

Passive sampling biota replacement feasibility study

Chief Scientist's Group research report

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Dr Robert Bradburne
Chief Scientist

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List of abbreviations

Abbreviation	Definition
AM	Artificial mussel
ANSES	French Agency for Food, Environmental and Occupational Health & Safety
BCF	Bioconcentration factor
BFR	Brominated flame retardant
C_l	Concentration of a chemical in a lipid at equilibrium
COI	Chemical of interest
C_p	Concentration of a chemical in a polymer at equilibrium
C_w	Concentration of a chemical in water at equilibrium
Defra	Department for Environment, Food and Rural Affairs
DGT	Diffusive gradients in thin films (passive samplers)
DOM	Dissolved organic matter
EEA	European Environment Agency
EQS	Environmental quality standard
GC-HRMS	Gas chromatography-high resolution mass spectrometry
GC-MS	Gas chromatography-mass spectrometry
GC-MS/MS	Gas chromatography-tandem mass spectrometry
HCBD	Hexachlorobutadiene
HCH	Hexachlorocyclohexane
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
K_{lp}	Lipid-polymer partition coefficient
K_{lw}	Lipid-water partition coefficient
K_{ow}	Octanol-water partition coefficient
K_{pw}	Polymer-water partition coefficient
LC-HRMS	Liquid chromatography-high resolution mass spectrometry
LC-MS	Liquid chromatography-mass spectrometry
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
LDPE	Low density polyethylene
LOD	Limit of detection
NERC	Natural Environment Research Council
NIEA	Northern Ireland Environment Agency
NORA	Natural Environment Research Council Open Research Archive

Abbreviation	Definition
NORMAN	The NORMAN network is the Network of Reference Laboratories, Research Centres and Related Organisations for Monitoring of Emerging Environmental Substances
NRW	Natural Resources Wales
OC	Organochloride (pesticides)
OPFR	Organophosphate flame retardant
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ether
PBT	Persistent, bioaccumulative, and toxic
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzofuran
PCP	Personal care product
PDMS	Polydimethylsiloxane
PE	Polyethene
PFAS	Per- and polyfluoroalkyl substance
PFCA	Perfluoroalkyl carboxylates
PFOS	Perfluorooctanesulfonic acid
POCIS	Polar organic chemical integrative sampler
POM	Polyoxymethylene
POP	Persistent organic pollutant
PRC	Performance reference compound
PSD	Passive sampling device
SEPA	Scottish Environmental Protection Agency
SPE	Solid-phase extraction
SPM	Suspended particulate matter
SPMD	Semi-permeable membrane device
TMF	Trophic magnification factor
UKRI	United Kingdom Research and Innovation
USGS	United States Geological Survey

Executive summary

The aim of the project was to review the scientific evidence to understand if passive sampling devices (PSDs) could provide a practical alternative to monitoring chemicals through sampling fish and shellfish. The outputs will help the Environment Agency to design suitable field studies to further test the use of PSDs for sustainable monitoring.

This project consisted of three distinct tasks:

1. A **literature review** to assess the current state of knowledge regarding the potential for PSDs to replace biota in the Environment Agency's monitoring programmes. The primary objective was to evaluate correlations between concentrations of chemicals of interest (COIs) measured in biota and those measured in the surrounding water via PSDs. A further key objective was to identify knowledge gaps and ultimately assess how equilibrium concentrations in PSDs can be translated to concentrations measured in biota.
2. Develop **recommendations of different PSD configurations** that could be used to support and eventually replace the Environment Agency's biota monitoring in freshwater and saline environments.
3. Provide a **workflow** that can be used to estimate the equilibrium concentration of a chemical in an aquatic organism using the concentration measured in a PSD operating under equilibrium conditions. Further objectives were to provide methods for estimating the freely dissolved equilibrium concentration of a chemical based on PSD data, as well as highlighting uncertainties associated with these estimations.

A systematic literature review was conducted to understand the applicability of PSDs as potential replacements for biota in chemical monitoring. The review identified European studies published since 2000 that investigated the occurrence of contaminants of interest in biota routinely monitored by the Environment Agency monitoring programmes and in associated water by abiotic passive sampling techniques.

Passive sampling devices show promise as a reasonable proxy for biota monitoring for certain contaminant groups. This is supported by strong correlations, reported in the literature, between PSDs and biota for contaminants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and metals, particularly when contaminant group summed concentrations are considered. Many studies in the scientific literature advocate for PSDs as complementary tools alongside biota monitoring.

Despite notable progress over the past 25 years, several knowledge gaps remain. Data on the suitability of passive samplers to act as proxies for biota monitoring is not available for some contaminant groups, e.g. rodenticides. Few studies have explicitly tested the predictive accuracy of PSDs for biota concentrations, and there is no standardised framework for correlating PSD and biota data. Biological processes such as metabolism, excretion and bioaccumulation, which PSDs cannot replicate, pose significant challenges.

For instance, some compound groups such as per- and polyfluoroalkyl substances (PFAS) can undergo transformation following uptake in biota. Additionally, PSDs may be less representative for contaminants taken up via dietary or particulate-bound pathways.

Nevertheless, PSDs can reliably estimate exposure in many scenarios and may serve as a first-tier screening tool to identify exceedances of environmental quality standards (EQSs). This could trigger targeted biota sampling where needed. While PSDs presently cannot fully replace biota monitoring, they offer a valuable means to reduce reliance on it and could also serve to the reduce destructive sampling of biota.

Insights from the literature review were used to evaluate and propose different practical configuration options for sampling that could be adopted by the Environment Agency. Three configurations were proposed, covering a range a chemicals, logistical complexities and costs.

A workflow was developed, based on equilibrium partitioning models. This approach begins by estimating the freely dissolved equilibrium concentration of a chemical in water. These values are then used to estimate the equilibrium concentration of a chemical in biota.

Section 1: Literature Review

Executive summary

This section presents the findings of a literature review that collated data on the occurrence of chemicals in biota and water using abiotic passive sampling techniques. Our primary objective was to evaluate correlations between concentrations of chemicals of interest measured in biota and those measured in the surrounding water via passive sampling devices (PSDs). A further objective was to assess the current state of knowledge with regards use of PSDs as a proxy for biota and ultimately assess how equilibrium concentrations in PSDs can be translated to concentrations measured in biota.

A systematic literature review was conducted to identify European studies published since 2000 that investigated the occurrence of contaminants of interest in both biota and abiotic passive sampling techniques. Biota included fish, crayfish, and mussels, which are routinely sampled in Environment Agency monitoring programmes. An evidence base was compiled to provide insight into the current understanding and practical applicability of PSDs as potential replacements for biota in chemical monitoring.

Passive sampling devices show promise as a reasonable proxy for biota in monitoring certain contaminant groups. This is supported by strong correlations reported in the literature between PSDs and biota for contaminants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and metals, particularly when summed concentrations are considered. Many studies advocate for PSDs as complementary tools alongside biota monitoring.

Despite notable progress over the past 25 years, several knowledge gaps remain. Data on the suitability of passive samplers to act as proxies for biota monitoring is not available for some important contaminant groups, e.g. rodenticides. Few studies have explicitly tested the predictive accuracy of PSDs for biota concentrations. Biological processes such as metabolism and excretion cannot be replicated by PSDs which poses challenges. For instance, per- and polyfluoroalkyl substances (PFAS) can undergo transformation following uptake in biota. Additionally, PSDs may be less representative for contaminants taken up via dietary or particulate-bound pathways.

Nevertheless, PSDs can reliably estimate exposure in many scenarios and may serve as a first-tier screening tool to identify likely exceedances of environmental quality standards (EQSs). This could trigger further targeted biota sampling where needed. While PSDs currently cannot fully replace biota monitoring, they offer a valuable means to reduce reliance on it.

1.1 Background

Monitoring of chemicals in aquatic biota such as fish is a well-established method for assessing the exposure of organisms to environmental contaminants. The levels of contaminants measured in biota can be compared with threshold levels such as environmental quality standards (EQSs). This approach continues to play a key role in the management of chemical risks to both the environment and human health. However, the sampling of biota is necessarily destructive, requiring the organisms to be sacrificed prior to chemical analysis. Biological processes such as metabolism can also alter contaminants following uptake by biota. Therefore, the chemical signature measured in an organism reflects those chemicals which bioaccumulate without significant biological transformation or excretion and thus may not be representative of all contaminants that the organism has been exposed to. These factors can complicate the interpretation of biota monitoring data as a proxy for environmental contaminant exposure. Additional challenges associated with chemical monitoring in biota include variability depending on the organism's life history (e.g. diet, age, spatial range), the necessity to sample only in areas with existing populations of the target species, and the fact that the body burden of contaminants of some species is integrated over various areas which may be geographically distinct from the site in which they are sampled.

The routine use of passive sampling devices (PSDs) to monitor the levels of organic contaminants in water was established in the early 1990s (Huckins et al., 1993, 1990). Since then, PSDs have become an increasingly widespread and accepted technique, supported by a growing body of scientific evidence. The underlying principle of PSDs is comparable to that which underpins the suitability of biota for contaminant monitoring, i.e. the substrate, such as liver tissue or passive sampler polymer, accumulates chemicals and provides a measure of the environmental occurrence of contaminants that is, to a degree, averaged over time, and in some cases, space.

PSDs offer potential advantages over biota for chemical monitoring. Unlike biota, PSDs can be deployed for a specified period at known locations and offer the chance for more repeatable and comparable measurements of contaminants in the aquatic environment, increasing confidence in the robustness of the data across geographic regions. Consequently, PSDs have the potential to be deployed as sustainable, ethical, and robust proxies for biological monitoring, sidestepping the challenges associated with traditional biological monitoring of contaminants.

However, to fully realise this ambitious goal, it is essential to understand differences in the chemical uptake between biota and PSDs. Furthermore, the robustness of these comparisons will depend on various factors, including both intra- and inter- class variability, PSD type, and species of interest.

The overall aim of this investigation was to assess the current state of knowledge regarding the potential for PSDs to replace biota in the Environment Agency's monitoring programmes. Specifically, this study focused on understanding the correlations between the concentrations of chemicals of interest (COIs; for the full list of COIs see Appendix 1)

measured in biota and in surrounding water using PSDs. The list of COIs was based on chemicals included in routine biota monitoring programmes and those that have been identified as of interest for future biota or PSD chemical monitoring by the Environment Agency. A key objective was to understand opportunities for use of PSDs in Environment Agency monitoring programmes and identify any knowledge gaps that would need to be addressed for this technology to be employed routinely.

To achieve this aim, a systematic literature review was conducted to identify European studies published since 2000 that investigated the occurrence of COIs in PSDs and biota monitored in the Environment Agency monitoring programmes. The information extracted from relevant studies identified in the literature search formed an evidence base, providing insight into the current understanding and applicability of PSDs as potential replacements for biota in chemical monitoring.

1.2 Methodology

1.2.1 Literature searches

Academic literature

Search strings were developed to capture search terms in the title, abstract, and keywords of published academic literature on the co-occurrence of chemicals of interest (COIs) in biota and PSDs in aquatic environments from Web of Science. Boolean operators and truncations were used to retrieve all variations of the key search terms. To capture studies which employed PSDs in conjunction with biota relevant for Environment Agency aquatic chemical monitoring programmes, “passive sampl*” and “AND (biota* OR fish* OR mussel* OR crayfish*)” were included as search terms. The variation in possible relevant ecosystem types were represented using “AND (water* OR surface water* OR river* OR lake* OR groundwater* OR estuary* OR saline* OR marine* OR aquatic*)”. In order to capture those publications which investigated the chemicals of interest (as identified by the Environment Agency Project Steering Group), organic chemicals in the COI list were classified into groups based on structural similarities, applications, or commonly used terminology (Appendix 1), represented by “OR PAH* OR PCB* OR PBDE* OR OCP* OR PFAS* OR antioxidant* OR flame retardant* OR dioxin* OR furan* OR pesticide* OR rodenticide*”. Metals were included as individual elements (“OR lead OR mercury OR nickel OR silver OR arsenic OR cadmium OR chromium OR copper OR zinc OR selenium”). To capture the chemicals that may not be covered by these classifications, broader terms were also included, namely “AND (PBT* OR hydrophob* OR POP* OR persistent organic pollutant* OR metal*)”. Search results were filtered to only include those published from 1st January 2000 onwards, to ensure modern advances in PSD technology were represented. Two academic literature searches were carried out, with an initial search (29/05/25) followed by a search with an expanded set of search terms relating to

COIs (20/08/25). The full search strings of the two academic literature searches are shown in Appendix 2.

Grey literature

In addition to the procedures for identifying relevant academic literature, searches were also carried out on number of repositories of “grey literature”. These included government reports, conference abstracts, and technical documents. These repositories included national and devolved UK government agencies, namely DEFRA, the Environment Agency, Natural Resources Wales (NRW), the Scottish Environmental Protection Agency (SEPA), the Northern Ireland Environment Agency (NIEA), in addition to the UKRI NERC Open Research Archive (NORA). Publications by European governmental environment agencies were also examined, e.g. German Environment Agency (Umweltbundesamt), Swedish EPA, Irish EPA, ANSES (France), Danish EPA. Two pan-European organisations were also searched for relevant information, specifically the European Environment Agency (EEA) and the NORMAN network. Due to the smaller volume of potentially relevant documents in these repositories than in Web of Science, and the lack of optimisation of the basic search function for technical interrogation of the databases, it was necessary and appropriate to apply much broader search terms than in the academic literature search. The search terms applied to these repositories consisted of the following terms: “passive sampler”, “PSD”, “passive sampl”, “passive sampler biota”, “passive sampling”. The grey literature search was conducted on 04/08/25.

1.2.2 Data extraction and clean-up

The initial literature search in Web of Science was completed on 29/05/25 and an expanded search with wider criteria completed on 20/08/25. The grey literature search was completed on 04/08/25. Search results were collated in databases and duplicate records removed. Each of the 510 studies identified in the search were screened to retain only those studies conducted in the UK and Europe. A manual filtering approach was taken to reduce false negatives and maximise the likelihood of identifying all relevant studies. Of the 222 identified European studies, each was assessed for relevance based on the following criteria:

- 1) If the studies contained empirical data regarding the concentrations of COIs (or very similar chemicals, e.g. pesticides not included on the COI list) in biota derived from established sacrificial sampling methods and in associated water (freshwater or saline water) derived from abiotic passive sampling.
- 2) Studies reporting techniques involving “biotic passive sampling” (e.g. uptake through mussels) were only included for data extraction if they also contained an abiotic passive sampling component.
- 3) Whilst the focus was primarily on organisms included in the Environment Agency chemicals monitoring programmes (primarily fish, mussels, and crayfish), studies of other taxa (e.g. *Daphnia magna*) were also included if they were deemed to be useful based on e.g. representative study areas, sampling approaches, or recommendations regarding PSDs.

Thirty-one studies were identified as containing relevant information and were selected for data extraction. Although the vast majority of these were field-based (30 studies, 97% of relevant studies), one laboratory study was also identified. From each relevant study, information regarding high-level sampling information (e.g. study area, study environment, chemical classes monitored), biota sampling (e.g. species, frequency, seasonal and temporal resolution), passive sampling (e.g. PSD class, technical details, use of performance recovery compounds, deployment duration, seasonal and temporal resolution), chemical analysis (e.g. instrumentation, extraction and clean-up methods), and PSD-biota comparisons (e.g. methods used, conclusions, recommendations) was extracted into a database. The database was quality controlled with independent double extraction of 7 papers (23%) by a secondary data recorder. All extracted data was finally validated by a reviewer to ensure data quality, relevance, and consistency across studies. The information extracted from the studies is included in the supplementary “Summary – studies and COIs.xlsx” file. Bibliographic information regarding the 31 studies used as the evidence base for this review is included in the “Database of collated publications.ris” file. These files are not included as part of this publication.

1.2.3 Partition coefficient search

A partition coefficient represents the ratio of the concentration of a compound between two phases at equilibrium. The coefficients of interest in this study were octanol-water (K_{ow}), polymer-water (K_{pw}), and lipid-polymer partition coefficients (K_{lp}). The K_{ow} (typically expressed as a base-10 logarithm, $\log K_{ow}$) is a measure of the hydrophobicity of a chemical, with $\log K_{ow}$ increasing with increasing hydrophobicity. $\log K_{ow}$ provides an indication as to how strongly a chemical may bind to soil or sediment particles, or how bioaccumulative it may be due to partitioning strongly to organic- or lipid-rich tissues. It is a useful parameter for understanding and predicting the behaviour of chemicals in the environment. K_{pw} and K_{lp} represent the equilibrium partitioning of a compound between a polymer (i.e. a passive sampler) and water (K_{pw}) or a lipid (K_{lp}). These coefficients can be used to estimate the freely dissolved water concentration (K_{pw}) or the biota lipid concentration (K_{lp}) of a contaminant from the amount measured in a passive sampler (see Section 1.7.3 for further information). These partition coefficients are therefore relevant for interpreting data acquired from passive sampling devices.

A search was carried out on Web of Science on 15/09/25 to identify papers which report partition coefficients for COIs (see Appendix 2 for the full search string). The initial search was not limited to European studies but also to those papers published since 1st January 2000. The search yielded 323 papers. Each of these papers were manually screened to determine if the paper contained partition coefficients relevant to passive sampling. Polymers/sampler types of interest included, silicone, polyethylene (PE), semi-permeable membrane devices (SPMDs), polar organic chemical integrative samplers (POCISs), and polyoxymethylene (POM). Partition coefficients ($\log K_{ow}$, K_{pw} , K_{lp}) were then extracted from the literature, with values from papers published since 1st January 2000 (where identified)

used to populate the initial database. For those compounds with identified values for a particular coefficient, up to four extra additional values for K_{pw} and K_{lp} were extracted from studies published since 1st January 2015 covering different polymer/passive sampler types. These additional values were extracted to capture potential variability in how these parameters were determined across different studies. Only values derived from empirical data were extracted from the literature. Predictive modelling studies were excluded. The polymer-water and lipid-polymer partition coefficients were further categorised into freshwater and saline studies. The collated literature values can be found in the supplementary spreadsheets “Partition coefficients – freshwater.xlsx” and “Partition coefficients – saline.xlsx”. These files are not included as part of this publication.

1.3 Overview of chemicals and compounds of interest

Polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and organochloride pesticides (OCs) were the most studied contaminants, with these compounds analysed in 55% (PCBs, n=17 studies), 48% (PAHs, n=15) and 35% (OCs, n=11) of all studies (Figure 1 and Appendix 3). (NB: Many studies analysed >1 class of chemical, and/or investigated both freshwater and saline samples, therefore the percentages for each type of study discussed in the text sum to >100%).

PCBs, PAHs, and OCs were not only the most frequently studied contaminants overall, but also the most analysed chemicals in both freshwater and saline environments.

Polybrominated diphenyl ethers (PBDEs, 16%, n=5) per- and polyfluoroalkyl substances (PFAS, 10%, n=3), alkylphenols (10%, n=3), and personal care products (PCPs, 10%, n=3) were the only other chemical classes to be analysed in ≥10% of studies. Metals were only measured in PSDs and biota in 2 saline studies, but not in freshwater.

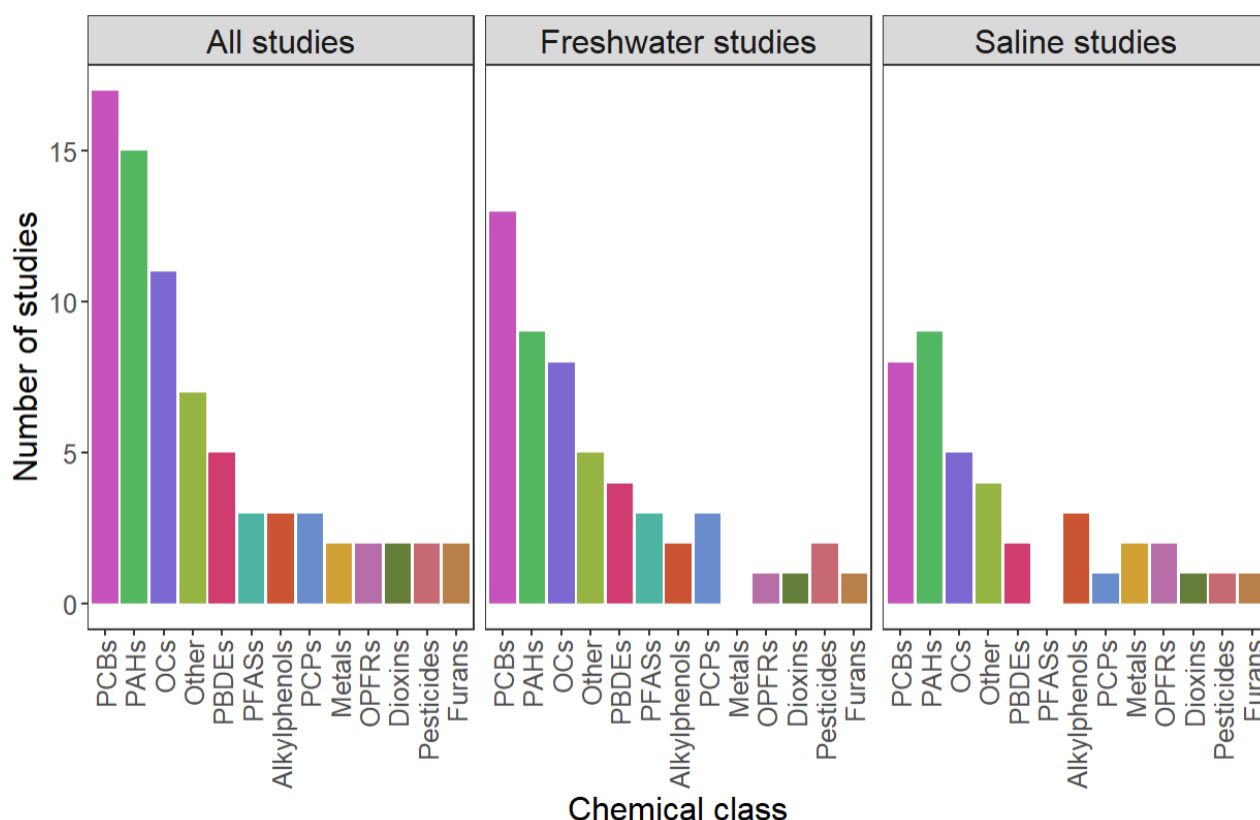


Figure 1: Number of studies that carried out targeted analysis of different chemical classes in biota and PSDs in water. “Other” includes brominated flame retardants, pharmaceuticals, organotins, extractable organofluorine, UV filters, antimicrobials, and industrial compounds (1 study each). A detailed breakdown of the data is shown in Appendix 3.

Of the 111 individual chemicals of interest (COIs), as defined by the Environment Agency (Appendix 1), 82 (74%) of these chemicals were investigated in at least one study. The most commonly investigated COIs reflect the results for compound classes (Figure 1 and Appendix 3), with PCB congeners 138, 180, 101, 52, 153, 118, and 28, and the PAHs pyrene, benzo(a)pyrene, anthracene, benzo(b) fluoranthene, fluoranthene, benzo(k) fluoranthene, benzo(a)anthracene, phenanthrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene, and chrysene the most commonly analysed COIs (>42% of studies). Of the metals in the COI list, 6 out of 10 elements were investigated in at least one study. A detailed list of which COIs were investigated in which study, including freshwater/saline categorisation, is included in the supplementary “Summary – studies and COIs.xlsx” file.

