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Water as a New Matrix for Global Assessment of Hydrophilic POPs

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1 **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
- XADTM, hydrophobic crosslinked polystyrene copolymer resin
- EmporeTM disk, particle loaded disk within an inert matrix of polytetrafluoroethylene
- OASIS HLBTM, 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

65 NOEC, No observable effect concentration

66

67 **1. Introduction**

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

76 With the addition of perfluorooctanesulfonate (PFOS) as well as the somewhat soluble
77 hexachlorocyclohexane (HCH) isomers, chlordecone, and endosulfan to the Stockholm Convention,
78 POPs can no longer be characterized solely as hydrophobic organics. There is in fact a wide range
79 of solubility with at least 7 POPs having water solubilities > 0.1 mg/L (Table 1). These 7, along
80 with their transformation products, also have lower organic carbon partition coefficients (K_{oc}) and
81 lower octanol-water partition coefficients (K_{ow}) than other POPs (Table 1). Thus their
82 environmental distribution is likely to be different from the more hydrophobic polychlorinated
83 biphenyls (PCBs), polybrominated diphenylethers (PBDEs) and polychlorinated dibenzo-p-dioxins
84 and dibenzofurans (PCDD/Fs). Indeed global ocean and large lake waters represent a major sink for
85 PFOS, HCHs and endosulfan and to a lesser extent for other POPs. Ocean and large lake waters can
86 also represent a source of POPs emissions to the atmosphere as a result of declining air
87 concentrations and climate change e.g. reduced ice cover, increased water temperatures [6-8].

88 Awareness is growing that transport via ocean currents may be an important pathway for
89 persistent chemicals to reach polar and other remote regions, especially for the more soluble
90 substances [9, 10]. Zarfl et al. [11] showed that Characteristic Travel Distances (CTDs) in water
91 were important for chemicals with long half-life in water and a low air-water partition coefficient
92 (K_{aw}). They concluded that PFOS, α -, β - and γ -HCH and chlordecone all have significant mass
93 fractions in water based on their known or estimated rates of degradation and K_{aw} values. Water and
94 air CTDs for the POPs discussed by Zarfl et al. [11] are compared in Table 2. These distances
95 should be compared only in a relative manner and are dependent on model parameterizations as
96 illustrated for γ -HCH where the CTD for water ranges from 72 to 1646 km depending mainly on the
97 half-life in water. Water soluble POPs such as PFOS and chlordecone have the highest CTDs in

98 water and greatest water/air CTD ratios. The CTD for PFOS is an underestimate since its half-lives
99 in all compartments, particularly in water and soil are greater than the 17,000 h used in the model
100 calculation. Indeed, PFOS and perfluorooctanoic acid (PFOA) have been proposed as stable
101 chemical tracers of global circulation of ocean waters [12].

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

112 PFOS, HCH isomers and endosulfan have been determined widely both in freshwater and
113 marine waters while reports on concentrations of dieldrin, endrin, and chlordecone in surface waters
114 are very limited [17, 18]. Sampling programs and selected individual investigations for POPs in
115 water were reported in the UNEP persistent toxic substances reports [19].

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

124

125 **2. Sampling considerations**

126 **2.1. Procedures and requirements for sampling**

127 A wide range of water collection methodology has been employed for obtaining samples for POPs
128 analysis, ranging from hand dipping of 1L bottles, to passive sampling, to *in situ* submersible

129 samplers collecting hundreds of liters. Standard operating procedures for selecting sites, cleaning
130 equipment, and avoiding contamination, e.g. by use of “clean hands/dirty hands” protocols are
131 available from USGS [22] with a focus on rivers and streams. Another USGS publication by
132 Alvarez [23] provides practical guidance for passive sampling. The European Commission [24] and
133 ISO [25] provide guidance for sampling of contaminants in freshwaters. HELCOM [26, 27] offers
134 useful advice on marine sampling design including seawater collection. Sampling procedures for
135 selected studies are summarized in Table 4.

