Water as a new matrix for global assessment of hydrophilic POPs

Derek Muir, Rainer Lohmann

With the addition of perfluorooctanesulfonate (PFOS), chlordecone, hexachlorocyclohexane (HCH) isomers and endosulfan to the Stockholm Convention, the chemicals addressed no longer comprise solely hydrophobic organics. Water has become a widely-used environmental matrix for monitoring persistent organic pollutants (POPs), particularly for the chlorinated pesticides, despite challenges related to collecting samples and determining trace levels.

We review sampling and analytical considerations for water sampling of less hydrophobic or hydrophilic POPs to identify and to recommend the best approaches, particularly for assessment of spatial and temporal trends on a global scale.

“Active” and “passive” methods are available for sampling water for hydrophilic POPs, but no single approach can be recommended. We recommend a performance-based approach, in which sampling and quantitative analysis are needed so that future global trends of hydrophilic POPs can be monitored.

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Keywords: Chlordecone; Dieldrin; Endosulfan; Hexachlorocyclohexane (HCH); Lake; Ocean; Passive sampling; Perfluorooctanesulfonate (PFOS); Persistent organic pollutant (POP); Seawater

Abbreviations: AWQC, Ambient water quality criteria; CTD, Characteristic travel distance; Empore disk, Particle-loaded disk within an inert matrix of polytetrafluoroethylene; EQG, Environmental quality guideline; EQS, Environmental quality standard; GMP, Global monitoring plan of the Stockholm convention; Kow, Octanol-water partition coefficient; LC-tandem MS, Liquid chromatography-tandem mass spectrometry; LDPE, Low-density polyethylene plastic; LLE, Liquid–liquid extraction; NOEC, No observable effect concentration; OASIS HLB, Polymeric reversed-phase sorbent; OCP, Organochlorine pesticides; PFASs, Perfluoro-alkyl and polyfluoro-alkyl substance; POCIS, Polar organic chemical integrative sampler; POM, Polyoxymethylene plastic; PRC, Performance reference compound; PUF, Polyurethane foam; QA/QC, Quality assurance/quality control; SPE, Solid-phase extraction; SPMD, Semi-permeable membrane device; TWA, Time-weighted average; WAX, Weak anion-exchange solid-phase cartridge; WBL, Water-boundary layer; XAD, Hydrophobic cross-linked polystyrene copolymer resin

1. Introduction

Water concentrations of persistent organic pollutants (POPs) in large lakes, coastal seas and open oceans reflect a dynamic balance of inputs via rivers and atmospheric deposition, re-release from sediments, and removal pathways (e.g., volatilization and sedimentation) [1,2]. Long-term data on POPs in water thus provide important information that can be used to assess the effectiveness of measures taken to reduce emissions. Concentrations of POPs in surface water are directly linked to their bioaccumulation in the food chain [3,4], so knowing dissolved concentrations in the water enables prediction of concentrations in aquatic species using bioaccumulation factors or lipid-water partitioning and food-web biomagnification models [5].

With the addition of perfluorooctanesulfonate (PFOS) and the somewhat soluble hexachlorocyclohexane (HCH) isomers, chlordecone, and endosulfan, to the Stockholm Convention, POPs can no longer be characterized solely as hydrophobic organics. There is a wide range of solubility with at least seven POPs having water solubilities >0.1 mg/L (Table 1). These seven POPs, with their transformation products, also have lower organic carbon partition coefficients (Koc) and lower octanol-water partition coefficients (Kow) than other POPs (Table 1). Thus, their environmental distribution is likely to be different from the more hydrophobic polychlorinated biphenyls (PCBs), polychlorinated dibenzo-pesticides (PCBs) and polychlorinated dibenzop-p-dioxins and dibenzofurans (PCDD/Fs). Indeed global ocean and large lake waters represent a major sink for PFOS, HCHs and endosulfan and, to a lesser extent, other POPs. Ocean and large lake waters can also represent a source of POP emissions to the atmosphere.
as a result of declining air concentrations and climate change (e.g., reduced ice cover, and increased water temperatures) [6–8].