The 29 COIs that were not investigated in studies comparing biota uptake with that of PSDs in water were rodenticides (n=9 compounds), non-PBDE brominated flame retardants (BFRs, n=6), metals (n=4), antioxidants (n=2), non-OC pesticides (n=2), pigments (n=1), and solvents (n=1). Consequently, there is no data available for any of these COIs.

Partition coefficients (Section 1.2.3) were identified for several COIs, with the most information available for the commonly studied compounds shown in Figure 1 (i.e. PCBs, PAHs, OCs and PBDEs). Polymer-water partitioning coefficients were more frequently reported than lipid-polymer coefficients, with lipid-polymer coefficients identified for only two polymer types (silicone and polyethylene). The most reported coefficients were for silicone, with 72 COIs (65%) having at least one reported partition coefficient for this polymer (either polymer-water or lipid-polymer), with multiple literature values available for the majority of these COIs.

A detailed description of the number of studies investigating each individual COI and the partitioning coefficients identified in the literature, including a breakdown of freshwater and saline studies, is included in the supplementary “Summary – studies and COIs.xlsx”, “Partition coefficients – freshwater.xlsx”, and “Partition coefficients – saline.xlsx” documents.

1.4 Study regions and environments

Studies investigating the co-occurrence of COIs in aquatic biota and PSDs were identified from 13 European countries (Figure 2). Northern and central Europe were the most frequently studied regions, with research carried out in Czechia (6 studies), Norway (6), Finland (4), and France (3). These four countries accounted for 61% of all identified studies. None of the published studies of the co-occurrence of COIs in aquatic biota and PSDs identified were from the UK.

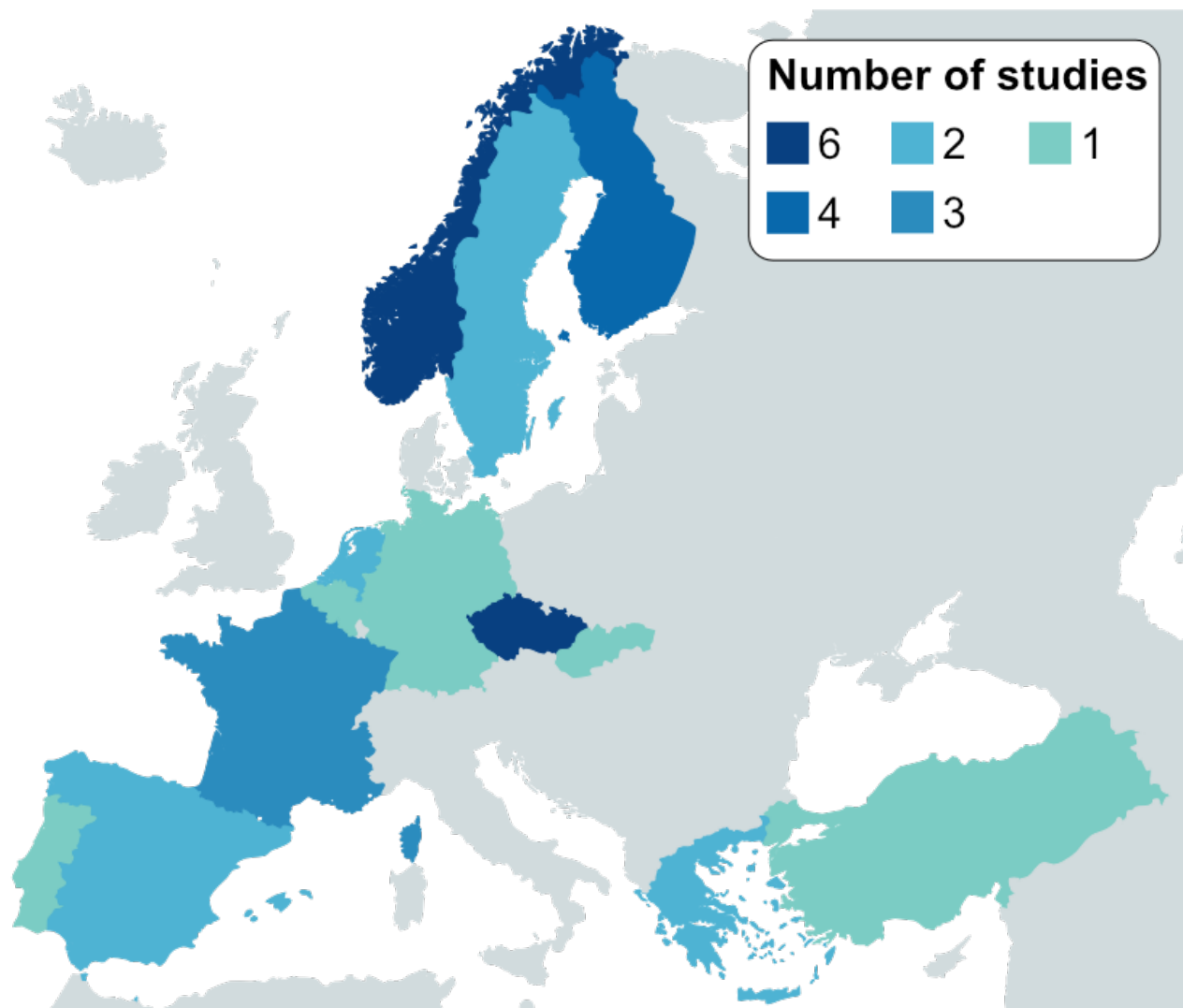


Figure 2: Study regions of the 31 identified publications investigating co-occurrence of COIs in aquatic biota and PSDs in Europe since 2000.

Most studies were carried out using samples collected in the field (97%), with only one laboratory freshwater mesocosm study (Gourlay et al., 2005; Table 1). The majority (70%) of studies sampled freshwater environments (22 studies), with 48% sampling saline environments (15 studies). Rivers were the most frequently investigated freshwater environment, featuring in just over half the studies (52%). Freshwater lakes were also relatively commonly studied (26% of investigations). Transition environments between freshwater and marine ecosystems, such as coastal, harbour, and estuary systems were also often investigated. In contrast, only four studies focused on offshore marine waters not classified as coastal. Of these marine studies, two were designed to investigate contamination arising from offshore oil production facilities (Aghito et al., 2024; Harman et al., 2011b).

Table 1: Number of studies that investigated the uptake of COIs (or closely related chemicals) in biota and PSDs in water.

Environment	Number of studies	% of studies ¹
River	16	52
Lake	8	26
Coastal	8	26
Harbour	6	19
Estuary	4	13
Marine	4	13
Freshwater mesocosm	1	3
Canal	1	3
Pond	1	3
Ditch	1	3
Lagoon	1	3

¹Many studies investigated >1 ecosystem, therefore the percentages for each type of study sum to >100%.

1.5 Biota

1.5.1 Biota species

Of the species routinely monitored by the Environment Agency (namely mussels, fish, and crayfish), mussels and fish were by far the most studied (17 studies each, 55% of total studies each; Table 2), with crayfish only studied in a single freshwater investigation (Rojo-Nieto et al., 2024). A marked difference was observed in the frequency with which these species were studied across freshwater and saline environments. Mussels were more commonly investigated in saline compartments, whereas fish were predominantly studied in freshwater systems. Specifically, mussels were studied in 45% of studies with a

freshwater component (10 studies), and 67% of studies with a saline component (10 studies), whilst fish were predominantly investigated in freshwater studies (64% of all freshwater studies, n=14), with their study in saline water less common (27% of saline studies, n=4). In the studies identified, several other species were also sampled alongside the fish, mussels, and crayfish, including invertebrates and aquatic flora (Table 2). Although these additional species are not the focus of this literature review, because they are not species routinely monitored for COIs by the Environment Agency (Appendix 1), data regarding the incidences of their study has been included in Tables 2 and 3, and the “Summary – studies and COIs.xlsx” document for completeness.

Table 2: Number of studies that carried out analysis of COIs (or closely related compounds) in different aquatic biota.

Biota	All studies ¹		Freshwater studies ¹		Saline studies ¹	
	n	%	n	%	n	%
Mussel	17	55	10	45	10	67
Fish	17	55	14	64	4	27
Invertebrate	3	10	3	14	0	0
Leach	2	6	2	9	0	0
Amphipod	1	3	0	0	1	7
Seagrass	1	3	1	5	1	7
Water flea	1	3	1	5	0	0
Shrimp	1	3	0	0	1	7
Clam	1	3	1	5	1	7
Plankton	1	3	1	5	0	0
Crayfish	1	3	1	5	0	0
Water moss	1	3	1	5	0	0
Pondweed	1	3	1	5	0	0

Biota	All studies ¹		Freshwater studies ¹		Saline studies ¹	
	n	%	n	%	n	%
Mollusc²	1	3	1	5	0	0

¹Many studies analysed >1 species, and/or investigated both freshwater and saline samples, therefore the percentages for each type of study sum to >100%. ²Unspecified species.

Fish and mussels were used in investigations in a comparable number of studies; however, fish were more comprehensively studied at species level. Across 17 publications, a total of 37 fish species were studied compared to just 8 mussel species (Table 3). The most studied fish were European perch (9 studies), common chub (6 studies), common roach (6 studies), asp (5 studies), and common bream (5 studies). The most studied mussel species were blue mussels (5 studies), duck mussels (5 studies), Mediterranean mussels (4 studies), Painter's mussels (3 studies), swollen river mussels and zebra mussels (2 studies each). Crayfish were represented by one species, the signal crayfish.

Table 3: Number of studies that carried out analysis of COIs (or closely related compounds) in different aquatic species; F = fish, M = mussel, I = invertebrate, Fl = flora, S = shrimp, C = crayfish, Mo = mollusc, P = plankton, Fw = freshwater studies, Sa = saline studies.

Species	Group	All ¹		Fw ¹		Sa ¹	
		n	%	n	%	n	%
European perch (<i>Perca fluviatilis</i>)	F	9	29	8	36	2	13
Common chub (<i>Squalius cephalus</i>)	F	6	19	6	27	0	0
Common roach (<i>Rutilus rutilus</i>)	F	6	19	6	27	0	0
Asp (<i>Leuciscus aspius</i>)	F	5	16	5	23	0	0
Blue mussel (<i>Mytilus edulis</i>)	M	5	16	1	5	5	33
Common bream (<i>Abramis brama</i>)	F	5	16	5	23	0	0

Species	Group	All ¹		Fw ¹		Sa ¹	
		n	%	n	%	n	%
Duck mussel (<i>Anodonta anatina</i>)	M	5	16	5	23	0	0
Mediterranean mussel (<i>Mytilus galloprovincialis</i>)	M	4	13	2	9	4	27
Northern pike (<i>Esox lucius</i>)	F	4	13	4	18	0	0
Common barbel (<i>Barbus barbus</i>)	F	3	10	3	14	0	0
Common bleak (<i>Alburnus alburnus</i>)	F	3	10	3	14	0	0
Common carp (<i>Cyprinus carpio</i>)	F	3	10	3	14	0	0
Common nase (<i>Chondrostoma nasus</i>)	F	3	10	3	14	0	0
Ide (<i>Leuciscus idus</i>)	F	3	10	3	14	0	0
Painter's mussels (<i>Unio pictorum</i>)	M	3	10	3	14	0	0
Zander (<i>Sander lucioperca</i>)	F	3	10	3	14	0	0
Atlantic cod (<i>Gadus morhua</i>)	F	2	6	1	5	2	13
Blue bream (<i>Ballerus ballerus</i>)	F	2	6	2	9	0	0
Brown trout (<i>Salmo trutta</i>)	F	2	6	2	9	1	7
European eel (<i>Anguilla anguilla</i>)	F	2	6	2	9	0	0
Gudgeon (<i>Gobio gobio</i>)	F	2	6	2	9	0	0
Leech (<i>Erpobdella</i> sp.)	I	2	6	2	10	0	0
Stone moroko (<i>Pseudorasbora parva</i>)	F	2	6	2	9	0	0
Swollen river mussel (<i>Unio tumidus</i>)	M	2	6	2	9	0	0

Species	Group	All ¹		Fw ¹		Sa ¹	
		n	%	n	%	n	%
Wels catfish (<i>Silurus glanis</i>)	F	2	6	2	9	0	0
Zebra mussel (<i>Dreissena polymorpha</i>)	M	2	6	2	9	0	0
Amur bitterling (<i>Rhodeus sericeus</i>)	F	1	3	1	5	0	0
<i>Anabolia</i> sp.	I	1	3	1	5	0	0
Arctic charr (<i>Salvelinus alpinus</i>)	F	1	3	1	5	1	7
Atlantic salmon (<i>Salmo salar</i>)	F	1	3	1	5	1	7
Baltic mussel (<i>Mytilus trossulus</i>)	M	1	3	0	0	1	7
Broad-leaved pondweed (<i>Potamogeton natans</i>)	Fl	1	3	1	5	0	0
Bronze bream (<i>Abramis brama</i>)	F	1	3	1	5	0	0
Burbot (<i>Lota lota</i>)	F	1	3	1	5	0	0
Caddisfly (<i>Hydropsyche</i> sp.)	I	1	3	1	5	0	0
<i>Chironomid</i> spp.	I	1	3	1	5	0	0
Common dab (<i>Limanda limanda</i>)	F	1	3	0	0	1	7
Common dace (<i>Leuciscus leuciscus</i>)	F	1	3	1	5	0	0
Common rudd (<i>Scardinius erythrophthalmus</i>)	F	1	3	1	5	0	0
Common shrimp (<i>Crangon crangon</i>)	S	1	3	0	0	1	7
Crucian carp (<i>Carassius carassius</i>)	F	1	3	1	5	0	0
<i>Daphnia magna</i>	I	1	3	1	5	0	0

Species	Group	All ¹		Fw ¹		Sa ¹	
		n	%	n	%	n	%
Dragonfly (<i>Odonata</i> sp.)	I	1	3	1	5	0	0
European bitterling (<i>Rhodeus amarus</i>)	F	1	3	1	5	0	0
<i>Gammarus</i> sp.	I	1	3	1	5	0	0
Grass carp (<i>Ctenopharyngodon idella</i>)	F	1	3	1	5	0	0
Great ramshorn (<i>Planorbis corneus</i>)	Mo	1	3	1	5	0	0
Littoral amphipods (<i>Gammarus</i> sp.)	I	1	3	0	0	1	7
Macrophyte spp.	Fl	1	3	1	5	0	0
Manila clam (<i>Ruditapes philippinarum</i>)	Mo	1	3	1	5	1	7
Mayfly (<i>Ephemeroptera</i> sp.)	I	1	3	1	5	0	0
Mediterranean tapeweed (<i>Posidonia oceanica</i>)	Fl	1	3	1	5	1	7
<i>Mollusca</i> spp.	Mo	1	3	1	5	0	0
Phytoplankton spp.	Fl	1	3	1	5	0	0
Pond slater (<i>Asellus aquaticus</i>)	I	1	3	1	5	0	0
Round goby (<i>Neogobius melanostomus</i>)	F	1	3	1	5	0	0
Rudd (<i>Scardinius erythrophthalmus</i>)	F	1	3	1	5	0	0
Signal crayfish (<i>Pacifastacus leniusculus</i>)	C	1	3	1	5	0	0
Silver bream (<i>Abramis bjoerkna</i>)	F	1	3	1	5	0	0
Stone loach (<i>Barbatula barbatula</i>)	F	1	3	1	5	0	0

Species	Group	All ¹		Fw ¹		Sa ¹	
		n	%	n	%	n	%
Swan mussel (<i>Anodonta cygnea</i>)	M	1	3	1	5	0	0
Tench (<i>Tinca tinca</i>)	F	1	3	1	5	0	0
Vimba bream (<i>Vimba vimba</i>)	F	1	3	1	5	0	0
Water moss (<i>Fontinalis</i> sp.)	Fl	1	3	1	5	0	0
Western tubenose goby (<i>Proterorhinus semilunaris</i>)	F	1	3	1	5	0	0
Zooplankton spp.	P	1	3	1	5	0	0

¹Many studies analysed >1 species, and/or investigated both freshwater and saline samples, therefore the percentages for each type of study sum to >100%.

1.5.2 Biota sampling – spatio-temporal aspects and tissue analysis

The sampling frequency of biota on the collated studies ranged from single sampling events to annual sampling across multi-year studies. Just over half of the identified studies collected biota in a single event or pooled samples from multiple events collected within days or weeks into a single sample. Approximately 20% of studies sampled biota monthly for anywhere between 2-12 months. 23% of studies sampled annually over longer timescales, e.g. every year for 2-5 years, with one monitoring study sampling biota annually for approximately 9 years (Allan et al., 2022).

For this project, sampling seasons were defined according to the meteorological calendar in the northern hemisphere (spring = March-May, summer = June-August, autumn = September-November, winter = December-February). Overall, biota was mainly sampled in summer (15 studies), followed by spring (14 studies), and autumn (12 studies), with organisms relatively rarely sampled in winter (6 studies). Of the total, 32% of studies sampled biota during a single season, 23% across two seasons, 13% across three seasons, and 10% across all four seasons. In 19% of studies (n = 6), the season during which biota sampling was conducted was not reported.

The spatial resolution of biota sampling varied greatly. Several studies conducted catchment-level approaches (e.g. Terzopoulou and Voutsas, 2017; Wernicke et al., 2022)

or targeted a specific river or lake (e.g. Bourgeault and Gourlay-Francé, 2013; Cervený et al., 2018; Figueiredo et al., 2017), typically with 3-5 sampling sites in these areas. Whereas others were national-level studies (e.g. Burkina et al., 2018; Cervený et al., 2016; Grabicová et al., 2022), and in these studies biota was generally collected from a greater number of sites with the maximum number of biota sites being ~10 (e.g. Burkina et al., 2018; Grabicová et al., 2022).

The specific tissue types collected for analysis were relatively consistent between studies. Of those studies which investigated uptake in mussels, soft tissues were analysed. For fish, muscle, occasionally reported as fillet, was the most analysed tissue (12 out of 31 studies). Fish livers were relatively commonly investigated (6 studies), whilst whole fish were analysed in 4 studies. This was typically when juvenile fish were sampled and the mass of muscle or liver alone would not be sufficient for analysis. Less frequently analysed fish samples include plasma (Grabicová et al., 2022; Tumova et al., 2017) and bile (Harman et al., 2011b). Multiple tissues from the same individuals were analysed in 5 studies. The most common multi-tissue assessment was that of fish muscle and liver (3 studies; Cervený et al., 2016; Claessens et al., 2015; Smedes et al., 2020), with plasma and muscle tissues also analysed in 2 studies (Grabicová et al., 2022; Tumova et al., 2017).

1.6 Passive sampling devices

Seven different types of passive sampling devices (PSDs) were used in the 31 studies identified in the literature search. The most frequently applied samplers were silicone-based PSDs (11 studies, 35% of total), semi-permeable membrane devices (SPMDs, 10 studies, 32%), and polar organic chemical integrative samplers (POCISs, 8 studies, 26%). Low density polyethylene (LDPE) samplers were used only in a minority of studies (3 studies, 10%). Three types of samplers were used in a single study each: they were artificial mussels (AM, Gonzalez-Rey et al., 2011), diffusive gradients in thin films (DGT) samplers (Schøyen et al., 2017), and polyoxymethylene (POM) samplers (Sobek et al., 2014). A further study used data from a monitoring programme where multiple types of PSD had been deployed (e.g. SPMDs, POCISs) but did not clearly report which PSDs generated the datasets discussed in the paper (Aghito et al., 2024). For a detailed discussion of the application of PSDs in the studies identified in the literature review, see Sections 1.6.1-1.6.4 and Appendix 4.

Table 4: Overview of the passive sampling devices (PSDs) used in the identified literature studies. A more detailed table of information on the application of the different PSDs used in literature (of the identified papers) is supplied in Appendix 4.

PSD	Number of studies (%)	Compounds analysed (number of studies)
Silicone	11 (35%)	PCBs (8), PAHs (7), OCs (6), PBDEs (3), OPFRs (2), (Personal care products (2), Pesticides (2), Organotins (1), BFRs (1), Alkylphenols (1), UV filters (1), Antimicrobials (1), Industrial (1)
SPMD	10 (32%)	PAHs (7), PCBs (6), OCs (5), PBDEs (2), Alkylphenols (2), Dioxins (1), Furans (1), Non-target screening (1)
POCIS	8 (26%)	PFAS (3), Pharmaceuticals (1), Alkylphenols (1), Personal care products (1), Extractable organofluorine (1)
LDPE	3 (10%)	PCBs (3)
Artificial mussel	1 (3%)	Metals (1)
DGT	1 (3%)	Metals (1)
POM	1 (3%)	PCBs (1), Dioxins (1), Furans (1)
Not reported	1 (3%)	-

Table 4 summaries the PSDs identified in the literature for monitoring the COI. Other PSDs are available on the market for monitoring a range of chemicals, however many are proprietary and potentially less readily available for Environment Agency use.

1.6.1 Polymer-based passive samplers

Three different types of polymer-based samplers were used in the identified literature studies, namely silicone, LDPE, and POM samplers. These samplers typically constitute sheets of polymer which are suspended in the water. Targeted chemicals are passively sorbed into the sheet over the deployment period.

Silicone passive samplers

Silicone samplers were the most widely used polymer-based sampler, representing 35% of all studies and ranking as the most used sampler overall (Allan et al., 2022; Apostolopoulou et al., 2014; Carlsson et al., 2018; Claessens et al., 2015; Lehtonen et al., 2019; Mäenpää et al., 2015; Pintado-Herrera et al., 2020; Rojo-Nieto et al., 2024; Schøyen et al., 2017; Smedes et al., 2020; Wernicke et al., 2022). They were used in 32% of studies that investigated freshwater environments, and 47% of studies that investigated saline environments. Among the studies that specify the type of silicone polymer that was used, the vast majority employed polydimethylsiloxane (PDMS, e.g. Allan et al., 2022; Rojo-Nieto et al., 2024). The silicone sheets were typically housed in stainless-steel cages (e.g. Apostolopoulou et al., 2014; Mäenpää et al., 2015), which were held in place using rope and weights. In studies which also carried out caged mussel sampling, the sheets were often attached directly to the mussel cages (e.g. Lehtonen et al., 2019).

Prior to deployment, the silicone sheets were often cleaned using Soxhlet extraction, typically with ethyl acetate for 72-100 hours (e.g. Allan et al., 2022; Apostolopoulou et al., 2014; Schøyen et al., 2017). A further pre-cleaning step was also reported by some studies, with sheets soaked in methanol for 24 hours following Soxhlet extraction (e.g. Pintado-Herrera et al., 2020). These steps were carried out to remove potential impurities such as non-polymerised monomers, which might impact the analysis and quantification of target compounds. Eight out of the 11 studies that used silicone PSDs (73%) incorporated the addition of performance reference compounds (PRCs). These mixtures consist of isotopically-labelled analogues of the selected compounds. These compounds were spiked into the polymer matrix to enable accurate estimates of average water concentrations by accounting for environmental variables affecting uptake. For further details about use and selection of PRCs, see Section 1.7.3.

