s \frac{\partial h}{\partial t} \qquad (2)$$

for a unit thickness.

To account for flow through the entire aquifer thickness, equation 2 is written in terms of transmissivity (T) which is hydraulic conductivity (K) times aquifer thickness (m). Also T_x is normally taken equal to T_y although T may vary within the aquifer--be a function of x and y. Equation 2 then can be written

$$T \frac{\partial^2 h}{\partial x^2} + T \frac{\partial^2 h}{\partial y^2} = m\, S_s \frac{\partial h}{\partial t} \qquad (3)$$

Compare equation 3 with equation 4 for the flow of electricity,

$$\frac{1}{R} \frac{\partial^2 v}{\partial x^2} + \frac{1}{R} \frac{\partial^2 h}{\partial y^2} = C \frac{\partial V}{\partial t} \qquad (4)$$

where R is resistance and C is capacitance and the basis for using electrical networks for modeling ground-water flow is apparent.

When flow is steady, head does not change with time and equation 3 can be written

$$T \frac{\partial^2 h}{\partial x^2} + T \frac{\partial^2 h}{\partial y^2} + W - Q = 0 \qquad (5)$$

where input (aquifer recharge, underflow) and output (well withdrawals, evapotranspiration, underflow) terms have been added. We can also write equation 5 in an approximate finite difference form for uniform T and a square network of nodes ($\Delta x = \Delta y$) as

$$(h_1 + h_2 + h_3 + h_4 - 4h_0) + \frac{W_0(\Delta x)^2}{T} - \frac{Q_0(\Delta x)^2}{T} = 0 \qquad (6)$$

where h_1 through h_4 are the heads at the four nearest neighbors of h_0 or alternately

$$h_0 = (h_1 + h_2 + h_3 + h_4) + \frac{W_0(\Delta x)^2}{4\,T} - \frac{Q_0(\Delta x)^2}{4\,T} = 0 \qquad (7)$$

Without recharge or discharge at a node, head is just the average of the head at the four nearest neighbors; recharge tends to raise the head and discharge to lower it. The above equations can be written in a more general form and the interested reader may refer to the thesis by Geisser (1975) or standard texts such as the one by Rushton and Redshaw (1979). In this report we will use the simpler forms of the equations for clarity.

The solution technique will be explained with a one-dimensional aquifer model. Figure 1 shows a typical cross-section for the Chipuxet aquifer and figure 2 an idealized model representing it. Assume that a series of wells is proposed to intercept ground water and induce river infiltration. As a first approximation flow is considered to be one dimensional towards the river and the line of wells to behave effectively as a slot. This means that head varies only with distance away from the river (x) and not along it (y). The governing flow equations can be written in finite difference

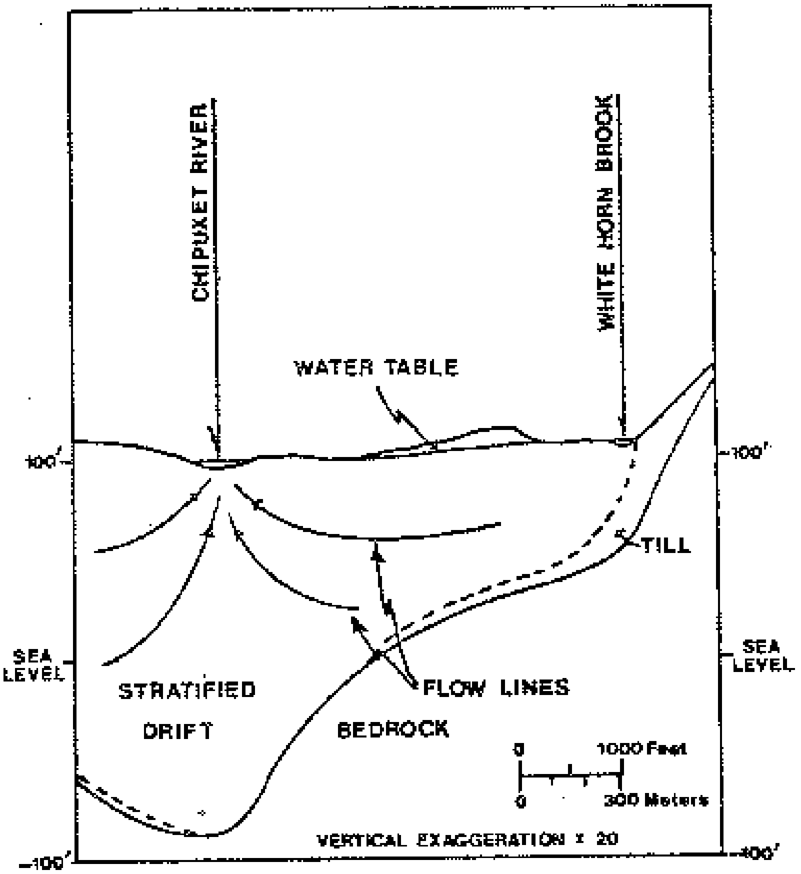

Figure 1.-- Generalized Cross-section of the Chipuxet Stratified-drift Aquifer.

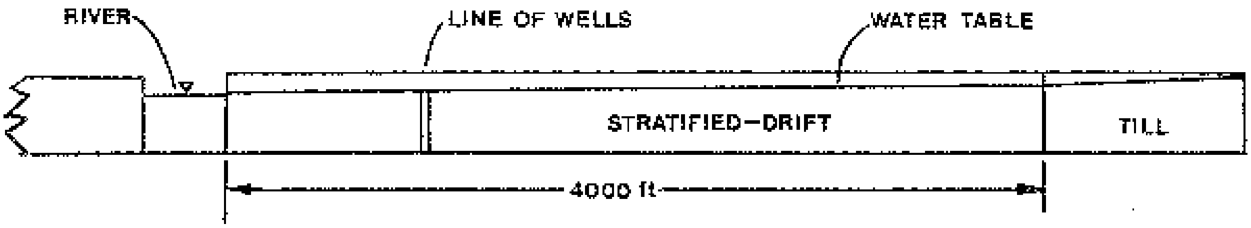

Figure 2.-- Cross-section of Idealized Aquifer.

form or represented by a resistor network.

To solve for the nodal heads the necessary boundary conditions must first be introduced. Boundary conditions in this case are the head at the river and the flow from the till area; values must also be assigned to input and output terms.

As an example, consider the following situation for the idealized aquifer, assume aquifer transmissivity is uniform at 8,000 ft.^{2}/day, nodes are spaced 1,000 ft. apart, average recharge is at the rate of 20 in/yr and leakage from the till area 4,000 feet from the river is negligible and can be ignored. A typical nodal equation is written as

$$h_{i-1} + h_{i+1} - 2h_{(i)} + W_{(i)} - Q_{(i)} = 0 \qquad (8)$$

Assume also that the head at the river is 95 ft. and that the proposal is to extract 73% of the average ground water recharge (20 in/yr.) at the first node, 1,000 ft. from the river. The equations are written in matrix form as

$$[A]\,[h] - \begin{bmatrix} hr \\ o \\ \\ o \\ o \end{bmatrix} + \begin{bmatrix} W_1 \\ W_2 \\ \\ W_3 \\ W_4 \end{bmatrix} + \begin{bmatrix} Q_1 \\ Q_2 \\ \\ Q_3 \\ Q_4 \end{bmatrix} = [o] \qquad (9)$$

The column matrices can be combined into a single matrix [b] so that

$$[A]\,[h] - [b] = 0 \qquad (10)$$

which for this problem in expanded form is

$$\begin{bmatrix} 2 & -1 & 0 & 0 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ 0 & 0 & -2 & 2 \end{bmatrix} \begin{bmatrix} h \\ h \\ h \\ h \end{bmatrix} = \begin{bmatrix} 93.90 \\ .57 \\ .57 \\ .28 \end{bmatrix}$$

The next step is to find the inverse of [A] and compute [h] from [h] $= [A]^{-1}$ [b]. If it is only necessary to solve this problem once we can compute [b] find $[A]^{-1}$, which in this case can be done with a programmable calculator, and multiply to obtain the heads [h]. Some results from this problem are tabulated below in Table 1.

TABLE 1 - Heads in idealized aquifer for development of 73% of average recharge rate

	Recharge rate in inches per year			
Node	20		10	5
Node	Head, water table altitude, in feet above mean sea level			
River	95		95	95
2	95.18	(96.85)	94.24	93.79
3	96.46	(98.13)	94.88	94.11
4	97.17	(99.84)	95.23	94.29
5	97.31	(98.98)	95.30	94.32
River infiltration as percent of development	0		28	34

Also shown in table 1 are heads for recharge rates of 10 and 5 in/yr, which could represent conditions more severe than the average. Withdrawals are still at the rate of 73% of the average recharge rate and during periods where recharge is less (5 and 10 in/yr for example) results show that heads are lowered and more water must be obtained from the stream. The number in parentheses for the 20in/yr rate are the heads if there were no pumping at that recharge rate. By comparison it can be seen that with pumping, heads are lowered nearly two feet. This is a crude model but it illustrates how a modeler may easily study a variety of conditions. Additional constraints could be imposed to account for partial penetration of the stream or leakage from the till area. Solutions with an analog model proceed similarly; after a model is set up voltages (heads) are measured.

If it is necessary to solve this type of problem many times on a digital computer, a program could be written which would take as input, transmissivities, heads, recharges, etc.; assemble the equations; and solve for heads and flows. When a program is developed and applied to a particular problem (data are introduced), a model of the ground water system is the result.

The reader may ask how good a crude model of the actual conditions shown in Figure 1 would be. The cross-section in Figure 1 is shown with vertical exaggeration because the aquifer's thickness is very small relative to its lateral dimensions. If the section were drawn without vertical exaggeration, the outwash would be visible only as a thin layer. Also shown in Figure 1 are some possible ground water flow lines; these are intended only to show that flow in the stratified drift aquifer is nearly horizontal except where ground water enters the Chipuxet River. Near the river where flow lines curve upward, there is a much greater head loss per horizontal foot of aquifer than in areas further from the river, even when conditions are otherwise the same. If flow is primarily toward the river, then flow can reasonably be approximated as 1-dimensional and modeled as shown in Figure 2. For conditions prior to the development of the Chipuxet ground water reservoir the assumption of one-dimensional or horizontal flow is reasonable. Some additional simplifications may also be explained using the one-dimensional model. In the idealized model (Figure 2), seepage from the till-bedrock area was neglected. This would not be reasonable for the Chipuxet aquifer, since inflow from the till-bedrock areas is an important input. On the loss side, wetlands adjacent to the river are areas of relatively high evapotranspiration losses which have not been directly modeled. Since in this case wetlands are adjacent to a river node, this node actually includes outflow by ground-water flow and by evapotranspiration from the adjacent wetlands. There would be no effect on the predicted heads in the aquifer but the modeled outflow would be larger than the observed outflow by the amount of evapotranspiration. Head losses near the stream due to curvature of flow lines and lower vertical hydraulic conductivities can be accounted for by inserting nodes immediately adjacent to the stream to impede flow.

Some of the simplifications necessary for representing real aquifers with idealized computer models have been discussed. Both the till-bedrock input and the evapotranspiration losses could be included in a computer model but were beyond the scope of this study.

In calibration, which will be discussed for the Chipuxet ground-water reservoir in the next section, both transient and steady-state simulations were used. Equation 11

$$\frac{T\partial^2 h}{\partial x^2} + W - Q = \frac{S\partial h}{\partial t} \qquad (11)$$

is the partial differential equation governing transient one-dimensional aquifer flow. For transient conditions, h is a function of time and the boundary conditions, recharge inputs and discharges which may all vary with time. If a modeler wants to calibrate a transient model against actual aquifer behavior, aquifer quantities must be known as a function of time. Often only a few values of head and some flows are known as a function of time and the need for or appropriateness of a transient model may be questionable. For example, in the Chipuxet aquifer which has been monitored in some detail, good records of streamflow (stream stage at one point) and water levels at one observation well are available. Withdrawal records at the URI well field have been until recently poor and other records are of relatively short duration. (Allen et al 1966).

To understand how steady-state simulations can be used in calibration it is necessary first to look at the physical meaning of the term $\frac{S\partial h}{\partial t}$. If the water level at an observation well drops [0.5 feet] in a month and the specific yield at that point is estimated to be .10 then

$$S_y \frac{\Delta h}{\Delta t} = -.10 \times \frac{.5 \times 12}{1/12} = -7.2 \text{ in/yr}$$

This means that the water table at the end of a month may be considered to result in part from an accretion of this magnitude. Equation 11 may then be written

$$\frac{T\partial^2 h}{\partial x^2} + (W - S\frac{\Delta h}{\Delta t}) - Q = 0$$

or

$$T\frac{\partial^2 h}{\partial x^2} + \overline{W} - Q = 0 \qquad (12)$$

where

$$\overline{W} = W - S\frac{\Delta h}{\Delta t} \qquad (13)$$

and $\overline{W}$ is the recharge which will simulate aquifer response at the desired time. This expedient is often used in calibrating aquifer models where measurements of aquifer conditions are known for only a few times and this is the approach we have used.

Another reason for assuming steady-state conditions would be to represent average yearly conditions. If water levels are not declining on a yearly basis, then $\frac{\partial h}{\partial t} = 0$ and equation 11 becomes

$$T\frac{\partial^2 h}{\partial x^2} + W - Q = 0 \qquad (14)$$

where W, Q, and h now would represent average yearly values.

Still retaining a one-dimensional model for simplicity model calibration will be explained. Before making predictions, a model must be calibrated to accurately represent field conditions. Assume the modeler has a water-table map constructed from water level measurements made in late summer, some stream-flow measurements made during the same period representing base flow conditions and is using the simplified model shown in Figure 2. Calibration would involve adjusting transmissivities, and recharge and underflow from the till-bedrock area until the predicted water table map matches the observed water table to any desired degree. Also outflow from the model should, in this case, match the observed baseflow with a recharge rate consistent with known specific yields and rates of water level decline, and an input from the till-bedrock area consistent with independent estimates. The degree of agreement between observed and predicted behavior is an indication of the accuracy with which a model represents the conditions under which it is calibrated.

After the model has been calibrated in steady-state, transmissivities, leakages, and underflows which are not time-dependent are fixed and the model is calibrated in a transient mode by introducing values for storage coefficients and time varying inputs and outputs and checking the model against a period of historical record. By adjusting storage coefficients and possibly underflows a match is obtained after which the model is considered to be calibrated for conditions similar to the period for which the model was calibrated. Verification would involve checking the calibrated model against another period of record.

For transient calibration two approaches are normally used. In the first the model is calibrated by testing it against a large-scale pumping test. The pumping must be great enough and of sufficient duration so that the modeled portion of the aquifer is stressed. Measurements of drawdowns and other relevant parameters must be available over the aquifer since these values are compared with modeled drawdowns. When a large-scale pumping test is not feasible the necessary data can be obtained by careful monitoring of existing large-scale ground water withdrawals.

In cases where a large-scale pumping test is not feasible and where the aquifer is undeveloped the alternative is to compare predicted natural fluctuations with observed natural fluctuations during a period of historical record. When a model is calibrated against natural conditions only, predictions of the effects of future development must be clearly qualified since development conditions will in general not be comparable with the conditions under which the model was calibrated.

When complete calibration and verification are not possible or when a modeler wants to learn more about aquifer behavior, a sensitivity analysis may be performed. A sensitivity analysis could consider the sensitivity of water levels to changes in transmissivity. Results from sensitivity analyses besides giving modelers a better feel for aquifer behavior may also be useful as a guide in decisions such as the need for additional field data and the types of data of most value.

Figure 3 shows an idealized two-dimensional model and Figure 4 some results from sensitivity analyses by Beckman. The model was operated in a transient mode with recharge applied over half the items; the response at a single observation node and the baseflow are shown. By the end of the second year of simulation, the effects of the initial conditions are negligible and the aquifer is

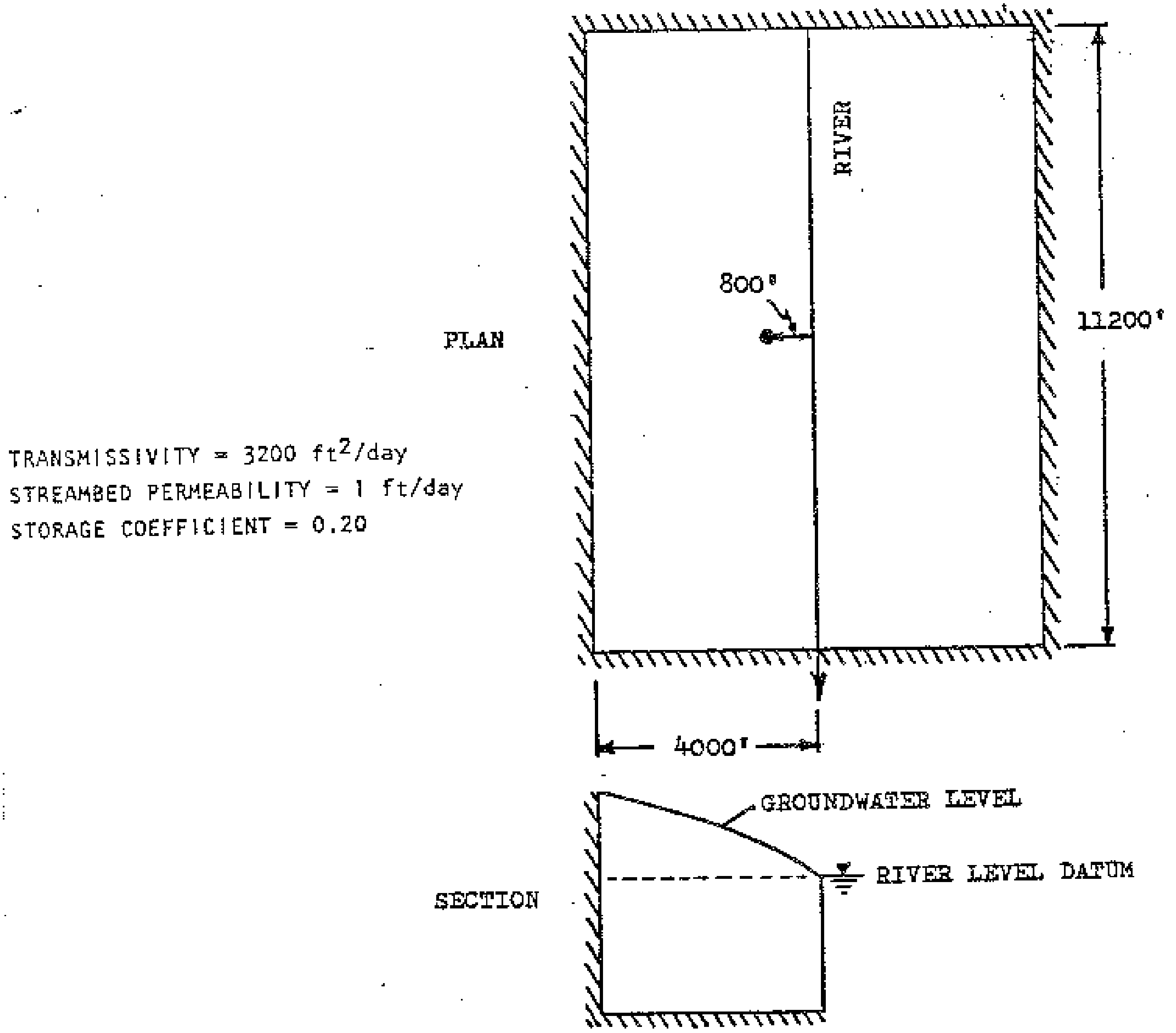

Figure 3.-- Idealized Two-dimensional Model.

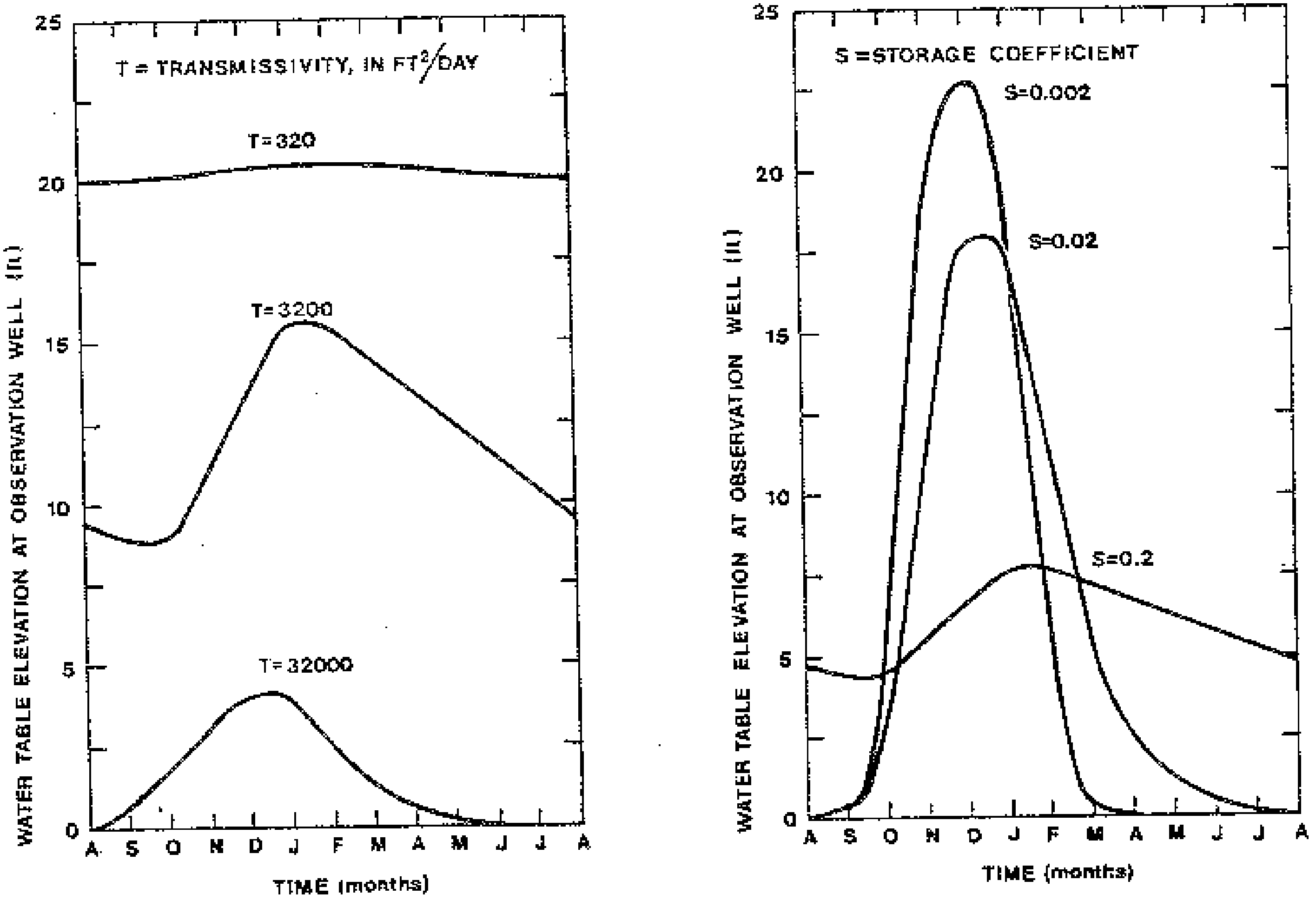

Figure 4 .-- Results of Sensitivity Analysis.

essentially in equilibrium with discharge balancing recharge. This condition could be considered representative of average aquifer conditions.

Figure 4 shown results of varying transmissivity and storage coefficient in the idealized two-dimensional model. Heads (water table elevation) are higher at any point in the aquifer as transmissivity is lowered, and the rate of aquifer discharge is greater at higher transmissivities. For storage coefficient, a higher storage coefficient mean slower rates of aquifer depletion.

DESIGN AND CONSTRUCTION OF THE CHIPUXET GROUND-WATER RESERVOIR MODELS

The first step in designing a model is to develop a conceptual model of the ground-water reservoir from available hydrologic information. Next decisions as to the actual area to be modeled are made. This will depend on several factors including the amount and quality of data available and the degree of detail desired. Figure 5 shows the area of the Chipuxet ground-water reservoir modeled, the mesh spacing, and the types of boundary conditions used. A constant mesh spacing of 400 feet was used mainly to take advantage of aerial photographs available at that scale. This scale is adequate for modeling, although, we have used variable mesh spacing in more recent digital models. With variable mesh spacing, areas of primary interest can be modeled with a finer mesh and areas of less interest with a coarser mesh. This may reduce computer storage requirements and execution time since less total nodes are generally involved. For the same number of nodes a more detailed water level picture

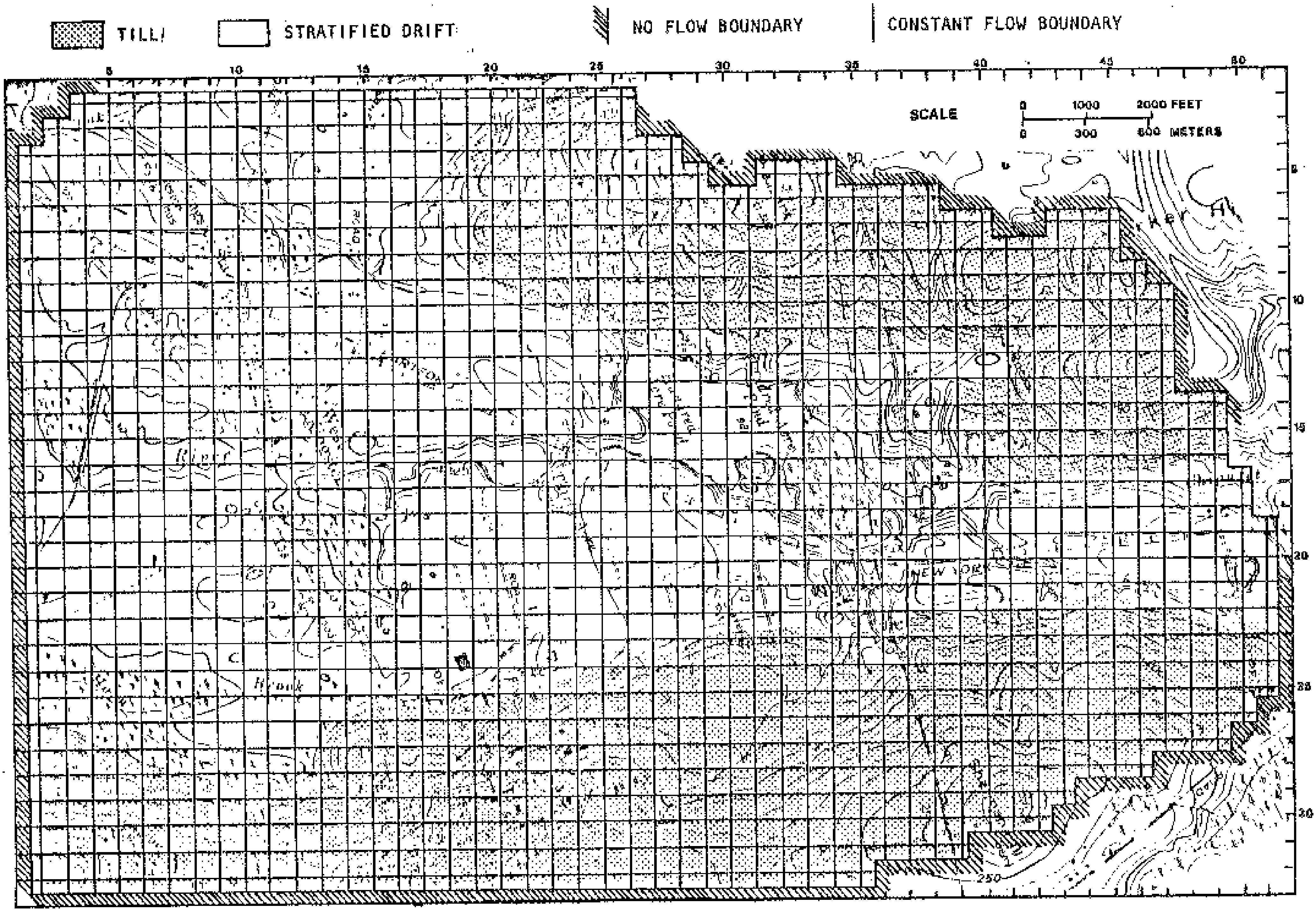

Figure 5.-- Finite Difference Grid and Boundary Conditions for Chipuxet Aquifer Model.

would be obtained in areas with a finer mesh. Unfortunately, with finite difference methods, mesh spacing may not be varied arbitrarily without introducing computational problems.

Initial values of transmissivity were estimated from saturated thicknesses and hydraulic conductivities given by Allen, et al. (1966). Transmissivities used in the digital model range from 135 ft.^{2}/day for till areas to 20,100 ft.^{2}/day for stratified-drift areas beneath and south of Thirty Acre Pond. In the analog model a transmissivity of 670 ft.^{2}/day was used in till areas, but proved to be too high. In the analog model the quantity affecting model performance is the rate of seepage from till areas which is proportional to the product of transmissivity and hydraulic gradient. In the analog model the final gradients determined in calibration are much smaller than those observed, compensating for the fact that the transmissivity used is higher than the probable value.

Streambed parameters were initially selected based on published data (Rosenshein et al. 1968; Gontnier et al., 1974). However, these estimates did not prove reasonable and it was necessary to resort to selection by trial and error. Leakage into or out of a stream is computed as

$$Q_S = K_S \left(\frac{h_s - h_a}{M_S}\right) A_S = \bar{K}(h_S - h_a) \qquad (15)$$

where Q_s is leakage h_s and h_a are heads in the stream and aquifer respectively, and A_s is the area of the streambed through which infiltration occurs. In reality it is impossible to separate the effects of hydraulic conductivity (K_s), area (A_s) and thickness (M_s) of the streambed which are effectively lumped together ($\bar{K}$). Also as indicated earlier, these parameters represent, in part, the increased head loss due to flow line convergence and anisotropy of the aquifer in the vicinity of the stream. Even heads in the aquifer are not well known beneath the streams. The absolute value of predicted water levels away from the stream are dependent on these streambed parameters which are not well defined physically. For example, depending on how flow-path dependent these parameters are, the values could change as a stream changes from gaining to losing in response to pumping.

For transient predictions a value of storage coefficient (specific yield) must be introduced (see equation 3). We used two values in the analog model .10 in till areas and .3 in stratified drift areas. In the digital model we used a value of .15 for both till and stratified drift. These values are based on values given by Allen et al. The storage coefficients affect transient simulations in several ways. First, when a well is pumped the volume of aquifer dewatered will be larger and the cone of pumping influence will expand faster for a lower storage coefficient. Second water levels and streamflows will decrease faster for a lower storage coefficient if all other factors remain constant.

Underflows are flows entering or leaving the modeled area as ground-water flow. Initial estimates of these quantities were made using the transmissivities used in the model and the hydrogeologic map given by Allen, et al (1960). Most underflow enters the model along its western boundary; this underflow was initially estimated to be about 460,000 gal/day which was reduced to 350,000 gal/day during calibration of the analog model.

MODEL CALIBRATION

Models were calibrated in the steady-state mode by matching the observed water table map from late summer 1959 (Allen, et al., 1966) and miscellaneous streamflow data.

The analog model was not equipped with an accretion (recharge) network; instead boundary conditions consisted of heads interpolated from water-level data along boundaries in the till areas and along streams, and estimated underflows. Initial simulations reproduced the general shape of the water table but absolute values of heads were too low. Heads were increased primarily by increasing streambed resistances and lowering boundary heads in the till area.

The different boundary conditions used in the analog and digital models required slightly different transmissivity distributions to calibrate them. However both these transmissivity distributions and the different boundary conditions led to essentially the same trial and error values for streambed hydraulic conductivities. Therefore, a discussion of the influence of the different boundary conditions on calibration will not be included. Geisser (1975) obtained a reasonably good water table match by trial and error adjustment of streambed resistors alone.

After a satisfactory water table match was obtained for the analog model, streambed hydraulic conductivities in the digital model were set equal to those obtained in the analog calibration.

In the digital model, steady-state calibration was slightly different since a uniform recharge rate was applied over the entire model. Except for till areas, streambed properties and transmissivities in the two models are essentially the same. Boundary conditions in the digital model are either constant flow (underflows) or no flow and constant head along the stream. Again the late summer 1959 water-table map and miscellaneous streamflow data were used for calibration. The final underflows in the digital model were determined to be 1,450,000 gpd versus 300,000 gpd in the analog model. This difference is significant and is the major difference between the two models. Geisser did not discuss it suggesting that the differences in underflows were small. Possible reasons for this difference will be discussed below.

Figure 6 shows the predicted and observed water table. Agreement is fair and could be improved by varying transmissivities and steady-state accretions. However, because of the limited water-table data available, further adjustment of transmissivities and accretions was not warranted.

Several points need clarification since they probably contribute, in part, to some of the discrepancies between measured and modeled water levels. White Horn Brook which appears to be a gaining stream when ground-water levels are high and a losing stream when water levels are low was not included in either model. Chickasheen Brook which appears from the water-table map (Allen, _et al._, 1966) to be a losing stream, at least as it crosses part of the aquifer in West Kingston, was also not included. With reliable measurements of stream flow loss along the Chickasheen Brook, an estimate of the recharge from this stream to the aquifer could be made and entered in the model.

The underflow along the western model boundary may include part of this recharge. Differences between measured and modeled water tables in the West Kingston area could then be due to the fact that recharge has been input to the modeled area as underflow but

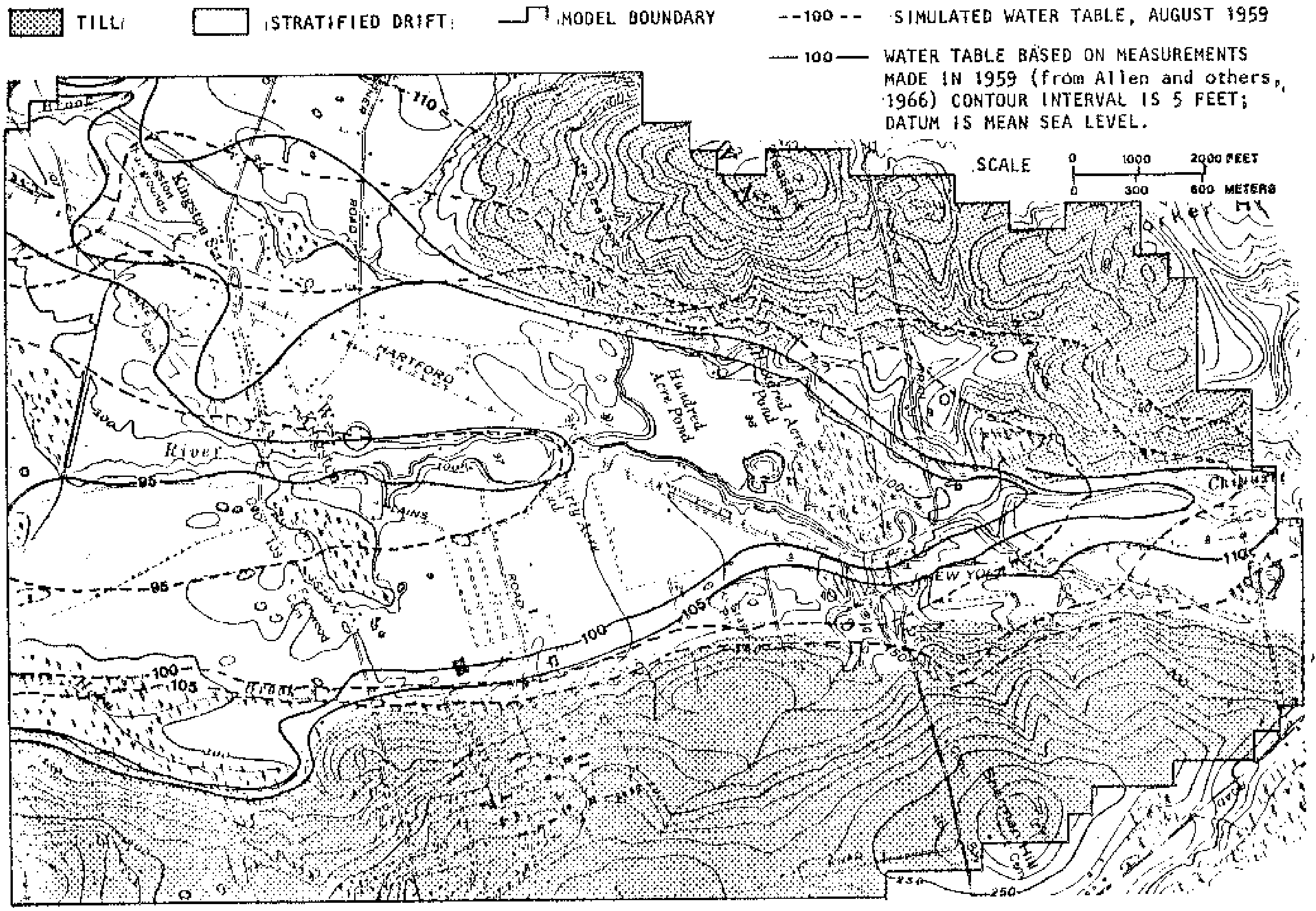

Figure 6.-- Comparison of Observed and Predicted Water Table Map

actually enters the aquifer as stream infiltration. Additional flow data and modeling would be necessary to resolve these questions. Sensitivity testing could be done to determine how sensitive model predictions are to these differences.

An additional check of model performance was to look at the variation of baseflow with accretion rate. To match the steady-state water table, underflows and accretions can be varied recognizing that the accretion rate is related to baseflow or ground-water runoff for a declining water table. Figure 7 shows the variation of predicted water level in the vicinity of SNW6 with accretion rate (solid line) and some average monthly baseflow rates with the corresponding average monthly water table altitudes. Here the steady-state simulation represents an average declining water table condition. Ground water baseflows are those reported by Allen, _et_ _al_. for summer and fall 1959 and the corresponding water levels are those reported by Allen, _et_ _al_. Additional runoffs were determined by Zeneski (1975) for the 1974 water year.

The models could be modified to improve the match between predicted and observed values. However, the parameters used in the models were based on the best data available and if the values of interest (heads) are relatively insensitive to minor changes in these parameters, little improvement in model performance would result from further parameter adjustment.

Figure 8 shows the variation of predicted water table altitude at SNW 6 for different ratios of the transmissivities used in the digital model. Variations of 20% have only a minor effect on water levels (less than .2 ft.). Figure 9 shows the variation of water level at SNW6 with model streambed hydraulic conductivity. Water

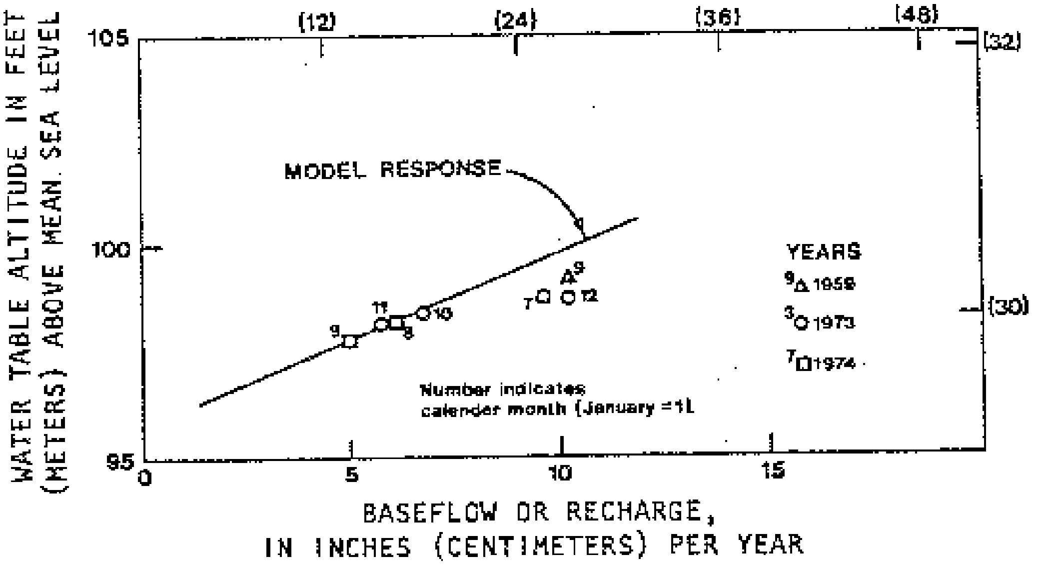

Figure 7.-- Modeled Ground Water Runoff versus Water Level SNW 6.

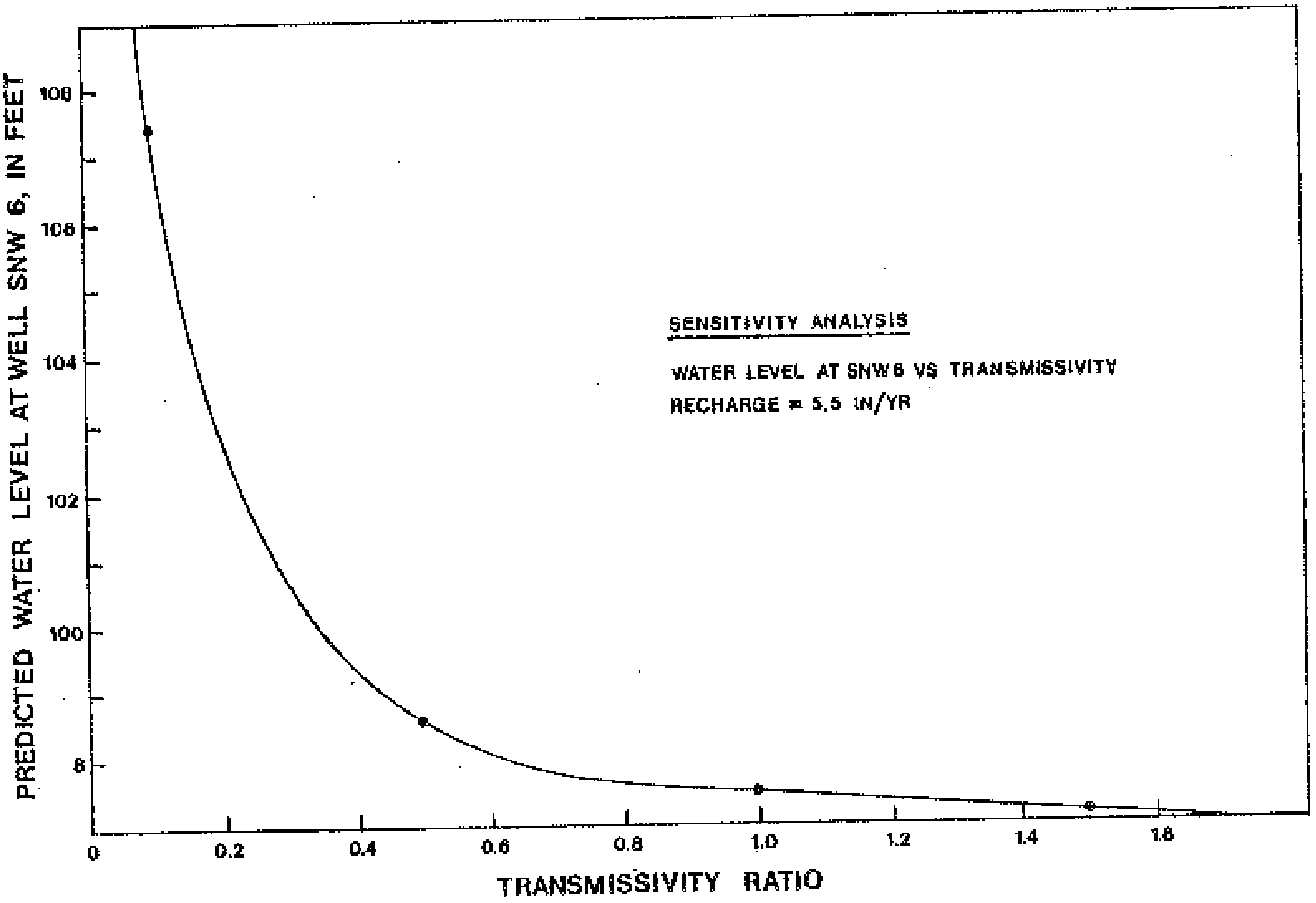

Figure 8.-- Sensitivity of Chipuxet Model to Variations In Transmissivity.

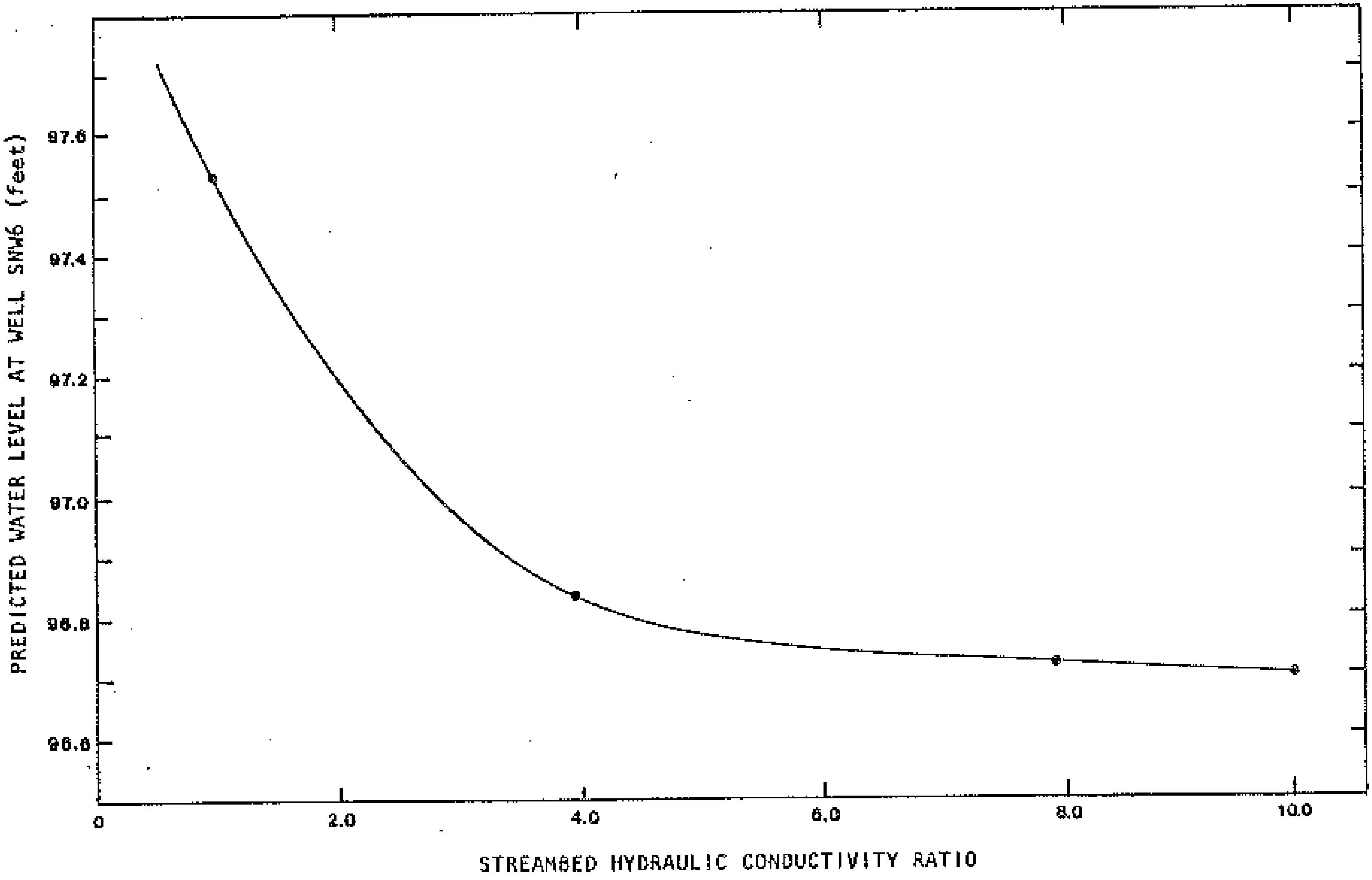

Figure 9.-- Sensitivity of Chipuxet Model to Variations in Streambed Hydaulic Conductivity.

levels are about as sensitive to streambed hydraulic conductivities as to aquifer transmissivities.

Finally, we may look at the streambed properties. These were determined by trial and error and because they are derived quantities and cannot be measured directly they need further discussion. In the models, streams are modeled as aquitards of limited areal extent. Kukenberger (1975) analyzed data from a pumping test at Thirty Acre Pond as a leaky confined aquifer and determined a transmissivity of 26,700 ft.^{2}/day and a leakance (Ks/Ms) of .11 gpd/ft^3. In the vicinity of Thirty Acre Pond these values may be compared with the leakance used in the models by Geisser since these are full 400 by 400 foot nodes. Values of model leakance are .62 gpd/ft^3 with a corresponding transmissivity of 20,100 ft.^{2}/day. These values are for practical purposes equivalent; for example, at a pumping rate of 650 gpm, steady-state drawdown 150 ft. from the pumping well would be about 1.6 ft. for the higher T, and 1.5 ft. for the lower T. This difference is insignificant when it is noted that Geisser calibrated steady-state behavior against a water-table map contoured in five foot intervals.

Very little transient calibration has been done since stresses imposed on the aquifer have so far been slight. One opportunity for which limited data is available is the pumping which occurred during dewatering for the sewage pumping station along White Horn Brook just south of Rte. 138 (Figure 6). Accurate records of pumpage are not available and as already noted White Horn Brook was not included in the model.

Dewatering started in April, 1976 and was crudely estimated to average 3 mgd. Dewatering continued at this rate for four months.

Predictions were made with the digital model using a uniform specific yield of .15. These predictions indicated only a light drop in water level at well SNW6 and very little drawdown was observed. Perhaps of more interest would be depleted streamflows which would lag dewatering by several months. Additional interpretation would be necessary to see if this effect could be separated from available streamflow and water level records.

Comparisons were made between the analog and digital models by comparing drawdowns due to pumping for several hypothetical schemes. Agreement was excellent.

MODEL SIMULATION OF PUMPING SCHEMES

Five pumping schemes have been proposed by the Rhode Island Water Resources Board for the Chipuxet ground-water reservoir. Proposed schemes I through V are summarized in table 2; the locations of existing and proposed pumping centers are shown in figure 10. To test these proposed pumping schemes two types of simulations were done: steady-state simulation and transient simulation. All simulation results reported, herein, were obtained with the digital model.

Steady-state simulations of low-flow conditions are the basis for comparing pumping schemes at this time. Under nonpumping conditions, the water table is falling and stream flow decreasing during late summer and fall. Therefore, on a monthly basis the water table may be assumed to be in steady-state equilibrium. With pumping the water table is assumed to reach a new equilibrium with average pumping rates. Under pumping conditions some water that

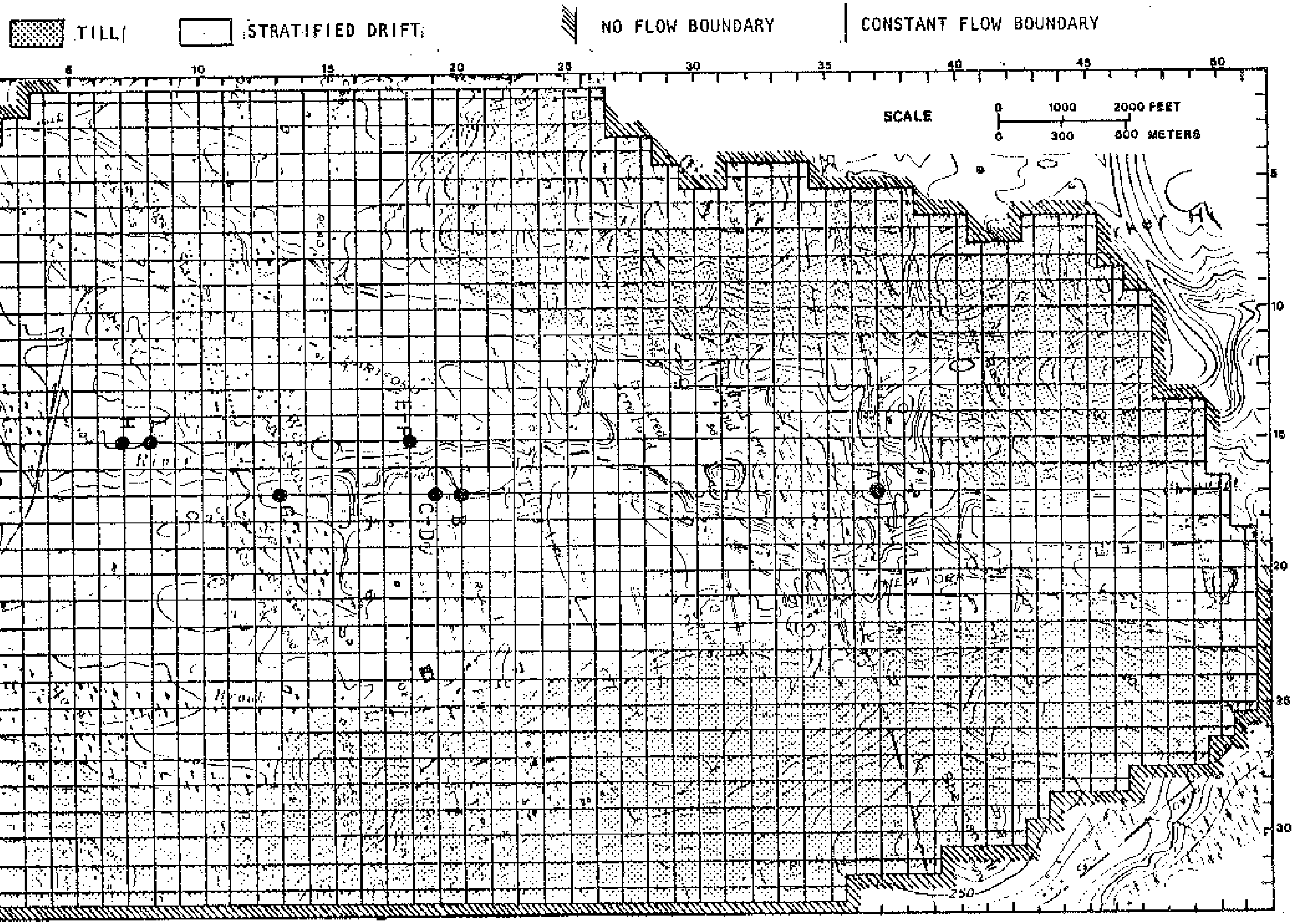

Figure 10.-- Location of Pumping Centers

would have become streamflow is diverted to wells, some streamflow is infiltrated, and the equilibrium water table is generally lower than under nonpumping conditions.

Figures 11 and 12 show the predicted steady-state water table for proposed pumping schemes I and V. Figure 13 shows how the predicted stream pickup would vary under steady state conditions for these two proposed pumping schemes.

Results from pumping schemes II, III and IV fall between Scheme V, which concentrates the pumping at Thirty Acre Pond, and Scheme I, which spreads the pumping througrout the basin. Scheme V would result in the greatest absolute lowering of the water table; it would also significantly modify flow patterns and induce large amounts of stream and pond infiltration in the Thirty Acre Pond Area. Figure 13 indicates that there would be little or no flow in the stream between 30 Acre Pond and the gage at Route 138 for Scheme V. Scheme I on the other hand, would result in less ground water lowering over a larger area, would not significantly modify existing ground water flow patterns and would involve more ground water interception and less induced infiltration.

Transient 180-day simulations were run under conditions similar to those used by Allen, _et al._ for an image well model. Simulation conditions were as follows:

1) the water table was assumed flat and equal to the stream elevation; 2) specific yield was assumed constant and equal to .15; and 3) there was no underflow - boundaries where underflow does occur were assumed to be no-flow boundaries.

Under these conditions there is no flow before pumping starts. Wells were pumped at the average rates shown in table 2. The

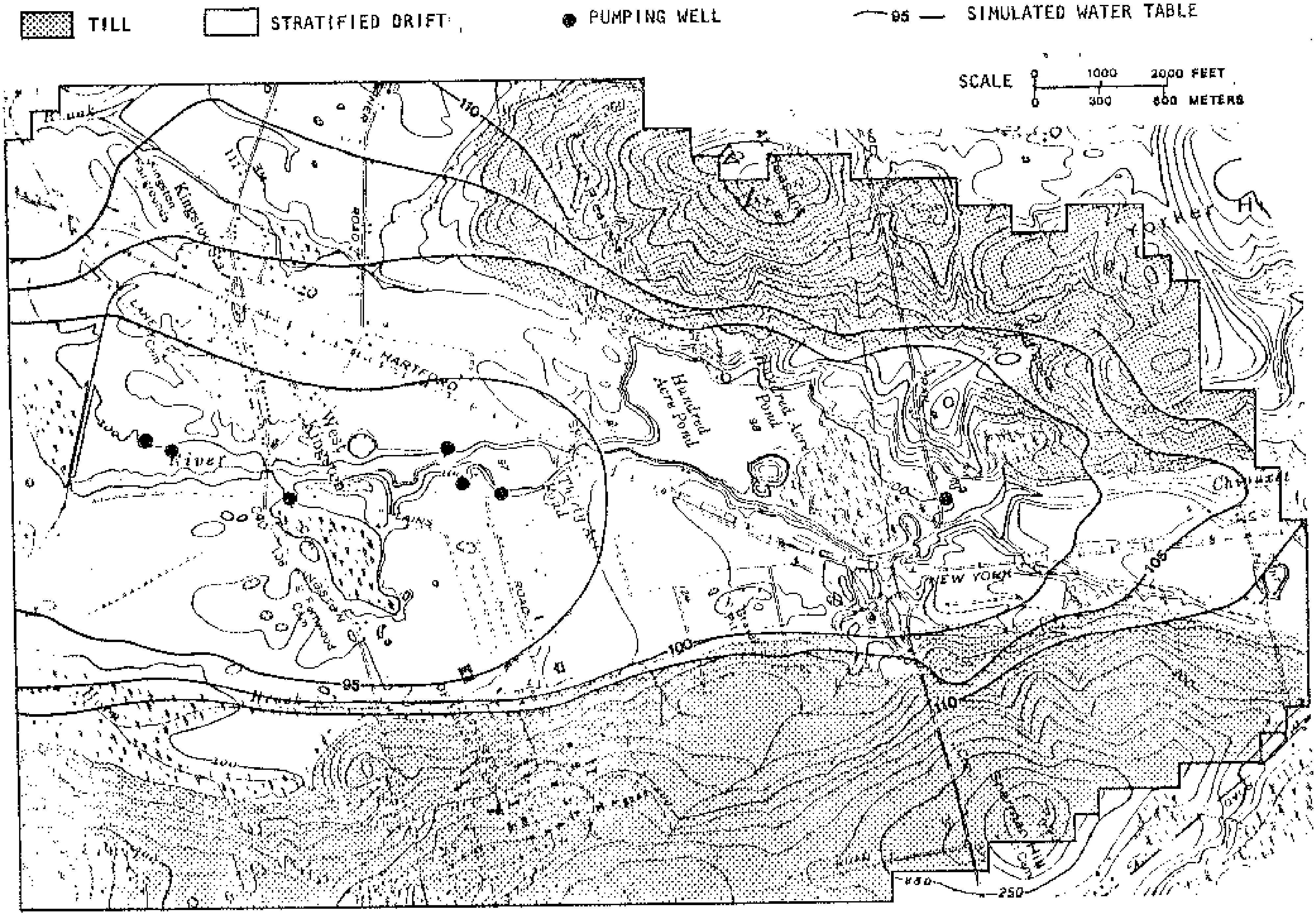

Figure 13.-- Predicted Steady-state Water Table with Proposed Scheme 1.

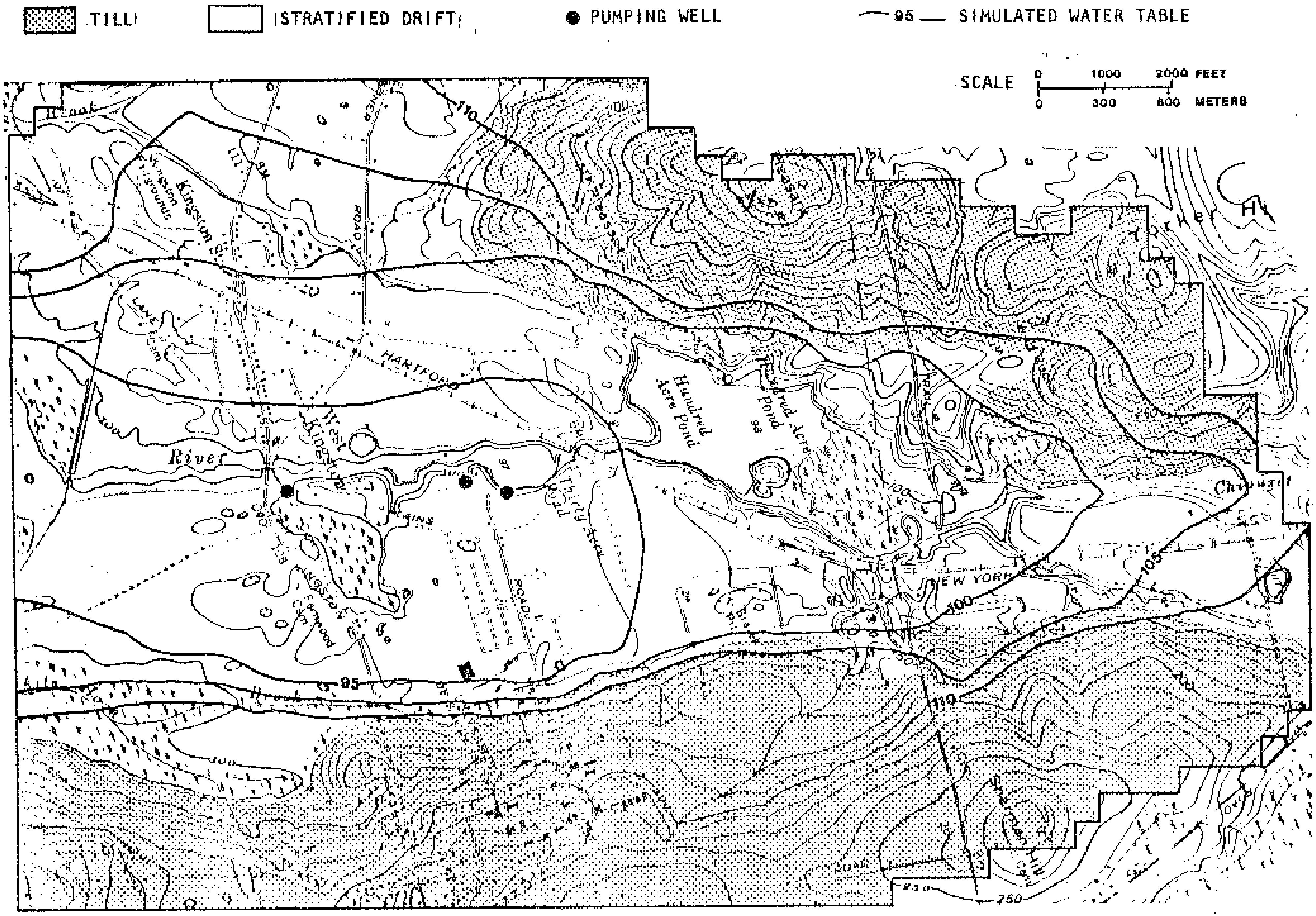

Figure 12.--Predicted Steady-state Water Table with Proposed Scheme V.

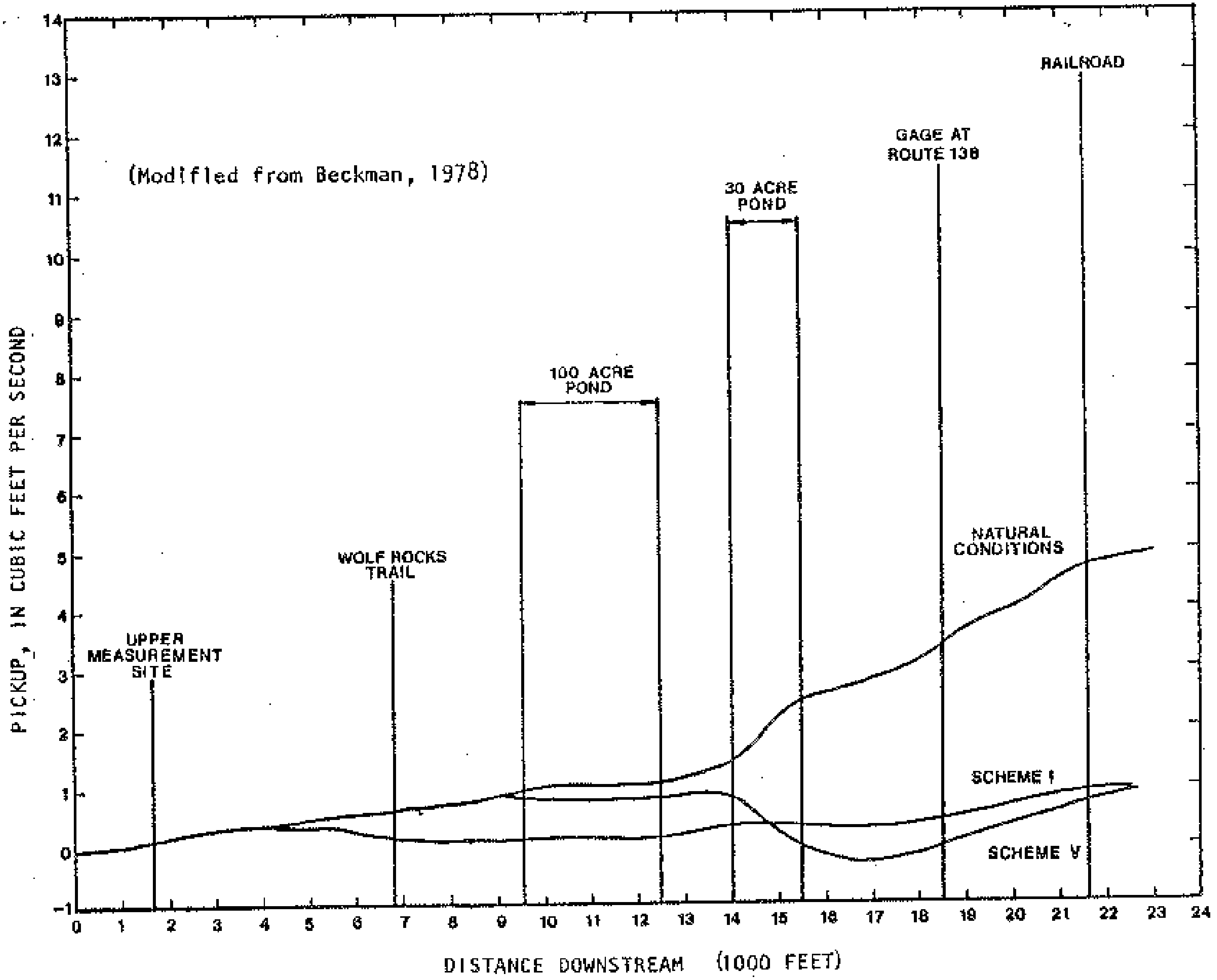

Figure 13.-- Stream Pickup for Natural Conditions and with Proposed Schemes I and V.

maximum predicted drawdowns at each pumping center after 180 days for each scheme are tabulated in table 3.

The sixth pumping scheme in table 2 is not proposed by the RIWRB; instead it is designed to test the higher withdrawal rates estimated by Allen et al. Results tabulated in table 3 show that even for pumping at these rates drawdowns are not excessive.

This type of transient simulation yields results comparable to image well models but allows a more accurate representation of the aquifer including the actual location of wells, varying transmissivities, storage coefficients and boundary conditions (heads, changes in stream infiltration) during a simulation period. These simulations accurately predict short term pumping effects. During a growing system the amount of induced infiltration and aquifer drawdowns increase and these changes can be predicted with this type of transient simulation. The absolute values of streamflow and water levels would depend on the initial conditions which are the conditions at the start of the growing season. A complicating factor is that streamflows and water levels decline naturally during the growing system and these changes as well as changes due to pumping would have to be accounted for in predicting actual late season conditions. Although this can be done, it involves a great deal of judgement.

More realistic transient modeling would involve simulating monthly or weekly water levels with and without pumping. With this type of modeling, conditions at the beginning of the growing season, the effects of pumping and seasonally declining water tables are accounted for in model predictions. Beckman (1978) modified Trescott's (1972) computer program so that monthly water levels could be simulated. Beckman's modifications were primarily to the input and output portions of the program. Beckman also did transient simulations on proposed Schemes I and V on a monthly basis. The resulting simulated water-table altitudes at observation well SNW6 are shown in figure 14. Also shown in figure 14 for comparison are the observed end-of-month water table altitudes at SNW6 for the 1959 water year (Allen et al, 1963). The model simulates only part of the ground water component of the hydrologic cycle so that on an annual basis, stream pick-up in the modeled area must equal aquifer recharge. Beckman used a recharge rate of approximately 14 inches/year which is representative of conditions occurring about once every ten years. Actually, these results are more representative of two successive years with a recharge rate of 14 in/year. It should be noted that Beckman found it necessary to increase some streambed leakances by a factor of two over those determined by Geisser.

Figure 15 compares results of stream pickup between transient simulations and steady-state simulation for pumping scheme I. This comparison suggests that the steady-state analysis is conservative. However, it should be noted that what is simulated with the transient model are average monthly baseflows and daily low flows will be considerably below monthly averages.

Results from continuous transient simulations confirm that for continuous withdrawals at constant rates, an equilibrium condition will be achieved in the aquifer where the reduction in streamflow will be approximately equal to the withdrawal rate. Figure 16 shows this comparison of nonpumping conditions with pumping conditions under the proposed pumping schemes I and V.

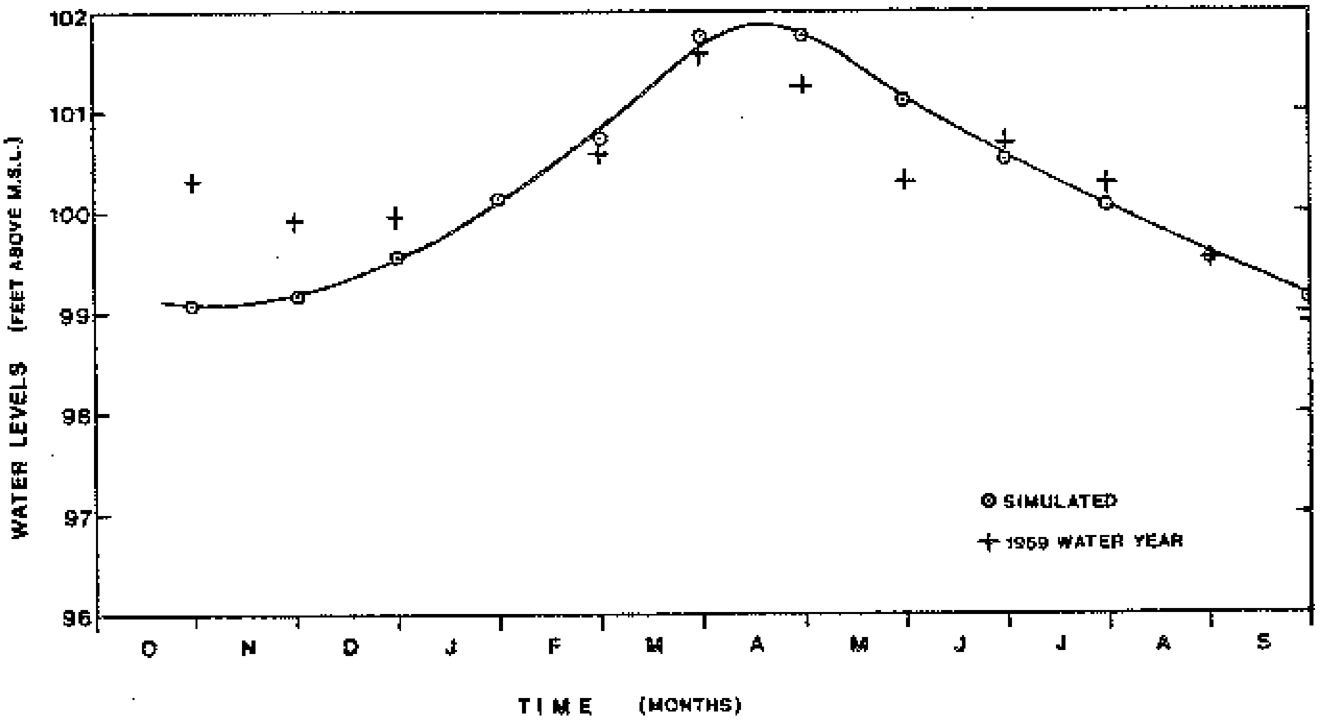

Figure 14-- Simulated and Observed Water Levels at Well SNW 6.

