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Water as a new matrix for global assessment of hydrophilic POPs

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Abstract

With the addition of perfluorooctanesulfonate (PFOS), chlordecone, hexachlorocyclohexane (HCH) isomers and endosulfan to the Stockholm Convention, the list of chemicals addressed by the Convention no longer consists solely of hydrophobic organics. 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. Here we review the sampling and analytical considerations for water sampling of POPs in general, and the hydrophilic POPs in particular, with the goal of identifying and recommending best approaches particularly for assessment of spatial and temporal trends on a global scale. Methods are available for both “active” and “passive” sampling of water for hydrophilic POPs, however, no single approach can be recommended at this time. A performance based approach in which the sampling and quantitative analysis is evaluated is needed so that future global trends of hydrophilic POPs can be monitored.

Keywords:
perfluorooctanesulfonate (PFOS), chlordecone, hexachlorocyclohexane (HCH), endosulfan, dieldrin, passive sampling, seawater, oceans, lakes

Abbreviations/glossary
GMP, global monitoring plan of the Stockholm Convention
POCIS, Polar organic chemical integrative sampler;
PRC, Performance and reference compound
QA/QC, quality assurance/quality control
SPE, Solid-phase extraction;
SPMD, Semi-permeable membrane device;
TWA, Time-weighted average
XAD™, hydrophobic crosslinked polystyrene copolymer resin
Empore™ disk, particle loaded disk within an inert matrix of polytetrafluoroethylene
OASIS HLB™, a polymeric reversed-phase sorbent
LDPE, Low-density polyethylene plastic
POM, polyoxymethylene plastic
PFASs, perfluoro- and polyfluoroalkyl substances
PUF, polyurethane foam
LC-tandem MS, liquid chromatography-tandem mass spectrometry
WAX, weak anion exchange solid phase cartridges
Kow, octanol-water partition coefficient
CTD, Characteristic Travel Distance
EQS, Environmental Quality Standard
EQG, Environmental Quality Guideline
AWQC, Ambient Water Quality Criteria
NOEC, No observable effect concentration
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 as well as release from sediments, and removal pathways such as volatilization and sedimentation [1, 2]. Long-term data on POPs in water thus provides 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]; hence 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) as well as the somewhat soluble hexachlorocyclohexane (HCH) isomers, chlordcone, and endosulfan to the Stockholm Convention, POPs can no longer be characterized solely as hydrophobic organics. There is in fact a wide range of solubility with at least 7 POPs having water solubilities > 0.1 mg/L (Table 1). These 7, along 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), polybrominated diphenylethers (PBDEs) and polychlorinated dibenzo-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 for other POPs. Ocean and large lake waters can also represent a source of POPs emissions to the atmosphere as a result of declining air concentrations and climate change e.g. reduced ice cover, 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 (Kaw). They concluded that PFOS, α-, β- and γ-HCH and chlordcone all have significant mass fractions in water based on their known or estimated rates of degradation and Kaw values. Water and air CTDs for the POPs discussed by Zarfl et al. [11] are compared in Table 2. These distances should be compared only in a relative manner and are dependent on model parameterizations as illustrated for γ-HCH where the CTD for water ranges from 72 to 1646 km depending mainly on the half-life in water. Water soluble POPs such as PFOS and chlordcone have the highest CTDs in
water and greatest water/air CTD ratios. The CTD for PFOS is an underestimate since its half-lives in all compartments, particularly in 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 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 more water soluble POPs (Table 3). These values provide a perspective on the detection limits 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 persistent toxic substances reports [19].

Here we review the sampling and analytical considerations for water sampling of the 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 for POPs [20] although, at present, water sampling is recommended in the GMP only for PFOS [21]. Thus we have focused 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 1L bottles, to passive sampling, to 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
Alvarez [23] provides practical guidance for passive sampling. The European Commission [24] and
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 centres, harbours, industrial waste water inputs, and
ocean dumpsites, and other sources of POPs, as to reflect concentrations typical of a large area
around the site. Requirements for water sampling sites selection include:

- ease of access by limnological or oceanographic vessels with capacity to deploy water sampling
equipment
- availability of suitable buoys or permanent stations for repeat sampling and for deployment of
  passive samplers
- knowledge of site depth and bottom sediment/substrate composition
- existence of an existing routine sampling program with water chemistry data
- availability physical measurements (temperature, pH, conductivity/salinity), tidal conditions,
  flow (e.g. outflow from a lake) from which to assess sampling depth e.g. consideration of
  vertical gradients such as thermal stratification
- meteorological observations
- trained personnel to conduct the sampling.
- availability of suitable laboratory facilities to prepare sampling media and subsequently extract
  and analyse 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 techniques such as 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 by use of Van Dorn, Niskin or “Glo-flo” samplers used in limnological and
oceanographic sampling. There is potential for wall effects (contamination, 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 subsurface to avoid contamination from surface
microlayers which can have elevated concentrations of POPs [30, 31] as well as to minimize
exposure to boat motor exhausts and airborne contaminants emanating from ships [23, 32].

Direct pumping thru 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 the use of in situ samplers which are programmed to turn on and
off underwater, and in line systems bringing seawater directly into clean rooms on ships (Table 4).

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 performed in the field with simple portable pumping equipment [33] and other
media such as divinylbenzene solid-phase disks have been shown to outperform XAD resins for
OCP and PCB extractions of filtered water [34].

### 2.3. Passive sampling

Passive sampling offers an alternative for widespread monitoring of POPs in water including the
hydrophilic POPs such as HCH isomers, endosulfan and dieldrin, as well as anionic PFOS [35]
(Table 4). Recent reviews by Harman et al. [36], Alvarez et al. [37] and Booij [38] have covered the
history and use of passive samplers in POPs monitoring in the aquatic environment. SPMDs
consisting of 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, such as LDPE
strips [41], polyoxymethylene (POM)[42] [43], and silicone [44-46] are also used.

Lohmann et al. [47] discuss 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 analysed 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 for several PAHs with similar log Kow to HCHs, dieldrin and endosulfan, as well as with the more hydrophobic POPs, p,p’-DDE, PCBs and hexachlorobenzene. They used fluoranthene-d10 and chrysene-d12 as performance reference compounds (PRC) and noted that amounts of these less hydrophobic PRCs were lost relatively quickly, particularly from LDPE. This 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 was less variable than that from “whole water” sampling since the latter may be strongly influenced by levels of suspended particulate matter.
2. Detection limits 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.

The period of time of deployment 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 either be deployed as equilibrium samplers or in the linear uptake phase (integrative sampling). For the various POPs, times to reach equilibrium will vary dramatically between e.g., the HCHs and DDTs. The long deployment periods that are still adequate for integrative sampling of very hydrophobic compounds (log $K_{ow} > 6$) such as 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$^{-1}$) 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 and polymers), and is determined in
laboratory calibration studies or via the use of PRCs in the field.

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

Equilibrium sampling can be achieved through the use of thin membranes, in which POPs
display high diffusivities, as often used in contaminated sediments and harbours. 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, as well as in 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 (POCIS) have mainly been used for passive water sampling of compounds with log Kow < 4 such as pharmaceuticals, pesticides and alkyl phenols [37, 52] but hydrophilic POPs including dieldrin, and lindane have also been determined, e.g. [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 analysed quantitatively in water using a POCIS modified with a weak anion exchange sorbent as a receiving phase. A 7 day deployment in Sydney harbour 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 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 POCIS in their current configuration are sufficient to overcome detection limits for targeted POPs at background sites.

2.4. Sampling for PFOS
PFOS and related perfluoro- and polyfluoroalkyl substances (PFASs) are water soluble and have relatively low Koc values compared to neutral halogenated compounds on the POPs list (Table 2). Thus the PFASs are preferentially found in the dissolved phase in surface and ground waters. 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 as well as 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] has 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] likely because of the lower suspended particulate material (SPM); thus filtration is not recommended, unless it can be done with an inline system or in a clean room [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].