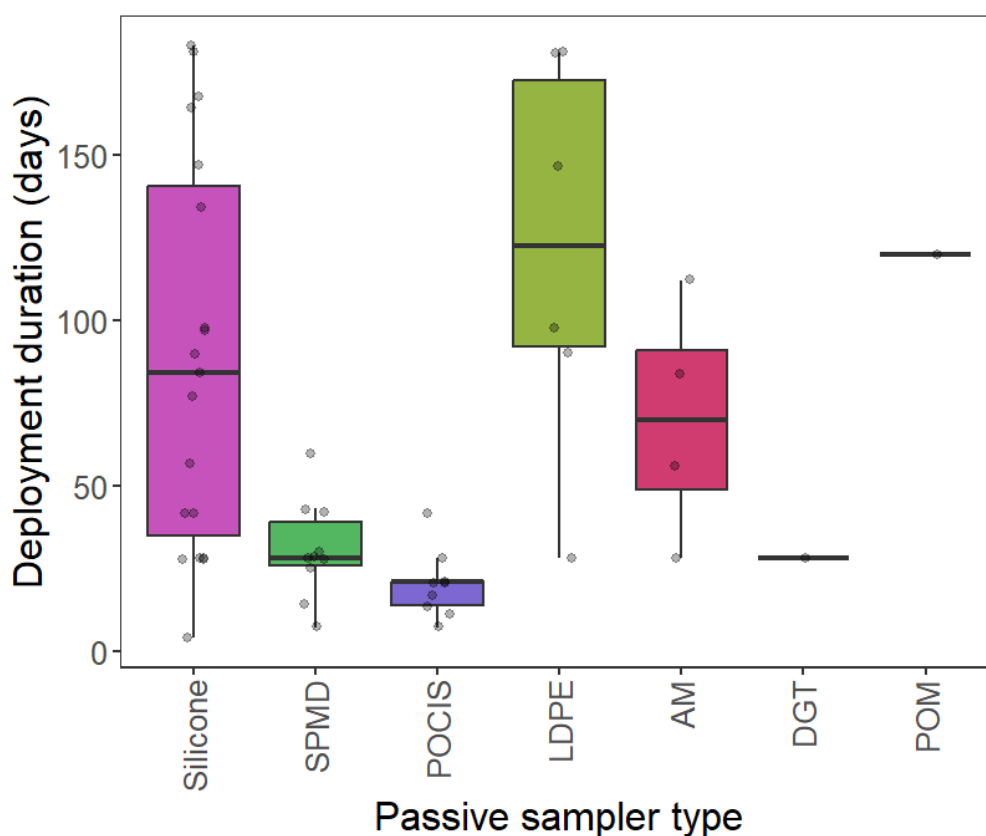


Figure 3: Deployment duration of the different types of PSD in the studies identified in this review. In studies where multiple passive sampler deployments were carried out for different lengths of time, each of these durations have been included as separate datapoint in the boxplots. Grey dots represent individual datapoints.

The studies described deployment periods ranging from 4 (Rojo-Nieto et al., 2024) to 183 days (Smedes et al., 2020), as presented in Figure 3. The mean and median deployments were 88 and 84 days, respectively. The selection of these relatively long exposure times is in part related to the compounds of interest in the studies. For instance, some persistent organic pollutants such as PCBs or OCs, which have been banned for decades (EEC, 1978; Scottish Government, 2020) and have very low solubilities in water, will be present in surface water in trace amounts. For these substances longer deployment times allow a sufficient volume of water to be sampled so that such analytes will be above the method detection limits. The choice of PSD deployment duration is also influenced by the rate at which target compounds reach equilibrium between the water and the polymer. As $\log K_{ow}$ increases, longer deployments are typically required to achieve equilibrium. Although equilibrium can be verified empirically (e.g., Mäenpää et al., 2015), many studies employ performance reference compounds (PRCs) to account for contaminant uptake kinetics (e.g., Claessens et al., 2015). These considerations are explored in detail in Section 1.7.3.

Multiple samplers were typically deployed at each sampling site, with duplicate or triplicate deployments common (e.g. Apostolopoulou et al., 2014; Mäenpää et al., 2015; Pintado-Herrera et al., 2020; Wernicke et al., 2022). The deployment of replicate samplers has

several advantages. It provides redundancy should one or more of the samplers become lost or damaged in the field. In addition, it increases the statistical robustness of the acquired data. Some studies also reported the deployment of field blanks which could be used to account for contamination associated with handling, transport, deployment and retrieval. For instance, several studies reported field blanks consisting of samplers exposed to the air during the deployment period, which were then retrieved and extracted following the same protocol as the other samplers (Carlsson et al., 2018; Claessens et al., 2015; Pintado-Herrera et al., 2020). These were also analysed in addition to PRC-spiked samplers stored in the freezer for the duration of the deployment, which were used in some studies to determine the initial quantity of PRCs present in the samplers (Carlsson et al., 2018; Pintado-Herrera et al., 2020).

To investigate accumulation of both organic and metal contaminants, Schøyen et al. (2017) co-deployed silicone samplers and diffusive gradients in thin film (DGT) samplers. Co-deployment with LDPE samplers was also carried out by Mäenpää et al. (2015), although in this instance the primary goal of the co-deployment was to compare the uptake of PCBs in both sets of samplers, as opposed to providing a wider range of quantified chemicals.

Silicone samplers were frequently deployed at a single time point (e.g. Rojo-Nieto et al., 2024; Smedes et al., 2020; Wernicke et al., 2022), although some studies implemented repeated deployments to capture temporal variation. For example, Pintado-Herrera et al. (2020) conducted a comprehensive year-long study involving monthly deployments of silicone samplers to monitor a wide range of analytes, including PAHs, PCBs, UV filters, and personal care products. Claessens et al. (2015) deployed silicone samplers annually over a 3-year period, each period lasting between 6 and 11 weeks. Carlsson et al. (2018) followed a similar approach, deploying samples annually for 2 years, while Allan et al. (2022) extended this approach and deployed silicone samplers over longer timescales, for approximately 9 years.

Deployment and sampling seasons for silicone samplers spanned the year, with deployments starting and finishing in each of the four seasons. Direct comparisons of spatial resolutions across the studies are challenging due to differing methodologies. The scale of deployment varies considerably; ranging from those at single monitoring stations (Carlsson et al., 2018) to a national-level monitoring study (Allan et al., 2022). Many studies were confined to a regional or catchment basis e.g. across coastal areas (e.g. Claessens et al., 2015; Pintado-Herrera et al., 2020) or river basins (e.g. Mäenpää et al., 2015; Smedes et al., 2020).

Studies often report cleaning the sheets to remove biofilms after sampler retrieval, for instance rinsing and wiping with de-ionised water and a tissue (Apostolopoulou et al., 2014). The chemicals of interest were typically extracted from the sheets using either Soxhlet extraction or agitation with organic solvent. Gas chromatography-mass spectrometry (GC-MS) based techniques were used exclusively to analyse the extracts from the silicone samplers, with studies commonly using single-quadrupole (GC-MS, e.g. Carlsson et al., 2018; Lehtonen et al., 2019), triple-quadrupole (GC-MS/MS, e.g. Pintado-Herrera et al., 2020; Wernicke et al., 2022) or high resolution (GC-HRMS, e.g. Rojo-Nieto

et al., 2024; Smedes et al., 2020) mass spectrometry-based methods. Further details of extraction and analysis methodologies are provided in Section 1.7.1 and 1.7.2.

Silicone samplers were used primarily to analyse hydrophobic organic pollutants such as PCBs (8 studies), PAHs (7 studies), OCs (6 studies), and PBDEs (3 studies). Less commonly studied compound classes included personal care products (2 studies), non-OC pesticides (2 studies). A range of other compound classes (e.g. non-PBDE brominated flame retardants and UV filters) were also studied using silicone-based passive samplers. These compounds were rarely analysed, with each compound appearing in only one study (see Table 4 and Appendix 4).

The PDMS sheets that were commonly used in the identified studies appear to be either purchased at the required dimensions (e.g. Claessens et al., 2015) or prepared to the correct dimensions in-house (e.g. Mäenpää et al., 2015). The dimensions of the sheets, where reported, were not standardised across all studies, although the sheets used were typically of a similar size, ranging from ~5-10 cm in width and from ~10-30 cm in length. The sheets were primarily sourced directly from manufacturers/supplier of silicone products, although silicone samplers are also available from dedicated PSD suppliers such as Affinisep (France). An advantage of using silicone passive samplers is that they are generally inexpensive to purchase, although may require extensive cleaning and preparation steps. One drawback of using silicone samplers in the field is the variability introduced by factors such as inconsistencies in polymer composition between production batches and differences in sheet thickness. These variables must be carefully considered to ensure reliable and reproducible sampling results.

Low density polyethene (LDPE) samplers

LDPE samplers were only deployed in 3 studies, all carried out by the same researchers. Each study was carried in the freshwater environment, with sampling occurring in a lake (Figueiredo et al., 2017, 2014; Mäenpää et al., 2015) and in a river basin (Mäenpää et al., 2015). Similarly to the deployment of silicone samplers, the LDPE samplers were housed in metal cages suspended in the water. The sheets were pre-cleaned by soaking in dichloromethane (DCM) for 48 hours, followed by methanol and ultrapure water for 24 hours each (Figueiredo et al., 2014; Mäenpää et al., 2015). The use of PRCs was not reported, with PCBs assumed to have reached equilibrium due to the length of the deployment times (90-181 days). The length of time for deployment was based on the results of a time-series experiment using the same samplers and analytes which showed that concentrations of PCBs did not change considerably after 147 days (Mäenpää et al., 2015). Between 3-6 replicate samplers were deployed at each sampling site, with each study conducting sampling over a single uptake period. The samplers were typically deployed in spring, and collected in autumn, spring, and summer (Figueiredo et al., 2017; Mäenpää et al., 2015).

LDPE-based samplers were co-deployed alongside silicone-based samplers in a single study (Mäenpää et al., 2015) to compare the use of both samplers for the analyses of PCBs. In this instance both PSDs revealed a good agreement in the concentrations of PCBs measured.

Following retrieval at the end of the sampling period, LDPE samplers were placed in glass vessels filled with water from the sampling site for transportation to the laboratory, followed by cleaning with lint-free tissue (Figueiredo et al., 2014; Mäenpää et al., 2015). PCBs were analysed in each study, with compounds extracted from the LDPE samplers by immersing in hexane and shaking for 24 hours. The extracts were then typically cleaned by acidification, with the hexane layer decanted and dried over sodium sulfate prior to analysis using GC-MS (see Section 1.7.1 and 1.7.2).

Similarly to silicone samplers, the LDPE samplers used in these studies appear to have been prepared in-house from LDPE film purchased from a polymer manufacturer as opposed to the dedicated PSD manufacturer. Therefore, it is likely that LDPE samplers share many of the same advantages and limitations as silicone samplers in this regard; they are inexpensive to purchase, but there may be issues with uniformity between the individual samplers.

Polyoxymethylene (POM) samplers

POM samplers were only used in one identified study in coastal and marine waters (Sobek et al., 2014). Samplers were suspended 1 metre above bed sediments using buoys and steel frames. The POM samplers were not spiked with PRCs, as equilibrium was assumed to have been reached over the single 120-day deployment period. This assumption was based on the findings from Cornelissen et al. (2008) and supported by the lack of correlation between sediment-to-water activity ratios and compound hydrophobicity. These ratios were calculated from concurrently collected bed sediment samples (Sobek et al., 2014). No pre-treatment (e.g. Soxhlet extraction) of the samplers was reported, possibly because the POM material was sold as 'additive free' (Sobek et al., 2014). However, field blanks were carried out to account for contamination during sampling and analysis. The values in the blanks were not reported, although they used to determine the limits of quantification in instances where analytes were detected in the blanks.

The number of PSDs deployed per site varied, ranging from 1 to 5 replicates. The samplers were deployed in spring and collected in autumn, at 8 sites along a ~500 km stretch of the Swedish coastline.

Samplers were cleaned with paper tissue at the end of the sampling period, with compounds extracted by shaking in hexane for 48 hours. The extracts were then subjected to three column clean-up steps, using multilayer silica and activated carbon columns, followed by a second multilayer silica clean-up. Dioxins, furans and PCBs were quantified using GC-HRMS (see Section 1.7.1 and 1.7.2 for further information). POM samplers were prepared in-house from POM material purchased from a plastic supplier.

POM samplers likely represent similar advantages and challenges as those discussed above for other polymer-based PSDs.

1.6.2 Semi-permeable membrane devices (SPMDs)

Semi-permeable membrane devices (SPMDs) typically comprise a flat LDPE tube containing ~1 mL of lipid, most commonly triolein, to act as the receiving phase for the compounds of interest. SPMDs were one of the first types of passive sampler to be applied to monitoring of hydrophobic contaminants in water (Huckins et al., 1993, 1990). They are comparably well-studied, with 10 studies (32% of total studies) which have investigated the occurrence of chemicals in biota and SPMDs in Europe (Booij et al., 2002; Bourgeault and Gourlay-Francé, 2013; Burkina et al., 2018; Castro et al., 2022; David et al., 2010; Gourlay et al., 2005; Harman et al., 2011b; Okay et al., 2017; Terzopoulou and Voutsas, 2017; Verweij et al., 2004). They were commonly used across freshwater and saline environments, with 8 studies (36% of freshwater studies) and 5 studies (33% of saline studies) identified, respectively.

SPMDs are typically housed in stainless steel cages (Castro et al., 2022; Okay et al., 2017), although some studies report using aluminium tubes (Bourgeault and Gourlay-Francé, 2013) or steel canisters (Harman et al., 2011b).

The use of PRCs was reported in the most studies (70%), with the triolein receiving phase commonly spiked with mixtures of isotopically labelled analogues of target compounds (typically PAHs, e.g. Bourgeault and Gourlay-Francé, 2013; Harman et al., 2011b). Some older studies also used PCB congeners which were not present in Aroclor formulations as PRCs, as these compounds, although not isotopically labelled, would therefore be unlikely to be present in the environment (Booij et al., 2002; Verweij et al., 2004). The practicalities of using PRCs with SPMDs may be simpler than PRC use with polymer-based samplers, as the triolein liquid can be spiked manually (or SPMDs can be purchased pre-loaded with PRCs), as opposed to more lengthy procedures involved with ensuring appropriate distribution of spiked PRCs in solid sheets of e.g. silicone or LDPE.

SPMDs were deployed for significantly shorter periods of time than polymer-based sampling devices (Figure 3), ranging from 7-60 days (Castro et al., 2022; Okay et al., 2017) with mean and median deployment durations for SPMDs of 31 and 28 days, respectively. The reason why SPMDs were deployed for shorter time periods may be related to the rate of uptake of compounds by the triolein receiving phase occurring more rapidly than for polymer-based samplers, negating the need for more lengthy deployments, although this is not explicitly stated in the studies.

There was no major difference in the types of compounds studied using SPMDs vs polymer-based samplers (Table 4), with SPMDs commonly used to measure PAHs (7 studies), PCBs (6 studies), OCs (5 studies), PBDEs (2 studies), alkylphenols (2 studies), and dioxins and furans (1 study each).

Deployment of duplicate SPMDs was common (Bourgeault and Gourlay-Francé, 2013; David et al., 2010; Verweij et al., 2004), although the number of SPMDs deployed per site was not reported in some studies. The use of field blanks was reported sometimes. For instance, field blanks were deployed in triplicates per sampling month by Bourgeault and Gourlay-Francé (2013). A single deployment was common, occurring in 60% of the identified studies, although one of these studies (Gourlay et al., 2005) was laboratory based (Burkina et al., 2018; Castro et al., 2022; David et al., 2010; Gourlay et al., 2005; Okay et al., 2017; Verweij et al., 2004). Four other studies applied more extensive sampling frequencies, e.g. sampling monthly or bi-monthly for a 6-12 month period (Bourgeault and Gourlay-Francé, 2013; Terzopoulou and Voutsas, 2017), or annually for two years (Harman et al., 2011b). Deployments generally covered multiple sites in a river basin (Bourgeault and Gourlay-Francé, 2013; Terzopoulou and Voutsas, 2017), estuary (Booij et al., 2002; Castro et al., 2022), or coastline and associated marine environment (David et al., 2010; Okay et al., 2017).

SPMDs were co-deployed with POCISs in 3 studies (Burkina et al., 2018; Castro et al., 2022; Harman et al., 2011b). Co-deployment of these samplers may allow for a wider range of contaminants to be measured, as SPMDs are typically suited to hydrophobic contaminants (e.g. PAHs, PCBs), whilst POCISs are more commonly used to study hydrophilic contaminants such as PFAS, pesticides, and pharmaceuticals (Table 4).

Biofouling was reported in several studies, therefore SPMDs were often cleaned after retrieval with distilled or ultrapure water (e.g. Bourgeault and Gourlay-Francé, 2013). Compounds of interest were typically extracted from the samplers by shaking with an organic solvent such as heptane for 24-72 hours (e.g. Bourgeault and Gourlay-Francé, 2013; David et al., 2010; Terzopoulou and Voutsas, 2017; Verweij et al., 2004). Some studies report clean-up steps after extraction such as size-exclusion chromatography (Harman et al., 2011b), or solid-phase column clean-up using, e.g. silica (Booij et al., 2002) or silica-alumina (Okay et al., 2017). Analytes were measured primarily using GC-MS(/MS) techniques (e.g. Harman et al., 2011b; Terzopoulou and Voutsas, 2017), with a handful of studies using GC-HRMS (Burkina et al., 2018; Castro et al., 2022; Okay et al., 2017). Further details of the extraction, clean-up, and analytical methodologies used are discussed in Sections 1.7.1 and 1.7.2.

SPMDs are commercially available, with a commonly cited supplier being ExposMeter, Sweden (Harman et al., 2011b; Terzopoulou and Voutsas, 2017). A minority of studies prepared SPMDs in-house (e.g. Verweij et al., 2004) by filling LDPE tubing with triolein and heat-sealing both ends. One potential advantage of preparing SPMDs in-house is increased control over the use of PRCs, as opposed to proprietary SPMDs which can be supplied pre-loaded with set mixtures of PRCs. Preparing SPMDs in-house is also likely to be less expensive than purchasing pre-assembled SPMDs.

1.6.3 Polar organic chemical integrative samplers (POCISs)

Polar organic chemical integrative samplers (POCISs) were developed by the United States Geological Survey (USGS) (Alvarez et al., 2004) with the aim of sampling less hydrophobic compounds than those that are captured by SPMDs (Alvarez, 2013). POCISs are used to sample compounds with a $\log K_{ow} < 3$, or those with an ionic nature, e.g. per- and polyfluoroalkyl substances (PFAS). A POCIS comprises a solid sorbent sandwiched between sheets of polyethersulfone membrane, encased in a steel disk. The sampled water passes through the device, with analytes captured by the sorbent.

POCISs were the third most used sampler in the identified literature studies, with 8 studies (32%) using POCISs (Aro et al., 2021; Burkina et al., 2018; Castro et al., 2022; Cervený et al., 2016, 2018; Grabicová et al., 2022; Harman et al., 2011b; Tumova et al., 2017). They were primarily deployed in freshwater environments (7 studies, 32% of all freshwater studies), with only 2 studies using POCISs in saline environments (13% of saline studies).

Stainless steel cages (Castro et al., 2022) and steel canisters (Harman et al., 2011b) were used to house the samplers, although the majority of POCIS studies did not report specific details as to how the POCISs were fixed *in situ*. Most studies did not report any pre-treatment of POCISs, this possibly being a consequence of the fact that POCISs were acquired as pre-assembled units from dedicated PSD manufacturers. Nevertheless, Castro et al. (2022) reported extensive pre-cleaning of POCIS components, which appeared to have been assembled in-house using sorbent taken from OASIS HLB solid phase extraction cartridges.

No studies reported using PRCs in POCISs, likely due to challenges such as PRCs binding very strongly to the sorbent (see Section 1.7.3. for further discussion of PRCs in POCISs).

Deployment durations for POCISs were the shortest of all PSD studies identified in the literature review (Figure 3), with mean and median duration of 20 and 21 days, respectively (range 7-42 days). POCIS samplers were deployed in duplicate (Aro et al., 2021; Harman et al., 2011b), or singularly (Tumova et al., 2017), although most studies did not report specific details as to the number of site-level replicates. Sampling frequencies of POCISs were varied, with some studies electing to deploy the samplers for a single event (Aro et al., 2021; Burkina et al., 2018; Castro et al., 2022; Cervený et al., 2016), whilst others repeat the process multiple times over 2-6 months (Cervený et al., 2018; Grabicová et al., 2022; Tumova et al., 2017) or annually (Harman et al., 2011b).

POCISs were also co-deployed with SPMDs in 3 studies (Burkina et al., 2018; Castro et al., 2022; Harman et al., 2011b), providing a greater range of compounds which could be analysed (see Section 1.6.2).

Spatial deployments of POCISs were generally some of the most widespread of the different PSDs used in the reviewed literature. There were several nationwide studies with multiple sampling points (Burkina et al., 2018; Cervený et al., 2016; Grabicová et al., 2022;

Tumova et al., 2017), in addition to regional ones (Castro et al., 2022; Cervený et al., 2018).

After the end of the POCIS deployment period, the sorbent is typically removed from the sampler and placed inside a solid phase extraction (SPE) column. The analytes are then eluted from the SPE column using a solvent (or a combination of solvents), e.g. methanol, with extracts often filtered prior to analysis (e.g. Grabicová et al., 2022). See Section 1.7.1. for further information regarding extraction and clean-up procedures. POCIS extracts are typically analysed using LC-MS(/MS) systems (e.g. (Aro et al., 2021; Grabicová et al., 2022), with some studies also using LC-HRMS (see Section 1.7.2 for further details, e.g. Cervený et al., 2018, 2016). POCISs were primarily used to analyse PFAS (3 studies), in addition to other water-soluble compounds such as pharmaceuticals, alkylphenols, and personal care products (1 study each, Table 4).

POCISs were typically purchased from a commercial supplier of PSDs, although some studies (e.g. Castro et al., 2022) prepared POCISs in-house using sorbent from OASIS HLB SPE cartridges. Most studies did not report any pre-cleaning of POCISs, possibly due to these samplers being sourced directly from dedicated manufacturers. Given that they involve a more complex design than polymer-based samplers, and to an extent, SPMDs, POCISs may be more expensive to purchase than other organic sampling devices. However, the POCIS housing is reusable if the sorbent is replaced and the device cleaned, whereas polymer-based samplers may be primarily single-use.

1.6.4 Passive samplers for metals analysis

Diffusive gradients in thin films (DGT) samplers

DGT passive samplers comprise a binding gel, a diffusive gel, and a filter membrane encased in a plastic cylinder with an opening at one end. The filter membrane is exposed at the open end of the tube. Water passes through the membrane and diffusive gel, with metals collected in the binding gel. DGT devices are patented, manufactured, and distributed by DGT Research, UK. DGT passive samplers have recently been applied to organic compounds (e.g. PAHs, Rong et al., 2024). The only study to apply DGT passive samplers in the reviewed literature used them to measure the levels of metals in water. In this review we focused on their applications to metals analysis.

DGT samplers were used in one study of saline water in a Norwegian harbour (Schøyen et al., 2017). They were used to measure concentrations of the COIs lead, nickel, cadmium, chromium, copper, and zinc, and were co-deployed with silicone-based samplers (for PAH, PCB, and OC analysis). No pre-treatment of the DGT samplers was reported, and the use of PRCs is not applicable for metals analysis.

The samplers were mounted to mussel cages, with the cages held in places with buoys and weights. The DGT samplers were deployed in duplicates, with a time duration limited

to a single 1-month deployment, due to biofouling at the surface of the sampler. Following the end of the deployment period, metals are extracted from the samplers by submersing in nitric acid for >24 hours. Schøyen et al. (2017) did not report which technique was used to quantify the metal concentrations in the extracts.