Awareness is growing that transport via ocean currents may be an important pathway for persistent chemicals to reach polar and other remote regions, especially for the more soluble substances [9,10]. Zarfl et al. [11] showed that characteristic travel distances (CTDs) in water were important for chemicals with long half-life in water and a low air-water partition coefficient ($K_{ow}$). They concluded that PFOS, α-HCH, β-HCH, γ-HCH and chlordecone all have significant mass fractions in water, based on their known or estimated rates of degradation and $K_{ow}$ values. Water and air CTDs for the POPs discussed by Zarfl et al. [11] are compared in Table 2. These CTDs should be compared only in a relative manner and depend on model parameters, as illustrated for γ-HCH where the CTD for water is 72–1646 km, depending mainly on the half-life in water. Water-soluble POPs (e.g., PFOS and chlordecone) have the highest CTDs in water and the greatest water/air CTD ratios. The CTD for PFOS is an underestimate, since its half-lives in all compartments, particularly water and soil, are greater than the 17,000 h used in the model calculation. Indeed, PFOS and perfluorooctanoic acid (PFOA) have been proposed as stable chemical tracers of global circulation of ocean waters [12].

Water has become a widely-used environmental matrix for monitoring POPs, particularly for the chlorinated pesticides, despite challenges related to collecting samples and determining trace levels. The availability of environmental quality standards, expressed in terms of concentrations in water (environmental quality standards (EQSs) [13], Environmental Quality Guidelines (EQGs) [14], Ambient Water Quality Criteria (AWQC) [15]) and peer-reviewed literature on thresholds for effects on aquatic biota (e.g., No observable effect concentration (NOECs)), is a major driver of continuing interest in these measurements as part of risk/exposure assessments [16]. EQSs, and EQGs, which are generally derived from NOECs for chronic or long-term aquatic toxicity tests, by including an assessment factor of 10, are available for some of the most water-soluble POPs (Table 3). These values provide a perspective on the limits of detection (LODs) required for exposure assessment of these POPs.

PFOS, HCH isomers and endosulfan have been determined widely both in freshwater and marine waters, while reports on concentrations of dieldrin, endrin, and chlordecone in surface waters are very limited [17,18].

Sampling programs and selected individual investigations for POPs in water were reported in the UNEP reports on persistent toxic substances [19].

Here, we review the sampling and analytical considerations for water sampling of these less hydrophobic or hydrophilic POPs with the goal of identifying and recommending best approaches. The focus is on the sampling and analytical considerations for performing water sampling for hydrophilic POPs, as the quantitative analysis aspects are similar for all matrices. The assumption is that the information would be useful for the Global Monitoring Plan (GMP) for POPs [20], although, at present, water sampling is recommended in the GMP for only PFOS [21]. Thus, we focus mainly on sampling of water for hydrophilic POPs at background sites on a global scale, rather than near sources of contamination.

2. Sampling considerations

2.1. Procedures and requirements for sampling

A wide range of water-collection methodology has been employed for obtaining samples for POPs analysis, ranging from hand dipping of 1-L bottles to passive sampling and in-situ submersible samplers collecting hundreds of liters. Standard operating procedures for selecting sites, cleaning equipment, and avoiding contamination (e.g., by use of “clean hands/dirty hands” protocols) are available from USGS [22] with a focus on rivers and streams. Another USGS publication by Alvarrez [23] provides practical guidance for passive sampling. The European Commission (EC) [24] and the International Organization for Standardization (ISO) [25] provide guidance for sampling of contaminants in freshwaters. HELCOM [26,27] offers useful advice on marine sampling design, including seawater collection. Sampling procedures for selected studies are summarized in Table 4.

While the collection methodology can be applied both near sources and at far field sites, special consideration needs to be given to identifying collection sites in remote areas. The sampling sites need to be sufficiently remote from urban centers, harbors, industrial wastewater inputs, ocean dumpsites, and other sources of POPs, so as to reflect concentrations typical of a large area around the site. Requirements for selection of water-sampling sites include:

1. ease of access by limnological or oceanographic vessels with capacity to deploy water-sampling equipment;
2. availability of suitable buoys or permanent stations for repeat sampling and deployment of passive samplers;
3. knowledge of site depth and bottom sediment/substrate composition;
4. an existing routine sampling program with water-chemistry data;
5. availability of physical measurements (temperature, pH, and conductivity/salinity), tidal conditions, flow (e.g., outflow from a lake), from which to assess sampling depth (e.g., consideration of vertical gradients (e.g., thermal stratification)).
(6) meteorological observations;
(7) trained personnel to conduct the sampling; and,
(8) availability of suitable laboratory facilities to prepare sampling media and subsequently extract and analyze the samples.