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

- 141 • ease of access by limnological or oceanographic vessels with capacity to deploy water sampling
142 equipment
- 143 • availability of suitable buoys or permanent stations for repeat sampling and for deployment of
144 passive samplers
- 145 • knowledge of site depth and bottom sediment/substrate composition
- 146 • existence of an existing routine sampling program with water chemistry data
- 147 • availability physical measurements (temperature, pH, conductivity/salinity), tidal conditions,
148 flow (e.g. outflow from a lake) from which to assess sampling depth e.g. consideration of
149 vertical gradients such as thermal stratification
- 150 • meteorological observations
- 151 • trained personnel to conduct the sampling.
- 152 • availability of suitable laboratory facilities to prepare sampling media and subsequently extract
153 and analyse the samples

154

155 **2.2. Active systems and Solid phase media**

156 “Active” sampling refers here to direct collection via various means ranging from hand dipping of
157 sample bottles to *in situ* sampler pumps which all provide a snapshot of prevailing concentrations.
158 Various large volume techniques such as pumping water through solid phase media (C18 disks or
159 columns, XAD resin, or polyurethane foam) have been employed for direct extraction of POPs
160 including HCHs and endosulfan. The water can also be collected by pumping into plastic, glass or

161 stainless steel vessels or by use of Van Dorn, Niskin or “Glo-flo” samplers used in limnological and
162 oceanographic sampling. There is potential for wall effects (contamination, sorption) particularly
163 with small volumes [28, 29] but these are less of a problem for hydrophilic POPs. Adsorption losses
164 can be evaluated using spikes of surrogates added to sample containers or to oceanographic bottles
165 once they have been brought to the surface.

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

169 Direct pumping thru a filter into a column holding the solid phase media has been widely
170 employed in studies of HCH and endosulfan in remote lake and ocean waters (Table 4). There are
171 many variations of this including the use of *in situ* samplers which are programmed to turn on and
172 off underwater, and in line systems bringing seawater directly into clean rooms on ships (Table 4).

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

178

179 **2.3. Passive sampling**

180 Passive sampling offers an alternative for widespread monitoring of POPs in water including the
181 hydrophilic POPs such as HCH isomers, endosulfan and dieldrin, as well as anionic PFOS [35]
182 (Table 4). Recent reviews by Harman et al. [36], Alvarez et al. [37] and Booij [38] have covered the
183 history and use of passive samplers in POPs monitoring in the aquatic environment. SPMDs
184 consisting of low density polyethylene (LDPE) tubing filled with triolein were originally developed
185 to determine bioavailable concentrations of hydrophobic organics ($\log K_{ow} > 5$) in water [39, 40],
186 and remain widely used for hydrophobic organics. Single-phase polymeric materials, such as LDPE
187 strips [41], polyoxymethylene (POM)[42] [43], and silicone [44-46] are also used.

188 Lohmann et al. [47] discuss the use of passive sampling devices for monitoring and
189 compliance checking of POP concentrations in water, highlighting the benefits over alternative
190 matrices applicable in trend monitoring (e.g. sediments or biota). The use of passive samplers
191 enables better control of analytical and natural environmental variance, which in turn results in a
192 reduction of the number of analysed samples required to obtain results with comparable statistical

193 power. Compliance checking with regulatory limits and analysis of temporal and spatial
194 contaminant trends have been suggested as two possible fields of application of passive sampling of
195 POPs [47].

196 Allan et al. [48] compared several passive devices (including LDPE, silicone and SPMDs) and
197 liquid-liquid extraction for several PAHs with similar log K_{ow} to HCHs, dieldrin and endosulfan,
198 as well as with the more hydrophobic POPs, *p,p'*-DDE, PCBs and hexachlorobenzene. They used
199 fluoranthene-d10 and chrysene-d12 as performance reference compounds (PRC) and noted that
200 amounts of these less hydrophobic PRCs were lost relatively quickly, particularly from LDPE. This
201 indicating that analytes with log K_{ow} values in the same range as these PRCs had reached or were
202 close to equilibrium. The major conclusions of the study were:

- 203 1. Passive samplers provided data that was less variable than that from “whole water” sampling
204 since the latter may be strongly influenced by levels of suspended particulate matter.
- 205 2. Detection limits were much better with passive samplers due to high sampling rates and
206 sampler/water partition coefficients.
- 207 3. While all passive devices performed well, LDPE samplers were found to be the most
208 reproducible.
- 209 4. Linear uptake was observed for the more hydrophobic contaminants during exposures of up
210 to one month
- 211 5. Despite different modes of calculation, relatively consistent time-weighted average (TWA)
212 concentrations were obtained for the different samplers; and
- 213 6. Biofouling induced only minor changes in estimates of TWA concentrations.