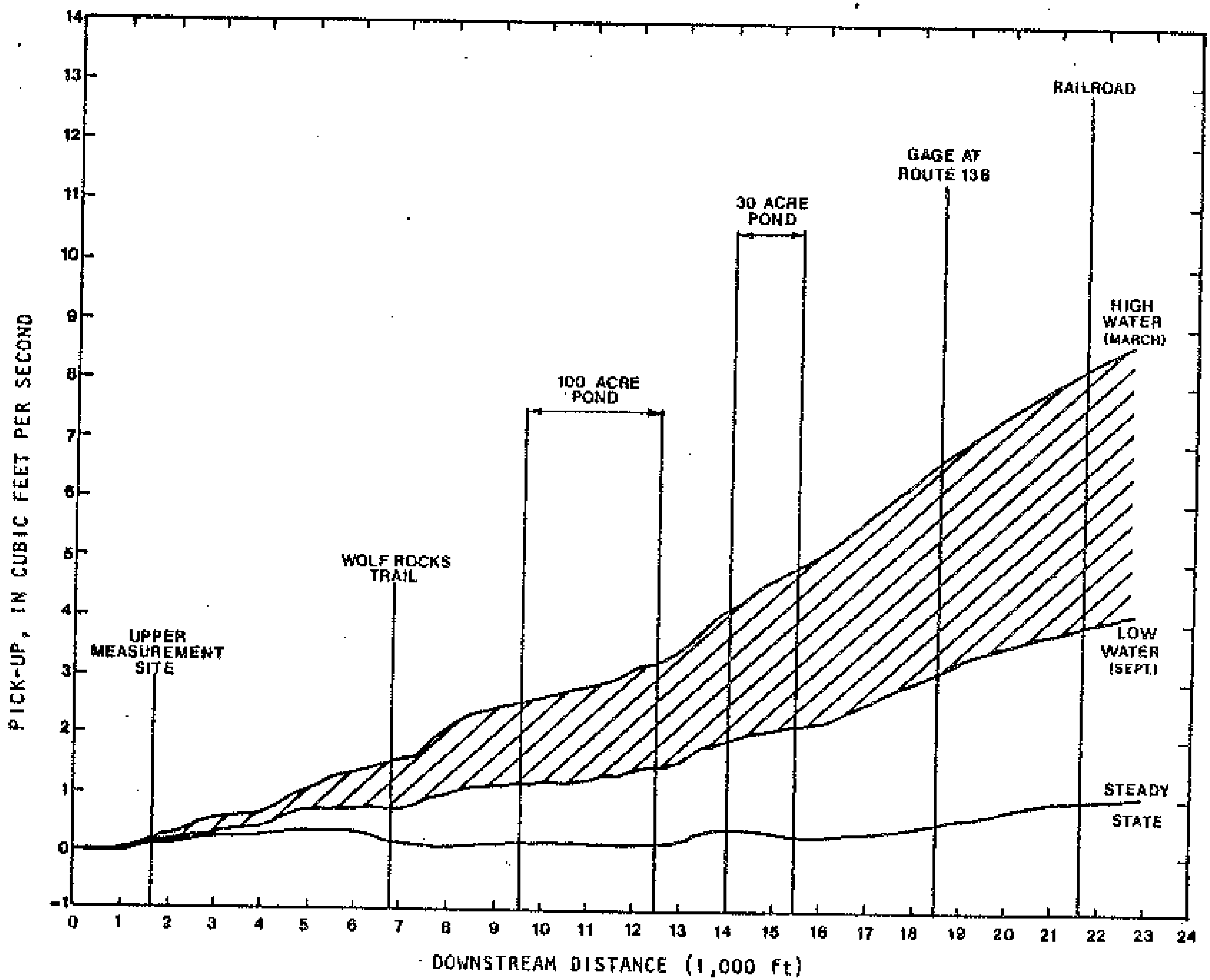

Figure 15.-- Comparison of Steady-state and Transient Simulations.

Table 2 - Average rates of continuous pumping used in transient 180-day simulation for proposed schemes

			Pumping Scheme					
Location	Well Site	Node^2	I	II	III	IV	V	VI
Wolf Rocks	A	(17,37)	.5	.75	-	-	-	1.5
Thirty Acre Pond	B	(17,20)	.5	.75	.75	1.0	1.0	1.0
	C-D	(17,19)	.5	.5	.75	1.0	1.75	2.5
	E-F	(15,18)	.5	-	.5	-	-	1.0
Kingston Fire District	G	(17,13)	.25	.25	.25	.25	.25	.5
Liberty Lane	I	(15, 8)	.35	.35	.35	.35	-	.8
	H	(15, 7)	.4	.4	.4	.4	-	.7
TOTAL (mgd)			3.0	3.0	3.0	3.0	3.0	8.0

1) See Figure 10 for well location.
2) See Figure 5 for node location.

Table 3 - Drawdowns for proposed pumping schemes after 180-day simulation with continuous pumping

Location	Well Site[1]	Node[2] (Row, Column)	Pumping Scheme I	II	III	IV	V	VI
			Drawdown[3] in Feet					
Wolf Rocks	A	(17,37)	6.56	9.88	-	-	-	19.69
Thirty Acre Pond	B	(17,20)	5.53	7.64	8.19	10.53	11.43	13.06
	C-D	(17,19)	6.12	6.11	8.98	11.16	18.78	27.27
	E-F	(15,18)	2.67	-	5.40	0	0	11.36
Kingston Fire District	G	(17,13)	2.81	2.71	2.93	2.87	2.72	5.97
Liberty Lane	H	(15, 8)	4.05	4.0	4.09	4.05	-	8.90
	I	(15, 7)	4.40	4.36	4.43	4.40	-	8.14

1) See Figure 10 for well location. Well radius assumed equal to 1/2 foot.
2) See Figure 5 for node location.
3) Drawdown not connected for dewatering, partial penetration, or well loss.

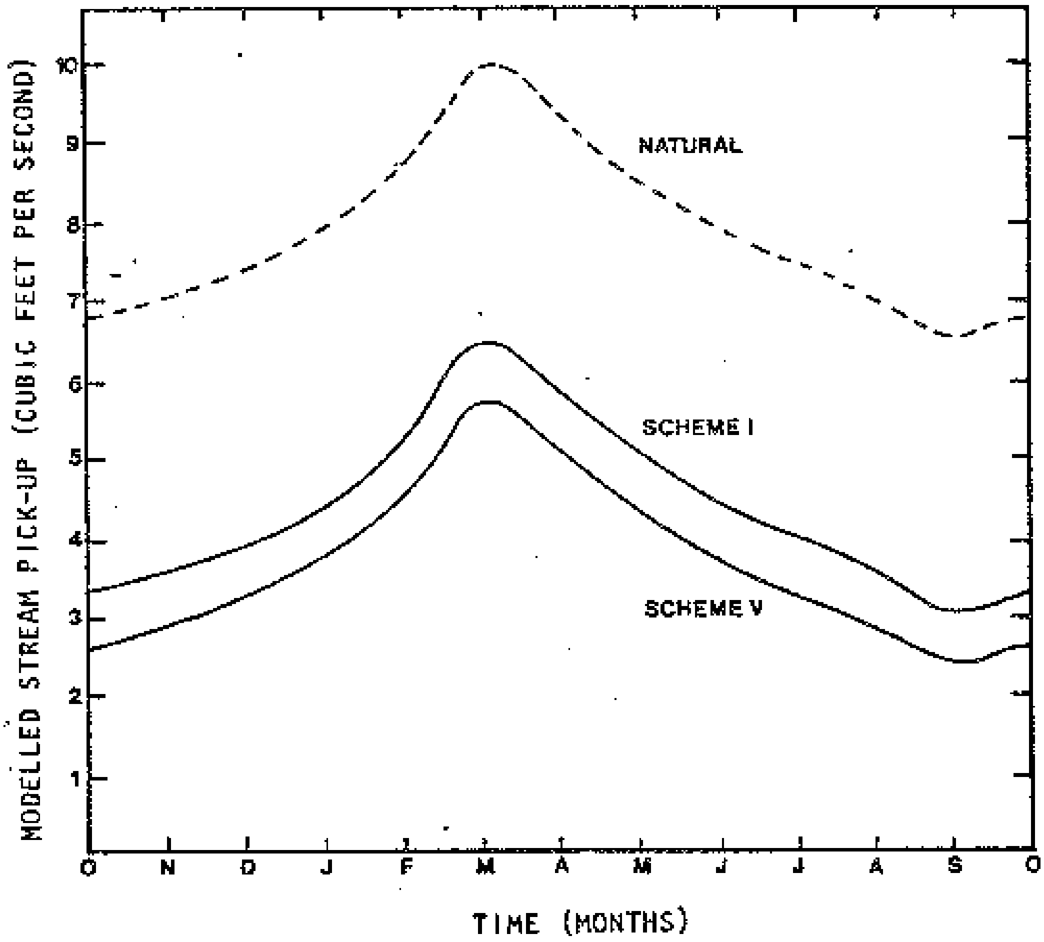

Figure 16.-- Comparison of Natural Conditions and Conditions with Proposed Pumping Schemes.

Conclusions

Results from analysis of the Chipuxet Ground-Water Reservoir with digital and analog computer models indicate that flow in the Chipuxet river will be reduced by an amount approximately equal to the average withdrawal rate and that groundwater levels will be lowered from less than 1 foot near the river to as much as 3-4 feet at points most distance from the stream.

All of the modeled pumping schemes have essentially the same effect on streamflow - a reduction in streamflow of approximately 3 mgd. Under field conditions there will probably be some reduction in evapotranspiration so that the actual reduction in streamflows are expected to be less than 3 mgd. A small difference in the effects on total flow at the gaging station between Schemes I and V will occur because planned withdrawals of .75 mgd at the Liberty Lane site would have little or no effect at the West Kingston gaging station. Scheme V would reduce flow at the gaging station by that additional amount.

Schemes that spread pumping out are able to derive more of their yield from ground-water runoff rather than induced infiltration. This means that ground-water moves directly to wells rather than moving into the stream and then to wells as induced infiltration. The percentage of induced infiltration will increase as the rate of ground-water runoff decreases. For scheme V during periods of low ground-water runoff, approximately 30 percent of the water would be infiltrated from the Chipuxet River in the Thirty Acre Pond area.

Because of the generally high transmissivity of the aquifer and the location of pumping wells near streams, drawdowns are relatively small. Even for scheme V drawdowns are not excessive. In a water emergency, the storage capacity of the aquifer could be utilized and the full yield of the aquifer, estimated by Allen et al (1966) to be more than 8.6 mgd, could be utilized. Withdrawals of this amount for short periods of time, half a year or less, would have little carry over effect on streamflow.

Further refinements in the model should be made as the sustained yield of the reservoir is more fully developed. Although the best available data and modeling techniques were used in this study, additional data has become available and modeling techniques are continually improving.

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APPENDIX A

Data Input for Steady-State Model

```
  TRANSIENT ANAYSIS OF THE CHIPUXET AQUIFER

PROBLEM OPTIONS:  ARTESIAN    LEAKAGE                                    CHECK                        NUMERIC     HEAD

ON ALPHAMERIC MAP:
 BASIC LENGTH UNIT IS MULTIPLIED BY        1.00 TO GET FEET
  NUMBER OF MAP UNITS PER INCH =   1000.00
 CONTOUR INTERVAL =        1.00

NUMBER OF PUMPING PERIODS =     1

NUMBER OF NODES IN COLUMN =    33

NUMBER OF NODES IN ROW =       51

PRINTOUT EVERY  100 STEPS

ERROR CRITERIA FOR CLOSURE =  0.9999999E-03

CONSTANT RECHARGE RATE(L/T) =  0.1586000E-07

SPECIFIC STORAGE OF CONFINING BED =  0.0

MAXIMUM PERMITTED NUMBER OF ITERATIONS =        100

TERMINATION OF COMPUTATION WHEN MAX(PHI(T)-PHI(T-1)) )  0.1000000D-02

EVAPOTRANSPIRATION RATE =  0.0

EFFECTIVE DEPTH OF ET =  0.0

PARAMETER MATRICES WERE ASSIGNED THE FOLLOWING INITIAL VALUES *

STRT =      140.00
S =       0.0
SY =      0.020000
RATE =  0.9999999E-10
RIVER =       -1.00
M =            1.00
T =     0.1540000E-03
PERM =  0.0
BOTTOM =       0.0
TOP =        92.00
LAND =      100.00
DELX =      400.00
DELY =      400.00

* THESE VALUES WERE REPLACED BY VARIABLE DATA IN ANY MATRICES PRINTED OUT IN FULL BELOW
```

RATE MATRIX

```
 1  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

 2  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

 3  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

 4  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

 5  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
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    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

 6  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
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    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

 7  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

 8  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

 9  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0



    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

10  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

11  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
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    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

12  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
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    0.0          0.0          0.0          0.0          0.967E-07    0.484E-07    0.484E-07    0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

13  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.967E-07    0.484E-07    0.967E-07    0.967E-07    0.484E-07    0.967E-0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

14  0.0          0.800E-06    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.967E-07    0.484E-07    0.484E-07    0.484E-07    0.484E-0
    0.242E-06    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

15  0.0          0.800E-06    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.967E-06    0.967E-06    0.484E-07    0.967E-07    0.484E-07    0.484E-07    0.484E-07    0.484E-0
    0.484E-07    0.242E-06    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

16  0.0          0.0          0.800E-06    0.800E-06    0.800E-06    0.800E-06    0.967E-06    0.967E-06    0.967E-06    0.967E-0
    0.967E-06    0.967E-06    0.967E-06    0.967E-06    0.967E-06    0.0          0.967E-06    0.967E-06    0.967E-06    0.967E-0
    0.967E-06    0.967E-06    0.0          0.0          0.0          0.0          0.967E-07    0.484E-07    0.967E-07    0.0
    0.967E-07    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

17  0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0          0.0          0.0          0.0          0.0          0.967E-06    0.0          0.0          0.0          0.967E-0
    0.967E-06    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.967E-07    0.0
    0.967E-07    0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.800E-06    0.800E-0
    0.801E-06    0.242E-06    0.484E-07    0.484E-07    0.967E-07    0.242E-06    0.242E-06    0.242E-06    0.242E-06    0.0
    0.0
```

```
18  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.967E-06    0.967E-06    0.967E-06    0.967E-06    0.967E-06    0.967E-06    0.967E-06    0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

19  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

20  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

21  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

22  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

23  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

24  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

25  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

26  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0



    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

27  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

28  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

29  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

30  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

31  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

32  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0

33  0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0     0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0          0.0
    0.0
```

RIVER HEAD MATRIX

```
1     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
2     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
3     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
4     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
5     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
6     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
7     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
8     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
9     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0   97.0   98.0   98.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0   97.0   97.0   98.0   98.0   99.0   99.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0   94.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0   97.0   97.0   98.0   98.0   99.0   99.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0   94.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0   95.0   96.0   96.0   97.0   97.0   98.0   98.0   99.0   99.0   99.0    0.0    0.0    0.0    0.0    0.0    0.0

      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0   94.0   94.0   94.0   94.0   94.0   94.0   94.0   94.0   94.0   94.0   94.0   94.0   94.0    0.0   94.0   94.0
     94.0   95.0    0.0    0.0    0.0    0.0   97.0   97.0   99.0    0.0   99.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0   94.0    0.0    0.0
     95.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0   98.0    0.0   99.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
    100.0  100.0  101.0  101.0  102.0  103.0  104.0  105.0  106.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0   99.0   99.0   99.0   99.0  100.0  100.0  100.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
      0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
```

```
     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0

 1   0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0

 2   0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0

 3   0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
     0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
```

```
                                                        TRANSMISSIVITY MATRIX
 1   0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0

 2   0.0       0.0       0.0       0.00154   0.00154   0.00154   0.00154   0.00154   0.07700   0.07700   0.19250   0.19250
     0.19250   0.11550   0.11550   0.11550   0.11550   0.03850   0.03850   0.03850   0.00154   0.00154   0.00154   0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0

 3   0.0       0.0       0.00154   0.00154   0.00154   0.00154   0.00154   0.07700   0.07700   0.11550   0.23100   0.23100
     0.19250   0.11550   0.11550   0.11550   0.11550   0.03850   0.03850   0.03850   0.00154   0.00154   0.00154   0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0

 4   0.0       0.00154   0.03850   0.03850   0.00154   0.00154   0.03850   0.07700   0.11550   0.15400   0.23100   0.23100
     0.19250   0.11550   0.11550   0.11550   0.11550   0.03850   0.03850   0.00154   0.00154   0.00154   0.00154   0.00154
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0

 5   0.0       0.00154   0.00154   0.00154   0.00154   0.07700   0.07700   0.11550   0.11550   0.15400   0.23100   0.23100
     0.19250   0.11550   0.11550   0.11550   0.07700   0.03850   0.03850   0.00154   0.00154   0.00154   0.00154   0.00154
     0.0       0.0       0.00154   0.00154   0.00154   0.0       0.0       0.0       0.0       0.0       0.0       0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0

 6   0.0       0.00154   0.00154   0.00154   0.00154   0.07700   0.07700   0.11550   0.15400   0.15400   0.15400   0.15400
     0.19250   0.11550   0.11550   0.11550   0.03850   0.03850   0.03850   0.00154   0.00154   0.00154   0.00154   0.00154
     0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.0       0.0       0.0
     0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0

 7   0.0       0.00154   0.00154   0.00154   0.00154   0.00154   0.11550   0.15400   0.15400   0.15400   0.15400   0.15400
     0.19250   0.11550   0.11550   0.11550   0.07700   0.03850   0.03850   0.00154   0.00154   0.00154   0.00154   0.00154
     0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.0
     0.00154   0.00154   0.0       0.0       0.0       0.0       0.0       0.0       0.0

 8   0.0       0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.15400   0.15400   0.15400   0.15400   0.15400
     0.19250   0.19250   0.11550   0.11550   0.11550   0.03850   0.03850   0.00154   0.00154   0.00154   0.00154   0.00154
     0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154
     0.00154   0.00154   0.0       0.0       0.0       0.0       0.0       0.0       0.0

 9   0.0       0.00154   0.00154   0.00154   0.00154   0.01540   0.15400   0.15400   0.15400   0.15400   0.15400   0.15400
     0.19250   0.19250   0.19250   0.11550   0.11550   0.07700   0.03850   0.03850   0.00154   0.00154   0.00154   0.00154
     0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154
     0.00154   0.00154   0.00154   0.0       0.0       0.0       0.0       0.0       0.0

10   0.0       0.00154   0.00154   0.00154   0.01540   0.15400   0.15400   0.11550   0.11550   0.11550   0.11550   0.11550
     0.19250   0.19250   0.19250   0.19250   0.11550   0.11550   0.07700   0.03850   0.03850   0.03850   0.00154   0.00154
     0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154
     0.00154   0.00154   0.00154   0.00154   0.0       0.0       0.0       0.0       0.0

11   0.0       0.03850   0.01540   0.01540   0.15400   0.15400   0.15400   0.11550   0.11550   0.11550   0.11950   0.11550
     0.19250   0.19250   0.19250   0.19250   0.19250   0.11550   0.11550   0.11550   0.11550   0.03850   0.03850   0.00154
     0.03850   0.03850   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154   0.00154
     0.00154   0.00154   0.00154   0.00154   0.0       0.0       0.0       0.0       0.0

12   0.0       0.01540   0.01540   0.01540   0.15400   0.15400   0.15400   0.11550   0.19250   0.11550   0.11550   0.11550
     0.19250   0.19250   0.19250   0.19250   0.19250   0.19250   0.19250   0.11550   0.11550   0.11550   0.11550   0.11550
     0.07700   0.07700   0.03850   0.00154   0.00154   0.03850   0.03850   0.03850   0.03850   0.03850   0.03850   0.03850
```

```
     0.00154  0.00154  0.00154  0.00154  0.0      0.0      0.0      0.0      0.0
13   0.0      0.15400  0.15400  0.15400  0.23100  0.23100  0.23100  0.19250  0.19250  0.19250  0.19250  0.19250
     0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.19250  0.15400  0.15400  0.15400  0.11550  0.11550
     0.11550  0.11550  0.11550  0.11550  0.11550  0.07700  0.07700  0.03850  0.03850  0.03850  0.03850  0.03850
     0.00154  0.00154  0.00154  0.00154  0.0      0.0      0.0      0.0      0.0
14   0.0      0.15400  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100
     0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.15400  0.15400  0.15400  0.15400  0.15400
     0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.03850  0.03850  0.03850  0.03850
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0      0.0      0.0
15   0.0      0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100
     0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.19250  0.15400  0.15400  0.15400  0.15400  0.15400
     0.15400  0.15400  0.15400  0.15400  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.03850
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0      0.0      0.0
16   0.0      0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100
     0.23100  0.23100  0.23100  0.23100  0.23100  0.19250  0.19250  0.15400  0.15400  0.15400  0.15400  0.15400
     0.15400  0.15400  0.15400  0.15400  0.15400  0.15400  0.15400  0.15400  0.15400  0.11550  0.11550  0.11550
     0.00154  0.00154  0.01540  0.01540  0.01540  0.01540  0.0      0.0      0.0
17   0.0      0.19250  0.19250  0.19250  0.19250  0.19250  0.23100  0.23100  0.23100  0.23100  0.23100  0.23100
     0.23100  0.23100  0.19250  0.19250  0.19250  0.19250  0.19250  0.15400  0.15400  0.15400  0.15400  0.15400
     0.15400  0.15400  0.15400  0.15400  0.15400  0.15400  0.15400  0.15400  0.15400  0.15400  0.11550  0.11550
     0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.0      0.0
18   0.0      0.11550  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250
     0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.15400  0.15400  0.15400  0.15400  0.15400
     0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.15400  0.15400  0.15400  0.15400
     0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.0      0.0
19   0.0      0.11550  0.11550  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250
     0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.19250  0.11550  0.11550  0.11550  0.11550  0.11550
     0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.15400  0.15400
     0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.0
20   0.0      0.11550  0.11550  0.11550  0.19250  0.19250  0.19250  0.19250  0.11550  0.11550  0.11550  0.11550
     0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550
     0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.07700
     0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.0
21   0.0      0.01540  0.07700  0.07700  0.07700  0.07700  0.07700  0.11550  0.11550  0.11550  0.11550  0.11550
     0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.11550  0.07700  0.07700  0.07700
     0.07700  0.07700  0.07700  0.07700  0.03850  0.07700  0.11550  0.11550  0.11550  0.11550  0.07700  0.03850
     0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.01540  0.0
22   0.0      0.01540  0.01540  0.01540  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700
     0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700
     0.03850  0.03850  0.03850  0.03850  0.03850  0.03850  0.03850  0.11550  0.07700  0.03850  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0
23   0.0      0.01540  0.01540  0.01540  0.01540  0.01540  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700
     0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.03850  0.03850  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0
24   0.0      0.01540  0.01540  0.01540  0.01540  0.01540  0.00154  0.00154  0.00154  0.00154  0.07700  0.07700
     0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.07700  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.03850  0.00154  0.00154  0.00154


     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0
25   0.0      0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0
26   0.0      0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0      0.0
27   0.0      0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0      0.0      0.0
28   0.0      0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.0      0.0      0.0      0.0      0.0      0.0
29   0.0      0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
30   0.0      0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
31   0.0      0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0      0.0
     0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
32   0.0      0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.00154
     0.00154  0.00154  0.00154  0.00154  0.00154  0.00154  0.0      0.0      0.0      0.0      0.0      0.0
     0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
33   0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
     0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
     0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0
     0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0      0.0

S ITERATION PARAMETERS:   0.9490-03   0.5410-02   0.3080-01   0.1750 00   0.1000 01

ING PERIOD NO.  1:   180.00 DAYS.

 IN HOURS =     606.316
ER OF TIME STEPS =   1
```

```
MULTIPLIER FOR TIME STEP = [illegible]

                    33 WELLS

          I          J      PUMPING RATE

         17         37        -0.77
         18         20        -0.77
         17         19        -0.77
         15         16        -0.77
         17         13        -0.39
         14          7        -0.62
         14          8        -0.54
          2          5         0.01
          2          6         0.01
          2          7         0.01
          2          8         0.01
          2          9         0.01
          2         10         0.13
          2         11         0.10
          2         12         0.10
          2         13         0.10
          2         14         0.32
          2         15         0.32
          2         16         0.11
          2         17         0.11
          2         18         0.11
          2         19         0.11
          2         20         0.12
          2         21         0.12
          2         22         0.12
          2         23         0.12
          2         24         0.12
         15         49         0.01
         16         48         0.01
         17         49         0.01
         18         49         0.01
         19         50         0.02
         20         50         0.02

*****STEADY STATE AT TIME STEP    3*****


                                                   TIME STEP NUMBER=          3
                                          SIZE OF TIME STEP IN SECONDS=        7366734.00

                                                 TOTAL SIMULATION TIME IN SECONDS=       15551994.00
                                                                          MINUTES=        259199.75
                                                                            HOURS=          4320.00
                                                                             DAYS=           180.00
                                                                            YEARS=             0.49

                                         DURATION OF CURRENT PUMPING PERIOD IN DAYS=          180.00
                                                                            YEARS=             0.49

                                                ITERATION NUMBER=          0

S BALANCE:
  CUMULATIVE                            L**3
     SOURCES:
             STORAGE =                   0.0
            RECHARGE =           51983984.00
       CONSTANT FLUX =            3500I214.00
       CONSTANT HEAD =                   0.0
             LEAKAGE =          -14665611.00
       TOTAL SOURCES =           72219584.00
     DISCHARGES:
EVAPOTRANSPIRATION =                     0.0
      CONSTANT HEAD =                    0.0
    QUANTITY PUMPED =            72231169.00
          TOTAL OUT =            72231168.00

  TOTAL OUT-SOURCES =               11584.00
 PERCENT DIFFERENCE =                   0.02

 RATES FOR THIS TIME STEP               L**3/T
           RECHARGE =                   3.34
      CONSTANT FLUX =                   2.23
   CONSTANT HEAD IN =                   0.0
  CONSTANT HEAD OUT =                   0.0
            PUMPING =                   0.0
                 ET =                   4.64
           LEAKAGE=                     0.0
              TOTAL =                  -0.94
             STEADY =                -260.33
THIS TIME STEP, STORAGE =               0.0
MUM CHANGE IN HEAD FOR THIS TIME STEP =        0.000
M OF THE ABSOLUTE VALUE OF HEAD CHANGES FOR EACH ITERATION:
```

Report No. FHWA-RI-RD-80-01

A STUDY OF THE EFFECTS OF SALT STORAGE PRACTICES ON SURFACE AND GROUND WATER QUALITY IN RHODE ISLAND

DEPARTMENT OF TRANSPORTATION • UNITED STATES OF AMERICA

February 1981
Final Report

Prepared for
FEDERAL HIGHWAY ADMINISTRATION
Offices of Research & Development
Washington, D.C. 20590

FOREWORD

This report presents the results of a fifteen month long study on the effects of salt storage practices on surface and ground water quality. The study includes descriptions and conclusions from detailed investigations at four selected sites, as well as general information and recommendations for all State of Rhode Island salt storage sites. The information contained is of interest to all persons or groups concerned with the protection of water resources.

Grateful acknowledgement is made of the assistance and financial support of the Rhode Island Department of Transportation and the Federal Highway Administration. Recognition is also due the College of Engineering for making space and testing facilities available for this work. During the research a number of individuals contributed in various ways. Especially helpful were representatives from the Planning and Maintenance Divisions of the Rhode Island Department of Transportation. Of the students and others in the College of Engineering who assisted, special note is made of Milton T. Huston, Research Associate, and John W. Grace, Graduate Student, who contributed to most phases of the project.

General distribution of this report is being made by the Rhode Island Department of Transportation. It is available to the public through the National Technical Information Service.

Daniel W. Urish	William E Kelly
Daniel W. Urish	William E. Kelly

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16. Abstract

The results of a fifteen month study of the effects of salt storage practice indicate significant increases in sodium and chloride are occurring in adjacent ground and surface water resources. Based on detailed monitoring of four sites, ground water is most severely impacted due to its limited dilution capacity. Data on sodium, chlorides, and specific conductance are used to quantify the impacts. The long-term solution is to eliminate or minimize salt runoff by utilizing permanent covered storage at all sites. Recommendations are made to improve surface drainage, to divert runoff away from sensitive areas, and to upgrade existing brine tank storage facilities.

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Definition of Terms

Aquifer - area containing saturated permeable material through which ground water moves and which is capable of yielding significant quantities of water to wells; also called groundwater reservoir.

Dispersion - the spreading out of a pollutant as it moves through an aquifer.

Dissolved Solids - salts, generally inorganic, which have been dissolved by the water and are now in solution.

Drainage Area of Stream at Specified Location - area measured in a horizontal plan and enclosed by a topographic divide from which direct surface runoff from precipitation normally drains by gravity into the stream above the specified point.

Ground Water Gradient - the rate of change of fluid pressure per unit distance in the direction of decreasing of pressure, and is the driving force of fluid flow in a porous medium.

Land-Surface Datum - a datum plane that is approximately at land surface at each ground water observation well.

Measuring Point - a reference point from which the distance to the water surface in a well is measured to obtain the water level.

Mineralized Water - water containing above normal content of dissolved solids.

Permeability - the capacity of rocks or soil to transmit water.

Plume - a zone of mineralized water.

Pollution - a change in the chemical quality of water, as a result of the activities of man, that adversely affects such water for water supply.

Specific Conductance - measures the ability of water to conduct an electric current and is a convenient way of checking the approximate amount of dissolved solids of a water solution.

<u>Stratified Drift</u> - well-sorted and layered deposits of gravel, sand, silt, and clay deposited by water from melting glacial ice having generally a high permeability and a low cation-exchange capacity.

<u>Till</u> - poorly-sorted unstratified mixture of gravel, sand, silt, and clay, carried or deposited by a glacier, and generally with a low permeability; it may have significant cation-exchange capacity.

<u>Water Table</u> - the upper surface of the zone of saturation, except where the surface is formed by an impermeable body.

<u>Zone of Aeration</u> - the zone between the land surface and the water table.

<u>Zone of Saturation</u> - the zone in which the functional permeable rocks are saturated with water under hydrostatic pressure.

Introduction

There have been a number of cases in New England where salt has moved from storage areas into the ground water causing pollution of wells (12). In some instances, salt has moved several thousand feet and affected wells 100 feet deep, and in a few cases wells 400 feet deep have been affected. According to Miller, et al. (12)

> "Most of the deeper wells tap crystalline rocks, which are particularly susceptible to relatively rapid movements of the pollutant through fracture zones and bedding planes with little chance for dispersion and dilution."

In Rhode Island there have been a number of cases of probable and possible pollution of wells from salt storage sites but they are not well documented.

The objective of this study was to quantify the pollution effects of salt storage in Rhode Island, and then to formulate recommendations to minimize the impact of salt storage by methods such as: improved siting, operational and storage practices and design of storage facilities.

Method of Study

All salt storage sites belonging to the Rhode Island Department of Transportation (RIDOT) were located, and a preliminary investigation made of each storage site. In the preliminary investigation an assessment was made of the potential for pollution of ground and surface water at each site.

Following the preliminary assessment, four sites were selected for detailed investigation. Three sites were chosen to represent the three broad hydrogeologic categories found in Rhode Island: outwash, till, and bedrock. The fourth site was included because of its potential impact on the proposed Big River Reservoir. The following State of Rhode Island agencies were asked to comment on the selected sites: The Department of Transportation, the Water Resources Board, the Department of Health, and the Department of Environmental Management. Comments were also requested and received from the U.S. Geological Survey.

At the sites selected for detailed study the following work was planned:

1. Placement of test and monitoring wells
2. Soil sampling
3. Electrical resistivity measurements of subsurface conditions
4. Water quality measurements of both ground and surface water
5. Laboratory studies of soil
6. Water level measurements

Water samples were collected from installed monitoring wells, nearby domestic wells, and ponds, lakes, and streams likely to be influenced by salt storage runoff. The water quality parameters tested were specific conductance, sodium and chloride, and limited testing for cyanide.

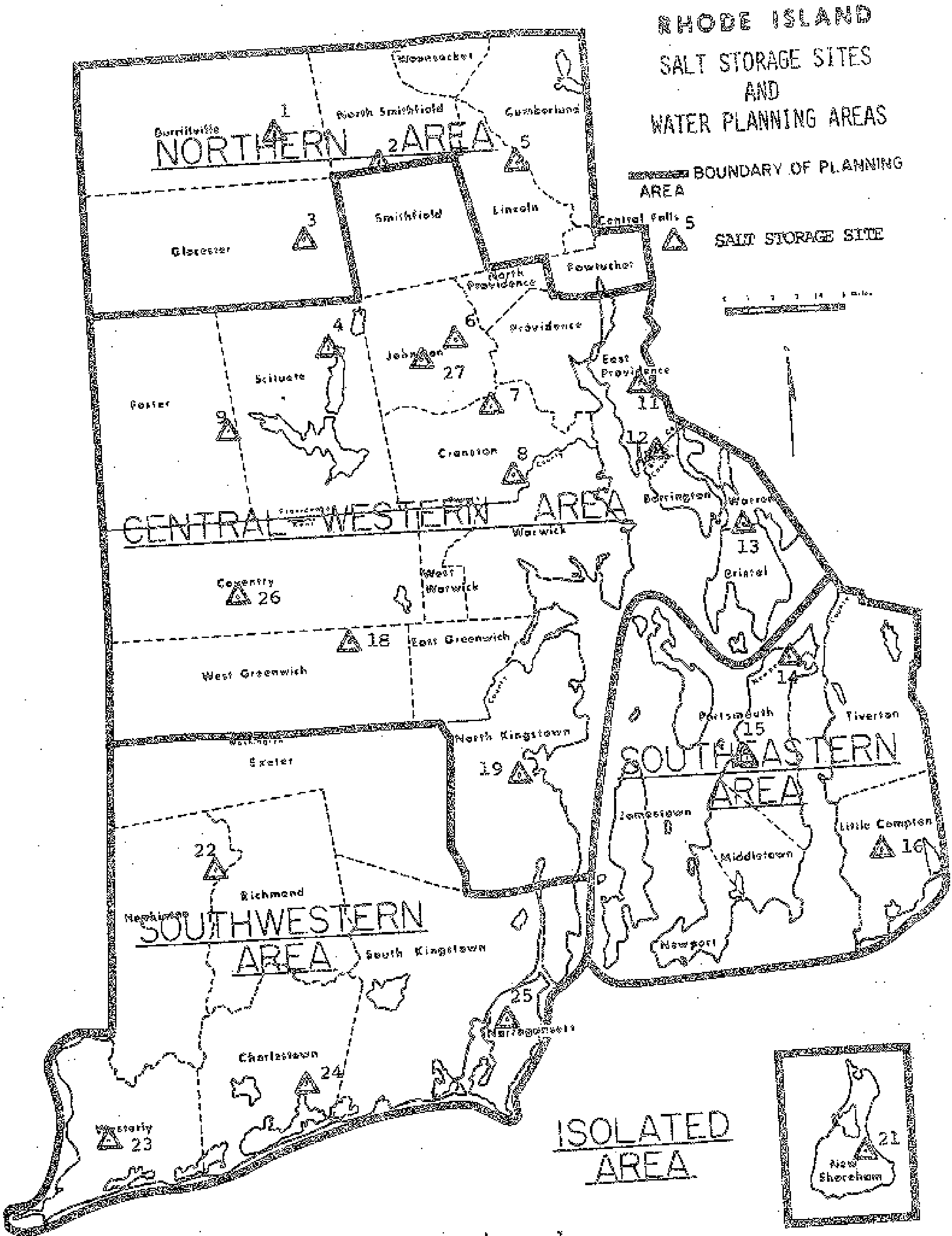
Monitoring wells were installed by a well driller at the rock and till sites and a test boring contractor at the outwash site.

From the results of the preliminary assessment and the detailed measurements the areas and hydrogeologic conditions most sensitive to salt storage were identified. From the four sites investigated in detail, the existing impact is quantified and future impacts under current and alternate operational conditions could be projected.

Methods for minimizing future salt storage impacts on water quality both non-structural (siting, handling procedures, etc.) and structural (covers, drainage, etc.) were reviewed and alternate storage practices are proposed.

Results of Study

All of the RIDOT salt storage sites, except for the Block Island site, were inspected. Figure 1 shows the approximate location of all of the sites; these are tabulated and further identified in Table 1. The numbering system used is modified from the one used by Bronstein in a report prepared for the RIDOT (2).


RHODE ISLAND
SALT STORAGE SITES
AND
WATER PLANNING AREAS
BOUNDARY OF PLANNING AREA
SALT STORAGE SITE
NORTHERN AREA
CENTRAL WESTERN AREA
SOUTHWESTERN AREA
SOUTHEASTERN AREA
ISOLATED AREA
Woonsocket
North Smithfield
Cumberland
Burrillville
Lincoln
Central Falls
Glocester
Smithfield
Pawtucket
North Providence
Providence
Foster
Scituate
Johnston
Cranston
East Providence
Barrington
Warren
Bristol
Warwick
West Warwick
Coventry
East Greenwich
West Greenwich
North Kingstown
Exeter
Richmond
Hopkinton
South Kingstown
Charlestown
Westerly
Narragansett
Jamestown
Middletown
Newport
Portsmouth
Tiverton
Little Compton
New Shoreham
1
2
3
4
5
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27

Figure 1.

Table 1. Impact of Existing Salt Storage Sites on Water Resources

Name - Location on Map		This Study		208 Study	Health Dept Report	RIDOT Records
		Ground Water	Surface Water			
Chapel Street	1	X		X		
Carpenter's Corner	2	O	O		X	O
Gloucester	3	X	O			O
Battey Mtg House	4	X	X		X	
Lincoln	5	X				
Cherry Hill	6		O			
Thornton	7		O			
Howard	8	X				
Clayville	9					
Pawtucket River Bridge	10					
Rt 6	11					
E. Prov.	12					
Warren Yard	13					
Portsmouth	14	X				
School House Lane	15		O			
Little Compton	16	O	O		O	
Lawton Valley	17					
Rts 95 & 3	18	X	O			
Belleville	19	X	O			
Jamestown	20					
Block Island	21					
Hope Valley	22	X	O			O
Westerly	23		X			
Charlestown	24	X			X	
Narragansett	25		X			
Rts 117&102	26		X			
Rts 195&295	27					

Table 1 shows qualitatively the results of our survey and information available in reports (7,14) and RIDOT files. An X indicates there was evidence of a possible or probable impact. An O indicates that salt pollution was considered confirmed. Except for this survey, all references are to ground water only.

From this survey, the most severe impact of salt storage as indicated by abnormal specific conductances (which can be correlated with chloride concentrations (9), is on ground water. Although elevated conductances were measured in small streams near salt storage sites, levels fell off rapidly downstream due to dilution and dispersion. Where ponds and lakes are nearby and are receiving runoff from salt storage sites, the effect is not as clear. In surface water bodies there is reportedly a tendency for density stratification (3,4) and for nuisance algal blooms (4). The effect of salt runoff on heavy metals which may be tied up in stream and lake bottom sediments is unknown.

The major effect of existing salt storage sites on ground water appeared to be on domestic wells. Table 2 was prepared from information presented in the salt storage study done as part of the 208 Study (14). In terms of major ground water resources, only the Hope Valley site has the potential for significant impact. The other locations appear to have less potential for impact either because there are other pollution sources nearby and the water quality is already poor, or they are not in close proximity to a ground water reservoir.

Based on the preliminary evaluation of all existing salt storage sites, a detailed investigation of the four sites listed in Table 3 was proposed. These sites had been reported as possible problem sites and our survey confirmed this. These sites also represent the three broad categories of hydrogeologic conditions proposed for study. The four sites proposed represent one more than originally proposed. The Routes 95 and 3 site was included because of concern that it might be affecting Cadwell Mill Pond and had the potential to affect the Big River Reservoir if and when it is built.

During August, 1979, water quality surveys were made in the vicinity of each of the four sites. Samples were collected from domestic wells, streams, and ponds adjacent to each site. Figures 2, 3, 4 and 5 show the locations of the sampling points at Routes 95 and 3, Charlestown, Glocester, and Little Compton,

Table 2. Salt Storage Sites in Relation To Ground Water Resources*

Location	Number	Ground Water Aquifer	Comments
Hope Valley	22	Upper Wood Area	Adjacent to ground water reservoir - no public wells existing or proposed - potential for development unknown
Rts 95 & 3	18	Mishnock Area	Not adjacent to ground water reservoir - sediments very fine silt and clay
East Prov.	12	Barrington Area	Not adjacent to ground water reservoir - sediments very fine silt or clay
Chapel Street	1	Upper Branch Area	In ground water reservoir at old Burrillville landfill
Howard	8	Providence-Warwick Area	In primary recharge area adjacent to ground water reservoir, landfill nearby - no public wells existing or proposed
Belleville	19	Annaquatucket-Pettaquamscutt Area	Not near ground water reservoir - sediments are stratified-drift mixed with till and of morainal origin

*From maps prepared by RIWRB for RISWPP and 208 Project.

Table 3. Sites Proposed for Detailed Evaluation

Site	Location Number	Geology	Potential Effect		Probably Affecting Ground Water
			Ground Water	Surface Water	
Glocester	3	Bedrock-Outwash	Domestic Wells	Small Stream	yes
Little Compton	16	Till	Domestic Wells	-	yes
Rts 95 & 3	18	Outwash	-	Streams & Ponds	yes
Charlestown	24	Outwash	Domestic Wells	Stream	yes

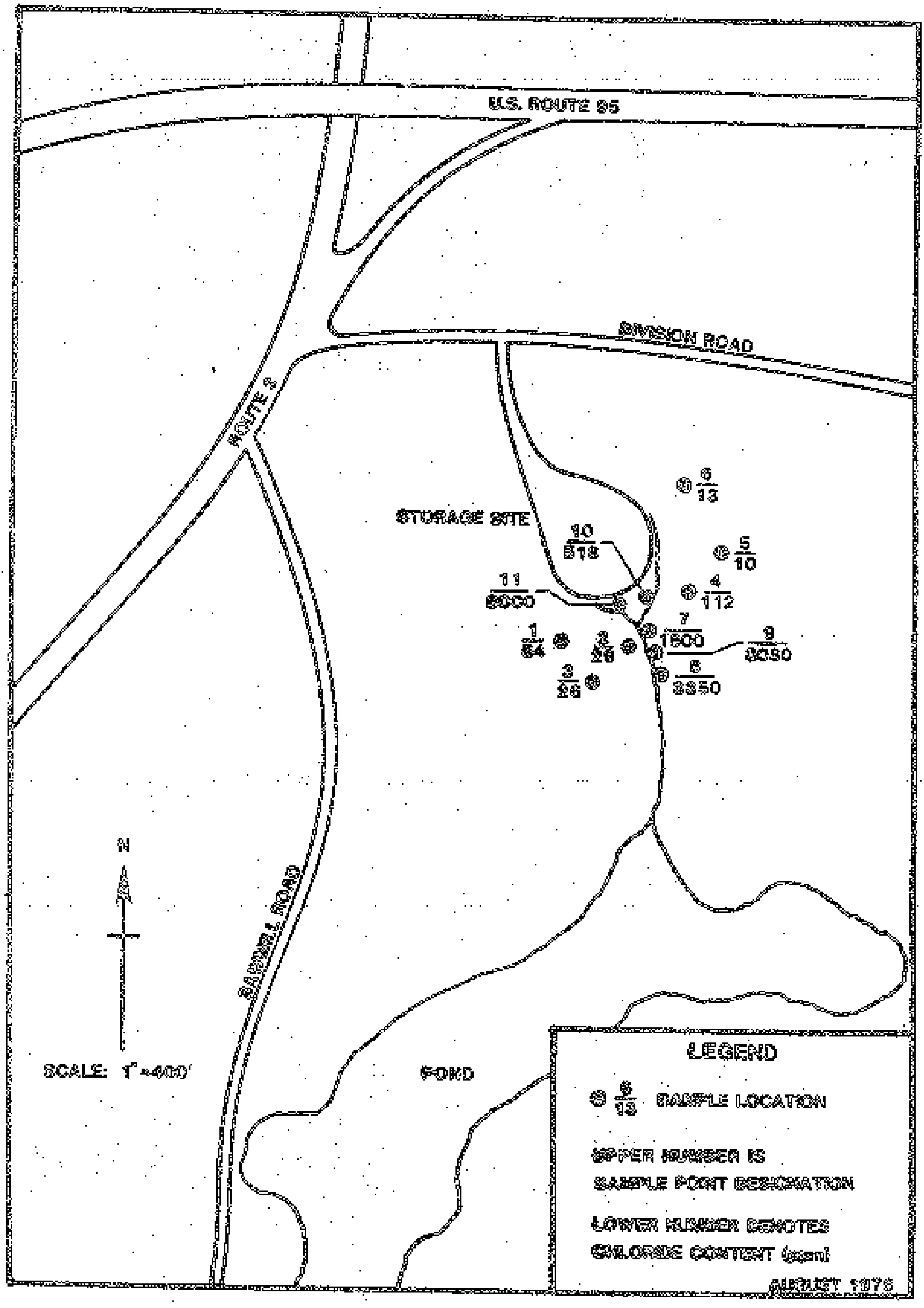
U.S. ROUTE 95
DIVISION ROAD
ROUTE 3
STORAGE SITE
SAWMILL ROAD
POND
N
SCALE: 1"=400'
6/13
10/518
5/10
11/8000
4/112
7/1500
1/54
2/26
9/3090
3/26
8/3350
LEGEND
6/13 SAMPLE LOCATION
UPPER NUMBER IS
SAMPLE POINT DESIGNATION
LOWER NUMBER DENOTES
CHLORIDE CONTENT (ppm)
AUGUST 1976

Figure 2.

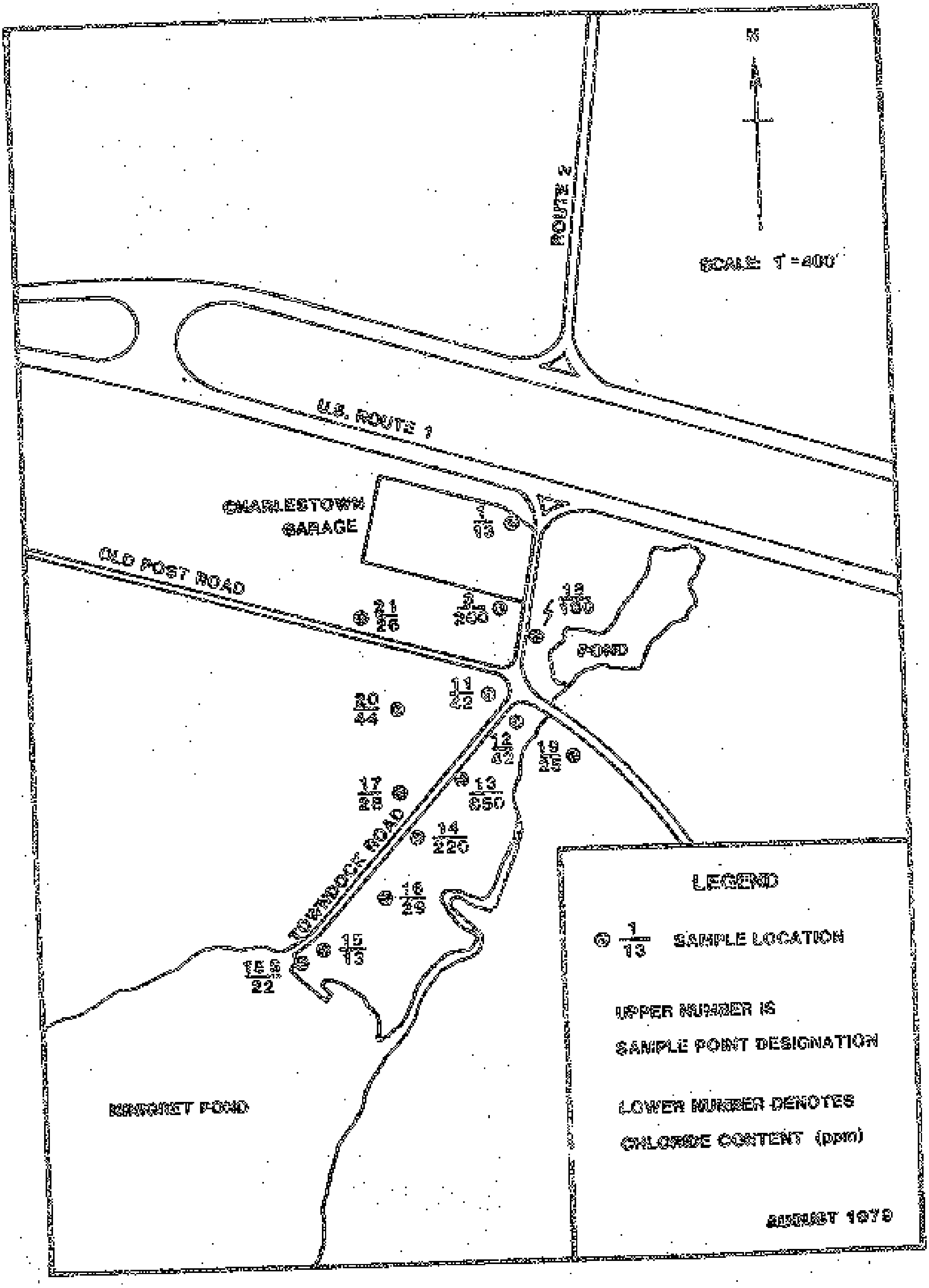

N
SCALE: 1" = 400'
ROUTE 2
U.S. ROUTE 1
CHARLESTOWN GARAGE
OLD POST ROAD
TOWNDOCK ROAD
POND
NINIGRET POND
1/13
2/200
18/100
21/26
11/42
20/44
12/42
19/35
17/28
13/650
14/220
16/29
15/13
15.5/22
LEGEND
1/13 SAMPLE LOCATION
UPPER NUMBER IS SAMPLE POINT DESIGNATION
LOWER NUMBER DENOTES CHLORIDE CONTENT (ppm)
AUGUST 1979

Figure 3.

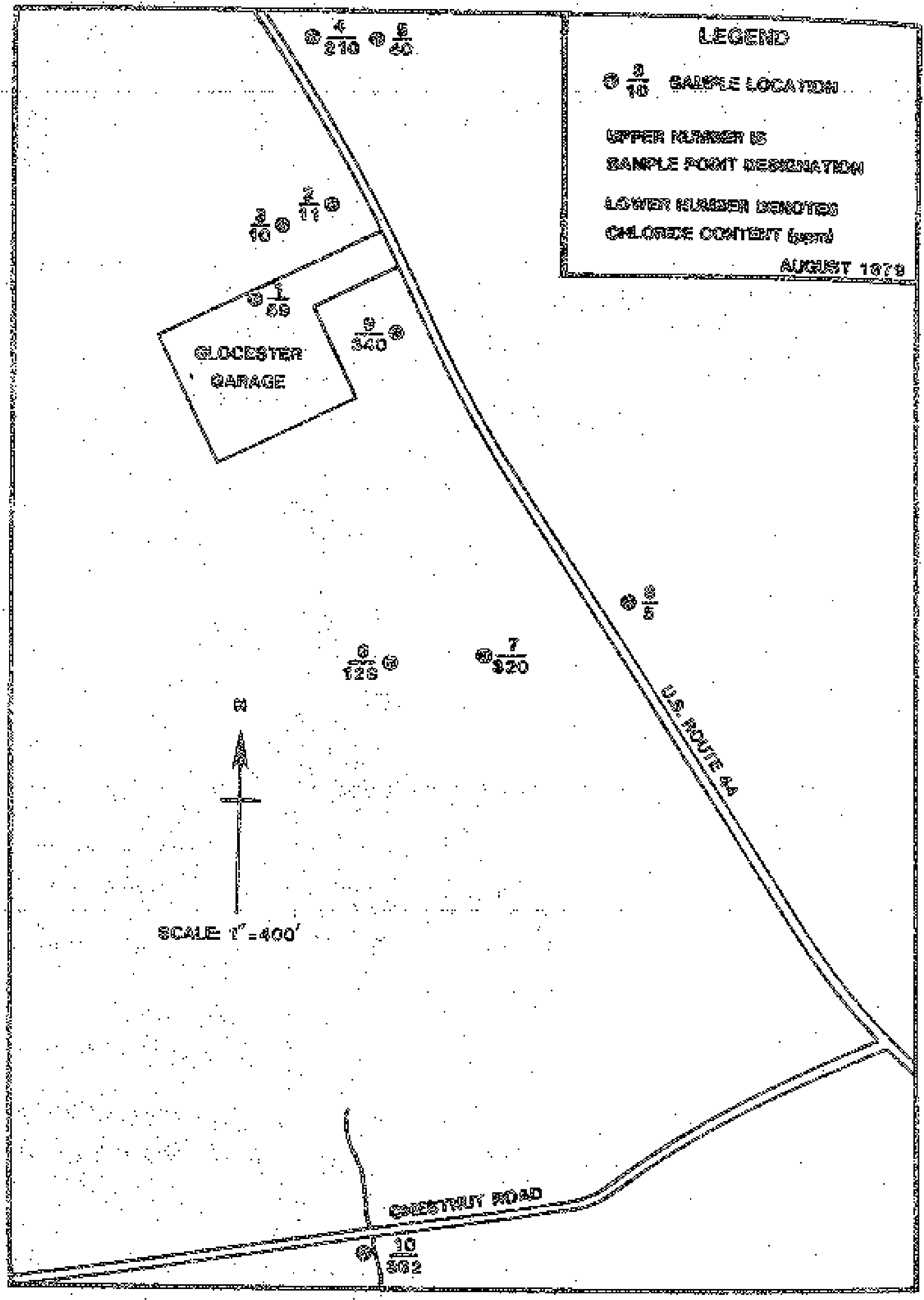

LEGEND
3/10 SAMPLE LOCATION
UPPER NUMBER IS SAMPLE POINT DESIGNATION
LOWER NUMBER DENOTES CHLORIDE CONTENT (ppm)
AUGUST 1979
4/210
5/40
3/10
2/11
1/59
9/340
GLOCESTER GARAGE
8/5
6/125
7/320
U.S. ROUTE 44
N
SCALE 1"=400'
CHESTNUT ROAD
10/302

Figure 4.

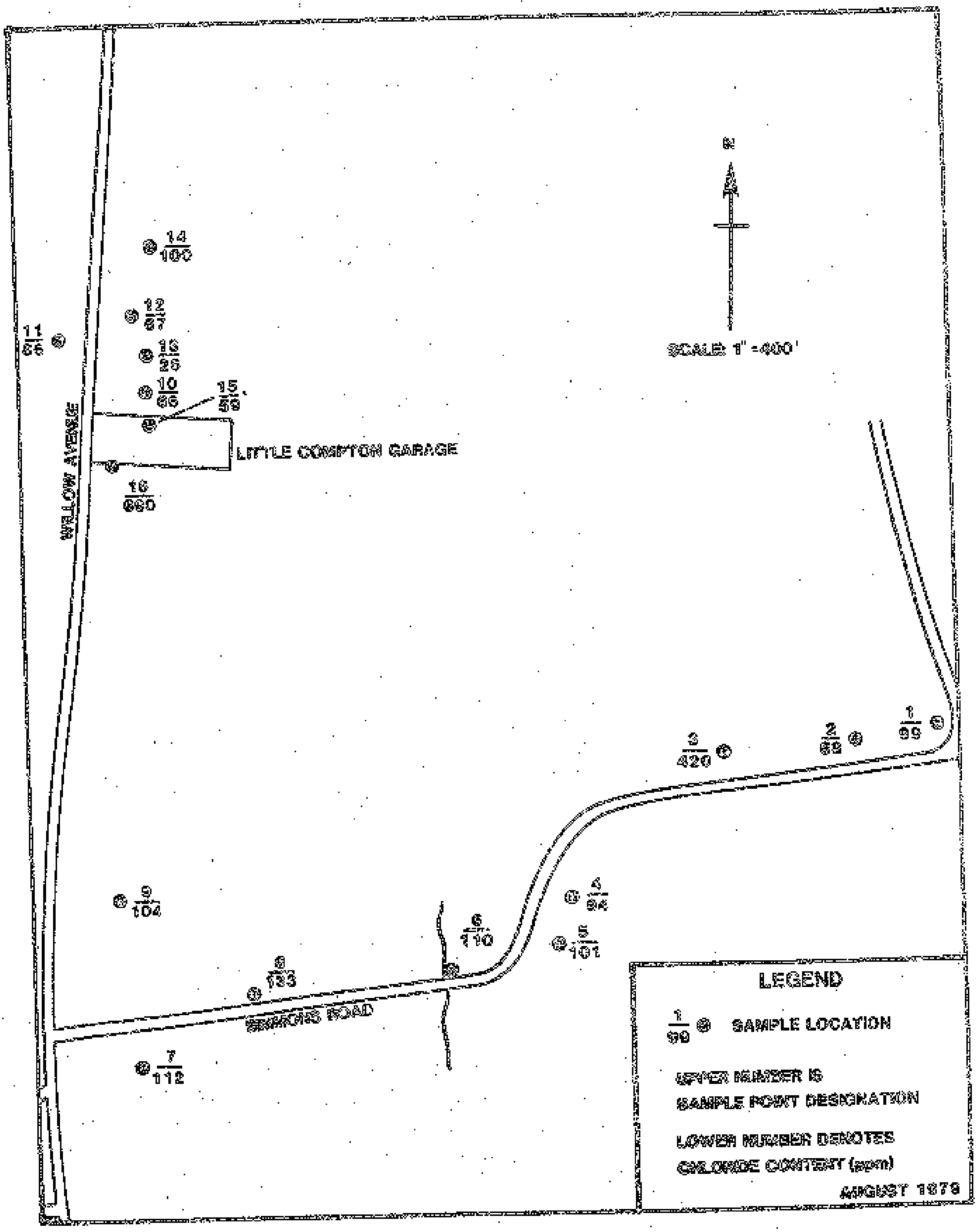

N
SCALE: 1" =400'
14
100
12
87
11
65
13
25
10
66
15
59
LITTLE COMPTON GARAGE
16
660
WILLOW AVENUE
3
420
2
89
1
99
9
104
4
94
6
110
5
101
8
135
SIMMONS ROAD
7
112
LEGEND
1
99
SAMPLE LOCATION
UPPER NUMBER IS
SAMPLE POINT DESIGNATION
LOWER NUMBER DENOTES
CHLORIDE CONTENT (ppm)
AUGUST 1979

Figure 5.

respectively. Tables 4, 5, 6 and 7 summarize survey results for each site. These results were used along with water level and geophysical data to estimate probable movement at each site. At the Charlestown, Rts. 95 and 3, and Glocester sites the probable direction of movement was reasonably well defined. The direction of movement at Little Compton was less certain. At all the sites, there was evidence that salt was moving into the ground water in significant quantities.

A preliminary analysis of the data collected in the August surveys was made. Figure 6 shows regression lines relating sodium to chloride concentrations. Also shown is the theoretical line for sodium chloride. In general, sodium is coming into solution in balance with the chloride ion as it should if the values are resulting from solution of salt. The suggested limit for sodium in drinking water is 20 mg/l and if this suggested limit is accepted, these results indicate significant increases in sodium concentrations in the vicinity of all four salt storage sites.

Deep monitoring wells were installed at the Charlestown, Glocester, and Little Compton sites and shallow well points were installed at all sites. Well points at the Charlestown, Glocester, and Little Compton sites were installed with the assistance of RIDOT personnel. Well points were set by excavating holes with a backhoe, placing the assembled well point, tapping to set, and backfilling with sand. Well points were monitored along with the deep monitoring wells and the other sampling points.

Charlestown

The location of the deep monitoring wells (24,25), the well points (22,23), the control well (1), and several offsite monitoring points (2,3,4,7) immediately adjacent to the site are shown in Figure 7.

Split spoon samples were collected during installation of monitoring well 25 and grain size distributions were run on the split-spoon samples. Well 25 extends 61.5 feet below the land surface. The material is generally medium dense, fine to medium sand. The well appears to just penetrate a layer of till. Bedrock was not encountered.

Figure 8 shows selected data for the Charlestown site.

Table 4. Water Quality Results
for Routes 95 and 3 Site
on August 24, 1979

SAMPLE NUMBER	SOURCE TYPE	SPECIFIC CONDUCTANCE µmhos/cm at 25°C	CHLORIDES (ppm)	SODIUM (ppm)
WG1	4" tube	230	54	22
WG2	4" tube	160	29	22
WG3	4" tube	115	26	13
WG4	4" tube	450	112	62
WG5	4" tube	87	10	6
WG6	1¼" W.P.	102	13	13
WG7 *	1¼" W.P.	1160	328	206
WG8	stream	8,800	3,350	2,250
WG9	stream	8,900	3,080	3,000
WG10	stream	1,320	518	320
WG11	stream	21,500	8,000	5,800

NOTE: *Denotes sample taken Sept. 14, 1979.

Table 5. Water Quality Results

for Charlestown Site

on August 6, 1979

SAMPLE NUMBER	SOURCE TYPE	SPECIFIC CONDUCTANCE µmhos/cm at 25°C	CHLORIDES (ppm)	SODIUM (ppm)
CH1*	drl. well	140	13	8
CH2*	dug well	1,110	260	155
CH11	well	215	42	34
CH12	drl. well	210	42	26
CH13	dug well	2,510	850	385
CH14	well pt.	760	220	122
CH15	dug well	80	13	11
CH16	dug well	155	29	16
CH17	well	310	28	16
CH18	well	520	180	84
CH19	dug well	255	25	32
CH20	drl. well	205	44	27
CH21	well pt.	395	26	16

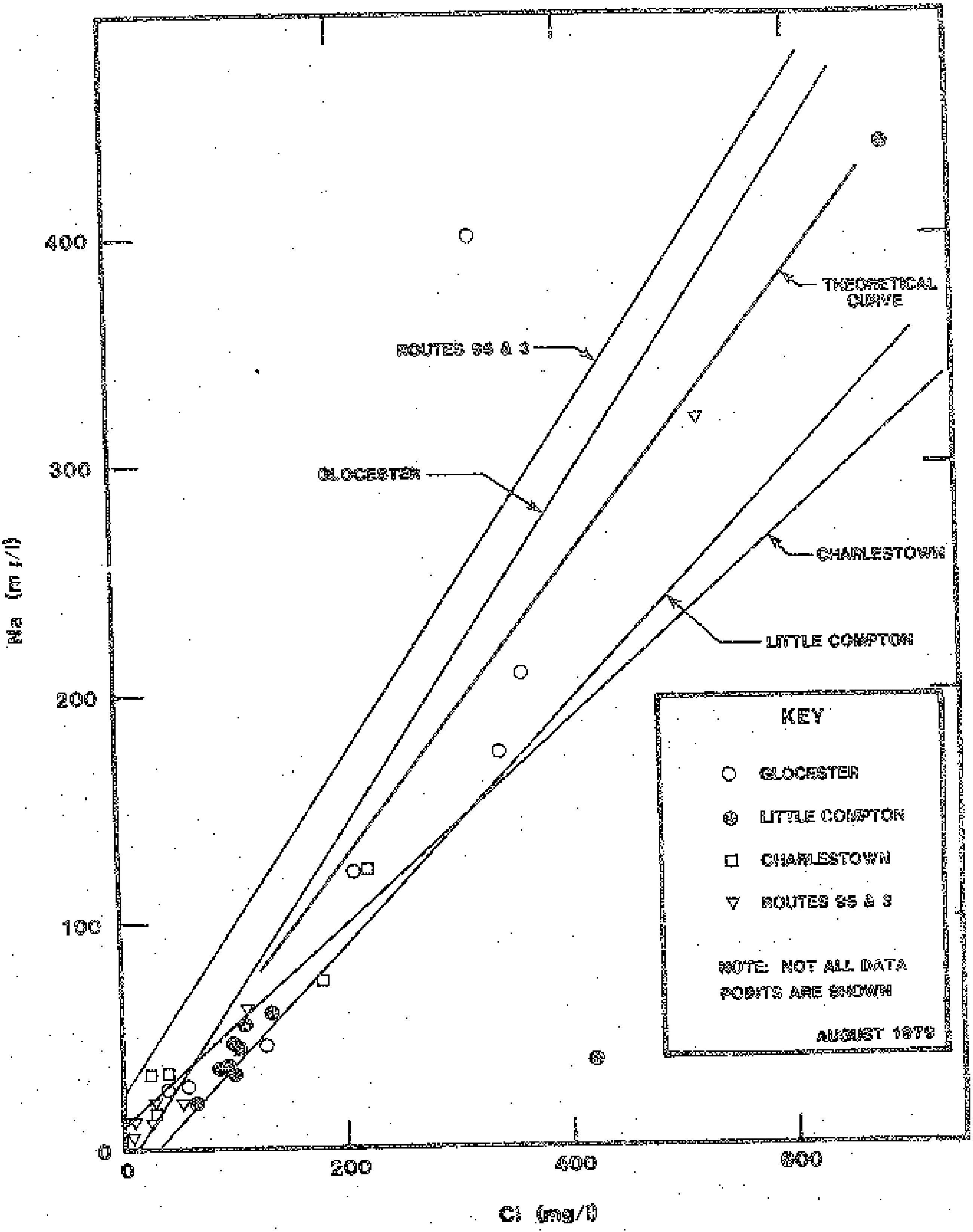
NOTE: *Denotes sample taken Sept. 14, 1979.

Table 6. Water Quality Results for Glocester Site on August 6, 1979

SAMPLE NUMBER	SOURCE TYPE	SPECIFIC CONDUCTANCE µmhos/cm at 25°C	CHLORIDES (ppm)	SODIUM (ppm)
GL1	drl. well	400	59	28
GL2	dug well	150	11	14
GL3	pond	50	10	8
GL4	drl. well	725	210	122
GL5	pond	230	40	27
GL6	drl. well	460	128	45
GL7	pond	1,030	320	400
GL8	drl. well	165	5	395
GL9	pond	1,170	340	174
GL10	stream	3,280	362	208

Table 7. Water Quality Results
for Little Compton Site
on August 17, 1979

SAMPLE NUMBER	SOURCE TYPE	SPECIFIC CONDUCTANCE µmhos/cm at 25°C	CHLORIDES (ppm)	SODIUM (ppm)
LC1	drl. well	445	99	46
LC2	drl. well	550	58	31
LC3	well	1,495	420	38
LC4	well	530	94	36
LC5	well	585	101	33
LC6	stream	450	110	54
LC7	well	640	112	55
LC8	drl. well	695	133	60
LC9	drl. well	630	104	45
LC10	drl. well	445	66	20
LC11	drl. well	1,045	86	36
LC12	drl. well	750	67	23
LC13	dug well	350	27	12
LC14	drl. well	1,135	100	36
LC15	drl. well	370	59	21
LC16	dug well	2,350	690	440



Na (mg/l)
400
300
200
100
0
0
200
400
600
Cl (mg/l)
ROUTES 95 & 3
GLOCESTER
THEORETICAL CURVE
CHARLESTOWN
LITTLE COMPTON
KEY
○ GLOCESTER
⊗ LITTLE COMPTON
□ CHARLESTOWN
▽ ROUTES 95 & 3
NOTE: NOT ALL DATA POINTS ARE SHOWN
AUGUST 1979

Figure 6.

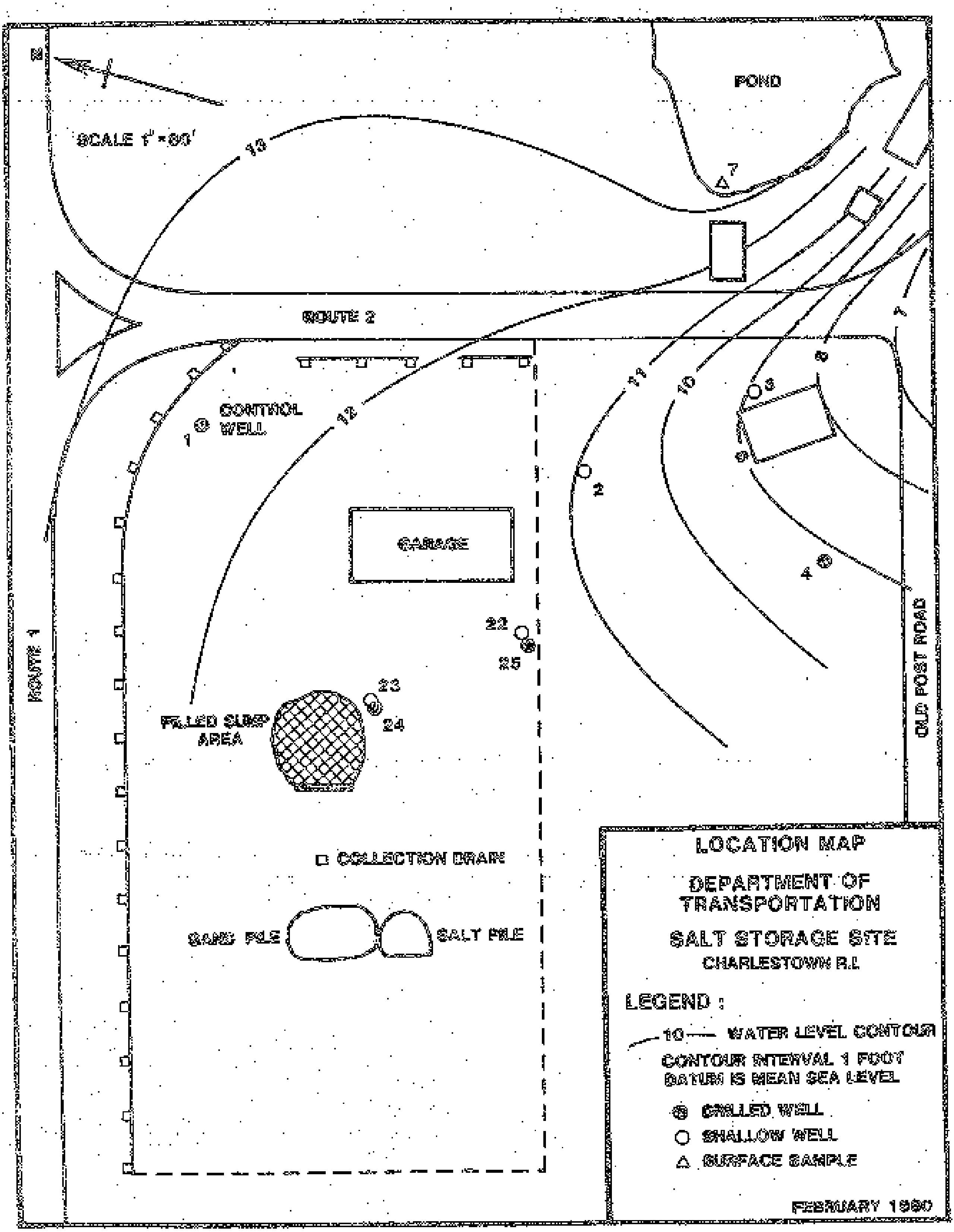

N
SCALE 1"=60'
POND
7
13
12
11
10
9
8
7
ROUTE 2
ROUTE 1
OLD POST ROAD
1
CONTROL WELL
2
3
4
GARAGE
22
25
23
24
FILLED SUMP AREA
COLLECTION DRAIN
SAND PILE
SALT PILE
LOCATION MAP
DEPARTMENT OF TRANSPORTATION
SALT STORAGE SITE
CHARLESTOWN R.I.
LEGEND :
10 WATER LEVEL CONTOUR
CONTOUR INTERVAL 1 FOOT
DATUM IS MEAN SEA LEVEL
DRILLED WELL
SHALLOW WELL
SURFACE SAMPLE
FEBRUARY 1980

Figure 7.