Artificial mussels

Artificial mussels, originally described by Wu et al. (2007), comprise a Perspex tube containing a chelating ligand suspended in artificial seawater. The ligand-artificial seawater solution is contained by layers of polyacrylamide gel at either end of the tube. The tube is then capped with perforated plastic caps to allow uptake of metal ions from the surrounding water into the solution. These samplers appear to have been constructed by the authors, given that the samplers used in this study are not available to purchase. Therefore, this may limit their broader use in monitoring studies.

Artificial mussels were used in one study identified in the literature search. Gonzalez-Rey et al. (2011) used them to measure the COIs cadmium, chromium, copper, lead, and zinc in water from 3 locations along the Portuguese coastline. Artificial mussels (n=10) were deployed in cages alongside live mussels for 1, 2, 3, and 4 months. Following retrieval, metals were extracted from the samplers by rinsing with ultrapure water, followed by extraction with nitric acid and filtration. The concentrations of the metals were also measured in the live mussels, to compare the results with those of the artificial mussels. Metals were quantified using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

1.7 Analytical methodologies for extraction of chemicals of interest from PSDs

1.7.1 Extraction and clean-up

The procedures used for the extraction of analytes from passive samplers varied with the type of sampler and the analytes in question (Table 5).

Table 5: Examples of extraction procedures for PSDs used in the studies identified in the literature search.

PSD Class	Example extraction and clean-up procedures	Compounds studied (number of studies)
Silicone	Two main methods are reported: 1) Soxhlet extracted, followed by solid-phase column clean-up (e.g. alumina or silica); 2) shake with organic solvent, followed by no clean-up or solid-phase column clean-up (e.g. alumina or silica).	PCBs (8), PAHs (7), OCs (6), PBDEs (3), OPFRs (2), Personal care products (2), Pesticides (2), Organotins (1), BFRs (1), Alkylphenols (1), UV filters (1), Antimicrobials (1), Industrial (1)
LDPE	Shake with hexane for 24 hours, acidify, take hexane layer for analysis, dry over sodium sulfate.	PCBs (3)
POM	Shake in hexane for 48 hours, pass through 3 solid-phase clean-up columns (multilayer silica and activated carbon).	PCBs (1), Dioxins (1), Furans (1)
SPMD	Shake with an organic solvent (e.g. heptane) for 24-72 hours. Some studies report further clean-up steps, e.g. solid-phase column clean-up (e.g. alumina or silica).	PAHs (7), PCBs (6), OCs (5), PBDEs (2), Alkylphenols (2), Dioxins (1), Furans (1), Non-target screening (1)
POCIS	Solid sorbent removed from samplers and placed in a solid phase extraction column. Analytes are eluted using solvents and filtered before analysis.	PFAS (3), Pharmaceuticals (1), Alkylphenols (1), Non-target screening (1), Personal care products (1), Extractable organofluorine (1)
Artificial mussel	Metals extracted by rinsing with water and addition of nitric acid, followed by filtration.	Metals (1)
DGT	Metals extracted by leaving in nitric acid for at least 24 hours.	Metals (1)

Four primary extraction methods were identified in the literature search:

1. The most commonly used method involved submersion of PSD membranes in a nonpolar organic solvent (e.g. hexane or heptane), followed by agitation (e.g. shaking,

rotating) for 24-72 hours (e.g. Figueiredo et al., 2017; Terzopoulou and Voutsas, 2017; Verweij et al., 2004). Extraction procedures based on this method were very commonly applied to polymer-based PSDs (silicone, LDPE, POM) in addition to SPMDs (e.g. David et al., 2010; Figueiredo et al., 2014; Sobek et al., 2014; Wernicke et al., 2022).

2. Soxhlet extraction was also applied in four studies, exclusively to silicone-based PSDs, using polar organic solvents (e.g. methanol, Carlsson et al., 2018; Smedes et al., 2020) or mixtures of polar and apolar solvents (e.g. 1:3 acetone:hexane v/v, Claessens et al., 2015).
3. Extraction of analytes from POCISs involved transfer of the sorbent to an empty solid phase extraction (SPE) column, where the analytes were then extracted from the sorbent by a polar organic solvent or mixture of solvents. A commonly used solvent combination for elution of analytes from POCIS sorbent is a 1:1:8 mixture of methanol:toluene:dichloromethane, which has been used to analyse pharmaceuticals (Grabicová et al., 2022), PFAS (Cervený et al., 2018, 2016), and personal care products (Tumova et al., 2017).
4. The fourth extraction methodology identified in the literature studies was that applied to the extraction of metals from either artificial mussels or DGT samplers. Metals were extracted from the receiving gel in these samplers by soaking in acid (e.g. 6 M nitric acid) for at least 24 hours (Gonzalez-Rey et al., 2011; Schøyen et al., 2017).

The optimal solvent choice for any extraction procedure is dependent on both the target analytes and the type of PSD being extracted. Many studies reported limited clean-up steps, possibly due to the relatively low complexity of the sample matrix. Where clean-up was employed, it typically involved eluting the extract through a clean-up column (e.g. silica or alumina chromatography), followed by filtration of the extract prior to instrumental analysis. A small number of studies carried out more extensive sample clean-up process, involving size-exclusion chromatography (Harman et al., 2011b; Schøyen et al., 2017) or acid clean-up (Figueiredo et al., 2017).

1.7.2 Instrumental analysis

Most studies were fully quantitative, with a semi-quantitative non-targeted screening approach taken in one study (Castro et al., 2022). Most studies used gas chromatography-mass spectrometry (GC-MS) based methods to identify and quantify analytes in the passive sampler extracts. GC-MS techniques were employed to analyse the most frequently investigated organic chemicals, namely the apolar POPs such as PAHs, PCBs, OCs, and PBDEs. As expected, alkylphenols, dioxins, and furans were also analysed using GC-MS. The most used detector for the GC was a single-quadrupole mass spectrometer, used in 12 studies. More sensitive triple-quadrupole instruments (GC-MS/MS) were used only in 6 studies. The use of GC-MS/MS typically achieves lower

instrument limits of detection (LODs) than for GC-MS analyses, but these instruments are more expensive to purchase and maintain than GC-MSs. High-resolution GC-MS instruments (GC-HRMS) were used in 6 studies. Some studies used a combination of different GC instruments to measure the target compounds. For instance, the analysis of dioxins, furans, PBDEs, OCs, and PCBs was split between GC-MS/MS and GC-HRMS instruments by Burkina et al. (2018). This may arise from e.g. the need for higher-throughput analyses, and/or specific instrument configurations (e.g. analytical columns, inlet configurations) being tailored towards specific groups of compounds. The expected concentration of a class of contaminants in the sample, will also guide the choice of instrument to be used in the analyses.

Liquid chromatography-MS (LC-MS) techniques were less frequently used than GC-MS. LC-MS/MS and quantitative LC-HRMS were applied in the analysis of typically polar organic compounds, such as PFAS (Aro et al., 2021; Cervený et al., 2018, 2016), personal care products (Tumova et al., 2017), and pharmaceuticals (Grabicová et al., 2022).

Two studies analysed metals in passive sampler extracts, using inductively coupled plasma mass spectrometry (ICP-MS) (Schøyen et al., 2017) and ICP-atomic emission spectroscopy (ICP-AES) (Gonzalez-Rey et al., 2011).

1.7.3 Calculation of freely dissolved concentrations and the use of performance reference compounds (PRCs)

The accumulation of chemicals by passive samplers can be conceptualised as occurring over two phases. The initial phase known as the “kinetic regime” occurs as chemicals are taken up by the passive sampler according to linear uptake kinetics. Eventually the chemical will reach an equilibrium state known as the “equilibrium regime”, between the passive sampler and the surrounding water. At this point the concentration in the passive sampler no longer changes considerably. In reality, as the concentration of the chemical approaches the equilibrium concentration, the uptake is neither linear nor at equilibrium, it is a transitional phase with a curvi-linear regime (Vrana et al., 2005).

The time taken to reach equilibrium will depend on the properties of the sampler, environmental factors (e.g. flow rate, biofouling) and the properties of the chemical. In terms of the compound properties, a key driver of uptake rate by the PSD is the $\log K_{ow}$. For compounds with a $\log K_{ow}$ of lower than 4, the equilibrium phase can be quickly reached in a matter of days or weeks (Vrana et al., 2019). Compounds with higher $\log K_{ow}$ values, such as many of the COIs in this study (Appendix 1), it can take months or longer to reach equilibrium (Joyce and Burgess, 2018; Vrana et al., 2019).

For those chemicals that are at equilibrium by the end of passive sampler deployment period, the freely dissolved concentration of each chemical in the water at equilibrium (C_w [ng/L]) can be estimated. C_w is determined by dividing the concentration of the chemical in

the passive sampler at equilibrium (C_p^∞ [ng/kg]) by the polymer-water partitioning coefficient for that chemical (K_{pw} [L/kg]):

$$C_w = \frac{C_p^\infty}{K_{pw}} \quad (1)$$

The assumption of equilibrium can be tested empirically by deploying passive samplers over varying durations and evaluating changes in concentration of accumulated chemicals over time (Mäenpää et al., 2015). An advantage of studying compounds in the equilibrium regime is that the estimation of the C_w is straightforward and avoids the use of performance reference compounds (PRCs), which are required to estimate C_w for those compounds which are in the kinetic uptake regime at the end of the PSD deployment time (see below). However, C_w determined for compounds at equilibrium is useful only when C_w has remained relatively constant over the sampling period (Booij et al., 2025). For compounds such as POPs (e.g. PCBs) this assumption of constant C_w may be acceptable, as concentrations of POPs in water are unlikely to fluctuate significantly over the sampling periods due to a lack of significant contemporaneous input. This assumption is less likely to be valid for current-use compounds such as PFAS, pharmaceuticals or pesticides, due to their ongoing production, use, and entry into the environment. Therefore, the deployment duration and type of passive sampler must be carefully considered based on the chemicals of interest and the questions that the investigation wishes to answer.

A further source of uncertainty in the estimation of C_w from C_p arises from the fact that there is variation in empirically-determined K_{pw} values among studies. Furthermore, in addition to the properties of the polymer and the chemical in question, additional factors such as temperature, salinity, and the presence of dissolved organic matter can all influence the solubility of a compound in the water phase, and therefore can affect K_{pw} values (Jonker, 2022). Therefore, the accuracy and relevance of the K_{pw} values used for a given environment will affect the overall uncertainty of estimates of C_w . For example, uncertainties in saline C_w estimates will be lower when K_{pw} values derived for saline conditions are used, compared to applying standard K_{pw} values typically determined for freshwater systems.

For chemicals with high $\log K_{ow}$ values that have not reached equilibrium during the PSD period of deployment, such as highly chlorinated PCB congeners, simply assuming that they have reached equilibrium and using equation (1) to calculate their concentration in the water will likely lead to underestimation of C_w . Assumptions of equilibrium will be more valid over longer deployment times (e.g. 3-6 months). However, it is best practice to use PRCs to account for these uncertainties associated with non-equilibrium conditions.

A PRC is typically an isotopically labelled compound analogous to the chemicals of interest. It is added to the passive sampler before its deployment. The level of the PRC in the sampler is measured at the beginning, ideally empirically, as opposed to theoretical estimates based on the amount added to the sampler, and at the end of the deployment. The proportion of the PRC that has been released over the sampling duration can be used

to more accurately estimate C_w . Calculations of C_w based on PRCs will generally yield more accurate results than those derived from simple assumptions of equilibrium.

There are several well-established methods that can be used to estimate C_w using PRC data (Booij and Smedes, 2010; Huckins et al., 2002; Joyce and Burgess, 2018; Thompson et al., 2015). Many of these methods are built on equation (1), but with the addition of a term that accounts for PRC loss. For instance, the uptake of chemicals and release of PRCs into the sampler can be modelled using a first-order kinetic model (Joyce and Burgess, 2018):

$$C_w = \frac{C_p^t}{K_{pw} \times (1 - e^{-kt})} \quad (2)$$

Where C_p^t (ng/kg) is the concentration of the chemical at the end of the deployment, t is the deployment duration (days), and k is the exchange rate constant (days^{-1}), calculated using PRC data:

$$k = -\left(\frac{\ln \frac{C_{PRC}^t}{C_{PRC}^0}}{t} \right) \quad (3)$$

Where C_{PRC}^0 (ng/kg) and C_{PRC}^t (ng/kg) are the concentrations of the PRC in the passive sampler at the beginning and end of the deployment period. The value of C_w estimated using equation 2 represents a time-weighted average concentration of that chemical in the water over the deployment period of the sampler. A challenge of using the approach detailed in equations (2) and (3) occurs when PRCs have very low retention in the sampler and most of the PRC was released over the sampling duration. or that had very high retention, where little PRC was released over the sampling duration, can cause similar challenges. In these cases, it can lead to being unable to quantify the change in the PRC concentrations because they are too close to the detection limit or too similar to the initial amounts at $t=0$, leading to inaccurate estimations of the sampling rate. Therefore, a common cited guideline in the literature is to use only those PRCs with between 20-80% of the initial amount remaining in the sampler at the end of the deployment period (Booij and Smedes, 2010).

There are also more complex modelling methods that can be used to account for PRC data aside from that detailed in equations (2) and (3), e.g. the calculation of sampling rates using nonlinear least squares modelling (Booij and Smedes, 2010), or the use of diffusion model methods (Thompson et al., 2015). These modelling approaches may reduce the impacts on PRC calculations when there is either very low or very high retention in the sampler for certain compounds (Joyce and Burgess, 2018).

The selection of PRCs requires careful consideration. Ideally, each chemical of interest will have an isotopically labelled version of itself used as a PRC, however this is rarely achievable due to limited availability of labelled compounds and the potentially prohibitive cost of purchasing, dosing, and quantifying these labelled compounds. A practical solution to this challenge is using multiple PRCs which capture the range of potential

physicochemical properties (e.g. $\log K_{ow}$ values) that may be represented by the compounds of interest. Of the studies that reported the use of PRCs, many use isotopically-labelled compounds from the different chemical classes of interest (e.g. Booij et al., 2002; Claessens et al., 2015; Wernicke et al., 2022). Labelling provides a more robust dataset that can be used to estimate the aqueous concentrations of the range of native compounds of interest, with the isotope analogous from each specific class used to correct the data. This allows for each chemical of interest to have a PRC assigned to it that matches its physiochemical properties as closely as possible and therefore reflect its uptake kinetics.

PRCs were used in most studies that used silicone (e.g. Pintado-Herrera et al., 2020; Smedes et al., 2020; Wernicke et al., 2022) and SPMD passive samplers (e.g. Bourgeault and Gourlay-Francé, 2013; Okay et al., 2017). Whilst PRCs can be applied to LDPE and POM samplers in a similar way as for silicone-based samplers, none of the studies using these samplers reported the use of PRCs. This may be partly due to the long deployment times in these studies (>120 days, Figueiredo et al., 2017, 2014; Mäenpää et al., 2015; Sobek et al., 2014) rendering the use of PRCs less applicable as equilibrium would be more likely to be reached. Although POCISs were the third most employed sampler (26% of studies), none of these studies reported the use of PRCs. The application of PRCs to POCISs has generally been less common than for other PSD types, as the interaction of compounds such as pharmaceuticals and pesticides with the sorbent used in POCISs is complex (Harman et al., 2011a), and many compounds are too strongly bound to the sorbent to act as PRCs (Liu et al., 2013). Therefore, studies wishing to derive aqueous contaminant concentrations from POCIS data have used laboratory calibrations as an alternative to in-field PRC use (e.g. Cervený et al., 2016). Nonetheless, efforts to develop an in-field PRC approach for POCISs have shown some success (e.g. Li et al., 2018).

1.8 Comparison of concentrations in aquatic biota with those in PSDs

1.8.1 Data analysis approaches and uncertainties

The extent to which concentrations in passive samplers, or water concentrations derived from passive sampler data, were formally compared with those measured in biota varied considerably across the identified body of literature. It should be noted that few studies were designed with the primary aim of correlating concentrations in biota with those measured in PSDs, therefore it is challenging to draw definitive conclusions regarding the suitability of different passive samplers to model concentrations in biota. Nevertheless, several different approaches were taken to directly or indirectly compare PSD concentrations with biota.

Some studies compared the levels of chemicals measured in passive samplers to those in biota using statistical models, e.g. through linear regression analysis and/or visualising them using scatterplots (e.g. Schøyen et al., 2017; Sobek et al., 2014). Other studies took more sophisticated approaches, for instance, using equilibrium models to predict concentrations in biota from passive sampler data (Claessens et al., 2015) or calculate and compare freely dissolved concentrations from biota, sediment, and passive sampler data (Verweij et al., 2004). A small number of studies, despite measuring the co-occurrence of contaminants in biota and PSDs, did not discuss their correlations. Nevertheless, they have been included in the supplementary “Summary – studies and COIs.xlsx” document to fully represent the targeted body of literature and ensure that potentially relevant underlying data is included.

Most studies (21 studies, 68%) employed approaches similar to those described in Section 1.7.3 to estimate the freely dissolved concentration of chemicals in the water. Whilst not explicitly required to compare concentrations in PSDs vs biota, the calculation of freely dissolved water concentrations, as opposed to using the amounts collected per sampler, was strongly recommended by Bourgeault and Gourlay-Francé (2013) to account for differences in exposure conditions influencing contaminant accumulation kinetics.

Calculation of freely dissolved concentrations can also enable the calculation of activity ratios (Allan et al., 2022; Mäenpää et al., 2015; Rojo-Nieto et al., 2024; Sobek et al., 2014). Comparing activity ratios of chemicals in biota and water, where water concentrations are derived from passive sampling, can reveal the extent to which a chemical has reached equilibrium between the water and biota. This, in turn, provides insight into the suitability of a passive sampling approach to model chemical concentrations in biota (e.g. Rojo-Nieto et al., 2024). Additionally, freely dissolved concentrations can be used to calculate other important toxicokinetic parameters such as bioconcentration factors (BCFs) and trophic magnification factors (TMFs).

There are limitations and uncertainties associated with using freely dissolved concentrations derived from PSDs to estimate concentrations in biota. For instance, whilst freely dissolved concentrations may act as an acceptable proxy for organisms that accumulate chemicals through exposure to contaminated water (bioconcentration), this approach may perform more poorly for organisms which accumulate contaminants through their diet (bioaccumulation), or through ingestion of compounds bound to particulates or dissolved organic matter. Furthermore, there are biotransformation processes which can alter certain chemicals following uptake by biota that cannot be mimicked in PSDs. These aspects are discussed in the context of individual studies in the following sections (1.8.3-1.8.8).

The contaminants discussed in the following sections (1.8.3-1.8.8) are the best-represented in the identified literature comparing concentrations in biota to those in passive samplers. Some other compound classes, e.g. alkylphenol, dioxins, furans, and personal care products were also analysed in a small number of studies. However, a lack of comparison of biota versus PSD-derived concentrations in these studies makes it challenging to draw conclusions on the suitability of the applied approaches in replacing biota in contaminant monitoring. Therefore, the focus of Section 1.8 will be on the

contaminants where either a sufficient body of literature exists to draw reasonable conclusions, or they are of particular interest from a regulatory or ecotoxicological perspective (PCBs, PAHs, OCs, PBDEs, PFAS, and metals).

1.8.2 Collection of additional field parameters

Some studies collected additional field samples, such as sediments, or measured environmental parameters such as river flow rate. These complementary measurements could provide valuable insights to better interpret the correlations observed between biota and water, as measured using water passive samplers.

Data relating to the biota studied, such as species, sex, age, size, and lipid content of sampled tissues are essential pre-requisites when interpreting the patterns of contaminant accumulation in biota and how these patterns may relate to those in PSDs. For instance, Figueiredo et al. (2017) found that the accuracy of equilibrium models to predict the concentrations of PCBs in a variety of fish species was both species- and age-dependent, with overpredictions in some species such as rudd, and considerable underpredictions in others, such as pike (see Section 1.8.3 for further details).

Sediment samples were used by Allan et al. (2022) to understand activity ratios in different environmental compartments, such as sediment-water, water-biota, and sediment-biota, to aid interpretation of accumulation of some compounds in biota. Sediments were also used in a comparative approach to evaluate whether contaminant estimates in biota were more accurately derived from water-based or sediment-based data. Findings generally indicated that estimations based on water concentrations provided greater accuracy (e.g. Figueiredo et al., 2014; Verweij et al., 2004).

Measuring chemical parameters of the water itself can enhance the interpretation of relationships between biota and passive sampler concentrations. Variables such as dissolved organic matter (DOM) have been shown to influence the relative uptake of contaminants by PSDs compared to biota. For instance, Gourlay et al. (2005) found that as DOM increased, the fractions of different PAHs that were bioavailable versus those that were SPMD-available diverged (see Section 1.8.4 for further details).

Although none of the studies used additional field data to specifically improve estimation of contaminant levels in biota, there are instances where such data could aid understanding observed correlations. However, substantial further research would be required before these additional parameters could be confidently used to account for observed deviations between predicted values and concentrations measured in biota.

1.8.3 Polychlorinated biphenyls (PCBs)

PCBs were the most widely studied COI. These contaminants were studied in 17 publications, with 12 of these attempting to link PSD-derived PCB concentrations to biota. Half of these 12 studies used silicone-based samplers, and 3 studies employed SPMDs (LDPE samplers (2 studies) and POM samplers (1 study)). The predictive power did not significantly differ between PSDs, possibly due to similar mechanisms of PCB uptake between polymer-based samplers and SPMDs.

Two studies were designed with a specific aim of testing empirically how passive samplers could be used to predict PCB concentrations in biota (Claessens et al., 2015; Figueiredo et al., 2017). Claessens et al. (2015) measured the levels of 9 PCB congeners in common dab, blue mussels, common shrimp, sediment, water, and suspended particulate matter (SPM) in harbour and coastal/marine environments using traditional spot/grab sampling. Silicone passive samplers were also deployed at these sites. They then applied equilibrium partitioning models to estimate concentrations in the fish, sediment, and SPM based on the PSD-derived water data. PSD-derived water concentrations were better predictors of the PCB and PAH concentrations measured in biota than they were for predicting levels in SPM or sediment. The predictions for biota were generally within 1 order of magnitude (e.g. 90% of fish muscle samples), with most samples generally within a factor of 5 (e.g. 70% of fish muscle, 73% of shrimp, 47% of fish liver). The difference in predictive power with a factor of 2 was quite similar across different species, ranging from 20% of shrimp samples to 31% of mussel samples. The equilibrium model was found to generally overpredict concentrations in biota. This overprediction was primarily attributable to compounds with $\log K_{ow} > 6.5$, which may be related to heavier congeners not being fully equilibrated between water and biota at lower trophic levels, resulting in less uptake and bioaccumulation in higher trophic levels than is predicted by the model (see below). The positive model bias does not preclude the use of these techniques as conservative “first-pass” approaches to identify potential trigger-level breaches, with subsequent targeted biota monitoring then applied. Indeed, similar tiered approaches were recommended by other studies which investigated the uptake of PCBs in PSDs and biota (Smedes et al., 2020; Terzopoulou and Voutsas, 2017).

Figueiredo et al. (2017) also used equilibrium models to predict the concentrations of PCBs in a variety of freshwater fish species. For many species, e.g. roach, the passive sampler data was able to accurately predict the concentrations in the fish (e.g. slope of 0.98, $R^2 = 0.89$). The accuracy of the model was species-dependent, with overpredictions in some species such as rudd, and considerable underpredictions in others, such as pike. The accuracy was also, to a lesser degree, dependent on the size (and thus potentially age) of the fish. Despite these uncertainties, the authors concluded that, based on their data, the use of passive sampling data can reliably estimate PCB concentrations in several freshwater fish species. The passive samplers in this study were deployed for 180 days, and thus PCBs were equilibrated between PSDs and the water column (i.e. were in the equilibrium regime, Section 1.7.3).

