

# 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

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## 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 bio-magnification 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 (K<sub>oc</sub>) and lower octanol-water partition coefficients (K<sub>ow</sub>) 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, other POPs. Ocean and large lake waters can also represent a source of POP emissions to the atmosphere

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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 ( $K_{aw}$ ). They concluded that PFOS,  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH and chlordecone all have significant mass fractions in water, based on their known or estimated rates of degradation and  $K_{aw}$  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  $\gamma$ -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 Alvarez [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)];

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