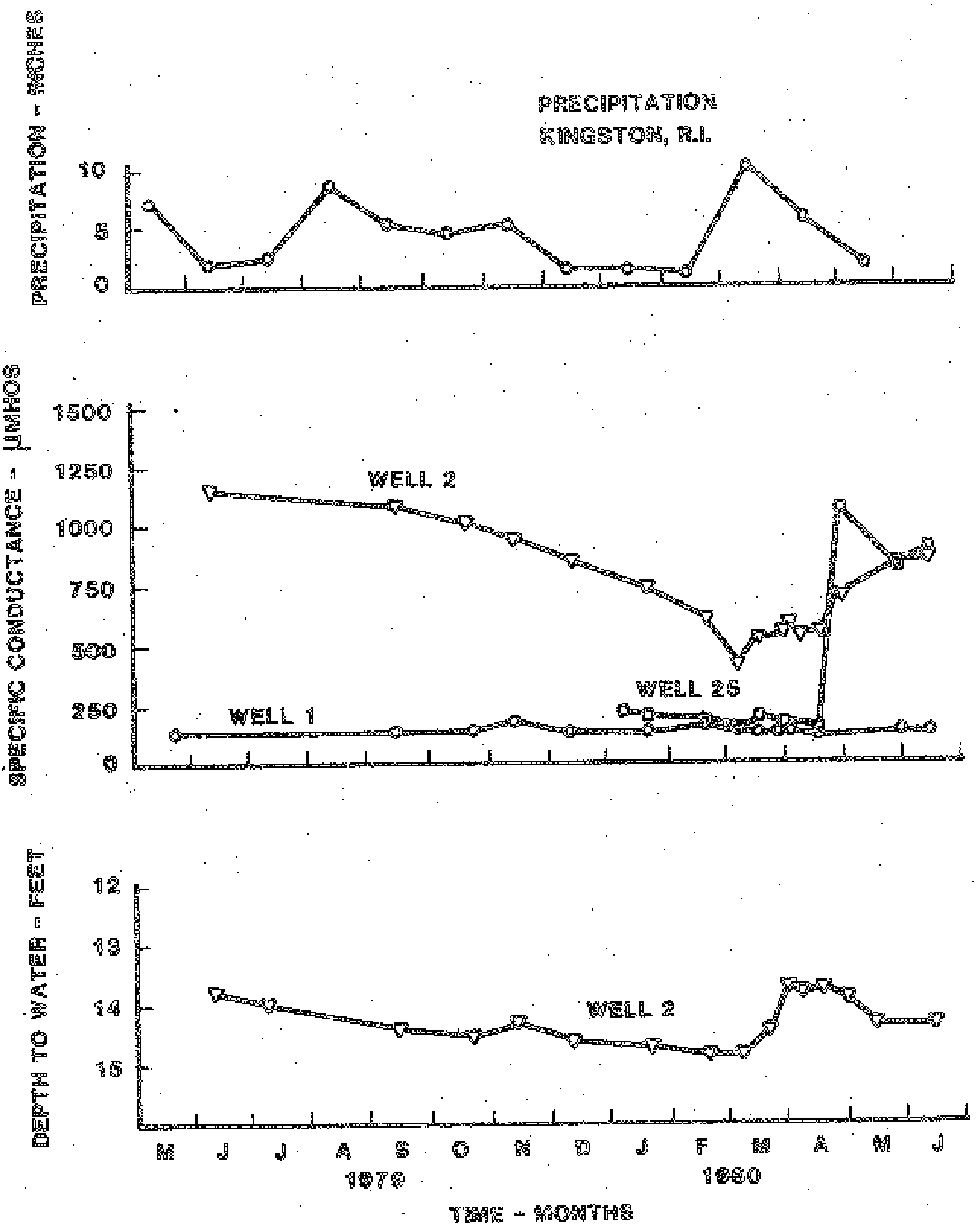

PRECIPITATION - INCHES
PRECIPITATION
KINGSTON, R.I.
10
5
0
SPECIFIC CONDUCTANCE - µMHOS
1500
1250
1000
750
500
250
0
WELL 2
WELL 25
WELL 1
DEPTH TO WATER - FEET
12
13
14
15
WELL 2
M
J
J
A
S
O
N
D
J
F
M
A
M
J
1979
1980
TIME - MONTHS

Figure 8.

Precipitation is the monthly precipitation at Kingston, R.I. Generally, water levels were declining and water quality was improving until the rains came in March; then, water levels and specific conductance generally began to rise. Water quality in the deep well near the sump (24) has remained near background (well 1). Well 25 which was at background shows a dramatic increase following recharge. All of the water level and water quality data is tabulated in Appendix A.

Figure 7 shows the water table configuration for February, 1980. The shape of the water table is not expected to vary greatly during the year although the actual elevations will vary somewhat. The water table is severely distorted due to the presence of a dam just east of Rt. 2 and north of old Post Road.

The specific conductances shown in Figure 8 translate approximately into maximum chloride levels of about 400 mg/l. Figure 9 shows the variation in sodium at the control well and well 2. These values will be reduced down gradient primarily by dispersion.

Estimates of probable maximum concentrations away from the site can be made using dispersion theory (5). To make such estimates, it is first necessary to estimate salt input to the ground water. Table 8 shows the amount of salt delivered to each of the four study sites for the three most recent years. Table 9 shows the pattern of salt deliveries for the past winter which is representative of RIDOT salt delivery practice.

This practice is briefly to deliver half of the expected salt usage by November 1 of each snow season. From November 1 to January 1 enough material is retained on site to fight three storms back-to-back, from January 1 to February 28 two storms back-to-back, and from then on just enough to handle what comes along. When salt is delivered to a garage 2/3 is immediately mixed with sand in a ratio of 3 sand to 1 salt by volume and the rest stored. Any sand-salt mix that is not used is covered with 7"-12" of sand for summer storage.

Based on the data in Tables 8 and 9, an average of 600 tons is estimated to be stored at Charlestown for the mid October to mid-March period. During this period an average of more than 23 inches of rain fell during the past three years. Rain is

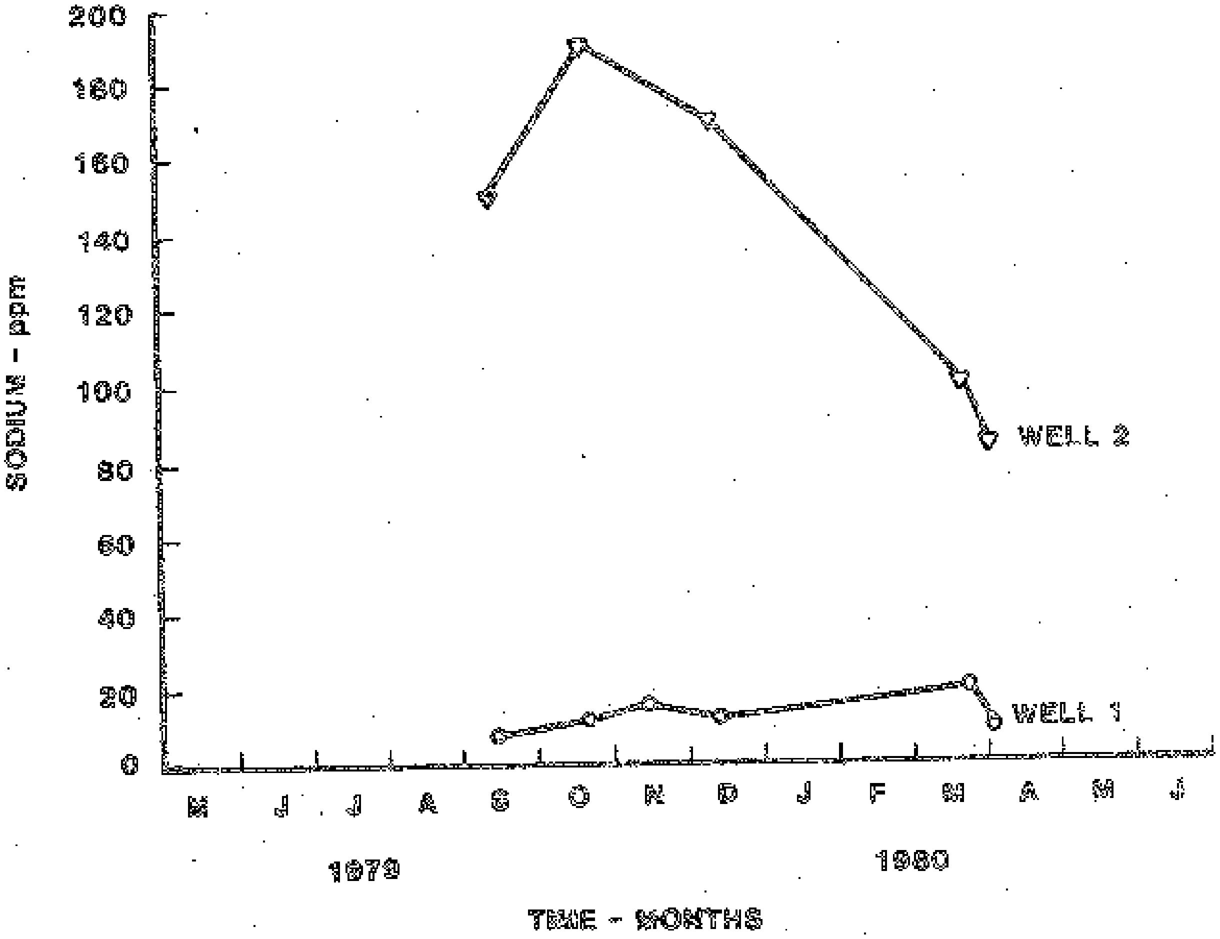

200
180
160
140
120
100
80
60
40
20
0
SODIUM - ppm
WELL 2
WELL 1
M
J
J
A
S
O
N
D
J
F
M
A
M
J
1979
1980
TIME - MONTHS

Figure 9.

Table 8.

SALT DELIVERIES - PAST THREE YEARS*

Site	1977-78 (tons)	1978-79 (tons)	1979-80 (tons)
Charlestown	1683	1104	783
Glocester	2857	2415	916
Little Compton	1436	611	447
Routes 95 and 3	2021	2787	991

*Data provided by T. Jackvony, RIDOT, 1980.

Table 9.

Salt Deliveries 1979-80*

Dates	Charlestown (tons)	Glocester (tons)	Little Compton (tons)	Rt. 95 and 3 (tons)
<u>1979</u>				
Oct. 22	-	133	64	-
23	-	170	-	-
24	-	234	-	-
26	-	135	-	-
29	251	-	-	-
30	187	92	-	-
31	60	62	-	-
Nov. 21	-	-	-	481
26	96	-	-	-
29	-	-	-	160
30	-	-	-	195
Dec. 3	-	-	-	156
<u>1980</u>				
Jan. 9	-	-	191	-
Feb. 18		-	93	-
19	95	-	-	-
20	94	-	-	-
Totals	783	726	446	992

*Data provided by T. Jackvony, RIDOT, 1980.

reported to reduce a salt pile at the rate of 0.25% per annual inch of precipitation (15). Assuming 600 tons for the half year storage period, an estimate of the salt runoff is 600x23x .0025 = 34.50 tons.

Assuming that half the salt eventually reaches the ground water, the salt input is estimated to be 17.25 tons x 2000 lb/ tons ÷ 180 days = 96 lbs/day NaCl, of which about 58 lbs/day is chloride. This analysis does not presume that any of the salt runoff is collected, though it is recognized that a limited collection tank capability exists now at Charlestown.

In addition to the salt input it is necessary to know or be able to estimate several aquifer properties in order to evaluate salt movement in the ground water. Assuming a uniform flow field, estimates of saturated thickness, seepage velocity and longitudinal and transverse dispersivity are needed. Dispersivities have been related to grain size (5), although at the field scale much larger values are reported.

To illustrate the solution technique which utilizes an analytic solution given by Wilson and Miller (17) the following conditions are estimated for Charlestown.

seepage velocity	.45 ft/day
porosity	.3
longitudinal dispersivity	30 ft
lateral dispersivity	6 ft
input of sodium chloride	96 lbs/day
distance of observation well	650 ft
saturated thickness	40 ft

Figure 10 shows the response to a uniform 180 day input of 96 lb/day. Figure 11 shows the response to five years of 180 day uniform inputs after which the input ceases. Note that the highest concentration is not observed until more than 3 years after the input ceased!

This example illustrates the magnitude of the impact that can be expected 650 feet down gradient from the Charlestown site. Obviously the estimate of the magnitude and timing of the input are important and at best approximate the actual conditions. However, Figure 12 indicates this to be a reasonable estimate of the magnitude of the effect being observed in a

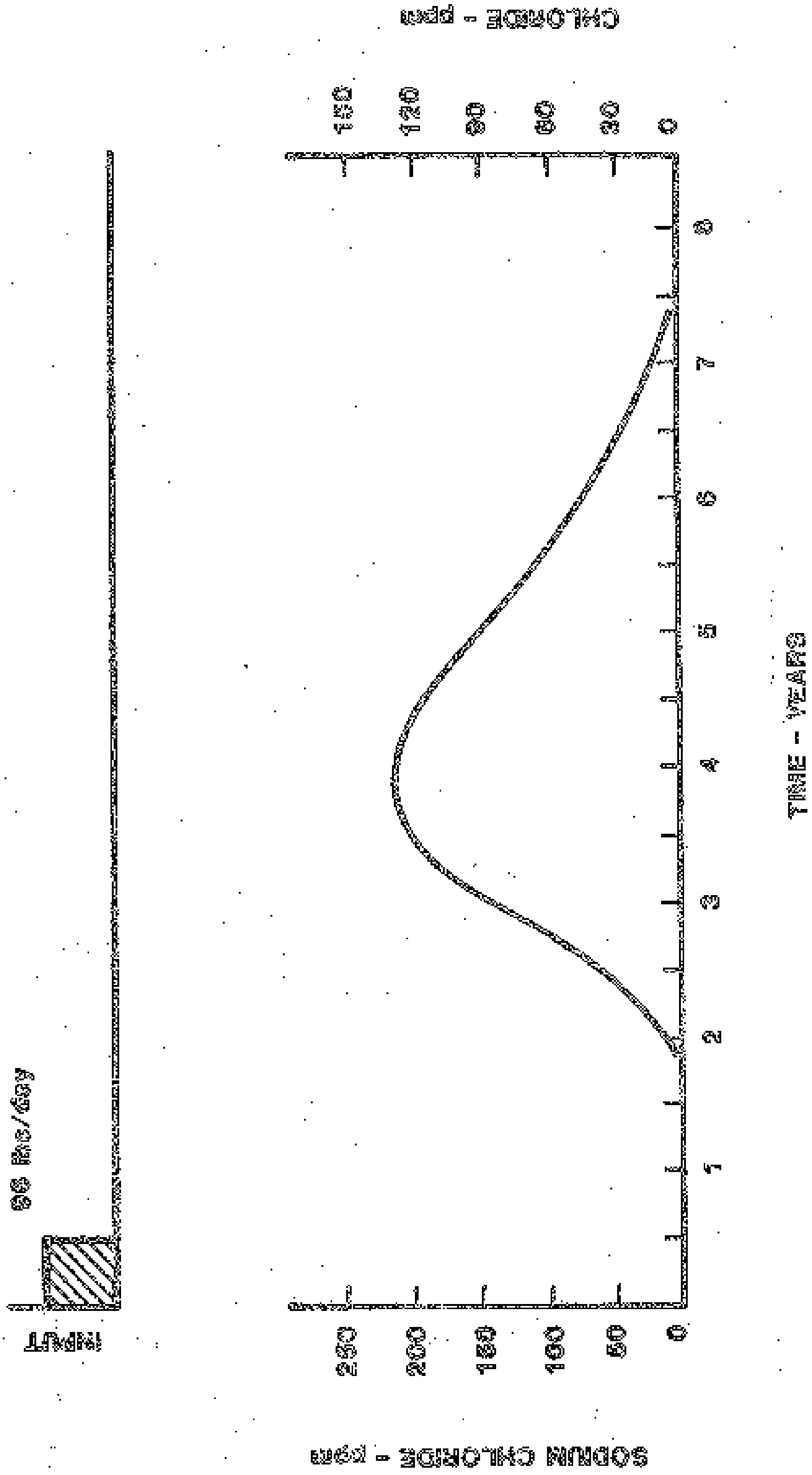

INPUT
90 Rns/day
SODIUM CHLORIDE - ppm
0
50
100
150
200
250
CHLORIDE - ppm
0
30
60
90
120
150
TIME - YEARS
1
2
3
4
5
6
7
8

Figure 10.

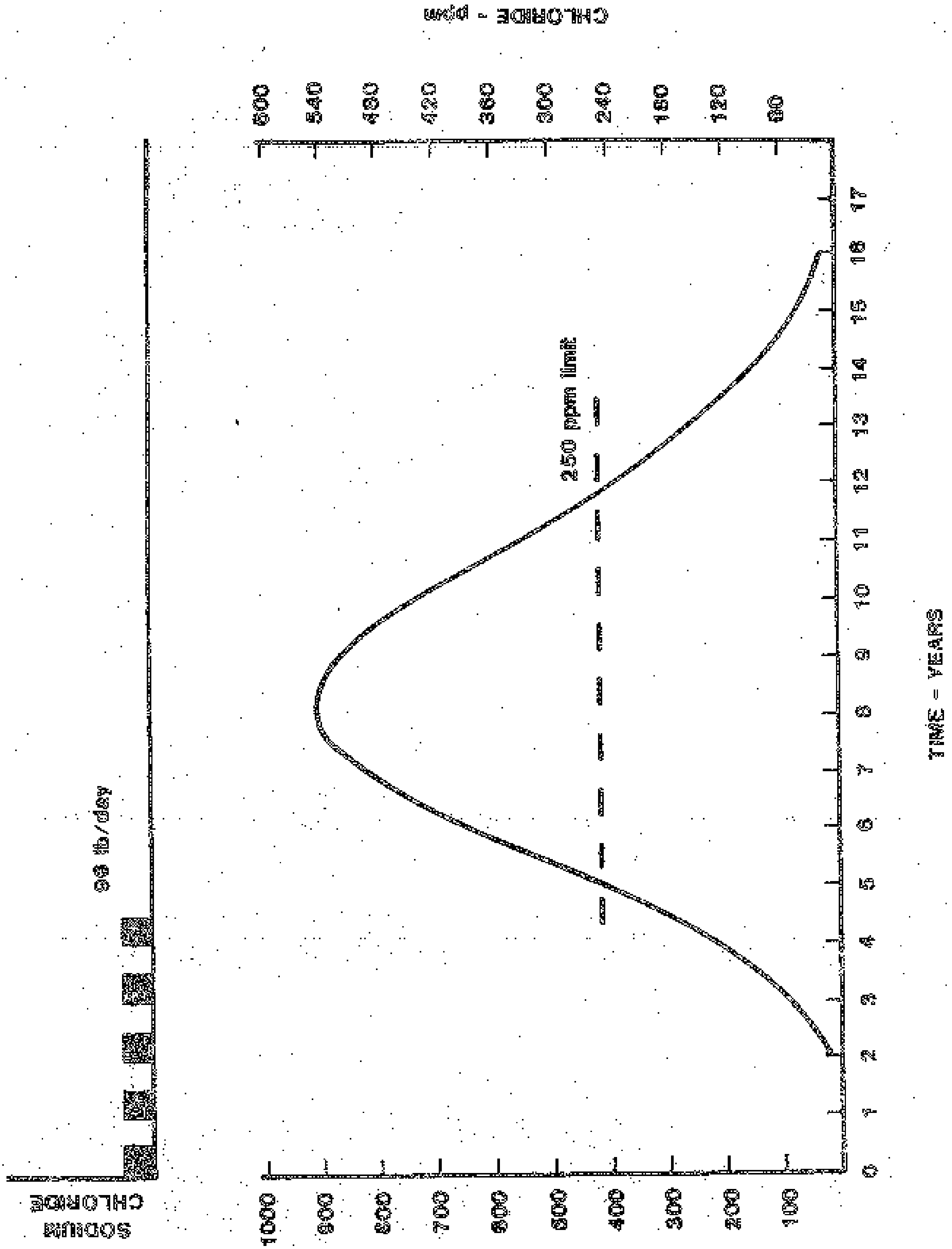

CHLORIDE - ppm
600
540
480
420
360
300
240
180
120
60
INPUT SODIUM CHLORIDE
90 lb/day
250 ppm limit
SODIUM CHLORIDE - ppm
1000
900
800
700
600
500
400
300
200
100
TIME - YEARS
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

Figure 11.

relatively narrow band down gradient from the storage site. Interestingly, the data collected did not show the "estimated" level of input at the site. This is probably due to the fact that in 1975 an asphalt mat with an underground tank was installed to control and collect brine from the stockpile.

Wells 13 and 14 (Figure 12) show the highest off-site values and the question was raised as to whether there could be salt water infiltrating from the adjacent stream, the the pond just east of the garage south to Ninigret Pond.

A survey was made to determine the stream profile downstream from Old Post Road. At Old Post Road the stream is approximately 5 feet above Ninigret Pond and at the final bend in the stream (see Figure 12) the level is approximately 1 foot above Ninigret Pond. Beyond this section the stream appears to be tidal. The high tide elevation of Ninigret Pond is estimated to be about .45 feet above the level at the time the survey was made so that under normal conditions the stream would not be expected to contain salt water, except very near its outlet.

Specific conductances were measured downstream from Old Post Road. Figure 13 shows the results of that survey. These results suggest that from 400 to 600 feet downstream from old Post Road, higher conductance ground water is entering the stream. This point corresponds to the upstream side of the last bend in the stream, the area where ground water flowing beneath the site would be expected to enter the stream.

Finally, samples were collected from two wells, wells 13 and 14 in Figure 12, and subjected to a complete analysis by the Rhode Island Department of Health. These results were analyzed using a Piper Diagram (9). The analysis is approximate because no analysis of Ninigret Pond water or mixes of road salt and native water were made. The analysis indicates that the water in the two wells, 13 and 14, is probably not a mix of sea water and natural ground water.

Table 10 compares the analysis of the two wells and the high and low values for 11 chemical analyses of ground water from the Lower Pawcatuck River Basin (6). Although no analysis has been run, Hagopian (7) indicates for salt purchased in 1968-69:

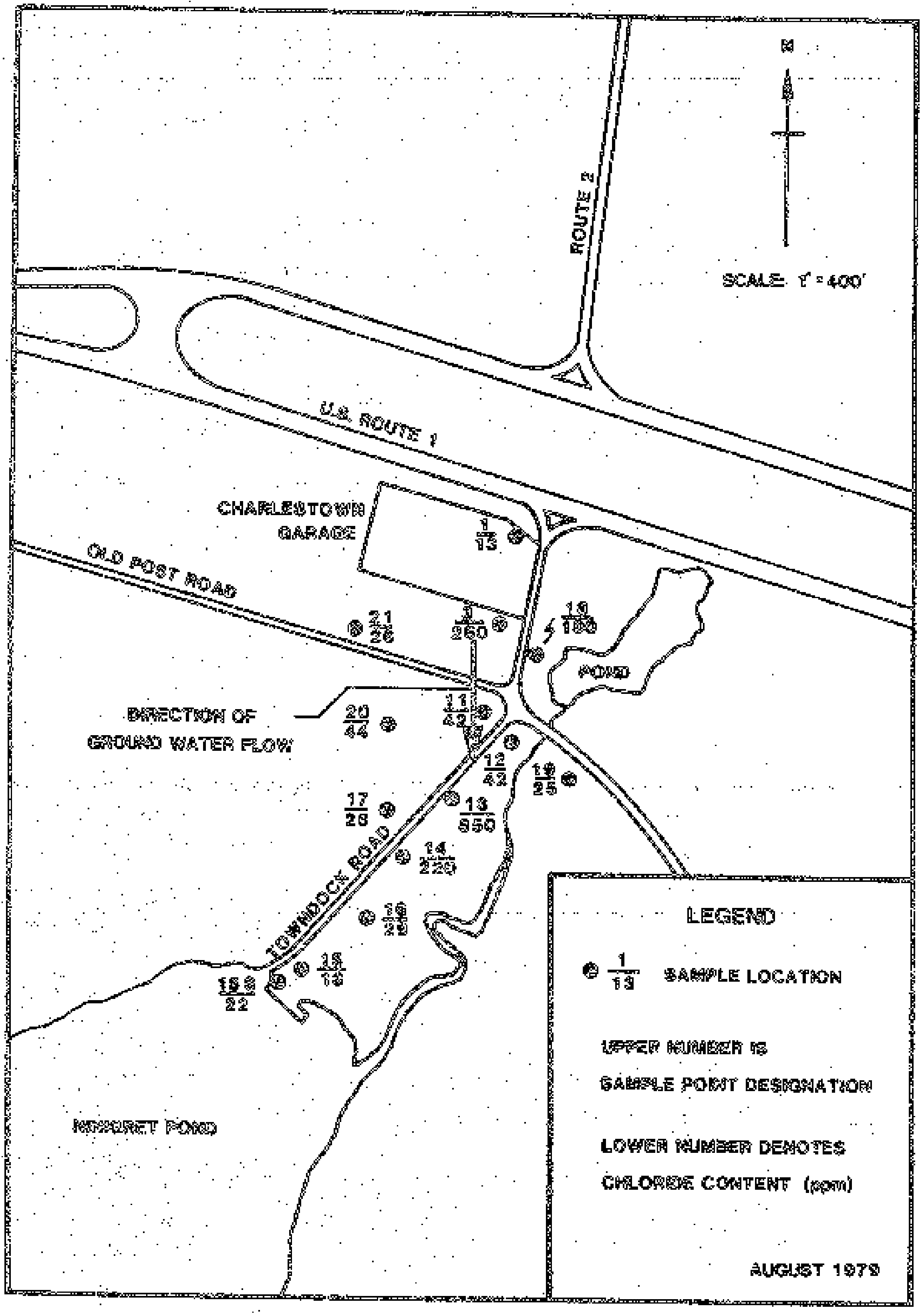

N
ROUTE 2
SCALE: 1" = 400'
U.S. ROUTE 1
CHARLESTOWN
GARAGE
OLD POST ROAD
1
13
21
26
260
19
160
POND
DIRECTION OF
GROUND WATER FLOW
20
44
11
42
12
42
19
25
17
26
13
550
14
220
TOWNDOCK ROAD
16
23
15
13
22
NINIGRET POND
LEGEND
1
13
SAMPLE LOCATION
UPPER NUMBER IS
SAMPLE POINT DESIGNATION
LOWER NUMBER DENOTES
CHLORIDE CONTENT (ppm)
AUGUST 1979

Figure 12.

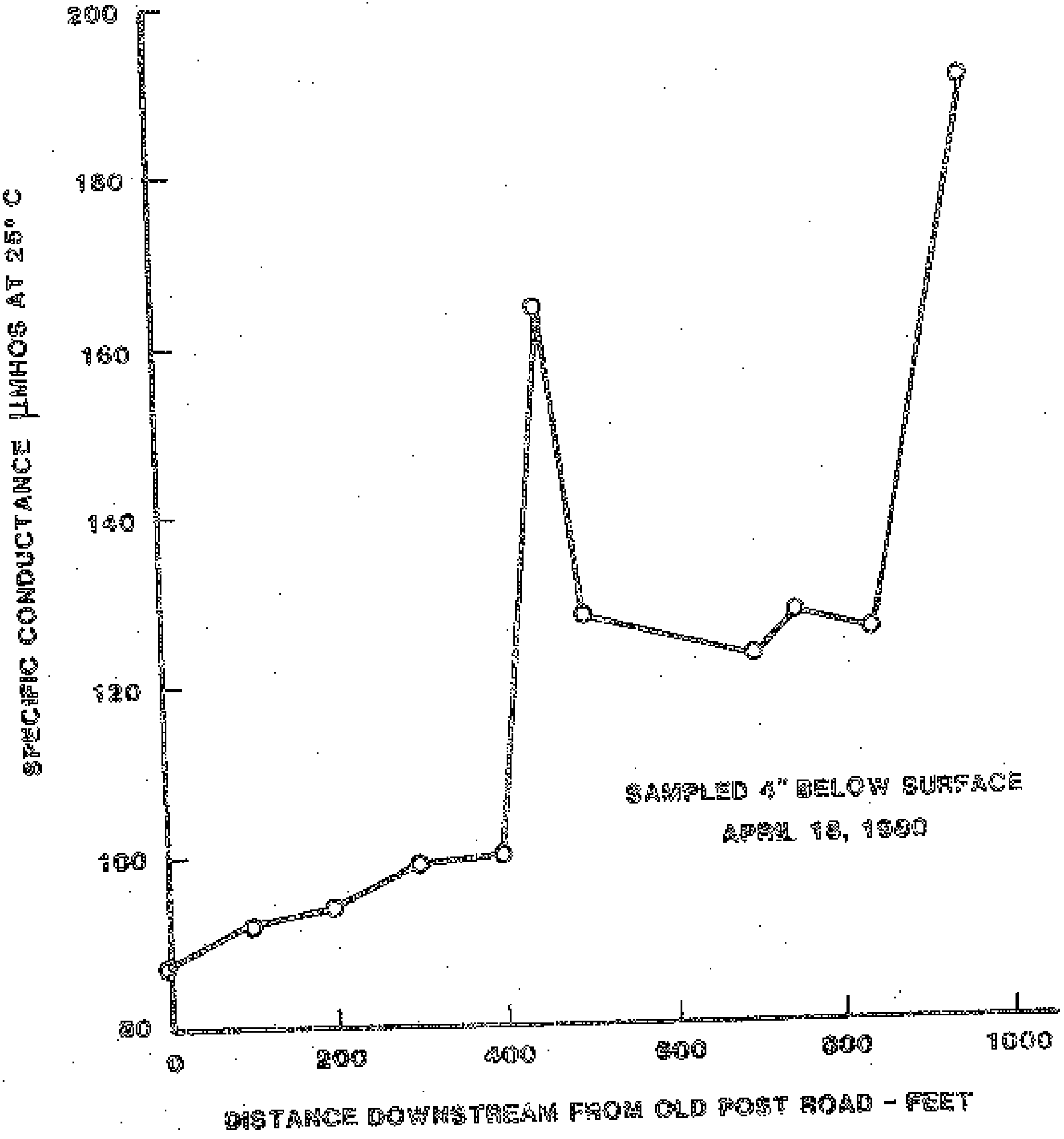

SPECIFIC CONDUCTANCE μMHOS AT 25° C
200
180
160
140
120
100
80
0
200
400
600
800
1000
DISTANCE DOWNSTREAM FROM OLD POST ROAD - FEET
SAMPLED 4" BELOW SURFACE
APRIL 18, 1990

Figure 13.

Table 10.

Water Quality Results
(mg/l)

Well or Identification	Sodium	Potassium	Calcium	Magnesium	Chloride	Nitrate	Sulphate
13	128	1.0	12.8	5.8	172	2.9	33
14	53.9	.2	4.0	8.2	72	.6	14
High values, Lower Pawcatuck*	16	3.4	9.5	3.1	23	14.3	17
Low values, Lower Pawcatuck*	2.7	.6	2.4	.2	3.2	0.0	4.1

*From Gonthier, et al., 1974.

> "The most abundant impurity is calcium sulfate with trace amounts of calcium carbonate, magnesium carbonate, silicon dioxide and ferric oxide."

The elevated values of calcium, magnesium, and sulphate appear to be consistent with the salt pile as a source.

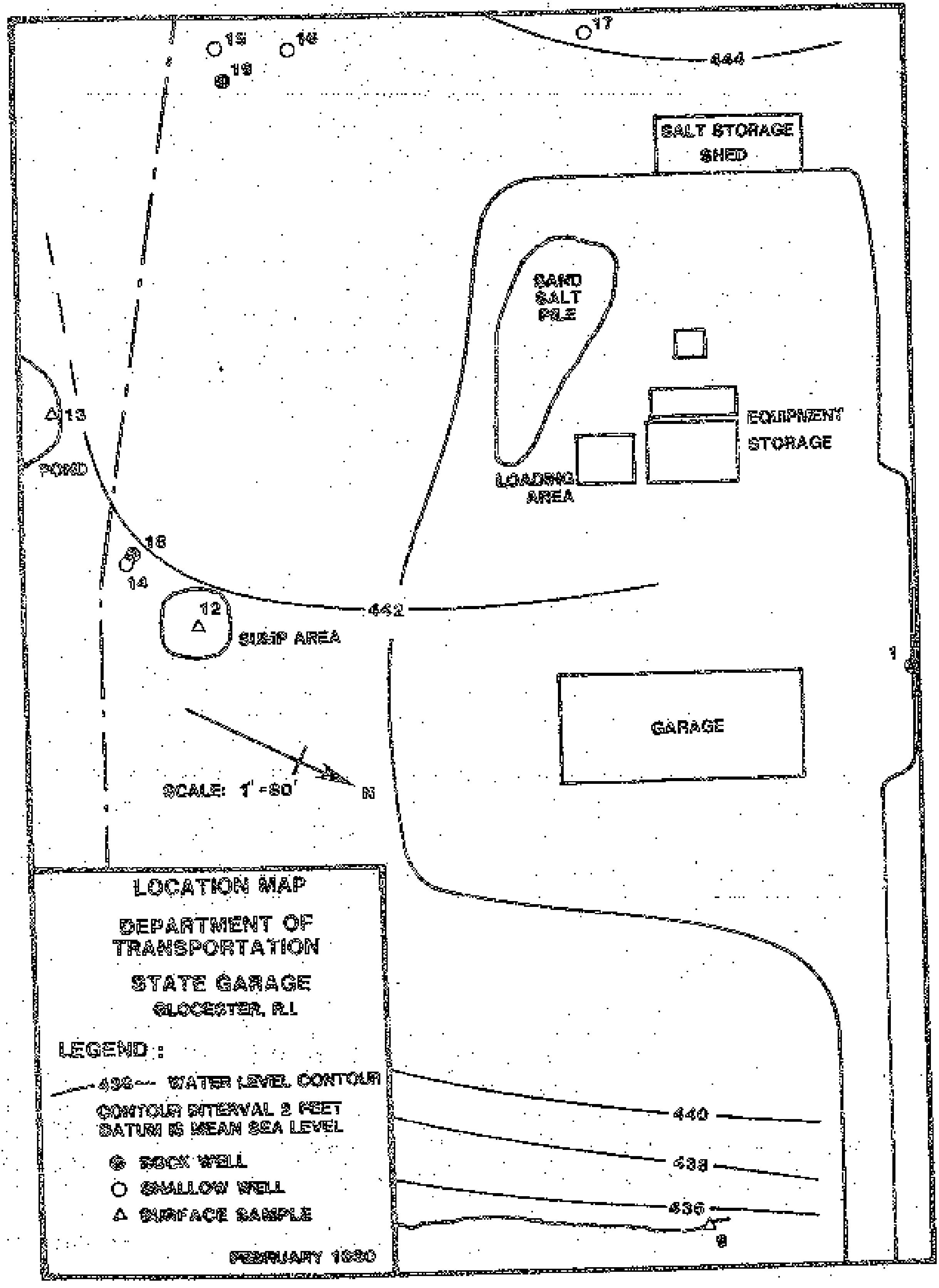
Although additional analysis could be done, it is reasonable to conclude at this point that runoff from salt storage is the cause of pollution at both wells. It is interesting to note that bedrock wells are not being affected. The reason is probably that the bedrock is discharging to the stratified drift in this area. Thus, rock replacement wells would appear to solve the immediate problem, provided they are not drilled too deep.

Glocester

The location of the deep monitoring wells (18,19), the well points (14,15,16,17), the garage well (1), and two surface sampling locations are shown in Figure 14.

Wells 18 and 19 are 70 and 59 feet deep, respectively. They were drilled with an air-rotary machine and are cased with 19 and 9 feet, respectively, of 6" diameter casing seated into the bedrock. The material above the bedrock appears to be outwash. This site was originally selected as a bedrock site and there are numerous bedrock outcrops in the area (8). The site is probably on or immediately adjacent to the till bedrock-outwash contact. Surface drainage is south by Peeptoad Brook.

The direction of ground water flow based on measurements made on February 13, 1980 is to the east towards Route 44. Figure 15 shows selected data for the Glocester site. Well 17, which is a well point just west of the salt storage shed, is relatively clean and will be used as a control well; all of the other sampling wells and surface water locations show evidence of salt. The highest levels are in the sump area southeast of the sand-salt pile. This area and the area to the southwest where wells 15, 16 and 19 are located appear to receive direct runoff from the sand-salt area. At both locations the shallow well points show higher levels of salt than the deeper wells, although the deep wells show significant levels. The well and



15
16
17
19
444
SALT STORAGE SHED
SAND SALT PILE
EQUIPMENT STORAGE
LOADING AREA
13
POND
18
14
12
442
SUMP AREA
1
GARAGE
SCALE: 1" = 80'
N
LOCATION MAP
DEPARTMENT OF TRANSPORTATION
STATE GARAGE
GLOCESTER, R.I.
LEGEND:
436 — WATER LEVEL CONTOUR
CONTOUR INTERVAL 2 FEET
DATUM IS MEAN SEA LEVEL
ROCK WELL
SHALLOW WELL
SURFACE SAMPLE
FEBRUARY 1990
440
438
436
9

Figure 14.

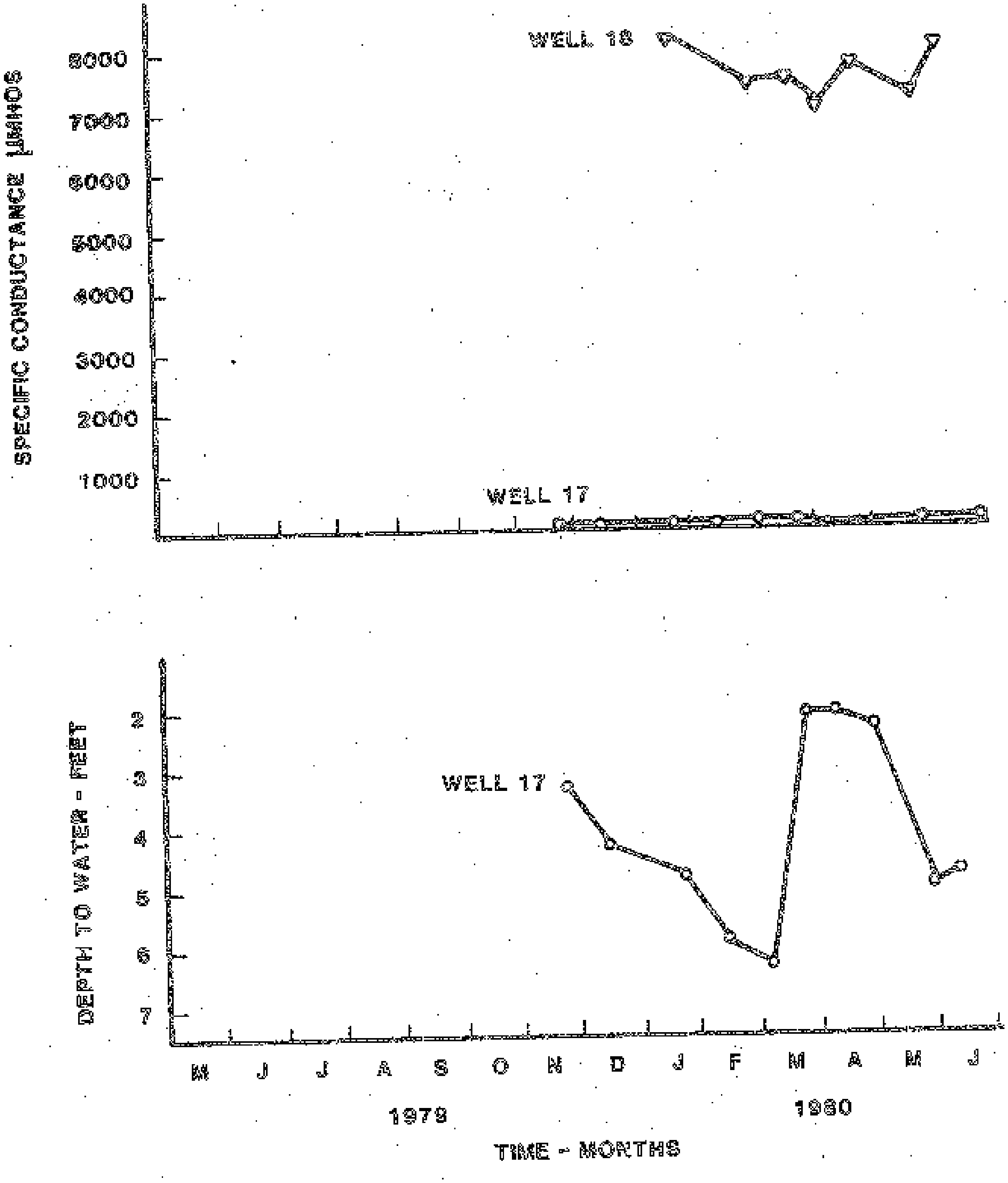

WELL 18
8000
7000
6000
5000
4000
3000
2000
1000
SPECIFIC CONDUCTANCE µMHOS
WELL 17
DEPTH TO WATER - FEET
2
3
4
5
6
7
WELL 17
M
J
J
A
S
O
N
D
J
F
M
A
M
J
1979
1980
TIME - MONTHS

Figure 15.

surface water data indicate that significant amounts of salt are leaving the site.

Little Compton

The locations of the deep monitoring wells (21,22), the well points (18,19,20), the garage well (15) and two additional sampling points (16 and 17) are shown in Figure 16. The deep wells were installed by the air rotary method. The wells are cased with 6" diameter casing into the bedrock. Wells 21 and 22 are 65 and 62 feet deep, and the depth to bedrock at each location is 16 and 14 feet, respectively. The water level data collected on site and in the survey (Figure 5) suggest that surface runoff and ground water flow are generally to the east.

The regional flow pattern is very uncertain. Some surface runoff appears to be draining to a swamp east of the site and just north of sampling point 18. The high salt levels at well 16 appear to be due primarily to runoff to the drainage ditch along Willow Avenue, infiltrating to the ground water just to the west of that well. Chlorides were measured in the drainage ditch (sampling point 17) and ranged from a low of 180 ppm to more than 15,000 ppm.

The data collected on site indicates significant amounts of salt are leaving the site. Well 15, the garage supply well, shows evidence of salt with an increase in chloride concentration from 28 to 130 ppm during the March recharge. Well 13, a shallow domestic well north of the site, had chlorides of 30 ppm or below.

Sampling point No. 6 which is an unnamed stream flowing south of the site shows evidence of salt runoff with chloride values ranging from 67 to 110 ppm during the sampling period.

Routes 95 and 3 Site

The fourth site investigated is a storage site located within the proposed Big River Reservoir area. No deep monitoring wells were installed at this site. All the sampling was through shallow well points or surface water sampling. Figure 17 shows the locations of all the sampling points. Results from the August, 1980, survey indicate very high levels of

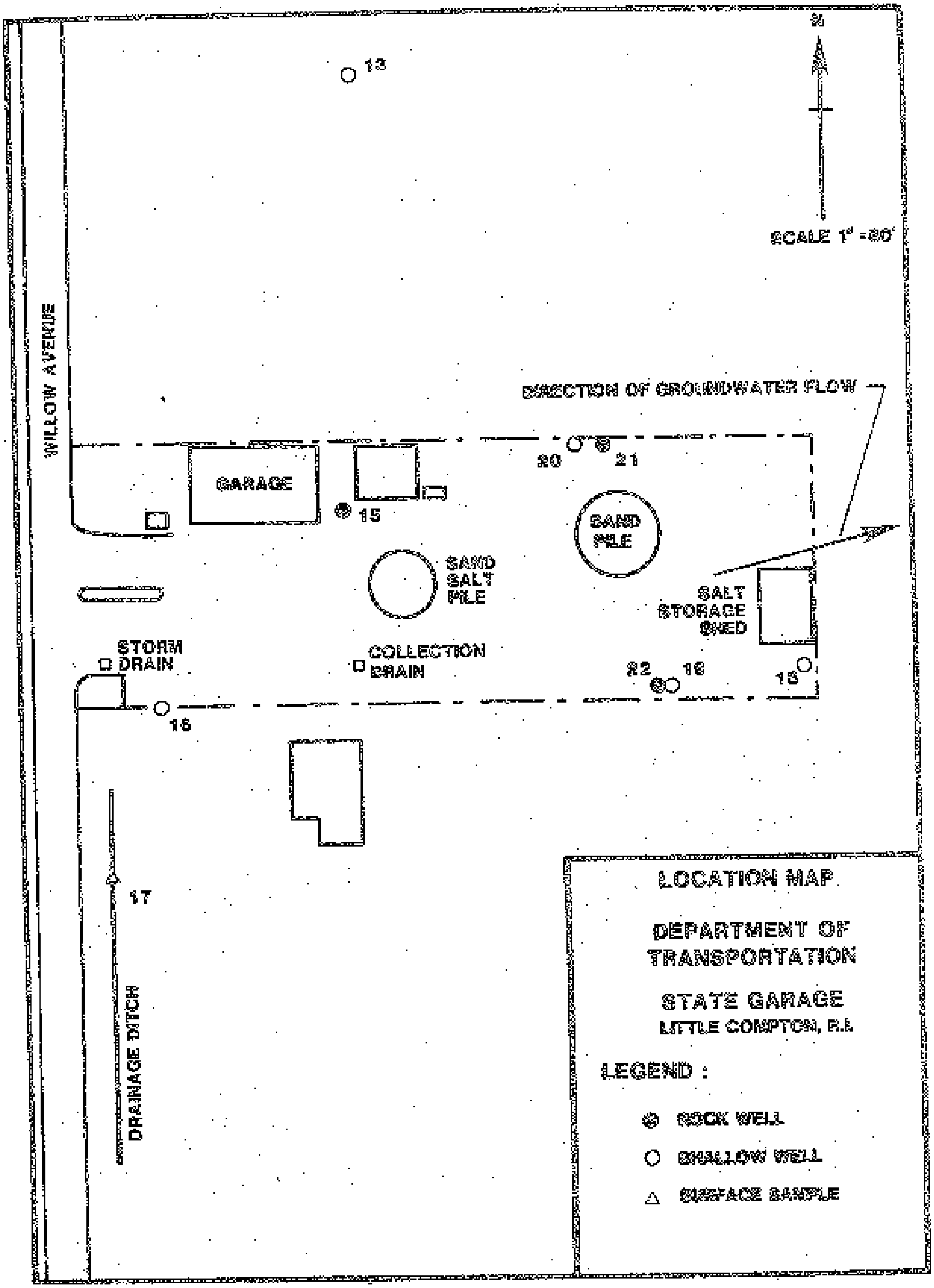

N
SCALE 1" =20'
13
WILLOW AVENUE
DIRECTION OF GROUNDWATER FLOW
20
21
GARAGE
15
SAND PILE
SAND SALT PILE
SALT STORAGE SHED
STORM DRAIN
COLLECTION DRAIN
22
19
18
16
17
DRAINAGE DITCH
LOCATION MAP
DEPARTMENT OF TRANSPORTATION
STATE GARAGE
LITTLE COMPTON, R.I.
LEGEND :
ROCK WELL
SHALLOW WELL
SURFACE SAMPLE

Figure 16.

chloride in an unnamed stream which appears to start beneath the site. The levels in the shallow wells are by contrast relatively low.

Allen, Johnston and Mason (1) indicate the site to be in glacial outwash with ground water flow to the south towards Cadwell Mill Pond just east of Sawmill Road. The pond drains to the west where it joins Big River.

The sand-salt and salt pile are located on what appears to be a rock fill covered with sand. Collapse holes are evident where sand has been washed down into the rock fill. The site appears to be highly pervious although there is evidence of some surface runoff.

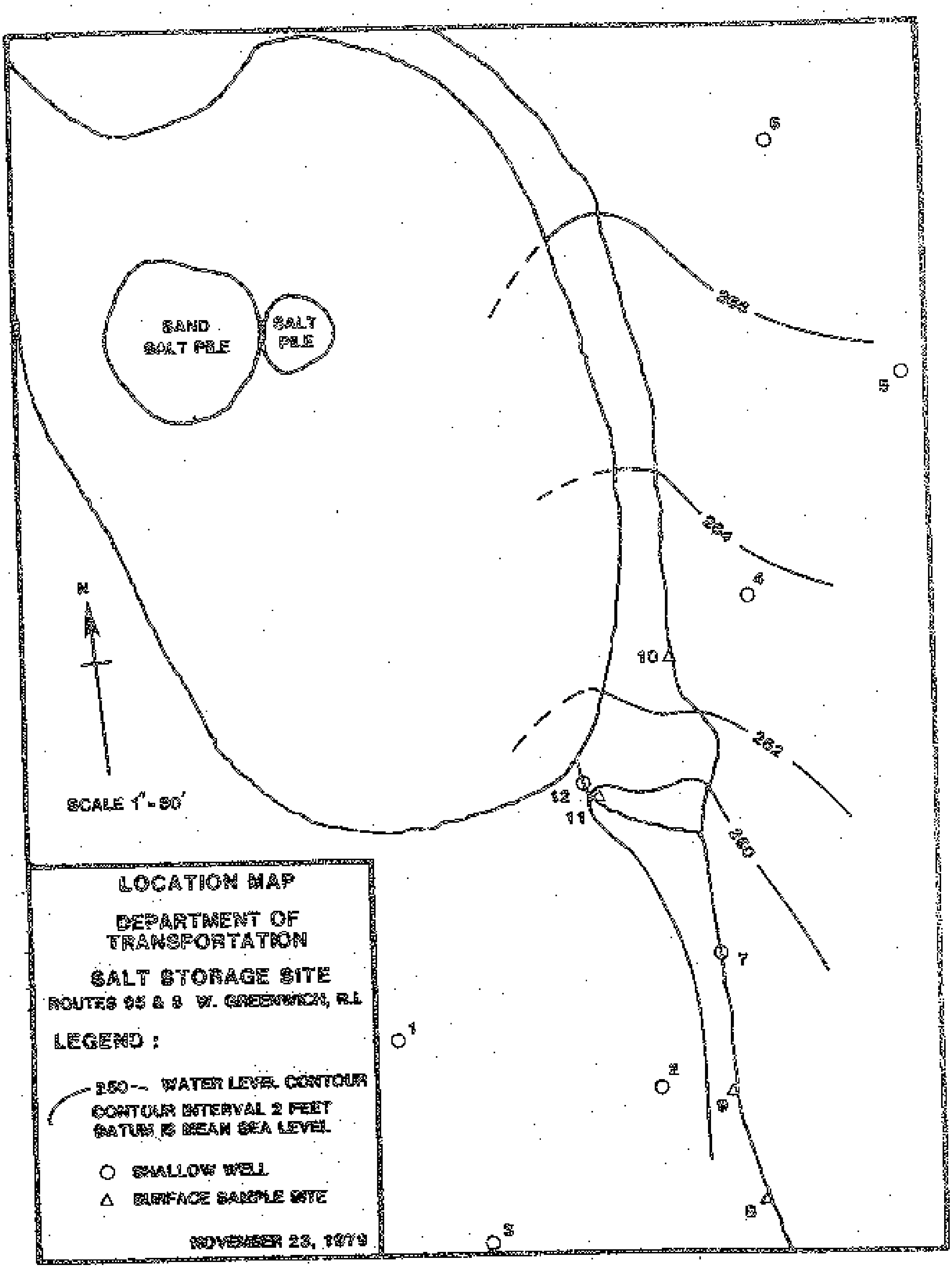
Wells 5 and 6 to the east of the pile are essentially unaffected. Measured chloride values ranged from 5 to 14 ppm at well 5, and 7 to 43 ppm at well 6. At surface sampling point 11 which is just below the edge of the fill, chlorides ranged from 2600 to more than 11,000 ppm during the same period. Figure 18 shows the average values for sampling points 7 and 8. These results indicate considerable runoff of salt from the site on a continuing basis.

A temporary plywood V-notch weir was installed to estimate the flow from beneath the site. On June 20, 1980, the flow was estimated to be .017 cfs at the approximate location of sampling point 11 in Figure 17. The salt (NaCl) concentration was measured and found to be 13,200 mg/l. This means that approximately 1200 lbs/day of salt was leaving the site at the time the measurement was made.

Based on the average of the salt delivered to the site over the last three years, this single measurement indicates a loss of about 11% of stored salt per year. This agrees closely with a 10 percent loss which would be predicted based on an average rainfall of 40 in/yr and the assumption that ¼% of the salt per inch of annual rainfall is lost from uncovered piles.

Control Measures

Covering of all salt storage and sand-salt mixtures is the long-term solution to eliminating salt runoff from storage areas. Construction of permanent storage facilities should be part of the establishment of new sites and any relocation of



SAND SALT PILE
SALT PILE
266
264
262
260
N
SCALE 1"=80'
1
2
3
4
5
6
7
8
9
10
11
12
LOCATION MAP
DEPARTMENT OF TRANSPORTATION
SALT STORAGE SITE
ROUTES 95 & 3 W. GREENWICH, R.I.
LEGEND :
250 — WATER LEVEL CONTOUR
CONTOUR INTERVAL 2 FEET
DATUM IS MEAN SEA LEVEL
○ SHALLOW WELL
△ SURFACE SAMPLE SITE
NOVEMBER 23, 1979

Figure 17.

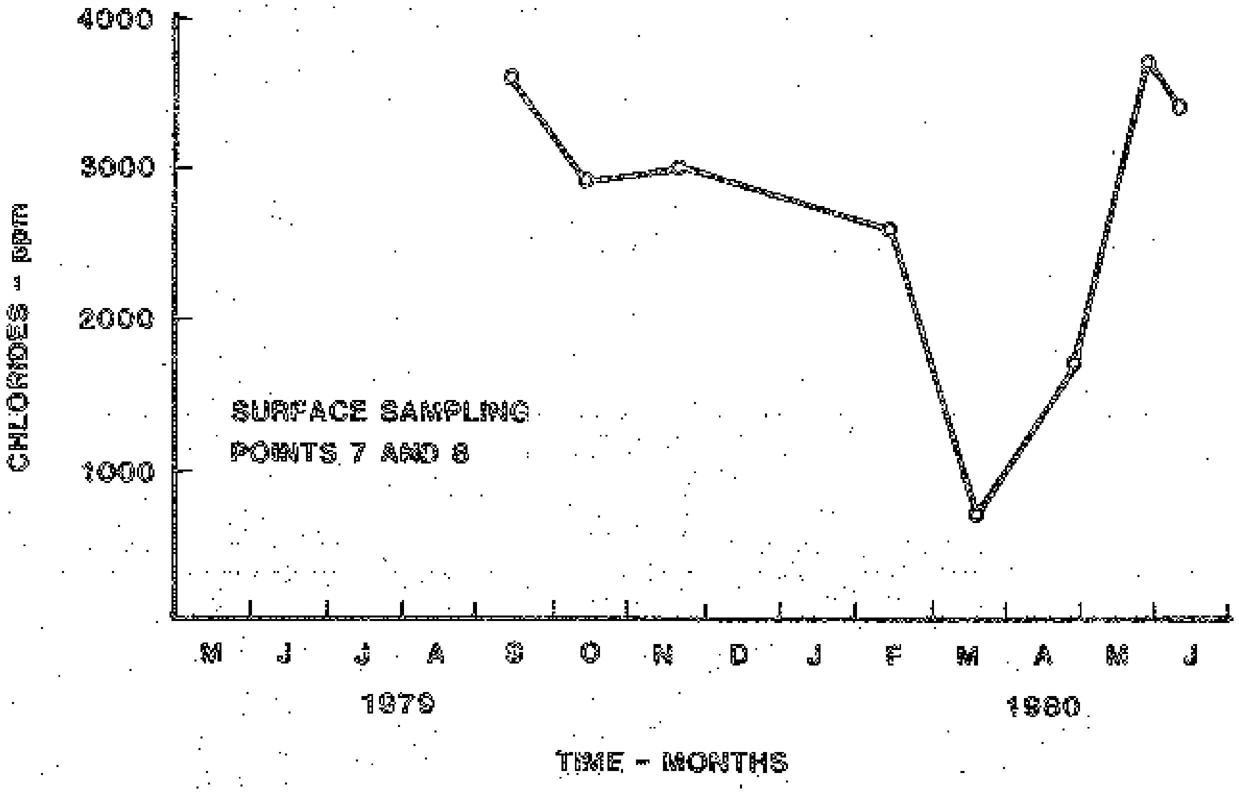

4000
3000
2000
1000
CHLORIDES - ppm
SURFACE SAMPLING
POINTS 7 AND 8
M
J
J
A
S
O
N
D
J
F
M
A
M
J
1979
1980
TIME - MONTHS

Figure 18.

existing facilities.

A survey was made of 13 agencies to determine their recent experience with salt storage and their current storage policies; the results are tabulated in Table 11. The trend is clear, salt is generally being stored in permanent structures, and in some cases the sand-salt mixtures. This is a relatively expensive proposition as indicated by cost data provided by several of the agencies and the EPA manual (15).

It is probably important to note that even if money were immediately available for permanent structures in Rhode Island some of the storage areas probably lack sufficient area for efficient storage and loading. The RIDOT needs to evaluate all garage and storage sites with regard to their overall adequacy, and in particular whether the sites can be upgraded to eliminate salt runoff. Each site should be considered with respect to the magnitude of impacts on water quality if there is salt runoff and whether the site is adequate to meet the Department's future needs including storage of salt in permanent structures with protected loading areas.

Some sites already have salt storage sheds and it should be possible to upgrade these sites at modest cost. One problem observed with several sheds is that surface drainage is directed through the shed. This is the case at Little Compton. Improving surface drainage so that it is diverted around or away from the sheds would reduce salt runoff. Where the floors of salt sheds are not paved, floors should be added.

Sand-salt mix is stored uncovered at all sites. Although it is difficult to separate runoff from salt areas, salt spillage and the sand-salt piles, the sand-salt piles appear to be a major source of salt runoff. In some cases relocation of the salt-sand piles and improvement of surface drainage would reduce salt runoff. Diversion of runoff to nearby streams could in some cases protect domestic wells, albeit with some reduction in surface water quality. Reasonable estimates of the salt loading on a stream and the dilution available can be made based on the data collected.

Figure 19 is a plot which shows the estimated increase in chloride runoff from a basin, assuming that 1/4% of the salt

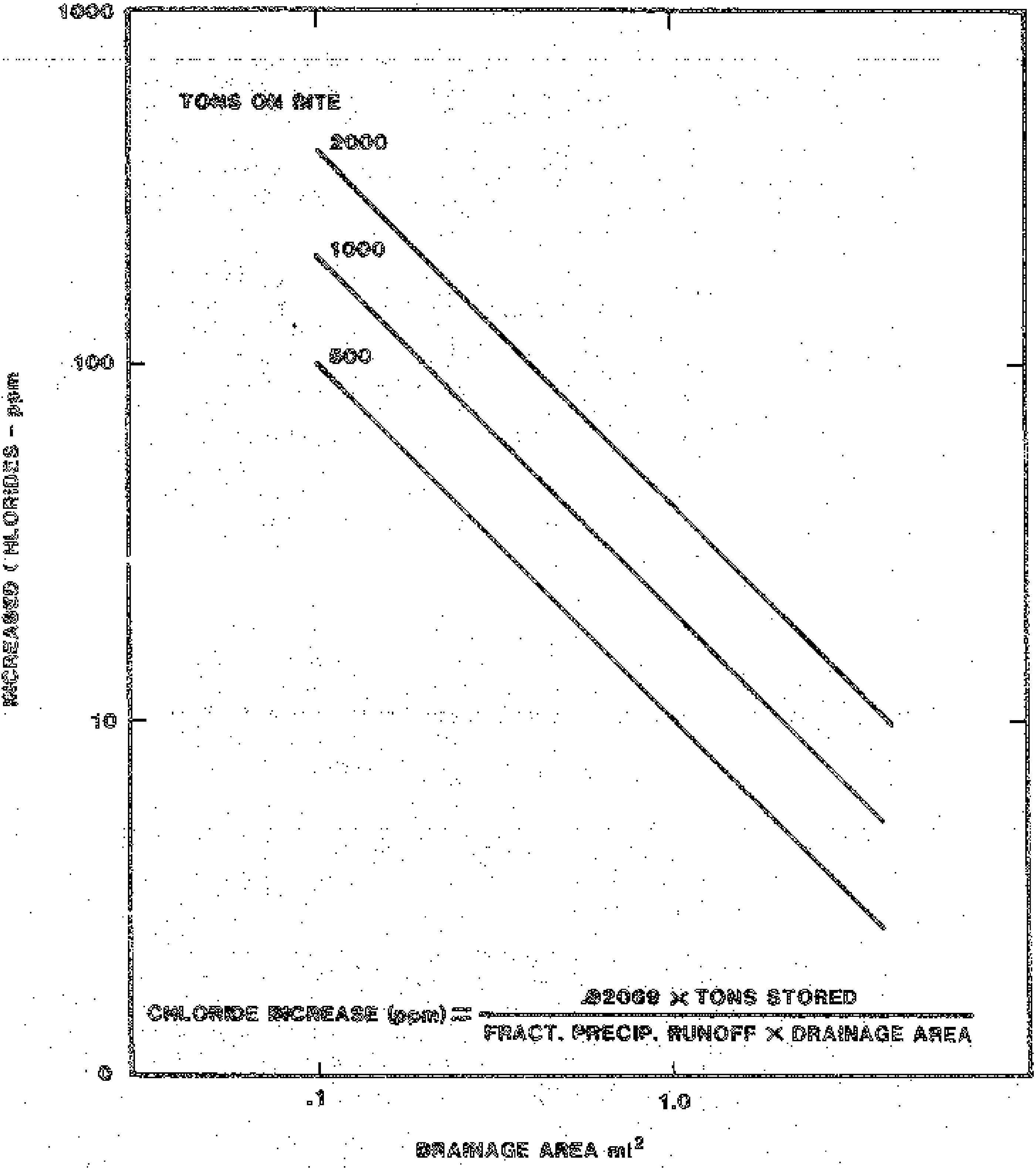

TONS ON SITE
2000
1000
500
1000
100
10
0
INCREASED CHLORIDES - ppm
CHLORIDE INCREASE (ppm) = .02069 × TONS STORED / FRACT. PRECIP. RUNOFF × DRAINAGE AREA
.1
1.0
DRAINAGE AREA mi²

Figure 19.

Table 11. Summary of Salt Storage Practices

	Covered Salt Storage	Permanent Salt Storage Structures	Type of Structure	Comments
Commonwealth of Mass.	yes	some	Wood frame	Moving to 100% storage in permanent salt sheds
Connecticut	yes	some	Wood	Storage capacity about 26,000 tons or 40% of annual use
Indiana	yes	some	-	100% inside storage within 5 yrs
Mass. Turnpike	yes	most	Wooden arch Wooden Rigid frame	1 of 9 site not in permanent structure
Maine	yes	some	Building constructed by M DOT	Capacity to store 50% of annual use; recognize leaching of salt-sand mix as a problem
Michigan	yes	some	Covered bins	Moving to completely closed systems of covered bins, paved handling areas, and lagoon runoff storage from covered bins, salt-sand piles and truck washing areas
New Hampshire	yes	some	Pole barn type wooden sheds	60,000 tons stored inside 60,000 tons in temporary storage on covered pads
NYS Thruway	yes	some	Concrete block Pole Domar	4 or 5 locations to upgrade; One in 1980 budget
No. Carolina	yes	some	Gravity bins Sheds; Sliding cribs; Domar	Storage capacity is 63,200 tons
Ohio	yes	some	Shed type	Increasing to 75% of annual use storage capacity
Ontario	yes	all	Sheds	Sand-salt mixture is stored in Dome Building
Rhode Island	some	some	Pole	
Vermont	yes	some	Pole Quonset Metal frame	Capacity of buildings between 60 and 70 percent of annual usage

stored per annual inch of precipitation will runoff and be diluted in the fraction of precipitation that actually becomes runoff. It can be seen that small drainage basins or headwaters of small basins should be avoided. If the runoff area available for dilution is greater than 5 mi^2, the impact is negligible (less than 10 ppm increase).

Paved areas are recommended for storage and handling of salt. Several areas that are not paved could be paved and at the same time drainage improved. Curbing may be used to divert drainage. Paved areas would make it easier to recover or divert salt runoff and recover spillage.

A possible remedial measure is to use recovery wells and evaporation lagoons at sites where ground water pollution is of concern. Recovery wells would be operated during the summer to recover salt runoff from the previous winter. Brine would be evaporated and the salt recovered. The ground itself would serve as a brine storage tank. Areas in rock and till would be the best candidates for this approach since the quantity of water handled would be less.

The feasibility of this approach could be tested at the Glocester or Little Compton site. First, estimates would have to be made of the quantity of water that would be pumped, rates of evaporation during the summer, and the area that would be needed for storage. If the approach appears feasible, a pilot study could be done using one or both of the existing deep monitoring wells. This approach is a variation of what is apparently being done in Michigan, storing surface runoff in lagoons year round.

Several sites are using brine tank storage facilities. These are not recommended as long term solutions since, if they fail, they pose a more severe threat to ground water than if they did not exist (15). The Rhode Island Department of Transportation should review the status of all brine storage facilities and insure that adequate operating procedures and safeguards have been established at each garage to insure both proper operation and maintenance. Properly maintained brine disposal tanks with overflow protection to nearby surface streams would appear to offer excellent low cost protection at many Rhode Island sites. This is on the assumption that brine can be discharged to nearby salt water bodies or into larger rivers. If this is not the case, then their effectiveness goes down dramatically.

Conclusions

The salt storage sites investigated are degrading surface and ground water in their immediate areas and some distance away. The effects on ground water are most severe primarily because of the limited dilution available.

Salt and sand-salt piles should be covered, preferably in permanent structures. This should be the goal. A priority plan should be implemented to upgrade sites in the order of the severity of existing problems. Although covered storage is the long-term solution, interim approaches are needed. Priority should be given to correcting problems at the four sites monitored. Two of the sites have salt sheds. The Glocester shed appears to be performing adequately, but surface drainage at the Little Compton site should be improved. At both sites the amount of salt-sand mix stored on site should be reduced. Areas where sand-salt mix is stored, mixed, and loaded should be paved so that improved housekeeping can be initiated. Runoff from the paved areas should be directed to a point where its effect is minimized if possible. A conscious effort to reduce and control salt runoff will bring results. The effectiveness of the control measures should be assessed by continued monitoring of specific conductance at the monitoring points.

Of the four sites monitored, the Routes 95 and 3 site is the one most difficult to evaluate. Upgrading this site would probably involve a significant expenditure of money which may not be warranted. If the site cannot be covered, then it should be relocated outside the proposed Big River reservoir area.

As the four sites monitored are upgraded, decisions on courses of action for the other sites listed in Table 1 should be made. Upgrading at the other sites should be based on effective procedures established with the first four sites.

APPENDIX A. References

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APPENDIX B.

Table 1.--Description of Wells

	Number	Installed	Owner	Altitude of LSD (ft)	Depth of Hole (ft)	Well Type	Well Diameter (in)	Well Screen Interval (ft)	Well Use	Well Depth to Bedrock (ft)	Measuring Point Elevation	Water Level Depth From Measuring Point (ft)	Water Level (date)	Water Bearing Material
R95&3	1	7/6/79	URI	267.0	4.2	OP	4.5	–	O	–	267.25	1.21	4/30/80	sand
	2	7/6/79	URI	262.3	4	OP	4.5	–	O	–	263.75	2.00	4/30/80	sand
	3	7/6/79	URI	264.8	5	OP	4.5	–	O	–	266.34	2.58	4/30/80	sand
	4	7/6/79	URI	263.8	3	OP	3.0	–	O	–	264.17	0.71	4/30/80	sand
	5	7/6/79	URI	267.6	4.5	OP	4.5	–	O	–	269.08	2.41	4/30/80	sand
	6	7/6/79	URI	267.5	4.5	WP	1.25	3.–4.5	O	–	271.5	3.25	4/30/80	sand
	7	8/24/79	URI	258.7	3.5	WP	1.25	2.–3.5	O	–	262.42	3.25	4/30/80	sand
	12	9/21/79	URI	260.3	3.5	WP	1.25	2.–3.5	O	–	264.06	3.31	4/30/80	sand
CN	1	1976	DOT	22.0	400	–	–	–	H	–	–	–	–	rock
	2	–	Melish	24.8	17	DUG	36	–	U	–	26.03	14.80	2/20/80	sand
	3	–	Melish	19.1	12	DUG	30	–	U	–	19.76	11.00	2/20/80	sand
	4	–	Melish	25.0	–	DRL	–	–	H	–	–	–	–	–
	22	11/79	URI	22.8	10.25	WP	1.25	8.75–10.25	O	–	24.56	–	–	sand
	23	11/79	URI	23.5	12.4	WP	1.25	10.9 –12.4	O	–	27.42	16.00	2/20/80	sand
	24	1/80	URI	23.5	58.5	T	1.25	8.5 –58.5	O	–	24.86	13.19	2/20/80	sand
	25	1/80	URI	22.8	58.3	T	1.25	8.3 –58.3	O	–	25.02	13.62	2/20/80	sand
GL	1	–	DOT	450.0	–	–	–	–	H	–	–	–	–	rock
	4	–	Kuvaska	440.0	75–80	–	–	–	H	–	–	–	–	rock
	14	10/79	URI	448.1	10	WP	1.25	8.5 –10.	O	–	450.06	8.21	3/05/80	s&g
	15	10/79	URI	449.6	9	WP	1.25	7.5 – 9.	O	–	452.60	9.34	3/05/80	sand
	16	10/79	URI	448.8	6	WP	1.25	4.5 – 6.	O	–	449.77	6.62	3/05/80	sand
	17	10/79	URI	448.7	5.8	WP	1.25	4.3 – 5.8	O	–	449.93	6.34	3/05/80	till
	18	12/79	URI	448.1	70	DRL	6	–	O	19	449.39	7.51	3/05/80	rock
	19	12/79	URI	449.4	59	DRL	6	–	O	9	450.60	8.22	3/05/80	rock
LC	9	1961	Farm	95.0	225.	DRL	–	–	H	–	–	–	–	rock
	13	–	Bouchard	–	22	DUG	36		H	22				till
	15	1974	DOT	80.5	300.	DRL	–	–	H	–	–	–	–	rock
	16	–	Briggs	78.5	14	DUG	30	0	H	14?	80.00	5.15	3/07/80	till
	18	11/79	URI	79.0	12	WP	1.25	11.75–12.	O	–	80.94	5.36	3/07/80	till
	19	11/79	URI	81.3	10.5	WP	1.25	10.25–10.5	O	–	82.76	6.75	3/07/80	till
	20	11/79	URI	80.6	11.5	WP	1.25	7.5 –11.5	O	–	83.10	7.97	3/07/80	till
	21	1/80	URI	80.6	65	DRL	6	–	O	16	82.15	7.40	3/07/80	rock
	22	1/80	URI	81.0	62	DRL	6	–	O	14	82.33	6.31	3/07/80	rock

Location: R95&3 – Routes 95 and 3 site
CN – Charlestown site
GL – Glocester site
LC – Little Compton site

Well Type: DRL – drilled well in rock
DUG – dug well
OP – open ended pipe
T – slotted PVC pipe
WP – well point

Water Use: H – domestic
O – observation
U – unused

Water Bearing Material: s&g – sand and gravel

APPENDIX B.