### 2.2. Active systems and solid-phase media

Active sampling refers here to direct collection via various means ranging from hand dipping of sample bottles to in-situ sampler pumps, which all provide a snapshot of prevailing concentrations. Various large-volume

<table>
<thead>
<tr>
<th>Chemical</th>
<th>t_{1/2} air (h)</th>
<th>t_{1/2} water (h)</th>
<th>t_{1/2} soil (h)</th>
<th>CTD Air (km)</th>
<th>CTD Water (km)</th>
<th>CTD ratio (W/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH</td>
<td>91.2</td>
<td>5256</td>
<td>1152</td>
<td>1527</td>
<td>389</td>
<td>0.255</td>
</tr>
<tr>
<td>β-HCH</td>
<td>1344</td>
<td>4320</td>
<td>2184</td>
<td>2903</td>
<td>443</td>
<td>0.153</td>
</tr>
<tr>
<td>γ-HCH</td>
<td>448</td>
<td>17000</td>
<td>9600</td>
<td>2591</td>
<td>1646</td>
<td>0.635</td>
</tr>
<tr>
<td>γ’-HCH</td>
<td>448</td>
<td>17000</td>
<td>9600</td>
<td>2418</td>
<td>175</td>
<td>0.073</td>
</tr>
<tr>
<td>Chlordecone</td>
<td>55.2</td>
<td>720</td>
<td>17520</td>
<td>918</td>
<td>72</td>
<td>0.079</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>31.3</td>
<td>4320</td>
<td>8640</td>
<td>638</td>
<td>194</td>
<td>0.305</td>
</tr>
<tr>
<td>α-endosulfan</td>
<td>31.3</td>
<td>4320</td>
<td>8640</td>
<td>638</td>
<td>194</td>
<td>0.305</td>
</tr>
<tr>
<td>HBB</td>
<td>4368</td>
<td>4320</td>
<td>8640</td>
<td>3617</td>
<td>553</td>
<td>0.531</td>
</tr>
<tr>
<td>BDE-99</td>
<td>264</td>
<td>3600</td>
<td>3600</td>
<td>2708</td>
<td>217</td>
<td>0.080</td>
</tr>
<tr>
<td>PeCB</td>
<td>3720</td>
<td>4656</td>
<td>4656</td>
<td>59562</td>
<td>216</td>
<td>0.004</td>
</tr>
<tr>
<td>PFOS</td>
<td>1830</td>
<td>17000</td>
<td>17000</td>
<td>1220</td>
<td>1717</td>
<td>1.407</td>
</tr>
</tbody>
</table>

1 Properties and half-lives (t_{1/2}) from Zarfl et al. [11] and from EPISuite V4.1 [96].
techniques [e.g., pumping water through solid-phase media (C18 disks or columns, XAD resin, or polyurethane foam)] have been employed for direct extraction of POPs, including HCHs and endosulfan. The water can also be collected by pumping into plastic, glass or stainless-steel vessels or using Van Dorn, Niskin or “Glo-Flo” samplers in limnological and oceanographic sampling. There is potential for wall effects (e.g., contamination and sorption) particularly with small volumes [28,29], but these are less of a problem for hydrophilic POPs. Adsorption losses can be evaluated using spikes of surrogates added to sample containers or to oceanographic bottles once they have been brought to the surface.

Sample collection is typically done sub-surface to avoid contamination from surface microlayers, which can have elevated concentrations of POPs [30,31], and to minimize exposure to boat-motor exhausts and airborne contaminants emanating from ships [23,32].

Direct pumping through a filter into a column holding the solid-phase media has been widely employed in studies of HCH and endosulfan in remote lake and ocean waters (Table 4). There are many variations of this, including use of in-situ samplers, which are programmed to turn on and off under water, and in-line systems bringing seawater directly into cleanrooms on ships [33,34].

Solid-phase extraction (SPE) cartridges have been widely used to extract relatively small volumes (1–5 L) for HCH, endosulfan and other chlorinated pesticides. They also have the advantage of being used in the field with simple, portable, pumping equipment [33] and other media (e.g., divinylbenzene solid-phase disks) have been shown to outperform XAD resins for organochlorine pesticides (OCP) and PCB extractions from filtered water [34].

2.3. Passive sampling

Passive sampling offers an option for widespread monitoring of POPs in water, including the hydrophilic POPs (e.g., HCH isomers, endosulfan, dieldrin, and anionic PFOS) [35] (Table 4). Recent reviews by Harman et al. [36], Alvarez et al. [37] and Booij [38] covered the history and the use of passive samplers in POPs monitoring in the aquatic environment. SPMDs comprising low-density polyethylene (LDPE) tubing filled with triolein were originally developed to determine bioavailable concentrations of hydrophobic organics (log Kow > 5) in water [39,40], and remain widely used for hydrophobic organics. Single-phase polymeric materials [e.g., LDPE strips [41], polyoxyyymethylene (POM) [42,43], and silicone [44–46]] are also used.