2. 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 is generally dictated by the characteristics of the water body, knowledge of the time dependence of loadings of POPs, and logistical considerations such as 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. POPs concentrations in lake and ocean waters may vary seasonally due to seasonality in phytoplankton and particulate organic matter [63], and other factors affecting inputs such as precipitation, runoff, seasonal chemical use, etc. 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 is also dependent 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 as well as 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 as well as support time trend modelling. An often used criterion is the ability to detection 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. To our knowledge 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 such as 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 such as 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 acetone followed by hexane) prior to use in extraction columns. Prepackaged media such as C18 disks and solid phase cartridges are conditioned by elution with a polar and 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 (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 the use of a water-miscible solvent (usually methanol or acetone) first to remove water followed by a solvent of intermediate polarity such as dichloromethane (DCM), methyl t-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 such as Speedisks and SPE cartridges are eluted with medium polarity solvents such as DCM or ethyl acetate [34, 66] as per manufacturer’s 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 that had been 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].

Liquid-liquid extraction of water has been used frequently, especially for OCPs [30, 31, 76-78] and was compared with XAD and PUF by Gómez-Bellnchón 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 liquid-liquid extractions at background sites due to potential for contamination from laboratory air, difficulty of separating particle and dissolved phase, solvent disposal concerns, and poor performance compared to solid phase methods [29, 33, 80]. However, this likely to be a problem mainly for hydrophobic POPs such as PCBs and PBDEs that are, or were, in consumer and industrial products (e.g., [32]). Most authors report low background blank contamination for hydrophilic POPs, e.g. [55, 66, 73].

Liquid-liquid extraction, 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 liquid:liquid extraction 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 liquid:liquid extraction using 35% ethyl-ether hexane mixture [82].

PFOS and other PFASs are extracted from water with weak anion exchange (WAX) solid phase cartridges [83, 84]. The cartridges are preconditioned by elution with 0.1% NH$_4$OH in methanol, and then methanol and (precleaned) water. Sample cartridges are eluted with 25mM ammonium acetate buffer (pH 4) and the target analytes then eluted with 0.1% NH$_4$OH in methanol [83, 84]. Water volumes of 0.5-1L are sufficient for pg/L measurements of PFOS. In general no further cleanup of extracts for PFOS is required and samples can be submitted for LC-tandem MS analysis.

Single phase passive samplers such as 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 cleanup may be required particularly for PCDD/Fs [50]. Two phase passives such as SPMDs are dialysed 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 the 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 needs to be included regularly to identify and 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/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, adequate training has to be performed to minimize contamination concerns.

For PFOS, snapshot sampling of small water volumes is possible, but for other hydrophilic POPs, larger water volumes need to be collected to achieve adequate detection limits. In view of the logistical and financial constraints of active sampling, passive sampling is a possible alternative for POPs such as HCHs, endosulfan, 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 passives particularly for deployment offshore in large water bodies. While there been many interlaboratory studies on analysis of PFOS and on chlorinated pesticides including the HCHs, there is a need to compare and contrast different sampling approaches (active, passive) for hydrophilic POPs, and 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 likely 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 quantitative analysis is evaluated using intra- and inter-laboratory comparisons is needed so that future global trends of hydrophilic POPs can be monitored.

6. References


[71] US EPA, Method 527 determination of selected pesticides and flame retardants in drinking water by solid phase extraction and capillary column gas chromatography/mass


Table 1. Water solubility, octanol-water, and organic carbon partitioning coefficients of selected individual components or transformation products of POPs