Table 2.--Water Levels in Observation Wells

Routes 95 and 3 Site

Date	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6
7/06/79	2.7	3.0	4.0	0.9	-	4.7
7/27/79	2.7	3.4	5.0	1.0	4.7	5.0
7/31/79	2.7	-	5.1	1.2	4.7	5.4
8/03/79	2.8	3.9	-	1.3	4.8	5.4
8/24/79	1.7	2.6	2.9	0.6	3.2	4.0
9/14/79	2.0	3.0	3.5	0.7	3.7	4.5
10/17/79	1.6	2.4	3.0	0.6	3.2	4.1
11/23/79	1.8	2.2	3.1	0.5	3.2	4.1
12/15/79	2.0	2.0	2.8	0.5	3.1	4.0
1/23/80	2.0	2.2	2.8	0.5	3.3	4.1
2/15/80	2.5	2.5	3.5	-	3.9	4.7
3/01/80	2.4	2.5	3.5	0.5	3.8	4.7
3/17/80	1.7	1.8	2.0	-	1.7	2.9
4/03/80	1.3	2.2	2.9	0.8	2.7	3.5
4/30/80	1.2	2.0	2.6	0.7	2.4	3.3
5/27/80	2.1	2.7	3.7	1.0	3.7	-

Charlestown Site

Date	Well 2	Well 3	Well 23	Well 24	Well 25
6/12/79	13.8	9.6	-	-	-
7/11/79	14.0	10.2	-	-	-
9/14/79	14.4	10.6	-	-	-
10/22/79	14.5	10.6	-	-	-
11/14/79	14.3	10.4	-	-	-
12/12/79	14.6	10.8	15.7	-	-
1/21/80	14.7	10.9	15.6	13.1	13.5
2/20/80	14.8	11.0	16.0	13.2	13.6
3/07/80	14.8	11.0	-	13.3	13.7
3/20/80	14.4	10.6	-	12.3	13.3
4/01/80	13.7	9.7	14.5	12.0	12.5
4/08/80	13.8	9.9	14.7	12.2	12.6
4/18/80	13.7	9.9	14.8	12.2	12.6
4/29/80	13.9	10.0	14.9	12.5	12.7
5/30/80	14.3	10.4	15.1	12.5	13.0
6/13/80	14.3	10.4	15.1	12.5	13.0

Glocester Site

Date	Well 14	Well 15	Well 16	Well 17	Well 18	Well 19
11/23/79	6.9	8.0	-	3.3	-	-
12/15/79	7.5	8.4	-	4.3	-	-
1/25/80	7.6	8.6	6.0	4.8	6.9	7.5
2/13/80	8.0	9.2	6.5	5.9	7.3	8.0
3/05/80	8.2	9.3	6.6	6.3	7.5	8.2
3/25/80	-	6.5	3.8	2.1	4.9	5.4
4/11/80	5.7	6.7	3.8	2.1	5.1	5.5
4/30/80	6.2	7.1	4.2	2.3	5.5	6.0
5/29/80	7.5	8.6	6.0	5.0	6.8	7.4
6/12/80	7.4	8.5	5.9	4.8	6.7	7.3

Little Compton Site

Date	Well 16	Well 18	Well 19	Well 20	Well 21	Well 22
9/21/79	9.0	-	-	-	-	-
10/26/79	5.1	-	-	-	-	-
11/14/79	3.0	3.0	4.5	4.9	-	-
12/15/79	2.7	3.2	4.4	5.3	-	-
1/02/80	3.3	4.1	5.0	5.9	-	-
2/18/80	5.0	5.0	6.6	8.0	7.3	6.2
3/07/80	5.2	5.4	6.8	8.0	7.4	6.3
3/25/80	1.6	2.7	3.2	3.3	2.8	2.9
4/11/80	-	2.9	3.6	3.8	3.1	3.2
5/05/80	2.7	3.7	4.3	5.2	5.3	4.0
5/29/80	4.3	4.9	5.9	7.1	6.3	5.5
6/12/80	3.9	4.3	5.7	7.5	6.3	5.3

APPENDIX B.

Table 3.--Specific Conductance

(micro mhos/cm at 25 degrees C;
all measurements were made in the laboratory
except those indicated with an asterisk]

Routes 95 and 3 Site

Date	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7
7/06/79	160*	130*	120*	320*	80*	100*	-
7/27/79	-	-	-	330*	-	-	-
8/03/79	-	200	-	340	120	210	-
8/24/79	230	160	115	450	87	102	-
9/14/79	235	130	110	630	90	210	1160
10/17/79	-	128	100	622	53	106	1300
11/23/79	220	125	100	510	55	95	1250
12/16/79	200	85	125	530	53	85	-
1/23/80	190	131	92	490	56	94	-
2/15/80	172	129	92	420	58	110	-
3/1/80	170*	109*	76*	-	52*	103*	-
3/18/80	210	128	90	-	56	106	970
4/03/80	147*	121*	61*	280*	52*	112*	860*
4/30/80	185	128	80	328	60	87	995
5/27/80	198	153	91	415	70	94	990

Routes 95 and 3 Site

Date	Surface 8	Surface 9	Surface 10	Surface 11	Well 12
8/24/79	8800	8900	1320	21500	-
9/14/79	8950	9260	1510	21800	-
10/17/79	9060	8870	1300	24500	1426
11/23/79	8200	8600	1330	25600	1050
12/16/79	8200	8820	1160	25000	1000
1/23/80	-	7180	1230	28300	1100
2/15/80	8600	9030	1290	21500	-
3/01/80	-	10600*	-	27200*	-
3/18/80	3540	3530	530	10600	1010
4/03/80	5180*	5320*	960*	8850*	1080*
4/30/80	5330	5540	820	12600	1450
5/27/80	8890	9880	1080	19750	1442
6/20/80	-	10000	-	18400	-

Charlestown Site

Date	Well 1	Well 2	Well 3	Well 4	Surface 7	Well 12	Well 13
5/23/79	125	-	-	-	85	-	-
6/12/79	-	1160	770	135	80	-	-
8/06/79	-	-	-	-	-	210	2510
9/14/79	140	1110	370	150	135	-	-
10/22/79	134	1050	270	133	86	-	-
11/14/79	180	950	305	125	85	-	-
12/12/79	130	850	435	125	65	-	-
1/21/80	133	735	504	-	88	-	-
2/20/80	157	608	473	135	90	-	-
3/07/80	130*	425*	390*	-	-	-	-
3/20/80	140	531	253	-	88	-	-
4/01/80	137	564	492	-	-	-	-
4/03/80	142	592	575	159	-	225	1130
4/08/80	-	540*	330*	-	94*	-	-
4/16/80	119*	564*	660*	-	82*	-	-
4/29/80	-	707	656	-	86	-	-
5/30/80	138	850	657	-	90	-	540
6/30/80	140	870	550	133	85	-	-

Charlestown Site

Date	Surface 15S	Well 16	Well 18	Well 20	Well 23	Well 24	Well 25
8/06/79	-	255	520	205	-	-	-
9/14/79	110	-	-	-	-	-	-
10/22/79	84	-	-	-	-	-	-
11/14/79	85	-	-	-	-	-	-
12/12/79	75	-	-	-	680	-	-
1/09/80	-	-	-	-	670	1260	235
1/21/80	74	-	1460	-	513	105	200
2/20/80	81	-	1462	-	530	113	186
3/07/80	65*	-	-	-	452*	106*	146*
3/20/80	76	-	1100	-	660	275	187
4/01/80	-	156	1450	-	840	140	167
4/03/80	80	-	-	414	875	184	161
4/08/80	69*	-	-	-	560*	105*	158*
4/18/80	66*	-	936*	-	820*	93*	185*
4/29/80	71	-	870	-	984	105	1066
5/30/80	69	-	-	-	1106	108	810
6/13/80	74	-	560	-	930	106	[illegible]

Appendix B. Table 3.--Specific Conductance

Glocester Site

Date	Well 1	Well 4	Surf. 9	Surf.10	Surf.11	Surf.12	Surf.13
8/06/79	400	725	1170	3260	-	-	-
9/14/79	340	590	390	1230	125	5100	300
10/12/79	536	-	910	-	-	6270	230
11/23/79	290	410	620	310	80	-	240
12/15/79	565	420	650	350	70	16800	270
1/25/80	360	370	880	492	86	-	-
2/13/80	347	368	670	774	103	-	-
3/05/80	290*	-	-	654*	82*	-	-
3/25/80	300	430	1440	370	77	15000	-
4/11/80	291*	-	1300*	135*	67*	2040*	-
4/30/80	251	880	1070	200	63	1070	133
5/29/80	456	995	1680	550	79	-	-
6/12/80	352	858	880	429	77	-	149

Glocester Site

Date	Well 14	Well 15	Well 16	Well 17	Well 18	Well 19
11/23/79	14400	1210	-	50	-	-
12/15/79	11800	1760	-	45	-	-
1/25/80	11300	1450	3200	46	8200	350
2/13/80	8060	1480	-	45	8170	420
3/05/80	7250*	1360*	-	88*	7420*	450*
3/25/80	-	1150	-	155	7500	430
4/11/80	3340*	540*	360*	68*	7030*	510*
4/30/80	11280	790	1086	54	7790	950
5/29/80	11850	710	1440	90	7300	300
6/12/80	7700	770	1760	80	8250	352

Little Compton Site

Date	Surface 6	Well 9	Well 13	Well 15	Well 16	Surface 17
8/01/79	-	-	-	420	-	-
8/17/79	450	630	350	370	2350	-
9/21/79	-	675	385	400	4560	-
10/26/79	422	714	360	360	5530	770
11/14/79	290	675	345	375	6600	47000
12/13/79	280	-	-	340	8250	5900
1/02/80	400	625	290	450	7000	11300
2/18/80	-	623	286	352	4070	9900
3/07/80	-	-	-	320*	3270*	24650*
3/25/80	320	-	240	740	3900	8400
4/11/80	312*	-	-	796*	3250*	2231*
5/05/80	300	-	-	450	2650	2800
5/29/80	326	-	273	383	2420	2720
6/12/80	363	715	-	374	2750	500

Little Compton Site

Date	Well 18	Well 19	Well 20	Well 21	Well 22
11/14/79	24700	35700	2700	-	-
12/13/79	24700	11500	2300	-	-
1/02/80	25600	10000	1650	1400	-
2/18/80	26900	9030	4380	1540	14000
3/07/80	24900*	8400*	5260*	1500*	17300*
3/25/80	29700	10000	1600	1650	21500
4/11/80	24000*	7680*	897*	1540*	15700*
5/05/80	25000	8200	1000	1800	-
5/29/80	30100	8890	2520	1640	20700
6/12/80	29700	9240	3190	1705	22000

APPENDIX B.

Table 4.--Chlorides

(parts per million)

Routes 95 and 3 Site

Date	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7
8/03/79	-	42	-	-	14	33	-
8/24/79	54	29	26	112	10	13	-
9/14/79	80	49	44	167	10	43	328
10/17/79	-	26	25	195	8.0	11	371
11/23/79	-	31	27	172	5.0	13	370
12/16/79	40	25	23	200	8.0	7	-
1/23/80	44	28	23	140	14	16	-
2/15/80	48	34	26	125	10	17	-
3/18/80	64	35	18	-	6.8	10	280
4/30/80	46	35	19	88	-	14	260
5/27/80	51	44	23	121	12	13	332

Routes 95 and 3 Site

Date	Surface 8	Surface 9	Surface 10	Surface 11	Well 12
8/24/79	3350	3080	518	8000	-
9/14/79	3600	3500	519	8400	-
10/17/79	2900	2960	420	10420	465
11/23/79	3100	3200	410	11200	310
12/16/79	3100	3000	400	10800	370
1/23/80	-	2300	360	7900	310
2/15/80	3200	2000	360	8000	-
3/18/80	700	720	98	2600	280
4/30/80	1680	1720	212	4200	390
5/27/80	4000	4400	391	9000	540
6/20/80	-	3400	-	8000	-

Charlestown Site

Date	Well 1	Well 2	Well 3	Well 4	Surface 7	Well 12	Well 13
5/27/79	11	-	-	-	14	-	-
6/12/79	-	300	200	18	12	-	-
8/06/79	-	-	-	-	-	42	850
9/14/79	13	260	57	20	21	-	-
10/22/79	13	313	35	17	12	-	-
11/14/79	16	205	25	14	11	-	-
12/12/79	13	340	92	17	14	-	-
1/21/80	18	155	108	-	20	-	-
2/20/80	10	76	60	33	9.2	-	-
3/20/80	9.4	124	-	-	10	-	-
4/01/80	15	123	155	-	-	-	-
4/03/80	13	120	140	20	-	42	270
4/29/80	-	150	142	-	15	-	172
5/30/80	15.5	222	208	-	20	-	128
6/13/80	15	221	125	21	17	-	-

Charlestown Site

Date	Surf.15S	Well 16	Well 18	Well 20	Well 23	Well 24	Well 25
8/06/79	-	29	180	44	-	-	-
9/14/79	22	-	-	-	-	-	-
10/22/79	13	-	-	-	-	-	-
11/14/79	10	-	-	-	-	-	-
12/12/79	17	-	-	-	-	-	-
1/09/80	-	-	-	-	160	420	53
1/21/80	18	-	480	-	105	17	44
2/20/80	7.8	-	360	-	100	14	34
3/20/80	8.6	-	300	-	196	56	46
4/01/80	-	-	410	-	245	26	44
4/03/80	15	18	-	105	240	38	34
4/29/80	12.8	-	212	-	235	-	262
5/30/80	16	-	-	-	335	23	268
6/13/80	15	-	147	-	280	16	300

Appendix B, Table 4.--Chlorides

Glocester Site

Date	Well 1	Well 4	Surf. 9	Surf.10	Surf.11	Surf.12	Surf.13
8/06/79	59	210	340	362	-	-	-
9/14/79	52	153	102	470	35	1710	80
10/12/79	135	-	406	-	-	1960	52
11/23/79	37	114	149	92	19	-	71
12/15/79	140	125	260	130	19	8000	84
1/25/80	65	92	260	145	19	-	-
2/13/80	68	92	150	230	25	-	-
3/25/80	32	70	340	30	12	3800	-
4/30/80	36	264	315	54	17	328	36
5/29/80	113	350	600	200	24	-	-
6/12/80	64	222	252	120	20	-	44

Glocester Site

Date	Well 14	Well 15	Well 16	Well 17	Well 18	Well 19
11/23/79	4560	350	-	4.0	-	-
12/15/79	5100	720	-	4.0	-	-
1/25/80	5500	400	1200	18	3200	94
2/13/80	4300	420	-	9	3200	115
3/25/80	-	220	-	22	1960	64
4/30/80	3900	233	312	12	2960	272
5/29/80	5560	240	510	12	4000	97
6/12/80	2800	182	642	17	3600	90

Little Compton Site

Date	Surface 6	Well 9	Well 13	Well 15	Well 16	Surface 17
8/01/79	-	-	-	45	-	-
8/17/79	110	104	27	59	690	-
9/21/79	-	115	22	53	1450	-
10/26/79	99	118	19	55	1760	180
11/14/79	67	98	25	45	1760	17200
12/13/79	74	-	-	52	3200	3600
1/02/80	100	110	30	82	2200	3300
2/16/80	-	60	13	28	800	1800
3/25/80	76	-	17	130	920	2500
5/05/80	72	-	-	78	690	910
5/29/80	84	-	21	59	820	640
6/12/80	97	112	-	53	742	83

Little Compton Site

Date	Well 18	Well 19	Well 20	Well 21	Well 22
11/14/79	8600	12400	700	-	-
12/13/79	11600	3900	490	-	-
1/02/80	6800	3600	320	245	-
2/06/80	5800	1520	680	260	3200
3/25/80	7400	6600	390	370	6200
5/05/80	8800	2560	220	470	-
5/29/80	12400	3200	860	540	8340
6/12/80	12000	3160	900	520	8000

APPENDIX B.

Table 5.--Sodium
(parts per million)

Routes 95 and 3 Site

Date	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7
8/03/79	-	19	-	-	10	21	-
8/24/79	22	22	13	62	6	13	-
9/14/79	19	21	10	43	7	21	206
10/17/79	-	11	10	58	9	13	190
11/23/79	27	11	11	59	7	6	210
12/16/79	19	11	15	46	12	10	-
1/23/80	19	12	11	35	11	13	-

Routes 95 and 3 Site

Date	Surface 8	Surface 9	Surface 10	Surface 11	Well 12
8/24/79	2250	3000	320	5800	-
9/14/79	1950	2000	265	5500	-
10/17/79	1960	1880	240	8400	300
11/23/79	2200	2500	115	7600	160
12/16/79	2600	2400	240	9600	200
1/23/80	-	1320	210	6800	140

Charlestown Site

Date	Well 1	Well 2	Well 3	Well 4	Surface 7	Well 12	Well 13
8/06/79	-	-	-	-	-	26	385
9/14/79	8	155	37	12	21	-	-
10/22/79	12	190	36	17	12	-	-
11/14/79	15	-	38	19	11	-	-
12/12/79	11	170	72	11	14	-	-
3/20/80	20	100	68	-	23	-	-
4/03/80	9	84	81	-	-	24	190
4/29/80	-	-	-	-	-	-	128

Charlestown Site

Date	Surface 15S	Well 16	Well 18	Well 20	Well 23	Well 24	Well 25
8/06/79	-	16	84	27	-	-	-
9/14/79	11	-	-	-	-	-	-
10/22/79	12	-	-	-	-	-	-
11/14/79	13	-	-	-	-	-	-
12/12/79	19	-	-	-	115	-	-
3/20/80	14	-	230	-	180	40	34
4/03/80	-	11	-	50	125	26	25

Appendix B, Table 5.--Sodium

Glocester Site

Date	Well 1	Well 4	Surf. 9	Surf.10	Surf.11	Surf.12	Surf.13
8/06/79	28	122	174	208	-	-	-
9/14/79	19	93	66	215	16	1020	52
10/12/79	38	-	180	-	-	1600	42
11/23/79	23	84	110	58	16	-	50
12/15/79	60	100	205	94	23	7200	76
1/25/80	62	90	190	105	23	-	-

Glocester Site

Date	Well 14	Well 15	Well 16	Well 17	Well 18	Well 19
11/23/79	-	230	-	4.0	-	-
12/15/79	6000	540	-	11	-	-
1/25/80	3200	300	1040	22	2200	78

Little Compton Site

Date	Surface 6	Well 9	Well 13	Well 15	Well 16	Surface 17
8/01/79	-	-	-	23	-	-
8/17/79	54	45	12	21	440	-
9/21/79	-	51	15	24	740	-
10/26/79	54	58	60	28	1120	155
11/14/79	40	44	13	15	1220	12400
12/13/79	39	-	-	27	1220	2600
1/02/80	65	62	26	47	1520	2800
2/18/80	-	-	-	-	720	1520
3/25/80	56	-	14	100	840	2200

Little Compton Site

Date	Well 18	Well 19	Well 20	Well 21	Well 22
11/14/79	6400	8400	240	-	-
12/13/79	6000	2000	400	-	-
1/02/80	6000	3000	280	90	-
2/18/80	3600	1080	-	150	2600
3/25/80	6400	3000	270	290	5600

APPENDIX B.

Table 6.--Cyanide
(parts per million)[a]

Routes 95 and 3 Site

Date	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7
9/14/79	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.
1/23/80	N.D.	N.D.	N.D.	0.15	N.D.	0.2	N.D.

Routes 95 and 3 Site

Date	Surface 8	Surface 9	Surface 10	Surface 11	Well 12
9/14/79	0.2	0.2	0.2	0.2	-
1/23/80	-	N.D.	N.D.	0.2	N.D.

Charlestown Site

Date	Well 1	Well 2	Well 3	Well 4	Surface 7
9/14/79	N.D.	N.D.	0.1	N.D.	N.D.
1/21/80	N.D.	N.D.	0.1	-	N.D.
2/20/80	N.D.	N.D.	N.D.	N.D.	N.D.
3/20/80	N.D.	N.D.	N.D.	N.D.	N.D.
6/13/80	-	-	-	-	-

Charlestown Site

Date	Surface 156	Well 18	Well 23	Well 24	Well 25
9/14/79	N.D.	-	-	-	-
1/21/80	N.D.	N.D.	N.D.	N.D.	N.D.
2/20/80	N.D.	N.D.	N.D.	N.D.	N.D.
3/20/80	N.D.	N.D.	N.D.	N.D.	N.D.
6/13/80	-	N.D.	N.D.	-	N.D.

Glocester Site

Date	Well 1	Well 4	Surf. 9	Surf.10	Surf.11	Surf.12	Surf.13
8/06/79	N.D.	N.D.	N.D.	0.1	-	-	-
3/25/80	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	-
6/12/80	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Glocester Site

Date	Well 14	Well 15	Well 16	Well 17	Well 18	Well 19
3/25/80	-	.05	-	.05	.2	.10
6/12/80	N.D.	N.D.	N.D.	N.D.	.2	N.D.

Little Compton Site

Date	Surface 6	Well 9	Well 13	Well 15	Well 16	Surface 17
9/02/79	-	.3	N.D.	N.D.	.1	-
3/25/80	N.D.	-	N.D.	N.D.	.15	.10
5/29/80	N.D.	-	N.D.	N.D.	.05	-
6/12/80	-	N.D.	-	-	-	-

Little Compton Site

Date	Well 18	Well 19	Well 20	Well 21	Well 22
3/25/80	.1	.05	.25	.3	N.D.
5/29/80	.2	.05	.25	.35	0.1

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[a] ND - not detected. Cyanide was measured with a Hach kit; the detection limit is .05 ppm.

FEDERALLY COORDINATED PROGRAM OF HIGHWAY RESEARCH AND DEVELOPMENT (FCP)

The Offices of Research and Development of the Federal Highway Administration are responsible for a broad program of research with resources including its own staff, contract programs, and a Federal-Aid program which is conducted by or through the State highway departments and which also finances the National Cooperative Highway Research Program managed by the Transportation Research Board. The Federally Coordinated Program of Highway Research and Development (FCP) is a carefully selected group of projects aimed at urgent, national problems, which concentrates these resources on these problems to obtain timely solutions. Virtually all of the available funds and staff resources are a part of the FCP, together with as much of the Federal-aid research funds of the States and the NCHRP resources as the States agree to devote to these projects.*

FCP Category Descriptions

1. Improved Highway Design and Operation for Safety

Safety R&D addresses problems connected with the responsibilities of the Federal Highway Administration under the Highway Safety Act and includes investigation of appropriate design standards, roadside hardware, signing, and physical and scientific data for the formulation of improved safety regulations.

2. Reduction of Traffic Congestion and Improved Operational Efficiency

Traffic R&D is concerned with increasing the operational efficiency of existing highways by advancing technology, by improving designs for existing as well as new facilities, and by keeping the demand-capacity relationship in better balance through traffic management techniques such as bus and carpool preferential treatment, motorist information, and rerouting of traffic.

3. Environmental Considerations in Highway Design, Location, Construction, and Operation

Environmental R&D is directed toward identifying and evaluating highway elements which affect the quality of the human environment. The ultimate goals are reduction of adverse highway and traffic impacts, and protection and enhancement of the environment.

4. Improved Materials Utilization and Durability

Materials R&D is concerned with expanding the knowledge of materials properties and technology to fully utilize available naturally occurring materials, to develop extender or substitute materials for materials in short supply, and to devise procedures for converting industrial and other wastes into useful highway products. These activities are all directed toward the common goals of lowering the cost of highway construction and extending the period of maintenance-free operation.

5. Improved Design to Reduce Costs, Extend Life Expectancy, and Insure Structural Safety

Structural R&D is concerned with furthering the latest technological advances in structural designs, fabrication processes, and construction techniques, to provide safe, efficient highways at reasonable cost.

6. Prototype Development and Implementation of Research

This category is concerned with developing and transferring research and technology into practice, or, as it has been commonly identified, "technology transfer."

7. Improved Technology for Highway Maintenance

Maintenance R&D objectives include the development and application of new technology to improve management, to augment the utilization of resources, and to increase operational efficiency and safety in the maintenance of highway facilities.

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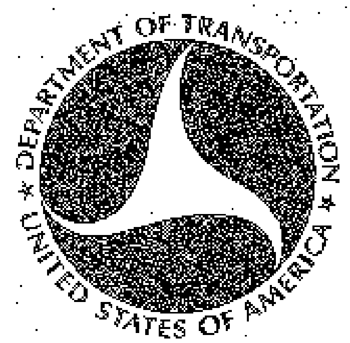
* The complete 7-volume official statement of the FCP is available from the National Technical Information Service (NTIS), Springfield, Virginia 22161 (Order No. PB 242057, price $45 postpaid). Single copies of the introductory volume are obtainable without charge from Program Analysis (HRD-2), Offices of Research and Development, Federal Highway Administration, Washington, D.C. 20590.


DEPARTMENT OF TRANSPORTATION
UNITED STATES OF AMERICA

WATER REUSE by METAL REMOVAL
from
INDUSTRIAL PLATING EFFLUENTS

UNIVERSITY OF RHODE ISLAND
1892

RHODE ISLAND
WATER RESOURCES CENTER

COMPLETION REPORT

Water Reuse by Metal Removal from Industrial Plating Effluents

Project No. A-073-RI

Agreement No.: 14-34-0001-1142

Principal Investigator: Frank J. DeLuise, Professor of Mechanical Engineering and Applied Mechanics

Consultant: Stanley M. Barnett, Professor of Chemical Engineering

Research Period: October, 1979 to September 1981

Research Category: VF

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WATER REUSE BY METAL REMOVAL FROM INDUSTRIAL PLATING EFFLUENTS

Objective

The purpose of this project was to study the removal of various metals in solution (chromium, cadmium, zinc, nickel, etc.) from liquid wastes discharged from the metal-plating and jewelry industries. The process which was used for this investigation employed microgas dispersions for flotation of the various metals. The process had been successfully used in a previous project (A-067-RI) for the removal of manganese from potable water.

Background

The metals found in the metal-plating and jewelry industry waste-waters can contribute significantly to stream pollution either directly or indirectly. Their direct effect is to destroy the stream flora and fauna. Indirectly, they may destroy the various organisms essential to the operation of a conventional sewage treatment plant and thereby render the plant ineffective. Since many of these metals are not removed by conventional processes used by municipal sewage treatment plants and since many of these metals in fact destroy the effectiveness of conventional processes, the wastewaters from plating and jewelry-making processes, in many instances, are not allowed to be discharged directly to municipal sewer systems. This means that these wastewaters must be pre-treated for removal of the metals and other possible toxic materials prior to discharge to the municipal sewer system.

Although technology is available for treating these wastewaters for reduction of the metals to any desired concentration, the cost of treatment is relatively high and therefore only the larger industrial plants can afford to employ this technology. There is a great need for a more economical system of treatment, particularly for the smaller plating and jewelry facilities. Many of the smaller plants are still discharging directly into municipal sewer systems, but municipal, state, and federal regulations will soon put an end to this practice. The jewelry industry must be in compliance with the federal standards shown in Table 1 in the near future. This means that pre-treatment to a desirable level must be accomplished before discharge to a municipal system.

On the local level, the City of Providence sewage treatment facility has been accepting wastes from a large number of plating and jewelry companies without pretreatment for many years. High concentrations of metals from these industrial wastes have been found in the Providence River and Narragansett Bay waters and sediments. Therefore, the Environmental Protection Agency will soon require that a maximum concentration level be set on various metals contained in the effluent discharged from the Providence treatment plant. The only way this result may be obtained is by pretreating the plating and jewelry wastewaters for removal of the metals before discharge to the sewer system. Since most of the companies involved in the industry are small, this means a more economical method of treatment than is currently available must be found if the companies are to survive.

Experimental Methods

Figure 1 is a schematic of the system used to produce the MGD and to effect removal of the various metals. The foam producing equipment consisted of a reservoir, paddle pump, heat exchanger, and venturi generator. A surfactant solution was made up to the desired concentration (usually 300 ppm) and was then added to the reservoir. The pump was used to circulate the dispersion throughout the system. Since the quality of the dispersion is

Table 1
Federal Standards(1)

Pollutant	Process Water Less than 10,000 GPD (PPM) 1 day	Process Water Less than 10,000 GPD (PPM) 30 days	Process Water Greater than 10,000 GPD (PPM) 1 day	Process Water Greater than 10,000 GPD (PPM) 30 day
Total Cyanide	-	-	0.8	0.23
Amenable cyanide	5.0	1.5	-	-
Copper	-	-	4.5	1.8
Nickel	-	-	4.1	1.8
Total chromium	-	-	7.0	2.5
Zinc	-	-	4.2	1.8
Lead	0.6	0.3	0.6	0.3
Cadmium	1.2	0.5	1.2	0.5
Silver	-	-	1.2	0.5
Total Metals	-	-	10.5	5.0

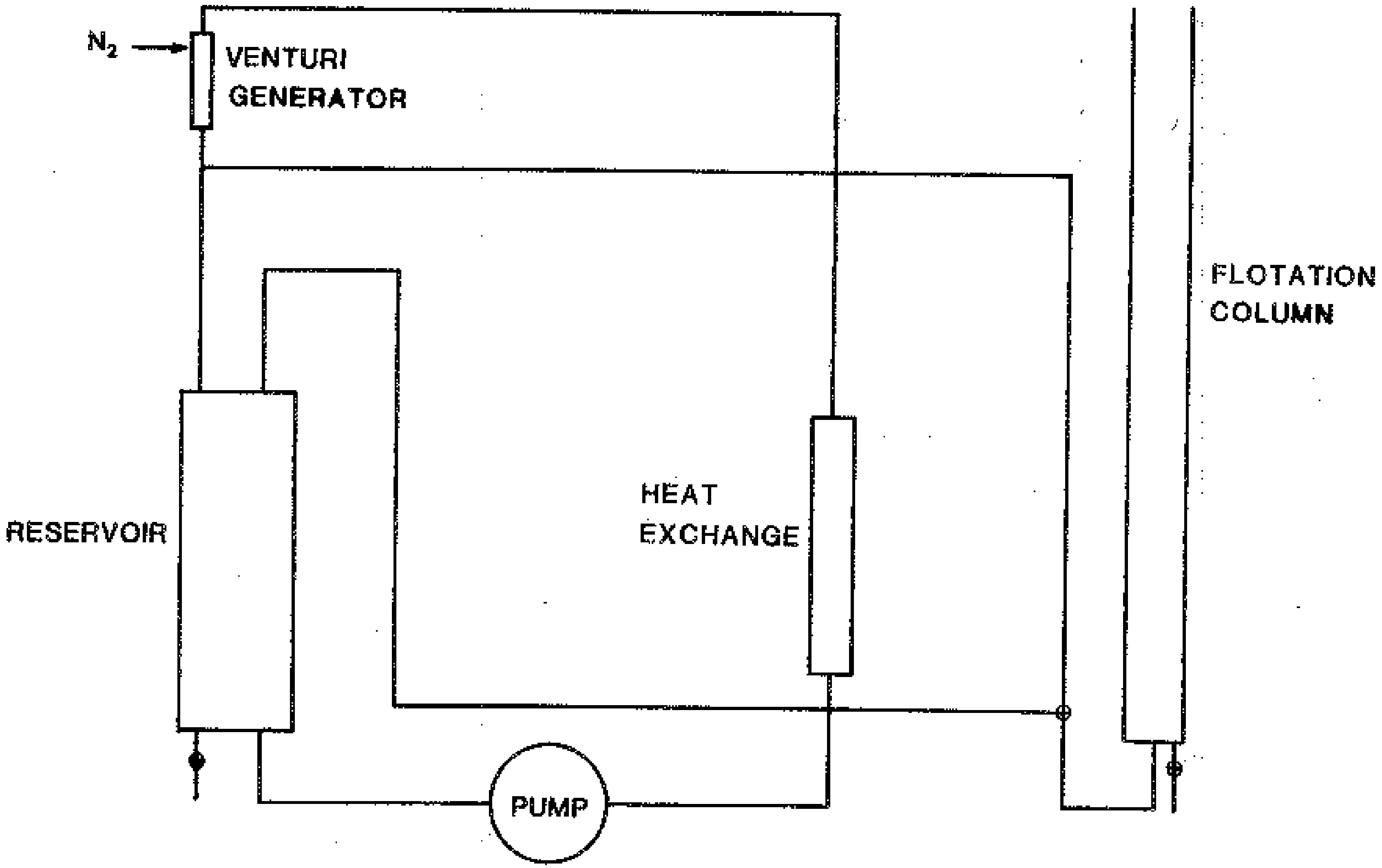

FIGURE 1. MICROGAS DISPERSION GENERATOR

obviously effected by temperatures much above room temperature, it was necessary to include a heat exchanger in the system. From the heat exchanger the dispersion, or surfactant solution at startup, passed through the generator which formed and maintained the dispersion. In the generator, Figure 2, the surfactant passed from an area of low velocity and high pressure, A, to a point of high velocity and low pressure, C. At point C, nitrogen gas or air was introduced and passed through the space, B. The space B, is similar to a loose ground-glass fitting. By this mechanism, the dispersion was formed. Once the foam was formed, the generator acted to maintain a constant foam quality by breaking up larger bubbles as they passed through. From the generator, the dispersion was circulated back to the reservoir. A baffle was present in the reservoir to evenly distribute the dispersion back into the reservoir. A secondary loop fed the MGD dispersion to a flotation column where sample solutions to be treated had been added. The flotation column measured 5.1 cm I.D. and 90 cm in height. The MGD foam entered the bottom of the column through a constriction (eyedropper).

Surfactant solutions which were used had a concentration of 300 ppm of either ethylhexadecyldimethylammonium bromide (EHDA), or sodium dodecylbenzene sulfonate (DBSS). These solutions were used to form the bubble structure. No further addition of surfactants was required.

Solutions of the metals were prepared by adding nitric acid to appropriate amounts of copper sulfate, chromium trioxide, lead nitrate, nickel nitrate, and zinc metal. Adjustments to pH were made under constant stirring, by adding required amounts of either sodium hydroxide or nitric acid. The flotation column was then filled with the metal solution and the MGD dispersion was introduced at the bottom of the column. Some runs were made using chitosan as a chelating or complexing agent. The same procedure was used in these runs except that prior to pH adjustment, the sample solutions

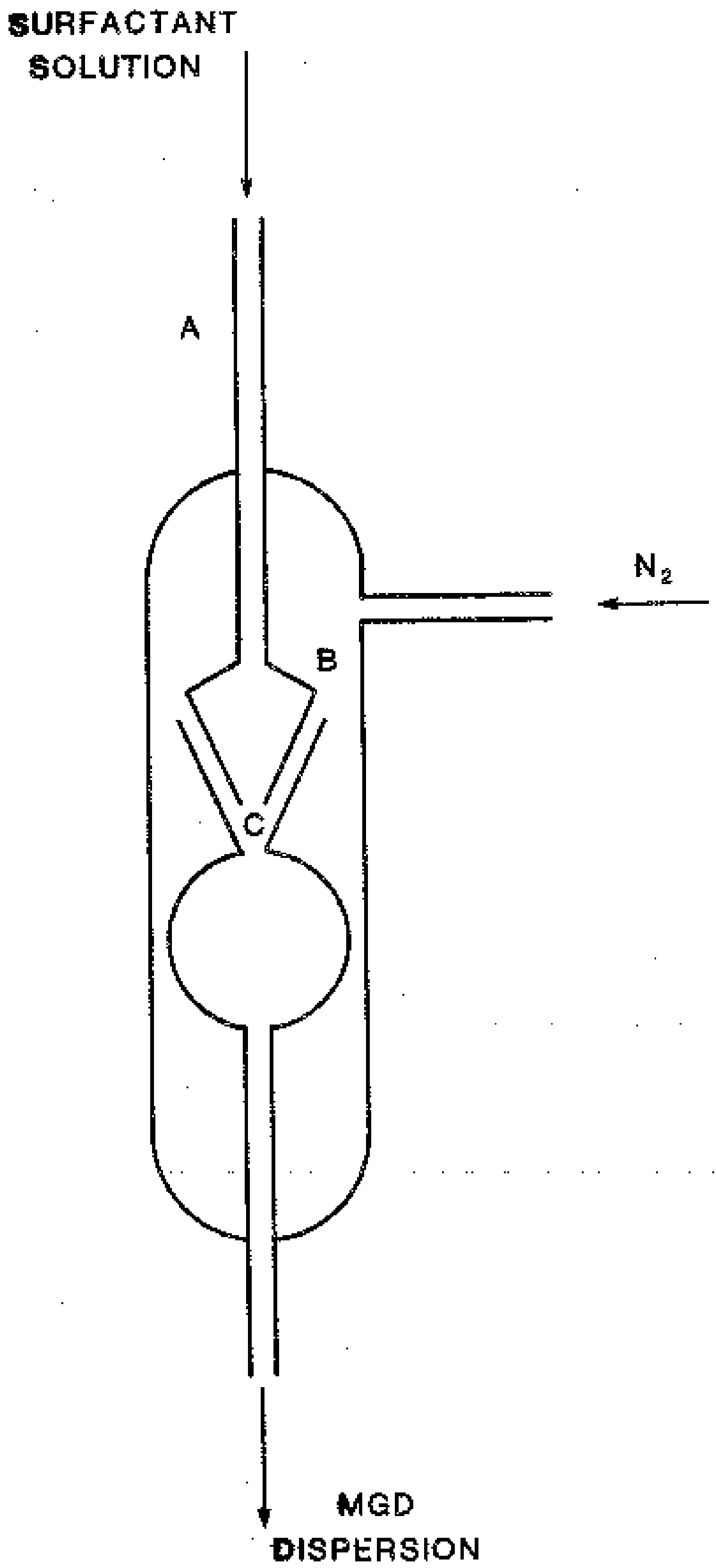

FIGURE 2. VENTURI GENERATOR

were made up to 6.0 ppm chitosan. For each run, a sample of MGD dispersion was taken to determine the quality which was defined as the percent entrained gas in the dispersion. Before making the initial run of each series of runs, it was necessary to circulate the MGD dispersion for about ten to fifteen minutes to assure a constant foam quality. A good MGD dispersion typically entrained about 50-65% gas. Nitrogen gas was introduced into the generator at about 25°C and 24 psig at a rate of 0.29 l/min. No difference in foam quality was found when air was used in place of the nitrogen gas. After the dispersion passed through the liquid column, a final liquid height was read, from which a dilution factor was calculated (initial height/final height). Samples of the treated water were withdrawn from an outlet at the bottom of the column, acidified, and quantified on an atomic absorption unit. Percent removals were obtained as follows.

$$\% \text{ Re} = \frac{CI - CF/DIL}{CI} (100)$$

CI = Initial concentration of metal
CF = Final concentration of metal
DIL = Dilution factor

Results

Percent removals have been calculated and are shown in Figures 3-11. Operating conditions and initial metal concentrations are also noted. The residual concentrations obtained in each of these runs are presented in Tables II and III.

Copper (Cu)

In aqueous solution at low pH, the cupric ion (Cu^{++}) was the stable ion present. This ion is highly soluble in water so the main mechanism of removal at low pH was ion flotation. In Figure 3, this can be seen as the pH region less than about 6. As alkali was added to the solution, the hydroxide was formed, $Cu(OH)_2$. This species corresponds to the pH region greater than approximately 6 or 7. As shown in Figure 3, 100% removal was attained at high pH. The vertical portion of the curve at pH 7 corresponds to the point where the removal mechanism changes from ion to precipitate flotation.

Nickel (Ni)

Removal of nickel is plotted in Figure 4. In aqueous solution nickel is present in the plus two state, Ni^{++}. When the pH is less than about 9, nickel is highly soluble, and ion flotation is the predominant mechanism of removal. As alkali is added to increase the pH, insoluble nickel hydroxide, $Ni(OH)_2$, is formed. The vertical portion of the curve, located at a pH of about 8.5 to 10, represents a change from ion to precipitate flotation.

Zinc

At low pH, less than 6.5, zinc exists in solution as Zn^{++} ions, and therefore ion flotation is the predominant mechanism of flotation in this pH range. Removal is plotted in Figure 5. The vertical portion of the curve is where the removal mechanism changes from ion to precipitate flotation. At a pH of about 8.5, $Zn(OH)_2$ is the main species present. Increasing the pH beyond 8.5 resulted in lower removal, since the precipitate became more soluble. This increased solubility is due to the formation of anionic hydroxo complexes such as $Zn(OH)_3^-$, and $ZN(OH)_4^=$ (1).

Lead (Pb)

Figure 6 shows the percent removal obtained for lead. At pH less than 6 lead is present as Pb^{++} ions. In this pH region, ion flotation is the main mechanism of removal. As alkali is added lead hydroxide is formed. This hydroxide is slightly soluble and exists as a giant molecule with no definite composition (2). The concentration of the solution, along with any impurities which may be present will effect both the composition and solubility of the precipitate. Consequently, there can be a reproducibility problem with this metal. Again, the vertical portion of the curve represents a change in mechanism from ion to precipitate flotation. Maximum removal was attained at pH 9.5. As the pH is increased, removal decreases due to the formation of soluble plumbites (2).

Chromium (Cr)

Figure 7 shows percent removal vs. pH for the flotation of chromium. Chromium, unlike the other metals studies, is present in solution as an anion, the species present being dependent on pH. At a pH less than 1, the main species present is H_2CrO4. In the pH range between 2 and 6 $HCrO_4^-$ and $Cr_2O_7^=$ are in equilibrium and above a pH of about 8, $CrO_4^=$ is present (1). All of these species are soluble in water and nowhere in the pH range is there any precipitation. Consequently, the main mechanism of removal throughout the entire pH range was ion flotation, and as shown, removal of only 26% was achieved. Maximum removal was attained in a pH range between 2.5 and 6.5. Beyond this, removals fell off, possibly due to the formation of the unfavorable $CrO_4^=$ ion, which will require a stoichiometric ratio of 2:1 surfactant to metal ion. There may also have been competition for the surfactant by the hydroxyl groups which were now in high concentration.

Since the removal of chromium was very poor when using the procedure used for the removal of the other metals, a modification was tried. The hexavalent chromium was reduced to the trivalent state by the addition of sodium sulfite under acidic conditions. Results are shown in Figure 11.

Mixture of Metals

Since it is unlikely that only one metal will exist in a waste to be treated, a mixture of several metals was examined to determine the effect on removal. Figure 8 shows the percent removal obtained from a mixture of Cu, Cr, Ni, Zn, and Pb. It can be seen that although the same general trend was followed, with higher removal being obtained at higher pH, the shapes of the curves differ from those of the pure components. This result was to be expected, since in a mixture of these metals, each metal species can be effected by every other metal in solution. Each metal is being removed from an environment different from that of the pure solution. There are also several anions present which have an effect on removal. As alkali is added and precipitation occurs, the composition of the precipitate is no longer easily described. The possibility of complexes between different metals and different anions make it impossible to guess the composition of the resulting precipitate. One obvious reaction, however, is that between chromium and lead, which gives precipitates of insoluble lead chromates. This may possibly explain the high removal of lead obtained in the mixture.

Wastewater Sample

Figure 9 shows the percent removal obtained from an actual wastewater sample obtained from a local plating firm. Again, the same general trend is observed with increased removals being realized as precipitate flotation begins. A slight similarity between the curves in Figure 9 and the corresponding curves in Figure 8 can be noted.

Wastewater with Chitosan

Figure 10 shows the data obtained for the flotation of metals from a plating firms wastewater using chitosan as a chelating or complexing agent.

Comparison of Figure 10 with Figure 9 indicates a much more efficient removal is obtained using chitosan as a chelating agent. Peak removals were obtained at a pH of 7.9 for all the metals except nickel which peaked at pH 9. Removal of copper, iron and zinc exceeded 90% with removal of Cu reaching 100%. Removal of chromium reached 50% as compared to only 15% obtained without chitosan.

Conclusions

It has been demonstrated that batch flotation of various metals from aqueous solution is an effective method for removal of these metals from wastewater. Solutions of single metals as well as solutions containing several metals have been treated and significant removal has been obtained. In addition, actual plating wastes containing several metals have been successfully treated. The most efficient system employed the use of a cationic surfactant with precipitate flotation.

Recommendations

Further study should be undertaken to determine the effect of operating conditions such as bubble feed rate, column size, and the use of other surfactants upon the degree of removal of the various metals. The use of chitosan and possibly other complexing agents should also be further investigated. The possibility of using the MGD dispersion in a continuous flow process should be investigated.

Publications

A paper based upon the work done during this project has been accepted for publication in Separation Science and Technology. The title of the paper is "Removal of Heavy Metals from Aqueous Solutions Using Microgas Dispersions."

Table II
Metal Removal from Synthesized Solutions of Pure and Mixed Metal Ions.***

	Individual Solutions			Synthesized Mixture		
	Initial Conc.	Final Conc.	% Removal	Initial Conc.	Final Conc.	% Removal
Cu	8.46	0.00	100.0	9.55	0.15	98.4
Ni	19.50	0.30	98.5	9.79	0.46	95.3
Zn**	18.11	0.90	95.1	9.46	0.48	94.9
Cr	10.10	7.40	26.7	3.80	3.01	20.8
Pb	10.92	2.28	79.1	0.233	0.00	100.0

**Surfactant: DBSS (300 ppm)
***Surfactant: EHDA (300 ppm)

Table III
Metal Removal from Industrial Effluent with and without Chitosan***

	Industrial Effluent			Industrial Effluent with Chitosan		
Cu	1.242	0.19	84.5	2.176	0.00	100.0
Ni	1.175	0.55	53.2	1.380	0.54	60.7
Fe	0.223	0.052	76.7	0.227	0.008	96.5
Cr	2.617	2.25	14.1	3.876	1.90	50.9
Zn	0.139	*	*	0.372	0.02	94.6

*Sample Lost
***Surfactant: EHDA (300 ppm)

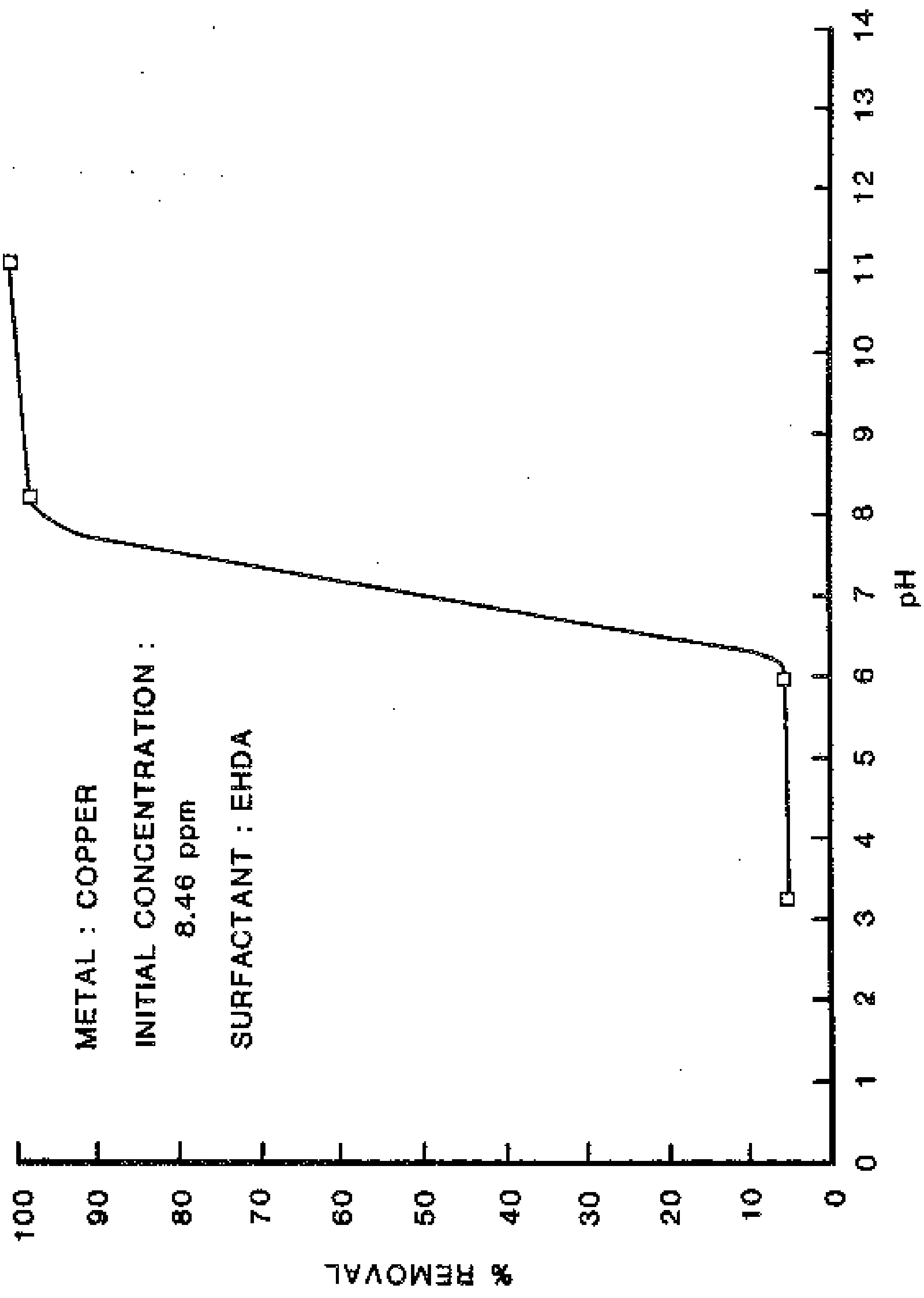

FIGURE 3. COPPER REMOVAL

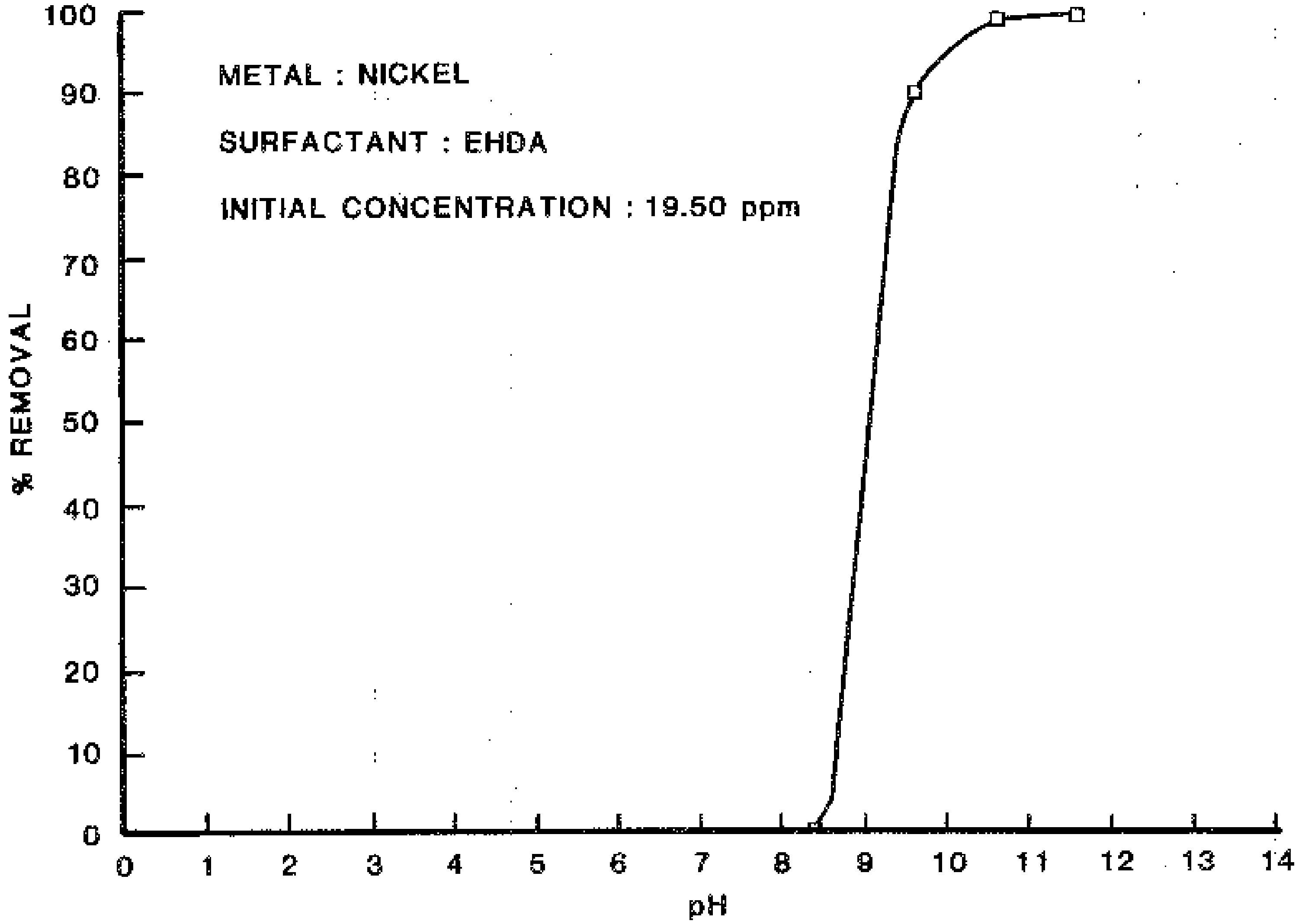

FIGURE 4. NICKEL REMOVAL

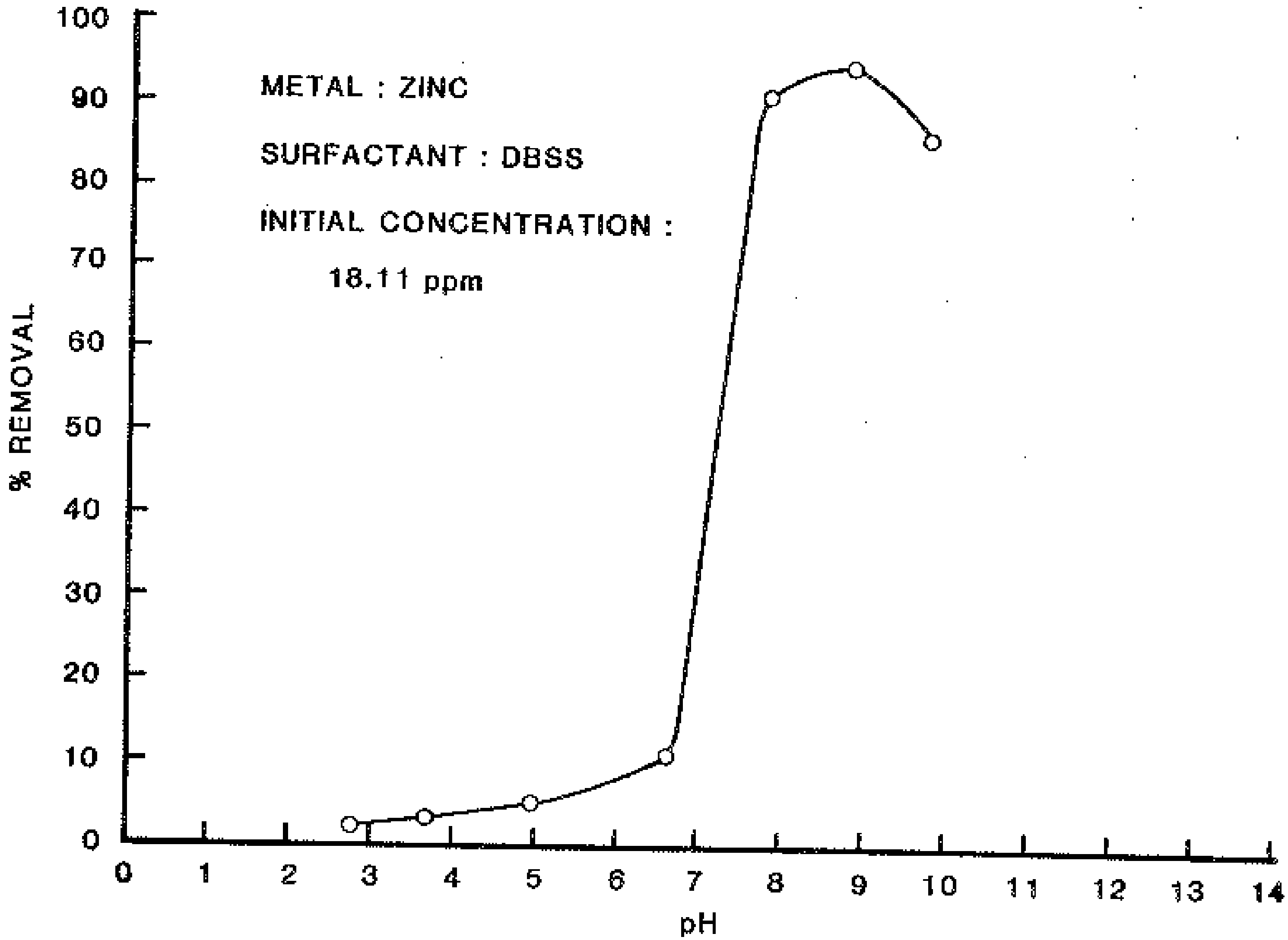

FIGURE 5. ZINC REMOVAL

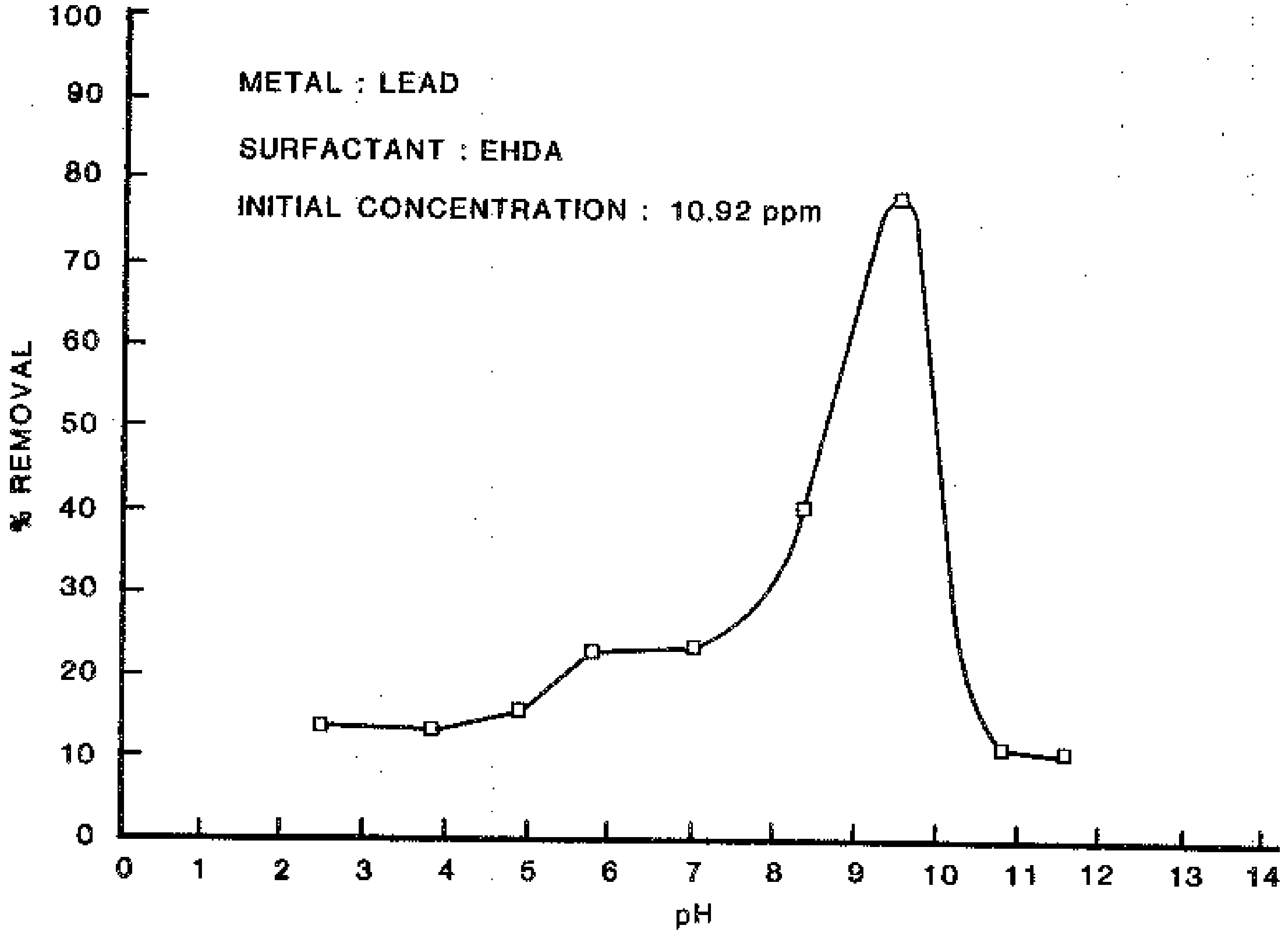

FIGURE 6. LEAD REMOVAL

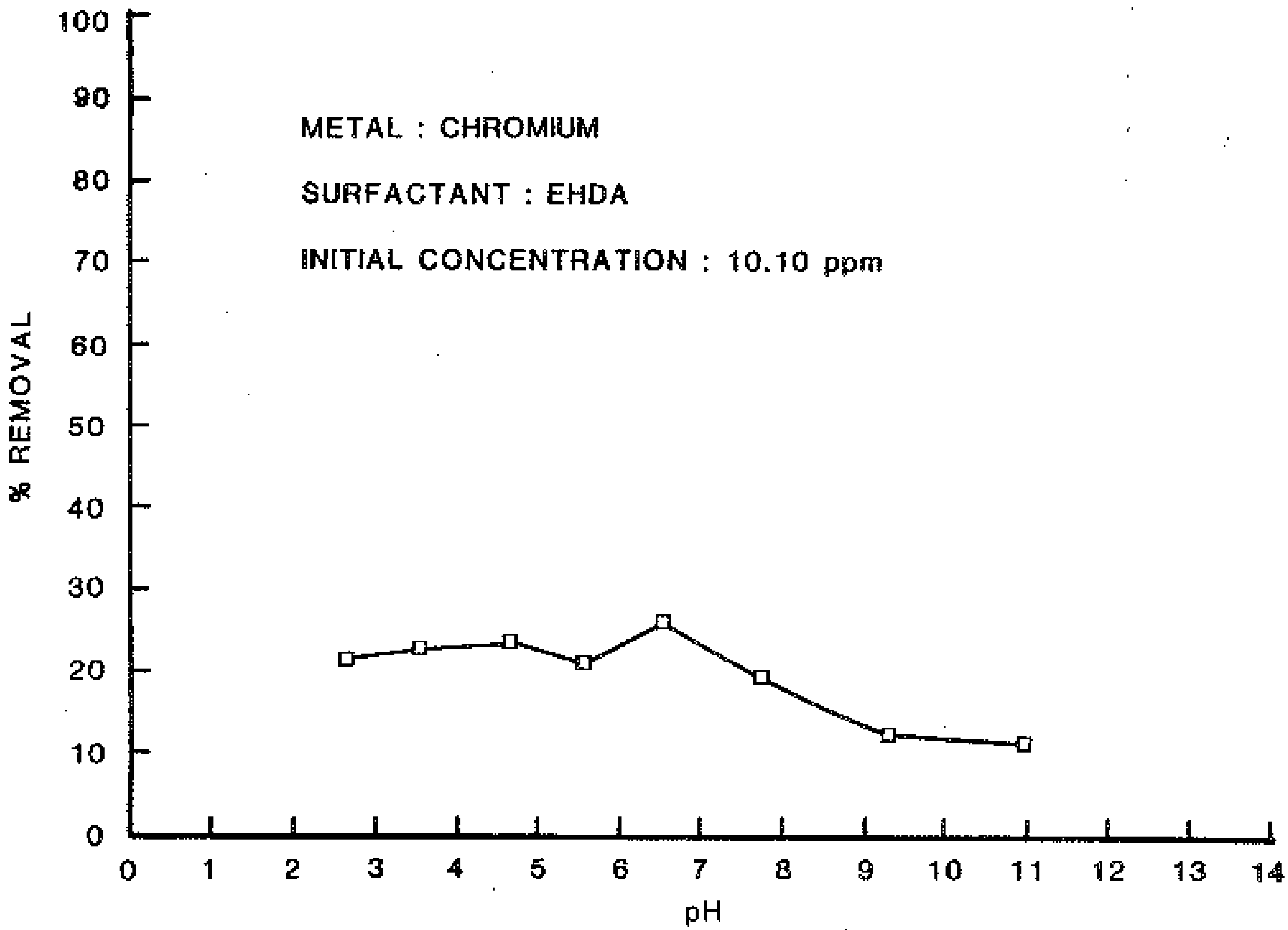

FIGURE 7. CHROMIUM REMOVAL

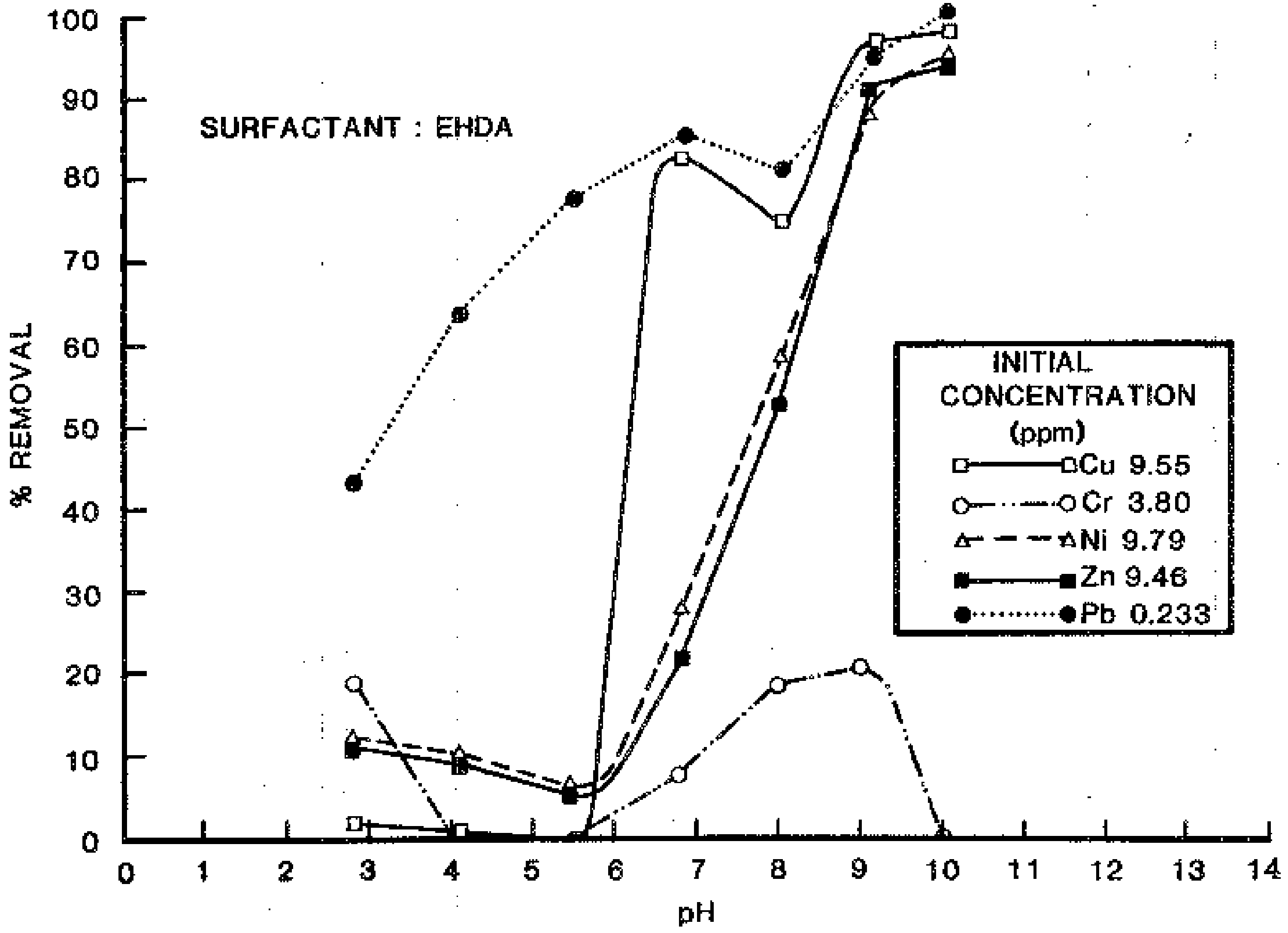

FIGURE 8. MIXED ION REMOVAL

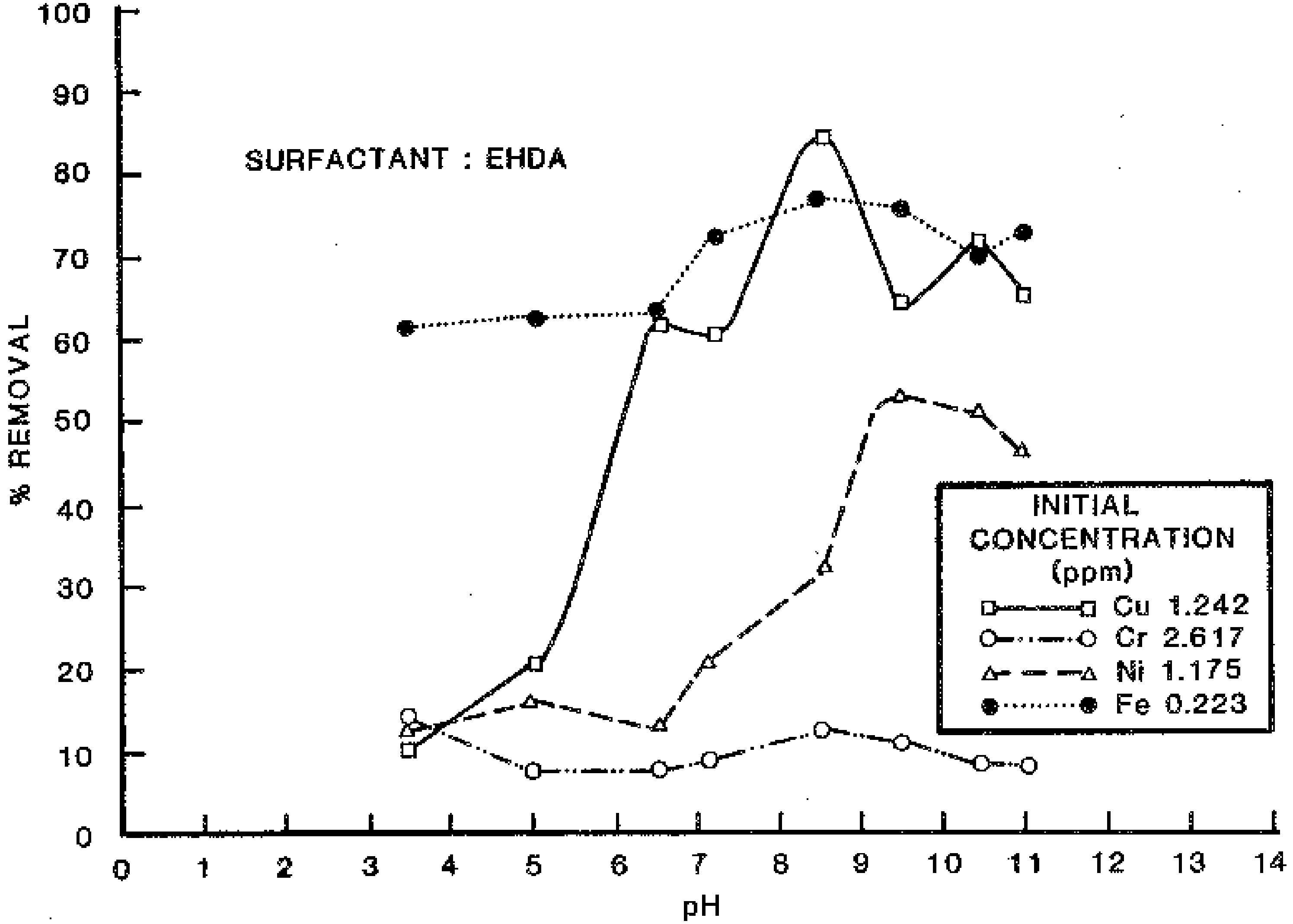

FIGURE 9. PURIFICATION OF WASTEWATER

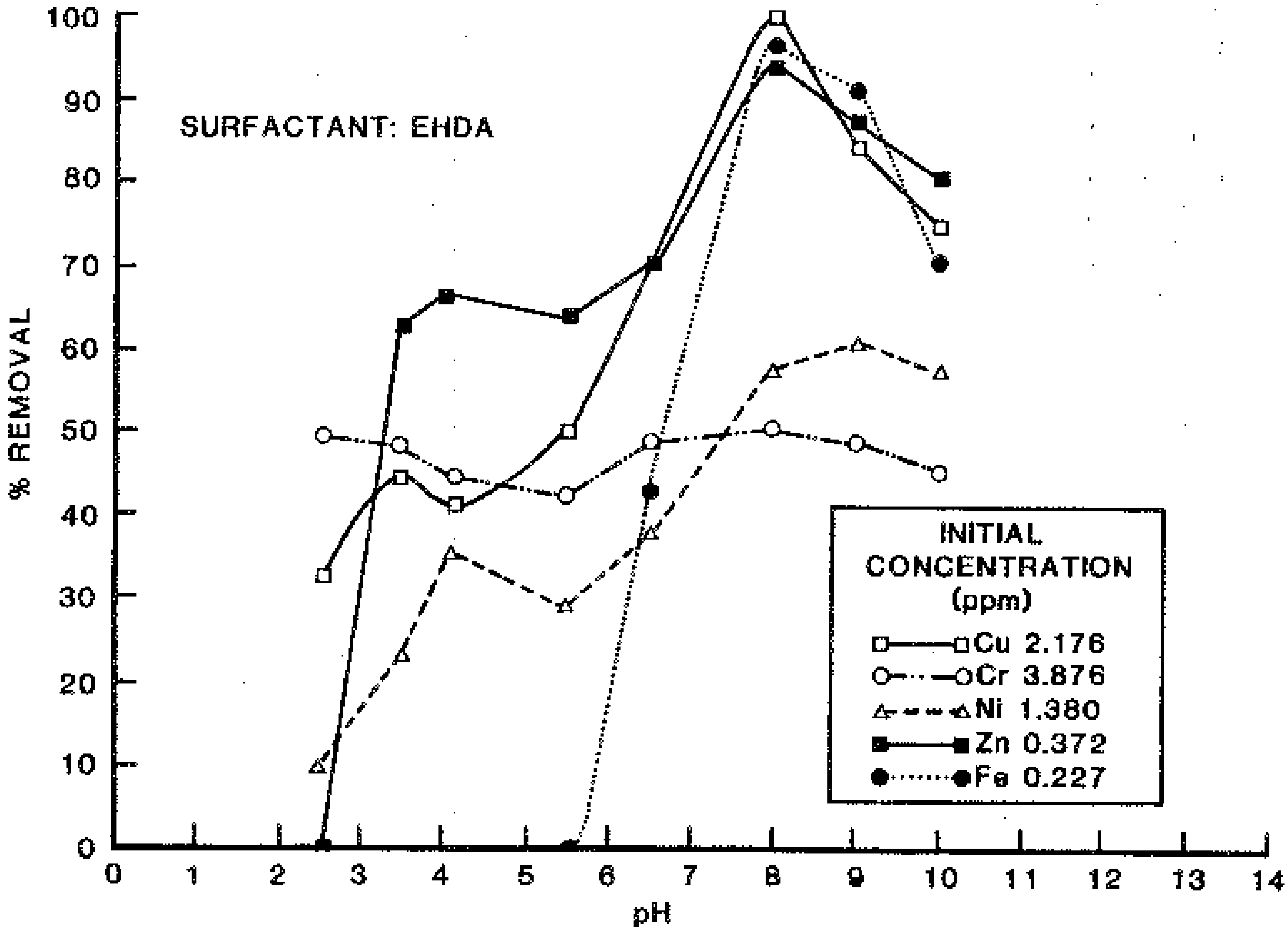

FIGURE 10. PURIFICATION OF WASTEWATER USING CHITOSAN

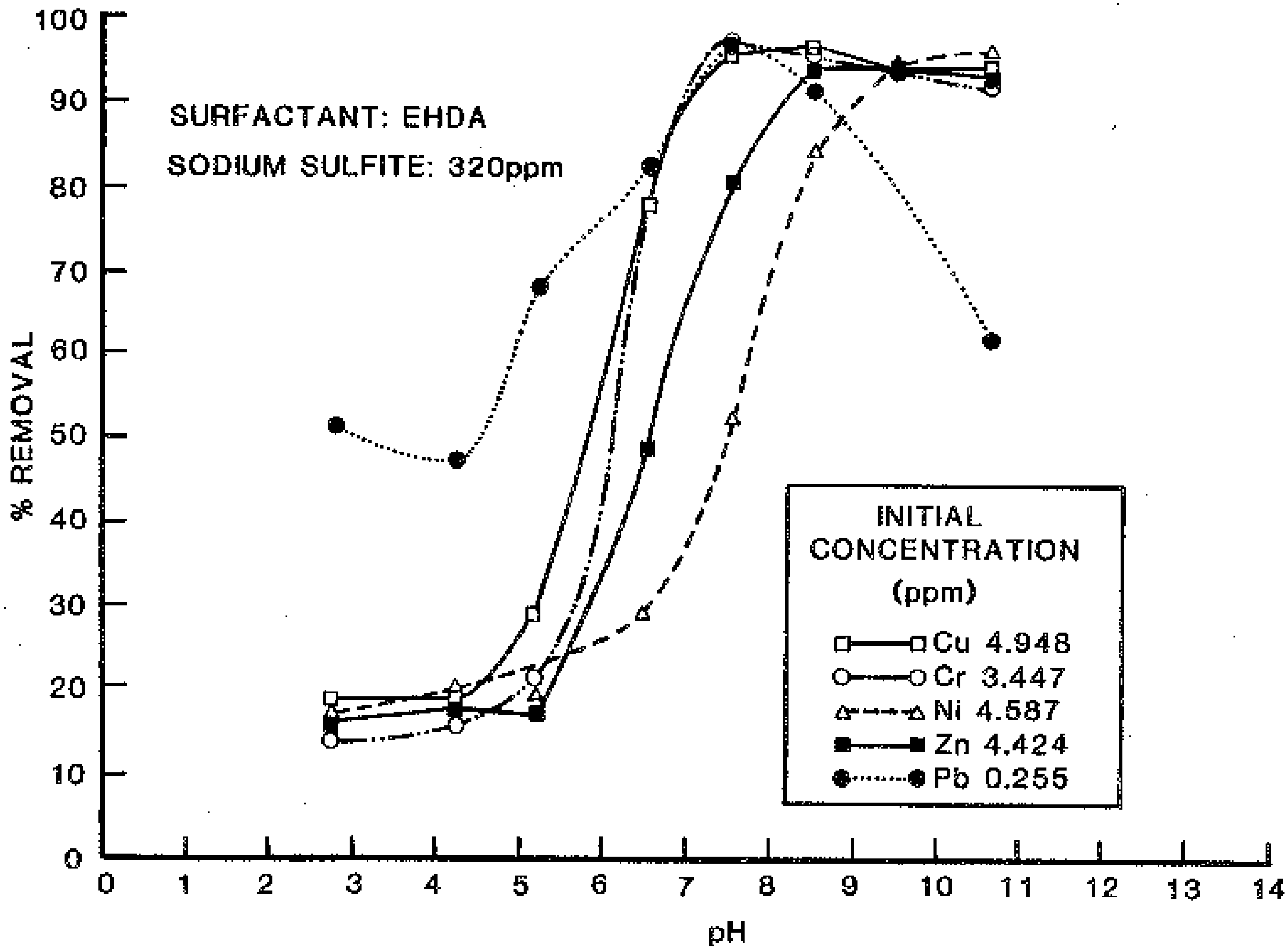

FIGURE 11. MIXED ION REMOVAL USING SODIUM SULFITE

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1981
RI-A-072

REMOVAL OF HALOMETHANES
FROM WATER
WITH OZONATION

UNIVERSITY OF RHODE ISLAND

1892

RHODE ISLAND
WATER RESOURCES CENTER

TECHNICAL REPORT NO. 3

RHODE ISLAND WATER RESOURCES CENTER

PROJECT NO. A-072-RI

TERMINATION REPORT

APRIL, 1981

1. TITLE OF PROJECT: REMOVAL OF HALOMETHANES FROM WATER WITH OZONATION

2. PROJECT STARTING AND TERMINATION DATES: October 1, 1979 -
February 28, 1981

3. PRINCIPAL INVESTIGATOR: Pei Wen Chang, Ph.D. , Professor
Charles E. Olney, Ph.D., Professor

4. NAME OF APPLICANT INSTITUTION: Department of Aquaculture Science
and Pathology
Department of Food Science and
Technology, Nutrition and Dietetics
College of Resource Development
University of Rhode Island
Kingston, RI 02881

5. ORIGINAL PROJECT OBJECTIVES AND ANY REVISED OBJECTIVES:

The objective of the project was to determine factors influencing the formation and removal of trihalomethane (THM) from water with ozonation.