Lohmann et al. [47] discussed the use of passive sampling devices for monitoring and compliance checking of POP concentrations in water, highlighting the benefits over alternative matrices applicable in trend monitoring (e.g., sediments or biota). The use of passive samplers enables better control of analytical and natural environmental variance, which, in turn, results in a reduction of the number of analyzed samples required to obtain results with comparable statistical power. Compliance checking with regulatory limits and analysis of temporal and spatial contaminant trends have been suggested as two possible fields of application of passive sampling of POPs [47].

Allan et al. [48] compared several passive devices (including LDPE, silicone and SPMDs) and liquid-liquid extraction (LLE) for several PAHs with similar log Kow to HCHs, dieldrin and endosulfan, and with the more hydrophobic POPs, p,p’-DDE, PCBs and hexachlorobenzene. They used fluoranthene-d10 and chrysene-d12 as performance-reference compounds (PRCs) and noted that amounts of these less hydrophobic PRCs were lost relatively quickly, particularly from LDPE, indicating that analytes with log Kow values in the same range as these PRCs had reached or were close to equilibrium. The major conclusions of the study were: (1) passive samplers provided data that were less variable than that from “whole water” sampling, since the latter may be strongly influenced by levels of suspended particulate matter; (2) LODs were much better with passive samplers, due to high sampling rates and sampler/water partition coefficients; (3) while all passive devices performed well, LDPE samplers were found to be the most reproducible; (4) linear uptake was observed for the more hydrophobic contaminants during exposures of up to one month; (5) despite different modes of calculation, relatively consistent time-weighted average (TWA) concentrations were obtained for the different samplers; and, (6) biofouling induced only minor changes in estimates of TWA concentrations.

Deployment time is an important consideration for passive samplers. There exists a trade-off between longer deployment periods to maximize uptake of POPs while limiting biofouling in the field. During their deployment, passive samplers integrate dissolved concentrations over time, until equilibrium is reached. Time to equilibrium is chemical specific for different sampler types and dependent on the sampler-water partition coefficient values (i.e. sorptive capacities for particular chemicals). Passive samplers can be deployed as equilibrium samplers or in the linear-uptake phase (integrative sampling). For the various POPs, times to reach equilibrium vary dramatically (e.g., between HCHs and DDTs). The long deployment periods that are still adequate for integrative sampling of very hydrophobic compounds (log Kow > 6) (e.g., DDT) will result in equilibrium sampling of less hydrophobic compounds. This means that the sampler might not reflect TWA concentrations of hydrophilic POPs if it is exposed for extended time periods.
For devices that operate in the linear or integrative mode, the sampling rate is given by the product of the overall analyte mass-transfer coefficient and the active surface area of the sampler. Sampling rate may be interpreted as the volume of water cleared of analyte per unit of exposure time (e.g., L/day) by the device and is independent of the analyte concentration in the sampled medium. It can be affected and modulated by the analyte diffusion and partition properties in the media along the diffusional path [water-boundary layer (WBL) and polymers] and is determined in laboratory-calibration studies or via use of PRCs in the field.

Often, the main barrier to mass transfer is the WBL located at the external surface of the sampler. In such a case, the sampling rate is significantly affected by environmental variables (e.g., water temperature, flow rate and biofouling). If laboratory calibration data are to be used for calculation of TWA concentrations, the effect of these variables has to be controlled or quantified. PRCs must be added to help understand if the sampler is approaching equilibrium and the degree to which environmental variables (e.g., temperature, turbulence and biofouling) affect the sampling kinetics [49]. The measurement of PRC dissipation provides information on contaminant-exchange kinetics between water and sampler. Use of multiple PRCs with a range of log Kow makes it possible to establish when kinetics of uptake into the sampler are controlled by the membrane or the WBL.

Equilibrium sampling can be achieved through use of thin membranes, in which POPs display high diffusivities, as often used in contaminated sediments and harbors. After equilibrium has been obtained in the field, dissolved concentrations are simply obtained by dividing the POP concentration in the passive sampler by its passive sampler-water partitioning coefficient, corrected for temperature and salinity, as appropriate for the deployment period [41].

Passive samplers are generally deployed in stainless-steel cages or frames attached to moorings, so that their position in the water column is maintained [23,50]. Deployment at background sites, as envisioned for the GMP for water, is challenging, since permanent moorings are needed. Lohmann and Muir [51] have suggested making use of existing monitoring buoys in key locations in major lakes and seas, and outer coastal areas. The major requirement for a given site is that it should be away from a major point source, and temperature (and salinity, where appropriate) data need to be available for the deployment period.