Future studies could test the accuracy of such predictive models in other species, environments, and with passive samplers operating under different uptake regimes such as shorter deployments. Overprediction of the occurrence of PCBs in some fish species had been previously recorded by the same authors (Figueiredo et al., 2014). In this study the authors used two food web models to predict concentrations of PCBs in plankton, benthic invertebrates, and fish species in a lake ecosystem. They found that using the free water concentrations from passive samplers as opposed to the sediment pore water generally provided more accurate estimates of biota concentrations, although they still tended to overestimate PCB concentrations for some fish species.

Several other studies reported generally good relationships between concentrations of PCBs in passive samplers (or freely dissolved PCB concentrations calculated from PSD data) and biota but did not test these relationships to such an extent as Claessens et al. (2015) and Figueiredo et al. (2017). Schøyen et al. (2017) reported good correspondence between the levels of PCBs measured in mussels and those in water derived from silicone passive samplers. They attribute this to the fact that mussels accumulate PCBs primarily via the bioconcentration route (i.e. from exposure/ingestion of the surrounding water) as opposed to the bioaccumulation route (i.e. through diet), and that the freely dissolved concentration measured by the passive samplers is representative of the bioconcentration pathway. This highlights that the applicability of passive samplers to estimate biota concentrations will be dependent on species and trophic level. For this reason, PSDs may be a closer representation of the uptake processes of PCBs (and potentially other contaminants) occurring in mussels than in some fish species. A very close correlation between total PCB concentrations in co-deployed SPMDs and mussels ($R^2 = 0.97$) was found by Okay et al. (2017), although there were differences in the profiles of individual PCBs. Comparable, but slightly weaker correlations between PSD-derived PCB concentrations and those measured in perch were reported by Sobek et al. (2014), with R^2 ranging from 0.49 to 0.74.

In contrast, a few studies did not find clear correlations between PSD-derived PCB concentrations and those in biota. For instance, Pintado-Herrera et al. (2020) found that the summed concentrations of contaminants measured using silicone samplers, including PCBs, did not consistently correlate with those measured in clams at the same sites. However, the authors did not break down the data by chemical class, and thus the lack of a relationship may have been influenced by contaminants other than PCBs, such as fragrances, rather than PCBs specifically. Consequently, it is challenging to draw a definitive conclusion from the data presented. Terzopoulou and Voutsas (2017) found the same individual PCBs in SPMDs and in fish tissues but did not attempt a direct comparison of the concentrations on the basis that metabolism of some of the PCB compounds would have altered the concentration of the compounds in the fish.

Considering the studies discussed above, the weight of evidence suggests that both polymer-based and SPMD passive samplers can be used to estimate concentrations of PCBs in some biota species, although they may sometimes overpredict actual tissue concentrations.

Several studies that used silicone passive samplers reported that the concentration of heavier PCB congeners (i.e. more hydrophobic, highly chlorinated compounds) were relatively low in biota at lower trophic levels (e.g. fish lipid values) when compared to the equilibrium concentration predicted between lipids and water by passive samplers (Allan et al., 2022; Rojo-Nieto et al., 2024; Smedes et al., 2020). This suggests that PCBs with higher logK_{ow} values can often be unequilibrated in lower trophic level species, with potential implications for the prediction of lipid values in these species. An earlier study using SPMDs reported similar results, which were also attributed to the fact that equilibrium of heavier PCB congeners was not reached between fish and water (Verweij et al., 2004). This behaviour appears not to be an artifact of using a specific sampler type and is more likely to be associated with toxicokinetic fate of different PCB congeners and their interactions between different matrices in an ecosystem (e.g. water, biota and sediment).

Allan et al. (2022) highlighted that water column sampling depth should be considered when designing studies of bioaccumulation of PCBs in aquatic biota. The representativeness of passive samplers as a model for fish depends on the species in question. For instance, samplers deployed in the top 2 metres of water column may be less representative for benthic species (e.g. cod in the case of Allan et al., 2022), but more representative of pelagic ones. Whilst this study was focused on PCBs, this principle will in theory apply to any contaminant or suite of contaminants.

1.8.4 Polycyclic aromatic hydrocarbons (PAHs)

Of the 16 studies that investigated PAHs, 11 carried out some degree of comparison between PAH concentrations measured in biota and passive samplers. Six of the studies used silicone samplers and five other studies applied SPMDs. Whilst some studies report reasonably good correlations between PSD-derived PAH concentrations and those in biota, there appear to be more challenges than those found with PCBs.

Like in the case of PCBs, Claessens et al. (2015) found that whilst concentrations of PAHs in different species could be relatively well-predicted using an equilibrium partitioning model, the equilibrium model was found to generally overpredict the concentrations in the biota. This, however, would not preclude the use of such techniques to initially identify threshold breaches that could be followed by subsequent targeted biota monitoring. This view is shared by Apostolopoulou et al. (2014), who concluded that whilst passive sampling couldn't replace the biota sampling entirely, it is a complementary technique to allow, for instance, an estimation of the freely dissolved PAH fraction to better understand exposure.

Levels of pyrene (a 4-ring PAH) in water estimated from SPMD data were significantly correlated with the levels of the metabolite 1-hydroxy-pyrene in fish bile (Verweij et al., 2004). Furthermore, no relationship was found between SPMD-derived sediment PAH concentrations and 1-hydroxy-pyrene in fish bile, indicating that water sampling is a better

tool for predicting PAH accumulation in fish. In addition to a strong correspondence between PCB levels in mussels and those in water estimated from silicone PSDs (see Section 1.8.4), Schøyen et al. (2017) also found a robust correlation between PSD-derived PAH concentrations and concentrations in mussels. The authors noted that this was unexpected for PAHs, as a significant amount of PAHs present in the water in the industrialised study harbours were thought to be associated with particulate matter which the silicone samplers would not be capable of accumulating. Given that the mussels weren't depurated prior to PAH extraction, any particles present in the gut would contribute to the PAH concentrations measured in the mussels. This suggests that uptake of freely dissolved PAHs from the water was the dominant accumulation route in mussels, at least in this particular study.

Further studies have reported that, whilst the sum concentrations of PAHs were found to correlate significantly between PSD-derived concentrations and those in mussels, the concentrations of some individual PAHs were not significantly correlated. For instance, Okay et al. (2017) reported a strong linear relationship ($R^2 = 0.99$) between sum PAH concentrations in SPMDs and in mussels. However, differences in the profiles of individual PAHs were identified. These differences were attributed to biotransformation and differences in uptake between the samplers and the mussels. Similar results were also observed in a study comparing concentrations in silicone passive samplers and mussels. Harman et al. (2011b) found that the uptake of some PAHs, e.g. alkylated phenanthrenes, in SPMDs was similar to mussels, but there were also clear differences in other compounds, e.g. naphthalene, a 2-ring PAH. It was hypothesised that because mussels were exposed to particulate bound PAHs the SPMDs would not have been capable of accumulating, contrary to the later findings of Schøyen et al. (2017), which suggested that uptake of freely dissolved PAHs was the primary accumulation pathway in mussels (see previous paragraph).

Harman et al. (2011b) also compared the relationships of PAH uptake in fish and SPMDs and found stronger relationships between PAHs and fish bile metabolite concentration than was found for mussels. This further suggests that the primary route of PAH uptake by mussels in this study may be through particulates, whereas the uptake route in the fish was predominantly through water.

The different uptake pathways of PAHs in mussels were also discussed by Bourgeault and Gourlay-Francé (2013), who measured the uptake of pyrene in mussels, and compared this to model estimates based on SPMD-derived data. The results suggested that pyrene accumulated predominantly through bioaccumulation (i.e. through a trophic pathway), as opposed to exposure through water. Therefore, for compounds such as pyrene, SPMDs did not appear to be a suitable proxy for mussels. However, this contrasted with the results of both Harman et al. (2011b) and Schøyen et al. (2017), discussed above. For instance, Schøyen et al. (2017) reported that, for mussels, model estimated concentrations of PAHs with $\log K_{ow}$ in the range 5-6 were relatively accurate when compared to PAHs with $\log K_{ow} < 5$, although the authors noted that the relationship broke down for PAHs with $\log K_{ow} > 6$. Bourgeault and Gourlay-Francé (2013) also highlighted the possible limitations of the use of equilibrium models to correlated PAHs in PSD-derived data with biota in cases where

biological processes alter the concentrations of the parent compounds in the organism. For these instances, the authors suggested the use of kinetic-based models as a possible alternative.

Not only the organisms, but also the properties of the waterbody itself can act to alter the relative PAH uptake in passive samplers and biota. For instance, Gourlay et al. (2005) investigated the effect of dissolved organic matter (DOM) on the uptake of PAHs in SPMDs and the commonly used model organism *Daphnia magna*. As the concentration of DOM increased, the fractions of different PAHs that were bioavailable versus those that were SPMD-available diverged. The effect appeared to be compound dependent, with fluoranthene and pyrene being increasingly less SPMD-available (relative to bioavailable) and benzo(a)pyrene increasingly more SPMD available as DOM increased. However, the authors note that for DOM concentrations typically found in temperate rivers, the difference in the uptake of PAHs was <50%. They concluded that SPMDs are useful tools to measure concentrations of unbound dissolved PAHs. However, because numerous physiological and biochemical processes occur in biota that cannot be replicated by passive samplers, extrapolating PSD data to predict bioaccumulation of PAHs remains challenging.

1.8.5 Organochloride pesticides (OCs)

Seven of the 11 studies of OCs identified in the literature review included some comparison of OC levels in biota and passive samplers, with 4 studies using silicone samplers and 3 using SPMDs. However, the extent and depth of these comparative analyses is much more restricted than for PCBs and PAHs, which were significantly more widely studied than any other class of compound.

OCs were almost exclusively studied alongside PCBs and therefore the comparisons of these compounds were often included in the analysis of PCBs (Section 1.8.3). For instance, the conclusions made by Rojo-Nieto et al. (2024), Terzopoulou and Voutsas (2017), Verweij et al. (2004), and Wernicke et al. (2022) discussed in Section 1.8.3 for PCBs were very similar, if not identical, for OCs.

Three studies reported findings specific to OCs that warrant attention. Smedes et al. (2020) found that the concentrations of the OC pentachlorobenzene across fish of different trophic levels were strongly correlated with predictions based on equilibrium passive sampler concentrations. These findings suggest that equilibrium of pentachlorobenzene between water and biota was present across all trophic levels, whereas deviations were observed for PCBs (Section 1.8.3) and PBDEs (Section 1.8.6). These differences were partly attributed to differences in uptake kinetics determined by $\log K_{ow}$. Okay et al. (2017) found a reasonable correlation ($R^2 = 0.83$) in the concentrations of DDT and its degradation products between SPMDs and mussels. However, this correlation was significantly worse than for PAHs or PCBs ($R^2 = 0.99$ and 0.97 respectively). This may reflect the greater diversity in the structures of compounds that are classified as OCs, as

opposed to PAHs and PCBs which form homologous series with clear trends in properties with increasing molecular size, degree of chlorination etc. The authors also suggested that uptake was variable across different sampling locations. For instance, at sites where OC concentrations were high in mussels but low in passive samplers, it was suggested that the primary uptake route of OCs for mussels was through binding to particulate matter followed by ingestion. Allan et al. (2022) reported lower chemical activity for OCs in fish, which indicated slow kinetics of transfer of OCs from water to organisms at the base of the food chain. These results suggest that trophic level of an organism influences the partitioning of OCs between water and organisms and should be considered when interpreting data co-derived from PSDs and biota.

1.8.6 Polybrominated diphenyl ethers (PBDEs)

Only two studies compared PBDE levels in biota and passive samplers. Booij et al. (2002) investigated the concentrations of PBDEs and PCBs in mussels and water using SPMDs in Dutch coastal waters. They reported that measured concentrations of PBDEs in mussels deviated more positively from the values predicted using an equilibrium model than PCBs did. This was attributed to bioaccumulation via food-chain ingestion, playing a more important role for PBDE uptake in mussels than water-biota partitioning (bioconcentration). However, the underlying reasons why this may be more relevant for PBDEs than PCBs remained unclear. The conclusions of the study of PBDEs (and PCBs and OCs) in freshwater fish by Smedes et al. (2020) were similar for PBDEs to those reported for PCBs, although the deviation of PBDE concentrations in fish as predicted by an equilibrium model using PSD-derived data were even greater at lower trophic levels than for PCBs. This greater deviation for PBDEs was attributed to properties of the compounds that were not captured by $\log K_{ow}$ values which influenced bioaccumulation.

1.8.7 Per- and polyfluoroalkyl substances (PFAS)

PFAS were studied in biota and POCISs in three studies. Cervený et al. (2016) measured 16 PFAS in POCISs and in fish liver and muscle tissue from 6 rivers in the Czech Republic. Sum PFAS concentrations were strongly correlated with those in the fish liver tissue ($R^2 = 0.88$, $p < 0.05$), with a slightly weaker but also strong relationship found in the muscle tissue ($R^2 = 0.71$, $p < 0.05$). However, no significant correlations were found for individual PFAS, and therefore the individual PFAS profiles in the POCISs and the fish were different. A later study carried out by the same authors also reported differences in the PFAS profiles between POCISs and fish (Cervený et al., 2018). Several PFAS compounds were dominant in POCISs that were never detected in fish, for instance perfluorohexanoic acid. Conversely, some compounds such as perfluorododecanoic acid were found in fish but not in POCISs. These differences in PFAS profiles were attributed to several factors related to differences in the physicochemical properties of individual PFAS

compounds, including rapid metabolism or excretion of certain PFAS in the fish, biotransformation of PFAS into other PFAS compounds; for example, PFOS is a breakdown product of various precursor PFAS, and the potential uptake of PFAS bound to particulate matter by fish, an exposure route not captured by the passive samplers.

A more recent study of 37 PFAS in fish and POCISs from a lake also reported considerable differences in the individual PFAS profiles in the passive samplers and the fish livers. They found that perfluoroalkyl carboxylates (PFCAs) with alkyl chain length C6 to C10 plus C12 were significantly more enriched in the fish liver than in the POCIS extracts (Aro et al., 2021). Due to the diversity of PFAS compound structures such as head group, chain length, and degree of branching, there are considerable differences in the physicochemical properties between different PFAS compounds. Therefore, whilst further work is required to understand the suitability of passive samplers for estimating PFAS concentrations in biota, the overall weight of evidence from these studies suggests that there may be considerable challenges associated with correlating concentrations of individual PFAS measured in passive samplers with those in biota.

It should be noted that none of these three studies calculated freely dissolved PFAS concentrations in the water, but instead PFAS concentrations were reported on a mass per sampler (ng sampler^{-1} or a $\text{ng sample extract}^{-1}$) basis. This reporting approach may reflect the challenges associated with applying performance reference compounds (PRCs) to POCISs, as discussed in Section 1.7.3.

1.8.8 Metals

Only two studies investigated the occurrence of metals in in co-deployed biota and passive samplers, with both investigating their uptake in mussels. Gonzalez-Rey et al. (2011) reported that the correlation of sum metal concentrations in mussels and artificial mussels (Section 1.6.4) co-deployed in the same cages in marine waters were significantly strongly correlated after 2, 3, and 4 months of sampling, but after 1 month the correlation was poor. This was attributed to the first month of deployment acting as an acclimatisation period for the transplanted live mussels. Although the concentrations of metals in the artificial and live mussels were correlated in months 2 to 4, absolute concentrations of metals were generally higher in the mussels. The exception was lead, likely due to efficient elimination and excretion of lead by the live mussels. Schøyen et al. (2017) examined the uptake of metals in mussels and DGT samplers deployed in coastal waters. Although no formal statistical analysis was carried out, the authors plotted the concentrations of the different metals in the mussels versus the concentration in water derived from DGT data. The relationship appears generally linear, although the divergence from linearity was variable and depended on the metal.

1.9 Conclusions

The findings of this literature review suggest that passive sampling devices serve as a reasonable proxy for biota in the monitoring of certain contaminant groups. A range of studies report strong correlations for some classes of contaminants in passive samplers and biota; CBS, PAHs, and metals. This is mostly true when the sum of the individual compounds was considered. Many studies recommend the use of passive samplers as a complementary technique to be deployed in conjunction with biota monitoring.

However, despite the progress demonstrated in the application of passive samplers over the past 25 years in Europe, as evidenced by the studies reviewed, several knowledge gaps remain. For instance, very few studies were designed with the explicit aim of testing how comparable equilibrium concentrations of contaminants in passive samplers are with estimates of measured concentrations in biota. Whilst conclusions can still be drawn from those studies that did not explicitly aim to model this relationship, there remains a lack of empirical data for many groups of compounds and species. Furthermore, it appears that there have been no attempts to produce a standard framework to reliably correlate concentrations of COIs (Appendix 1) measured in passive samplers to those in biota. This represents a significant challenge that would need to be overcome before PSDs could be used as a proxy for biota monitoring. It highlights the need for further exploration to better understand factors that will influence variability including multiple sampling environments, passive sampler types, biota species, and chemical classes.

A major challenge in estimating concentrations of contaminants in biota from passive sampler-derived data lies in accounting for biological processes that occur after uptake, such as metabolism, excretion, and transformation, which passive samplers cannot replicate. The rate and extent of biotransformation of contaminants is species and contaminant dependent. Therefore, passive sampling may be more suitable for those compounds that undergo no or slow biotransformation.

Another challenge is to understand the extent that certain compounds can be taken up by passive samplers relative to uptake by biota. Passive samplers measure the freely dissolved concentrations of contaminants in water, which may serve as a reasonable proxy for organisms and compounds where bioconcentration is the primary uptake route. However, this approach may be less representative for substances with very low water solubility, where uptake by organisms is more likely to be via dietary uptake or ingestion of particles.

The influence of water quality parameters such as dissolved organic matter and pH on contaminant partitioning between water and passive sampling devices, and whether these parameters influence the uptake of contaminants in biota in a similar manner is not sufficiently well understood yet.

Significant challenges remain before biota monitoring could be completely replaced with passive sampling devices. However, they can provide reliable estimates of exposure in many scenarios. Passive samplers may be suitable as a “first-pass” tool within a tiered

monitoring approach, helping to identify locations with likely exceedances of EQSs (environmental quality standards) for specific contaminants and hot spots of contamination for further investigation. In case where such exceedances are detected, targeted sampling of biota could then be triggered to further assess ecological risk. Passive samplers can thus help to reduce the reliance on biota sampling, even if not eliminating the need entirely.

Section 2: Passive sampling device recommendations

Executive summary

This section recommends different passive sampling device (PSD) configurations that could be used to support the Environment Agency's biota monitoring in freshwater and saline environments. It builds on the findings of a comprehensive literature review of European studies published from 2000 to 2025, which investigated the co-occurrence of chemicals of interest (COIs) in aquatic biota and passive sampling devices (Section 1). Insights from the literature review have been used to evaluate and propose different practical configuration options for sampling. Three configurations have been proposed, each providing a different starting point for pilot deployments in the field. The configurations are presented in order of increasing cost.

Configuration 1 represents the most affordable configuration. It involves the use of silicone PSDs to investigate PCBs, PAHs, OCs, and PBDEs. Sampling would occur over a 6-month period, with two annual deployments. The analytical suite included in Configuration 1 represents 56% of the chemicals which are currently monitored in biota by the Environment Agency, making it a practical and economical choice for initial implementation.

Configuration 2 uses SPMDs to monitor PCBs, PAHs, OCs, and PBDEs, in addition to brominated flame retardants, dioxins, and furans. This expanded analytical suite in Configuration 2 covers around 81% of the COIs investigated in the Environment Agency biota monitoring programmes, offering a more comprehensive assessment of contaminant presence. Configuration 2 involves four deployments per year, each lasting 2 months. This approach provides higher temporal resolution compared to Configuration 1, enabling more detailed insights into fluctuations in chemical exposure across different seasons.

Configuration 3 represents the most comprehensive as well as the most expensive configuration, expanding upon Configuration 2 to deliver the greatest analytical breadth and the highest temporal resolution. This configuration investigates 99% of the COIs currently monitored in biota by the Environment Agency ensuring near-complete alignment, in terms of COI, with existing monitoring programmes. To achieve this breadth of compounds, this configuration uses SPMDs, POCISs and DGTs. These PSDs cover additional groups such as PFAS, pesticides, and metals. Configuration 3 involves six deployments per year, providing a highly detailed dataset that captures short-term fluctuations and seasonal trends in contaminant concentrations.

These three proposed configurations offer distinct starting points from which the Environment Agency could begin to support their biota monitoring programmes, with the long-term objective of replacing traditional biota monitoring in selected scenarios.

2.1 Background

Insights from the literature review described in Section 1 have been used to evaluate and propose different configuration options for sampling. The rationale for the configuration and the benefit and limitations of each option are described below. Our aim is to ensure that the recommended configurations are evidence-based, reflect current best practices, and address the challenges identified in recent research.

2.2 PSD configurations

2.2.1 Criteria considered and overview of configurations

Several key factors were considered when developing the different PSD configurations. To provide clear options for implementation, three configurations were selected, differentiated primarily by their relative cost: low, medium, and high. Costs associated with the sampler devices themselves, deployment, and chemical analysis were all considered.

Considerations include: the compound groups to be analysed and consequently the number of different analytical methods required, PSD type, deployment frequency and duration, and seasonality, were then optimised within the predefined cost parameters (i.e. low, medium and high). An overview of the recommendations is presented in Table 6.

Table 6: Recommendations for passive sampler deployments. The approximate relative costs of PSDs, sampling and chemical analysis are relative within each column, and cannot be directly compared between columns. E.g. the cost of analysis for Configuration 1 is lower than Configuration 2, but the absolute cost will likely be greater than the cost of sampling for Configuration 1. Costs for PSDs and analysis for Configurations 2 and 3 are given as ranges, due to the use of performance recovery compounds in these configurations. Cost estimates are based on information available in 2025.

No.	PSD type	Compounds analysed	Deployment			Estimated annual cost per sampling site ¹	Approx. relative cost		
			Duration (months)	Frequency	Seasonality		PSD	Sampling	Analysis
1	Silicone	PCBs, PAHs, OCs, PBDEs	6	Twice annually	Autumn/Winter, Spring/Summer	£2200-£3300	1	1	1
2	SPMD	PCBs, PAHs, OCs, PBDEs, BFRs, Dioxins, Furans	2	Four times annually	Each season	£6300-£9500	2-3	2	2-3
3	SPMD, POCIS, DGT	PCBs, PAHs, OCs, PBDEs, BFRs, Dioxins, Furans, PFAS, pesticides, metals	1-2	Six times annually	Each season	£16000-£24000	4-5	5	4-5

¹ February 2026

The three PSD configurations outlined in Table 6 vary in analytical breadth, temporal resolution, and associated cost implications. They provide flexible options that can accommodate different monitoring objectives and resource constraints. It is important to emphasise that for many compounds included on the COI (Chemicals of Interest) list, there was little or no data regarding their uptake in passive samplers and biota identified in Section 1. This limitation has influenced the analytical suites discussed in Sections 2.2.5-2.2.7, which will therefore be focussed primarily on broader classes of contaminants (e.g., pesticides) rather than targeting individual compounds with insufficient evidence. Each of these configurations will be discussed in detail in the following Sections (2.2.5-2.2.7), including a critical evaluation of the advantages and limitations of each approach.