<table>
<thead>
<tr>
<th>Listed Chemical</th>
<th>Representative Analyte in water</th>
<th>Water solubility$^1$ (mg/L) at 25°C</th>
<th>Log Kow</th>
<th>Log Koc$^2$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorooctane sulfonate</td>
<td>PFOS</td>
<td>680</td>
<td>-</td>
<td>2.6</td>
<td>[86, 87]</td>
</tr>
<tr>
<td>Hexachlorocyclohexane, gamma isomer</td>
<td>γ-HCH</td>
<td>7.3</td>
<td>3.7</td>
<td>3.0</td>
<td>[88]</td>
</tr>
<tr>
<td>Chlordane</td>
<td>Chlordane</td>
<td>2.7</td>
<td>4.5</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Hexachlorocyclohexane, alpha isomer</td>
<td>α-HCH</td>
<td>1.0</td>
<td>3.8</td>
<td>3.8</td>
<td>[88]</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>PeCBz</td>
<td>0.55</td>
<td>5.2</td>
<td>4.5</td>
<td>[88]</td>
</tr>
<tr>
<td>Endosulfan, alpha isomer</td>
<td>α-Endosulfan</td>
<td>0.50</td>
<td>4.9</td>
<td>3.6</td>
<td>[89] [90]</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>Heptachlor epoxide</td>
<td>0.35</td>
<td>5.0</td>
<td>4.0</td>
<td>[88]</td>
</tr>
<tr>
<td>Endrin</td>
<td>Endrin</td>
<td>0.23</td>
<td>5.2</td>
<td>4.0</td>
<td>[88]</td>
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<td>Endosulfan transformation product</td>
<td>Endosulfan sulfate</td>
<td>0.22</td>
<td>3.6</td>
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<td>[89] [90]</td>
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<td>Dieldrin</td>
<td>Dieldrin</td>
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<td>5.2</td>
<td>4.1</td>
<td>[88]</td>
</tr>
<tr>
<td>PCB congener</td>
<td>PCB 28</td>
<td>0.16</td>
<td>5.8</td>
<td>5.3</td>
<td>[88]</td>
</tr>
<tr>
<td>Chlordane, cis isomer</td>
<td>cis-(α)chlordane</td>
<td>0.056</td>
<td>6.0</td>
<td>5.5</td>
<td>[88]</td>
</tr>
<tr>
<td>DDT transformation product</td>
<td>4,4’-DDE</td>
<td>0.04</td>
<td>5.7</td>
<td>5.0</td>
<td>[88]</td>
</tr>
<tr>
<td>PCB isomer</td>
<td>PCB 52</td>
<td>0.03</td>
<td>6.1</td>
<td>5.6</td>
<td>[88]</td>
</tr>
<tr>
<td>Aldrin</td>
<td>Aldrin/dieldrin</td>
<td>0.02</td>
<td>3.0</td>
<td>2.6</td>
<td>[88]</td>
</tr>
<tr>
<td>Toxaphene congener</td>
<td>P26</td>
<td>-</td>
<td>5.5</td>
<td>5.0</td>
<td>[91]</td>
</tr>
<tr>
<td>Toxaphene congener</td>
<td>P50</td>
<td>-</td>
<td>5.8</td>
<td>5.3</td>
<td>[91]</td>
</tr>
<tr>
<td>Hexabromobiphenyl congener</td>
<td>HBB 153</td>
<td>0.011</td>
<td>6.4</td>
<td>5.9</td>
<td>[92]</td>
</tr>
<tr>
<td>Pentabromo diphenyl ethers</td>
<td>BDE 47</td>
<td>0.011</td>
<td>6.8</td>
<td>6.3</td>
<td>[93] [94]</td>
</tr>
<tr>
<td>PCB isomer</td>
<td>PCB 101</td>
<td>0.01</td>
<td>6.4</td>
<td>5.9</td>
<td>[88]</td>
</tr>
<tr>
<td>DDT isomer</td>
<td>4,4’-DDT</td>
<td>0.0055</td>
<td>6.2</td>
<td>5.4</td>
<td>[88]</td>
</tr>
<tr>
<td>HCB</td>
<td>HCB</td>
<td>0.005</td>
<td>5.5</td>
<td>5.0</td>
<td>[88]</td>
</tr>
<tr>
<td>PBDE isomer</td>
<td>BDE 99</td>
<td>0.0024</td>
<td>7.3</td>
<td>6.8</td>
<td>[93] [94]</td>
</tr>
<tr>
<td>PCB isomer</td>
<td>PCB 153</td>
<td>0.001</td>
<td>6.9</td>
<td>6.4</td>
<td>[88]</td>
</tr>
<tr>
<td>Polychlorinated dibenzofurans isomer</td>
<td>2,3,7,8-TCDF</td>
<td>0.000419</td>
<td>6.5</td>
<td>6.0</td>
<td>[88]</td>
</tr>
<tr>
<td>Mirex</td>
<td>Mirex</td>
<td>0.000065</td>
<td>6.9</td>
<td>6.0</td>
<td>[88]</td>
</tr>
<tr>
<td>Polychlorinated dibenzo-p-dioxin isomer</td>
<td>2,3,7,8-TCDD</td>
<td>0.0000193</td>
<td>6.8</td>
<td>6.3</td>
<td>[88]</td>
</tr>
<tr>
<td>Heptabromo BDE congener</td>
<td>BDE 183</td>
<td>-</td>
<td>8.3</td>
<td>7.8</td>
<td>[94]</td>
</tr>
</tbody>
</table>

