Understanding the Importance of Soil and Water Chemistry in Relation to Fish Kills

For the April 2022 Workshop on Production Practices and Strategies to Boost the Milkfish Industry in the Philippines –NIFTDC-BFAR-Bonuan Binloc, Dagupan City

Michael A. Rice, Ph.D.
Rhode Island Cooperative Extension
Dept. of Fisheries, Animal & Veterinary Sciences
Benthic processes

(This is why URI Fisheries students are made to take chemistry)
Oxygen demand

• The decomposition of organic matter uses oxygen. Measures of demand for oxygen have standard tests used in analysis of wastewater:
  – Biological (or Biochemical) Oxygen Demand (BOD) – measures oxygen used by microbial oxidation (test is 5- or 7-d sealed bottle test)
  – Chemical Oxygen Demand (COD) – measures oxygen used chemically for oxidation of both organic matter and inorganic matter like ammonia and nitrite (test is lab assay using potassium dichromate)
  – Both are expressed in mg/L
  – Used by environmental engineers for TMDL, etc.
Redox (reduction-oxidation)

- Redox reactions occur when electrons are transferred between atoms or molecules
- Reduction reaction – electrons accepted
- Oxidation reaction – electrons given off
- Reduction – oxidation number (relative charge) of an atom is reduced
  - Cu\(^{++}\) (aq) + 2e\(^{-}\) → Cu (s)  (reduction)
  - Zn (s) → Zn\(^{++}\) (aq) + 2e\(^{-}\)  (oxidation)
Redox reactions

Reduced compound A (reducing agent)  Oxidized compound B (oxidizing agent)
A is oxidized, losing electrons  B is reduced, gaining electrons
Oxidized compound A  Reduced compound B

Light bulb  Electron flow through the wire
Zinc  Salt bridge
Water  Blue solution of Cu^{2+} ions

ALKA-CELL
Zn  MnO_2
OH^-
Redox reactions

• In a galvanic cell, electrons flow from a zinc electrode to a copper electrode, because Cu has a greater affinity for electrons than does Zn.

• In general, reactions proceed spontaneously in the direction that causes the energy of the products and reactants to decrease. When the energy of the reactants and products has reached an equal, minimal level, there is no longer any driving force for the reaction and the resulting steady state is called thermodynamic equilibrium.
Globally…

• On a global basis, redox processes do not reach equilibrium, because solar energy continuously arrives at the earth’s surface, bringing about photosynthetic activity by plant cells – yielding \( \text{O}_2 \) and organic matter
• This energy is then used by heterotrophic organisms to fuel their metabolic processes
• Although equilibrium is not achieved globally, we can still use thermodynamic principles to predict the direction and rates of redox reactions
Redox potential

- The flow of electrons in a galvanic cell can be measured with a voltmeter – the voltage is referred to as the cell potential or redox potential.

- \[ Pe_{\text{cell}} = \frac{(F E_{\text{cell}})}{(2.303RT)} \]

- The redox potential is proportional to the equivalent free energy change per mole of electrons associated with a given reduction.
Redox potential (cont.)

- Although aqueous solutions do not contain free protons and electrons, it is possible to define proton activity and electron activity:
  - \( \text{pH} = -\log (H^+) \)
  - \( \text{pE} = -\log (e^-) \)

- \( \text{pE} \) is large and positive in strongly oxidizing solutions and negative in strongly reducing solutions

- Redox potential is strongly influenced by \( H^+ \) ions (i.e., pH), so it is customary to express redox potential corrected to a pH of 7; thus, redox potential is often expressed as \( E_h \) or \( E_7 \)
Global redox - oxidation reactions

- Respiration: \( \text{O}_2 + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{CO}_2 \)
- Oxidation reactions using \( \text{O}_2 \):
  \[
  \begin{align*}
  \text{O}_2 + \text{CH}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
  \text{O}_2 + \text{N}_2 & \rightarrow \text{NO}_3^- + \text{H}_2\text{O} \\
  \text{O}_2 + \text{H}_2\text{S} & \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} \\
  \text{O}_2 + \text{CH}_4 & \rightarrow \text{CO}_2 + \text{H}_2\text{O}
  \end{align*}
  \]
Global redox – reduction reactions