The estimated cost for a single sampling site for each configuration relates to the estimated cost of samplers and associated materials (e.g. housing, PRCs), extraction, and chemical analysis (including staff time for chemical analysis) for an annual deployment of that configuration. Field sampling costs, including staff time, are not included. The estimated costs have been calculated using available data from PSD suppliers and in-house estimates of analytical costs and therefore represent very broad approximate ranges. Cost estimates are based on costs in 2025 and included for context and comparison between configurations only and should be interpreted with caution.

Table 7: Overview of compounds of interest recommended for analysis in each PSD configuration. Only compound groups which are currently monitored in aquatic biota by the Environment Agency are shown. The solvent hexachlorobutadiene (HCBd) is the only COI which is not included in the analysis in any configuration, as during Section 1 no evidence of suitability for investigation by passive samplers was identified.

Compound class	Configuration		
	1	2	3
PAHs	Y	Y	Y
PBDEs	Y	Y	Y
PCBs	Y	Y	Y
BFRs		Y	Y
Dioxins and Furans		Y	Y
Pesticides (OC)	Y	Y	Y
Pesticides			Y

Compound class	Configuration		
	1	2	3
PFAS			Y
Solvent (HCBd)			
Metals			Y

The evaluation considered factors such as analytical coverage, practicality of deployment, cost-effectiveness, suitability for long-term monitoring programmes, and potential sources of uncertainty (e.g. time take to reach equilibrium). By comparing these configurations, the section provides a clear basis for selecting the most appropriate strategy under varying operational and budgetary conditions.

2.2.2 Freshwater and saline deployments

The configurations outlined in Sections 2.2.5-2.2.7 have been designed to be deployed in both freshwater and saline environments. However, when applying PSDs to the saline environment, several additional considerations must be addressed to ensure accurate performance and data integrity.

For instance, the ionic strength of saline waters may influence the behaviour and uptake of certain classes of contaminant by the PSDs, in particular ionic contaminants such as per- and poly-fluorinated alkyl substances (PFAS) and metals. Consequently, interpretations for these contaminants in saline environments may carry more uncertainty compared to freshwater data.

To mitigate this uncertainty, it is recommended that for analysis of ionic contaminants in saline deployments (as is the case in Configuration 3), measurements of the ionic strength of the seawater are taken, e.g. conductivity measurements. These measurements provide valuable metadata to aid interpretation of the sampling data by indicating the degree to which salinity may have affected contaminant uptake.

In Configuration 3, two types of samplers are recommended for ionic contaminants: DGT samplers for metals, and POCISs for PFAS. DGTs suitable for saline environments are commercially available. Furthermore, both studies on metals identified in Section 1 were conducted in saline waters and reported relatively strong correlations between concentrations measured in PSDs and biota (Section 1.8.8). However, none of the studies using POCISs to measure PFAS identified in Section 1 were carried out in saline waters, introducing greater uncertainty surrounding the performance of POCIS deployments in the

marine environment. To address this pilot deployments would be valuable to assess the potential effects of salinity on PFAS uptake.

Contaminant concentrations in the marine environment are often lower than in freshwater systems such as rivers and therefore may justify consideration of longer deployment times. For instance, Castro et al. (2022) used a deployment time of 1 week for SPMDs and POCISs in rivers, which was doubled to 2 weeks for deployment in estuaries. However, this study used non-target screening as opposed to quantitative approaches, and it was likely that many contaminants had not reached equilibrium in the samplers for these relatively short deployment periods. Nevertheless, a longer deployment in the saline environment was justified as ambient concentrations of contaminants were likely to be lower.

Concentrations of contaminants will also vary considerably according to hydrological conditions (e.g. periods of high and low flow), meaning that the relative difference between saline and freshwater concentrations may ultimately be small. This is supported by the fact that many of the studies identified in Section 1 deployed samplers in saline waters for comparable lengths of time to those recommended in the configurations suggested in Sections 2.2.5-2.2.7. Nevertheless, longer deployments in saline environments introduce additional challenges, including increased biofouling and a higher risk of sampler loss or damage. These factors should be carefully considered when determining optimal deployment durations.

2.2.3 Additional field data

In addition to salinity, other water quality parameters can influence the uptake of contaminants in PSDs. As described in Section 1, Gourlay et al. (2005) investigated the effect of dissolved organic matter (DOM) on the uptake of PAHs in SPMDs and the commonly used model organism *Daphnia magna*. As the concentration of DOM increased, the fractions of different PAHs that were bioavailable versus those that were SPMD-available diverged. The authors noted that for DOM concentrations typically found in temperate rivers, the difference in the uptake of PAHs was relatively small (<50%).

Contaminants can also bind to particulates, e.g. clay and silt, present in freshwater or the marine water column. Because passive samplers measure contaminants which are freely dissolved, high levels of turbidity may limit the ability of passive samplers to capture contaminants which are bound to particulates. High turbidity may also have an impact on bioavailability.

The pH of water may influence the behaviour and uptake of certain contaminant classes, particularly metal ions or ionic compounds such as PFAS, both of which are measured in Configuration 3. Water temperature and water flow rate can also influence the rates of contaminant uptake. Partition coefficients also vary as a function of temperature.

Measurements of DOM, turbidity, flow rate, and temperature should be taken in Configurations 1-3, to provide additional data which may aid comparisons of PSD data

with biota concentrations. Additionally, it is recommended that water pH is also measured in Configuration 3, due to potential effects on the uptake of ionic contaminants measured in this configuration.

2.2.4 Collection of water and sediment spot samples

In addition to the measurements of water quality parameters described in Sections 2.2.2-2.2.3, the collection of water and sediment spot samples could also be considered to assist with estimating equilibrium concentrations between matrices. A spot sample is taken at a specific time and location, providing a snapshot of water or sediment quality at that moment in time. Chemical analysis of the levels of contaminants in these samples could be carried out alongside those for PSDs, to provide additional data to interpret the levels measured in PSDs (and biota). There would, however, be additional costs associated with this additional sample collection and analysis.

Whilst spot water samples may provide some additional insight, their relevance to understanding the levels of contaminants in biota is potentially limited. For instance, spot water samples capture contaminant concentrations only at the specific time of collection, making it challenging to interpret in the context of contaminant data in biota and passive samplers, both of which integrate exposure over time.

Some studies identified in the literature review (Section 1) used sediments in a comparative approach to evaluate whether contaminant estimates in biota were more accurately derived from water-based or sediment-based data. Whilst findings generally indicated that estimations based on water concentrations provided greater accuracy (e.g. Figueiredo et al., 2017; Verweij et al., 2004), the collection of sediment samples may be of value when trying to understand patterns of bioaccumulation in benthic organisms based on PSD data.

The collection of additional water and sediment samples may be useful in some instances, for example exploring spatial or temporal fluctuations. However, spot samples may be less applicable to routine longer-term aquatic PSD deployment for monitoring.

2.2.5 Configuration 1

2.2.5.1 Introduction to configuration

This configuration employs silicone passive samplers, followed by extraction and gas chromatography-mass spectrometry (GC-MS) analyses to quantify an analytical suite which is comprised primarily of hydrophobic persistent organic pollutants (POPs) included in the COI list provided by the Environment Agency. The suite is comprised of PCBs,

PAHs, OCs, and PBDEs. These four groups were the most well-studied in literature as identified in the literature review, with PCBs, PAHs, OCs, and PBDEs investigated in 55%, 48%, 35%, and 16% of studies (Section 1). Together these compound classes represent 46% of the COI list, and 56% of the chemicals which are currently monitored in biota by the Environment Agency. Consequently, these groups are relevant for regulatory monitoring requirements. However, some of these substances are rarely or never detected, as their use has been restricted. They could be considered no longer environmentally relevant and therefore less need for monitoring.

2.2.5.2 Sampler specification and deployment

One key advantage of using silicone PSDs for the monitoring of POPs is that they are relatively inexpensive to purchase and prepare. The silicone polymer polydimethylsiloxane (PDMS) was employed in most of the studies identified in Section 1, making it the recommended material for this configuration. A silicone sampler typically constitutes a sheet (or sheets) of polymer which is suspended in the water, where targeted chemicals are passively sorbed into the sheet over the deployment period. Furthermore, larger PDMS sheets can be purchased from suppliers (e.g. Altec Extrusions Ltd, UK was a commonly cited supplier in the literature review), and cut to the required dimensions in-house, further reducing costs. It is recommended to prepare sheets to commonly used dimensions, for instance those recommended by the International Council for the Exploration of the Sea (ICES; 5.5 x 9.0 cm with a thickness of 0.5 mm; Smedes and Booij, 2012).

Prior to deployment, the silicone sheets should be cleaned using Soxhlet extraction in organic solvent with ethyl acetate for 72-100 hours, as reported in the literature (e.g. Allan et al., 2022; Apostolopoulou et al., 2014). It is essential to perform this pre-cleaning step to remove potential impurities that could interfere with the analysis and quantification of target compounds. A potential challenge of preparing silicone samplers in-house is that the properties of the PDMS may vary slightly across batches. These inconsistencies may have small impacts on the validity of the partition coefficients which have been measured for PDMS.

Multiple sheets (e.g. between 3-6) should be simultaneously deployed per site to provide increased silicone surface area, thus lowering detection limits, and providing redundancy should some of the sheets become damaged or lost during the deployment period. The sheets retrieved from a site can be combined and extracted together to increase the concentration of the chemicals in the sampler (see below). Stainless-steel cages are appropriate housing for the silicone sheets. These cages can be attached to e.g. buoys, pier supports, or bottom-weights depending on the environment. Deployment depth will depend on cost and practicalities associated with the sampling environment but will ideally be representative of the depth that relevant species occupy in the water column, e.g. benthic or pelagic. The use of procedural/field blank silicone strips (i.e. those that travel to the field but aren't deployed in the water) is strongly recommended, to establish baseline levels of any contamination originating from the silicone itself, or contamination associated with storage, handling and transport of the samplers.

To reduce the cost associated with Configuration 1, it is recommended that the samplers only be collected once equilibrium has been established, as opposed to operating in the kinetic regime (see Section 1.7.3). This approach would eliminate costs associated with the use, chemical analysis, and data analysis of performance recovery compounds (PRCs), while also simplifying the overall data analysis workflow. PRCs can also be a significant expense, given that isotopically labelled compounds are costly to purchase. Therefore, an equilibrium approach is recommended for Configuration 1. However, should the use of PRCs in Configuration 1 also be considered, the use and selection of appropriate PRCs discussed in Section 2.2.6, in the context of Configuration 2, is equally applicable to Configuration 1. For instance, the specific PRCs that are provided as suitable examples for Configuration 2 in Section 2.2.6 are also suitable for deployment in Configuration 1. The chemical classes to which they belong are present in the recommended analytical suites of both Configuration 1 and 2. Further information regarding PRCs can also be found in Section 1.7.3.

A limitation of the equilibrium approach is that it requires an assumption that equilibrium has been reached between the passive samplers and the water. Therefore, in order for the compounds of interest to reach equilibrium between the PSD and the water, the PSDs should be deployed for 6 months. The duration of 6 months deployment is based on the findings of Mäenpää et al. (2015), who observed that equilibrium of 16 PCBs (ranging from tri- to hepta-chloro) was reached after ~5 months (147 days). Figueiredo et al. (2017) built on these results and deployed silicone samplers for 6 months (181 days) to collect PCBs and reported that the passive sampler data was able to accurately predict concentrations in many fish species (e.g. slope of 0.98, $R^2 = 0.89$), although the accuracy of the model was species-dependent (see Section 1.8.3 for further details). Further details of the range of typical deployment durations for silicone passive samplers, and other passive sampler types, can be found in Section 1.6.

Longer deployment durations may increase biofouling to the surface of the samplers, which can reduce compound uptake rate and therefore lengthen the time taken to reach equilibrium. Significant biofouling may also reduce the accuracy of model predictions, although systematic studies of the effects of biofouling on estimations of chemical concentrations of biota based on PSD data are limited. PRCs could be used to account for biofouling, although their inclusion adds additional costs and complexity in chemical and data analysis (see above, Section 2.2.6, and Section 1.7.3). Assumptions of equilibrium can be evaluated in the field by deploying passive samplers for different lengths of time and assessing the changes in the concentrations of contaminants over time. Conducting these tests across different saline and freshwater environments could increase confidence in the reliability of the results in different environments and their applicability under different scenarios.

A sampling period of 6 months would allow for biannual deployments, e.g. September-February and March-August, thereby capturing temporal variability in contaminant concentrations. This would allow for comparisons, for instance, of periods of relatively low biological activity (autumn/winter) with those where species are more active (spring/summer). Whilst the use of these relatively lengthy deployment timescales limits

the temporal resolution of the data, this does not preclude a robust comparison with biota (e.g. Figueiredo et al., 2017). Furthermore, deployment of samplers for 6 months provides arguably better temporal resolution than biota monitoring can offer, where the concentration of POPs and PAHs in fish livers, for instance, are averaged over the lifetime of the fish. The use of stationary PSDs also reduces complexities associated with poor or unclear spatial resolution inherent in the monitoring of many aquatic species. Nevertheless, there are disadvantages with long deployment times including potential loss of samplers during storm events, and significant biofouling on the surface of the samplers. Many studies reported biofilms which needed to be removed prior to analyte extraction (Section 1.6). The removal of biofilms will add extra time and resources to the procedure.

2.2.5.3 COIs to be analysed – methodology and analytical suites

An advantage of analysing a targeted suite of key POPs and PAHs is that these compounds can be extracted from the PSDs using a single method. Two commonly used extraction procedures were reported for silicone samplers, namely Soxhlet extraction, and shaking with an organic solvent (see Section 1.7.1). The costs and time necessary for both extraction procedures are broadly comparable, although Soxhlet extraction may be preferred as it is a stronger extraction procedure due to the use of heat and the continuous circulation of solvent through the samples. This process can result in higher extraction efficiency compared to shaking-based methods. It should be noted, however, that none of the studies reviewed in Section 1 directly compared the relative performance of these two approaches. It is not likely that there will be considerable matrix effects associated with passive sampler extracts, therefore clean-up of the extracts may not be required. However, column clean-up could be used to clean the extracts before instrumental analysis if this is found to be necessary, for instance using alumina columns which can be prepared inexpensively in-house by plugging a Pasteur pipette with glass wool and packing the pipette with alumina.

Another advantage of the analytical suite in Configuration 1 is that the knowledge regarding the applicability of PSDs as replacements for monitoring of these compounds in biota is considerably more developed than for other contaminants. POPs (PCBs, OCs, PBDEs) and PAHs are amongst the most well-studied contaminants in the environmental sciences. Consequently, key parameters such as partitioning coefficients and bioaccumulation factors are more readily available for these compounds. This availability reduces the barrier to estimation of their levels in biota based on those levels detected in the PSDs (see Section 1.3). Additionally, the behaviour and fate of these compounds in abiotic matrices (e.g. water, sediment) and biota is relatively well-understood, with most of these compounds known to bioaccumulate and bioconcentrate (Environment Agency, 2024).

The instrumental techniques used to quantify these compounds can also be harmonised. For instance, it is recommended that these compounds are analysed using GC-MS, thereby making efficient use of consumables and costs associated with instrument upkeep

and maintenance. These compounds can be analysed using at most three separate instrument configurations (PCBs and OCs can have a combined analysis), which may require different instrument settings and GC columns. However, it may also be possible to combine these analyses into fewer individual instrument analyses depending on the instruments, resources available and number of COIs to be analysed. Detailed methods for the analysis of these compounds are available in the literature and described in Section 1.7.2. Furthermore, given that these compounds are currently monitored by the Environment Agency, the application of these instrument methodologies would reduce costs associated with method development and validation.

Although the analytical suite in Configuration 1 excludes substances of emerging concern to minimise analytical costs, this does not preclude their analysis should additional funds become available. For instance, subsamples of the sampler extracts could be archived for long-term storage and subsequent analysis. Given the wide range of compounds that are accumulated by silicone samplers (see Section 1.6), these archived extracts could later be used to quantify the concentrations of several substances in addition to those initially recommended.

2.2.6 Configuration 2

2.2.6.1 Introduction to configuration

This configuration uses SPMDs to investigate not only the contaminants included in Configuration 1 (PCBs, OCs, PBDEs, PAHs) but also other hydrophobic organic compounds, including other POPs, namely non-PBDE brominated flame retardants (BFRs), polychlorinated dibenzodioxins (aka. PCDDs, dioxins), and polychlorinated dibenzofurans (aka. PCDFs, furans).

BFRs, dioxins and furans are POPs, and many of these compounds are no longer used as they are restricted by the Stockholm Convention. These compounds are known to bioaccumulate and are persistent, so remain in the environment despite restrictions on use. However, they have been less frequently studied in biota compared to other POPs such as PCBs and OCs (Section 1.3). The extended suite proposed in this configuration builds on Configuration 1 by expanding the analytical suite to include additional legacy compounds (e.g. PCDFs), as well as relatively more recently used compounds (e.g. BFRs).

SPMDs typically comprise a flat LDPE tube containing ~1 mL of lipid (most commonly triolein) to act as the receiving phase for the compounds of interest. SPMDs were one of the first types of passive sampler to be applied to monitoring of hydrophobic contaminants in water (Huckins et al., 1993, 1990) and are comparatively well-studied.

Many of the advantages of silicone samplers discussed in Section 2.2.5 also apply to SPMDs. They allow for straightforward deployment and targeted compounds can be

extracted in one relatively simple extraction. Furthermore, SPMDs are a very well-established technique for monitoring hydrophobic contaminants in water and have been used in this capacity for over three decades (Huckins et al., 1993, 1990). Consequently, SPMDs were the second most frequently used sampler identified in Section 1 (32% of studies). This widespread application has resulted in a large body of associated supporting literature regarding their use (Section 1.6.2). There is also some evidence to suggest that SPMDs can act as accurate proxies for the uptake of hydrophobic contaminants in biota (see Section 1.8). For instance, Okay et al. (2017) found strong correlations between the sum amounts of PCBs, PAHs, and OCs in mussels and SPMDs. Associated partition coefficients for triolein SPMDs are also well-established (see Section 1.2.3).

2.2.6.2 Sampler specifications and deployment

SPMDs may offer a more standardised approach than silicone samplers, as the purity of the triolein receiving phase is easier to control compared to that of the silicone polymer receiving phase. For example, triolein with 99% purity is often used in SPMDs and is readily available from suppliers such as Merck (Germany). The SPMD specification developed by the USGS and patented in the United States (Huckins et al., 2004) consists of a flat, low density polyethylene (LDPE) tube with dimensions of 91.4 cm x 2.5 cm (75-90 µm thickness), filled with 1 mL of triolein. SPMDs of this specification are available from suppliers in the United States (Environmental Sampling Technologies, 2025).

NyaExposMeter (Sweden) was a commonly cited supplier in the studies identified in Section 1, with standard SPMD specifications of 15.5 cm x 2.5 cm (75-90 µm thickness) filled with 0.17 mL of triolein (ExposMeter, 2008). Despite the standardised specification commercially available, the SPMDs used in the studies identified in the literature review exhibited considerable variation. The length of the tubing ranged from 30 cm (Booij et al., 2002; Verweij et al., 2004) to 91.4 cm (David et al., 2010; Harman et al., 2011), with a width of 2.5 cm (Harman et al., 2011) or 2.54 cm (David et al., 2010; Verweij et al., 2004). SPMDs were typically filled with 1 mL of triolein (Bourgeault and Gourlay-Francé, 2013; David et al., 2010; Harman et al., 2011; Terzopoulou and Voutsas, 2017), although other quantities were used, such as 0.3 mL (Booij et al., 2002), 0.27 g (Verweij et al., 2004), and 0.7 mL (Okay et al., 2017). Other studies have reported preparation of SPMDs in-house, using additive-free flat LDPE (low density polyethylene) tubing, filled with 99% purity triolein (e.g. Verweij et al., 2004, see Section 1.6.2).

The final specifications to which SPMDs are procured or prepared for use in Configuration 2 are unlikely to have a large impact on their suitability or robustness, providing that they are within the ranges commonly described in the literature and the specific dimensions and mass of triolein are known. The use of SPMDs is however, likely to be relatively more expensive than silicone samplers, as the samplers themselves are multi-component and therefore would be more costly to purchase and prepare.

Another consideration is whether to assume equilibrium as with the silicone samplers in Configuration 1, or to use performance recovery compounds (PRCs) to provide more accurate estimates of compound concentrations. A typical deployment period for SPMDs is up to 60 days (Section 1.6.2). For hydrophobic compounds with $\log K_{ow}$ values between 4 and 5, this is likely to be a sufficient length of time that assumptions of equilibrium are acceptable (Booij et al., 2002). However, for more hydrophobic compounds (e.g. $\log K_{ow} > 5.5$), this assumption becomes increasingly less valid as $\log K_{ow}$ increases, potentially leading to an underestimation of freely dissolved water concentrations (Section 1.7.3).

SPMDs can be purchased pre-loaded with PRCs, or a custom mix can be added to SPMDs that have been prepared in-house. If PRCs are to be used in Configuration 2, it is recommended to use a range of PRCs which are representative of the classes of compounds to be analysed. For instance, isotopically-labelled (e.g. H^2 or C^{13}) analogues of compounds spanning the range of $\log K_{ow}$ values could be used, for instance α -HCH ($\log K_{ow}$ 3.8), fluoranthene (4.6), PCB 29 (5.6), PCB 101 (6.4), PBDE 99 (7.3), and PBDE 196 (8.3). The exact number and identity of the PRCs to be used will depend on the number of compounds to be analysed as well as budget. Based on the results of previous studies (e.g. Figueiredo et al., 2017; Mäenpää et al., 2015; see Section 2.2.5 for further details), increasing the deployment duration of the SPMDs in Configuration 2 would lead to increasingly valid assumptions of equilibrium in the samplers. However, for a 60-day deployment time, the use of PRCs is recommended. If samplers were deployed for less than 60 days, the use of PRCs would also become increasingly more important.

An advantage of SPMDs is that the samplers do not require pre-cleaning prior to deployment. A deployment schedule of 60 days (2 months), with four deployments annually, would capture more finely resolved seasonal variation than Configuration 1. For instance, SPMDs could be deployed in December-January, March-April, June-July, and September-October, representing seasonal variability. The used of field and laboratory blanks is recommended. It is recommended to deploy SPMDs in duplicate or triplicate, to mitigate for potential loss of samplers. To reduce analytical costs, however, only one of the SPMDs per site could be analysed, with the other SPMD(s) archived. If the samplers were deployed in triplicate this would provide additional statistical power should analysis of the replicates be carried out for some sites, e.g. where anomalous results were identified in the first sampler to be analysed. This would, however, incur additional analytical costs.

2.2.6.3 COIs to be analysed – methodology and analytical suites

Extraction and analyses of targeted compounds from SPMDs is relatively straightforward. The most frequently used method identified in the literature review, involves submersion of PSD membranes in a nonpolar organic solvent (e.g. hexane or heptane), followed by agitation (e.g. shaking, rotating) for 24-72 hours. This extraction process is repeated between 2-3 times per sampler. Whilst many studies do not report any clean-up steps, some others used size-exclusion chromatography (Harman et al., 2011), or solid-phase column clean-up using, e.g. silica (Booij et al., 2002) or silica-alumina (Okay et al., 2017).

Solid-phase clean-up is less costly than size-exclusion chromatography, although may not remove as much of the sample matrix interferences.