214 The period of time of deployment is an important consideration for passive samplers. There
215 exists a trade-off between longer deployment periods to maximize uptake of POPs while limiting
216 biofouling in the field. During their deployment, passive samplers integrate dissolved
217 concentrations over time, until equilibrium is reached. Time to equilibrium is chemical-specific for
218 different sampler types and dependent on the sampler-water partition coefficient values, i.e. sorptive
219 capacities for particular chemicals. Passive samplers can either be deployed as equilibrium samplers
220 or in the linear uptake phase (integrative sampling). For the various POPs, times to reach
221 equilibrium will vary dramatically between e.g., the HCHs and DDTs. The long deployment periods
222 that are still adequate for integrative sampling of very hydrophobic compounds ($\log K_{ow} > 6$) such
223 as DDT will result in equilibrium sampling of less hydrophobic compounds. This means that the

224 sampler might not reflect TWA concentrations of hydrophilic POPs if it is exposed for extended
225 time periods.

226 For devices that operate in the linear or integrative mode, the sampling rate is given by the
227 product of the overall analyte mass transfer coefficient and the active surface area of the sampler.
228 Sampling rate may be interpreted as the volume of water cleared of analyte per unit of exposure
229 time (e.g. L day⁻¹) by the device and is independent of the analyte concentration in the sampled
230 medium. It can be affected and modulated by the analyte diffusion and partition properties in the
231 media along the diffusional path (water boundary layer and polymers), and is determined in
232 laboratory calibration studies or via the use of PRCs in the field.

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

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

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

255 Polar Organic Chemical Integrative Samplers (POCIS) have mainly been used for passive water
256 sampling of compounds with log Kow <4 such a pharmaceuticals, pesticides and alkyl phenols [37,
257 52] but hydrophilic POPs including dieldrin, and lindane have also been determined, e.g. [53].
258 Unlike other passive water samplers, POCIS consists of solid sorbent sandwiched between two
259 microporous polyethersulfone diffusion-limiting membranes. The most widely used absorbent is
260 OASIS HLB (a polymeric reversed-phase sorbent). PFOS was analysed quantitatively in water using
261 a POCIS modified with a weak anion exchange sorbent as a receiving phase. A 7 day deployment in
262 Sydney harbour yielded concentrations, calculated based on a sampling rate determined in a
263 calibration study, that were within 78% of results in grab water samples from the same site [35].
264 Thus modified POCIS samplers may represent an alternative to grab sampling for PFOS and other
265 PFASs. Morin et al. [52] have noted the need for standardized protocols for deployment and
266 QA/QC of POCIS, and validation of calibration procedures (e.g., intercomparison exercises). It is
267 unclear whether POCIS in their current configuration are sufficient to overcome detection limits for
268 targeted POPs at background sites.

269

270 **2.4. Sampling for PFOS**

271 PFOS and related perfluoro- and polyfluoroalkyl substances (PFASs) are water soluble and have
272 relatively low Koc values compared to neutral halogenated compounds on the POPs list (Table 2).
273 Thus the PFASs are preferentially found in the dissolved phase in surface and ground waters. PFOS
274 and other PFASs are readily detected in all surface waters at pg/L to ng/L. There have already been
275 a large number of surveys of PFOS and other PFASs in rivers and lakes as well as measurements in
276 all the major world oceans [12, 54, 55]. Collection of seawater samples has been done through ship
277 intake systems [54] and via Niskin bottles [56] into plastic or glass bottles. In lakes and large
278 rivers, direct pumping into sampling bottles [57] and collection from Niskin type samplers [58, 59]
279 and from ship intakes [60] has been used. Sampling procedures used for selected studies are
280 summarized in Table 4.

281 Samples for PFOS analysis have generally not been filtered prior to extraction. A study of
282 waters in the Elbe River (Germany) and the North Sea indicated that on average 14% of PFOS was
283 in the particulate phase [60]. In ocean waters PFOS was not detectable on particles [54] likely
284 because of the lower suspended particulate material (SPM); thus filtration is not recommended,
285 unless it can be done with an inline system or in a clean room [60] because it could introduce
286 contamination. Contamination is also introduced from polytetrafluoroethylene (PTFE) materials due

287 to the use of PFOA as a processing aid for PTFE production. Common sources are PTFE tubing, o-
288 rings and other seals. PTFE bottles or bottles with fluorinated interior coatings should therefore be
289 avoided [61].