• Photosynthesis: \( H_2O + CO_2 \rightarrow O_2 + CH_2O \)

• Reduction reactions using \( CH_2O \):
  - \( CH_2O + O_2 \rightarrow H_2O + CO_2 \)
  - \( CH_2O + NO_3^- \rightarrow N_2 + CO_2 \)
  - \( CH_2O + SO_4^{2-} \rightarrow H_2S + CO_2 \)
  - \( CH_2O + CO_2 \rightarrow CH_4 + CO_2 \)
Organic matter

• The ratio of C:N:P in seawater (Redfield-Richards ratio) is 106:16:1. Assuming that phytoplankton take up molecules in the same ratio, average molecule of organic matter should be given by:

• $106\text{CO}_2 + 122\text{H}_2\text{O} + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 \rightarrow (\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 138\text{O}_2$
Aerobic decomposition

• The decomposition of POM in the presence of O₂ (respiration) returns C, N and P to their soluble forms:

\[
(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightarrow 106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4
\]
But what happens when we run out of O$_2$?
Anaerobic decomposition

• Nitrates can be used as electron acceptors in the absence of O$_2$:

  \[ (\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 84.8\text{HNO}_3 \rightarrow 106\text{CO}_2 + 148.8\text{H}_2\text{O} + 42.4\text{N}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4 \]

• So can sulfates:

  \[ (\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 53\text{SO}_4^{--} \rightarrow 106\text{CO}_2 + 106\text{H}_2\text{O} + 16\text{NH}_3 + 53\text{S}^{--} + \text{H}_3\text{PO}_4 \]
Layers of sediment redox

Oxidation of organic matter

This sequence also occurs in stratified lakes with anoxic hypolimnia
Sedimentation

• As POM settles on the benthos, it gets decomposed by one of the above processes
• In most areas of the ocean, rate of settlement is not too high and POM is degraded by aerobic processes
• In upwelling areas, rate of settlement is much higher and degradation may be by anaerobic processes
• Thus, marine sediment chemists are quite familiar with these processes
• Animal bioturbation oxygenates sediment
Organic loading

• In immediate area of sewage loading, biodiversity and population biomass are low and DO is low
• With increasing distance, biomass increases, but biodiversity (species richness) remains low
• Further distance increases biodiversity but with decreasing biomass
• Eventually at even further distance, normal benthic faunal assemblages occur & DO is high

Benthic communities

Figure 25. A diagrammatic representation of the sea bottom in the vicinity of a sewage discharge point.
Organic enrichment

- These benthic processes occur in bangus and shrimp ponds, under/around fish cages and high intensity shellfish farms.
- The rate of POM input to the benthos in relation to the ability of the microbes of the benthos to degrade it determines aerobic/anaerobic.
- If anaerobic, worry about outgassing of ammonia, hydrogen sulfide, methane.
New Brunswick salmon farms

- Studies by DFO St. Andrews (Holmer, Hargrave) documented sediment chemistry and benthic community structure to establish database of relationships between the two.
- Farms are inspected annually by a contractor – sediment sampling (among other things considered) done a) under cage, b) at edges of farm, c) 30 m downstream.


Relative monitoring costs

- **Benthic community structure (BCS)**
  - Field – 22 min.
  - Lab – 185 min.

- **Sediment chemistry**
  - Field – 9 min.
  - Lab – 0 min.
## Monitoring rating scale

<table>
<thead>
<tr>
<th>$E_h$ ($mV$)</th>
<th>Sulfides ($\mu$mol)</th>
<th>Degree of effect/BCS</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; -100</td>
<td>&gt;6000</td>
<td>High</td>
<td>Anoxic C</td>
</tr>
<tr>
<td>-100 to 0</td>
<td>1300-6000</td>
<td>Medium</td>
<td>Hypoxic B</td>
</tr>
<tr>
<td>0 to +100</td>
<td>300-1300</td>
<td>Medium</td>
<td>Oxic B</td>
</tr>
<tr>
<td>&gt; +100</td>
<td>&lt;300</td>
<td>Low</td>
<td>Normal A</td>
</tr>
</tbody>
</table>
Conclusion

- Given a sufficient database of relationships between community structure and sediment chemistry, latter can be used to monitor aquaculture farms at great cost savings
Maraming Salamat sa Inyong Lahat