6. FINDINGS, RESULTS AND CONCLUSIONS:

"The work upon which this publication is based was supported in part by funds provided by the Office of Water Research and Technology, (Project No. A072-RI_, U S Department of the Interior, Washington, D.C."

A. Effects of Sparging and Ozone on THM Concentration

Ozone from a laboratory generator was sparged at rates of 30-60 mg/min into 100 ml water solutions containing 100 ppb concentrations of the halogenated methane, ethane and ethylene compounds. After sparging a 10 ml aliquot was shaken with 5 ml petroleum ether to extract the residual THMs, which were analyzed by electron capture gas chromatography. Peaks were identified by retention time on two columns and quantitated by comparing peak heights with those of standards. Similar samples were treated with oxygen gas to assess the effect of sparging, and the ozone oxidative effect was measured by their differences. Diluted standards and extracts of untreated spiked water were run with each set of treated samples.

Sparging alone caused considerable reduction in THM concentration. When the gas flow rate was at 2 liters per min (Table I) the reduction of carbon tetrachloride (CCl_4), trichloroethylene ($CCl_2{=}CHCl$) and bromoform ($CHBr_3$) were approximately the same under oxygen or ozone treatment. It was therefore not possible to determine the reduction of THM due to ozone oxidation.

In a second experiment (Table II), eight (8) THM compounds were treated with oxygen or ozone at a gas flow rate of 2 liters per min. There were no differences in THM reduction between the oxygen and ozone treatment at 300 seconds post-treatment. However, at 60 seconds post-treatment dibromochloromethane ($CHBr_2Cl$), chloroform ($CHCl_3$), methyl iodide (CH_3I), bromodichloromethane ($CHBrCl_2$) and tetrachloroethylene ($CCl_2{=}CCl_2$) all showed a reduction, which was due to ozone oxidation. These reductions were 16%, 14%, 17%, 42% and 12% respectively.

Because it was difficult to distinguish the oxidative effect between ozone and oxygen at a gas flow rate of 2 liters per min, the flow rate was reduced to 0.65 liter/min. The voltage for the ozone generator was also increased from 3 KV to 4 KV. Under these conditions, ozone production was approximately 56 mg/min. A comparison of six compounds under these conditions is given in Table III. The percentages of reduction due to one minute of ozone oxidation were 10, 12, 38, 10, 9 and 16% at 0C and 19, 18, 33, 12, 10 and 19% at 25 C for methyl iodide, chloroform, trichloroethylene, bromotrichloromethane, tetrachloroethylene and dibromochloromethane, respectively. The THM which responded to ozone most effectively was trichloroethylene. It was reduced 38% at 0C and 33% at 25 C.

Five of these compounds reported in Table III (at low rate of sparging, 0.65 l/min) were also reported in Table II (at high rate of sparging, 2 l/min). Their comparison showed that volatility losses were slightly reduced at the lower gas flow rate and ozone oxidation was more apparent at 30 seconds after the start of ozonation. At 60 seconds after treatment oxidative values were similar between the two treatments.

B. Reduction of THM Compounds by Residual Ozone in Water

In this study, residual ozone in water was added to the chlorinated hydrocarbons for determining the oxidation ability of ozone. Five compounds, methyl iodide (CH_3I), chloroform ($CHCl_3$), trichloroethylene (CCl_2=$CHCl$), bromotrichloromethane ($CBrCl_3$), and tetrachloroethylene (CCl_2=CCl_2) were selected for this test. Each compound was made up to 10 ppm in acetone and 0.1 ml of it was added to a test tube, followed by 10 ml of ozonated water. The solution was mixed and held for 3 min at 0 C. The concentration of the residual ozone in the water at pH 7 was 14 mg per liter.

Results in Table IV showed that ozone partially oxidized all five compounds at pH 7. The percent of reduction of each compound due to ozone was CCl_2=$CHCl$, 97%; CCl_2=CCl_2, 45%; $CBrCl_3$, 37%; $CHCl_3$, 32%; and CH_3I, 31%. It appears that ozone is particularly effective in destroying trichloroethylene.

The significant slower reaction of tetrachloroethylene as compared with trichloroethylene may be explained by the electron withdrawing effect of the extra chlorine atom and an increase in stearic hindrance.

C. Effects of Ozone on THM Precursors

Experiments with combinations of chlorination and ozonation on solutions of phenol, toluene, acetone and methanol were conducted.

Phenol: In this study, one ppth of phenol in water solution was used. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C. Chlorination was carried out by adding to the one ppth water solution, 3.1 ppth sodium hypochlorite for 2 hours.

Ozonated phenol solution was divided into 2 aliquots, one of which was chlorinated immediately after ozonation. The results of this study are presented in Table V. Ozonation alone did not reduce the phenol concentration (20%) as much as chlorination alone (29%). Chlorination after ozonation reduced 33% of phenol from water solution, while chlorination after oxygen reduced 30% of the phenol. When ozonation followed chlorination, 43% of phenol was removed as compared to 25% with oxygen. It is evident that chlorination alone, ozonation alone and in combination partially removes phenol, a precursor of THM. The best sequence for the removal of phenol is chlorination followed by ozonation.

Chlorination of phenol-water solution may convert some of the phenol in the water to chlorophenols; at least three new compounds were formed in this study (Table V). Ozone, before or after chlorination, reduced the levels of chlorophenols by 30%.

Chloroform formed during the chlorination of phenol was 402 ppb and the following ozonation reduced 63% of it. In the ozonation-chlorination treatment, the chloroform produced was higher than that produced by chlorine treatment alone. The amounts were 1236 and 402 ppb, respectively. This was probably due to the formation of small molecular weight fragments during ozonation, which provided more chances for chloroform formation during the subsequent chlorination process (Eisenhauer, J. Water Poll. Contr. Fed. 40, 1887, 1968). If ozonation-chlorination is applied in the field, there should be an additional treatment between ozonation and chlorination to remove the small molecular weight fragments produced by ozonation. That could be accomplished by either filtration or adsorption onto activated charcoal.

Toluene: In this study, the same procedure applied to the phenolic water solution was applied to toluene. The results are presented in Table VI.

When chlorination of toluene-water solution was carried out, no chlorinated toluene was formed as seen with the phenol-water solution. Chlorination alone had little effect on toluene, while ozone and oxygen both reduced the concentration of toluene from water solution. This is probably due to aeration, since toluene is a volatile compound. There was a 67% reduction following both treatments.

Chloroform formed during chlorination of toluene was 712 ppb. This was reduced to 400 ppb when chlorination was followed by ozonation. Comparison with the chlorine-oxygen treatment, where 698 ppb of chloroform was formed, it suggests that the removal of chloroform was at least partially due to oxidation by ozone.

Acetone: The same procedure applied to the phenolic water solution was applied to acetone. The results are presented in Table VII.

Acetone is highly volatile; it is also water soluble. After ozone or oxygen treatment 78-80% of the acetone remained in the water. Chlorination alone seemed to be less effective than ozonation, since 96% of acetone was still detectable in the water solution.

Acetone was a stronger precursor of chloroform than phenol, toluene or methanol. Chloroform formed was so high with acetone that later ozonation did not show any effect on its removal.

Methanol: The same procedure applied to phenol, acetone and toluene was applied to methanol. The results are presented in Table VIII.

Methanol like acetone, is volatile and water soluble. Like acetone, ozone and oxygen treatment did not reduce the concentration of the compound in water. This is due to its water solubility. After ozone and oxygen treatment, there were still 91 and 98% left in the solution, respectively. Chlorination of methanol produced a compound(s) which had shorter retention time than that of methanol. The new product was not identified, nor reduced by subsequent ozone treatment. Chlorination alone produced 783 ppb of chloroform, which was lower than that produced by ozonation followed by chlorination (4500 ppb).

Table IX summarizes the formation of chloroform following chlorination and/or ozonation. Ozonation alone does not produce any chloroform. Chlor -

ination alone or in combination with ozone all produces chloroform. With phenol and methanol, treatment with ozone prior to chlorination increases the amount of chloroform 3 and 6 times respectively over that formed by chlorination alone. With phenol and toluene, ozonation after chlorination reduced chloroform level 63% and 43% respectively.

D. Conclusion

In the Study of the reduction of THM in water by ozonation, it was found that in the application of ozone by sparging, the sparging alone caused considerable reduction of THM.

To better assess the oxidative effect of ozone, residual and dissolved ozone were used in the treatment of THM. Under these conditions, oxidative losses of methyl iodide, chloroform, bromotrichloromethane, tetrachloroethylene and trichloroethylene were 31, 32, 40, 56 and 97%. Ozonation is effective in destroying a number of THM particularly trichloroethylene. Experiments with combinations of chlorination and ozonation on solution of phenol, toluene, acetone and methanol were conducted. Sparging with ozone or oxygen for 3 minutes at 0 C and pH 7 reduced toluene levels, but had little effect on the total concentration of the other three compounds, which are water soluble. With all four compounds treatment with ozone alone does not produce any chloroform, however, treatment with chlorine produced 400-870 ppb of chloroform. With phenol and methanol, treatment with ozone prior to chlorination increased the amount of chloroform 3 and 6 times respectively over that formed by chlorination alone. With phenol and toluene, ozonation after chlorination reduced chloroform level 63% and 43% respectively.

7. A STATEMENT DESCRIBING THE RESEARCH RESULTS IN LANGUAGE A LAYMAN CAN UNDERSTAND

Chloroform and other trihalomethanes are carcinogens and their prevention and/or removal from drinking water is essential to the health of the population.

The formation of chloroform and other THM results from the interaction between chlorine and precursors present in the water. The precursors could be any organic matter in the surface or ground water. Thus the removal of chlorine and/or precursors from water will reduce the THM in the finished water. In addition the removal of any THM already formed in water would be a beneficial step in the treatment of water.

In this study, ozone, an alternative disinfectant, produced no THM from organic matter. Ozone had little effect on the removal of three precursors of THM (phenol, acetone and methanol). However, when precursors such as phenol and toluene were treated with chlorine followed by ozone, the chloroform level (a form of THM) was reduced 63% and 43% respectively from that produced by chlorination alone. In other experiments, ozone was shown to partially reduce other THMs in water.

It appears from these studies that ozonation is a better disinfectant for drinking water with its ability to reduce and limit THM formation.

8. A STATEMENT DESCRIBING HOW THE RESULTS ARE BEING APPLIED IN THE WATER RESOURCES FIELD

The majority of water plants in the U.S. currently use chlorine as their source of disinfectant. However, since the discovery of THM formation following chlorination was reported, alternative means of disinfecting water are being studied.

This study showed that ozonation, an alternative means of water disinfection, reduces and limits THM formation in water and is therefore a better disinfectant.

9. PUBLICATIONS

"Ozonation of trihalomethanes, pesticides and four common organic compounds in water" by You Lu. Masters Thesis in Food Science and Nutrition, University of Rhode Island, Kingston, 1980.

TABLE I. Reduction of THM[a] following sparging with oxygen or ozone gas at 2 l/min flow rate[b]

Compound	pH	Sparging Time (sec)	% Reduction		
			Ozone	Oxygen	Ozone Oxidation
CCl_4	2	20	69	78	-9[c]
		40	96	96	0
		60	98	98	0
	7	20	69	78	-9
		40	96	94	2
		60	98	98	0
CCl_2=CHCl	2	20	63	67	-4
		40	91	92	-2
		60	100	100	0
	7	20	75	67	8
		40	95	92	3
		60	100	100	0
$CHBr_3$	2	20	25	12	13
		40	26	33	-7
		120	58	56	2
	7	20	14	10	4
		60	22	28	-6
		120	55	55	0

a. The concentration of CCl_4, CCl_2=CHCl and $CHBr_3$ in untreated water solution were 49, 75, and 72 ppb, respectively.

b. The operation conditions were: Oxygen flow rate = 2 l/min; Generator voltage = 3 KV; Temperature = 25 C.

c. (-) sign indicates that the reduction of THM compound was greater with oxygen than with ozone.

TABLE II. Reduction of eight THM compounds following sparging with oxygen or ozone gas at 2 liters per min flow rate[a]

Compounds[b]	Sparging[c] Time (sec)	% Reduction		
		Ozone	Oxygen	Ozone Oxidation
$CHBrCl_2$	30	29	15	14
	60	46	4	42
	120	67	48	19
	360	90	79	11
$CHBr_2Cl$	30	33	38	-5[d]
	60	70	54	16
	120	100	71	29
	360	100	100	0
CH_3I	30	43	28	15
	60	70	53	17
	120	90	76	14
	360	100	99	1
$CHCl_3$	30	36	35	1
	60	70	56	14
	120	91	97	-6
	360	100	95	5
CCl_2=CCl_2	30	70	67	3
	60	84	72	12
	120	94	87	7
	360	100	100	0
CH_2BrCl	30	66	63	3
	60	87	84	3
	120	96	96	0
	360	100	100	0
$CBrCl_3$	30	43	41	2
	60	58	61	-3
	120	81	83	-2
	360	95	97	-2
CH_3CCl_3	30	35	47	8
	60	72	80	-8
	120	91	95	-4
	360	100	100	0

a. The ozone production was approximately 27 mg/min

b. The concentrations of $CHBrCl_2$, $CHBr_2Cl$, CH_3I, $CHCl_3$, CCl_2=CCl_2, CH_2BrCl, $CBrCl_3$ and CH_3CCl_3 in untreated water were 119, 98, 86, 124, 141, 134, 96 and 87 ppb, respectively.

c. Operation conditions were: Flow rate = 2 l/min; Generator voltage = 3 KV; pH = 7; Temperature = 25°

d. (-) sign indicates that the reduction of THM compounds was greater with oxygen than with ozone.

TABLE III. Reduction of THM following sparging with oxygen or ozone gas at 0.65 l/min flow rate

Compound[b]	Temp. C	Sparging[c] Time (sec)	% Reduction		
			Ozone[a]	Oxygen	Ozone Oxidation
CCl_2=CHCl	0	30	60	27	33
		60	75	37	38
		240	100	72	28
	25	30	89	49	40
		60	97	64	33
		240	100	96	4
CH_3I	0	30	37	23	14
		60	47	31	16
		240	74	68	6
	25	30	65	41	24
		60	72	53	19
		240	94	93	1
$CHBr_2Cl$	0	30	28	9	19
		60	32	16	16
		240	52	45	9
	25	30	56	29	27
		60	62	43	19
		240	100	100	0
$CHCl_3$	0	30	30	19	11
		60	33	21	12
		240	48	44	4
	25	30	50	33	17
		60	59	41	18
		240	76	78	-2
$CBrCl_3$	0	30	39	24	15
		60	46	36	10
		240	78	73	5
	25	30	66	45	21
		60	73	61	12
		240	100	100	0
CCl_2=CCl_2	0	30	52	40	12
		60	61	52	9
		240	87	85	2
	25	30	77	59	18
		60	84	74	10
		240	100	100	0

a. The ozone production was approximately 56 mg/min

b. The concentration of CCl_2=CHCl, CH_3I, $CHBr_2Cl$, $CHCl_3$, $CBrCl_3$ and CCl_2=CCl_2 measured in untreated water solution were 120, 109, 121, 116, 112 and 124 ppb, respectively.

c. Operation conditions were: Flow rate = 0.65 l/min; Generator voltage = 4 KV; pH = 7.

TABLE IV. Reduction of THM following treatment with residual ozone in water (at pH 7 and 0 C).

	% Reduction		
Compound[a]	Ozone[b]	Oxygen	Ozone Oxidation
$CCl_2=CHCl$	100	3	97
$CCl_2=CCl_2$	45	0	45
$CBrCl_3$	37	0	37
$CHCl_3$	40	8	32
CH_3I	48	17	31

a. The concentration of $CCl_2=CHCl$, $CCl_2=CCl_2$, $CBrCl_3$, $CHCl_3$ and CH_3I measured in water solution were 67, 64, 63, 99 and 67 ppb, respectively.

b. Residual ozone concentration was 14 mg per liter.

TABLE V. Chloroform formation following ozonation[a] and/or chlorination[b] of Phenol

	Relative amount (%) in the water solution							
Compounds	None	O_3	O_2	Cl_2	O_3+Cl_2	O_2+Cl_2	Cl_2+O_3	Cl_2+O_2
Phenol	100	80	94	71	67	70	57	75
Chlorophenols[c]	0	0	0	100	73	116	70	130
$CHCl_3$	0	0	0	100[d]	307[e]	45	37[f]	(-)[g]

a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7.
b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.
c. Three new products were formed, which were not identified. They are presumed to be chlorophenols based on retention time.
d. The actual amount of chloroform formed was 402 ppb.
e. The actual amount of chloroform formed was 1236 ppb.
f. The actual amount of chloroform formed was 149 ppb.
g. Sample lost

TABLE VI. Chloroform formation following ozonation[a] and/or chlorination[b] of toluene

	Relative amount (%) in the water solution							
Compounds	None	O_3	O_2	Cl_2	O_3+Cl_2	O_2+Cl_2	Cl_2+O_3	Cl_2+O_2
Toluene	100	33	33	90	22	22	19	23
$CHCl_3$	0	0	0	100[c]	70[d]	58	56[e]	97[f]

a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7.
b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.
c. The actual amount of chloroform formed was 720 ppb.
d. The actual amount of chloroform formed was 510 ppb.
e. The actual amount of chloroform formed was 400 ppb.
f. The actual amount of chloroform formed was 698 ppb.

TABLE VII. Chloroform formation following ozonation[a] and/or chlorination[b] of acetone

	Relative amount (%) in the water solution							
Compounds	None	O_3	O_2	Cl_2	O_3+Cl_2	O_2+Cl_2	Cl_2+O_3	Cl_2+O_2
Acetone	100	80	78	96	85	90	91	73
$CHCl_3$	0	0	0	100[c]	100	107	100	100

a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7.

b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.

c. The actual amount of chloroform formed was 8680 ppb.

TABLE VIII. Chloroform formation following ozonation[a] and/or chlorination[b] of methanol

	Relative amount (%) in the water solution							
Compounds	None	O_3	O_2	Cl_2	O_3+Cl_2	O_2+Cl_2	Cl_2+O_3	Cl_2+O_2
Methanol	100	91	98	0	89	99	0	0
New Products	0	0	0	100	0	0	100	97
Chloroform	0	0	0	100[c]	574[d]	58	112[e]	52

a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7.

b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.

c. The actual amount of chloroform formed was 733 ppb.

d. The actual amount of chloroform formed was 4500 ppb.

e. The actual amount of chloroform formed was 877 ppb.

TABLE IX. Summary: Chloroform formation following ozonation[a] and/or chlorination[b] of organic compounds

	Amount of chloroform (ppb) formed			
Compounds	O_3	Cl_2	O_3+Cl_2	Cl_2+O_3
Phenol	0	402	1236	149
Toluene	0	720	510	400
Acetone	0	8680	8680	8680
Methanol	0	783	4500	877

a. Ozonation was carried out by the continuous sparging method at an ozone dose of 56 mg/min for 3 min at 0 C and pH 7

b. Chlorination was carried out by adding 3.1 ppth of sodium hypochlorite to one ppth of water solution of phenol for 2 hours.

ANOXIC NUTRIENT REGENERATION
and the
EUTROPHICATION OF ESTUARINE WATERS

UNIVERSITY OF RHODE ISLAND

1892

RHODE ISLAND
WATER RESOURCES CENTER

PROJECT FINAL REPORT

Title: Anoxic Nutrient Regeneration and the Eutrophication of Estuarine Waters

Project Dates: 10/01/78 - 02/28/81

Project Number: B-082-RI

Principal Investigator: Dr. Scott W. Nixon
Professor of Oceanography
University of Rhode Island

Co-investigator: Patrick F. Roques
School of Oceanography
University of Rhode Island

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ABSTRACT

In the Pettaquamscutt Estuary, RI, the sedimentation of organic matter is high and water circulation is reduced. Consumption of oxygen in the water and sediments exceeds renewal processes and anoxic conditions develop. The accumulation of regenerated nutrients in the stagnant bottom water permits a test of recent models for organic matter decomposition under anoxic conditions. The stoichiometry of nutrient concentrations in the anoxic bottom water (C:S:N:P:Si of 108:59.4:14.3:1.0:3.43) indicates that the nitrogen and phosphorus regenerated is greater than predicted from anoxic zone sediment trap material (C:N:P of 140:14.0:1). Rates of organic matter oxidation and the stoichiometry of nutrient regeneration were measured directly by placing *in situ* chambers over the sediment and monitoring concentration changes in the isolated bottom water. The rate of carbon oxidation (14.8 mmol C m^{-2} day^{-1}) based upon sulfide release is equal to that in nearby oxygenated sediments and about half of the rate observed in Narragansett Bay (RI) sediments at the same temperature (11°C). The atomic ratio of nitrogen:phosphorus released is close to the observed ratio of these metabolic products accumulating in the anoxic bottom water.

PROJECT OBJECTIVES

Using the Pettaquamscutt River as a natural laboratory, we proposed to investigate the rates and stoichiometry of nutrient regeneration from sedimenting organic matter under anoxic and oxic conditions. Since the water column is stratified, the water and sediments below 7 meters are permanently anoxic and the products of anaerobic metabolism accumulate in the stagnant bottom water. We proposed to monitor the changes in concentration and stoichiometry of these regenerated nutrients and gases on a seasonal basis. The source material was to be collected over the annual cycle in sediment traps suspended at several depths in the oxic zones of the water column. The elemental composition of the sedimenting organic matter can be related to the composition of decomposing organic matter which produces the accumulating metabolites.

Residual material is left behind in the accumulating sediment. We proposed to investigate further decomposition in buried sediment by examining the composition of this residual organic matter at various depths in sediment cores from the oxic and anoxic environments.

It has been suggested that organic matter oxidation under reducing conditions is very slow and leads to the preservation of organic matter in anoxic environments. We proposed to measure the <u>in situ</u> rate of sulfate reduction with chambers placed over the anoxic sediment. The flux of sulfide and regenerated nutrients is used as a measure of the total sediment metabolism. Similarly, we proposed to measure oxygen consumption in shallow water sediments.

Originally, we intended to investigate the effect of organic loading and temperature on anaerobic metabolism in the laboratory, using intact sediment cores. We were unable to maintain the cores for long enough periods of time under conditions similar to the field. As an alternative, the sediment was sectioned into depth intervals and incubated *in vitro* at various temperatures. The reactivity of the organic matter and response of metabolism to temperature was investigated using this method.

PROJECT RESULTS AND CONCLUSIONS

1. The Upper Pond of the Pettaquamscutt River, RI, is a fjord type estuary. The water column is stagnant for periods of several years. Partial ventilation probably occurs every year in late winter with the intrusion of cold dense oxygenated water into the deep part of the basin. In some years, low rainfall and rapid fall cooling makes the surface water dense enough to permit mixing of the entire water column for several weeks. A few weeks after stratification occurs oxygen is depleted in the bottom water and the products of anerobic metabolism accumulate.

2. A year long survey of the elemental composition of suspended matter in the surface water of the Upper Pond resulted in a C:N:P ratio of 135:17.8:1. Organic material was collected in sediment traps over the yearly cycle in the oxic and anoxic parts of the water column. Near-surface oxic water traps were depleted in nitrogen and phosphorus (C:N:P of 167:15.6:1) relative to the traps in the low oxygen zone (C:N:P of 141:16.6:1) where the most abundant plankton were found. In the anoxic zone, sedimenting material showed only small losses of nitrogen and phosphorus (C:N:P of 140:14.0:1) before reaching the sediment surface (C:N:P of 180:19.9:1) where most of the decomposition occurred.

3. The potential sources of carbon, nitrogen and phosphorus in the sedimenting organic matter can be compared to the products of this decomposition in the water column. In the stagnant bottom water, the ratio of sulfate reduced to carbon dioxide produced is close to the predicted value (0.517 observed, 0.50 predicted, see Figure 12a). The nitrogen to phosphorus ratio of sedimenting organic matter collected in

the 7.0 and 10.0 meter traps (14.4 and 13.6 respectively), is very close to the ratio of changes observed in the bottom water of 14.3. Only about 80 percent of the carbon is oxidized relative to nitrogen and phosphorus metabolized when the carbon content of the sedimenting organic matter is compared to the sulfide or inorganic carbon produced (108/140 or 2(59.4)/140). This is reflected in the high C/N and C/P ratios in the sediment. Silica is regenerated at 3.43 times that of phosphorus.

4. The elemental composition of the surface sediment is a function of its degree of decomposition. Organic material that sediments in the shallow water sediments has already undergone more decomposition than material sedimenting in the anoxic zone which has its origin in the deeper and abundant plankton community at the oxic-anoxic interface. The shallow water sediments are mixed to a depth of several centimeters by bioturbating organisms. Thus the age and degree of decomposition, indicated by a higher C/N and C/P ratio, is greater in the surface sediment under oxic water than in the undisturbed surface sediment in the anoxic zone. Inorganic phosphorus is retained to a greater extent by the oxic sediments where it is adsorped onto iron oxyhydroxide particles. The sediment accumulating at the depth of transition from oxic to anoxic conditions showed the least retention of inorganic phosphorus.

5. The organic carbon oxidation rate in the anoxic sediment, calculated from sulfide flux using <u>in situ</u> chambers, was between 55 and 72 g C m^{-2} yr^{-1}. This was slightly higher than the rate for the oxic shallow water environment of 48-50 g C m^{-2} yr^{-1}. The higher rate for the anoxic sediment can be attributed to input of labile organic matter from the productive plankton community at the oxic-anoxic interface. At the same

temperature, total benthic metabolism in the sediments of the anoxic environment is about half that in nearby Narragansett Bay where primary production is similar. Thus areal rates of oxidation by sulfate reduction can be high. This rate is a function of the supply of organic matter when it is at low rates and becomes limited by the supply of electron acceptor, sulfate, at high rates .

6. Laboratory incubation of isolated sediment slices (2 cm thick) was used to investigate the reactivity of sediment organic matter and the response of metabolism to temperature. The production of porewater ammonium was taken as a measure of sediment metabolism. The surface sediment (top 2 cm) accumulating in the anoxic environment is more reactive at 7°C by a factor of 3.2 than the surface sediment in the oxic environment. Even at 10 centimeters the sediment from the anoxic environment is more reactive by a factor of 2.1. A large portion of the organic matter for the permanetly anoxic sediment comes from the very productive plankton community near the oxic-anoxic interface. This is a source of relatively fresh and labile organic matter in the form of fecal pellets and it has not been exposed to aerobic oxidation. In contrast, the organic matter in the top 2 centimeters of the oxic sediment has been exposed to oxic conditions before and after decomposition.

7. The effect of temperature on metabolic rate (pore water ammonium production) was investigated by incubating sediment sections at two temperatures, 7° and 20°C. The metabolism of the anoxic sediment increased by a factor of 2.9 at the sediment surface. The metabolism of the sediment from the oxic environment increased by a factor of 1.5. Greater increases occurred deeper in the sediment.

develops in oxygenated sediments defines the aerobic zone through burrowing and pumping activities (Aller 1978) and may increase the rate of denitrification and other geochemical processes at the oxic-anoxic interface (Grund manis and Murray 1977; Hendriksen et al. 1980).

The anoxic deep water of lakes, stratified estuaries, and fjords is periodically mixed upward into the surface water. This often occurs yearly as the conditions of temperature or salinity stratification are broken up. The release of nutrients, temporarily stored in the hypolimnion, may result in massive plankton blooms. Mixing upward of the bottom water temporarily reduces the dissolved oxygen levels in the entire water column through dilution and a chemical oxygen debt (Cline and Richards 1969). In addition to this stress of low oxygen on marine organisms, a transient condition of hydrogen sulfide in the water column can result in mass mortality.

A better understanding of processes controlling the occurrence of anoxic conditions is especially timely since conditions of low oxygen or anoxic significantly contribute to the mobilization and transport of heavy metals within estuaries (Holmes et al. 1974). Although the presence of sulfide resulting from anoxic conditions may act to precipitate toxic metals as insoluble sulfides, the reduction and dissolution of Fe and Mn hydroxides (which co-precipitate toxic metals under oxygenated conditions) may lead to their mobilization (Khalid et al. 1978).

While a substantial amount of research is now underway on the geochemical dynamics of aerobic coastal marine sediments, less is known about these processes in low oxygen or anoxic sediment-water systems. Research into this area is increasingly important since coastal waters are receiving

INTRODUCTION

The relationship between the flow of energy and the cycling of nutrients in the water of the open sea was described over 35 years ago by A.C. Redfield (1934). Since then, it has become increasingly clear that this relationship is considerably more complicated in coastal and inland waters where the metabolism of bottom sediments becomes important. The production of organic matter in shallow water is often large and the settling time is relatively short, so that the oxidation of much of the primary production and allochthonous organic input takes place in the sediment rather than in the water column. This oxidation is accompanied by a flux of regenerated inorganic nutrients which add significantly to the productivity of shallow water systems (Lee 1970; Keeny 1973; Rowe et al. 1975; Nixon et al. 1975). In some environments, the relationship between nutrient cycling and the decomposition of organic matter is further complicated by very low oxygen concentrations or by anoxic conditions that greatly influence the changes in organic substrate, oxidation rates, and end products of metabolism. Since the supply of oxygen for decomposition in the sediment must come by diffusion from the overlying water, the metabolism of deeper sediment is always anaerobic, regardless of the oxygen content of the overlying water. However, since most of the decomposition of organic matter takes place in the upper few centimeters of the sediment, the presence or absence of oxygen in this layer and the overlying water have dramatic influence on sediment nutrient flux. Denitrification and inorganic mineral reactions, which occur at the interface where oxygenated sediment meets anoxic sediment, act to mediate the flux of nutrients out of the anoxic zone. The abundant benthic fauna which usually more nutrient and organic loading every year from human activities which results in oxygen depletion in bottom waters and sediments. It is important that we understand the processes which lead to the formation, maintenance, and dissipation of anoxic conditions in estuaries and the ways in which the flux of materials from oxic and anoxic sediments differ.

METHODS

Sampling the Water Column

Profiles of nutrients and physical parameters in the water column were always made from the same location, near the center of the pond (Figures 1 and 2). A raft constructed from plywood and urethane foam floatation logs provided a platform for sampling and taking sediment cores. The physical parameters of temperature, conductivity, and salinity were measured with a Beckman Model RS5-3 Induction Salinometer. Water samples were pumped to the surface with a peristaltic pump through a Tygon tube. The end of the tube was attached to the salinometer probe so that water samples were obtained at exactly the same depth as physical parameters.

Water samples for dissolved oxygen and sulfide were collected in 60 ml BOD bottles after several volumes had overflowed and fixed immediately with reagents. Samples for total inorganic carbon, methane, and sulfate were similarly collected in separate 125 milliliter glass bottles and closed with poly-seal caps. Whole water samples for dissolved and particulate nutrients were taken by pumping directly into a nitrogen filled one liter polypropylene bottle, through a stopper hole. As a result, samples collected in this manner were not aerated before filtering and freezing in the lab. All sample bottles were kept on ice until processed in the lab several hours later.

<u>In situ</u> Benthic Chambers

In order to measure the rate of organic matter oxidation in the sediments, bell jar chambers were placed on the bottom. This isolated an area of bottom surface and the overlying water (see Figure 3). Changes in the concentration of dissolved nutrients in the closed system were used to calculate organic matter oxidation and nutrient release on an areal basis. Incubation of ambient water for controls was done at the same depth in 60 milliter BOD bottles.

The benthic chambers were constructed from 12 inch diameter clear Lucite tubing and closed on the top with a sheet of Lucite. Benthic production in some chambers was eliminated by painting the exterior opaque. The edges of the chambers penetrated about 20 centimeters into the soft anoxic mud and about 10 centimeters into the oxic shallow water mud. The area of bottom covered was .0675 square meters and from 7 to 15 liters of water were enclosed. The chambers were carefully placed in the sediments by SCUBA divers to assure position and depth penetration. Volume of the chambers was determined at the end of each experiment by the dilution of a flourescent dye and independently by calculation from the line of scum formed on the walls at the mud-water interface.

Samples were taken through Tygon tubes attached to a surface float. Water was pumped with a peristaltic pump to the surface and back down through another tube to thoroughly mix the enclosed volume of water before a sample was removed. As sample water was withdrawn, an equal volume of ambient water displaced it. These water samples were collected and transported in the same manner as the water column samples. Smaller bottles were used to conserve the water enclosed in the chamber. The volume of water withdrawn was so small that tedious corrections (usually less than 1% and always less than 3%) for dilution by ambient water were not made.

Sediment Traps

Sedimenting organic matter was collected in traps deployed in two locations and at four depths (see Figure 2). Sediment trap design was developed from a consideration of published studies of trap design performance, materials available, and ease of handling in the field. A funnel design with 1.2 centimeter square baffles was chosen particularly because the sedimented material would concentrate in the throat of the funnel and not wash out when the trap was retrieved (see Figure 4). An assessment of sediment performance by Gardner (1980) suggests that a cylindrical trap shape, with a depth to diameter ratio of about 3, most accurately samples sedimenting materials both quantitatively and qualitatively. A trap of this design was tested during one of the deployments of the baffled funnel traps. A visual inspection of the materials contained in both types of traps indicated that both collected the same amount of material. Some material was lost since the traps were not designed to close during recovery.

The traps were buoyant and were tethered on a string tied to an anchor. There was no surface buoy in the vacinity of the traps to attract floating particles, boaters, or birds. About 30 hours after the traps were deployed, they were recovered and emptied into polyethylene bottles. This deployment time was sufficient to collect an adequate sample for analysis but not long enough for the shallow water samples to go anoxic while in the trap. About an hour after collection the samples were filtered onto precombusted glass fiber filters and analyzed according to the procedure outlined below for particulate organic matter.

Sediment Cores

Sediment core samples were taken along a transect from the shallow nearshore oxic bottom to the deeper and permanently anoxic bottom near the center of the pond (see Figure 2). The anoxic mud was unconsolidated and easily stirred up. Ordinary coring techniques, using a gravity corer or SCUBA divers with hand held core liners, failed to collect the top few centimeters of mud intact. A coring device was constructed that could be slowly lowered from the surface, closed on the top and bottom, and retrieved. It is similar in design to that of Craib (1965). A 0.75 meter diameter plate came to rest on the mud surface to prevent further sinking after the plastic core liner (9.0 centimeter diameter) had penetrated the mud. The top and bottom of the removable plastic core liner were closed with rubber stoppers before the core was lifted from the bottom, preventing loss of material. The sediment cores were taken to the laboratory in the core liners with the stoppers still in place.

Cores were kept at in situ temperatures for several hours until sectioned. The water overlying the core was siphoned away and the sediment was pushed up with a piston from below in measured intervals. Sediment was scraped into glass drying vials or onto a 1.0 millimeter screen for sieving.

Incubation of Isolated Sediment Sections

The production of ammonia in portions of sediment isolated at particular depth intervals was used to assess rates of organic matter decomposition. Two water depths were chosen, 2.0 and 8.5 meters, as characteristic of oxic and anoxic bottom environments, respectively. Several cores with overlying water were taken at each of these depths using the coring device described above.

Cores were stored at field temperatures for several hours before sectioning. Water over the core was pumped out and displaced by an overpressure of nitrogen gas. The core was pushed up with a neoprene piston which made a gas-tight seal inside the core liner. As discrete depth sections were removed from the core, they were placed in 1 liter glass chambers and combined with sediment from the same depth in the other cores. The chamber containing the sediment was continuously flushed with nitrogen gas. After mixing, the combined sediment was injected into two nitrogen filled 300 milliliter BOD bottles and sealed with rubber septa. The head space in the bottles, about

100 milliliters, was flushed with about 10 volumes of nitrogen. The bottle was shaken intermittently to bring out any gas bubbles that may have been trapped in the sediment. The bottles were then transferred to a nitrogen filled dessicator.

The cores were sectioned into four discrete depth sections. The oxic cores were sectioned into intervals of 0-2, 2-4, 5-7, and 12-14 centimeters. The anoxic cores were sectioned into intervals of 0-2, 2-4, 8-10, and 16-18 centimeters. Homogenized sediment from each of these depths was put into two bottles for incubation and kept in the dark at 7°C or 20°C.

After the biochemical conditions in the bottles had stabilized, the first analysis of pore water ammonium was made. The bottles were brought to room temperature and shaken to homogenize. About 50 cubic centimeters of sediment was removed from each bottle with a syringe and put into polycarbonate centrifuge tubes. This entire procedure was performed under a stream of nitrogen gas. The bottles were resealed and the head space was flushed with nitrogen. The sediment was centrifuged for 15 minutes at 2200 xG. The supernant was filtered through a 0.45 micron Nucleopore filter and diluted to the proper range for analysis by the indophenol method described below. Analysis of carbon, nitrogen and phosphorus in the solid phase is also described below.

Analysis of Dissolved Components

Dissolved oxygen was determined by the Winkler method (Carritt and Carpenter 1966). Sulfide interferes with the Winkler titration, resulting in a stoichiometric underestimation of oxygen concentration. The following precautions were taken when sulfide was expected to occur in low oxygen water samples. Sulfide was precipitated immediately upon collection with zinc hydroxide. Oxygen in the clear supernatant was then determined by the Winkler method (Ingvorsen and Jorgensen 1979). Precision was ± 2.50% (1 S.D.), average for duplicate samples over the range 0.1 - 0.7 mg-at O_2 - Oxygen liter^{-1}.

Sulfide was determined by iodometric titration. (American Public Health Service 1976). This method measured sulfide and other reducing forms of sulfur. Precision was ± 1.13% (1 S.D.), average for triplicate samples over the range 0.17 - 5.3 mg-at H_2S - Sulfur liter^{-1}. Colorimetric measurements by the methylene blue method which is specific for sulfide however gave the same results over this range (Grassoff 1976).

Total dissolved inorganic carbon was determined on an infrared gas analyzer using the procedure described by Johnson et al. (1981). Precision was ± .60% (1 S.D.), average for duplicate samples over the range 0.7 - 7.8 mg-at CO_2 - Carbon liter^{-1}.

Methane samples were equilibrated with an equal volume of air in a 50 milliliter syringe. Methane was then determined in the air phase by gas chromatography (Rudd et al. 1974). Precision was ± 1.68% (1 S.D.), average for duplicate samples over the range 7 - 81 μg at CH_4 - Carbon liter^{-1}.

Samples for dissolved nutrients were returned to the lab on ice and filtered within several hours through precombusted (425°C for 4 hours) Reeve Angel Type 934A glass fiber filters. The filtrate was diluted to the appropriate range for analysis. Ammonium was run immediately and other samples were frozen in polyethylene bottles for later analysis. The filters were dried at 60°C for 24 hours and stored in a dessicator at -40°C for later analysis of the particulate fraction.

Ammonium was determined by the indiphenol method (Grassoff 1976) after dilution and air oxidation of sulfide. Precision was ± 1.07% (1 S.D.), for triplicate determinations over the range 5 - 1410 µg-at NH_4^+ - Nitrogen liter^{-1}.

Orthophosphate was determined by the molybdate-blue method (Grassoff 1976) after dilution and air oxidation of sulfide. Precision was ± .84% (1 S.D.), average for duplicate determinations over the range 2-93 µg-at PO_4^{-3} - Phospherus liter^{-1}.

Total phosphorus was determined by the molybdate-blue method after wet digestion with an acidified potassium persulfate solution (Grassoff 1976). Precision was ± .48% (1 S.D.) average for duplicate determinations over the range 2 - 94 µg-at Phosphorus liter^{-1}. Dissolved organic phosphorus was calculated as the difference between the total phosphorus and the orthophosphate concentration.

Reactive silicate was determined colorimetrically by reaction with molybdate and reduction with metol (Strickland and Parsons 1968). Precision was ± .22% (1 S.D.), average for duplicate determinations over the range 8 - 355 µg-at SiO_2 - Silicon liter^{-1}.

Nitrate and nitrate analysis were made using a Technicon Autoanalyzer II. Nitrite was determined by diazotizing with sulfanilamide and coupling with N-(-1-naphthyl)-ethylene diamine. Nitrate was determined by the same reaction after reduction to nitrite in a cadmium-copper reduction column (Strickland and Parsons 1968). Precision was ± 3.85% (1 S.D.), average for triplicate determinations over the range 0.05 - 0.15 and ± .62% over the range 0.85 - 6.3 µg-at NO_2^- or NO_3^- - Nitrogen liter^{-1}.

Total nitrogen was determined by alkaline persulfate oxidation and analysis of nitrate in the buffered digest by the automated method outlined above (Solorzano and Sharp 1980). Precision was ± 1.28% (1 S.D.), average for triplicate determinations over the range 17 - 1348 ug-at Nitrogen liter^{-1}. Dissolved organic nitrogen was calculated by subtracting the total sum of the other forms of inorganic nitrogen (ammonium, nitrate and nitrite) from the total persulfate nitrogen value.

Analysis of Particulate Organic Matter

Particulate carbon and nitrogen in dried sediments, and in samples collected on filters from the sediment traps and water column, were analyzed by combustion in a Carlo Erba Model 1106 Elemental Analyzer. Sediments were dried at 105°C for 48 hours and ground to a fine powder before weighing. Water and salt content were calculated from weight loss during drying. The sediment subsample to be used for organic carbon and nitrogen analysis was treated to remove inorganic carbonates before drying by adding enough HCl to bring the normality of the sample to 0.5 N. Pretreatment of filter samples to remove inorganic carbon was not necessary.

Although the precision for analysis of a weighed organic standard was always less than 1%, the variability in duplicate subsamples of the sediment trap collection and water column samples resulted in a precision of ±5.98% (1 S.D.), over the range 49 - 438 μg-at Carbon liter^{-1} and ±8.35% over the range 6.0 - 64.3 μg-at Nitrogen liter^{-1}. The precision for duplicate determinations of sediment samples was ±0.87% (1 S.D.), over the range 4.2 - 16.9 mg-at Carbon per gram dry sediment and ±1.02%, over the range 0.26 - 1.91 mg-at Nitrogen per gram dry sediment.

The phosphorus content of sediment and particulate matter on filters was determined using a modification of the method of Williams et al. (1967) developed by Beach (1981). Samples were ashed and then leached with hydrochloric acid. The leachate was analyzed for phosphorus colorimetrically after the formation of a blue phosphomolybdate complex.

Variability in duplicate subsamples from sediment trap collections and water column samples resulted a precision of ±7.53% (1 S.D.), over the range 0.33 - 3.41 µg-at Phosphorus liter^{-1}. The precision for duplicate determinations of sediment samples was ±0.76% (1 S.D.), over the range 0.015 - 0.089 mg-at Phosphorus per gram dry sediment .

Temperature, conductivity and salinity were measured in the field with an induction salinometer. Accuracy was ±0.50 °C for temperature, ±0.50 millimhos/cm for conductivity, and ±0.50 parts per thousand for salinity. Precision on any given day was about ±0.10 °C temperature, ±0.10 millimhos/cm conductivity and ±0.10 parts per thousand salinity.

RESULTS AND DISCUSSION

Development of Anoxic Conditions In Aquatic Environments

In aquatic systems where vertical water mixing is not complete, the production of organic matter and oxygen through photosynthesis is separated in time and space from its eventual consumption or oxidation, and a dissolved oxygen deficit develops in the deeper water. Additional organic inputs from leaves, marsh grasses, stream borne detritus, and sewage often increase oxygen demand in estuarine waters. The oxidation of these organic inputs is accompanied by accumulation of inorganic nutrients in the bottom water.

Low oxygen concentrations are characteristic of the bottom waters in many estuaries and coastal environments which develop stratified water columns during parts of the year due to strong temperature and salinity gradients. In estuaries this may result in part from somewhat restricted circulation, but even in more open marine environments the productivity of the surface water may be sufficiently high that consumption of oxygen in the water very near the bottom may exceed the rate of renewal by circulation. For example, anoxic bottom water conditions developed in the New York Bight in the summer of 1976. A naturally occurring, though greater than usual, carbon load accurred when the residence time of the bottom water may have been slightly increased by atypical freshwater run off, temperature and wind conditions (Falkowski et al. 1980). Oxygen conditions in the deep water of the Baltic have been deteriorating at an accelerating rate in recent years, with periodic intrusion of hydrogen sulfide from anoxic bottom water and sediments.

Matthaus (1973) in a long term study of the oxygen trends concludes that the discharge of industrial and urban sewage into the Baltic, and not changes in hydrographic features, are the cause.

Along temperate coasts, anoxic conditions often develop in estuaries when the flushing of bottom water is reduced by a shallow sill near the mouth (Richards 1965). Primary production occurs in the less saline and less dense surface water, then sinks and decomposes in the stagnant bottom water, depleting the oxygen. These conditions are well documented in the Upper and Lower Basins of the Pettaquamscutt River, Rhode Island, a fjord type estuary (Gaines 1975).

Anoxic Conditions in the Pettaquamscutt Estuary

The Pettaquamscutt Estuary is a drowned type river estuary. In the upper part of the estuary are two deep basins separated by a sill less than a meter deep (see Figure 1). A long shallow river of six kilometers connects the upper basins with Rhode Island Sound. Fresh water enters the Upper Basin from Gilbert Stuart Stream and through ground water seepage. The geomorphology and hydrography of the Pettaquamscutt system are described in detail by Gaines (1975).

During the two years of this study, measurements of the physical parameters controlling water column stability were made bimonthly (see Figures 5a-d and Appendix I). During the fall of 1979, the surface water remained about 5 ppt. lower in salinity, due to fresh water input, than the anoxic bottom water. This difference in density, due to salt content, was adequate to prevent the cooler surface water from mixing downward until sometime in January or February, when snow and ice trapped most of the fresh water input, and about 30 percent of the bottom water was exchanged. This is indicated by a dilution of the high levels of sulfide and nutrients in the anoxic bottom water and a slight drop in bottom water temperature (see Figures 5a and 7).

The stability of the water column is strengthened in the spring, first by increased fresh water input after the snow melt and then by rapidly rising surface water temperature. The summer and fall of 1980 were the driest in almost a decade. The inadequate supply of fresh water input resulted in increasing surface water salinity during the fall. As the temperature dropped, the stability of the water decreased until mixing occurred top to bottom in November. This condition persisted for several weeks. Oxygen was present in the entire water column until 11/13/80, but by 12/1/80 the bottom meter water sample was anoxic and sulfide present (see Figures 5c and 7). By the late spring of 1981 the conditions of anoxia had been established long enough for nutrients and sulfide to build to high levels in the bottom 6 meters of the water column (see Figure 6).

The persistence of the same anoxic water mass in which nutrients build up during the year is best illustrated with a T-S diagram (see Figure 6). The bottom six meters for two of the fall 1979 sample days coincide indicating that they are the same water mass. The spring and late summer 1980 water masses also coincide with each other. The exchange of about 30 percent of the bottom water during the winter of 1979-1980 is indicated by a drop in temperature and slight decrease in salinity. The bottom water in the fall of 1980, after the water column mixed top to bottom, is a distinctly different water mass.

Complete mixing of the water column, observed in the fall of 1980, occurs only every few years. Partial exchange of bottom water, such as

30 percent exchanged during the winter of 1979-1980, probably occurs more often. The few weeks that the deep water sediment is exposed to oxygenated water above it are not sufficient to alter the biological or textural characteristics of the mud. Due to the oxygen debt caused by high levels of sulfide in the sediment and the lack of bioturbation by burrowing organisms, oxygen is not likely to penetrate more than a few millimeters. Oxygen consuming oxidation processes occurring during this time represent only a fraction of the oxidation by sulfate reduction during the anoxic period. Some bacterial species may establish themselves temporarily on the mud surface. Chemosynthetic bacteria such as Beggiatoa and Thiothrix use oxygen in the water to oxidize hydrogen sulfide diffusing out of the sediments. Such organisms are common on the sediment at the water depths of 3.5 to 5 meters in the summer and fall as the pycnocline moves deeper in the water and the oxygenated water comes in contact with the previously anoxic and sulfide rich surface sediment. These transitional events may lead to the barely visable varves which occur every few millimeters in sediment cores taken at water depths of 5 meters or more.

At the interface between the deep nutrient rich anoxic water mass and the illuminated surface water, the presence of hydrogen sulfide and adequate light permits continuous growth of the photosynthetic bacteria Chlorobium and Chromatium. These organisms are obligate anaerobes and use hydrogen sulfide in respiration as an electron doner. Except during the winter months, the population of these bacteria are high enough to impart a pink color to the water in the upper most part of the anoxic zone. The high densities of photosynthetic and chemosynthetic bacteria near the interface limited light penetration to the upper meter or less of the anoxic zone (see Appendix 1b).

Stoichiometric Models of Nutrient Cycling

Nutrient Regeneration Under Oxygenated Conditions

Redfield et al. (1963) have described the classic model for the decomposition of organic marine detritus under oxygenated conditions:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \rightarrow 106\ CO_2 + 122H_2O + 16NHO_3 + H_3PO_4$$

This model works well for the surface water of the open ocean. In near-shore and estuarine environments, stoichiometry of the benthic flux of nutrients regenerated from sedimenting organic matter deviates from the predictions of this model (Nixon et al. 1975; Nixon 1981). This may be due in part to processes occurring at the sediment-water interface after the decomposition has taken place such as adsorption, precipitation of minerals or denitrification, as well as a different stoichiometry for the decomposing organic matter.

Nutrient Regeneration Under Anoxic Conditions

After depletion of molecular oxygen, the oxidation of organic matter proceeds by the reduction of nitrate. This process is denitrification and is represented by Richards (1965) with the following equations:

$$(CH_2O)_{106}(NH_3)_{16}(H_3\ PO_4) + 84.8\ HNO_3 \rightarrow 106\ CO_2 + 42.4N_2 + 148.4H_2O + 16NH_3 + H_3PO_4$$

Some of the ammonia liberated in this process may be oxidized:

$$5NH_3 + 3HNO_3 \rightarrow 4N_2 + 9H_2O$$

The overall reaction can be represented by the equation:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 94.4\ HNO_3 \rightarrow 106CO_2 + 55.2N_2 + 177.2H_2O + H_3PO_4$$

After depletion of nitrate and nitrite, sulfate reduction occurs. Due to the high concentration of sulfate, the oxidizing capacity of seawater through sulfate reduction is many times that of the oxygen normally present. According to Richard's (1965) model this reaction takes place:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{-2} \rightarrow 106CO_2 + 53\ S^{-2} + 16\ NH_3 + H_3PO_4 + 106\ H_2O$$

Almgren et al. (1975) have recently suggested a model photosynthetic substance with nitrogen in peptides and phosphate in esters which requires less sulfate for oxidation:

$$(CH_2O)_{89}(NHCO)_{16}C(H_2PO_4)^- + 45SO_4^{-2} \rightarrow 106CO_2 + 45S^{-2} + 73H_2O + 16NH_3 + H_2PO_4^-$$

Just as oxygen consumption and carbon dioxide production can be used to measure the amount of oxidation in aerobic systems, sulfide and carbon dioxide production provides a measure of oxidation in anoxic marine systems by sulfate reduction (Gaines and Pilson 1972; Richards 1965). This reduction of carbon to methane, may lead to underestimates of organic matter oxidation based solely upon sulfide or CO_2 production (Richards 1971). Methane can be formed under anoxic conditions either by anaerobic fermentation or by the reduction of CO_2 (Richards 1971). The most likely pathway when sulfate is still present is acetate fermentation (Atkinson & Richards 1967; Reeburgh 1976). Richards (1971) gives this overall reaction:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CH_4 + 53CO_2 + 16NH_3 + H_3PO_4$$

Since sulfate does not participate in the reaction, no sulfide is produced. One half of the carbon is oxidized to CO_2; the other half is reduced to methane. This process may be important in the sediments of anoxic basins (Nissenbuam et al. 1973) and in the deeper anoxic zone of sediments in aerobic environments (Martens and Berner 1977).

Recent studies have shown that the production of methane in sediments (Nikaido 1977; Oremland and Taylor 1978) can occur while sulfate is still available for oxidation. Methane is gaseous, but unlike gaseous nitrogen it is not conservative in anoxic waters and may be oxidized by micro-organisms (Reeburgh and Heggie 1977).

Composition of Plankton and Detritus

In shallow water environments, decomposition of organic matter in the sediments plays an important part in the cycling of nutrients and energy in the system. The ratios of elements returned to the water column may or may not approximate those in the organic matter sedimented or oxidized. Predictions of these ratios have traditionally been based upon model reactions with plankton of statistically average composition. However, in estuarine environments the composition of the sedimenting organic detritus may differ considerably from that of plankton. Inputs of stream litter, consisting mainly of leaves, which are deficient in phosphorus and nitrogen (Howarth and Fisher 1976) as well as the particulate and dissolved organic matter in sewage effluent may often equal or exceed primary production (Teal 1957; Minshall 1967). The death and decay of anadromous fish may also contribute to the phosphorus and nitrogen budgets of some estuarine systems (Durbin 1976).

In order to model the decomposition process it is necessary to know the composition of organic input to the sediments. Sediment traps were deployed in this study to collect organic matter settling in the water column. Strong currents which sometimes bias sediment trap measurements by resuspending material (Oviatt and Nixon 1975) are virtually absent in the anoxic and low oxygen zones of the water column. Traps were placed far from the shoreline to avoid input of resuspended material from the shallow water sediments.

In the open ocean suspended matter is formed by the plankton. Fleming (1940 cited in Redfield 1963) reported that statistically average plankton has an elemental C:N:P ration of 106:16:1. Organic particles which sink in the water column are not likely to be exactly the same in elemental composition as the living plankton. Some decomposition of these particles takes place. Honjo (1980) studied this process at several locations in the open ocean using sediment traps. Nitrogen and phosphorus were lost preferentially with depth. The C/N ratio changed from 7-8 in the plankton to 9 in the material collected at 400 meters and to 10 in the traps at depths greater than 2800 meters. In the deeper water traps, the atomic ratio of C:N:P was typically 100: 10:1.

Knauer et al. (1979) used sediment traps to assess the sedimentation of organic matter in areas of differing surface water productivity. In a coastal upwelling area with high productivity the C:N:P was 180:18:1 with a C/N of 10. These samples had elevated carbon levels but otherwise did not have ratios much different than that expected for living phytoplankton. Changes in these ratios with depth were far less than in a coastal nonupwelling area of low productivity which already had a C:N:P of 260:27:1 in the shallowest trap and rapidly lost phosphorus in the deepest samples (N/P exceeding 24, C/P of 260-370).

Chester and Larrance (1981) in a study of sedimenting organic matter in an Alaskan fjord report a C/N ratio averaging 9.2 in sediment traps near the bottom. This ratio was consistently higher than that in the overlying water which averaged 6.8.

A year long survey of the elemental composition of suspended matter in the surface water of the Upper Pond resulted in a C:N:P ratio of 135:17.8:1. This reflects the composition of the plankton and is typical of estuarine waters (see Table 2 and Appendix 3a). The highest densities of plankton are found near the oxic-anoxic interface where nutrient concentrations are high due to the upward diffusion of nutrients from the bottom water and the level of light is adequate to support photosynthesis (Miller 1972). Turbulence at this depth is not adequate to resuspend many phytoplankters. On the other hand, the higher density of water below the interface may be adequate to prevent them from sinking into the anoxic zone. These factors contribute to the accumulation of plankton at the oxic-anoxic interface. This is evidenced by the higher levels of particulate organic carbon in this zone (Figures 10a and 10b). The sediment trap at 3.5 meters usually coincided with the upper part of this zone. Annual sedimentation in this trap (see Table 1) is higher than at any other depth due to the settling of live phytoplankton as well as the input of fecal pellets from the abundant zooplankton (Vargo 1974). As a result of the input of this fresh organic matter, elemental composition of material collected in this trap is closest to the composition of statistically average plankton discussed below.

The elemental composition of phytoplankton grown in culture has been shown to reflect the levels of nutrients in the medium. There is evidence that this process may be occurring in the water column. The particulate C/N and C/P ratios are much higher in the nutrient poor surface water than in the nutrient rich water near the interface (Figures 10a and 10b). The high N/P ratio indicates that phosphorus may be limiting in the surface waters (as is typical of systems with significant fresh water input). Material trapped at 1.5 meters reflects the lower nitrogen and phosphorus content which is characteristic of the suspended material in this part of the water column.

The traps at 7.0 and 10 meters are below the particulate carbon maximum and the productive region of the water column. Most of the material settling into these traps was clearly identifiable as fecal pellets which appeared as black specks on the glass fiber filters. Although the C/N for fresh fecal pellets typically is higher than for plankton (Honjo and Roman 1978), this material has also undergone additional decomposition in the water column. The difference in composition between 7.0 and 10.0 meters is slight which is probably due to the additional sinking distance of only three meters.

Composition of Sediment Organic Matter

The rate of sedimentation in the Upper Pond of the Pettaquamscutt Estuary was established with radiocarbon dating to be about 1.4 mm per year (Orr and Gaines 1974). Surface sediment samples were taken to a depth of 50 mm, giving an average depth of 25 mm. The age of these sediments in the anoxic zone is about 18 years. In shallow water, bioturbation by benthic macrofauna, worms and amphipods, mixes the sediment to a depth of about 2-4 centimeters. At less than about 3.5 meters water depth, the age of the surface sediment is about 143 to 286 years.

The surface sediment sample originates with sedimenting particulate matter but has undergone far greater decomposition due to its age than material collected in the traps. The composition of the sediment surface material reflects this decomposition (see Figures 13a and 13b and Table 1). As the water depth increases, the sediment is not mixed as effectively by bioturbating organisms and the relative age of the surface sediment decreases. The more recent surface sediment in deep water has undergone less decomposition as evidenced by the increase in organic carbon (partly due to less clastic materials than in the shallowest samples), the decrease in carbon to nitrogen ratio, and the decrease in carbon to organic phosphorus with depth (see Figure 13a). In the organic fraction, the N/P ratio is slightly lower in the shallower sediments indicating that some nonhydrolyzable phosphorus might be retained preferentially over nitrogen in oxidizing conditions. This N/P ratio is always at least twice as high as that in the sediment traps. In the oxic sediment at 2.5 meters water depth, it increases from 38 to 45, just a few centimeters below the depth of bioturbation. In the permanently anoxic sediment, the ratio changes very little from a value of slightly less than 45 at the sediment surface. Clearly, most of the preferential loss of phosphorus over nitrogen takes place in the first few years of decomposition following sedimentation.

In the organic fraction the increase in both the carbon to nitrogen and carbon to phosphorus ratio is more rapid near the sediment surface than at depth. In the shallowest water (2.0 meters) oxic sediments, the surface sediment C/N is already 15 and it drops rapidly to about 10 at a water depth of 4.0 meters where bioturbating organisms are excluded. In the deep water, with recently deposited material on the sediment surface, the C/N is about 9. Since extensive decomposition has already taken place in the surface sediment at 2.5 meters the increase in C/N down core is from 14 to slightly more than 16 at 20 centimeters depth in the core. In the permanently anoxic sediment with no bioturbation, the more recent organic matter at the surface has a C/N of 9 and looses more carbon with depth than the oxic sediment resulting in a C/N ratio of almost 14 at a depth of 20 centimeters in the core.

The organic carbon to organic phosphorus ratio in the surface sediment is highest (more than 500) at the shallow oxic depths. It drops to about 450 at water depths characterized by low oxygen conditions and then gradually decreases to about 400 in the permanently anoxic sediments. The organic fraction is about 35% in the shallower oxic surface sediment and 45% in the permanently anoxic sediment. The carbon to inorganic phosphorus ratio increases from about 300 in shallow water to 450 in the zone of transition from low oxygen to anoxic conditions (4.5 m - 6.0 m) before dropping to 340 at permanently anoxic depths (see Appendix 6c). This is not due to increased decomposition since the carbon to organic phosphorus ratio decreases gradually. In the transition zone bioturbating macrofauna are effectively excluded by the condition of low oxygen and periodic anoxia. The recently deposited sediment is not mixed downward, and though the age of the surface sediment probably decreases gradually, it is closest to that of the deeper sediments. Inorganic phosphorus is removed from the sediments in this transition zone by chemical dissolution, and as a result, the fraction of the phosphorus which is inorganic decreases.

There is a loss of organic phosphorus relative to carbon with depth in the sediments. This is due to decomposition of the organic matter. The loss of total phosphorus to organic carbon, however is more rapid and this difference is due to the continued loss of phosphorus from the inorganic fraction buried in the sediments. As a result, the organic fraction as a percentage, increases. The increase in this fraction with depth occurs most rapidly in the shallow oxic sediment where it goes from 35 to 73 percent in the top ten centimeters. In the permanently anoxic sediment, a change from 46 to 73 percent takes place over the top thirty centimeters. The rapid loss of inorganic phosphorus with depth in the shallow water sediments is due to the release from adsorption sites on oxyhydroxide sediment particles during the anoxic reduction of iron (Krom and Berner 1981) as conditions become more reducing and begin to resemble the environment from which the anoxic sediments were taken. This process is evident during the transition from oxic to anoxic water conditions in shallow water cores (see Figure 11a and 11b). At the depth that the degree of organic matter decomposition (as evidenced by similar nitrogen to organic phopshorus ratios) becomes similar in the sediment from the two environments (10 centimeters in the oxic sediment and 30 centimeters in the anoxic sediment), the fraction of the total phosphorus which is organic is also similar, at 73 percent. In both environments, at this depth in the sediment, the conditions have been reducing for many years.

Stoichiometry of Anoxic Bottom Water

Because anoxic conditions arise when bottom water is stagnant, this water accumulates the products of organic matter decomposition. Investigations of the chemistry of anoxic basin waters have been used to examine the preceeding models of decomposition. As might be expected, complicating factors require that a number of assumptions and qualifications be made before a test of the relationship between the stoichiometry of inorganic nutrients in the bottom water and the composition of decomposing organic matter can be made. The composition of sedimenting organic detritus entering the anoxic zone, the degree and nature of decomposition in the anoxic water column, the processes of uptake and release of inorganic nutrients which occur in the sediments, and the preformed nutrients and original oxygen content of the water, must be known.

Sedimenting material was captured at various depths in the water column. Significant differences in elemental composition were found between traps in the oxic and those in the anoxic zone. It is clear that the material falling into the anoxic traps had undergone some decomposition. Changes taking place in the water column however are slight due to the short time that they are suspended. Changes with depth in sediment cores however, reflect changes in the elemental composition of the solid phase over long periods of time. These elements contribute to the benthic flux and accumulate in dissolved form in the water column. The preformed nutrients in the anoxic bottom water can be inferred from the positive deviation along the axis in regressions between various nutrients.

Sedimenting organic matter and changes in the anoxic bottom water nutrient concentration in the Pettaquamscutt and other anoxic basins are presented in Table 2. The mode of organic matter oxidation by sulfate reduction, $(CH_2O)_2 + SO_4^{-2} = H_2S + 2(HCO_2^-)$, predicts that two carbon molecules are oxidized for each sulfur molecule which is reduced. The potential sources of carbon, nitrogen, and phosphorus in the sedimenting organic matter can be compared to the products of this decomposition in the water column. In the stagnant bottom water, the ratio of sulfate reduced to carbon dioxide produced is close to the predicted value (0.517 observed, 0.50 predicted, see Figure 12a). The nitrogen to phosphorus ratio in sedimenting organic matter collected in the 7.0 and 10.0 meter traps (14.4 and 13.6 respectively), is very close to the ratio of changes observed in the bottom water of 14.3 (see Figure 12f). Only about 80 percent of the carbon is oxidized relative to nitrogen and phosphorus metabolized when the carbon content of the sedimenting organic matter is compared to the sulfide or inorganic carbon produced (108/140 or 2(59.4)/140). This is reflected in the high C/N and C/P ratios in the sediment.

The origin of phosphorus released from the sediments in the anoxic deeps of the Baltic is both organic and mineral (Balzer 1980). Sen Gupta and Korleff (1973) considered this in a stoichiometric model of nutrients in the Baltic. They compared surface water plankton composition to nutrient regeneration of oxidative origin in the anoxic water and found close agreement. If they assumed organic matter lost only a few percent of the nitrogen and phosphorus before reaching the anoxic zone, the sulfide produced would be equivalent to the carbon supplied in organic matter of plankton origin. The amount of carbon oxidized (or sulfide produced) relative to nitrogen and phosphorus regenerated was higher than that in the Pettaquamscutt. When compared to the Black Sea, Byfjorden and Lake Nitinat, the anoxic sediment of the Pettaquamscutt oxidizes less carbon per molecule of nitrogen and phosphorus regenerated. This is probably due to the relatively higher content of nitrogen and phosphorus in the organic matter actually reaching and decomposing in the anoxic zone in this shallow basin.

Although the stoichiometry of the oxidative processes in the bottom water of the Baltic indicates that the organic matter actually decomposing is very similar in composition to the surface plankton, this does not mean that the organic matter supplied to the anoxic zone is as rich as surface plankton in nitrogen and phosphorus. This also applies to the other anoxic basins in Table 2, where no analysis of sedimenting organic matter has been made. The depletion in nitrogen and phosphorus of accumulating sediments indicates that sedimenting organic matter is enriched in carbon.

Silica is regenerated at 3.43 times that of phosphorus. This is considerably slower than the Si/P of 16 typical of some surface waters, algal decomposition experiments and observations in anoxic Lake Nitinat (Richards et al. 1965).

The ratio for the change in methane to inorganic carbon concentration remains constant throughout the anoxic bottom water at about 1 percent. This suggests that methane is not oxidized after it escapes from the sediment. Methane is produced deep in the sediment below the zone of maximum sulfate reduction but much of it may be oxidized by sulfate reducing bacteria at shallow sediment depths before it can escape into the water column.

Rates of Oxidation and Nutrient Regeneration

There is little question that sediments accumulating under anoxic (water column) conditions contain more organic carbon than those accumulating under oxidizing conditions (Richards 1970). The organic carbon content of marine sediments accumulating under oxic water columns range from about 0.2 to 4 percent by weight, while organic carbon in sediments accumulating under anoxic water columns range from 1.0 to 20 percent (Demaison and Moore 1980). This observation has lead to the suggestion that the rate of organic matter oxidation in anoxic marine environments is slower than under oxic conditions.