290

291 **2. Sampling frequency, spatial scale and time series**

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

307 A goal of global monitoring of water for hydrophilic POPs should be the development of statistically
308 powerful time series, where feasible, as has been done for POPs in the atmosphere in some locations [20].
309 This would allow assessment of the effectiveness of global, regional and national programs to control POPs
310 as well as support time trend modelling. An often used criterion is the ability to detection a 5% change in
311 concentration after a sampling period of 10 years at a power of 80% [20, 27] although this definition has
312 mainly been used for trends of POPs in biota. To our knowledge there are no published time series for
313 hydrophilic POPs in water from background sites although, as illustrated by the studies cited in Table 4,
314 multiple year sampling is occurring in some regions such as the Great Lakes, the Baltic, the Mediterranean,
315 the Sea of Japan/North Pacific, and the Arctic Ocean.

316

317 **4. Analytical considerations**

318 **4.1. Background contamination**

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

325 Additional precautions for solid phase sampling systems are (1) field blanks consisting of
326 the same media that are attached temporarily to the pumping system during the sampling period (2)
327 procedural blanks prepared at the same time as the field blanks and held in the laboratory.
328 Comparison of the field and procedural blanks permits an assessment of contamination during
329 sampling [67]. The same approach is used for passive samplers. Field blanks are exposed to air for
330 the same time as the deployed samplers allowing comparison with procedural blanks held in the
331 laboratory [41, 68].

332

333 **4.2. Extraction procedures**

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

340 Solid-phase media such as Speedisks and SPE cartridges are eluted with medium polarity
341 solvents such as DCM or ethyl acetate [34, 66] as per manufacturer's recommendations. Speedisks
342 can be air-dried prior to extraction [71, 72]. Residual water in the eluate is also sometimes removed
343 by pipette and the extracts are further dried with sodium sulfate that had been baked at 400-450 °C.

344 Breakthrough of target analytes on XAD or PUF is generally monitored using secondary
345 columns [67, 73]. Recovery surrogates (usually mass labeled standards) are added prior to the
346 extraction step. In addition some investigators add standards to resin columns prior to deployment
347 [74, 75].

348 Liquid-liquid extraction of water has been used frequently, especially for OCPs [30, 31, 76-
349 78] and was compared with XAD and PUF by Gómez-Bellnchón et al. [79]. Extraction of seawater
350 with cyclohexane was shown to have equivalent results for PCBs in samples of 300-400 L. More

351 recent studies have come out against liquid-liquid extractions at background sites due to potential
352 for contamination from laboratory air, difficulty of separating particle and dissolved phase, solvent
353 disposal concerns, and poor performance compared to solid phase methods [29, 33, 80]. However,
354 this likely to be a problem mainly for hydrophobic POPs such as PCBs and PBDEs that are, or
355 were, in consumer and industrial products (e.g., [32]). Most authors report low background blank
356 contamination for hydrophilic POPs, e.g. [55, 66, 73].

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

363 PFOS and other PFASs are extracted from water with weak anion exchange (WAX) solid
364 phase cartridges [83, 84]. The cartridges are preconditioned by elution with 0.1% NH₄OH in
365 methanol, and then methanol and (precleaned) water. Sample cartridges are eluted with 25mM
366 ammonium acetate buffer (pH 4) and the target analytes then eluted with 0.1% NH₄OH in methanol
367 [83, 84]. Water volumes of 0.5-1L are sufficient for pg/L measurements of PFOS. In general no
368 further cleanup of extracts for PFOS is required and samples can be submitted for LC-tandem MS
369 analysis.

370 Single phase passive samplers such as LDPE, POM and silicone strips are wiped with a
371 damp paper tissue to remove biofilms and then extracted with pentane [48], hexane [50] or DCM
372 [85]. At this stage sample extracts may be suitable for GC analysis although additional cleanup may
373 be required particularly for PCDD/Fs [50]. Two phase passives such as SPMDs are dialysed with
374 hexane [39]. Residual triolein is removed from the extract through a size-exclusion
375 chromatographic column with DCM as the mobile phase [48, 68].

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

380

381 **5. Conclusions**

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

394 For PFOS, snapshot sampling of small water volumes is possible, but for other hydrophilic
395 POPs, larger water volumes need to be collected to achieve adequate detection limits. In view of the
396 logistical and financial constraints of active sampling, passive sampling is a possible alternative for
397 POPs such as HCHs, endosulfan, chlordecone and recent developments suggest it may have future
398 application to PFASs. Passive sampling provides TWA concentrations, which are more meaningful
399 for biological exposure and arguably more suitable for trend analysis. However, there are logistical
400 challenges with passives particularly for deployment offshore in large water bodies. While there
401 been many interlaboratory studies on analysis of PFOS and on chlorinated pesticides including the
402 HCHs, there is a need to compare and contrast different sampling approaches (active, passive) for
403 hydrophilic POPs, and agree on best practices.