The analytical suite builds on that proposed for Configuration 1, by the addition of BFRs, dioxins, and furans. Dioxins and furans are commonly analysed using GC-MS. Non-polar BFRs can be analysed by GC-MS and polar BFRs are more suited to analysis by liquid chromatography (LC) techniques, e.g. LC-tandem mass spectrometry (LC-MS/MS). In total, the compounds investigated in Configuration 2 account for 68% of the COI list, and 81% of those currently monitored in biota by the Environment Agency. The expanded analytical suite is more expensive than that recommended in Configuration 1, because it includes a wider range of compounds. Whilst the analytical suite in Configuration 2 does not include compounds of emerging interest, this configuration has the flexibility to increase the number of specific compounds that are quantified. For instance, the BFR suite could be expanded to include emerging brominated compounds, although the feasibility depends on the properties of the emerging compound to be added, as well as time, budget and analytical considerations. Consequently, this configuration does offer some scope for expanding the analytical suite to potentially include emerging BFRs.

2.2.7 Configuration 3

2.2.7.1 Introduction to configuration

This configuration builds upon the SPMDs used in Configuration 2 by incorporating two additional types of PSD. It expands the breadth of compounds that can be analysed. The co-deployment of POCISs is recommended alongside SPMDs. A POCIS comprises a solid sorbent sandwiched between sheets of polyethersulfone membrane, encased in a steel disk. The sampled water passes through the device, with analytes captured by the sorbent. POCISs can capture hydrophilic compounds such as PFAS, many pesticides, and personal care products. POCISs are suitable for co-deployment with SPMDs as these samplers collect hydrophilic compounds spanning a lower range of $\log K_{ow}$ values. SPMDs are suitable for hydrophobic compounds ($\log K_{ow} > 4$), and POCISs suitable for hydrophilic or ionic compounds ($\log K_{ow} < 4$).

This configuration further expands the analytical scope by incorporating metals on the COI list, which can be measured using DGT passive samplers. DGTs comprise a binding gel, a diffusive gel, and a filter membrane encased in a plastic cylinder with an opening at one end. The filter membrane is exposed at the open end of the tube. Water passes through the membrane and diffusive gel, with metals collected in the binding gel.

The combined deployment of these three PSD types (SPMDs, POCISs, DGTs) could enable measurement of the vast majority (85%) of the compounds on the COI list, and nearly all (99%) of those currently monitored in biota by the Environment Agency. The only exception is hexachlorobutadiene, a solvent for which in the literature we found no evidence of use of passives samplers for sampling.

The main advantage of Configuration 3 is its ability to cover the broadest possible range of compound groups, therefore delivering the most comprehensive data regarding exposure. This extensive coverage would create the largest possible evidence base for evaluating the suitability of passive sampling devices as proxies for prescribed biota monitoring in aquatic environments. A further benefit of this configuration is its capability to measure several other substance groups of interest, e.g. PFAS and pesticides.

2.2.7.2 Sampler specifications and deployment

POCISs containing a combination of carbonaceous sorbent (Ambersorb 1500) and polymer-based sorbent (ISOLUTE ENV+) are often referred to as the 'pesticide configuration' in the literature. They can be used to measure pesticides and have also been used to measure PFAS (Cerveny et al., 2018, 2016) and personal care products (Tumova et al., 2017). Consequently, POCISs with this specification could be employed in Configuration 3 to investigate most of the hydrophilic compounds on the COI list.

A variety of DGT samplers are also available, with each sampler based on a binding layer of Chelex resin and a metal oxide. The metal oxide present in the binding layer controls which metals can be sampled by the DGT sampler. Consequently, a range of metals can be analysed using DGT samplers, with the choice of binding layer to be used determined by the deployment conditions and target analytes.

The primary limitation of Configuration 3 is its higher costs and time requirements when compared with Configurations 1 and 2. Deploying multiple sampler types increases overall expenses, particularly because both POCISs and DGTs are proprietary samplers and may involve significant procurement costs. However, one advantage of purchasing pre-assembled samplers is that they don't require pre-cleaning and can provide more standardised, robust and repeatable measurements than samplers prepared in-house. It also reduces labour costs associated with preparing samplers in-house. In studies examined in the literature review, POCISs were commonly purchased from NyaExposMeter, Sweden (e.g. Cerveny et al., 2018; Harman et al., 2011). DGT devices are patented, manufactured, and distributed by DGT Research, UK.

To achieve a high-resolution temporal dataset, it is recommended that samplers in Configuration 3 are deployed six times per year. As in Configuration 2, SPMDs should remain in place for 2 months, while POCISs and DGTs should be deployed for 1 month. The 1-month deployment period for POCISs and DGTs aligns with the most used protocols identified in Section 1 (Section 1.6.3 and 1.6.4). Although the pre-cleaning of these samplers is not necessary, the use of field and procedural blanks is still recommended.

2.2.7.3 COIs to be analysed – methodology and analytical suites

SPMDs should be extracted and analysed as described in Configuration 2. Extraction of analytes from POCISs can be carried out by transferring the sorbent to an empty solid phase extraction (SPE) column, followed by extracting the analytes using a mixture of organic solvents. For instance, a 1:1:8 mixture of methanol:toluene:dichloromethane, has been used to analyse pharmaceuticals (Grabicová et al., 2022), PFAS (Cervený et al., 2018, 2016), and personal care products (Tumova et al., 2017). Metals can be extracted from DGT samplers by soaking in 6 M nitric acid for at least 24 hours (Schøyen et al., 2017).

Based on the results of the literature review, the measurement of substances such as PFAS analysed by POCISs, and metals using DGT samplers, are considerably less well-studied than hydrophobic organic contaminants in passive samplers and biota. For instance, PFAS and non-OC pesticides were investigated in only a small number (10% and 6% respectively) of studies identified. Consequently, relating the occurrence of these compounds in passive samplers to concentrations measured in biota may require a greater amount of method development than for some more well studied substances such as PCBs. In addition, there are also increased uncertainties and complexities in interpreting the results. Unlike more commonly used PSDs such as silicone samplers or SPMDs, where contaminants reach equilibrium between the water and the receiving phases, both DGT samplers and POCISs are sorbent-based, and therefore operate primarily in the first-order kinetic regime (Section 1.7.3). Thus, the frameworks based on equilibrium partitioning applied to SPMDs, cannot be readily applied to DGT samplers or POCISs. This presents an additional challenge when comparing concentration data from these samplers with levels in biota.

For instance, compound-specific sampling rates of POCISs are required in order to estimate time-weighted average concentrations in water. However, these rates can vary significantly with environmental factors such as flow rates or temperature (Wang et al., 2020). Therefore, the levels of contaminants in POCISs, e.g. PFAS, in studies identified in the literature review were reported in units of mass per sampler, e.g. ng sampler⁻¹ (e.g. Aro et al., 2021; Cervený et al., 2016). An advantage of this reporting method is that uncertainties with conversion to water and biota concentrations are eliminated.

Calculation of time-weighted average water concentrations may not be required for POCISs to act as a proxy for biota monitoring in some cases. For instance, Cervený et al. (2016) found that sum PFAS concentrations were strongly correlated with those in fish liver tissue when using units of ng POCIS⁻¹ ($R^2 = 0.88$, $p < 0.05$), although concentrations of individual PFAS were not significantly correlated. In theory, these relationships could act as the basis for predictive models of levels of certain groups of PFAS (and potentially other hydrophilic contaminants) in biota, for example through regression analysis. However, this would require extensive validation of model equations using field-collected data of contaminants in co-deployed PSDs and biota. The associated uncertainties would also need to be determined. Model development would need to be carried out for all species of interest, in addition to validation in different freshwater and saline environments.

Therefore, POCISs may be able to act as a reasonable proxy for PFAS uptake in biota at a lower resolution (i.e. sum concentrations), but considerable uncertainties remain in their application at the level of individual compounds (see Section 1.8.7 for further information).

Given the diversity of PFAS and their ionic nature, these compounds behave differently to many other classes of organic compound groups. This can add further challenges to the interpretation of the relationships between their occurrence in PSDs and biota (Section 1.8.7). Additionally, little appears to be known about the suitability of PSDs as proxies for biota for many other hydrophilic compounds captured by POCISs, such as some pharmaceuticals, pesticides, and personal care products (Section 1.3).

Metals analysis by DGT samplers were reported in only one study identified in the literature review (Sections 1.6.4 and 1.8.8). Although the results appeared promising (e.g. the relationship between metals in the DGTs and in mussels was generally linear), no formal statistical analysis was carried out (Schøyen et al., 2017).

In Configuration 3, each sampler type requires different extraction, clean-up and instrumental techniques for the identification and quantification of the compounds of interest. This implies that a greater number of analytical instruments are required, although it is likely the Environment Agency may already possess the necessary equipment and technical capability for these methodologies. In addition to the analysis of SPMD extracts, LC-MS/MS and inductively coupled plasma mass spectrometry (ICP-MS) would be required to analyse the extracts of POCISs and DGT samplers respectively. Therefore, whilst expanding the analytical suite to cover a wider range of compounds offers clear advantages, it also introduces limitations and uncertainties associated with the analysis of these less commonly studied compound groups.

2.3 Conclusions

This section describes three distinct PSD configurations designed to monitor a range of contaminants both in freshwater and saline environments. The specifics of each of the configurations discussed in this section are informed by evidence gathered in the literature review (Section 1). Key factors such as the compound groups to be analysed, PSD type, deployment frequency and duration, seasonality were optimised within low, medium and high-cost categories.

Configuration 1 represents the most affordable configuration, using silicone PSDs to investigate POPs. The targeted suite in Configuration 1 includes PCBs, PAHs, OCs, and PBDEs. Collectively, these contaminants represent 56% of the chemicals which are currently monitored in biota by the Environment Agency, and 46% of the COI list. PSDs in this configuration are suggested to be deployed for 6 months at a time, providing a biannual insight into the levels of these contaminants in the aquatic environments where they are installed.

Configuration 2 builds on Configuration 1 by employing the use of SPMDs to monitor all contaminants included in Configuration 1 (PCBs, OCs, PBDEs, PAHs) along with additional hydrophobic organic compounds. This expanded suite includes other POPs, namely BFRs, dioxins, and furans. This analysis covers for 81% of the COIs currently monitored in biota by the Environment Agency, and 68% of the COI list. The incorporation of PRCs in Configuration 2 enables enhanced temporal resolution compared to Configuration 1. This approach involves four annual deployments of 2 months each, thereby providing seasonal information about contaminant concentrations. Consequently, Configuration 2 incurs higher costs than Configuration 1 due to the increased deployment frequency and associated analytical requirements.

Configuration 3 represents the most expensive option, offering the widest analytical scope and highest temporal resolution. This configuration combines SPMDs in addition to POCISs and DGT samplers, enabling comprehensive monitoring across multiple contaminant classes. The combined deployment of these three PSD types would enable the measurement of nearly all (99%) of the COIs monitored in biota by the Environment Agency, and 85% of those on the COI list. Configuration 3 delivers the most highly resolved temporal dataset, with six deployments per year: 1 month for POCISs and DGTs) and 2 months for SPMDs.

These three configurations offer distinct starting points from which the Environment Agency could begin to support biota monitoring programmes.

Section 3: Analysis workflow

Executive Summary

This section describes a workflow that can be used to estimate the equilibrium concentration of a chemical in an aquatic organism using the concentration measured in a passive sampling device (PSD) operating under equilibrium conditions. This approach is based on equilibrium partitioning models and begins by estimating the freely dissolved equilibrium concentration of a chemical in water. These values are then used to estimate the equilibrium concentration of a chemical in biota. Uncertainties associated with these estimations are also discussed.

The workflow presented offers several advantages including ease of use, applicability to most compounds of interest, and a relatively well-established body of literature of partition coefficients. However, uncertainties remain, including assumptions of equilibrium, suitability of partition coefficients, biological processes (e.g. bioaccumulation, bioconcentration, and biotransformation), and limitations in the workflow application to some hydrophilic compounds.

3.1 Introduction

Polymer-based PSDs, such as silicone rubbers or SPMDs, take up chemicals whilst they are deployed in water. Initially, chemical uptake by the PSD follows linear uptake kinetics (Allan et al., 2025; Joyce and Burgess, 2018; Vrana et al., 2005). As the concentration of the chemical in the PSD increases, it gradually approaches equilibrium. Eventually an equilibrium state will be reached between the PSD and the surrounding water, meaning that the concentration of the chemical in the passive sampler stabilises, assuming that the concentration in the water is relatively constant (Vrana et al., 2005).

A partition coefficient represents the ratio of the concentration of a compound between two phases at equilibrium. Partition coefficients are available in the scientific literature (see Section 1.2.3) and various chemical property databases. The robustness and reliability of partition coefficients will affect the accuracy of calculating chemical concentrations between matrices, so selection of reliable values is important. Where possible, recognised test guidelines should be followed when generating partition coefficients, such as those published by the Organisation for Economic Co-operation and Development (OECD). The partition coefficients relevant for interpreting passive sampling data include:

- The polymer-water partition coefficient (K_{pw}), which represents the equilibrium partitioning of a compound between a polymer (i.e. a polymer-based passive sampler) and water.
- The lipid-polymer partition coefficient (K_{lp}), which represents the equilibrium partitioning of a compound between a lipid (for instance fish oil or triolein) and a passive sampler. This coefficient that can be used as a proxy for lipid partitioning in biota.
- The lipid-water partition coefficient (K_{lw}), which represents equilibrium partitioning between a lipid and water. This coefficient can be calculated from K_{pw} and K_{lp} .

Partition coefficients can be used to estimate the freely dissolved concentration of a contaminant in water or the lipid concentration in biota from the equilibrium amount measured in a PSD (Figure 4).

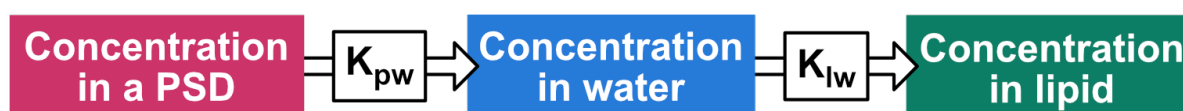


Figure 4: Overview of the relationships between the equilibrium concentrations in different media, including the associated partition coefficients used to estimate the equilibrium concentrations.

Here, we provide a guide for estimating the concentration of a chemical in an aquatic organism using the equilibrium concentration measured in a PSD. We also outline how to estimate the freely dissolved concentration of a chemical based on PSD data. The

workflow presented in Section 3.2.3 builds upon previously reported calculations (e.g. Allan et al., 2025; Joyce and Burgess, 2018). Finally, the uncertainties associated with these estimations are discussed.

3.2 Estimation of contaminant concentrations

The accuracy of the workflow relies on several assumptions, for instance:

- The chemical has reached equilibrium by the end of the deployment period.
- The concentration of the chemical in the water remained relatively constant over the deployment period.
- The partition coefficients are accurate and suitable for the chemical in question.
- No significant PSD degradation or biofouling occurred.

Additional uncertainties, in addition to potential mitigation strategies, are detailed in Section 3.3.

The equations presented in Section 3.2.3 are applicable to hydrophobic chemicals only, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), brominated flame retardants (BFRs), organochloride pesticides (OCs), and polychlorinated dioxins and furans (PCDDs and PCDFs). Taken together, these hydrophobic compounds comprise 81% of the chemicals of interest that are currently monitored in aquatic biota by the Environment Agency. The use of equilibrium partition models is not readily applicable to the passive sampling devices used to measure hydrophilic or ionic chemicals (e.g. PFAS, metals, see Section 3.3.4 for further details).

3.2.1 From passive sampling devices to water

For those chemicals that have reached equilibrium by the end of passive sampler deployment period (i.e. when the samplers are removed from the aqueous environment), the freely dissolved concentration of each chemical in the water at equilibrium (C_w) can be estimated by dividing the concentration of the chemical in the passive sampler at equilibrium (C_p) by the polymer-water partitioning coefficient for that chemical (K_{pw}).

$$C_w = \frac{C_p}{K_{pw}} \quad (1)$$

The details of the terms required for Equation 1 are shown in Table 8.

Table 8: Description of the terms used in Equation 1.

Term	Description	Units
C_w	Freely dissolved concentration of the chemical in water at equilibrium	ng L ⁻¹
C_p	Concentration of the chemical in passive sampler at equilibrium	ng kg ⁻¹
K_{pw}	Polymer-water partitioning coefficient for that chemical	L kg ⁻¹

3.2.2 From water to biota

Concentrations of hydrophobic organic contaminants in biota are commonly reported as lipid-weighted values, as lipids are the primary storage tissues for these contaminants. Therefore, the equilibrium concentration of a contaminant in lipids, derived from the concentration in water, can be used as a proxy for the levels of that chemical in aquatic biota.

The equilibrium concentration of an organic contaminant in (biota) lipids (C_l) can be estimated as the product of the concentration of the chemical in water (C_w), derived from Equation 1, and the lipid-water partition coefficient (K_{lw}).

$$C_l = C_w \times K_{lw} \quad (2)$$

If K_{lw} is known for the compound in question, then Equation 2 can be used. However, K_{lw} values are not readily available in the literature, and therefore are typically calculated using the lipid-polymer (K_{lp}) and polymer-water (K_{pw}) partition coefficients (Allan et al., 2025).

$$K_{lw} = K_{lp} \times K_{pw} \quad (3)$$

Combining Equations 2 and 3 yields Equation 4, which estimates the concentration of an organic chemical in biota lipids at equilibrium.

$$C_l = C_w \times K_{lp} \times K_{pw} \quad (4)$$

The details of the terms required for Equations 2-4 are shown in Table 9.

Table 9: Description of the terms used in Equations 2-4.

Term	Description	Units
C_l	Concentration of the chemical in lipids at equilibrium	ng kg ⁻¹
C_w	Freely dissolved concentration of the chemical in water at equilibrium	ng L ⁻¹
K_{lw}	Lipid-water partitioning coefficient for that chemical	L kg ⁻¹
K_{lp}	Lipid-polymer partitioning coefficient for that chemical	kg kg ⁻¹
K_{pw}	Polymer-water partitioning coefficient for that chemical	L kg ⁻¹

3.2.3 Summary workflow

A schematic overview of the data workflow detailed in Sections 3.2.1 and 3.2.2 is shown in Figure 5.

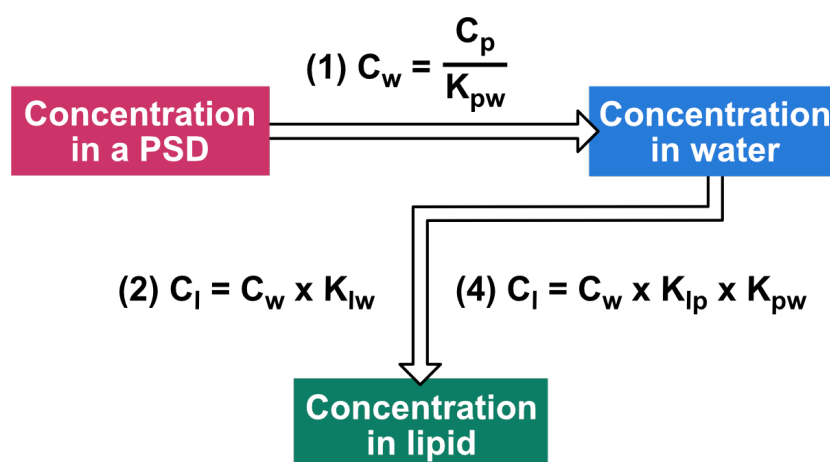


Figure 5: The workflow required to estimate the equilibrium concentrations of a chemical in water and aquatic biota using the equilibrium concentration measured in a passive sampling device (PSD). Numbers in paratheses refer to the Equations detailed in Sections 3.2.1 and 3.2.2. For details of the terms in each equation, including the units, see Sections 3.2.1 and 3.2.2.

3.3 Uncertainties and mitigations

3.3.1 Assumptions of equilibrium

A possible source of uncertainty in the estimates of biota concentrations using the workflow described in Section 3.2.3 arises from the assumption that all compounds have achieved equilibrium between the water and the PSD by the end of deployment period. For compounds with $\log K_{ow}$ of ~ 4 , equilibrium can be quickly reached (i.e. in a matter of days or weeks, Vrana et al., 2019). In contrast, compounds with higher $\log K_{ow}$ values (e.g. highly chlorinated PCB congeners) it can take longer to reach equilibrium (Joyce and Burgess, 2018; Vrana et al., 2019). For instance, Mäenpää et al. (2015) found that equilibrium of 16 PCBs (ranging from tri- to hepta-chloro, with $\log K_{ow}$ as high as 8.6, was only reached after ~ 5 months (147 days).

For compounds that have not reached equilibrium, using the workflow in Section 3.2.3 to calculate their concentration in water and lipid will likely lead to underestimation of these estimates. Assumptions of equilibrium become increasingly valid over longer deployment times (e.g. 3-6 months), although longer deployment times may result in increased biofouling or PSD degradation, both of which may vary depending on the environment in which they are deployed. Therefore, the deployment time is a compromise between allowing sufficient time for the compounds of interest to attain equilibrium, whilst also minimising the biofouling and/or PSD degradation. This uncertainty can be partially mitigated by deploying passive samplers over varying exposure durations and monitoring changes in concentrations of accumulated chemicals over time (e.g. Mäenpää et al., 2015). Conducting pilot experiments under different environmental scenarios (e.g. freshwater/saline, high/low flow, and across different seasons) would allow for an assessment of the timescales over which equilibrium is reached.

If PRCs are used in equilibrium trials, the amount of each PRC that is released over the deployment period can be used to estimate water concentrations based on first-order kinetics. The use of PRCs is relatively well-established, having been applied in both saline (e.g. Carlsson et al., 2018; Schøyen et al., 2017) and freshwater (e.g. Smedes et al., 2020; Wernicke et al., 2022) environments. Additionally, there are a number of well-documented workflows that describe how to use PRC data to estimate water concentrations, for instance see Smedes and Booij (2012), Joyce and Burgess (2018), and Booij et al. (2025). Further information regarding the application, selection, and the workflows for estimating COI concentrations in water can also be found in Section 1.7.3.

3.3.2 Accuracy and suitability of partition coefficients

A further source of uncertainty in the estimation of C_w and C_l arises from the fact that there is variation in determined K_{pw} and K_{lp} values among studies according to how they have been derived. Furthermore, in addition to the properties of the polymer and the chemical in question, additional factors such as temperature, salinity, and the presence of dissolved organic matter can all influence the solubility of a compound in the water phase, and consequently affect partition coefficient values (Jonker, 2022). The accuracy and relevance of the K_{pw} and K_{lp} values used in each environment will affect the overall uncertainty of estimates of C_w and C_l . For example, uncertainties in saline C_w estimates will be lower when K_{pw} values derived for saline conditions are used, compared to applying standard K_{pw} values typically determined for freshwater systems.

Measuring chemical parameters of the water itself can enhance the interpretation and provide a better understanding of relationships between biota and passive sampler concentrations. Uncertainties regarding the suitability and accuracy of partition coefficients can be partially mitigated by measuring key environmental parameters such as water temperature, levels of dissolved organic matter (DOM), ionic strength, and pH.

For instance, high levels of DOM have been shown to alter the relative bioavailability and SPMD-availability of different PAHs in the model organism *Daphnia magna* (Gourlay et al., 2005; see Section 1.8.4 for further details). Contaminants can also bind to particulates, e.g. clay and silt, which may limit the ability of passive samplers to capture those particulate bound contaminants. High turbidity may also have an impact on bioavailability. The pH of water may influence the behaviour and uptake of certain contaminant classes, particularly metal ions or ionic compounds such as PFAS.