The indirect evidence for this is not trivial. The most basic argument is thermodynamic. In any aquatic system there is the tendency for reduced substances, in this case organic matter, to loose electrons and become oxidized. The low pE under anoxic conditions means that there is high electron activity (many electrons available to reduce the oxidized substances). This redox potential is proprotional to the free energy change per mole of electrons in a given reaction. In an anoxic system, oxidation of organic matter yields less free energy than oxidation under oxic conditions (high pE). It has been proposed that this reduced electron drive results in preservation of a greater proportion of the sedimenting organic matter under reducing (anoxic) conditions (Claypool and Kaplan 1974).

In some aquatic systems where the origin of the organic matter is terrestrial (or from higher plant materials) much of the carbon is in the form of celluloses. Organisms responsible for the breakdown of these compounds, primarily certain fungi, are eliminated under anoxic conditions and organic preservation relative to oxic conditions is readily demonstrated

(Tenney and Waksman 1930). Peat bogs are an extreme example of this process of organic matter preservation. The ability of the system to supply oxygen by mixing and diffusion is overwhelmed by the rapid supply of higher plant material and the high demand for oxygen to decompose it.

Observations of terrestrial organic matter preservation and thermodynamic arguments for slow rates of oxidation under anoxic conditions only indirectly support the relation between high organic content in the sediments of anoxic basins and the rate at which processes of oxidation occur in these sediments. Richards (1970) suggested that the greater quantities of organic matter normally found in these areas are a function of higher rates of organic sedimentation. There is considerable evidence that the organic carbon content in fossilized sediment from oxic sedimentary environments is a function of the sedimentation rate (Heath et al. 1977; Muller and Suess 1979).

The effect that the rate of sediment thickness increase alone causes was determined by Muller and Suess (1979) to follow an emperical relationship. They show that the organic carbon content of accumulating sediments doubles with each ten-fold increase in the bulk sedimentation rate if the primary productivity is constant. However, since the primary productivity usually increases with sedimentation rate, the organic carbon content increases typically by a factor of two with each four-fold increase in sedimentation rate. The change in both the reactivity and the concentration of organic matter accumulating in the sulfate reducing zone of marine sediments is presumably a function of the time that the organic matter has remained in the zone of bioturbation and was exposed to aerobic processes of decomposition. The more rapid the sedimentation rate, the shorter the time of exposure.

Once the organic matter has entered the zone of bioturbation, continued oxidation depends upon the reactivity of the organic matter and the adequate supply of the electron acceptor, sulfate. In a review of factors influencing sulfate reduction in marine sediments, Goldhaber and Kaplan (1975) argue that the rate of sulfate reduction (per unit volume basis, porewater) is positively correlated with the rate of sediment accumulation as a result of these factors: (1) sediment total organic carbon is correlated with high sedimentation rate; (2) rapidly sedimented organic matter is less degraded and complexed; (3) these rapidly accumulating sediments tend to occur in shallow water environments where time for degradation in the water column is short and temperatures are higher.

The reactivity of organic matter is often expressed on a weight or volume basis. When the entire sediment column is considered, the areal rate of oxidation is less dependent on reactivity. Westridge (1981) using radiosulfur isotopes determined that the rate of sulfate reduction on an areal basis (integrated value to depth of zero sulfate) was about the same in an anoxic rapidly sedimenting environment and central Long Island Sound. In the organic rich, anoxic environment, most of the sulfate reduction took place at or near the sediment surface. In Long Island Sound, sulfate reduction took place below the zone of bioturbation and extended over a much deeper section of sediment. The reactivity of the organic matter below the zone of sulfate reduction in the rapidly accumulating sediment remained quite high, but sulfate was depleted at a much shallower depth in the sediment than in Long Island Sound. The organic carbon content of the sediment accumulating in the anoxic environment remained at about 4.0 percent even after burial. In Long Island Sound, the organic carbon content near the sediment surface was 2.0 percent and decreased to 1.5 percent at the depth of porewater sulfate depletion. Thus it seems probable that in rapidly accumulating sediments, the depletion of sulfate may limit the degree of organic matter decomposition and result in a higher organic content in the fossilized sediment.

Only a small percent of the primary production in the water column is permanently buried in the sediments. Orr and Gaines (1973) calculated that 6 percent of the primary production was fossilized in the Upper Pond of the Pettaquamscutt Estuary. They assumed that productivity was comparable to similar nearshore environments, 300 grams of carbon m^{-2} per year. The organic carbon content of the sediments is about 15 percent. If the sulfate reduction rate was increased by only 8 percent, the organic carbon content of the accumulating sediment would be reduced to half of its present value. Similarly, if the sulfate reduction rate in the Black Sea were increased by only about 20 percent, the organic carbon content of the sediment would decrease from 4 percent (Dueser 1971) to 2 percent. Clearly, small changes in the rate of sulfate reduction on an areal basis in anoxic basins can result in large differences in the organic carbon content in the sediment. The same argument applies to sediments accumulating under oxic water columns. The total metabolism of the benthos is a function of the depth of the mixed layer and the primary production (Hargrave 1973). The portion of the organic matter preserved in various sediments is always relatively small over a wide range of areal rates of benthic metabolism. Exceptions to this are in areas with very high organic matter accumulation rates such as some estuarine and upwelling areas, and areas with very high bulk sedimentation rates such as deltas. In these environments, oxidation of organic matter is limited by the supply of electron acceptors through diffusion (Berner 1978).

The reactivity of the organic matter is a function of its source and the time that it has spent in contact with an adequate supply of electron acceptors. In areas of slow and medium sedimentation rate, the only organic carbon preserved may be in organic compounds formed after sedimentation or the remains of bacterial biomass (Lijmbach 1975). The amount of recalcitrant organic matter remaining may also be related to the source. Johnson and Brinkhurst (1971) attribute the higher organic carbon content of their nearshore sediments to relatively lower utilization of organic matter of terrestrial origin. Similarly, Lyons and Gaudette (1979) attributed lower reactivity of organic matter from some sediment sites in Great Bay, N.H., to its terrestrial source. Higher plants, growing on land and in shallow water, contain lignin and waxes that are more resistant to microbial attack than plankton derived organic material, even under oxic conditions (Aizenshtat et al. 1973). Terrigenous material supplied by rivers has as its source subaerial soils where considerable degradation has already taken place, leaving organic material which is quite refractory in nature (Demaison and Moore 1980). In the Pettaquamscutt Estuary, structural materials in tree leaves are resistant to microbial attack under anoxic conditions and leaves are found preserved in varved sediments which are over two hundred years old.

The absence of oxygen during the early diagenesis of organic matter in sediments effects not only the amount and reactivity of accumulating organic matter, but also the composition (Demaison and Moore 1980; Price 1976). The organic matter accumulating in anoxic environments is more abundant and lipid rich than that from similar, but oxic areas, even if it has undergone extensive degradation. These differences can be attributed to the presence of benthic animals in sediments with oxic water columns. Bioturbation by these organisms greatly increases the time that sediment particles are exposed to aerobic oxidation and decomposition before burial in the zone of sulfate reduction. Oxygen rich surface water is pumped down to a depth of several centimeters and particles are mixed throughout a depth of about 10 centimeters. Mechanical breakdown of larger particles increases the reactive surface area and bacteria-eating organisms constantly clean and expose new surfaces (Gerlach 1978). Metazoans themselves digest organic matter with enzymes not produced by bacteria, and excrete inorganic phosphorus and nitrogen. The introduction of a steady supply of electron acceptors through the downward pumping of surface water acts to overcome limitations on the rate and extent of oxidation that exist where diffusion alone provides these reactants (Hylleburg and Hendriksen 1980).

Isolated sections of sediment from the oxic and anoxic water depths were incubated in the laboratory to investigate the reactivity of the organic matter. Pore water ammonium production was taken as a measure of reactivity. The percentage of the organic nitrogen remineralized per day at each depth in the sediment is shown in Figure 18. No correction for adsorption of ammonium by the sediment has been made. The absolute rates are probably underestimated by about one-half, but the relative portion absorbed should be constant (Rosenfeld 1977).

The surface sediment (top 2 cm) accumulating in the anoxic environment is more reactive at 7°C by a factor of 3.2 than the surface sediment in the oxic environment. Even at 10 centimeters the sediment from the anoxic environment is more reactive by a factor of 2.1. A large portion of the source of organic matter for the permanently anoxic sediment is the very productive plankton near the aoxic-anoxic interface. This is a source of relatively fresh and labile organic matter in the form of fecal pellets and it has not been exposed to aerobic oxidation. In contrast, the organic matter in the top 2 centimeters of the oxic sediment has been exposed to oxic conditions before and after deposition. The oxic sediment also has a greater contribution from recalcitrant organic matter of terrestrial origin since it is near the shore.

The rate of ammonium production (7°C) at 10 centimeters in the sediment under anoxic water is about 6 percent of the rate at 1 centimeter sediment depth. In contrast, the rate decreases to only 10 percent in the sediment under the oxic water column. The more gradual attenuation of ammonium production rate in the oxic environment can be attributed in part to bioturbation which mixes the more reactive surface organic matter downward and less reactive older material upward.

Rate of Supply of Organic Matter to the Benthos

The supply of organic matter to the benthos is a function of the primary production, allochthonous organic inputs and subsequent decomposition in the water column (Hargarve 1980; Nixon 1981; Zeitzchel 1980; Harrison 1980). A long residence time in the water column caused by a deep mixed layer of very deep water, decreases the portion of the primary production remineralized by the benthos. Organic carbon production in nearshore waters ranges from 100 to 150 g C m^{-2} yr^{-1} and the percentage oxidized by the benthos is from 25 to 60% (Zeitzchel 1980). This oxidation amounts to 25 to 90 g C m^{-2} yr^{-1}. Primary production in estuaries and upwelling areas is at least twice as high as in nearshore areas.

Dueser (1971) estimated organic input to the anoxic zone of the Black Sea to be 20 g C m^{-2} yr^{-1} and that about 80 percent of this is oxidized. Orr and Gaines (1974) calculated carbon oxidation in the anoxic bottom waters and sediments of the Upper Basin of the Pettaquamscutt River from sulfide production after overturn and restratification (in 1971 through 1972). The rate of carbon oxidation was 9.16 g-at m^{-2} yr^{-1} (110 g C m^{-2} yr^{-1}) and remained constant for more than a year. This rate is quite high and comparable to rates in aerobic systems.

The traps used in this study to collect organic matter sedimenting into the anoxic zone do not permit a quantitative estimate of the sedimentation rate. The traps collected only 2 percent of the sedimenting organic matter (see Table 1). This was due to loss of material upon recovery and the occasional deployment, six times during the year, which may not have corresponded to periods of maximum sedimentation.

Rate of Organic Matter Oxidation in the Sediment

Since most of the organic carbon input to the sediments is oxidized, benthic oxidation rates on an areal basis can be quite high in anoxic environments. Oxidation rates of some anoxic marine basins and anoxic sediments are summarized in Table 4. The amount of carbon oxidized in the sediments of anoxic basins can equal that below oxic water columns. The portion of organic matter oxidized by anaerobic processes in the anoxic zone of sediment below oxic water columns can be almost 50 percent where the rate of organic input is high.

The annual sediment organic carbon oxidation rate calculated from sulfide flux using in situ chambers was between 55 and 72 g C m^{-2} yr^{-1} (see Appendix 5a). This is a little more than half of the estimate of Orr and Gaines (1974). The rate in the anoxic zone is slightly higher than in situ rates for the shallower oxic sediments (48-50 g C m^{-2} yr^{-1}, see Appendix 5b). This may be due to lower organic input. Although allochthonous input of leaves and marsh grass is higher in shallow water, input from the considerable productivity of the plankton community near the oxic-anoxic interface is available to the anoxic zone. Benthic metabolism in the anoxic zone of the Pettaquamscutt Estuary is about half of that in nearby Narragansett Bay (at the same temperature) where the primary production rate is similar (Hale 1976).

Effect of Temperature on Oxidation Rate

In studies of benthic metabolism based upon oxygen uptake, changes in metabolism have been correlated with seasonal temperatures (Hale 1976, Hargrave 1969). Pamatmat (1977) in a review of factors affecting benthic oxygen uptake, found that the supply of fresh organic matter was most important. Hargrave (1973) was unable to correlate temperature with benthic production except on a local basis. He suggested (1978) that seasonal oxygen uptake was related to the supply of freshly sedimented organic matter rather than temperature and that the time of highest temperature usually corresponds to the time of highest organic input from primary productivity. Nixon et al. (1980) investigated the response of laboratory cores to a temperature increase similar to the in situ winter-spring warming. The effect of temperature on the phosphate and ammonium flux was considerably greater from cores collected after the intense winter-spring phytoplankton bloom than from cores collected in the late fall. A relatively greater response of phosphate to the warming may be due in part to chemical remobilization of oxidized complexes as oxygen demand by organic matter at the sediment-water interface brings reducing conditions nearer the sediment surface (Klump and Martens 1981).

Kaplan and Rittenberg (1964) demonstrated a significant effect of temperature on sulfate reduction in culture. An increase in temperature from 5° to 25° C increased the rate by a factor of 5. The population of sulfate-reducing bacteria in a salt marsh sediment was examined by Abdollahi and Nedwell (1979) over an annual cycle for response of sulfate reduction rate to temperature. The temperature characteristic of the population remained relatively constant over the year and was equivalent to a Q_{10} of 3.5. Jorgensen (1977) found a similar Q_{10} of 3.4 in a study of sulfate reduction in the shallow water sediment of a Danish fjord. Westbridge (1981) found the Q_{10} of Long Island Sound sulfate reducers to be about 4.0.

In environments with widely varying temperatures, temperature may be the environmental variable of primary importance. Nedwell and Abram (1979) compared the relative importance of temperature, electron donor (lactate) and electron acceptor (sulfate) in controlling sulfate reduction rates in a salt marsh pan. Temperature had the greatest importance, followed by the electron donor and then sulfate, but only when sulfate was at low concentrations. The seasonal temperature range in the bottom water and sediments of anoxic basins is usually only a few degrees. As a result, seasonal rates of organic matter oxidation are not likely to be controlled by temperature. Indrebo et al. (1979) investigated primary production and sulfate reduction in a stratified fjord.

Primary production and organic matter sedimentation were highest during the summer months and in excess, at this time, of sulfate reduction in the anoxic zone. In the winter months, the sulfate reduction continued at a high rate although the production of new organic material was low. In another anaerobic process, methane production, Kelly and Chynoweth (1981) observed a rapid increase in rate with temperature (Q_{10}=2.4). But since in situ hypolimnetic temperatures are low and relatively constant, the rate of methane production was linearly related to organic input in several lakes.

Orr and Gaines (1974) found that production of sulfide in the Pettaquamscutt was constant for over a year following overturn. An intense phytoplankton bloom preceeding stratification provided a large supply of fresh organic material to the sediments. In the present study, measurements of benthic sulfide production using in situ benthic chambers indicate that late spring rates are about 30 percent higher than early fall rates, although the temperatures are the same. This may be the result of a phytoplankton bloom in the spring and subsequent organic matter sedimentation as some of nutrient rich bottom water is displaced upward to enrich the surface water.

The effect of temperature on ammonium production was investigated by incubation of sediment sections at two temperatures 7° and 20°C. Sediment cores were taken from the shallow water with an overlying water column that is always oxic and from the permanently anoxic deep water sediments (see Figure 18 and Appendix 7a and 7b). The ammonium production rate in the sediment from the anoxic zone increased by a factor of 2.9-5.5 over this temperature range. In contrast the rate increased only by a factor of 1.5-2.0 in the sediment from the oxic environment. These increases were greatest in the deepest sediment sections. Aller and Yingst (1980) reported a Q_{10} of 3.4-3.0 for sulfate reduction rate in a similar experiment on the Long Island Sound sediments over a temperature range of 4° to 22°C.

Depth Below Surface (m)	Location	Carbon (g-at m^{-2} yr^{-1})	Nitrogen (g-at m^{-2} yr^{-1})	Phosphorus (g-at m^{-2} yr^{-1})	Average C : N : P	Average C/P	Average N/P	Average C/N
1.5	A	3.056	0.306	.0203	106 : 9.91 : .647	163.8	15.31	10.69
1.5	B	3.527	0.355	.0225	106 : 9.85 : .619	171.2	15.91	10.76
1.5	Average of A and B	3.289	0.331	.0214	106 : 9.88 : .634	167.4	15.60	10.73
3.5	A	5.490	0.675	.0363	106 : 12.79 : .688	154.1	18.60	8.28
3.5	B	4.852	0.556	.0391	106 : 12.15 : .820	129.2	14.82	8.72
3.5	Average of A and B	5.171	0.616	.0377	106 : 12.47 : .754	140.6	16.54	8.50
7.0	A	1.725	0.167	.0131	106 : 10.21 : .738	143.6	13.83	10.38
7.0	B	1.540	0.183	.0122	106 : 11.19 : .744	142.5	15.04	9.48
7.0	Average of A and B	1.632	0.185	.0126	106 : 10.70 : .741	143.1	14.44	9.91
10.0	A	1.313	0.144	.0108	106 : 10.50 : .757	140.0	13.87	10.09
10.0	B	2.347	0.251	.0191	106 : 10.45 : .788	134.4	13.25	10.15
10.0	Average of A and B	1.830	0.198	.0149	106 : 10.47 : .773	137.15	13.55	10.12
			Sediment Surface Samples					
At 11.0 meters water depth, total phosphorus calculation					106 : 11.82 : .611	174.	19.35	8.97
At 11.0 meters water depth, organic phosphorus calculation					106 : 11.82 : .281	378.	42.08	8.97
At 8.5 meters water depth, total phosphorus calculation					106 : 11.73 : .589	180.	19.93	9.04
At 8.5 meters water depth, organic phosphorus calculation					106 : 11.73 : .274	386.	42.77	9.04

Table 1. Annual sedimentation of organic carbon, nitrogen, and total phosphorus into sediment traps. Average ratios are calculated from ratios from collection on each sampling day, omitting sample when water column was mixed. Sediment surface (0.0 to 0.5 cm) samples are included for comparison.

Location	Organic Matter Source	Organic Matter Elemental Ratio		Change in Nutrient Concentration in Overlying Anoxic Water Column		
		C:N:P	C:N	C:S:N:P:Si	C:N	S:N
Pettaquamscutt (this study)	Surface Plankton integrated sample 0-6.5m	135:17.8:1	7.56	108:59.4:14.3:1:3.43	7.88	4.04
	Sediment Trap					
	Oxic zone 1.5m	167:15.6:1	10.73			
	Oxic zone 3.5m	141:16.6:1	8.50			
	anoxic zone 7.0m	143:14.4:1	9.91			
	anoxic zone 10.0m	137:13.6:1	10.12			
	Sediment Surface 8.5m	180:19.9:1	9.04			
Baltic Sea (Sen Gupta and Korleff 1973)	Surface Plankton	154:13.3:1	11.58	-:87.0:13.7:1:- (calculated from P of oxidative origin only)	-	6.35
				-:10.2:1.62:1:- (includes inorganic P leaching out of sediments)	-	5.60
Byfjorden, Sweden (Almgren et al. 1975)				80:36.8:6.64:1:- (calculated from bottom water nutrient profiles)	12.05	5.54
Black Sea (Skopintsev et al. 1958 cited in Richards et al. 1963)					13.18	4.49
Lake Nitinat, B.C. (Richards et al. 1965)				194:69.0:22.0:1:16	8.81	3.14

Table 2. Elemental composition of organic matter sedimenting in anoxic basins and the changes in nutrient concentrations observed in the bottom water.

Location and Method	Flux, mmol m^{-2} day^{-1} CO_2-C	 H_2S-S	 NH_4^+-N	 PO_4^{-3}-P	 SiO_2-Si	Elemental Ratio C:S:N:P:Si
Pettaquamscutt, anoxic basin (this study) *in situ* chambers average of 5 chambers	–	7.42	2.06	0.168	0.993*	–:51.0:14.3:1:5.87 (from conc. changes in chamber water)
Baltic Sea, anoxic water (Hallberg et al. 1976 cited in Dyrssen and Hallberg 1979) *in situ* chambers	–	6.4	0.55	.18	–	–:35.6:3.06:1:–
Byfjorden, Sweden, anoxic basin (Almgren et al. 1975) calculated from bottom water nutrient profiles	6.6	3.0	0.55	0.083	–	80:36.8:6.64:1:–
Cariaco Trench, anoxic basin (Fanning and Pilson 1972) sulfide flux calculated from vertical diffusion-advection model, silica flux from pore water profile	–	0.606	–	–	0.134	(S/Si = 4.52)

Table 3. Benthic flux of dissolved nutrients in anoxic marine basins.

Location	Method	Temp °C	Sulfate Reduction mmol SO_4^{2-} m^{-2} day^{-1}	Total Oxygen Consumption at this temp. g C m^{-2} yr^{-1}	Anaerobic Oxidation at this temp. g C m^{-2} yr^{-1}	Total Oxidation at this temp. g C m^{-2} yr^{-1}
Overlying Water Anoxic:						
Pettaquamscutt (this study)	*in situ* chambers	10° 12°	8.17 6.31	- -	71.6(spring) 55.3(fall)	-
Pettaquamscutt (this study)	sulfide accum. in anoxic water	8-9°	8.71	-	76.4 (annual)	-
Pettaquamscutt (Gaines 1975)	sulfide accum. in anoxic water	8-9°	12.6	-	110 (annual)	-
Baltic Sea (Bagander 1977)	*in situ* chambers	10°	4.3-5.1	-	38-45(fall)	-
Black Sea (Deuser 1971)	stable isotope ratios in anoxic water	9°	1.14	-	10 (annual)	-
Cariaco Trench (Fanning and Pilson 1972)	sulfide accum. in anoxic water	17°	.606	-	5.31(annual)	-
Byfjorden, Sweden (Almgren et al. 1975)	bottom water nutrient profile	10°	3.0	-	28.1(annual)	-
Saelenvann, Norway (Indrebo et al. 1975)	^{35}S incub. water column and sediment	10-11°	3.1-4.5	-	27.1-39.1 (annual)	-
Overlying Water Oxic:						
Pettaquamscutt (this study)	*in situ* chambers	18° 20°	- -	21.9 22.9	- -	48.0(spring) 50.2(fall)
Narragansett Bay (Hale 1976)	*in situ* chambers	11°	-	54	-	118(spring)
Limfjorden, Denmark (Jorgensen 1977)	^{35}S incub. and sediment oxygen uptake	11°	9.5	68	83	158(annual)
Randers & Kysing Fjords, Denmark (Sorensen et al. 1979)	^{35}S incub. and sediment oxygen uptake	3° 18°	2.6-7.6 9.8-15.1	60 170-180	23-67 86-132	131(winter) 383(summer)

Table 4. Oxidation rates in anoxic marine basins and anoxic sediments.

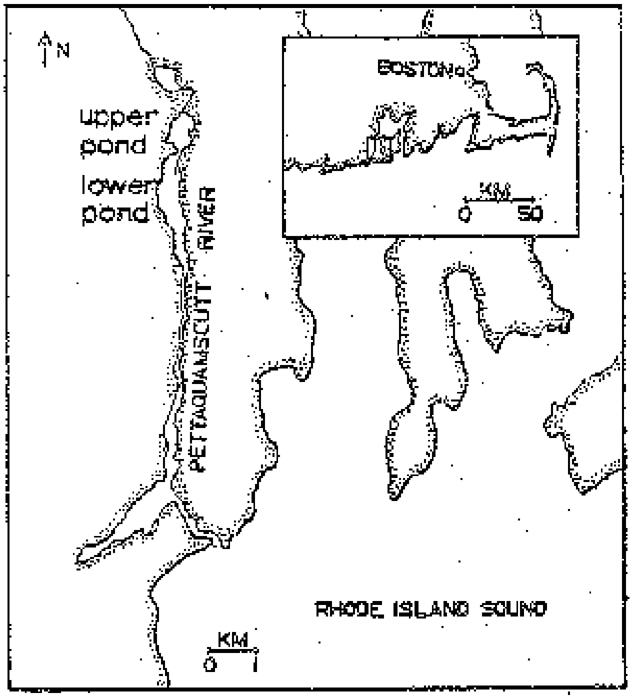


Figure 1a) Location of the Pettaquamscutt Estuary (from Gaines, 1975)

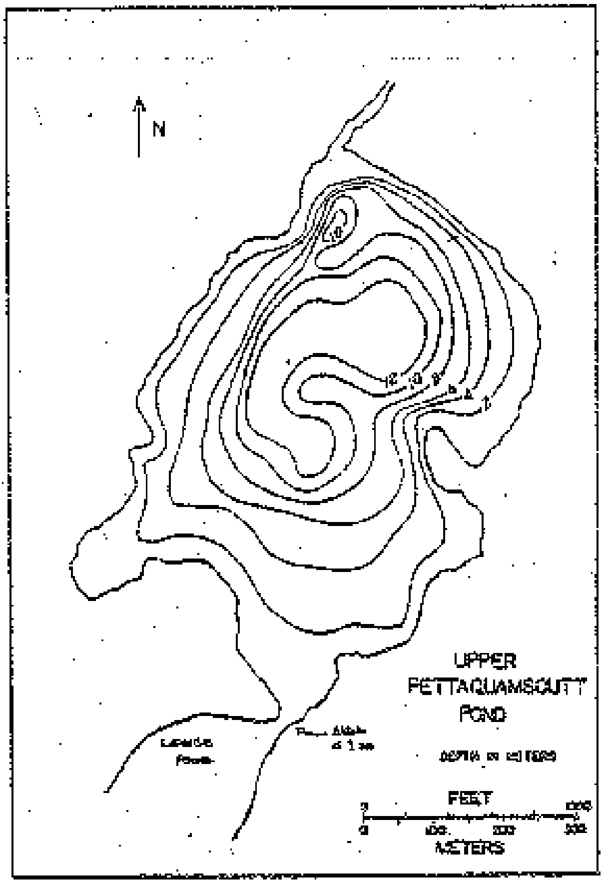


Figure 1b) Bathymetry of the upper pond (from Gaines, 1975)

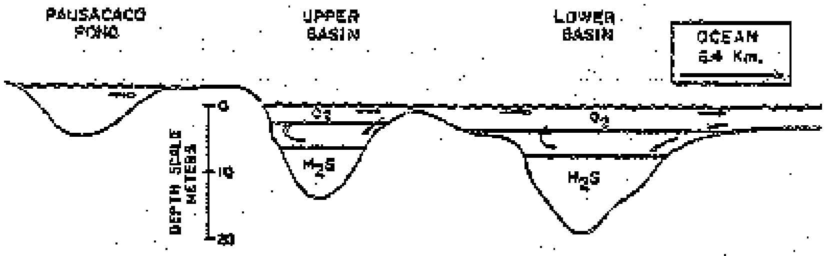


Figure 1c) Tidal and density circulation scheme (from Gaines, 1975)

PETTAQUAMSCUTT RIVER BASINS
VERTICAL EXAGGERATION CA.40:1

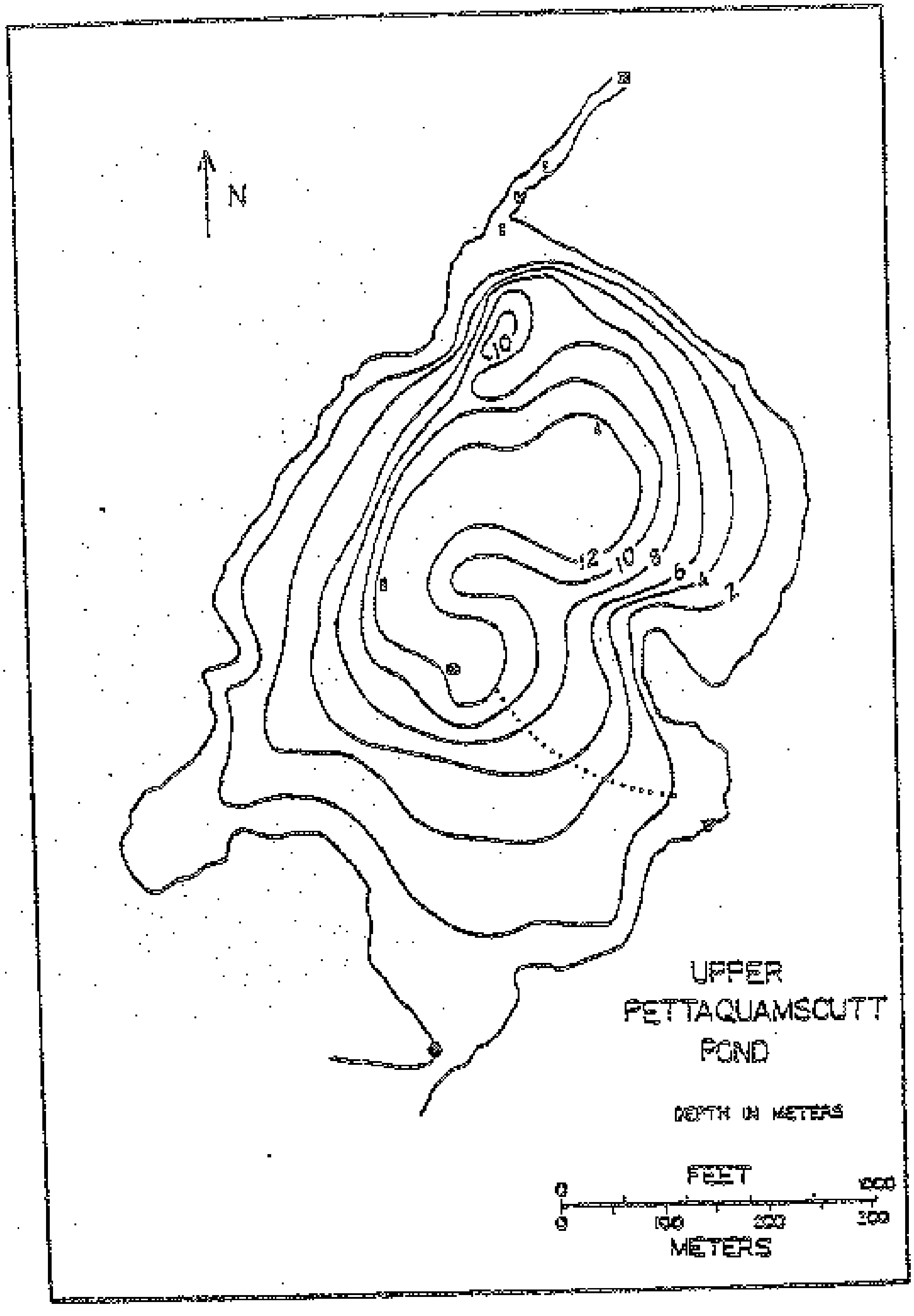


Figure 2. Map of Upper Pettaquamscutt Pond sampling sites. Permanent water column sampling location (◉). Sediment trap deployment area (A and B). Allochthonous detritus sampling sites: spillway (not shown, about 400 meters upstream), stream (⊠), shore leaves (▽) and sill (⊛). Freshwater stream sediment surface sample sites (C, D and E). Transect for sediment surface and core samples (indicated by dotted line). *In situ* benthic chambers were placed a few meters north of this transect. (Adapted from Gaines 1975).

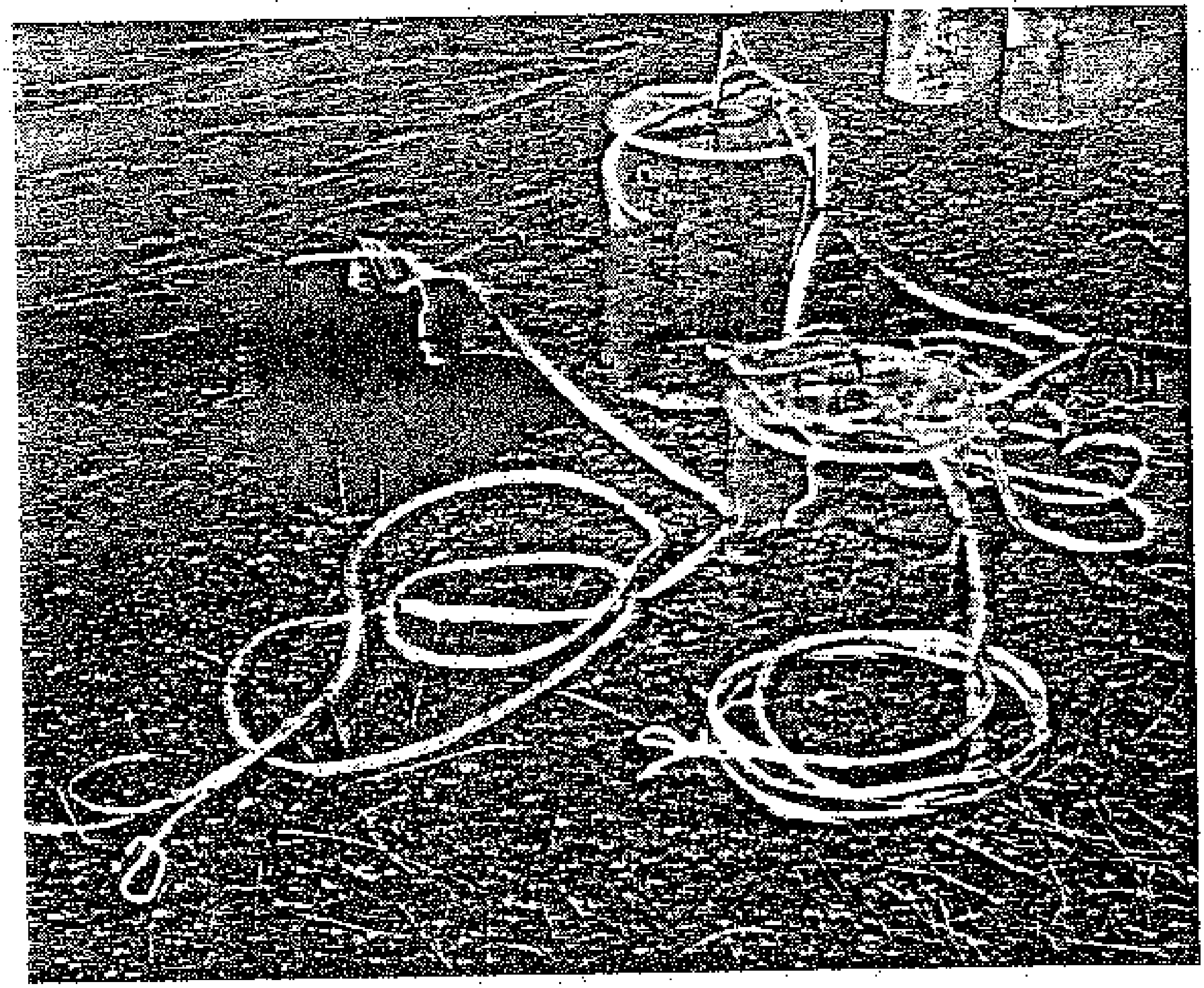


Figure 3. Photograph of in situ benthic chambers. Chambers were made from clear Lucite. After placement on the sediment, rubber stoppers with Tygon tubes extending to the surface, were inserted. The tubes were attached to floats and closed with plastic clamps.

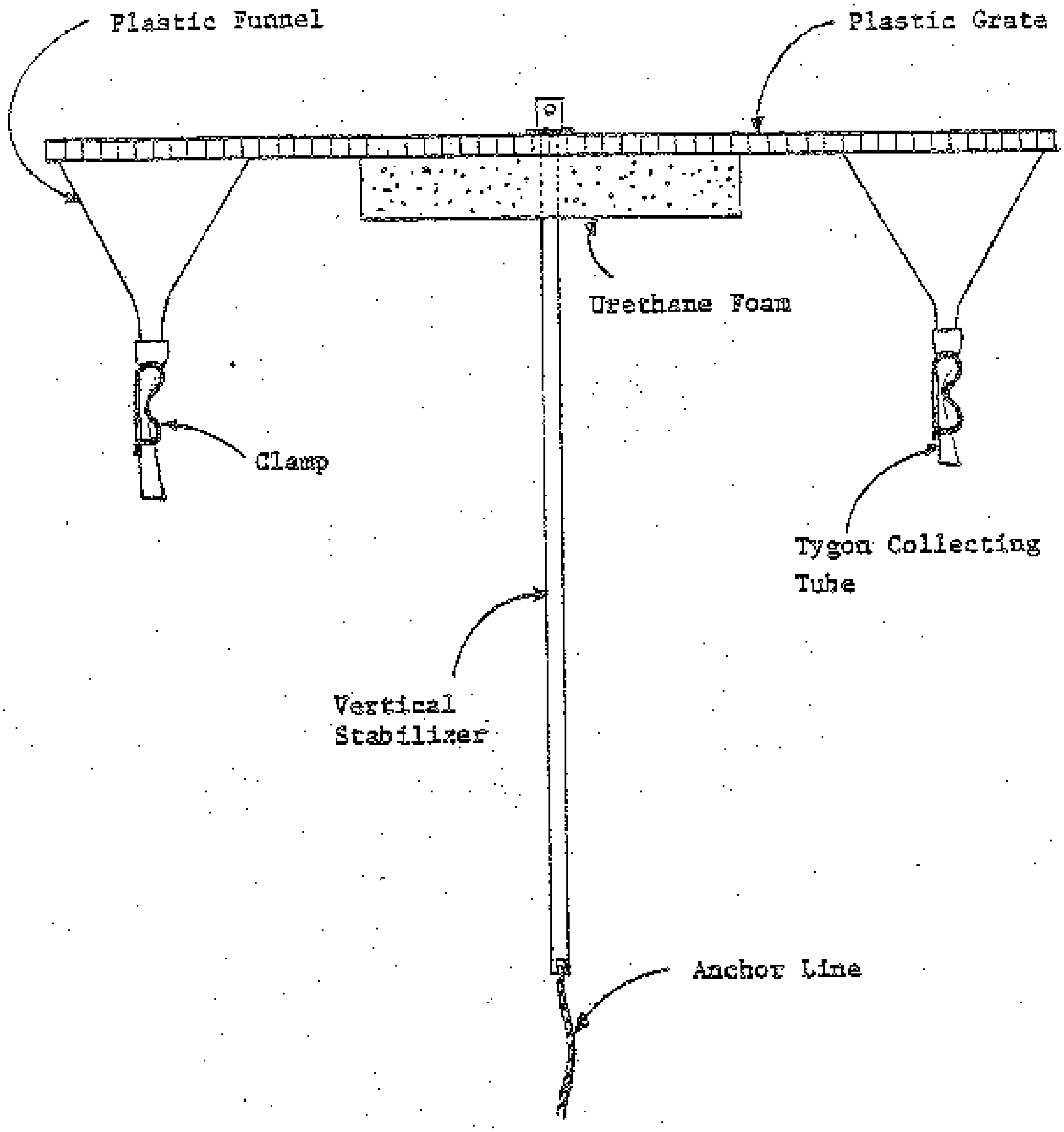


Figure 4. Sediment trap design. Sedimenting particles fell through the plastic grate with 1 cm holes and into a short length of Tygon tube at the bottom of the funnel. Samples were removed by opening a plastic clamp at the end of the tube. A urethane foam block made the trap positively bouyant. Four traps at various depths were strung together and anchored.

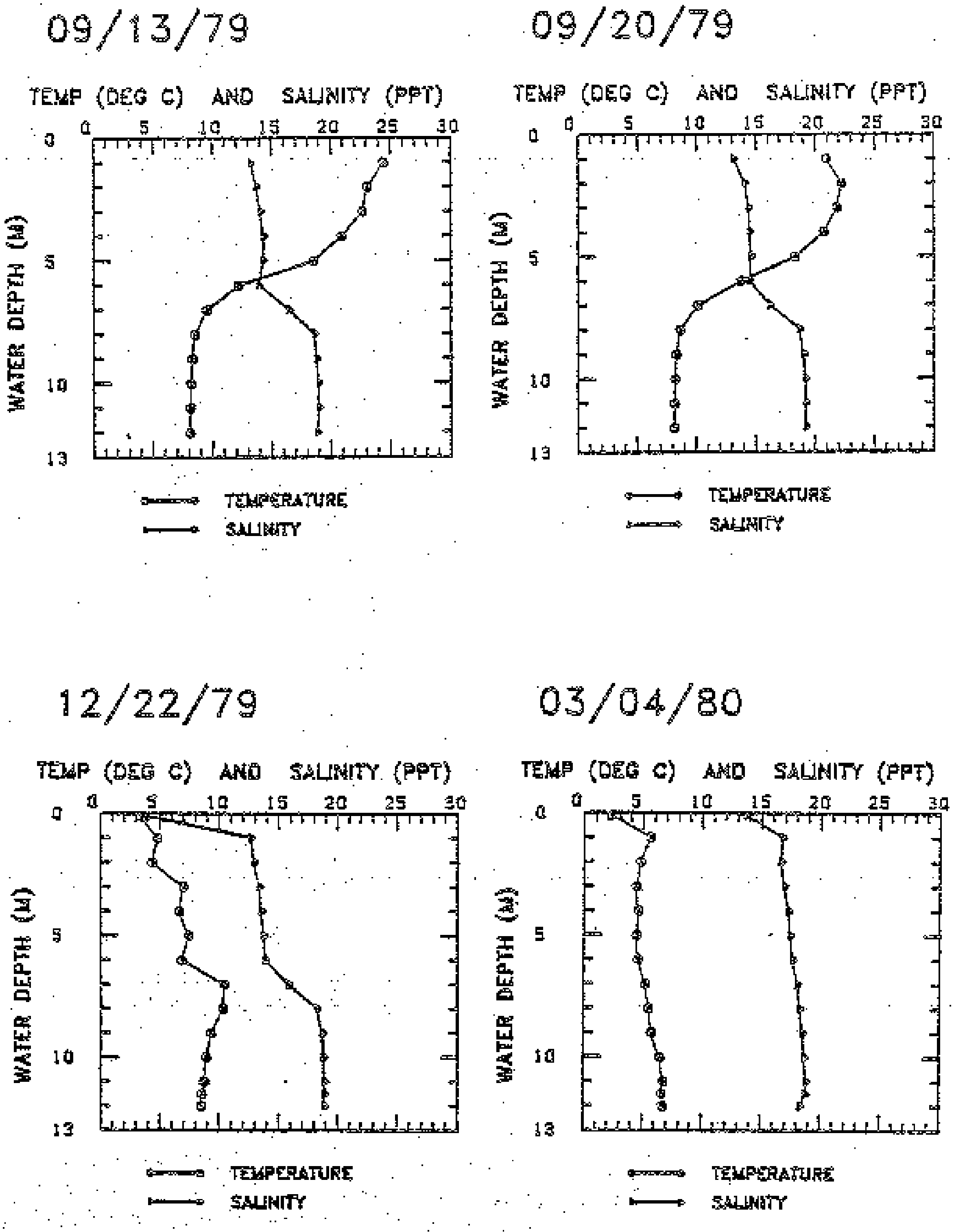


Figure 5a. Temperature and salinity profiles on 09-13-79, 09-20-79, 12-22-79 and 03-04-80.

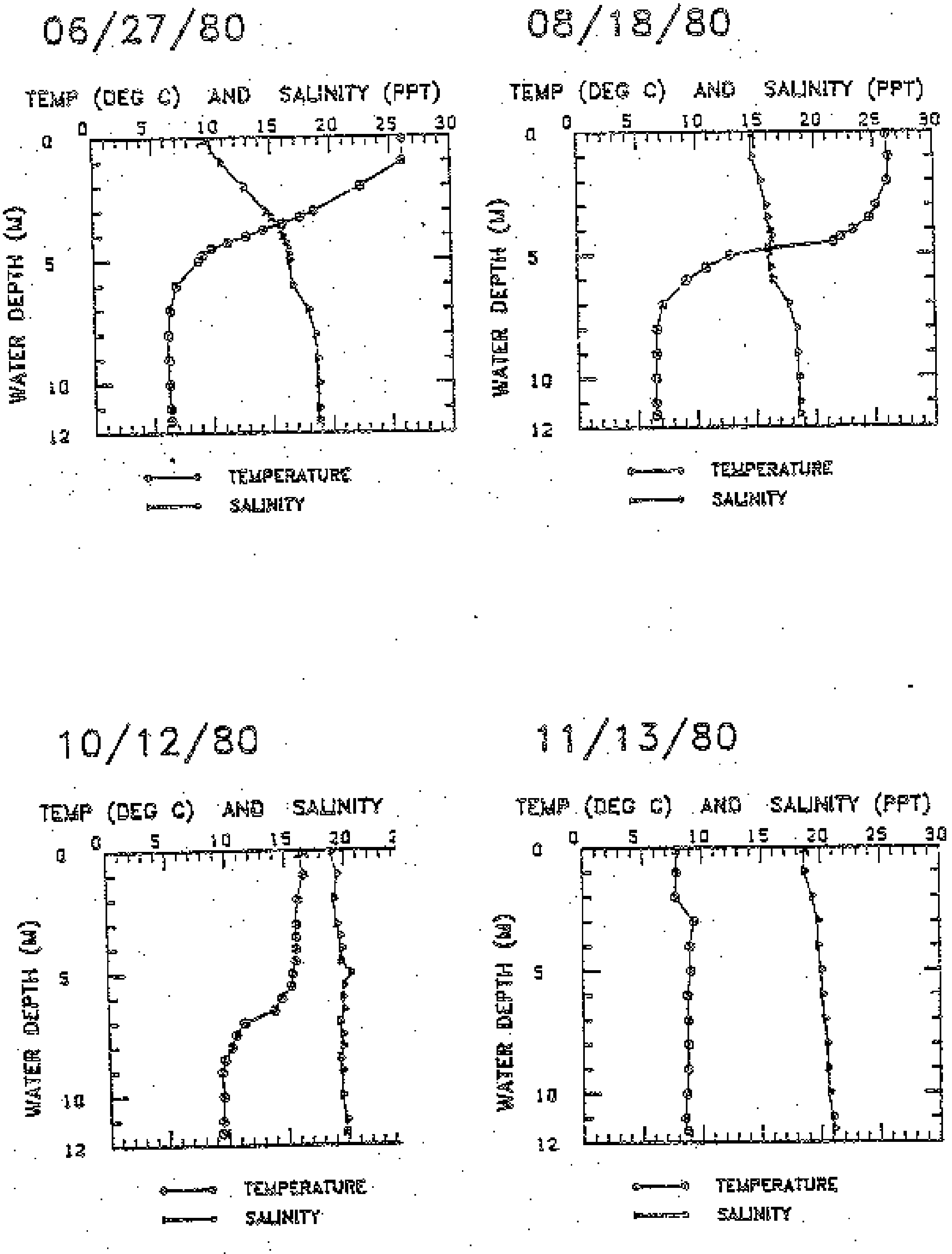


Figure 5b. Temperature and salinity profiles on 06-27-80, 08-18-80, 10-12-80 and 11-13-80.

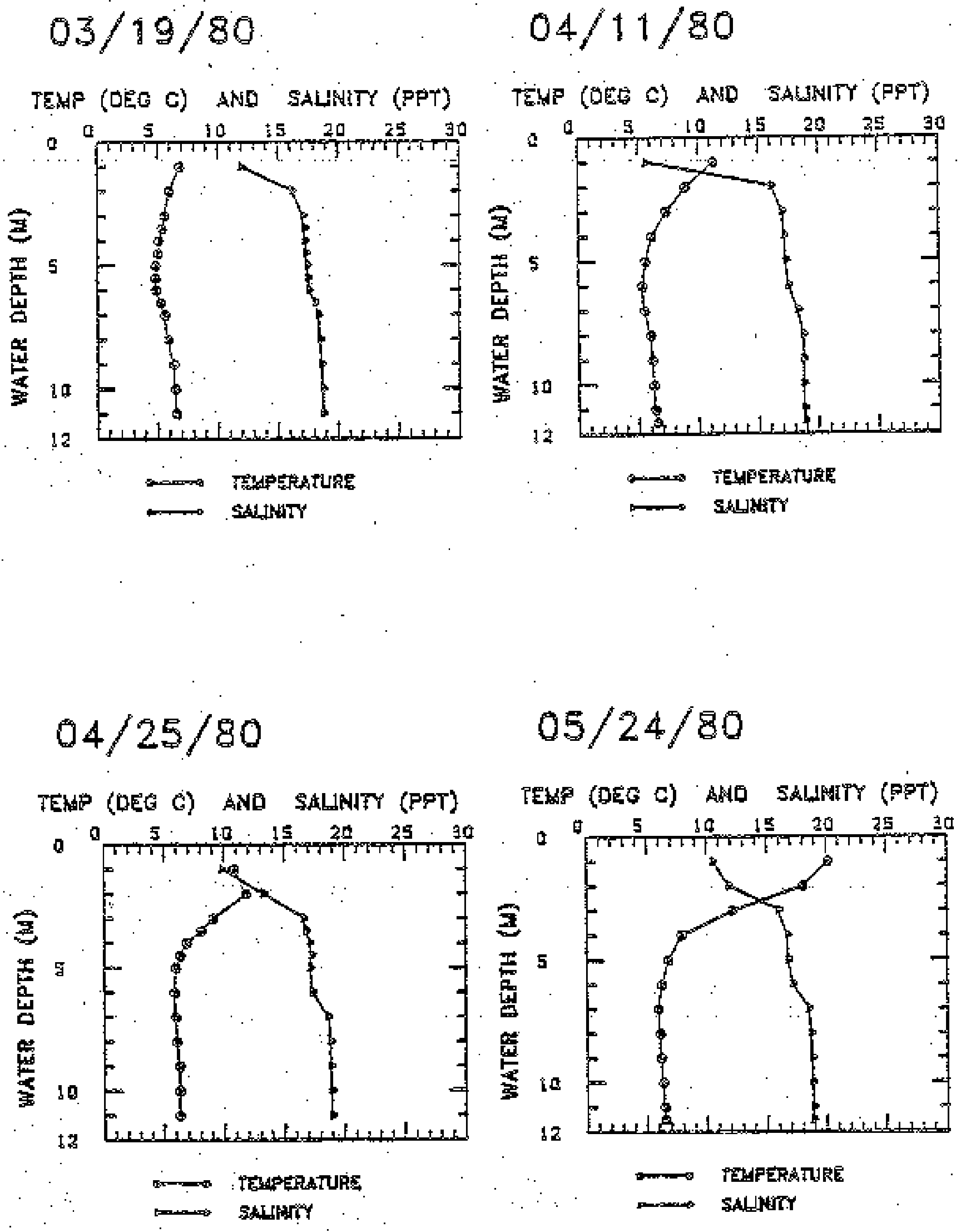


Figure 5c. Temperature and salinity profiles on 03-19-80, 04-11-80, 04-25-80 and 05-24-80.

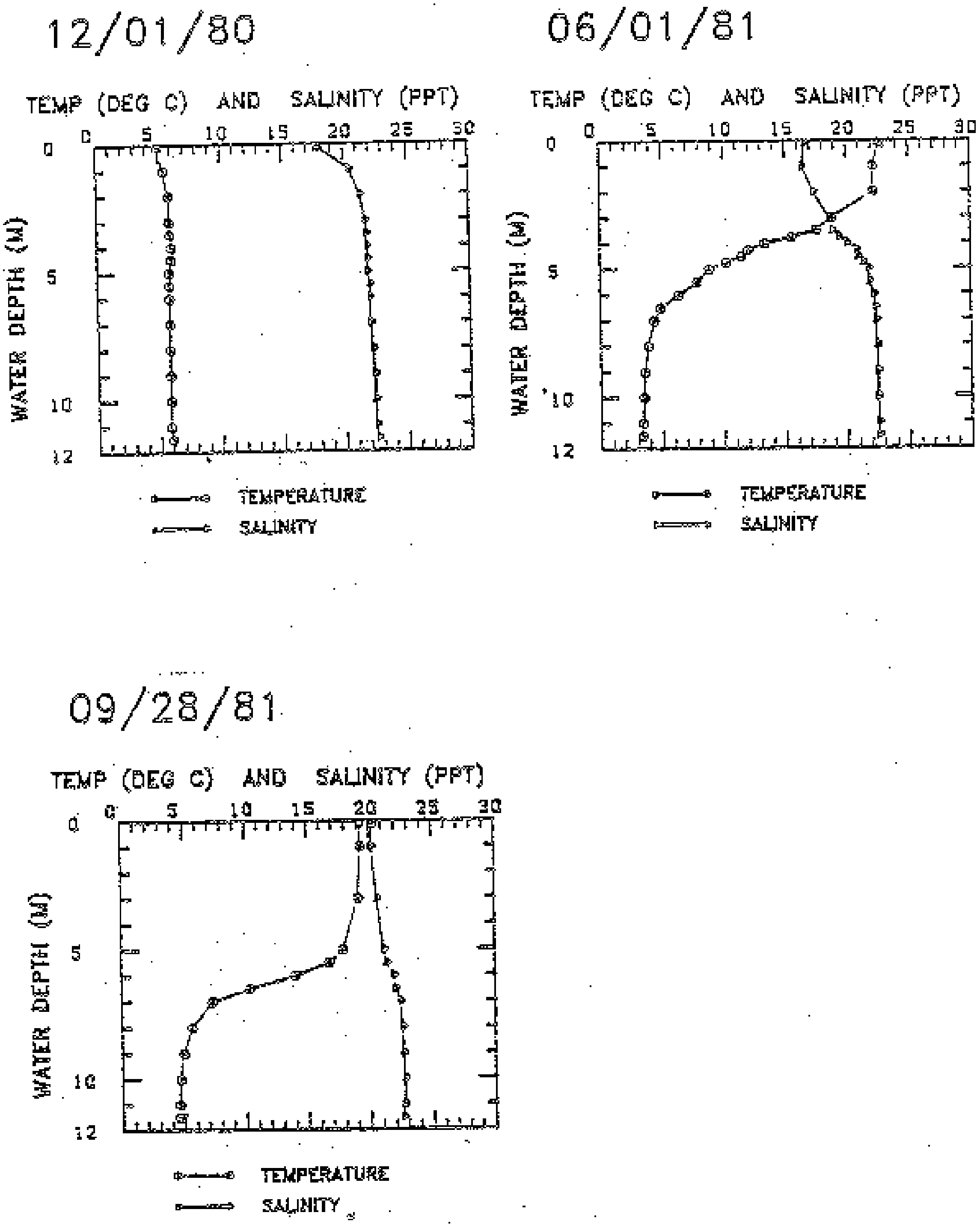


Figure 5d. Temperature and salinity profiles on 12-01-80, 06-01-81 and 09-28-81.

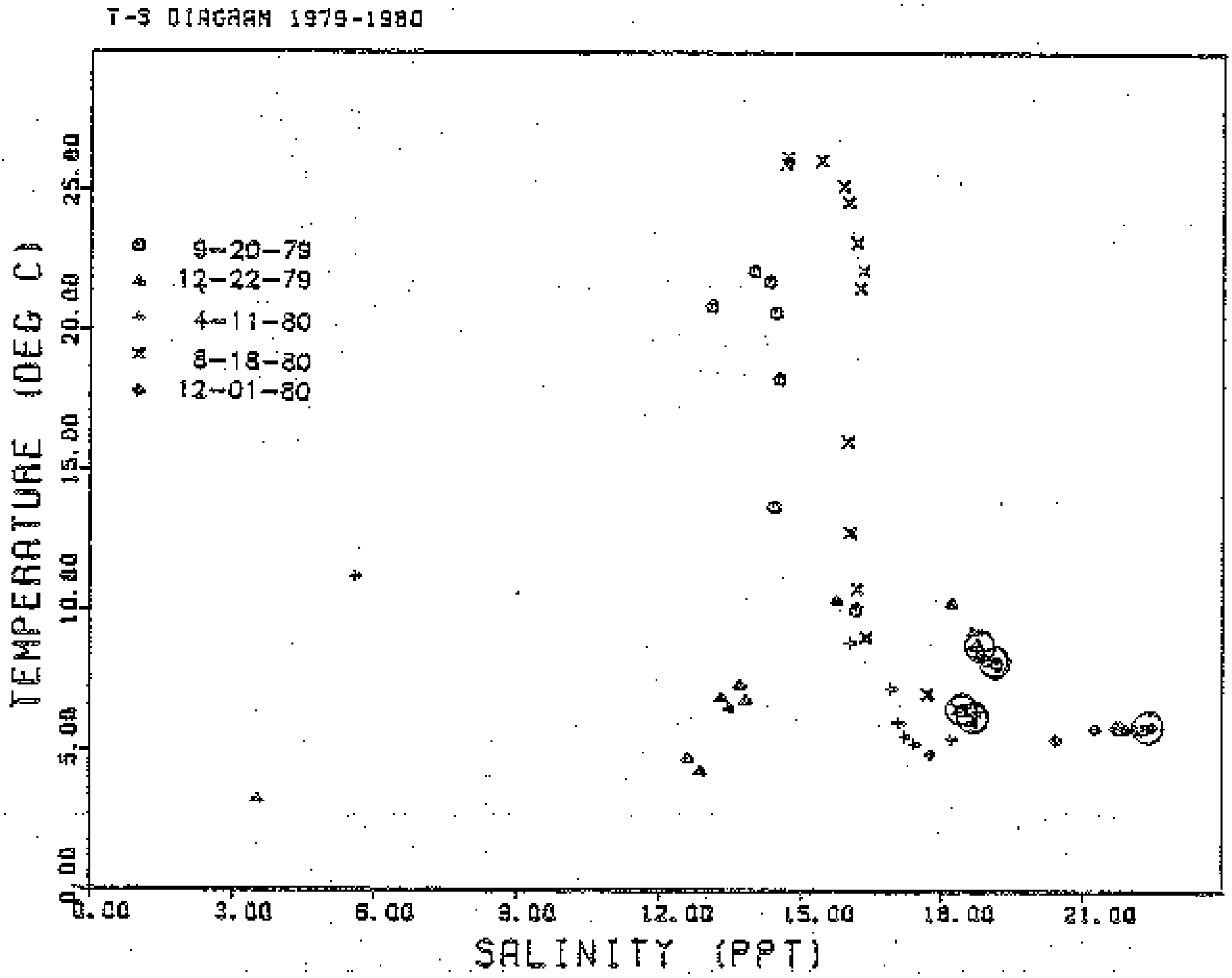
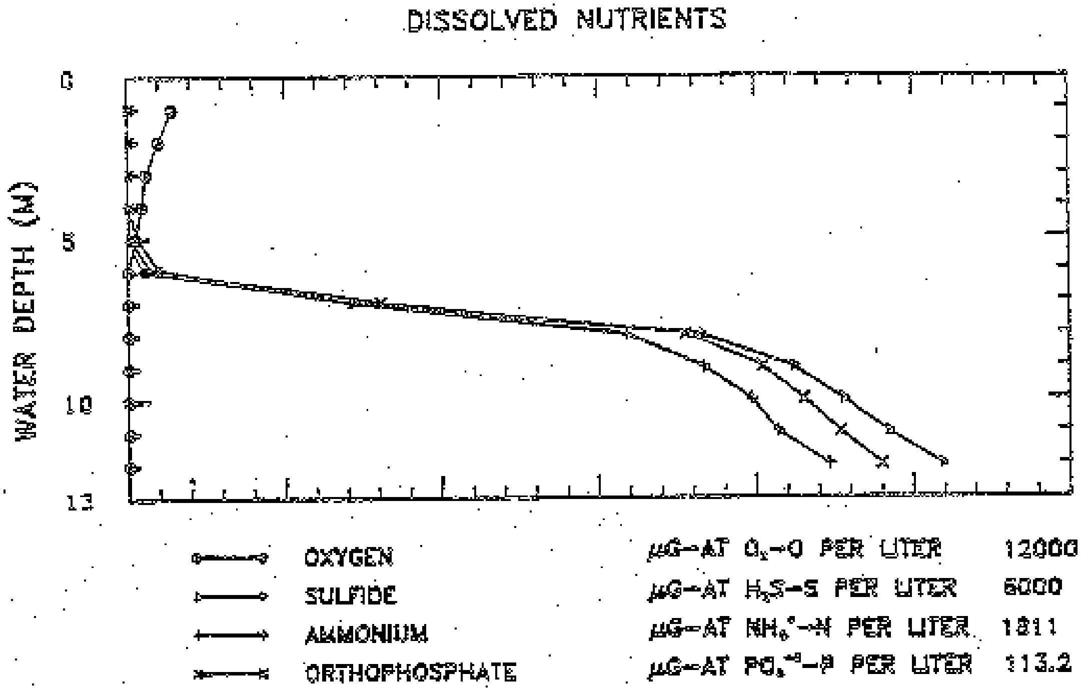


Figure 6. T-S diagram for selected water column dates. The points representing the bottom five meters for each profile are circled. The anoxic bottom water mass for 09-20-79 and 12-22-79 is represented by points which overlap. Similarly, the water mass on 04-11-80 and 08-18-80 is the same. Accuaracy of the salinity determination between different sampling days is ± 0.5 ppt.

09/20/79



12/22/79

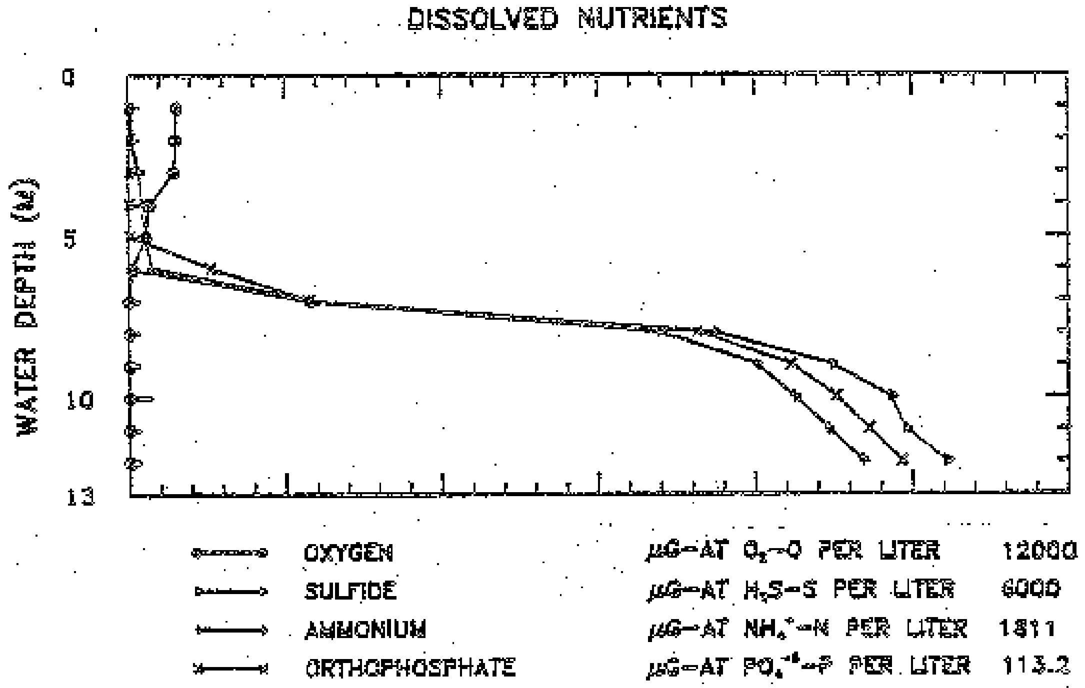
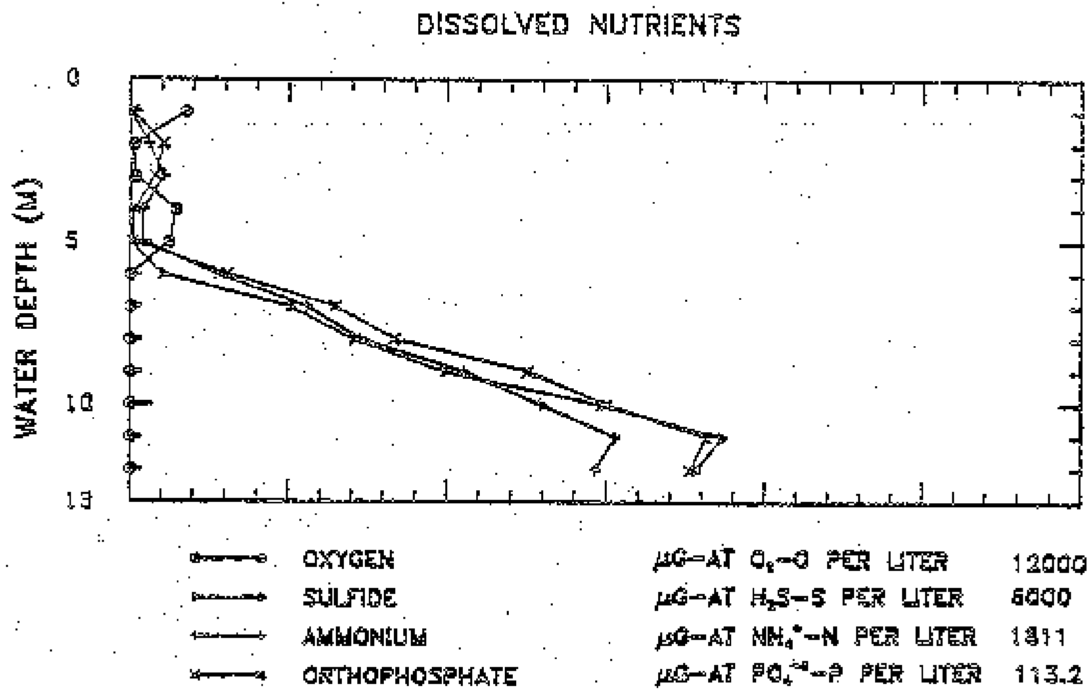


Figure 7a. Dissolved oxygen, sulfide, ammonium and phosphate profiles on 09-20-79 and 12-22-79.

03/04/80



03/19/80

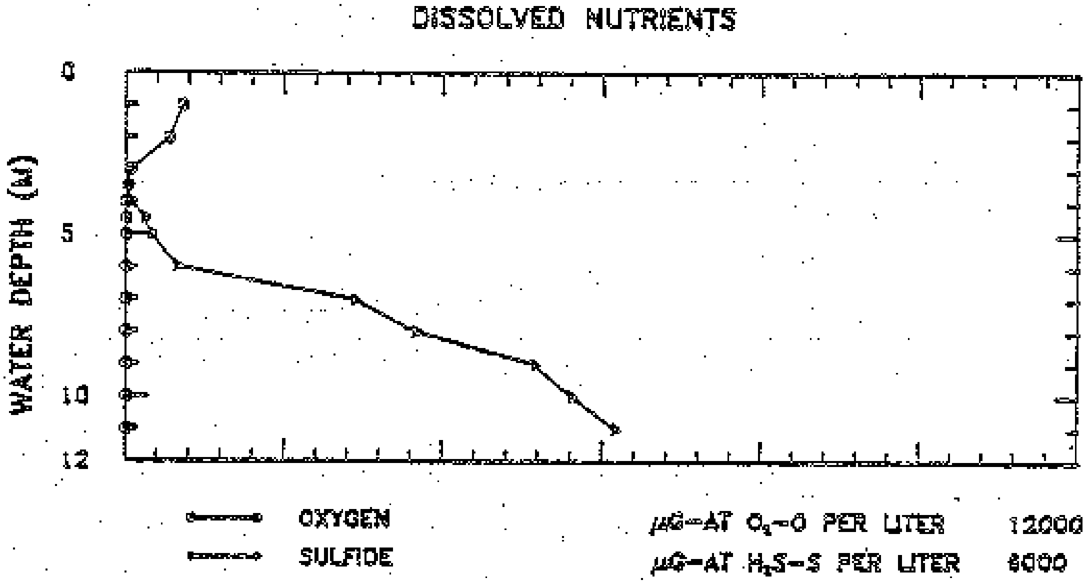
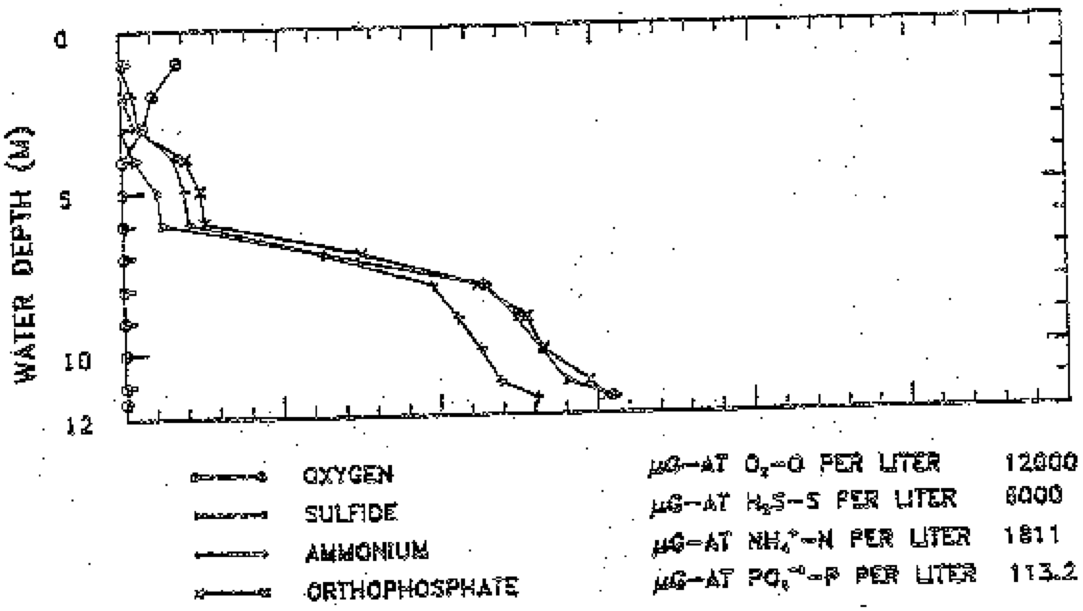


Figure 7b. Dissolved oxygen, sulfide, ammonium and phosphate on 03-04-80. Dissolved oxygen and sulfide on 03-19-80.

04/11/80

DISSOLVED NUTRIENTS



04/25/80

DISSOLVED NUTRIENTS

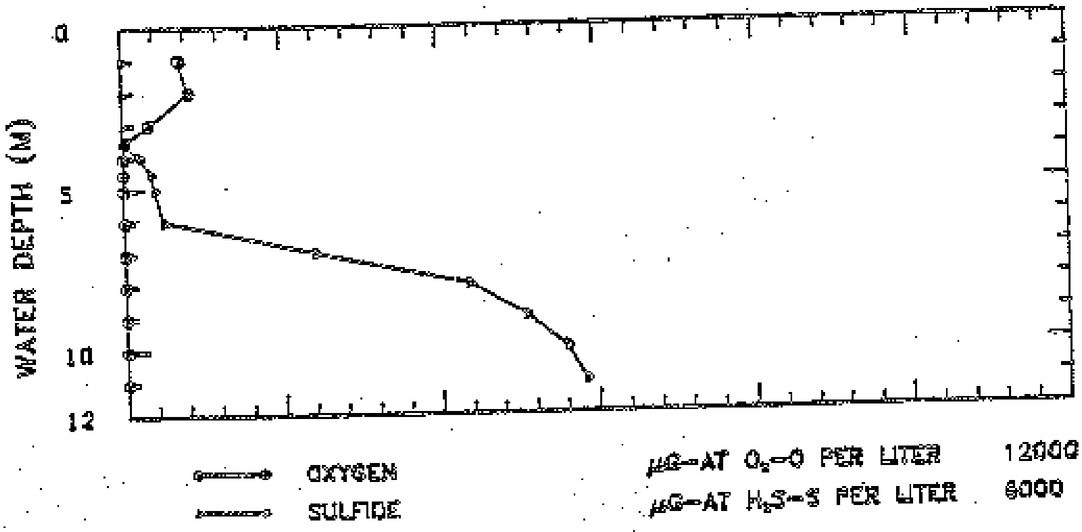
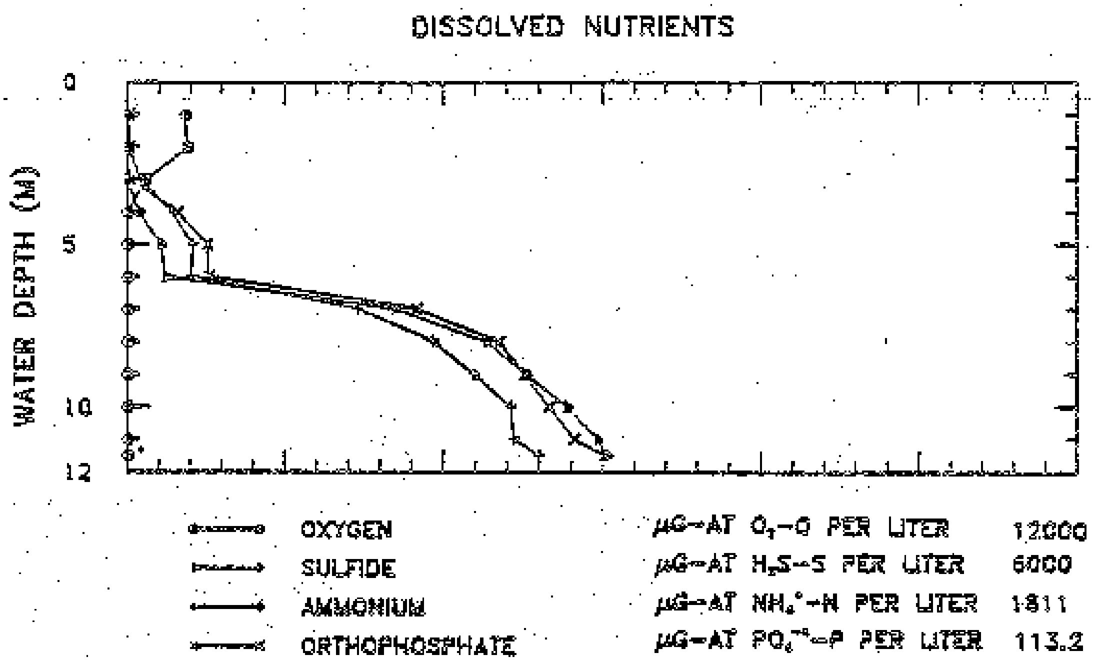


Figure 7c. Dissolved oxygen, sulfide, ammonium and phosphate on 04-11-80. Dissolved oxygen and sulfide on 04-25-80.