Polar organic chemical integrative samplers (POCISs) have mainly been used for passive water sampling of compounds with log Kow < 4 (e.g., pharmaceuticals, pesticides and alkyl phenols) [37,52] but hydrophilic POPs, including dieldrin, and lindane, have also been determined [53]. Unlike other passive water samplers, POCIS consists of solid sorbent sandwiched between two microporous polyethersulfone diffusion-limiting membranes. The most widely used absorbent is OASIS HLB (a polymeric reversed-phase sorbent). PFOS was analyzed quantitatively in water using a POCIS modified with a weak anion-exchange (WAX) sorbent as a receiving phase. A seven-day deployment in Sydney harbor yielded concentrations, calculated based on a sampling rate determined in a calibration study, that were within 78% of results in grab water samples from the same site [35]. Thus, modified POCIS samplers may represent an alternative to grab sampling for PFOS and other perfluoroalkyl and polyfluoro-alkyl substance (PFASs). Morin et al. [52] have noted the need for standardized protocols for deployment and QA/QC of POCIS, and validation of calibration procedures (e.g., intercomparison exercises). It is unclear whether POCISs in their current configuration are sufficient to overcome LODs for targeted POPs at background sites.

### 2.4. Sampling for PFOS

PFOS and related PFASs are water soluble and have relatively low Koc values compared to neutral halogenated compounds on the POPs list (Table 2). Thus the

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**Table 3. Summary of water solubility, EQGs, AWQCs, EQSs, and NOECs for the most water-soluble POPs**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>WS<strong>2</strong>(mg/L)</th>
<th>EQG (ng/L) (Canada)</th>
<th>AWQC (ng/L) (USA)<strong>1</strong></th>
<th>EQS (ng/L) (EU)<strong>1</strong></th>
<th>NOEC (ng/L)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH</td>
<td>1.0</td>
<td>50 (Daphnia)</td>
<td>32,000 (Medaka)</td>
<td>20 (all isomers)</td>
<td>2100 (Brook trout)</td>
<td>[97]</td>
</tr>
<tr>
<td>β-HCH</td>
<td>7.3</td>
<td>80</td>
<td>2500 (Daphnia)</td>
<td>5</td>
<td>50 (Rainbow trout)</td>
<td>[100]</td>
</tr>
<tr>
<td>Chlordecone</td>
<td>2.7</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>120 (Rainbow trout)</td>
<td>[101,102]</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>0.5</td>
<td>56</td>
<td>50 (Daphnia)</td>
<td>56</td>
<td>49,000</td>
<td>[103]</td>
</tr>
<tr>
<td>Dieldrin/aldrin</td>
<td>0.17</td>
<td>10</td>
<td>50 (Rainbow trout)</td>
<td>10</td>
<td>120 (Rainbow trout)</td>
<td>[101,102]</td>
</tr>
<tr>
<td>PFOS</td>
<td>680</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**1** EQG = Environmental Quality Guideline; AWQC = Ambient water quality criteria; EQS = Environmental Quality Standard; NOEC = No observable effect concentration.

**2** WS = Water solubility.
Table 4. Summary of selected water-sample collection and extraction techniques for hydrophilic POPs in ocean, large lake and remote lake waters