$^1$Water solubility of the solid and reported in mg/L

$^2$Koc estimated from Seth et al. [95]
Table 2. Characteristic Travel Distances (CTD) in water for selected POPs using the OECD LRTAP tool\(^1\)

<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>(\alpha)-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>(\beta)-HCH</td>
<td>1344</td>
<td>4320</td>
<td>2184</td>
<td>2903</td>
<td>443</td>
<td>0.153</td>
</tr>
<tr>
<td>(\gamma)-HCH</td>
<td>448</td>
<td>17000</td>
<td>9600</td>
<td>2591</td>
<td>1646</td>
<td>0.635</td>
</tr>
<tr>
<td>(\gamma)-HCH</td>
<td>448</td>
<td>1700</td>
<td>9600</td>
<td>2418</td>
<td>175</td>
<td>0.073</td>
</tr>
<tr>
<td>(\gamma)-HCH</td>
<td>55.2</td>
<td>720</td>
<td>17520</td>
<td>918</td>
<td>72</td>
<td>0.079</td>
</tr>
<tr>
<td>Chlordecone</td>
<td>10000</td>
<td>4320</td>
<td>8640</td>
<td>396</td>
<td>444</td>
<td>1.121</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>27.8</td>
<td>4320</td>
<td>8640</td>
<td>542</td>
<td>295</td>
<td>0.543</td>
</tr>
<tr>
<td>(\alpha)-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>3669</td>
<td>353</td>
<td>0.096</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]
Table 3. Summary of EQSs, EQGs, AWQCs, and NOECs for the more water soluble POPs

<table>
<thead>
<tr>
<th>Chemical</th>
<th>WS (mg/L)</th>
<th>EQG (Canada) ng/L</th>
<th>AWQC (USA) ng/L</th>
<th>EQS (EU) ng/L</th>
<th>NOEC ng/L</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td>50 (Daphnia)</td>
<td>[97]</td>
</tr>
<tr>
<td>β-HCH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>32000 (Medaka)</td>
<td>[97]</td>
</tr>
<tr>
<td>γ-HCH</td>
<td>7.3</td>
<td>10</td>
<td>80</td>
<td>20 (all isomers)</td>
<td>2100 (Brook trout)</td>
<td>[98]; [99]</td>
</tr>
<tr>
<td>Chlordecone</td>
<td>2.7</td>
<td></td>
<td></td>
<td></td>
<td>2500 (Daphnia)</td>
<td>[100]</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>0.5</td>
<td>3</td>
<td>56</td>
<td>5</td>
<td>50 (Rainbow trout)</td>
<td>[101]; [102]</td>
</tr>
<tr>
<td>Dieldrin/aldrin</td>
<td>0.17</td>
<td></td>
<td>56</td>
<td>10</td>
<td>120 (Rainbow trout)</td>
<td>[17]; [99]</td>
</tr>
<tr>
<td>PFOS</td>
<td>680</td>
<td>49000</td>
<td></td>
<td></td>
<td>49000</td>
<td>[103]</td>
</tr>
</tbody>
</table>