05/24/80



06/27/80

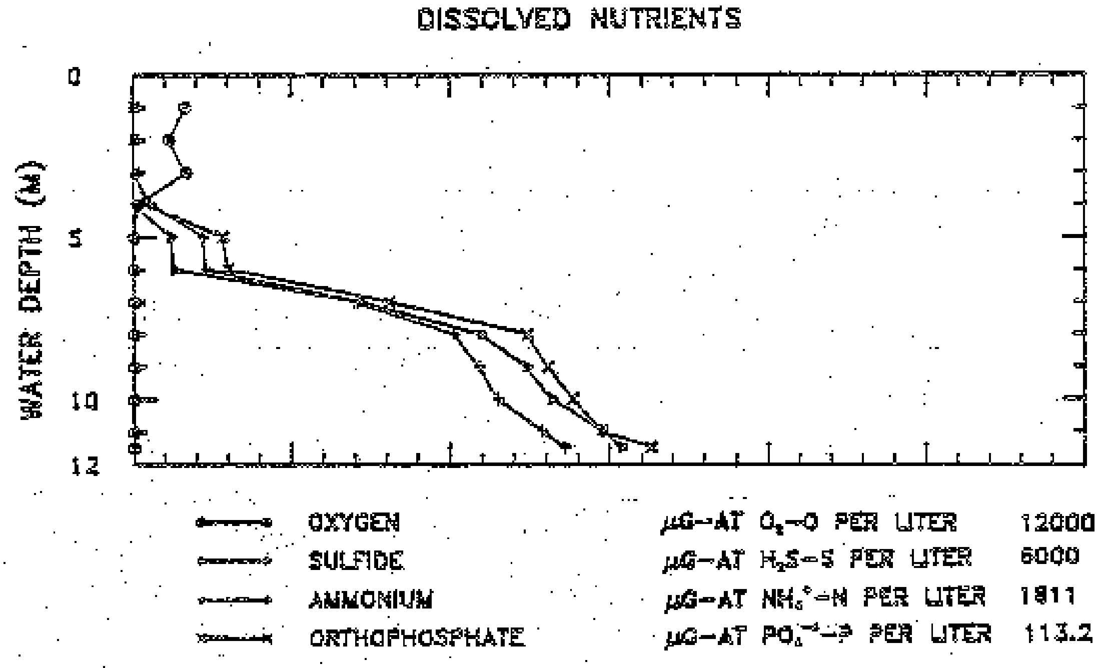
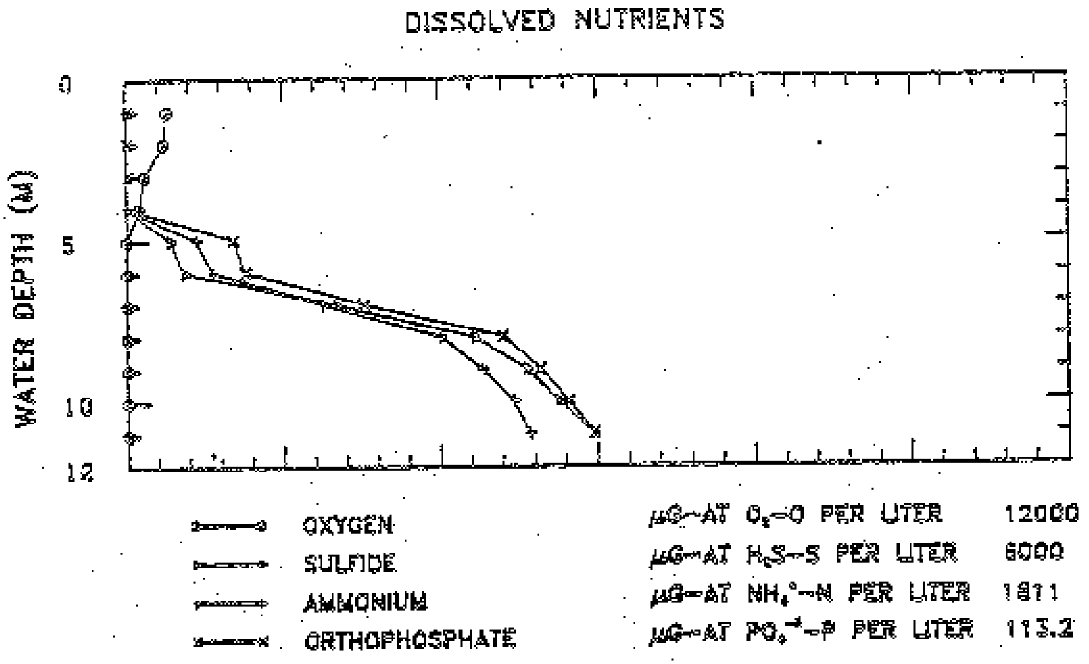


Figure 7d. Dissolved oxygen, sulfide, ammonium and phosphate on 05-24-80 and 06-27-80.

08/18/80



10/12/80

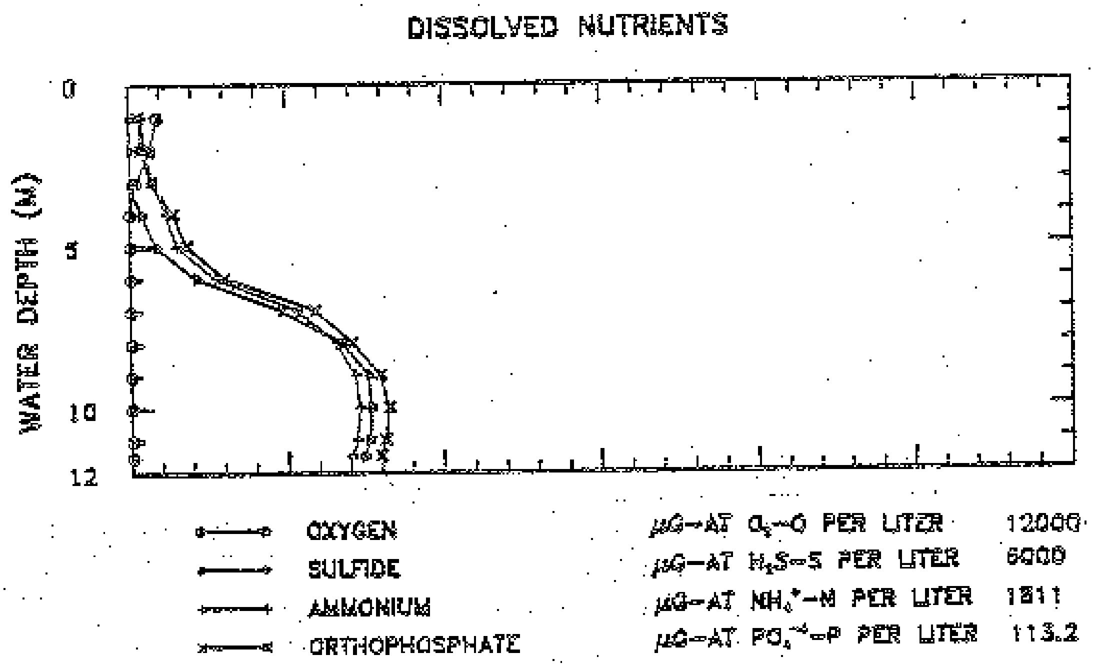
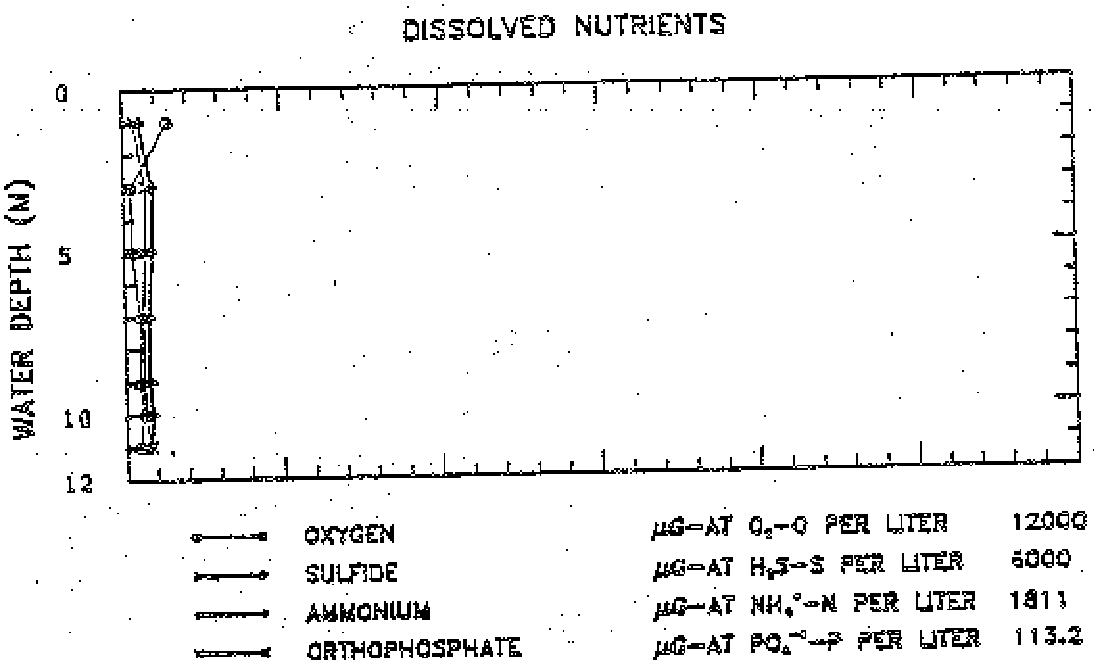


Figure 7e. Dissolved oxygen, sulfide, ammonium and phosphate on 08-18-80 and 10-12-80.

11/13/80



12/01/80

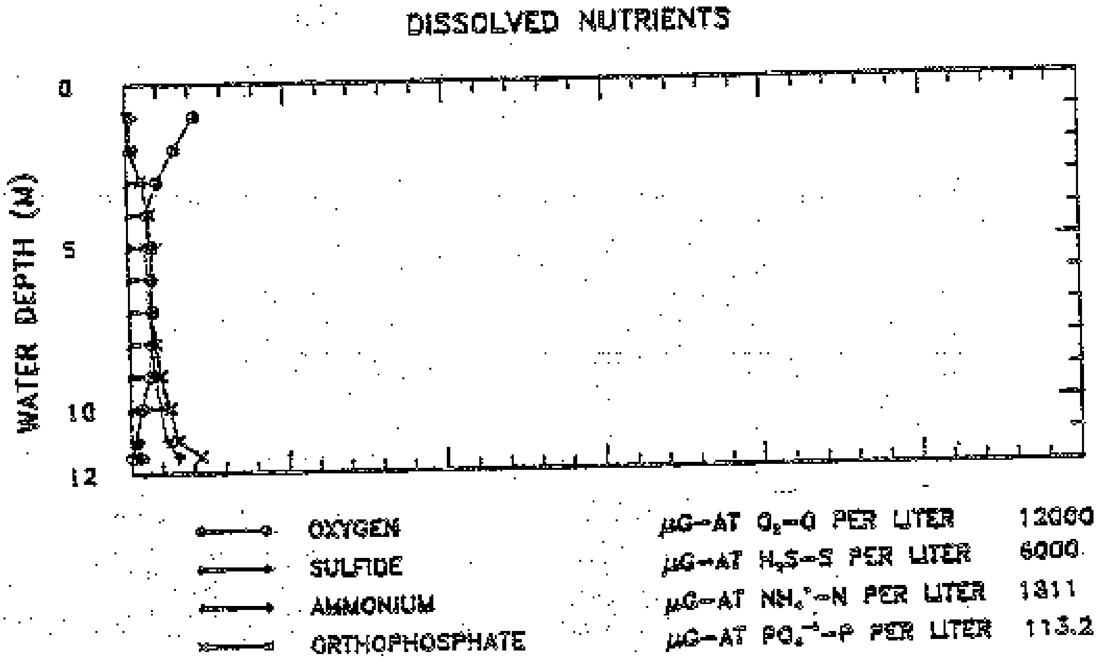
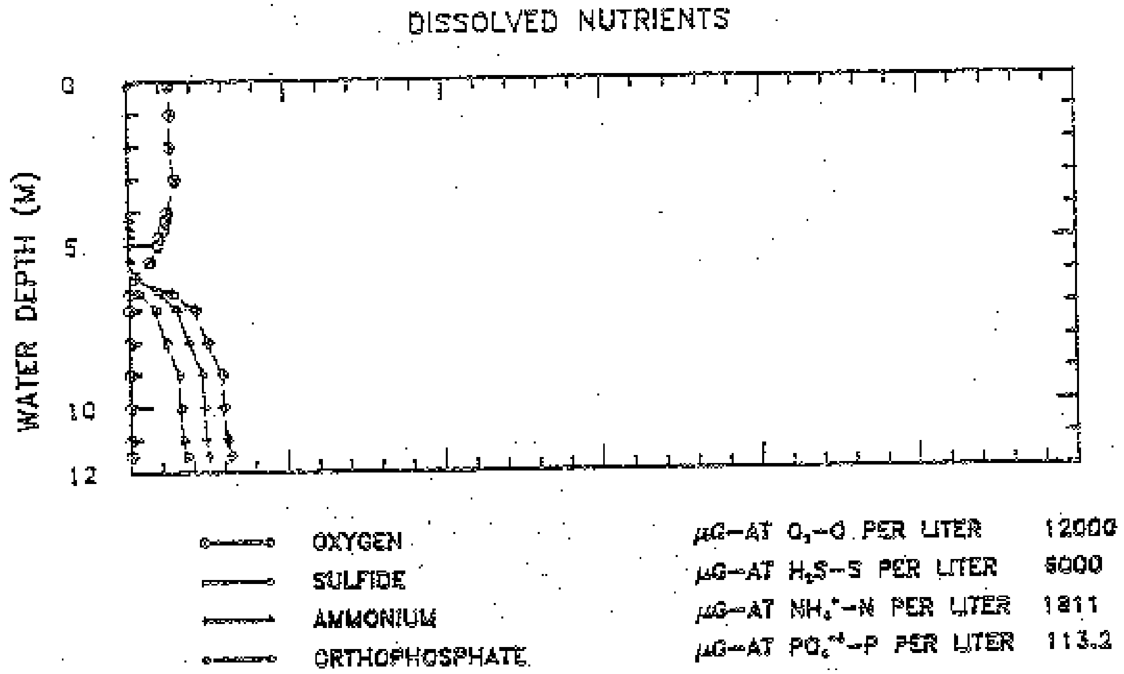


Figure 7f. Dissolved oxygen, sulfide, ammonium and phosphate on 11-13-80 and 12-01-80.

06/01/81



09/28/81

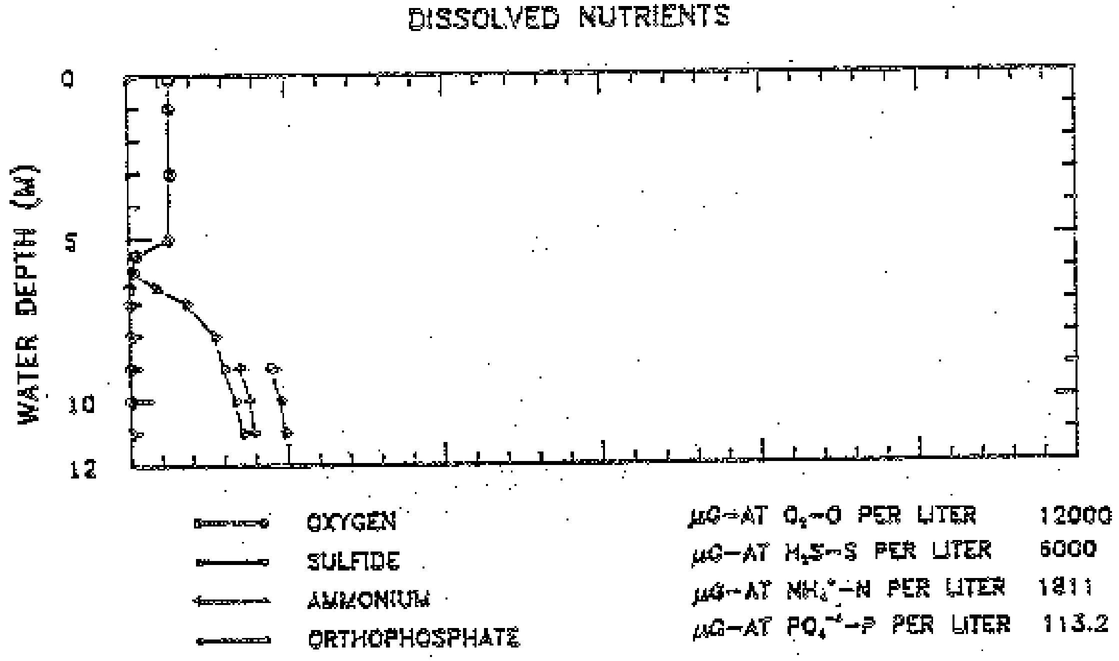
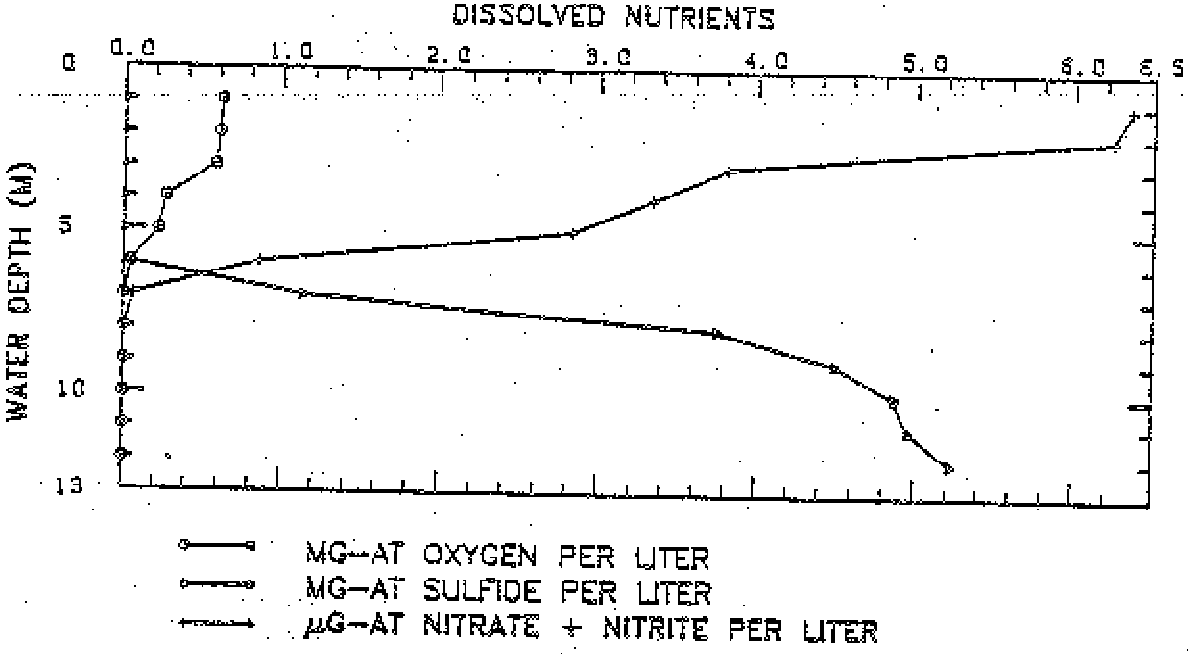


Figure 7g. Dissolved oxygen, sulfide, ammonium and phosphate on 06-01-81 and 09-28-81.

12/22/79



06/27/80

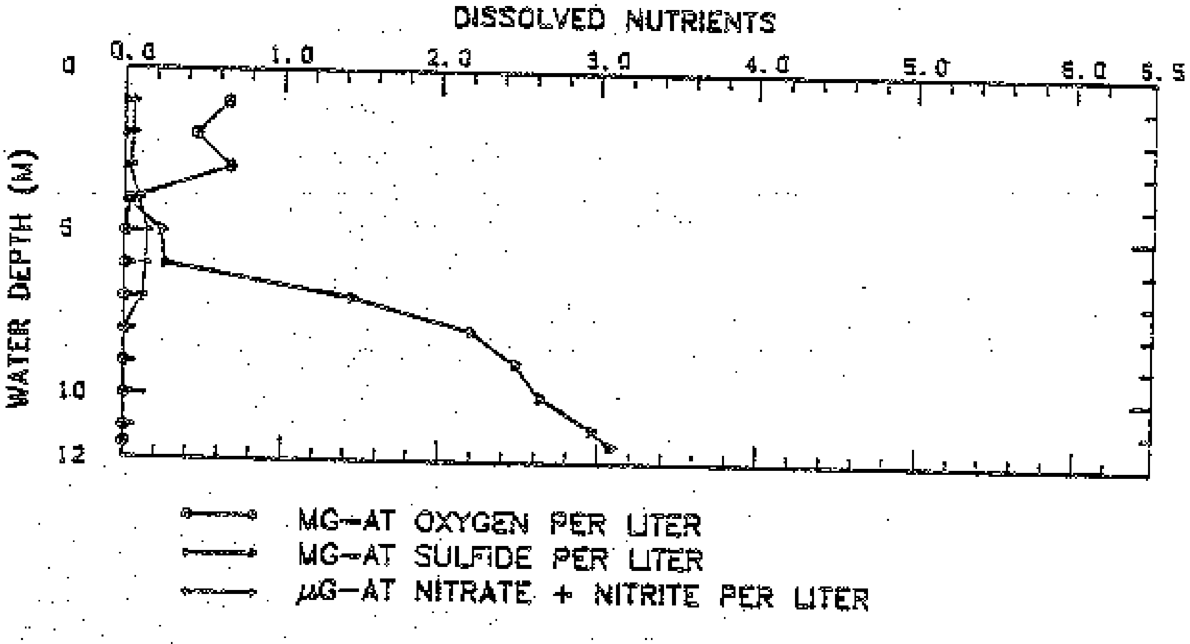


Figure 8. Dissolved oxygen, sulfide and nitrate plus nitrite on 12-22-79 and 06-27-80.

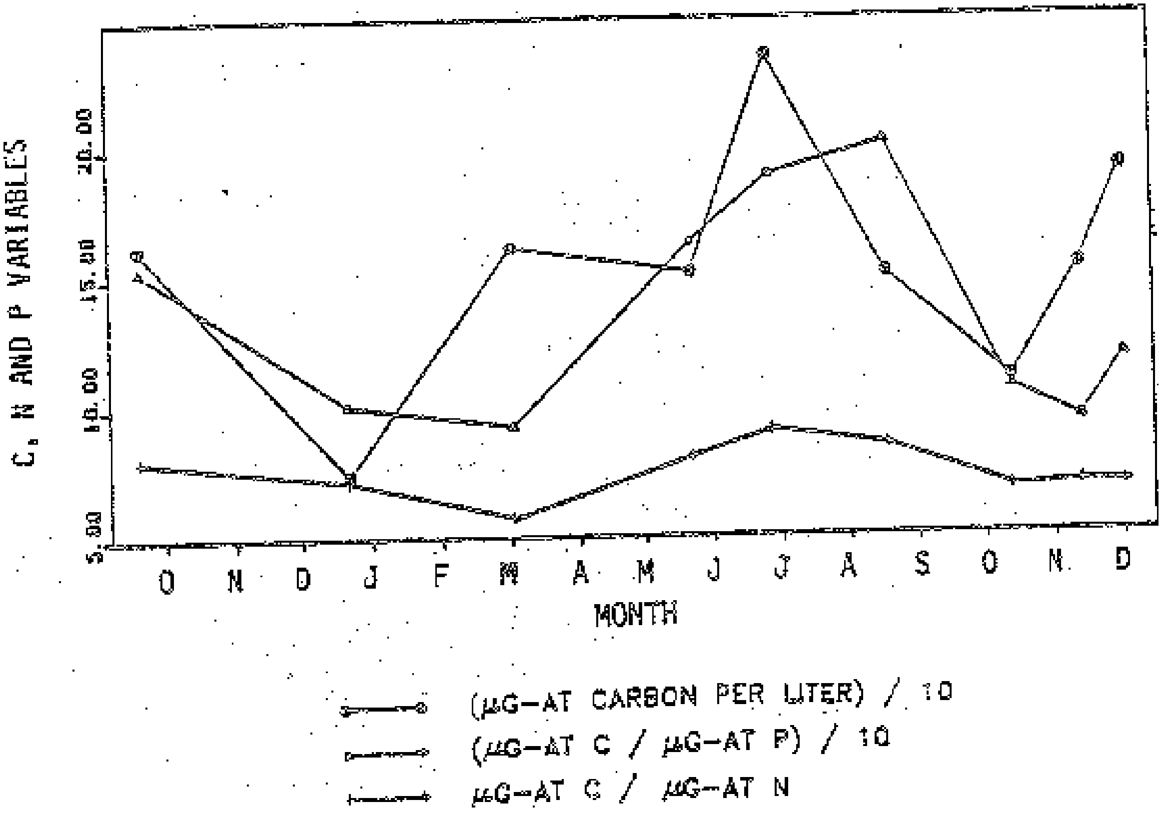
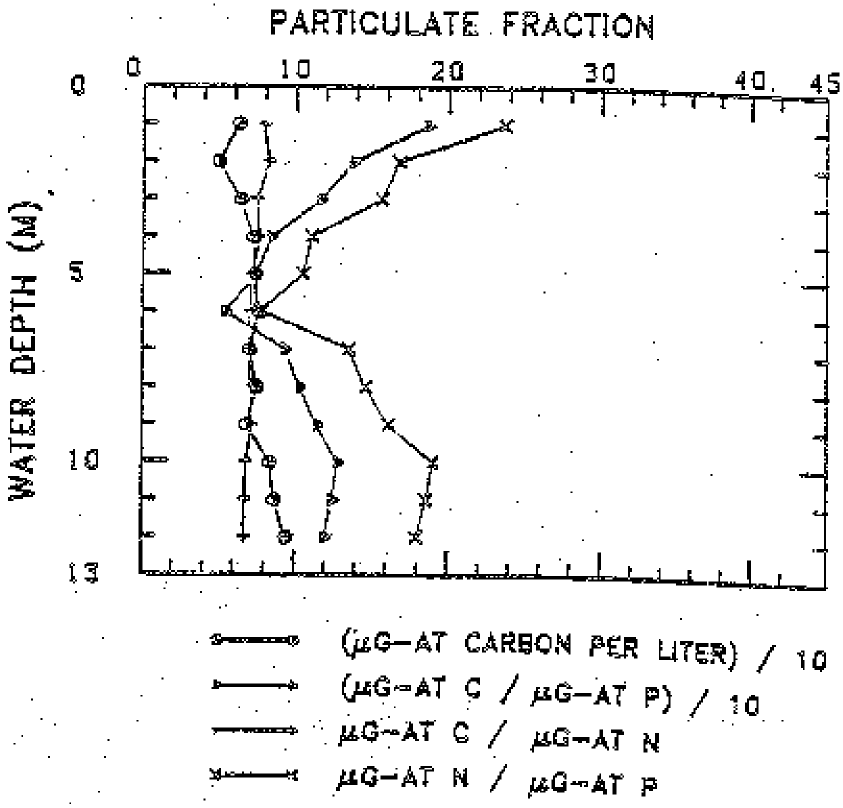


Figure 9. Particulate carbon, carbon to phosphorus ratio, carbon to nitrogen ratio and nitrogen to phosphorus ratio in the surface water on 09-20-79 through 12-10-80. Average for two determinations of an integrated sample from 0.5 to 6.5 meters.



12/22/79

Figure 10a. Particulate carbon, carbon to phosphorus ratio, carbon to nitrogen ratio and nitrogen to phosphorus ratio in the water column on 12-22-79.

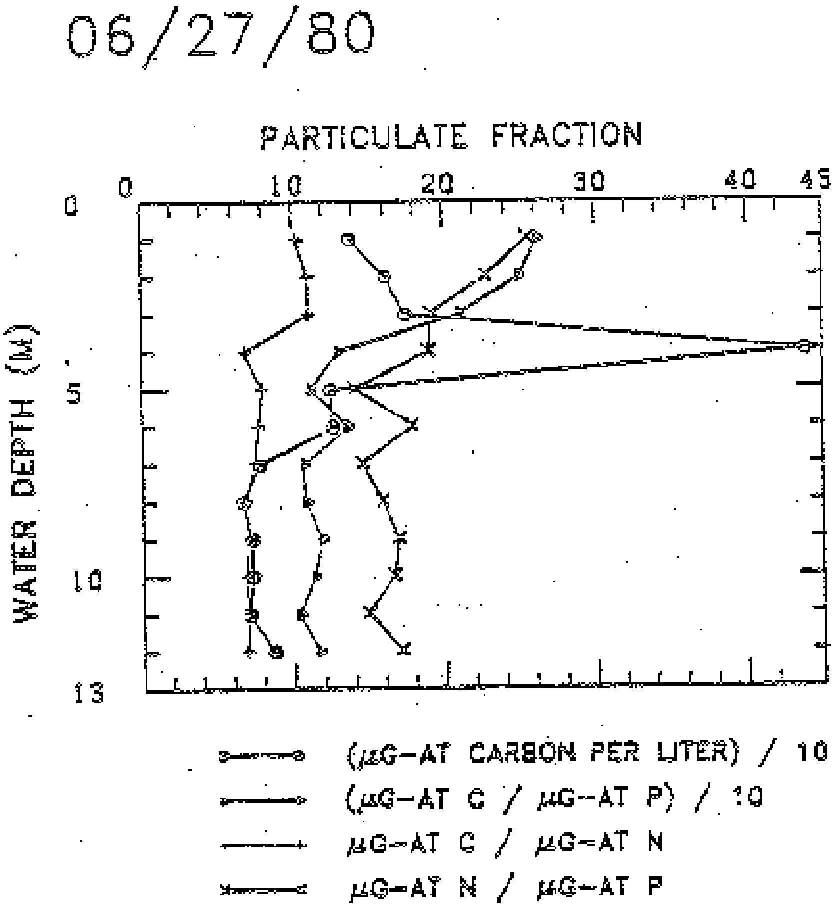


Figure 10b. Particulate carbon, carbon to phosphorus ratio, carbon to nitrogen ratio and nitrogen to phosphorus ratio in the water column on 06-27-80.

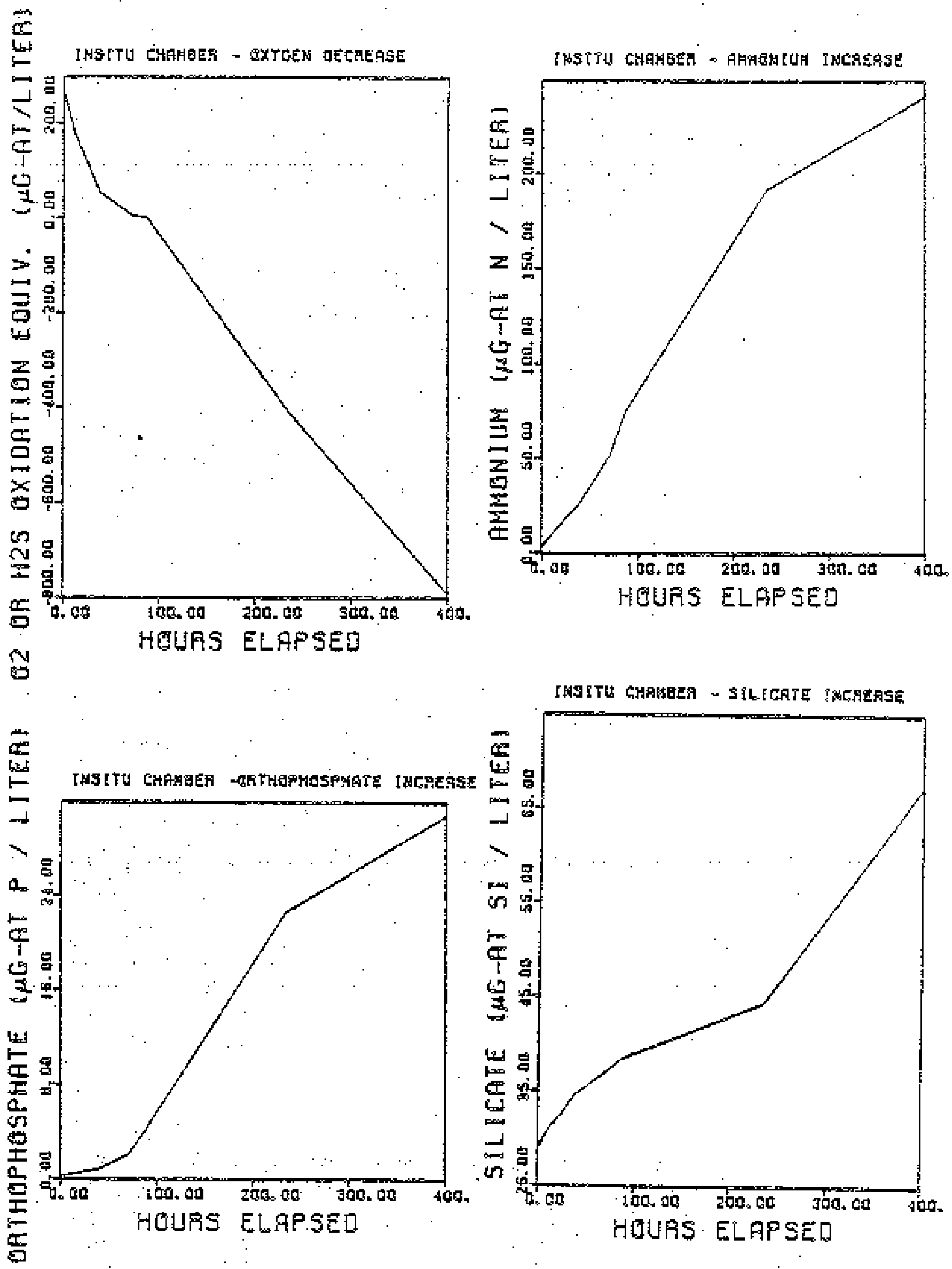


Figure 11a. Transition from oxic to anoxic conditions. Change in oxygen, sulfide, ammonium, phosphate and silicate concentration in an *in situ* bottom chamber at 2.5 meters water depth.

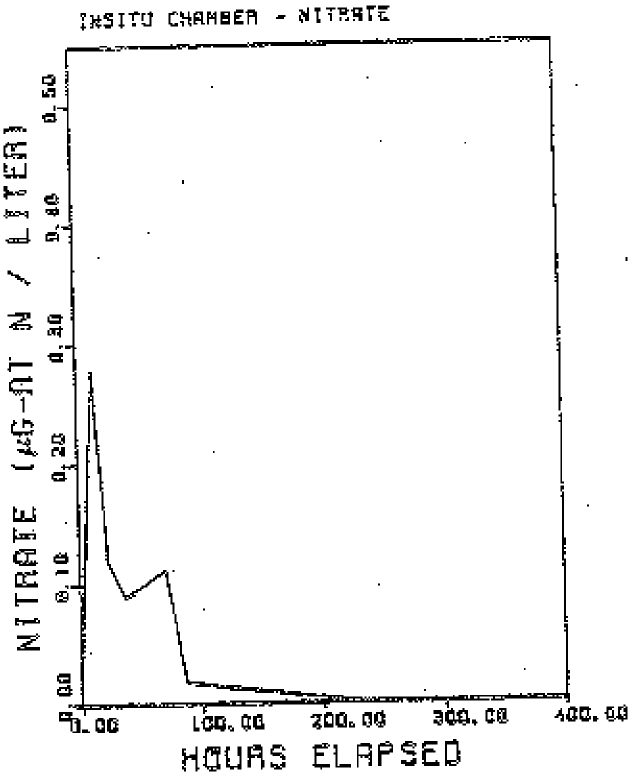


Figure 11b. Transition from oxic to anoxic conditions. Change in nitrate concentration in an *in situ* bottom chamber at 2.5 meters water depth.

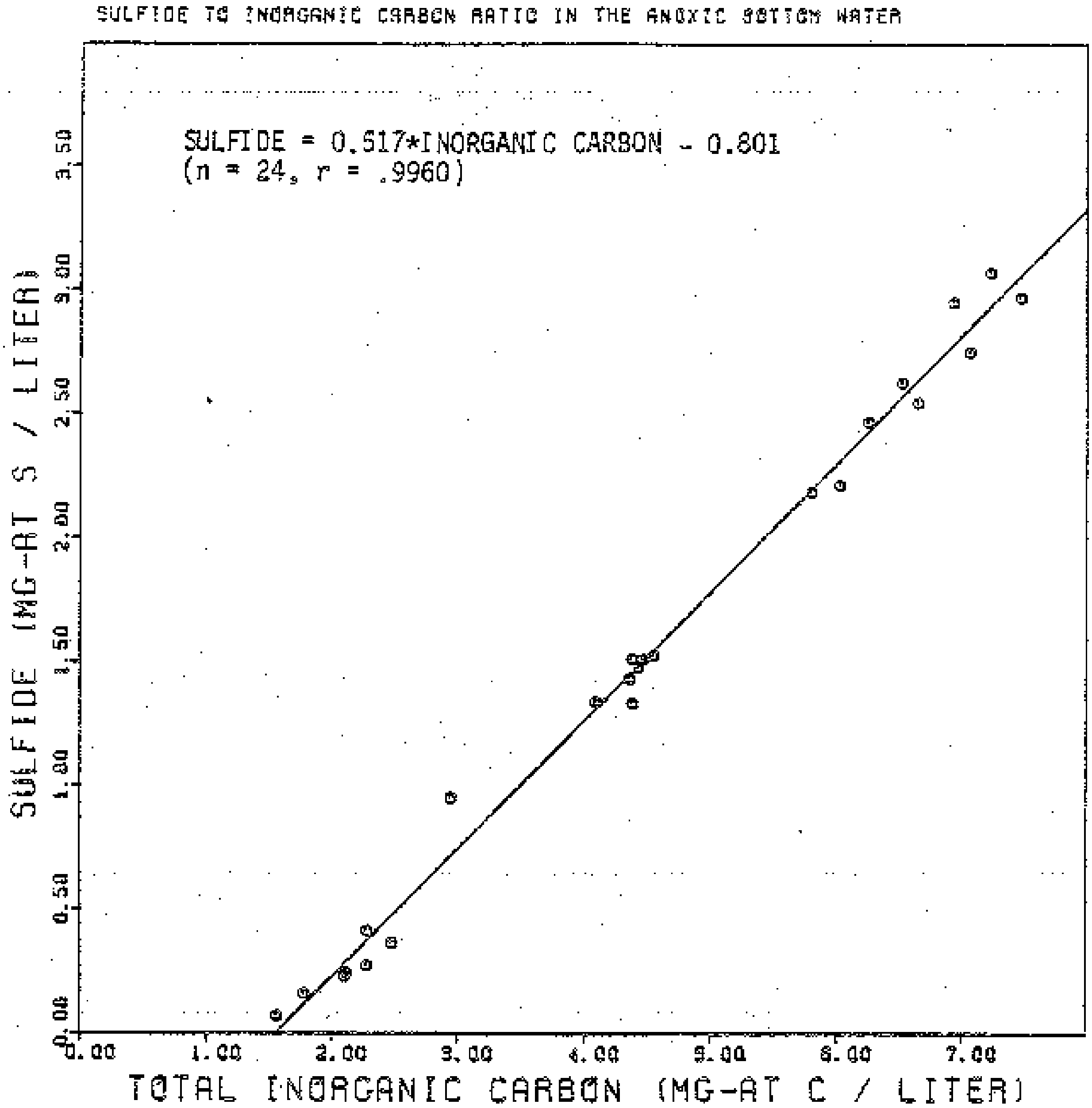


Figure 12a. Sulfide to inorganic carbon ratio in the anoxic bottom water. The least squares regression equation, denoted by the solid line, is $Y = -0.801 + 0.517\ X$. R-squared is 99.1 percent with (24-2) d.f.

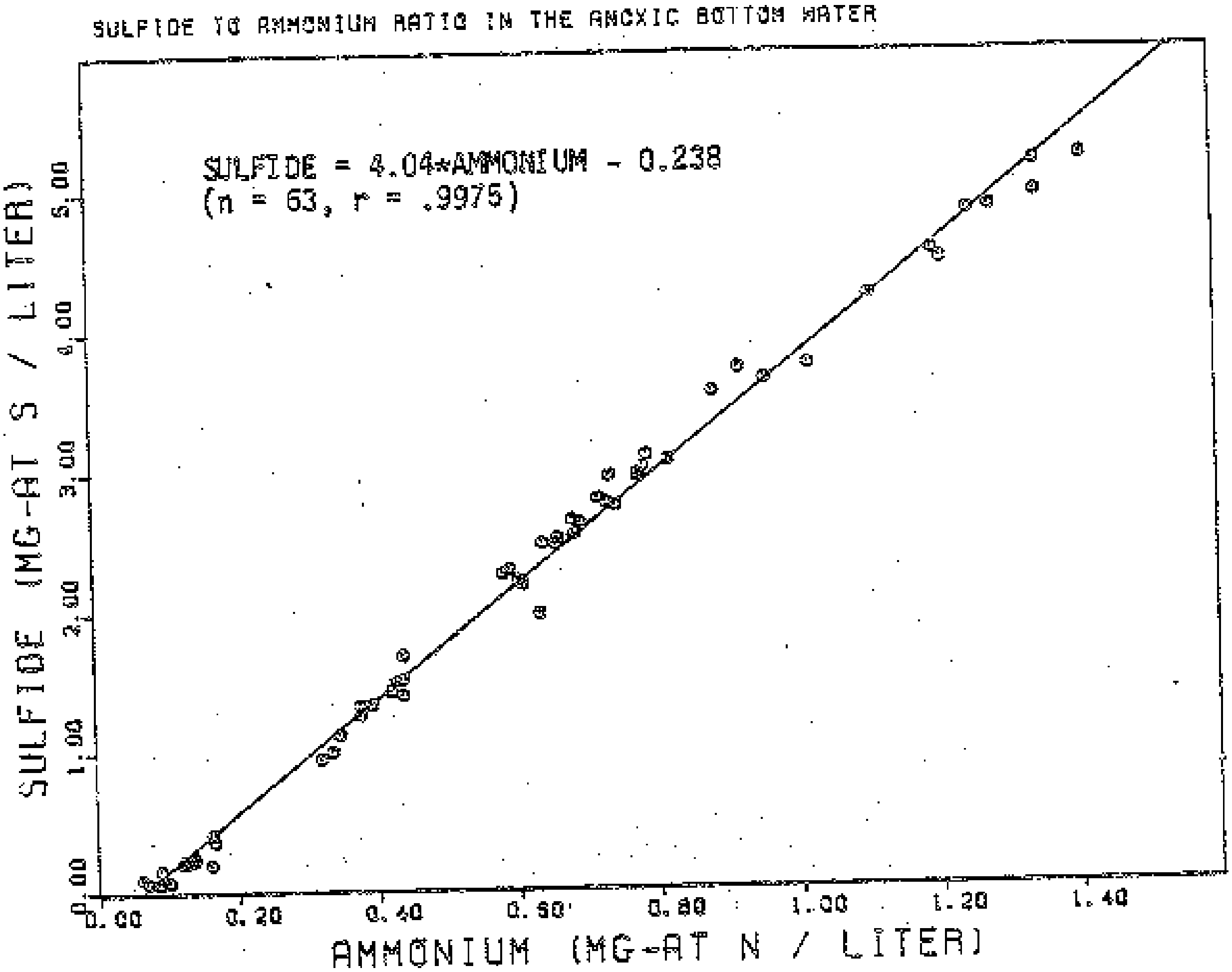


Figure 12b. Sulfide to ammonium ratio in the anoxic bottom water. The least squares regression equation, denoted by the solid line, is $Y = -0.238 + 4.04 X$. R-squared is 99.4 percent with (63-2) d.f.

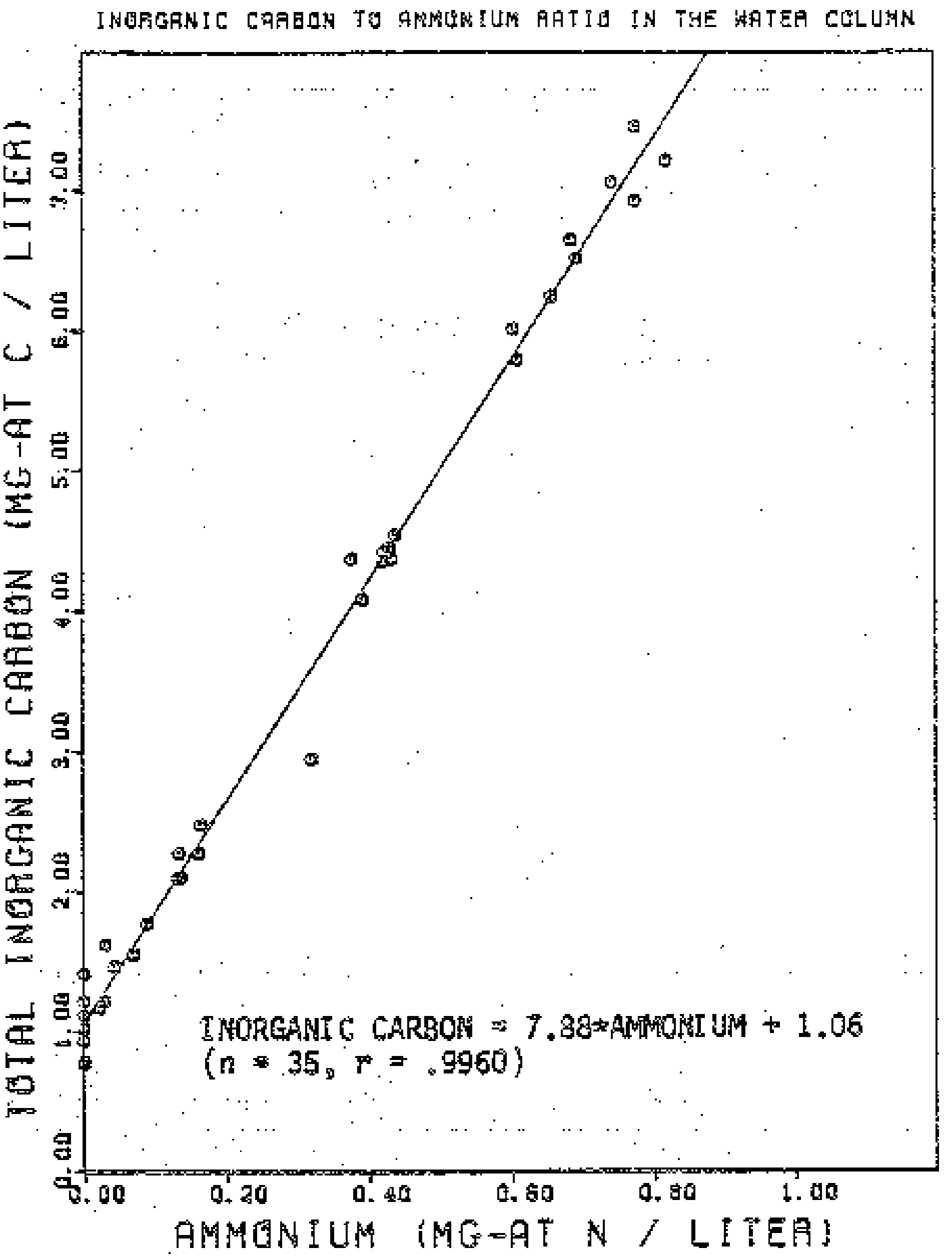


Figure 12c. Inorganic carbon to ammonium ratio in the water column. The least squares regression equation, denoted by the solid line, is Y = 1.06 + 7.88 X. R-squared is 99.2 percent with (35-2) d.f.

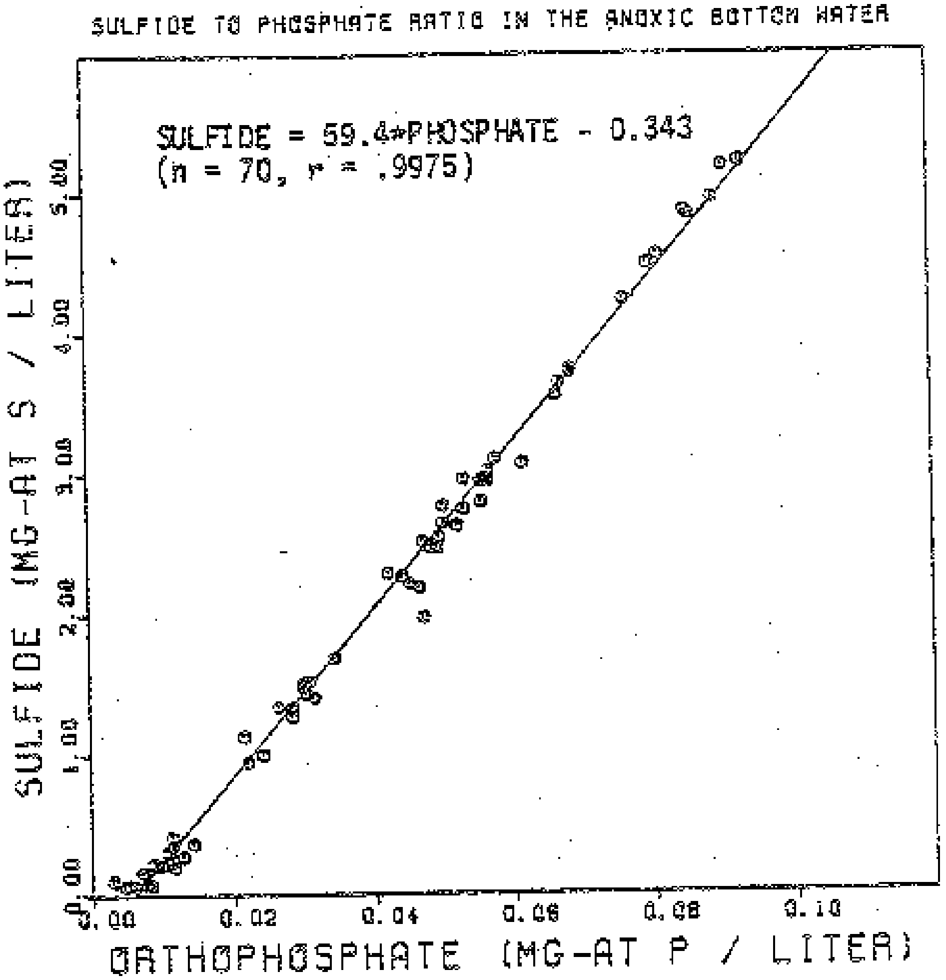


Figure 12d. Sulfide to phosphate ratio in the anoxic bottom water. The least squares regression equation, denoted by the solid line, is $Y = -0.343 + 59.4\ X$. R-squared is 99.5 percent with (70-2) d.f.

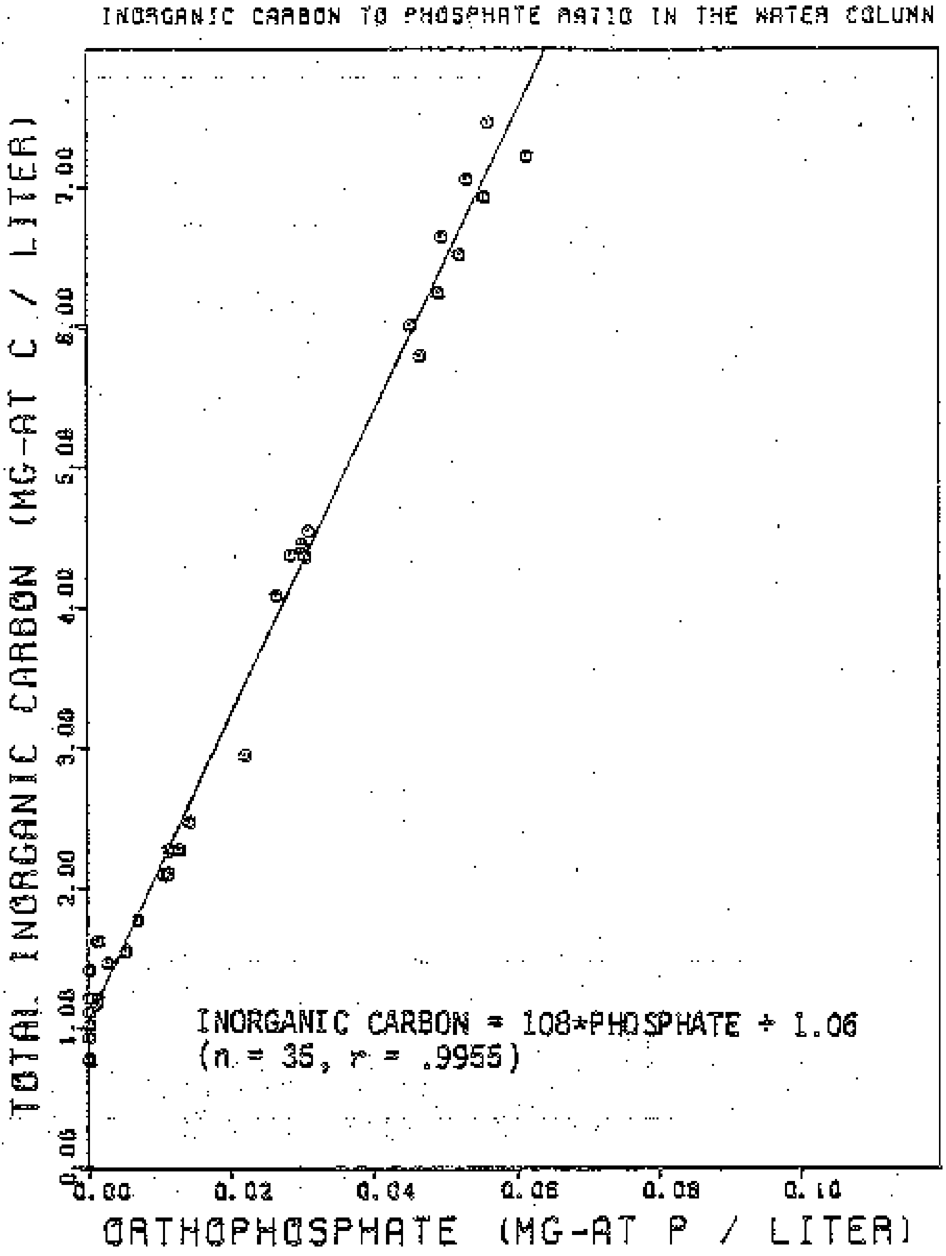


Figure 12e. Inorganic carbon to phosphate ratio in the water column. The least squares regression equation, denoted by the solid line, is Y = 1.06 + 108 X. R-squared is 99.0 percent with (35-2) d.f.

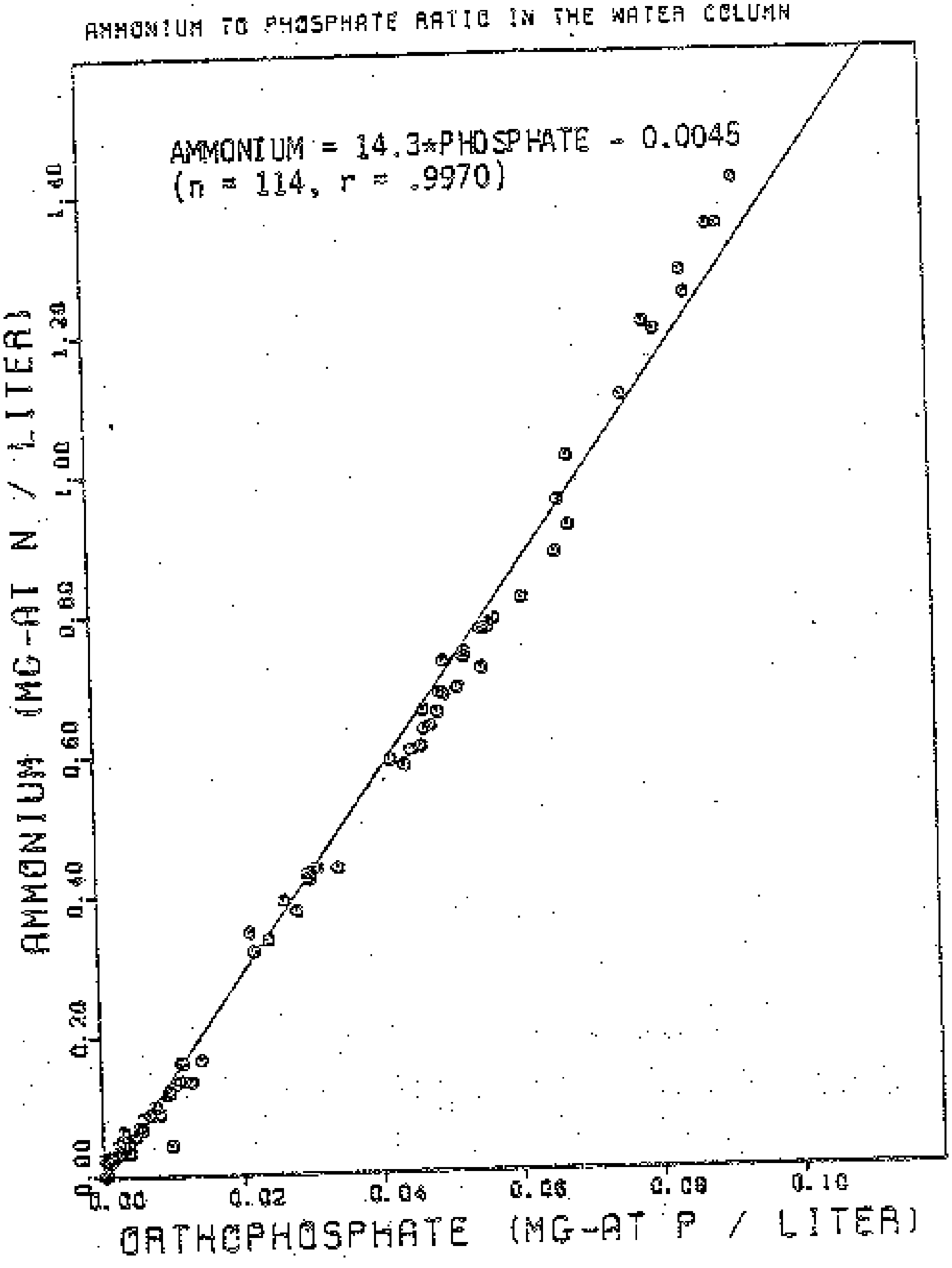


Figure 12f. Ammonium to phosphate ratio in the water column. The least squares regression equation, denoted by the solid line, is $Y = -0.0045 + 14.3\ X$. R-squared is 99.4 percent with (114-2) d.f.

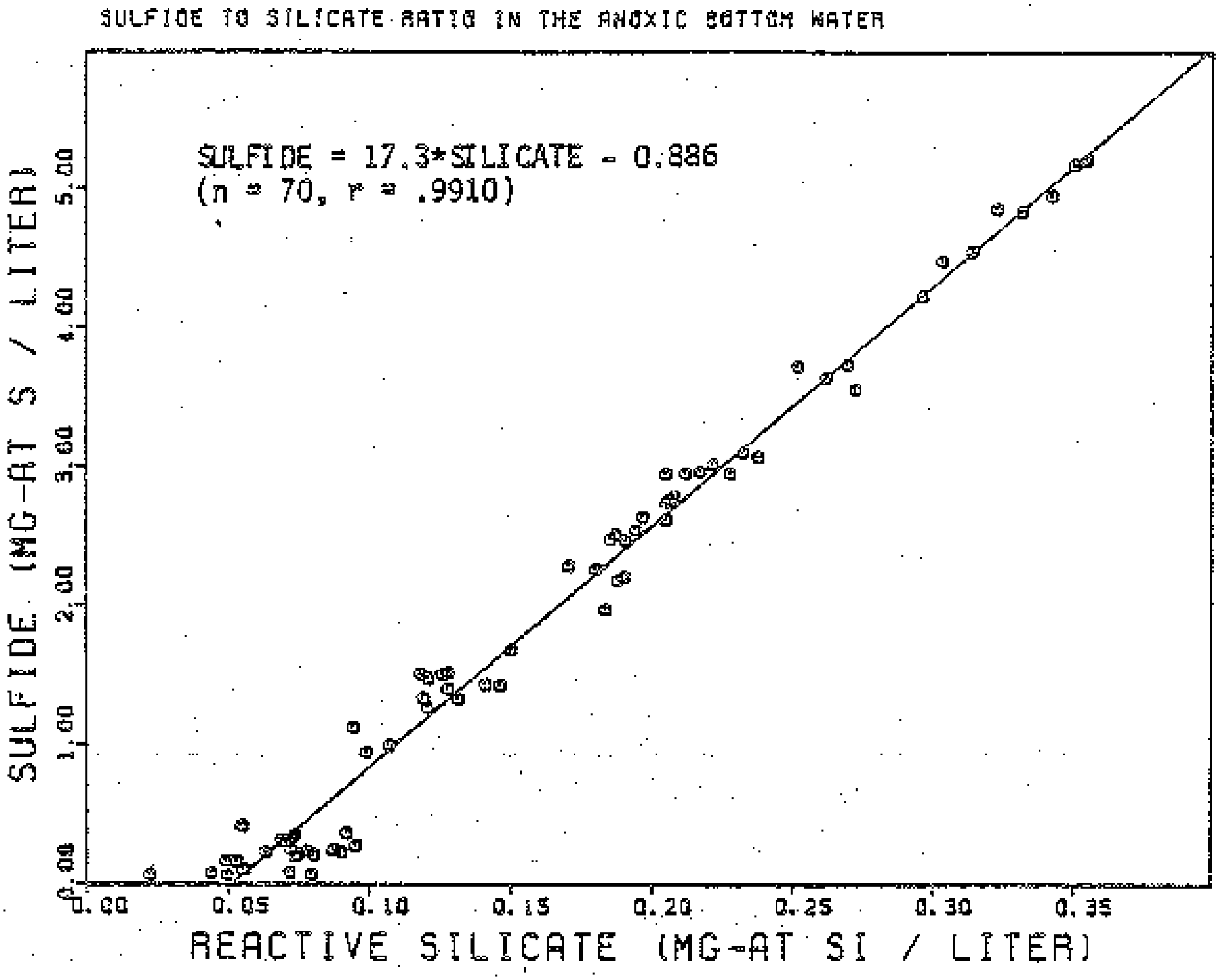


Figure 12g. Sulfide to silicate ratio in the anoxic bottom water. The least squares regression equation, denoted by the solid line, is $Y = -0.886 + 17.3\ X$. R-squared is 98.2 percent with (70-2) d.f.

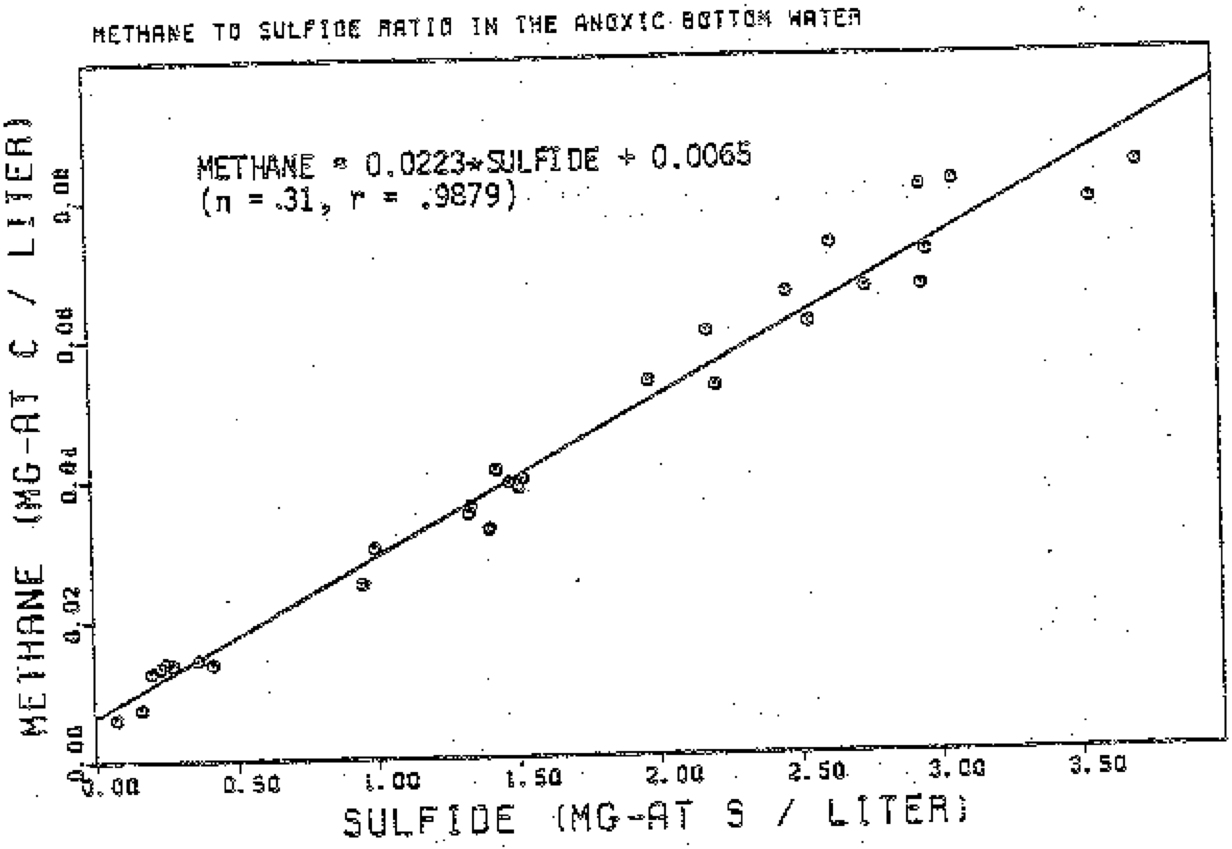


Figure 12h. Methane to sulfide ratio in the anoxic bottom water. The least squares regression equation, denoted by the solid line, is Y = .0065 + .0223 X. R-squared is 97.5 percent with (31-2) d.f.

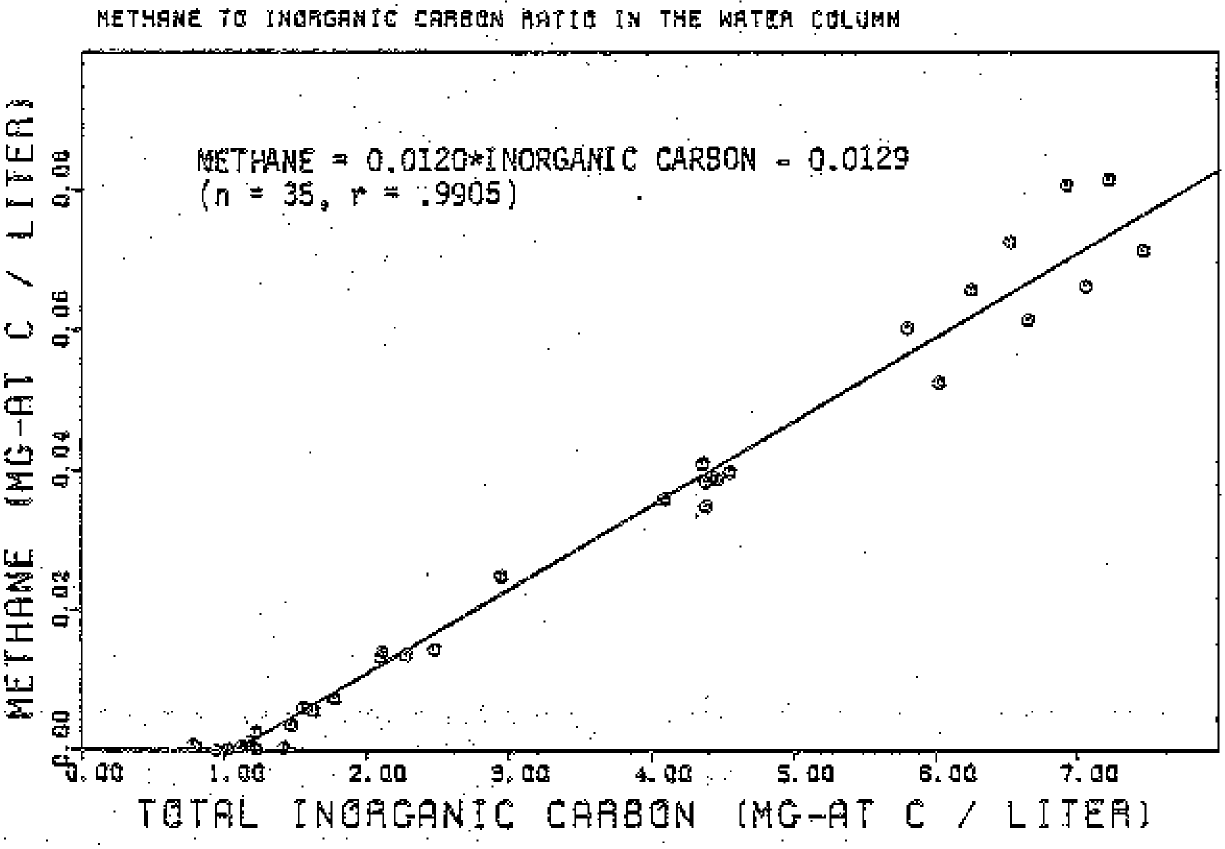


Figure 12i. Methane to inorganic carbon ratio in the water column. The least squares regression equation, denoted by the solid line, is Y = -0.0129 + 0.0120 X. R-squared is 98.0 percent with (35-2) d.f.