<table>
<thead>
<tr>
<th>General type</th>
<th>Analytes</th>
<th>Equipment</th>
<th>Extraction methodology</th>
<th>Vol (L)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Active sampling</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake water and glacial melt</td>
<td>HCHs, endosulfan</td>
<td>GF/A filters (0.6 μm)</td>
<td>DCM on water from continuous flow centrifuge</td>
<td>~65</td>
<td>[76]</td>
</tr>
<tr>
<td>In-situ sampling; lake water</td>
<td>HCHs, endosulfan</td>
<td>AXYS “Infiltrex” in situ sampler; submersible pumping system</td>
<td>GFF (1 μm); modified Speedisks divinylbenzene solid-phase extraction device</td>
<td>50</td>
<td>[34,104]</td>
</tr>
<tr>
<td>In-situ sampling; lake water</td>
<td>HCHs, endosulfan</td>
<td>AXYS “Infiltrex” in situ sampler; submersible pumping system</td>
<td>GFF (1 μm) and XAD-2 resin (75 g)</td>
<td>100</td>
<td>[105]</td>
</tr>
<tr>
<td>Pumping from a reservoir;</td>
<td>HCHs</td>
<td>Submersible pump to 20 L stainless-steel cans</td>
<td>GFF (0.7 μm); 200 mg “ENV+”(polystyrene–divinylbenzene (DVB) copolymer) cartridge</td>
<td>4–20</td>
<td>[7,66]</td>
</tr>
<tr>
<td>Ocean, Great Lakes water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea cruise, Mediterranean</td>
<td>α-HCH</td>
<td>Towfish intake to on-board in-line system</td>
<td>Unfiltered; Oasis WAX cartridge</td>
<td>0.5–1</td>
<td>[55]</td>
</tr>
<tr>
<td>Ocean cruise, Arctic, Atlantic</td>
<td>PFOS and PFCAs</td>
<td>Ship intake, in-line sampling</td>
<td>GFF (1.2 μm); Oasis WAX cartridge</td>
<td>2</td>
<td>[54]</td>
</tr>
<tr>
<td>Ocean cruise, Atlantic</td>
<td>PFOS and PFCAs</td>
<td>Ship intake, in-line sampling and rosette-sampler for depth profile</td>
<td>GFF (0.7 μm); Oasis WAX cartridge</td>
<td>1</td>
<td>[106]</td>
</tr>
<tr>
<td>Ocean cruise Pacific, Arctic</td>
<td>PFOS and PFCAs</td>
<td>Stainless-steel bucket</td>
<td>GFF (1.2 μm); Serdolit PAD-3 (DVB styrene) self-packed column</td>
<td>176–1120</td>
<td>[107,108]</td>
</tr>
<tr>
<td>Ocean cruise Pacific, Arctic</td>
<td>HCHs, endosulfan</td>
<td>Ship intake, in-line sampling</td>
<td>GFF (0.45 μm); C18 ENVI 18 SPE cartridge</td>
<td>4</td>
<td>[109]</td>
</tr>
<tr>
<td>Ocean cruise Pacific, Arctic</td>
<td>HCHs, endosulfan</td>
<td>Stainless-steel bucket and Niskin for depth profile</td>
<td>GFF (0.7 μm) and XAD-2 resin</td>
<td>100</td>
<td>[110]</td>
</tr>
<tr>
<td>Estuary and open ocean water</td>
<td>HCHs, endosulfan</td>
<td>AXYS Infiltrex sampler and on-board extraction</td>
<td>GFF (0.7 μm) and XAD-2 resin</td>
<td>720–1250</td>
<td>[73]</td>
</tr>
<tr>
<td>Open ocean water</td>
<td>HCHs</td>
<td>Ship intake, in-line sampling</td>
<td>GFF (0.7 μm) and XAD-2 resin</td>
<td>~100</td>
<td>[111]</td>
</tr>
<tr>
<td>Under ice and open ocean</td>
<td>HCHs</td>
<td>AXYS Infiltrex sampler</td>
<td>Liquid-liquid extraction with hexane</td>
<td>10</td>
<td>[31]</td>
</tr>
<tr>
<td>Ocean – Singapore Strait</td>
<td>HCHs</td>
<td>Pumping system</td>
<td>Hexane</td>
<td>14–90</td>
<td>[51]</td>
</tr>
<tr>
<td><strong>Passive sampling</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Global scale</td>
<td>HCHs</td>
<td>LDPE</td>
<td>Hexane</td>
<td>14–90</td>
<td>[51]</td>
</tr>
<tr>
<td>Plymouth Harbour UK</td>
<td>γ-HCH, dieldrin</td>
<td>Chemcatcher type - C18 Empore disks; Ecoscope – hexane-filled dialysis bag</td>
<td>Empore disk extracted with acetone then 1:1 (v/v) ethylacetate: isoctane</td>
<td>7–14</td>
<td>[53]</td>
</tr>
<tr>
<td>Godthåbsfjord Greenland</td>
<td>HCHs</td>
<td>Polyoxyymethylene</td>
<td>n-hexane extraction</td>
<td>~90</td>
<td>[43]</td>
</tr>
<tr>
<td>Sydney Harbor, AU</td>
<td>PFOS and PFCAs</td>
<td>Modified POCIS - Strata XAW weak-anion exchanger</td>
<td>Methanol extraction</td>
<td>2–7</td>
<td>[35]</td>
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</table>
PFASs are preferentially found in the dissolved phase in surface waters and groundwaters. PFOS and other PFASs are readily detected in all surface waters at pg/L to ng/L. There have already been a large number of surveys of PFOS and other PFASs in rivers and lakes, and measurements in all the major world oceans [12,54,55]. Collection of seawater samples has been done through ship-intake systems [54] and via Niskin bottles [56] into plastic or glass bottles. In lakes and large rivers, direct pumping into sampling bottles [57] and collection from Niskin-type samplers [58,59] and from ship intakes [60] have been used. Sampling procedures used for selected studies are summarized in Table 4.