EQSs = Environmental Quality Standards, EQGs = Environmental Quality Guidelines; AWQCs = ambient water quality criteria, NOECs = no observable effect concentrations
WS = water solubility
For protection of freshwater aquatic life – chronic effects [15]
Inland surface waters. From Borchers [99]
<table>
<thead>
<tr>
<th>General type</th>
<th>Analytes</th>
<th>Equipment</th>
<th>Extraction Methodology</th>
<th>Vol (L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Active sampling”</td>
<td>HCHs, endosulfan</td>
<td>GF/A filters (0.6 um)</td>
<td>DCM on water from continuous flow centrifuge</td>
<td>~65</td>
<td>[76]</td>
</tr>
<tr>
<td>“Active sampling”</td>
<td>HCHs, endosulfan</td>
<td>AXYS “Infiltrex” in situ sampler; submersible pumping system</td>
<td>GFF (1 um); modified “Speedisks” divinylbenzene solid-phase extraction device</td>
<td>50</td>
<td>[34]; [104]</td>
</tr>
<tr>
<td>“Active sampling”</td>
<td>HCHs, endosulfan</td>
<td>AXYS “Infiltrex” in situ sampler; submersible pumping system</td>
<td>GFF (1 um) and XAD-2 resin (75 g)</td>
<td>100</td>
<td>[105]</td>
</tr>
<tr>
<td>Pumping from a reservoir; ocean water, Great Lakes water Sea cruise, Mediterranean Ocean cruises, Arctic, Atlantic</td>
<td>HCHs</td>
<td>Submersible pump to 20 L stainless steel cans</td>
<td></td>
<td>4-20</td>
<td>[7, 66]</td>
</tr>
<tr>
<td>Ocean cruise, Atlantic</td>
<td>α-HCH</td>
<td>Towfish intake to on board inline system</td>
<td>Unfiltered; Oasis WAX cartridge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ocean cruise, Atlantic</td>
<td>PFOS and PFCAs</td>
<td>Ship intake, in line sampling</td>
<td>GFF (1.2 um); Oasis WAX cartridge</td>
<td>2</td>
<td>[54]</td>
</tr>
<tr>
<td>Ocean cruise, Pacific, Arctic</td>
<td>PFOS and PFCAs</td>
<td>Ship intake, in line sampling and rosette-sampler for depth profile</td>
<td>GFF (0.7 um); Oasis WAX cartridge</td>
<td>1</td>
<td>[106]</td>
</tr>
<tr>
<td>Ocean cruise, Pacific, Arctic</td>
<td>HCHs, endosulfan</td>
<td>Stainless steel bucket</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ocean cruise, Pacific, Arctic</td>
<td>HCHs, endosulfan</td>
<td>Ship intake, in line sampling</td>
<td>GFF (1.2 um); 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>Stainless steel bucket and Niskin for depth profile</td>
<td>GFF (0.45 µm); C18 ENVI 18 SPE cartridge</td>
<td>4</td>
<td>[109]</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 um) and XAD-2 resin</td>
<td>100</td>
<td>[110]</td>
</tr>
<tr>
<td>Open ocean water</td>
<td>HCHs</td>
<td>Ship intake, in line sampling</td>
<td>GFF (0.7 um) and XAD-2 resin</td>
<td>720–1250</td>
<td>[73]</td>
</tr>
<tr>
<td>Under ice and open ocean water</td>
<td>HCHs</td>
<td>AXYS “Infiltrex” sampler</td>
<td>GFF (0.7 um) and XAD-2 resin</td>
<td>~100</td>
<td>[111]</td>
</tr>
<tr>
<td>Ocean – Singapore Strait</td>
<td>HCHs</td>
<td>Pumping system</td>
<td>Liquid-liquid extraction with hexane</td>
<td>10</td>
<td>[31]</td>
</tr>
<tr>
<td>“Passive sampling”</td>
<td>Media</td>
<td>Extraction system</td>
<td>Deployment (d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Global scale</td>
<td>HCHs, endosulfan</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: isooctane n-hexane extraction</td>
<td>7-14</td>
<td>[53]</td>
</tr>
<tr>
<td>Godthåbsfjord,</td>
<td>HCHs</td>
<td>Polyoxymethylene</td>
<td></td>
<td>~90</td>
<td>[43]</td>
</tr>
<tr>
<td>Location</td>
<td>PFOS and PFCAs</td>
<td>Methodology</td>
<td>Range</td>
<td>Reference</td>
<td></td>
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<td>-------------------</td>
<td>----------------</td>
<td>--------------------------------------</td>
<td>-------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>Greenland</td>
<td></td>
<td>Modified POCIS - Strata XAW weak anion exchanger</td>
<td>2-7</td>
<td>[35]</td>
<td></td>
</tr>
</tbody>
</table>

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