404 There is currently a lack of standard reference materials for water analysis, but the use of
405 spiked blanks and inter-laboratory comparisons can help with ensuring QA/QC aspects of water
406 sampling. The choice of sampling technology and analytical methods will likely vary globally and
407 no single approach can be recommended at this time. A performance based approach in which the
408 entire series of steps from sampling through quantitative analysis is evaluated using intra- and inter-
409 laboratory comparisons is needed so that future global trends of hydrophilic POPs can be
410 monitored.

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412 6. References

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

Listed Chemical	Representative Analyte in water	Water solubility ¹ (mg/L) at 25°C	Log Kow	Log Koc ²	Ref
Perfluorooctane sulfonate	PFOS	680	-	2.6	[86, 87]
Hexachlorocyclohexane, gamma isomer	γ-HCH	7.3	3.7	3.0	[88]
Chlordecone	Chlordecone	2.7	4.5	3.4	[89]
Hexachlorocyclohexane, alpha isomer	α-HCH	1.0	3.8	3.8	[88]
Pentachlorobenzene	PeCBz	0.55	5.2	4.5	[88]
Endosulfan, alpha isomer	α-Endosulfan	0.50	4.9	3.6	[89] [90]
Heptachlor	Heptachlor epoxide	0.35	5.0	4.0	[88]
Endrin	Endrin	0.23	5.2	4.0	[88]
Endosulfan transformation product	Endosulfan sulfate	0.22	3.6	3.2	[89] [90]
Dieldrin	Dieldrin	0.17	5.2	4.1	[88]
PCB congener	PCB 28	0.16	5.8	5.3	[88]
Chlordane, cis isomer	<i>cis</i> -(α)chlordane	0.056	6.0	5.5	[88]
DDT transformation product	4,4'-DDE	0.04	5.7	5.0	[88]
PCB isomer	PCB 52	0.03	6.1	5.6	[88]
Aldrin	Aldrin/dieldrin	0.02	3.0	2.6	[88]
Toxaphene congener	P26	-	5.5	5.0	[91]
Toxaphene congener	P50	-	5.8	5.3	[91]
Hexabromobiphenyl congener	HBB 153	0.011	6.4	5.9	[92]
Pentabromo diphenyl ethers	BDE 47	0.011	6.8	6.3	[93] [94]
PCB isomer	PCB 101	0.01	6.4	5.9	[88]
DDT isomer	4,4'-DDT	0.0055	6.2	5.4	[88]
HCB	HCB	0.005	5.5	5.0	[88]
PBDE isomer	BDE 99	0.0024	7.3	6.8	[93] [94]
PCB isomer	PCB 153	0.001	6.9	6.4	[88]
Polychlorinated dibenzofurans isomer	2,3,7,8-TCDF	0.000419	6.5	6.0	[88]
Mirex	Mirex	0.000065	6.9	6.0	[88]
Polychlorinated dibenzo- <i>p</i> -dioxin isomer	2,3,7,8-TCDD	0.0000193	6.8	6.3	[88]
Heptabromo BDE congener	BDE 183	-	8.3	7.8	[94]

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

659 ²Koc estimated from Seth et al. [95]

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 662 Table 2. Characteristic Travel Distances (CTD) in water for selected POPs using the OECD
 663 LRTAP tool¹

Chemical	t _{1/2} air (h)	t _{1/2} water (h)	t _{1/2} soil (h)	CTD Air (km)	CTD Water (km)	CTD ratio (W/A)
α-HCH	91.2	5256	1152	1527	389	0.255
β-HCH	1344	4320	2184	2903	443	0.153
γ-HCH	448	17000	9600	2591	1646	0.635
γ-HCH	448	1700	9600	2418	175	0.073
γ-HCH	55.2	720	17520	918	72	0.079
Chlordecone	10000	4320	8640	396	444	1.121
Dieldrin	27.8	4320	8640	542	295	0.543
α-endosulfan	31.3	4320	8640	638	194	0.305
HBB	4368	4320	8640	3669	353	0.096
BDE-99	264	3600	3600	2708	217	0.080
PeCB	3720	4656	4656	59562	216	0.004
PFOS	1830	17000	17000	1220	1717	1.407

664 ¹Properties and half-lives (t_{1/2}) from Zarfl et al. [11] and from EPISuite V4.1 [96]
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668 Table 3. Summary of EQSs, EQGs, AWQCs, and NOECs for the more water soluble POPs¹