Samples for PFOS analysis have generally not been filtered prior to extraction. A study of waters in the Elbe River (Germany) and the North Sea indicated that, on average, 14% of PFOS was in the particulate phase [60]. In ocean waters, PFOS was not detectable on particles [54], probably because of the lower amount of suspended particulate material (SPM); thus, filtration is not recommended, unless it can be done with an in-line system or in a cleanroom [60], because it could introduce contamination. Contamination is also introduced from polytetrafluoroethylene (PTFE) materials due to the use of PFOA as a processing aid for PTFE production. Common sources are PTFE tubing, O-rings and other seals. PTFE bottles or bottles with fluorinated interior coatings should therefore be avoided [61].

3. Sampling frequency, spatial scale and time series

Consideration needs to be given on how frequently to sample and the spatial scale of the program, although detailed discussion is beyond the scope of this article. Frequency and scale of sampling are generally dictated by the characteristics of the water body, knowledge of the time dependence of loadings of POPs, and logistical considerations (e.g., ease of access and funding). The ISO water-sampling guidance document [25] provides practical advice for water-quality sampling of natural waters. Ort et al. [62] have critically reviewed sampling of wastewater systems and much of their advice is applicable for river and stream sampling. POP concentrations in lake and ocean waters may vary seasonally due to seasonality in phytoplankton and particulate organic matter [63], and other factors affecting inputs (e.g., precipitation, run-off, and seasonal use of chemicals). Seasonal cycles in water concentrations of POPs have been found in remote ocean waters in the Canadian Archipelago [64,65]. The spatial scale of a water-sampling program also depends on anticipated spatial heterogeneity and the goals of the monitoring program (i.e., whether it is designed to detect differences between global regions or between background and urban/industrial or agriculturally influenced waters) [20,24]. For water, this heterogeneity could occur between near-shore and open waters of lakes and seas, and with depth.

A goal of global monitoring of water for hydrophilic POPs should be the development of statistically powerful time series, where feasible, as has been done for POPs in the atmosphere in some locations [20]. This would allow assessment of the effectiveness of global, regional and national programs to control POPs and support time-trend modeling. A frequently used criterion is the ability to detect a 5% change in concentration after a sampling period of 10 years at a power of 80% [20,27], although this definition has mainly been used for trends of POPs in biota. There are no published time series for hydrophilic POPs in water from background sites, although, as illustrated by the studies cited in Table 4, multiple year sampling is occurring in some regions (e.g., the Great Lakes, the Baltic, the Mediterranean, the Sea of Japan/North Pacific, and the Arctic Ocean).

4. Analytical considerations

4.1. Background contamination

Sorbents (e.g., XAD resin and PUFs) are pre-cleaned by sequential Soxhlet extraction using a combination of polar and non-polar solvents (e.g., acetone: hexane and/or acetonitrile followed by hexane) prior to use in extraction columns. Prepackaged media (e.g., C18 disks and solid-phase cartridges) are conditioned by elution with a polar/non-polar solvent combination in the analytical laboratory or (if conditions permit) in the field prior to use [34,66]. Glass-fiber filters must also be baked (350–450°C) prior to use and stored in a sealed container.

Additional precautions for solid-phase-sampling systems are:

1. field blanks consisting of the same media that are attached temporarily to the pumping system during the sampling period; and,
2. procedural blanks prepared at the same time as the field blanks and held in the laboratory.

Comparison of the field and procedural blanks permits an assessment of contamination during sampling [67]. The same approach is used for passive samplers. Field blanks are exposed to air for the same time as the deployed samplers, allowing comparison with procedural blanks held in the laboratory [41,68].

4.2. Extraction procedures

The elution of reversed-phase or XAD resin water-sampler cartridges generally involves use of a water-miscible solvent (usually methanol or acetone) first to remove water followed by a solvent of intermediate polarity [e.g., dichloromethane (DCM), methyl-1-butyl ether or ethyl acetate]. Combined extracts are then partitioned into hexane [67,69]. Other investigators have directly
extracted media without removing residual water [70] and removed water with a Dean Stark apparatus or by pipette [66].

Solid-phase media (e.g., Speedisks and SPE cartridges) are eluted with medium-polarity solvents (e.g., DCM or ethyl acetate) [34,66], as per manufacturers’ recommendations. Speedisks can be air-dried prior to extraction [71,72]. Residual water in the eluate is also sometimes removed by pipette and the extracts are further dried with sodium sulfate baked at 400–450°C.

Breakthrough of target analytes on XAD or PUF is generally monitored using secondary columns [67,73]. Recovery surrogates (usually mass-labeled standards) are added prior to the extraction step. In addition, some investigators add standards to resin columns prior to deployment [74,75].