Although no studies were identified in the literature review that used additional field data to specifically improve estimation of contaminant levels in biota, there are instances where such information could potentially aid data interpretation. For example, the sensitivity of the estimations of C_w and C_l to the variable values for partition coefficients could be assessed by carrying out the estimations using multiple different literature values if available for K_{pw} and K_{lp} . For some groups of compounds, the relative homogeneity and predictability of their physicochemical properties (e.g. PAHs, PCBs) could potentially enable class-based predictions of the effects of water quality parameters on PSD uptake, although for more diverse compound groups, e.g. PFAS, this will be more complex. Further research would be required to understand the extent that these additional parameters account for deviations between predicted values and concentrations measured in biota.

3.3.3 Bioaccumulation, bioconcentration, and biotransformation

There are inherent limitations and uncertainties associated with using freely dissolved concentrations (C_w) to estimate concentrations in biota (C_b). While freely dissolved concentrations may act as a reasonable proxy for organisms at lower trophic levels that accumulate chemicals primarily through direct exposure to contaminated water (i.e. bioconcentration), this approach may be less reliable for organisms at higher trophic levels that accumulate contaminants primarily through their diet (i.e. bioaccumulation), or through ingestion of compounds bound to particulates or dissolved organic matter (see Bourgeault and Gourlay-Francé, 2013; Schøyen et al., 2017). In addition, there are biotransformation processes within the biota that can alter certain chemicals following their uptake, a mechanism that cannot be mimicked in PSDs. These aspects are discussed extensively in the context of individual studies in Sections 1.8.3-1.8.8.

Whilst it is challenging to account for the differences between bioconcentration and bioaccumulation routes, an understanding of the trophic position and feeding behaviour of the species of interest is useful in providing context for interpreting results.

3.3.4 Application to hydrophilic compounds and metals

The workflow outlined in Section 3.2.3 is applicable to most of the COIs that the Environment Agency routinely monitor in biota (>80%), as these hydrophobic compounds can be effectively sampled using polymer-based PSDs (e.g. silicone samplers or semi-permeable membrane devices, SPMDs). However, a minority of contaminants cannot be sampled using equilibrium-based devices. For instance, PFAS and metals are typically measured using POCISs and DGTs. Comparisons between the levels of hydrophilic organic compounds and metals between PSDs and biota are considerably less well-studied than those of hydrophobic organic compounds (see Sections 1.3 and 1.8).

Unlike more commonly used PSDs such as silicone samplers or SPMDs, where contaminants reach equilibrium between the water and the receiving phases, both DGT samplers and POCISs are sorbent-based. This means that they operate primarily in the first-order kinetic regime (Section 1.7.3). This presents an additional challenge when comparing concentration data from these samplers with those in biota.

For instance, POCIS sampling rates of different compounds are required in order to estimate time-weighted average concentrations in water. However, these rates can vary significantly with environmental factors such as flow rates or temperature (Wang et al., 2020). The application of PRCs to POCISs has generally been less common than for other PSD types. For instance, none of the POCIS studies identified in the literature review used PRCs. The interaction of compounds such as pharmaceuticals and pesticides with

the sorbent used in POCISs is complex (Harman et al., 2011), and many compounds are too strongly bound to the sorbent to act as PRCs (Liu et al., 2013). Consequently, studies that derived aqueous contaminant concentrations from POCIS data have also used laboratory calibrations as an alternative to in-field PRC use (e.g. Cervený et al., 2016).

The equilibrium partition models discussed in 3.2 also cannot be readily applied to DGT samplers. However, there are several alternative approaches that can be used to estimate the concentration of metals in water using data from DGTs (e.g. Jiménez-Piedrahita et al., 2017).

Whilst the workflow described in 3.2 cannot be readily applied to DGT samplers or POCISs, there is some evidence suggesting that, at least in some cases, reasonable correlations of levels of hydrophilic contaminants in PSDs and biota can be observed without estimating concentrations in water. For instance, Gonzalez-Rey et al. (2011) reported that the correlation of sum metal concentrations in mussels and PSDs (“artificial mussels”) co-deployed in the same cages in marine waters were significantly strongly correlated after 2, 3, and 4 months of sampling (see Section 1.8.8). Additionally, Cervený et al. (2016) found that the summed PFAS concentrations were strongly correlated with those in fish liver tissue when using units of mass per sampler, ng POCIS⁻¹ ($R^2 = 0.88$, $p < 0.05$), although concentrations of individual PFAS were not significantly correlated (see Section 1.8.7).

In theory, these relationships could act as the basis for predictive models of levels of certain groups of hydrophilic contaminants in biota, e.g. through regression analysis. However, this would require very extensive validation of model equations using field-collected data of contaminants in co-deployed PSDs and biota. The associated uncertainties would also need to be calculated. This model development would need to be carried out for all species of interest, in addition to validation in different environments (e.g. freshwater and saline).

3.4 Summary

This section describes a partition coefficient-based workflow that can be used to estimate the equilibrium concentration of hydrophobic organic contaminants in biota using equilibrium concentrations measured in passive sampling devices. The workflow also enables the estimation of freely dissolved equilibrium concentrations of hydrophobic organic contaminants in water.

Key advantages of this workflow include ease of use, applicability to the majority of the compounds of interest, and the availability of a relatively well-established literature of partition coefficients. However, several uncertainties remain, including assumptions of equilibrium, suitability of partition coefficients, biological processes (e.g. bioaccumulation, bioconcentration, and biotransformation), as well as limitations in its application to hydrophilic compounds.

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Appendices

Appendix 1

The 111 chemicals of interest (COIs) investigated in this study; 'Species monitored' refers to those species monitored in the Environment Agency monitoring programmes; C = crayfish; M = mussels; F = fish; fw = freshwater; sw = saline water; chemicals which are not routinely monitored are denoted by '-' and have been identified as of interest for future biota/PSD chemical monitoring.

Group	Chemical Compound	CAS	Species monitored
PAH	Anthracene	120-12-7	C (fw), M (sw)
	Pyrene	129-00-0	M (sw)
	Benzo(g,h,i)Perylene	191-24-2	C (fw), M (sw)
	Indeno(1,2,3-cd)pyrene	193-39-5	C (fw), M (sw)
	Benzo(b)Fluoranthene	205-99-2	C (fw), M (sw)
	Fluoranthene	206-44-0	C (fw), M (sw)
	Benzo(k)Fluoranthene	207-08-9	C (fw), M (sw)
	Chrysene	218-01-9	M (sw)
	Benzo(a)Pyrene	50-32-8	C (fw), M (sw)
	Benzo(a)anthracene	56-55-3	M (sw)
	Phenanthrene	85-01-8	M (sw)
	Naphthalene	91-20-3	M (sw)
PBDE	BDE 209	1163-19-5	-
	BDE 99	60348-60-9	F (sw)

Group	Chemical Compound	CAS	Species monitored
	BDE 47	32534-81-9	F (sw)
	BDE 47	32534-81-9	F (fw), M (sw)
	BDE 154	36483-60-0	F (fw), M (sw), F (sw)
	BDE 28	39635-85-7	F (fw), M (sw)
	BDE 99	40538-88-1	F (fw), M (sw)
	BDE 28	41318-75-6	F (sw)
	BDE 100	60348-60-9	F (fw), M (sw), F (sw)
	BDE 153	60348-61-0	F (fw), M (sw)
	BDE 154	68631-49-2	F (sw)
PCB	PCB 118	31508-00-6	F (fw), M (sw), F (sw)
	PCB 169	31508-06-2	F (fw)
	PCB 138	31508-11-9	M (sw), F (sw)
	PCB 180	3168-64-3	M (sw), F (sw)

Group	Chemical Compound	CAS	Species monitored
	PCB 167	32537-33-8	F (fw)
	PCB 114	32537-34-9	F (fw)
	PCB 81	32537-35-0	F (fw)
	PCB 156	32537-36-1	F (fw)
	PCB 105	32537-37-2	F (fw)
	PCB 77	32537-38-3	F (fw)
	PCB 123	32537-46-4	F (fw)
	PCB 157	32774-47-5	F (fw)
	PCB 28	3387-41-5	M (sw), F (sw)
	PCB 189	36466-07-8	F (fw)
	PCB 101	53671-42-6	M (sw), F (sw)
	PCB 126	57465-28-8	F (fw)
	PCB 153	6805-21-4	M (sw), F (sw)

Group	Chemical Compound	CAS	Species monitored
	PCB 52	74472-68-7	M (sw), F (sw)
BFR	g-HBCDD	134237-50-6	F (fw), F (sw)
	b-HBCDD	134237-51-7	F (fw), F (sw)
	TTB-TAZ	25713-60-4	-
	HBCDD (total)	3194-55-6	F (fw), M (sw), F (sw)
	a-HBCDD	3194-57-8	F (fw), F (sw)
	TBBPA	79-94-7	-
Dioxins and Furans	2378-TCDD	1746-01-6	F (fw)
	OCDD	3268-87-9	F (fw)
	1,2,3,7,8-Pentachlorodibenzo-p-dioxin	40321-76-4	F (fw)
	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	57653-85-7	F (fw)
	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	57653-87-9	F (fw)
	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	57653-89-1	F (fw)

Group	Chemical Compound	CAS	Species monitored
	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	57653-91-5	F (fw)
	WHOTEQ Lower Bound (dioxins and furans)	N/A	F (fw)
	Octachlorodibenzofuran (OCDF)	39001-02-0	F (fw)
	2,3,7,8-Tetrachlorodibenzofuran (2378TCDF)	51207-31-9	F (fw)
	1,2,3,7,8-Pentachlorodibenzofuran	57117-30-3	F (fw)
	2,3,4,7,8-Pentachlorodibenzofuran	57117-31-4	F (fw)
	1,2,3,7,8,9-Hexachlorodibenzofuran	57653-84-6	F (fw)
	1,2,3,6,7,8-Hexachlorodibenzofuran	57653-86-8	F (fw)
	1,2,3,4,7,8-Hexachlorodibenzofuran	57653-88-0	F (fw)
	1,2,3,4,7,8,9-Heptachlorodibenzofuran	57653-90-4	F (fw)
	1,2,3,4,6,7,8-Heptachlorodibenzofuran	57653-92-6	F (fw)
	2,3,4,6,7,8-Hexachlorodibenzofuran (234678HxCDF)	60851-34-5	F (fw)
Industrial	4-(1-Methyl-1-phenylethyl)-N-[4-(1-methyl-1-phenylethyl) phenyl]aniline	10081-67-1	-

Group	Chemical Compound	CAS	Species monitored
	Bis(2,6-diisopropylphenyl)carbodiimide	2162-74-5	-
Pesticide (OC)	HCB	118-74-1	F (fw), M (sw), F (sw)
	a-HCH	319-85-7	F (fw), M (sw)
	b-HCH	319-87-9	F (fw), M (sw)
	d-HCH	319-91-5	F (fw), M (sw)
	DDT	50-29-3	M (sw)
	g-HCH	58-89-9	F (fw), M (sw)
	PCB	608-93-5	F (fw), M (sw)
	DDD	72-54-8	M (sw)
	DDE	72-55-9	M (sw)
	Heptachlor	76-44-8	F (fw), M (sw), F (sw)
Personal care product	Galaxolide (HHCB)	1222-05-05	-
Pesticide	cis-Heptachlor epoxide	1024-56-2	F (fw), M (sw), F (sw)
	trans-Heptachlor epoxide	1024-57-3	F (fw), M (sw), F (sw)
	Quinoxifen	124495-18-7	F (fw)
	Tributyl Tin	56-35-9	F (fw), M (sw)

Group	Chemical Compound	CAS	Species monitored
PFAS	Perfluorooctane sulfonate (PFOS)	1763-23-1	F (fw), F (sw)
	Perfluorooctanoic acid (PFOA)	335-67-1	F (fw), F (sw)
	PFHxS	355-46-4	-
	PFNA	375-95-1	-
Pigment	Perylene-3,4:9,10-tetracarboxydiimide	81-33-4	-
Rodenticide	Difethialone	104653-34-1	-
	Bromadiolone	28772-56-7	-
	Chlorophacinone	3691-04-5	-
	Difenacoum	56073-07-5	-
	Brodifacoum	56073-10-0	-
	Coumatetralyl	5836-29-3	-
	Warfarin	81-81-2	-
	Diphacinone	82-66-6	-
	Flocoumafen	90035-08-8	-
Solvent	Hexachlorobutadiene (HCBD)	87-68-3	F (fw), M (sw), F (sw)

Group	Chemical Compound	CAS	Species monitored
UV filter	2-Ethylhexyl salicylate	118–60-5	-
	UV-350 (2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol)	36437-37-3	-
Antioxidant	4,4'-methylene bis(dibutyldithiocarbamate)	10254-57-6	-
	Tris(4-nonylphenyl, branched and linear) phosphite (TNPP) with $\geq 0.1\%$ w/w of 4-nonylphenol, branched and linear (4-NP)	Not available	-
Metal	Lead	7439-92-1	F (fw), M (sw), F (sw)
	Mercury	7439-97-6	F (fw), M (sw), F (sw)
	Nickel	7440-02-0	M (sw), F (sw)
	Silver	7440-22-4	M (sw)
	Arsenic	7440-38-2	M (sw), F (sw)
	Cadmium	7440-43-9	F (fw), M (sw), F (sw)
	Chromium	7440-47-3	M (sw), F (sw)
	Copper	7440-50-8	M (sw), F (sw)
	Zinc	7440-66-6	M (sw), F (sw)

Group	Chemical Compound	CAS	Species monitored
	Selenium	7782-49-2	M (sw), F (sw)

Appendix 2

Search strings used in the academic literature searches of Web of Science.

Initial search

passive sampl* AND (biota* OR fish* OR mussel*) AND (water* OR surface water* OR river* OR lake* OR groundwater* OR estuar* OR saline* OR marine* OR aquatic*) AND (PBT* OR hydrophob* OR POP* OR persistent organic pollutant* OR metal*)

Expanded search

passive sampl* AND (biota* OR fish* OR mussel* OR crayfish*) AND (water* OR surface water* OR river* OR lake* OR groundwater* OR estuar* OR saline* OR marine* OR aquatic*) AND (PBT* OR hydrophob* OR POP* OR persistent organic pollutant* OR metal* OR PAH* OR PCB* OR PBDE* OR OCP* OR PFAS* OR antioxidant* OR flame retardant* OR dioxin* OR furan* OR pesticide* OR rodenticide* OR lead OR mercury OR nickel OR silver OR arsenic OR cadmium OR chromium OR copper OR zinc OR selenium)

Partition coefficient search

passive sampl* AND partition* AND coefficient* AND (water* OR surface water* OR river* OR lake* OR groundwater* OR estuar* OR saline* OR marine* OR aquatic*) AND (PBT* OR hydrophob* OR POP* OR persistent organic pollutant* OR metal* OR PAH* OR PCB* OR PBDE* OR OCP* OR PFAS* OR antioxidant* OR flame retardant* OR dioxin* OR furan* OR pesticide* OR rodenticide* OR lead OR mercury OR nickel OR silver OR arsenic OR cadmium OR chromium OR copper OR zinc OR selenium)

Appendix 3

Number of studies that carried out targeted analysis of different chemical classes in biota and PSDs in water. A study that used a non-target screening approach (Castro et al., 2022) is not represented in the table. Many studies analysed >1 class of chemical, and/or investigated both freshwater and saline samples, therefore the percentages for each type of study sum to >100%.

Chemical class	All studies		Freshwater studies		Saline studies	
	n	%	n	%	n	%
PCBs	17	55	13	59	8	53
PAHs	15	48	9	41	9	60
OCs	11	35	8	36	5	33
PBDEs	5	16	4	18	2	13
PFAS	3	10	3	14	0	0
Alkylphenols	3	10	2	9	3	20
Personal care products	3	10	3	14	1	7
Metals	2	6	0	0	2	13
OPFRs	2	6	1	5	2	13
Dioxins	2	6	1	5	1	7
Pesticides	2	6	2	9	1	7
Furans	2	6	1	5	1	7
Non-target screening	1	3	1	5	1	7
Brominated flame retardants	1	3	0	0	1	7
Pharmaceuticals	1	3	1	5	0	0

Chemical class	All studies		Freshwater studies		Saline studies	
	n	%	n	%	n	%
Organotins	1	3	0	0	1	7
Extractable organofluorine	1	3	1	5	0	0
UV filters	1	3	1	5	1	7
Antimicrobials	1	3	1	5	1	7
Industrial compounds	1	3	1	5	0	0

Appendix 4

Overview of passive sampling devices used in the identified literature studies. Some studies used more than one type of sampler, and/or investigated both freshwater and saline samples, therefore the percentages for each type of study sum to >100%.

Deployment durations were calculated only where specific times were given in the studies. If a study had multiple deployments, these were included in the calculation of the summary statistics, with all datapoints weighted equally. The “Studies” column refer to the study numbers in the “Summary – studies and COIs.xlsx” spreadsheet.

Class	Overview of sampler	Number of studies (% of studies)			Compounds studied (number of studies)	Sampler source	Typical extraction procedure	Cost	Deployment duration (mean, median, range)	PRC use reported?		Studies
		All	Fw	Sa						Yes	No	
Silicone	Typically a sheet of silicone-based polymer (e.g. polydimethylsiloxane, PDMS). Analytes are sorbed directly in/to the polymer.	11 (35%)	7 (32%)	7 (47%)	PCBs (8), PAHs (7), OCs (6), PBDEs (3), OPFRs (2), Personal care products (2), Pesticides (2), Organotins (1), BFRs (1), Alkylphenols (1), UV filters (1), Antimicrobials (1), Industrial (1)	Studies commonly report using PDMS sheets which appear to be either purchased in the required dimensions or cut in-house. They are sourced from silicone manufacturers, and do not appear to be dedicated PSD suppliers/manufacturers.	Two main methods are reported: 1) Soxhlet extracted, followed by solid-phase column clean-up; 2) shake with organic solvent, followed by no clean-up or solid-phase column clean-up.	£	88, 84, 4-183	8 (73%)	3 (27%)	8, 11, 12, 15, 20, 22, 23, 24, 26, 28, 30

Class	Overview of sampler	Number of studies (% of studies)			Compounds studied (number of studies)	Sampler source	Typical extraction procedure	Cost	Deployment duration (mean, median, range)	PRC use reported?		Studies
		All	Fw	Sa						Yes	No	
SPMD (semi-permeable membrane device)	One of the first types of passive sampler to be applied to monitor water. Typically comprises an LDPE lay-flat tube containing ~1 mL of lipid (most commonly triolein) to act as the receiving phase for analytes.	10 (32 %)	8 (36 %)	5 (33 %)	PAHs (7), PCBs (6), OCs (5), PBDEs (2), Alkylphenols (2), Dioxins (1), Furans (1), Non-target screening (1)	Can be purchased from a PSD supplier/manufacturer (e.g. from NyaExposmeter AB, Sweden), or, less commonly, prepared in-house.	Shake with an organic solvent (e.g. heptane) for 24-72 hours. Some studies report further clean-up steps, e.g. solid-phase column clean-up.	£-£££	31, 28, 7-60	7 (70 %)	3 (30 %)	1, 2, 3, 4, 6, 7, 14, 17, 19, 29

Class	Overview of sampler	Number of studies (% of studies)			Compounds studied (number of studies)	Sampler source	Typical extraction procedure	Cost	Deployment duration (mean, median, range)	PRC use reported?		Studies
		All	Fw	Sa						Yes	No	
POCIS (polar organic chemical integrative sampler)	Developed by the USGS in order to sample less hydrophobic compounds than those that SPMDs are capable of capturing (typically < logK _{OW} of 3, or those with an ionic nature). Comprises a solid sorbent sandwiched between sheets of polyethersulfone membrane, within a steel disk. The water passes through the device, with analytes captured by the sorbent.	8 (26 %)	7 (32 %)	2 (13 %)	PFAS (3), Pharmaceuticals (1), Alkylphenols (1), Non-target screening (1), Personal care products (1), Extractable organofluorine (1)	The majority of studies report that POCIS were purchased from a PSD supplier/manufacturer (e.g. from NyaExposmeter AB, Sweden).	Solid sorbent removed from samplers and placed in a solid phase extraction column. Analytes are eluted using solvents, and filtered before analysis.	££-£££	20, 21, 7-42	0 (0 %)	8 (100 %)	6, 13, 18, 19, 21, 25, 27, 29

Class	Overview of sampler	Number of studies (% of studies)			Compounds studied (number of studies)	Sampler source	Typical extraction procedure	Cost	Deployment duration (mean, median, range)	PRC use reported?		Studies
		All	Fw	Sa						Yes	No	
LDPE (low density polyethene)	A sheet of low density polyethene plastic. Analytes are sorbed directly in/to the sheet.	3 (100%)	3 (100%)	-	PCBs (3)	Studies commonly report using LPDE sheets which appear to be either purchased in the required dimensions or cut in-house. They are sourced from plastic manufacturers, and do not appear to be dedicated PSD suppliers/manufacturers.	Shake with hexane for 24 hours, acidify to remove impurities, take hexane layer for analysis, dry over sodium sulfate.	£	121, 123, 28-181	0 (0%)	3 (100%)	9, 11, 16

Class	Overview of sampler	Number of studies (% of studies)			Compounds studied (number of studies)	Sampler source	Typical extraction procedure	Cost	Deployment duration (mean, median, range)	PRC use reported?		Studies
		All	Fw	Sa						Yes	No	
Artificial mussel	A Perspex tube containing a chelating ligand suspended in artificial seawater. The artificial seawater/ligand solution is capped by a polyacrylamide gel. The tube is then capped with perforated plastic caps to allow uptake of metal ions from the surrounding water into the artificial seawater/ligand solution.	1 (3%)	-	1 (7%)	Metals (1)	The artificial mussel was developed by Wu et al. (2007). Does not appear to be manufactured and therefore would require in-house preparation.	Metals extracted by rinsing with water and addition of nitric acid, followed by filtration.	££-£££ (not manufactured, but would require extensive in-house preparation)	70, 70, 28-112	0 (0%)	1 (100%)	5

Class	Overview of sampler	Number of studies (% of studies)			Compounds studied (number of studies)	Sampler source	Typical extraction procedure	Cost	Deployment duration (mean, median, range)	PRC use reported?		Studies
		All	Fw	Sa						Yes	No	
DGT (diffusive gradients in thin films)	Typically comprises a binding gel, a diffusive gel, and a filter membrane encased in a plastic cylinder with an opening at one end (which the filter membrane is exposed to). Metals are collected in the binding gel.	1 (3 %)	-	1 (7 %)	Metals (1)	DGT samplers are proprietary, and are supplied by DGT Research, UK.	Metals extracted by leaving in nitric acid for at least 24 hours.	££	28, 28, 28- 28	0 (0 %)	1 (10 0%)	15

Class	Overview of sampler	Number of studies (% of studies)			Compounds studied (number of studies)	Sampler source	Typical extraction procedure	Cost	Deployment duration (mean, median, range)	PRC use reported?		Studies
		All	Fw	Sa						Yes	No	
POM (polyoxy methylen e)	A sheet of polyoxymethylene plastic. Analytes are sorbed directly in/to the sheet.	1 (3 %)	-	1 (7 %)	PCBs (1), Dioxins (1), Furans (1)	Studies commonly report using POM sheets which appear to be either purchased in the required dimensions or cut in-house. They are sourced from plastic manufacturers, and do not appear to be dedicated PSD suppliers/manufacturers.	Shake in hexane for 48 hours, pass through 3 solid-phase clean-up columns.	£	120, 120, 120- 120	0 (0 %)	1 (100 %)	10

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