Chemical	WS ² (mg/L)	EQG ng/L (Canada)	AWQC ng/L (USA) ³	EQS ng/L (EU) ⁴	NOEC ng/L	References
α -HCH	1.0				50 (Daphnia)	[97]
β -HCH					32000 (Medaka)	[97]
γ -HCH	7.3	10	80	20 (all isomers)	2100 (Brook trout)	[98]; [99]
Chlordecone	2.7				2500 (Daphnia)	[100]
Endosulfan	0.5	3	56	5	50 (Rainbow trout)	[101]; [102]
Dieldrin/aldrin	0.17		56	10	120 (Rainbow trout)	[17]; [99]
PFOS	680				49000	[103]

669 ¹EQSs = Environmental Quality Standards, EQGs = Environmental Quality Guidelines; AWQCs =
670 ambient water quality criteria, NOECs = no observable effect concentrations671 ² WS= water solubility672 ³For protection of freshwater aquatic life – chronic effects [15]673 ⁴Inland surface waters. From Borchers [99]

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676 Table 4. Summary of selected water sample collection and extraction techniques for hydrophilic
 677 POPs in ocean, large lake, and remote lake waters

General type	Analytes	Equipment	Extraction Methodology	Vol (L)	Reference
“Active sampling”					
lake water and glacial melt	HCHs, endosulfan	GF/A filters (0.6 µm)	DCM on water from continuous flow centrifuge	~65	[76]
In situ sampling; lake water and snow melt	HCHs, endosulfan	AXYS “Infiltrex” in situ sampler; submersible pumping system	GFF (1 µm); modified “Speedisks” divinylbenzene solid-phase extraction device	50	[34];[104]
In situ sampling; lake water	HCHs, endosulfan	AXYS “Infiltrex” in situ sampler; submersible pumping system	GFF (1 µm) and XAD-2 resin (75 g)	100	[105]
Pumping from a reservoir; ocean water, Great Lakes water	HCHs	Submersible pump to 20 L stainless steel cans	GFF (0.7 µm); 200 mg “ENV+” (polystyrene-divinylbenzene (DVB) copolymer) cartridge	4-20	[7, 66]
Sea cruise, Mediterranean	α-HCH	Towfish intake to on board inline system	GFF and XAD column	90 to 350	[63]
Ocean cruises, Arctic, Atlantic	PFOS and PFCAs	Ship intake, in line sampling	Unfiltered; Oasis WAX cartridge	0.5-1	[55]
Ocean cruise, Atlantic	PFOS and PFCAs	Ship intake, in line sampling and rosette-sampler for depth profile	GFF (1.2 µm); Oasis WAX cartridge	2	[54]
Ocean cruise Pacific, Arctic	PFOS and PFCAs	Stainless steel bucket	GFF (0.7 µm); Oasis WAX cartridge	1	[106]
Ocean cruise Pacific, Arctic	HCHs, endosulfan	Ship intake, in line sampling	GFF (1.2 µm); Serdolit PAD-3 (DVB styrene) self-packed column	176–1120	[107]; [108]
Ocean cruise Pacific, Arctic	HCHs, endosulfan	Stainless steel bucket and Niskin for depth profile	GFF (0.45 µm); C18 ENVI 18 SPE cartridge	4	[109]
Estuary and open ocean water	HCHs, endosulfan	AXYS “Infiltrex” sampler and on-board extraction	GFF (0.7 µm) and XAD-2 r	100	[110]
Open ocean water	HCHs	Ship intake, in line sampling	GFF (0.7 µm) and XAD-2 resin	720-1250	[73]
Under ice and open ocean	HCHs	AXYS “Infiltrex” sampler	GFF (0.7 µm) and XAD-2 r	~100	[111]
Ocean – Singapore Strait	HCHs	Pumping system	Liquid-liquid extraction with hexane	10	[31]
“Passive sampling”					
Global scale	HCHs, γ-HCH,	LDPE	hexane	Deployment (d)	
Plymouth harbour UK	dieldrin	“Chemcatcher” type - C18 Empore disks; Ecoscope - hexane filled dialysis bag	Empore disk extracted with acetone then 1:1 (v/v) ethylacetate: isooctane	14-90 7-14	[51] [53]
Godthåbsfjord,	HCHs	Polyoxymethylene	n-hexane extraction	~90	[43]

Greenland Sydney harbor, AU	PFOS and PFCAs	Modified POCIS - Strata XAW weak anion exchanger	Methanol extraction	2-7	[35]
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