LLE of water has been used frequently, especially for OCPs [30,31,76–78] and was compared with XAD and PUF by Gómez-Bellmán et al. [79]. Extraction of seawater with cyclohexane was shown to have equivalent results for PCBs in samples of 300–400 L. More recent studies have come out against LLEs at background sites due to:

1. potential for contamination from laboratory air;
2. difficulty of separating particle and dissolved phase;
3. solvent disposal concerns; and,
4. poor performance compared to solid-phase methods [29,33,80].

However, this is likely to be a problem mainly for hydrophobic POPs (e.g., PCBs and PBDEs) that are, or were, in consumer and industrial products [32]. Most authors report low-background blank contamination for hydrophilic POPs [55,66,73].

LLE, particularly of pre-filtered water [30], may be suitable in certain situations where higher levels of POPs (i.e. ng/L) are anticipated. Another large-volume application uses LLE of water from a continuous-flow centrifuge allowing larger samples to be extracted [81]. Blais et al. [76] determined HCHs and endosulfan in remote alpine lake waters using DCM extraction with this approach. Chlordecone was extracted from water by LLE using 35% ethyl-ether hexane mixture [82].

PFOS and other PFASs were extracted from water with WAX solid-phase cartridges [83,84], which were preconditioned by elution with 0.1% NH₄OH in methanol, and then methanol and (precleaned) water. Sample cartridges were eluted with 25 mM ammonium-acetate buffer (pH 4) and the target analytes then eluted with 0.1% NH₄OH in methanol [83,84]. Water volumes of 0.5–1 L were sufficient for pg/L measurements of PFOS. In general, no further clean-up of extracts for PFOS was required and samples could be submitted for LC-tandem MS analysis.

Single-phase passive samplers (e.g., LDPE, POM and silicone strips) are wiped with a damp paper tissue to remove biofilms and then extracted with pentane [48], hexane [50] or DCM [85]. At this stage, sample extracts may be suitable for GC analysis, although additional clean-up may be required, particularly for PCDD/Fs [50]. Two-phase passive samplers (e.g., SPMDs) are dialyzed with hexane [39]. Residual triolein is removed from the extract through a size-exclusion chromatographic column with DCM as the mobile phase [48,68].

Overall, the analysis of hydrophilic POPs in water has been performed by various technologies. Common to all is the need for careful preparation and analysis of sampling materials to minimize contamination concerns in the laboratory and field. Blank sampling materials need to be included regularly to identify and to correct for artifacts during sampling and analysis.

5. Conclusions

The first chemicals that were targeted by the Stockholm Convention, the so-called “dirty dozen” were all hydrophobic compounds. The recent inclusion of endosulfan, chlordecone, HCHs and PFOS means that there are several water-soluble compounds now subject to global regulation, bans, and phase outs. For the first time, water has been recommended as a sampling medium in the GMP (for PFOS). Setting up a monitoring network for water is more challenging than for air, the current recommended matrix [20], due to analytical requirements and sampling constraints. Location of sampling sites that both reflect background conditions and can be accessed regularly is a key issue. Ideally, this should involve collaboration with oceanographers and meteorologists to make use of existing stations and monitoring networks. Critical components of any water-sampling campaign involve continuous access, contamination concerns, and financial sustainability. If routine sampling is performed by non-specialists, there has to be adequate training to minimize contamination concerns.

For PFOS, snapshot sampling of small volumes of water is possible, but, for other hydrophilic POPs, larger water volumes need to be collected to overcome LODs. In view of the logistical and financial constraints of active sampling, passive sampling is a possible alternative for POPs (e.g., HCHs, endosulfan and chlordecone) and recent developments suggest it may have future application to PFASs. Passive sampling provides TWA concentrations, which are more meaningful for biological exposure and arguably more suitable for trend analysis. However, there are logistical challenges with passive samplers, particularly for deployment offshore in large water bodies. While there have been many inter-laboratory studies on analysis of PFOS and on chlorinated pesticides, including the HCHs, there is a need to compare and to contrast different sampling approaches (active and passive) for hydrophilic POPs, and to agree on best practices.
There is currently a lack of standard reference materials for water analysis, but the use of spiked blanks and inter-laboratory comparisons can help with ensuring QA/QC aspects of water sampling. The choice of sampling technology and analytical methods will probably vary globally, and no single approach can be recommended at this time. A performance-based approach, in which the entire series of steps from sampling through to quantitative analysis is evaluated using intra-laboratory and inter-laboratory comparisons, is needed so that future global trends of hydrophilic POPs can be monitored.

References