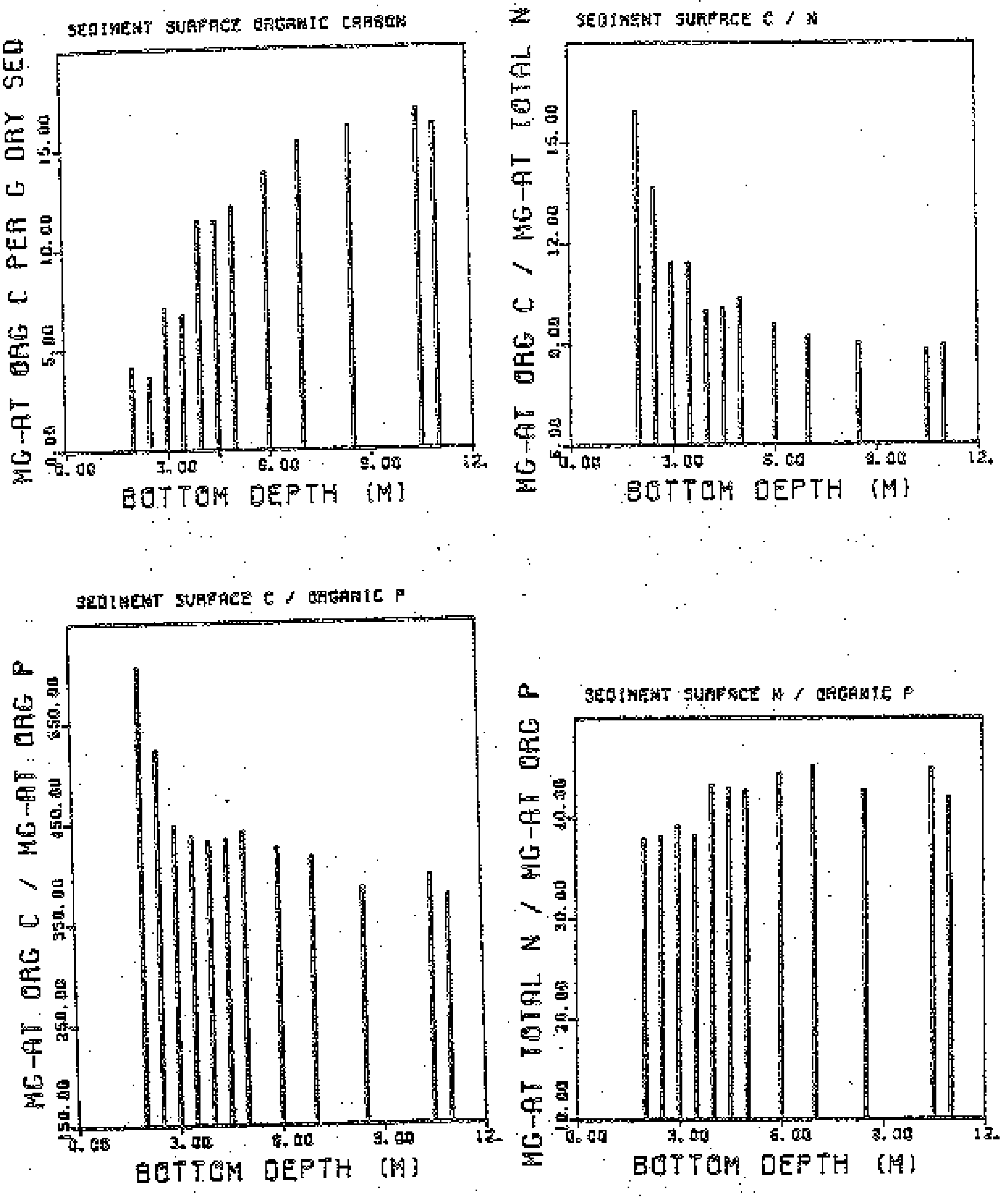


Figure 13a. Carbon, nitrogen and phosphorus in the surface sediment (0.0–0.5 cm) along a gradient from 2.0 to 11.5 meters water depth.

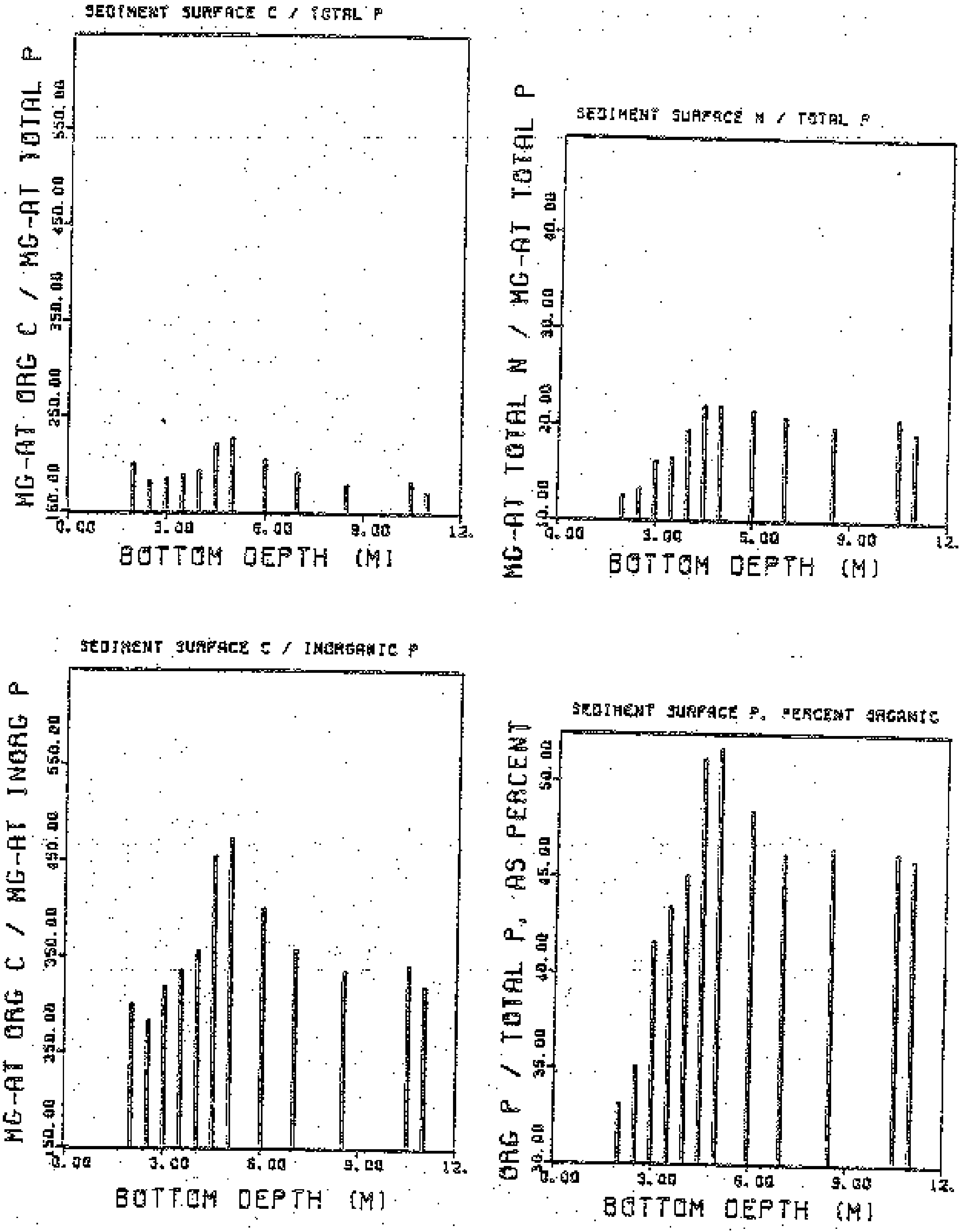


Figure 13b. Carbon, nitrogen and phosphorus in the surface sediment (0.0-0.5 cm) along a gradient from 2.0 to 11.5 meters water depth.

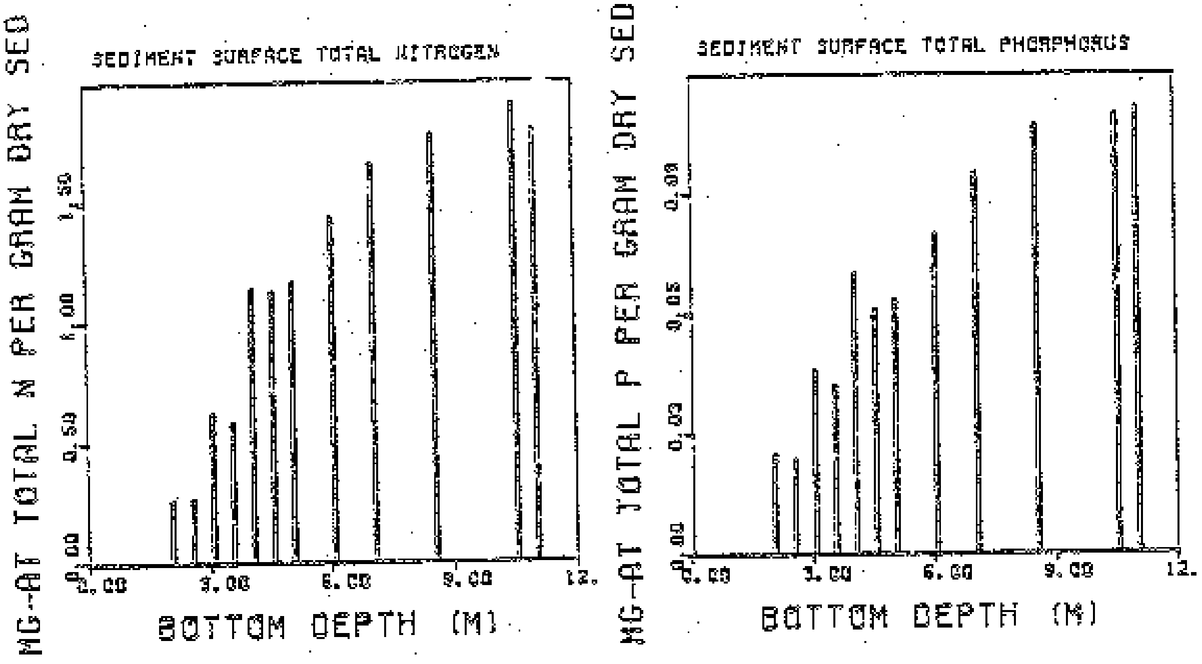


Figure 13c. Carbon, nitrogen and phosphorus in the surface sediment (0.0-0.5 cm) along a gradient from 2.0 to 11.5 meters water depth.

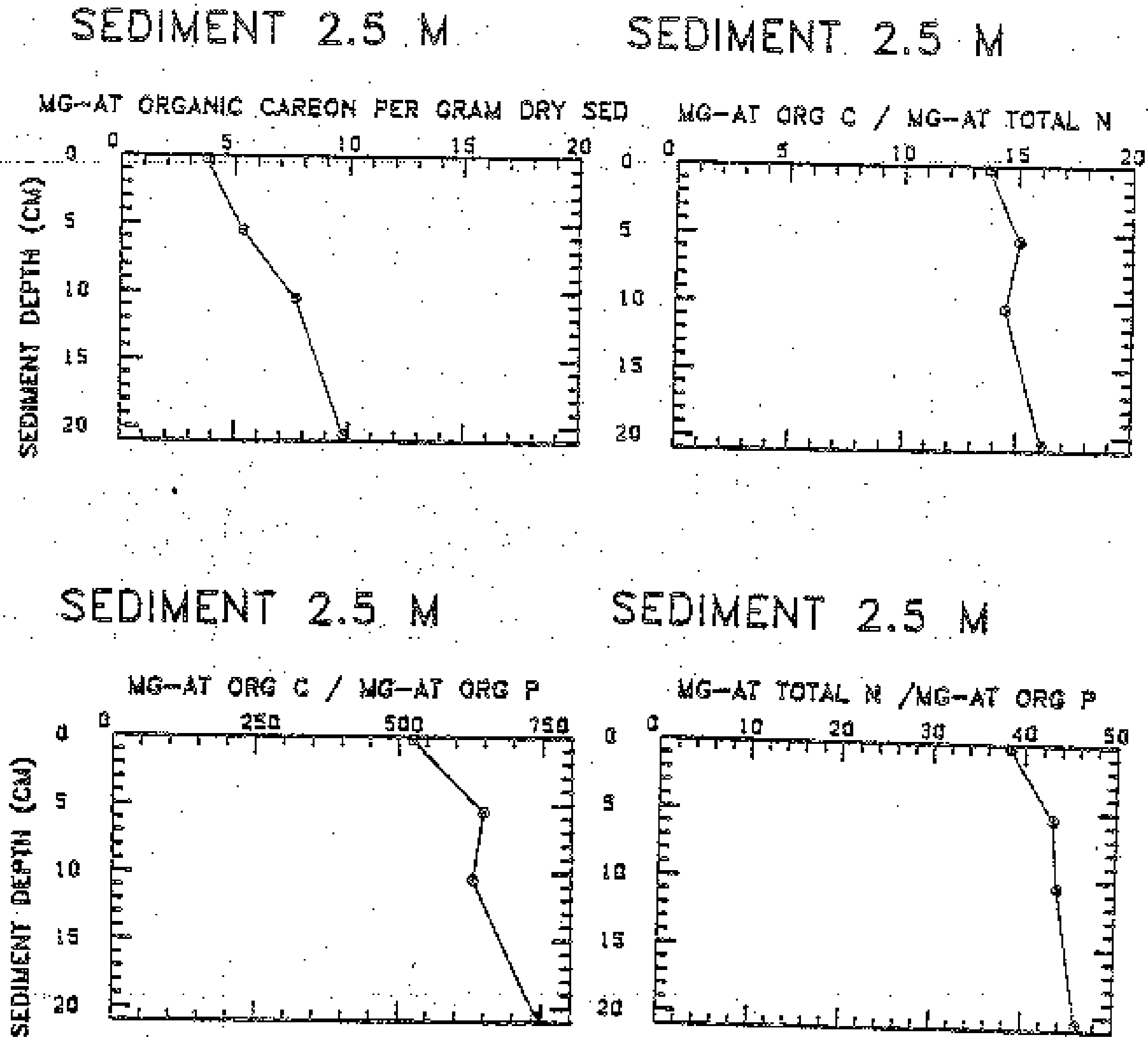


Figure 14a. Carbon, nitrogen and phosphorus in the sediment at 2.5 meters water depth.

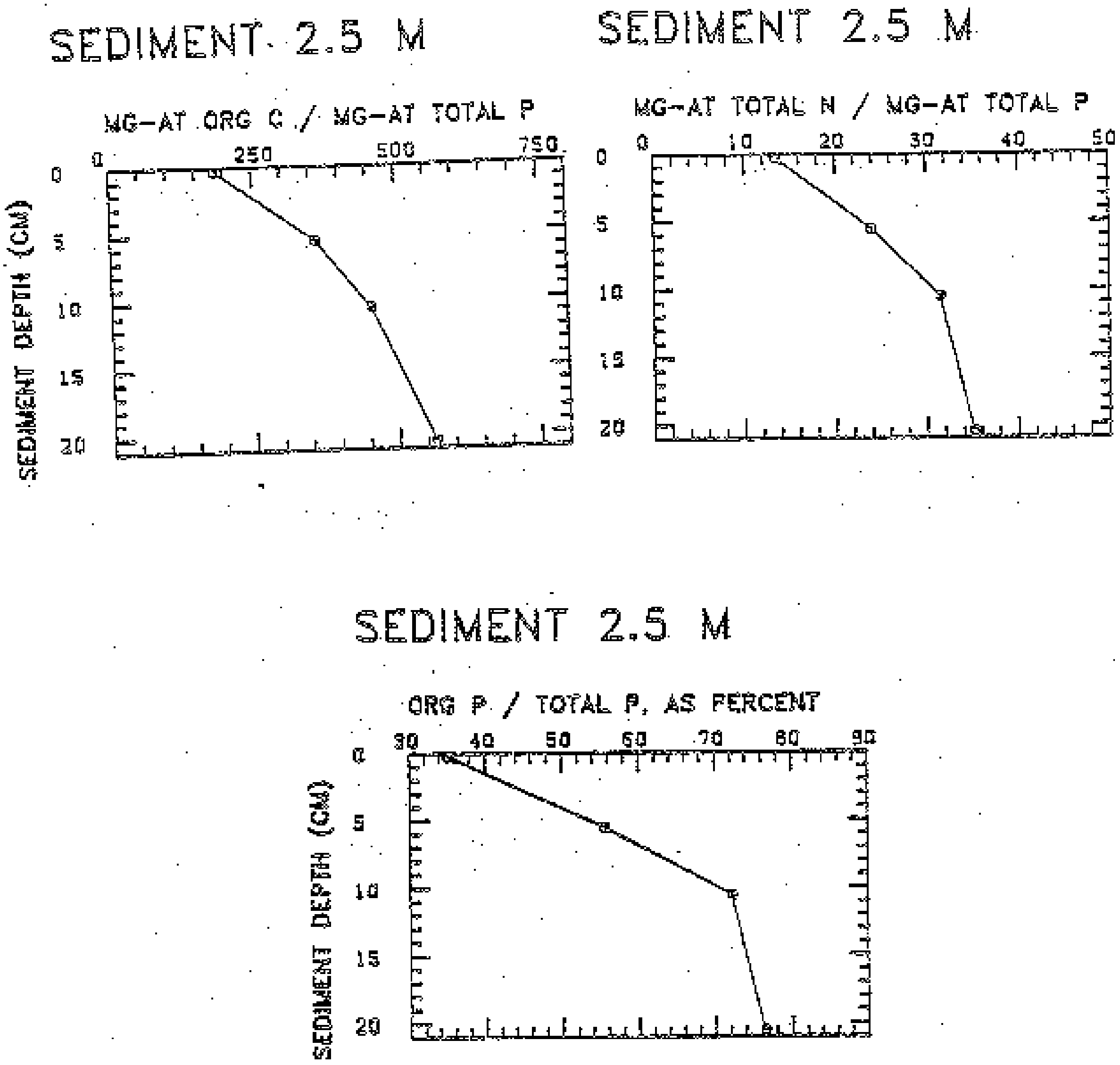


Figure 14b. Carbon, nitrogen and phosphorus in the sediment at 2.5 meters water depth.

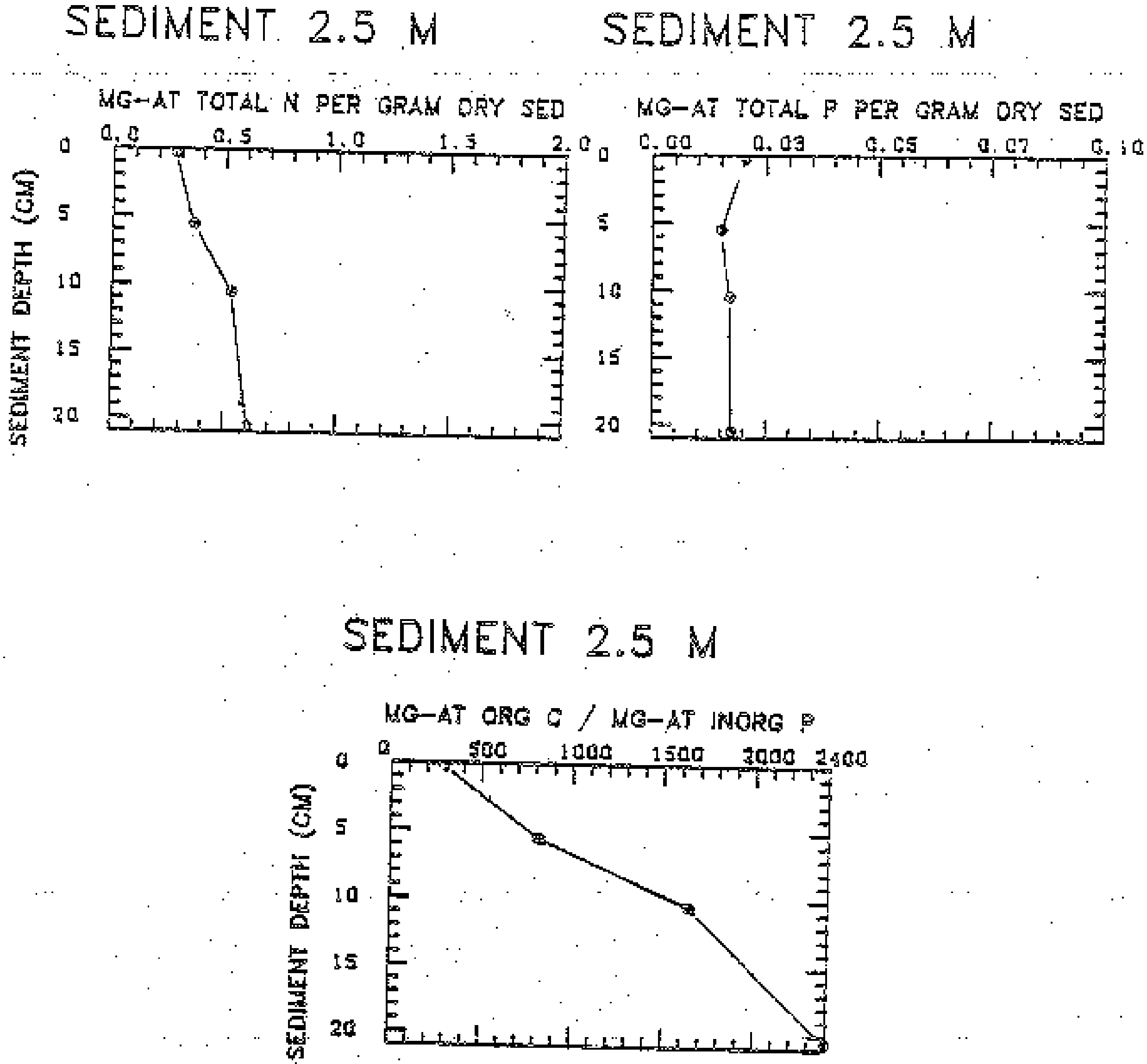


Figure 14c. Carbon, nitrogen and phosphorus in the sediment at 2.5 meters water depth.

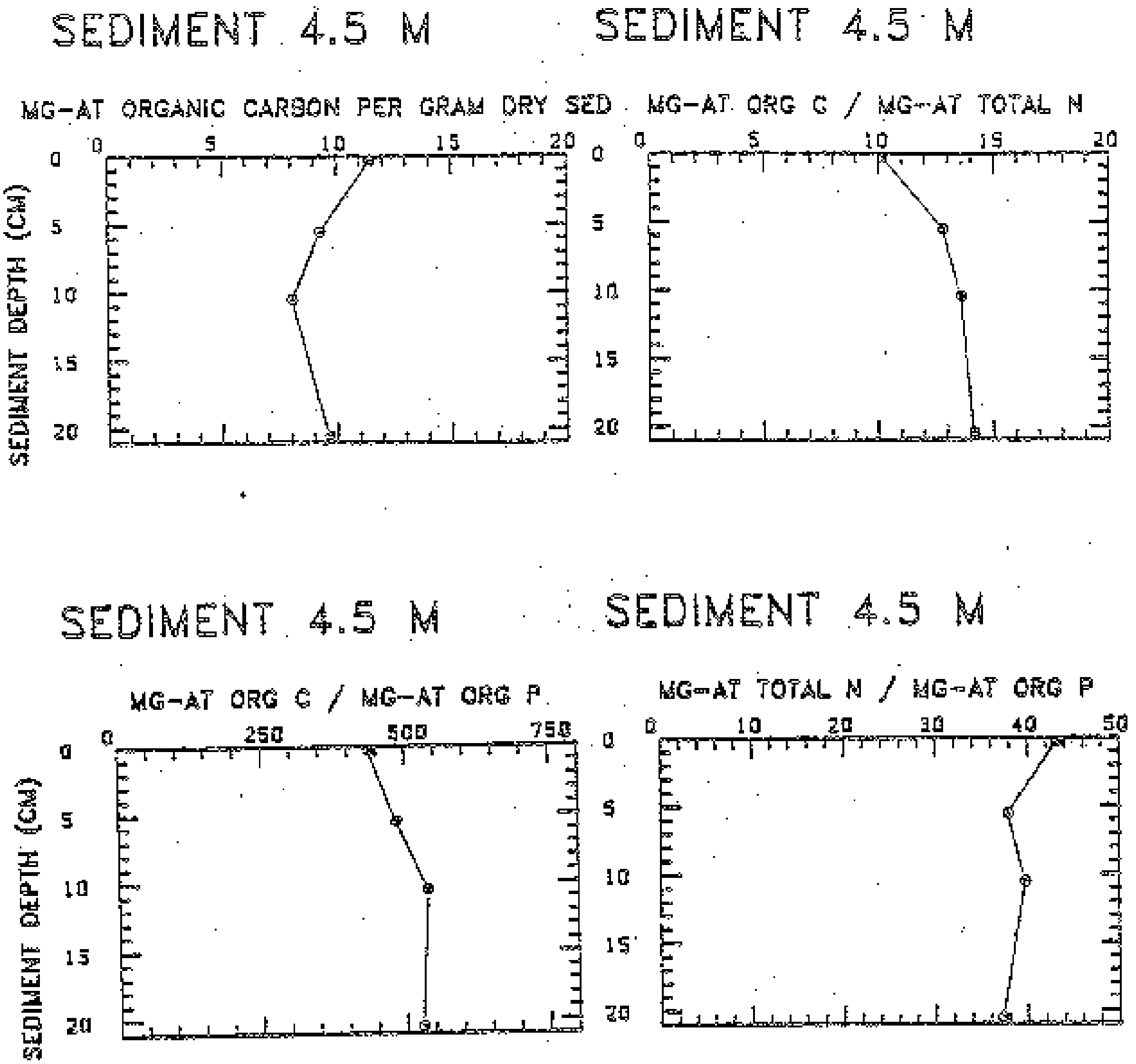


Figure 15a. Carbon, nitrogen and phosphorus in the sediment at 4.5 meters water depth.

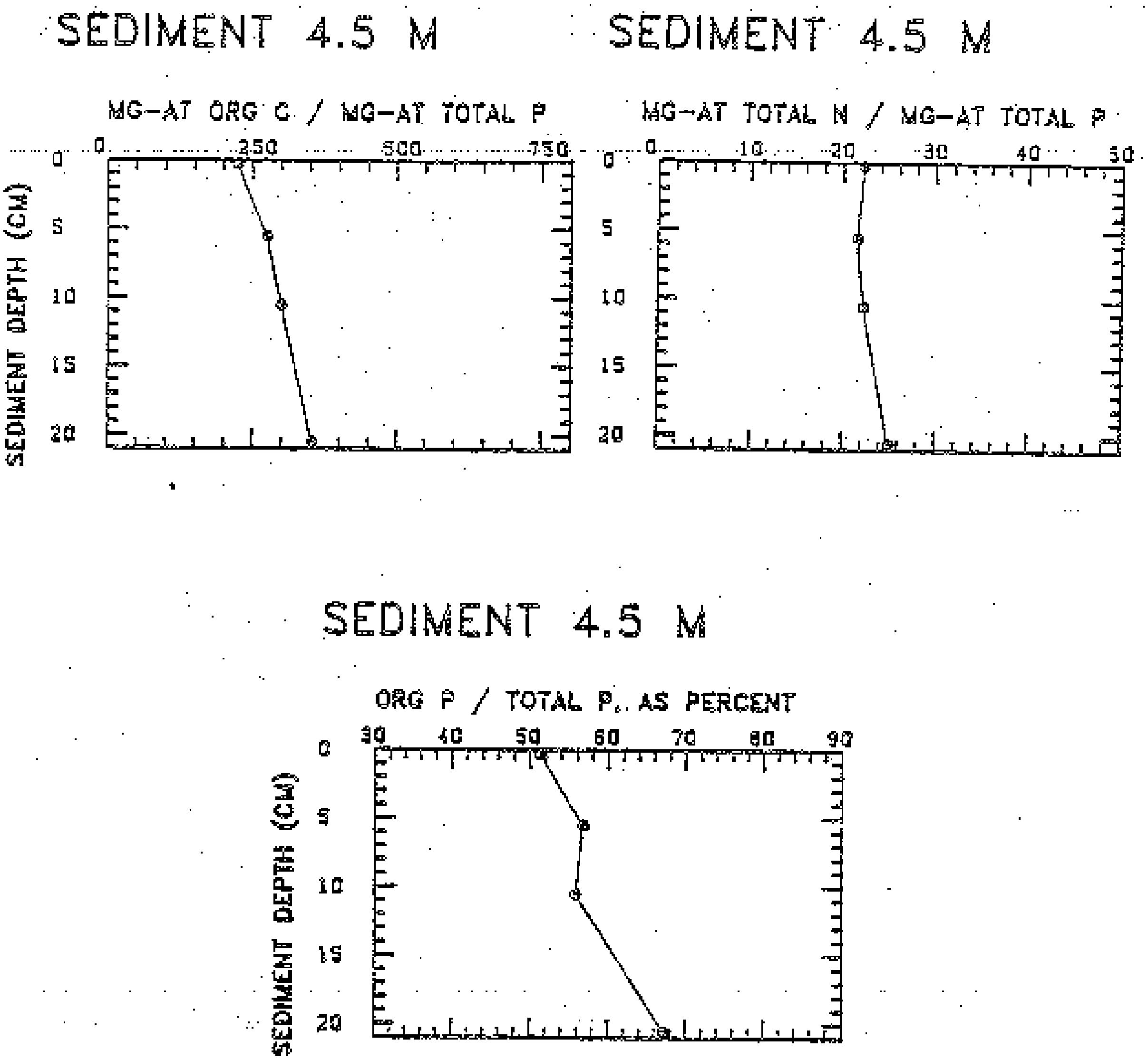


Figure 15b. Carbon, nitrogen and phosphorus in the sediment at 4.5 meters water depth.

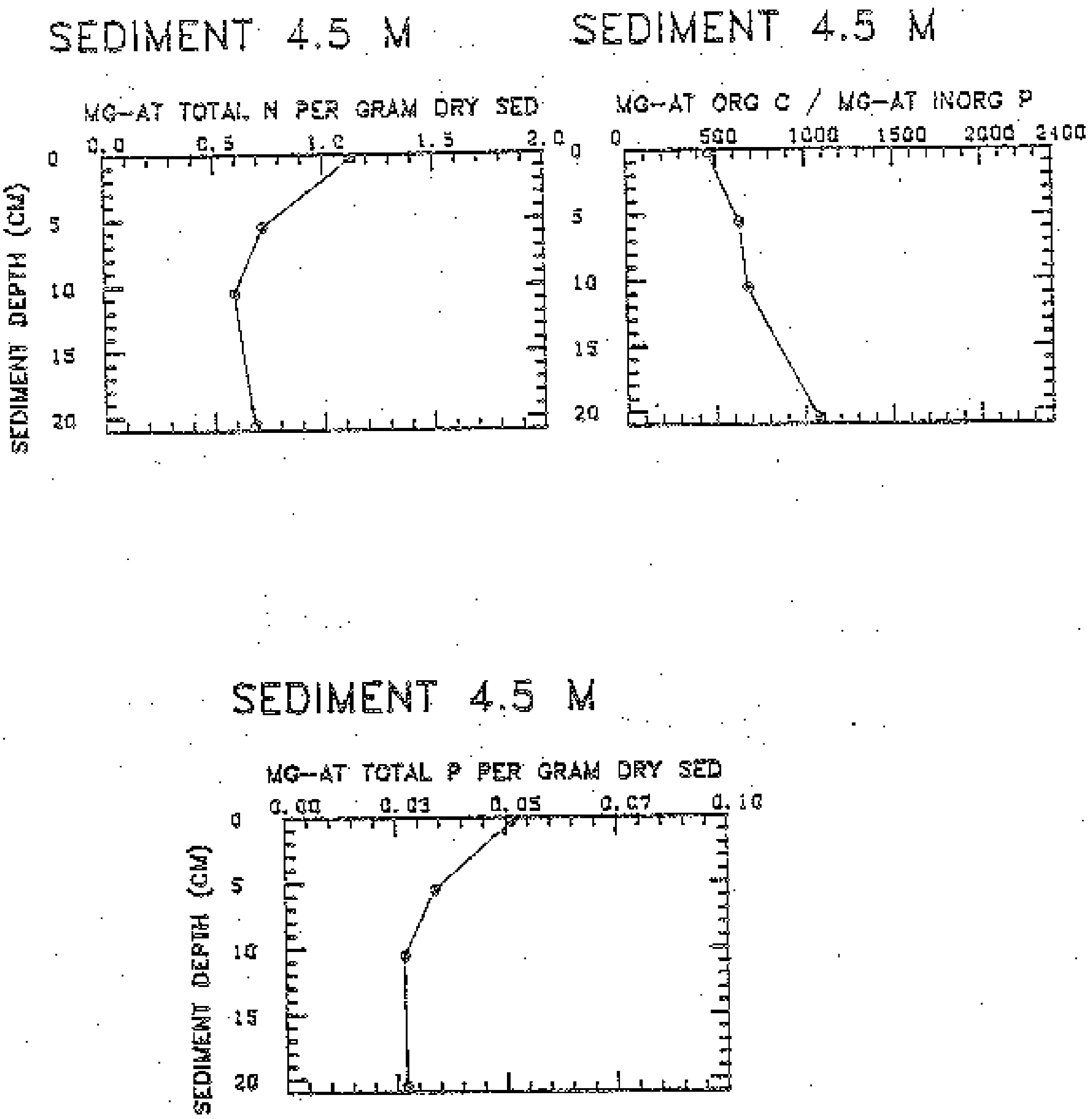
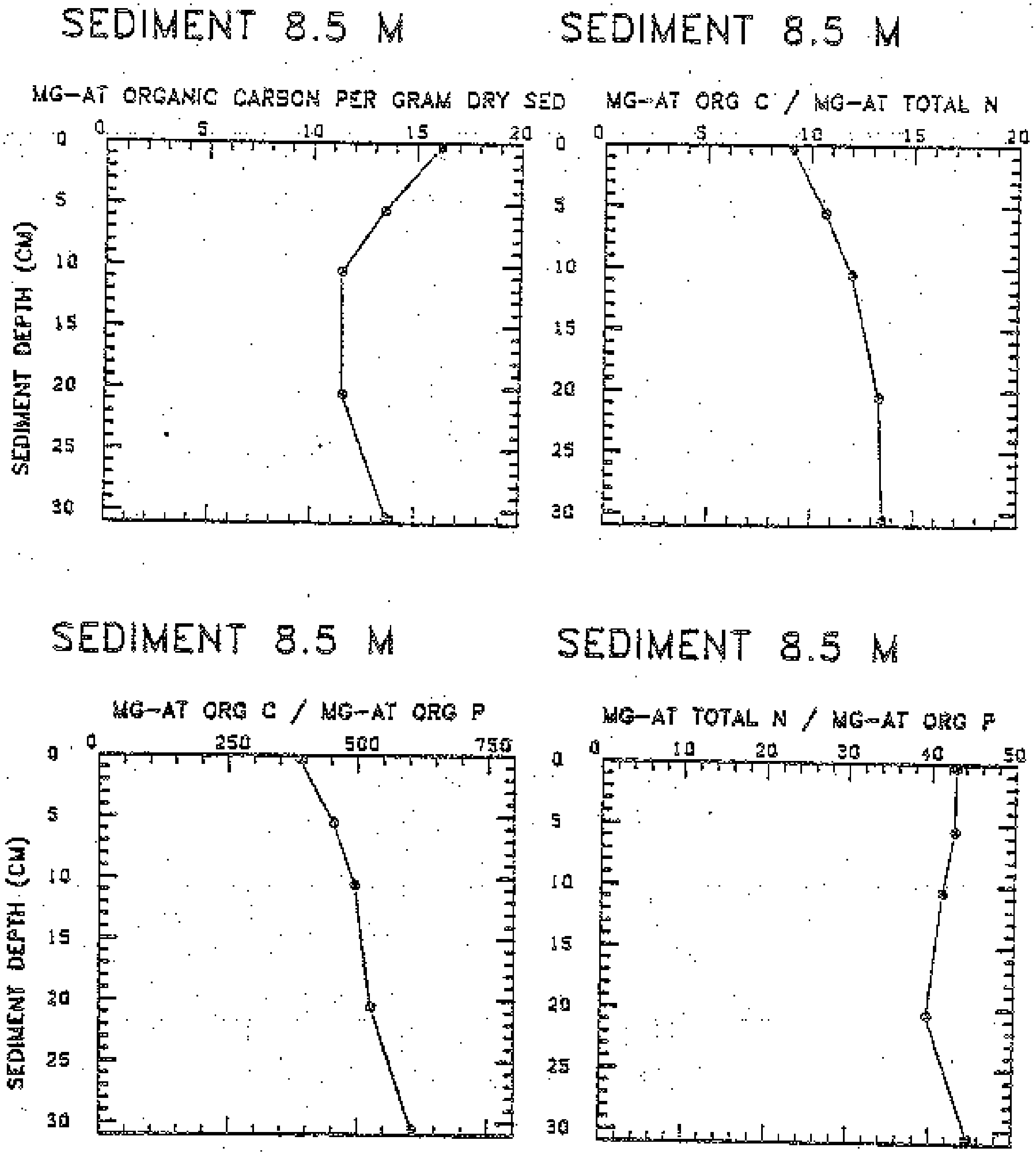


Figure 15c. Carbon, nitrogen and phosphorus in the sediment at 4.5 meters water depth.



SEDIMENT 8.5 M

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Figure 16a. Carbon, nitrogen and phosphorus in the sediment at 8.5 meters water depth.

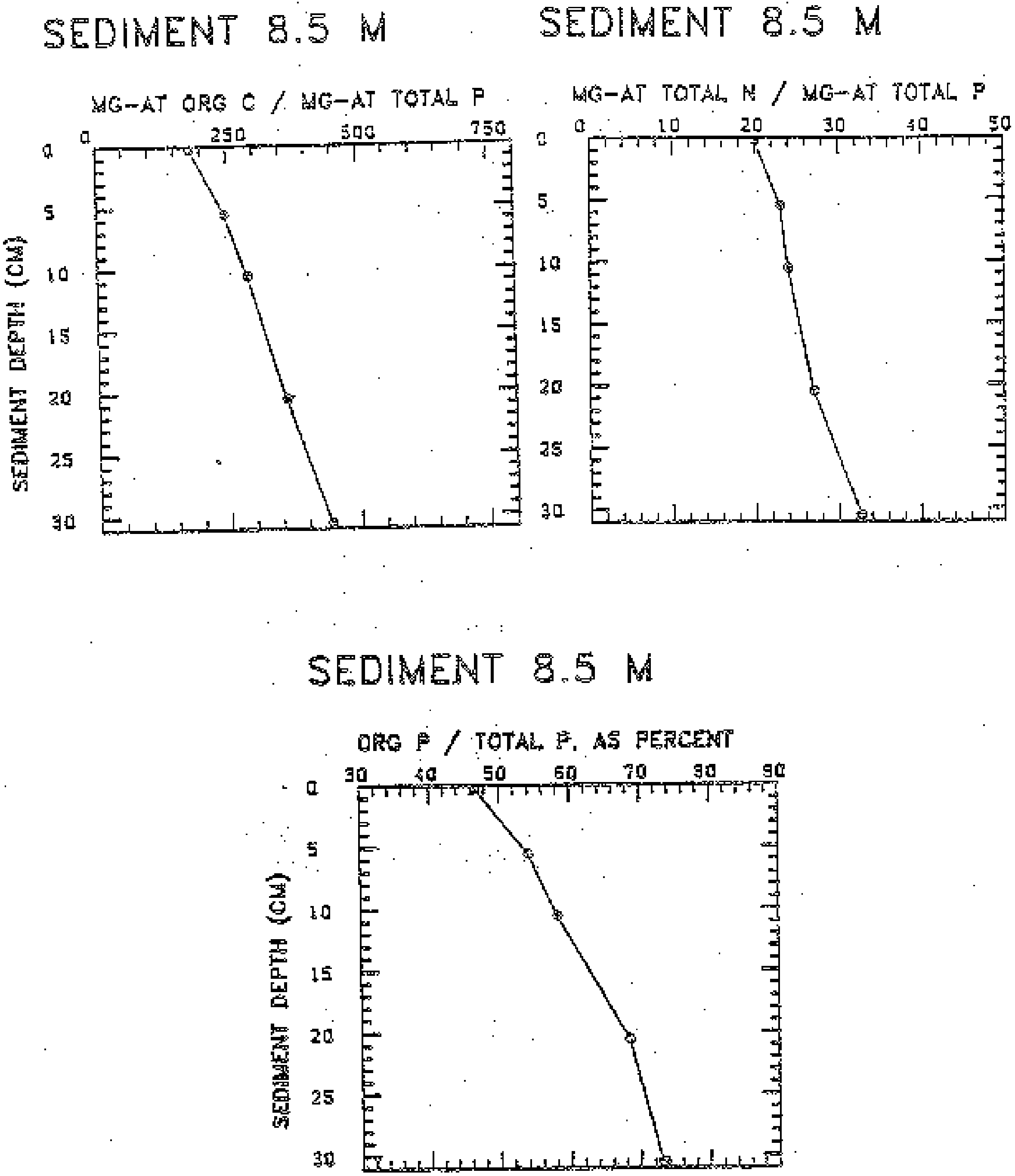

Figure 16b. Carbon, nitrogen and phosphorus in the sediment at 8.5 meters water depth.

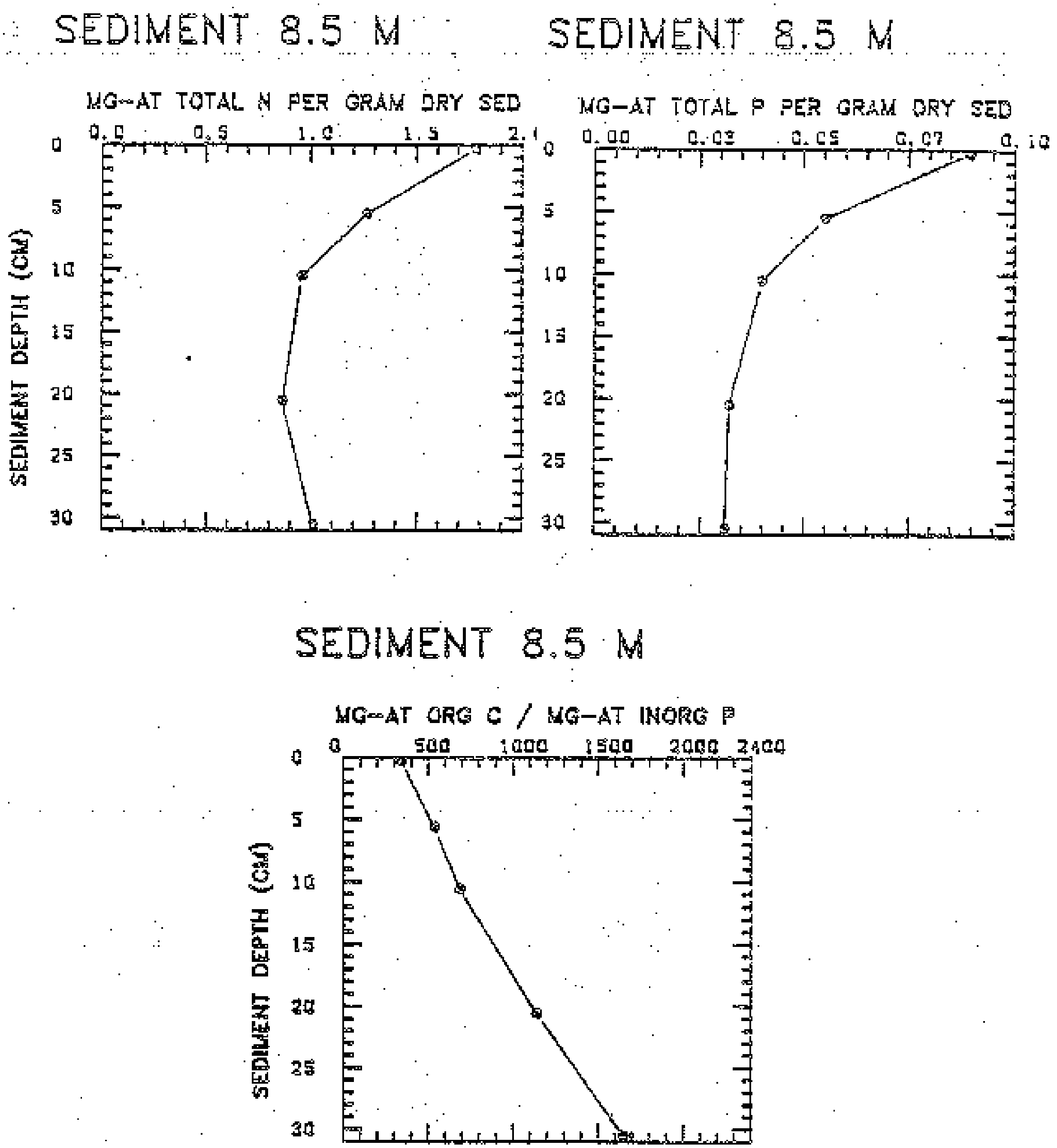

Figure 16c. Carbon, nitrogen and phosphorus in the sediment at 8.5 meters water depth.

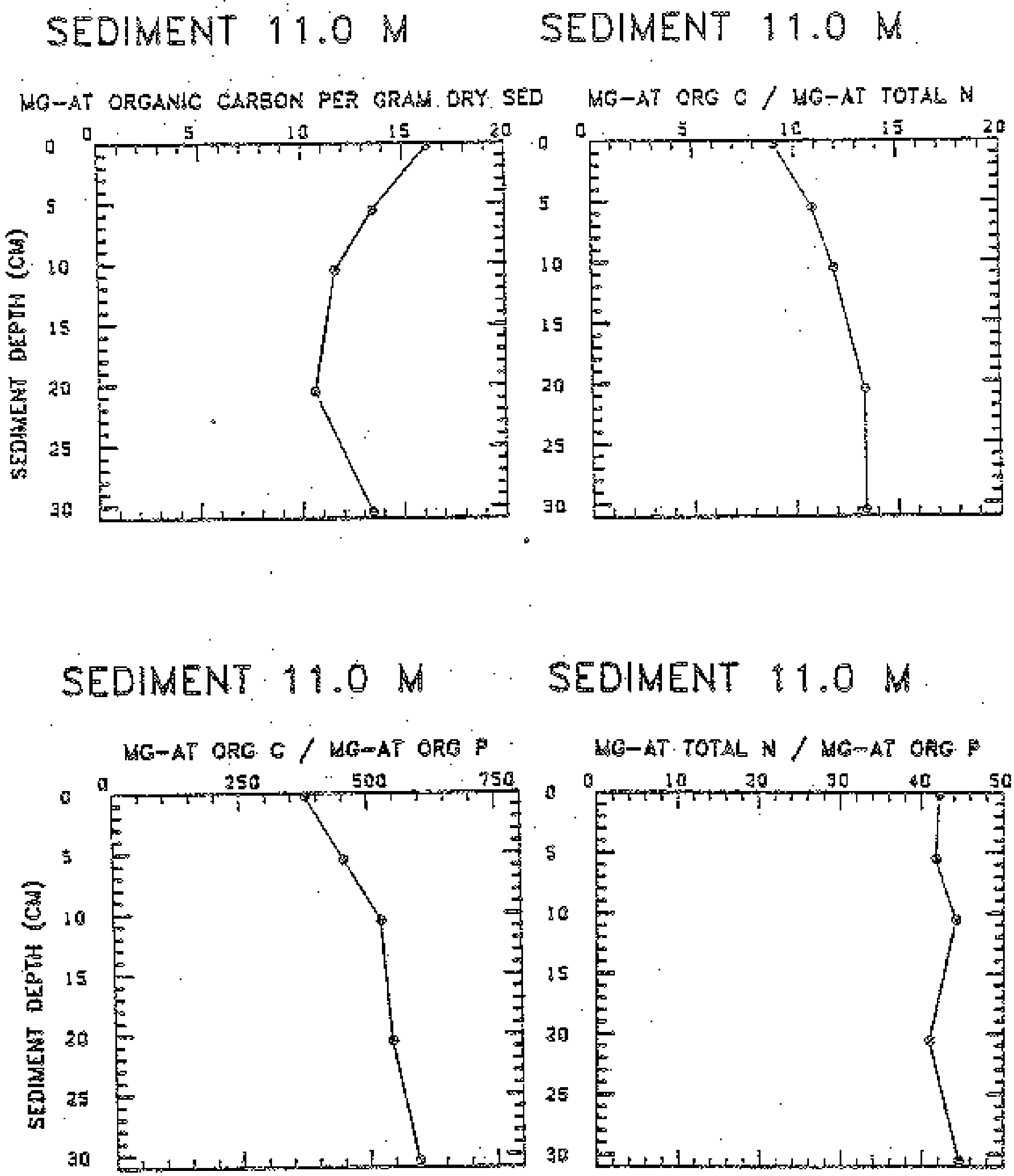

Figure 17a. Carbon, nitrogen and phosphorus in the sediment at 11.0 meters water depth.

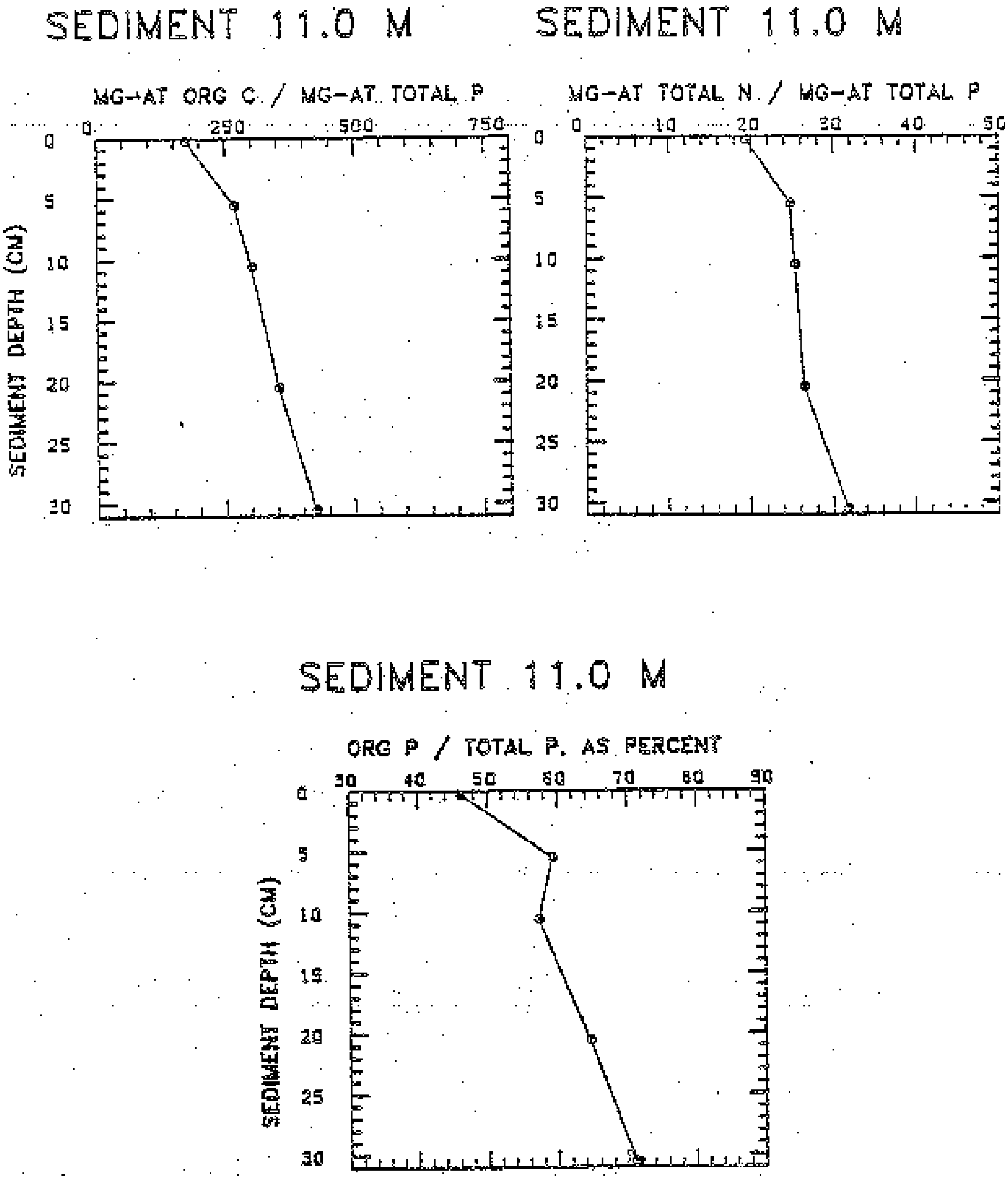

Figure 17b. Carbon, nitrogen and phosphorus in the sediment at 11.0 meters water depth.

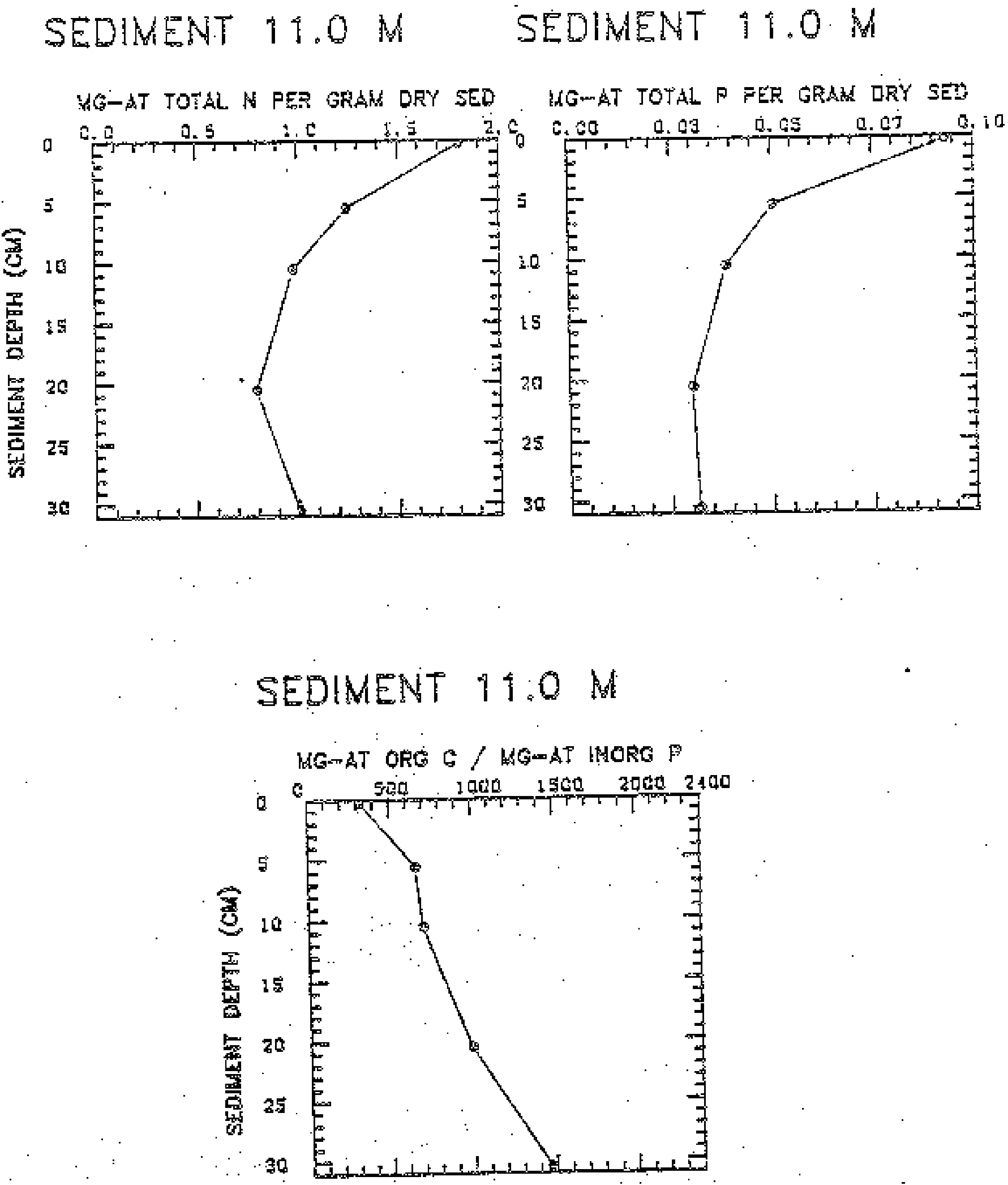

Figure 17c. Carbon, nitrogen and phosphorus in the sediment at 11.0 meters water depth.

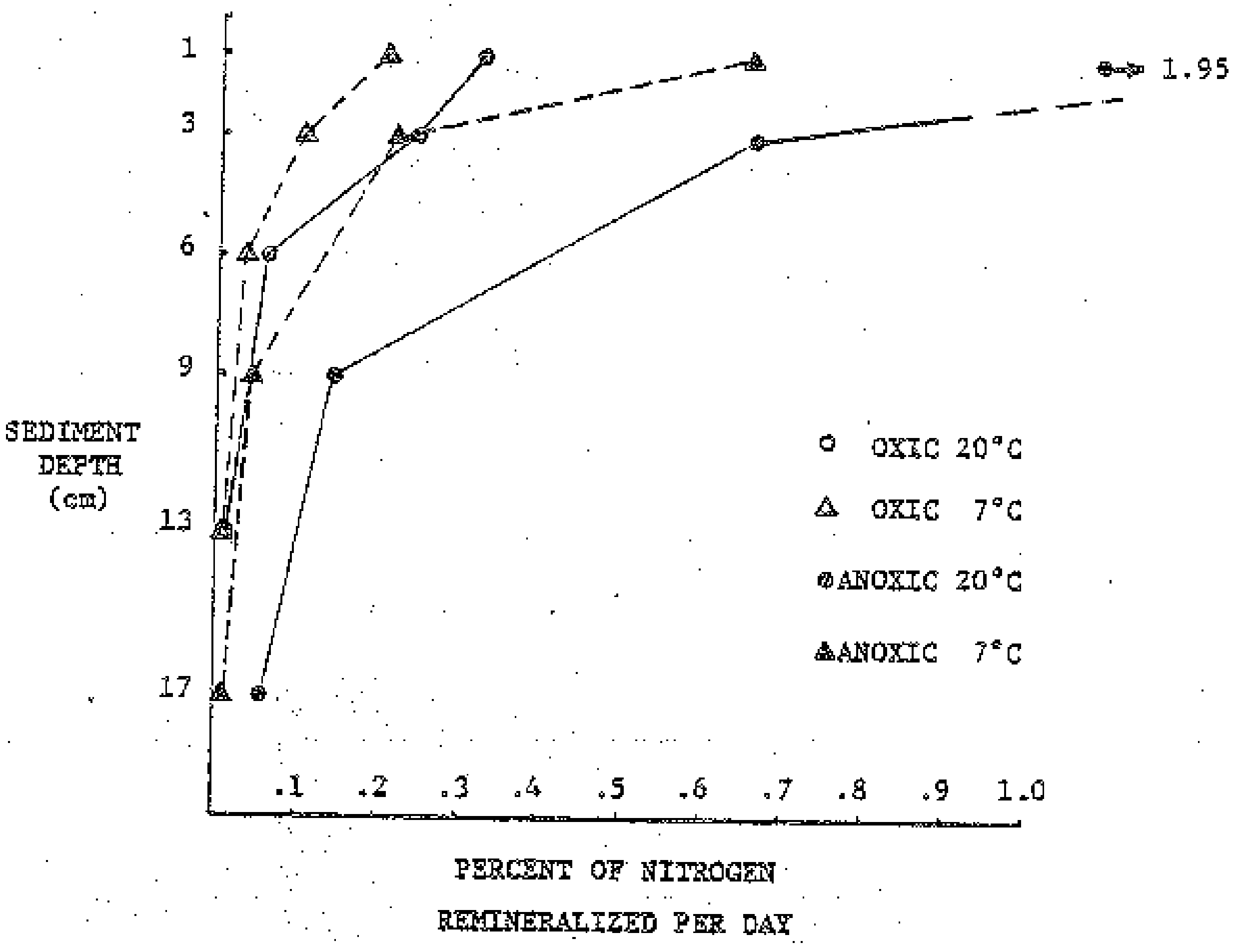

Figure 18. Percent of sediment organic nitrogen remineralized per day in isolated sediment sections from oxic and anoxic environments. Incubation at 7°C (dashed line) and 20°C (solid line).

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APPENDICES

The following is a list of detailed data appendices available from the authors. Appendix 1b, 3a and 6c are included with this report:

Appendix 1a.	Physical parameters of the water column, Fall 1979 through Fall 1981.
Appendix 1b.	Light measurements in the water column, Spring 1980 through Summer 1981.
Appendix 2a.	Chemical parameters of the water column, Fall 1979 through Fall 1981.
Appendix 2b.	Additional chemical parameters measured in the water column on 12-22-79 and 06-27-80.
Appendix 2c.	Total inorganic carbon and methane in the water column in the Spring and Summer of 1980.
Appendix 3a.	Particulate carbon, nitrogen and phosphorus in the surface water 09-20-79 through 19-01-80.
Appendix 3b.	Particulate carbon, nitrogen, and phosphorus in the water column on 12-22-79 and 06-27-80.
Appendix 4a.	Parameters for estimating sedimentation of carbon, nitrogen and phosphorus using sediment traps.
Appendix 4b.	Carbon, nitrogen and phosphorus content of a allocthonous detritus.
Appendix 5a.	Parameters for calculating the anoxic benthic flux of dissolved nutrients using <u>in situ</u> benthic chambers at 7.5 meters water depth.
Appendix 5b.	Parameters for calculating the oxic benthic flux of dissolved nutrients using <u>in situ</u> benthic chambers at 2.5 meters water depth.
Appendix 6a.	Parameters for calculating the porosity and salt content of sediment samples.
Appendix 6b.	Parameters for calculating the carbon, nitrogen and phosphorus content of sediment samples.
Appendix 6c.	Summary of carbon, nitrogen and phosphorus content of sediment samples and various ratios of these elements.
Appendix 7a.	Parameters for calculating the ammonium production rate during incubation of isolated sections of anoxic sediment.
Appendix 7b.	Parameters for calculating the ammonium production rate during incubation of isolated sections of oxic sediment.
Appendix 8a.	pH measurements in the water column on 03-19-80 and 04-25-80.

PUBLICATIONS AND MANUSCRIPTS

Manuscripts in preparation:

Patrick F. Roques and Scott W. Nixon. Rates and stoichiometry of anoxic nutrient regeneration in a permanently stratified estuary.

Patrick F. Roques and Scott W. Nixon. Flux and preservation of particulate carbon, nitrogen and phosphorus in an anoxic basin.

Patrick F. Roques. 1982. Anoxic nutrient regeneration in estuarine sediments: Rates and Stoichiometry. Ph.D. Thesis, University of Rhode Island, Kingston, RI.

Appendix 1b. Light measurements in the water column. Spring 1980 through Summer 1981. Depth (meters) and light measured in microeinsteins with percent of surface intensity on 03-04-80, 07-18-80, 11-13-80, 05-13-81 and 06-24-81. Data collected by Diana Kennett, University of Rhode Island.

	03-04-80		07-18-80		11-13-80		05-13-81		06-24-81	
DEPTH	µE	%	µE	%	µE	%	µE	%	µE	%
0.01	1330	100.0	1862	100.0	532	100.0	2128	100.0	2194	100.0
0.50			1064	57.1	279	52.4				
1.00	718	53.9	798	42.8	146	27.4	798	37.5	931	42.4
2.00	106	7.9	399	21.4	99	18.6	399	18.7	385	17.5
2.50			292	15.6						
3.00			266	14.2	80	15.0	266	12.5	169	7.7
3.50			133	7.1	73	13.7				
4.00			66	3.5					65	2.9
4.50			34	1.8						
5.00			29	1.5					26	1.1
5.50										
6.00									16	0.7
7.00										
8.00										

Appendix 3a. Particulate carbon, nitrogen, and phosphorus in the surface water 09-20-79 through 12-01-80. Determinations on an integrated sample from 0.5 to 6.5 meters. C1-date. C2 and C5-organic carbon determinations, µg-at C liter^{-1}. C3 and C6-total nitrogen determinations, µg-at N liter^{-1}. C4 and C7-total phosphorus determinations, µg-at P liter^{-1}. C8-average of carbon determinations. C9-standard deviation for carbon. C10-coefficient of variation for carbon as a percent. C11-average of nitrogen determinations. C12-standard deviation for nitrogen. C13-coefficient of variation for nitrogen as a percent. C14-average of phosphorus determinations. C15-standard deviation for phosphorus. C16-coefficient of variation for phosphorus as a percent. C17-carbon to nitrogen ratio. C18-nitrogen to phosphorus ratio. C19-carbon to phosphorus ratio.

C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19
092079	160.18	20.403	1.0169	163.25	19.982	1.0906	161.718	2.1666	1.3397	20.1925	0.29769	1.4743	1.05375	0.052114	4.9455	8.00881	19.1625	153.469
122279	80.19	11.401	0.8287	67.47	9.227	0.6394	73.838	8.9958	12.1832	10.3140	1.53725	14.9045	0.73405	0.133855	18.2352	7.15901	14.0508	100.590
030480	151.33	25.658	1.6541	171.57	30.563	1.8393	161.454	14.3118	8.8643	28.1105	3.46836	12.3383	1.74670	0.130956	7.4973	5.74355	16.0935	92.434
052380	152.00	19.118	0.9291	150.62	18.381	0.9266	151.315	0.9716	0.6421	18.7495	0.52114	2.7795	0.92785	0.001768	0.1905	8.07035	20.2075	163.081
062780	229.36	27.583	1.1856	240.26	24.178	1.2999	234.811	7.7067	3.2821	25.8805	2.40770	9.3031	1.24275	0.080822	6.5035	9.07291	20.8252	188.945
081880	152.86	18.622	0.7776	148.39	17.052	0.7176	150.625	3.1608	2.0984	17.8370	1.11016	6.2239	0.74760	0.042426	5.6750	8.44452	23.8590	201.478
101280	111.27	16.244	1.0712	108.04	16.140	0.9952	109.656	2.2861	2.0848	16.1920	0.07354	0.4542	1.03320	0.053740	5.2013	6.77226	15.6717	106.133
111280	162.13	23.853	1.7479	144.20	20.441	1.5310	153.171	12.6777	8.2768	22.1470	2.41265	10.8938	1.63945	0.153371	9.3550	6.91613	13.5088	93.429
120180	184.20	26.211	1.6259	196.91	29.204	1.6074	190.560	8.9887	4.7170	27.7075	2.11637	7.6383	1.61665	0.013081	0.8092	6.87756	17.1388	117.873

Appendix 6c. Summary of carbon, nitrogen and phosphorus content of sediment samples and various ratios of these elements. The symbol * indicates no data or no appropriate calculation. C1-sample location. C2-depth in the sediment. Surface sediment sample was a 0.0 to 0.5 cm section. A 1.0 cm section was taken for deeper samples. C3-organic carbon content of dry salt-free sediment, µg-at C mg^{-1}. C4-total nitrogen content of dry salt-free sediment, µg-at N mg^{-1}. C5-total phosphorus content of dry salt-free sediment, µg-at P mg^{-1}. C6-organic phosphorus content of dry salt-free sediment, µg-at P mg^{-1}. C7-organic carbon to nitrogen ratio. C8-organic carbon to total phosphorus ratio. C9-nitrogen to total phosphorus ratio. C10-organic carbon to organic phosphorus ratio. C11-nitrogen to organic phosphorus ratio. C12-inorganic phosphorus to total phosphorus ratio. C13-organic phosphorus to total phosphorus ratio. C14-organic phosphorus to inorganic phosphorus ratio. C15-organic carbon to inorganic phosphorus ratio.

C1	C2	C3	C4
Water depth 2.0 m	0.2500	4.21222	0.264074
Water depth 2.5 m	0.2500	3.69507	0.269870
Water depth 2.5 m	5.5000	5.34166	0.354923
Water depth 2.5 m	10.5000	7.63226	0.527884
Water depth 2.5 m	20.5000	9.76772	0.607295
Water depth 3.0 m	0.2500	7.15436	0.625673
Water depth 3.5 m	0.2500	6.73953	0.589421
Water depth 4.0 m	0.2500	11.44352	1.143327
Water depth 4.5 m	0.2500	11.42909	1.130522
Water depth 4.5 m	5.5000	9.23283	0.721277
Water depth 4.5 m	10.5000	8.00986	0.590804
Water depth 4.5 m	20.5000	9.61352	0.679966
Water depth 5.0 m	0.2500	12.14859	1.170635
Water depth 6.0 m	0.2500	13.82509	1.439260
Water depth 7.0 m	0.2500	15.34346	1.660761
Water depth 8.5 m	0.2500	16.11044	1.782967
Water depth 8.5 m	5.5000	13.44463	1.263122
Water depth 8.5 m	10.5000	11.41360	0.951792
Water depth 8.5 m	20.5000	11.47331	0.861470
Water depth 8.5 m	30.5000	13.64724	1.008041
Water depth 10.5 m	0.2500	16.88068	1.907226
Water depth 11.0 m	0.2500	16.14758	1.800159
Water depth 11.0 m	5.5000	13.49845	1.243754
Water depth 11.0 m	10.5000	11.60895	0.976310
Water depth 11.0 m	20.5000	10.59000	0.792745
Water depth 11.0 m	30.5000	13.40723	1.002300
Freshwater Stream Site C	0.2500	1.45856	0.076363
(see map of Site D	0.2500	7.00057	0.416060
sample sites) Site E	0.2500	3.94038	0.226240

Appendix 6c (continued)

C5	C6	C7	C8	C9	C10
0.0209029	0.0069470	15.95088	201.513	12.6334	606.336
0.0200682	0.0070564	13.69204	184.126	13.4476	523.648
0.0148731	0.0082537	15.05019	359.149	23.8634	547.183
0.0167904	0.0121212	14.45822	454.561	31.4396	629.662
0.0172967	0.0132146	16.08397	564.716	35.1105	739.161
0.0382990	0.0159449	11.43466	186.803	16.3365	448.693
0.0353754	0.0153792	11.43415	190.515	16.6619	438.224
0.0585178	0.0264199	10.00896	195.556	19.5381	433.140
0.0513172	0.0262577	10.10956	222.715	22.0301	435.266
0.0336771	0.0190737	12.80066	274.157	21.4174	484.061
0.0267177	0.0148907	13.55758	299.796	22.1128	537.911
0.0272385	0.0182839	14.13824	352.939	24.9634	525.792
0.0530252	0.0274063	10.37778	229.110	22.0770	443.277
0.0668154	0.0323997	9.60570	206.915	21.5408	426.704
0.0795259	0.0367744	9.23881	192.937	20.8833	417.232
0.0894570	0.0416921	9.03575	180.091	19.9310	386.415
0.0548511	0.0296353	10.64397	245.111	23.0282	453.669
0.0397408	0.0230963	11.99169	287.201	23.9500	494.174
0.0319499	0.0218458	13.31828	359.103	26.9632	525.195
0.0308803	0.0225929	13.53838	441.940	32.6435	604.050
0.0915882	0.0424206	8.85091	184.311	20.8239	397.936
0.0930091	0.0427719	8.97009	173.613	19.3546	377.528
0.0503750	0.0298296	10.85299	287.959	24.6899	452.319
0.0386396	0.0221165	11.89064	300.442	25.2671	524.900
0.0301016	0.0194149	13.35865	351.809	26.3356	549.457
0.0316429	0.0225042	13.37646	423.704	31.6754	595.766
0.0046995	0.0014437	19.10041	310.365	16.2491	1010.293
0.0203550	0.0091950	16.32610	343.929	20.4402	761.356
0.0134400	0.0056050	17.41683	293.183	16.8333	703.012

Appendix 6c (continued)

C11	C12	C13	C14	C15
38.0127	0.667653	0.332347	0.49778	301.82
38.2447	0.648377	0.351623	0.54231	283.98
43.0017	0.445061	0.554939	1.24688	806.97
43.5504	0.278086	0.721913	2.59600	1634.60
45.9564	0.236006	0.763994	3.23718	2392.82
39.2397	0.583672	0.416329	0.71329	320.05
38.3258	0.565258	0.434742	0.76910	337.04
43.2752	0.548514	0.451486	0.82311	356.52
43.0549	0.488325	0.511675	1.04782	456.08
37.8153	0.433628	0.566372	1.30612	632.24
39.6760	0.442663	0.557337	1.25905	677.25
37.1893	0.328748	0.671252	2.04185	1073.58
42.7141	0.483145	0.516855	1.06977	474.20
44.4220	0.515087	0.484913	0.94142	401.71
45.1608	0.537579	0.462421	0.86019	358.90
42.7651	0.533943	0.466057	0.87286	337.29
42.6222	0.459714	0.540285	1.17526	533.18
41.2097	0.418827	0.581173	1.38762	685.73
39.4341	0.316248	0.683751	2.16207	1135.51
44.6176	0.268374	0.731626	2.72614	1646.75
44.9599	0.536833	0.463167	0.86278	343.33
42.0874	0.540132	0.459868	0.85140	321.43
41.6953	0.407849	0.592151	1.45189	657.01
44.1440	0.427622	0.572378	1.33851	702.89
40.8318	0.355021	0.644979	1.81674	990.95
44.5384	0.288808	0.711192	2.46251	1467.08
52.8938	0.692804	0.307196	0.44341	447.99
45.2485	0.548268	0.451732	0.82392	627.30
40.3640	0.582961	0.417039	0.71538	502.92