



## Passive sampling in support of biota monitoring of hydrophobic substances under the Water Framework Directive

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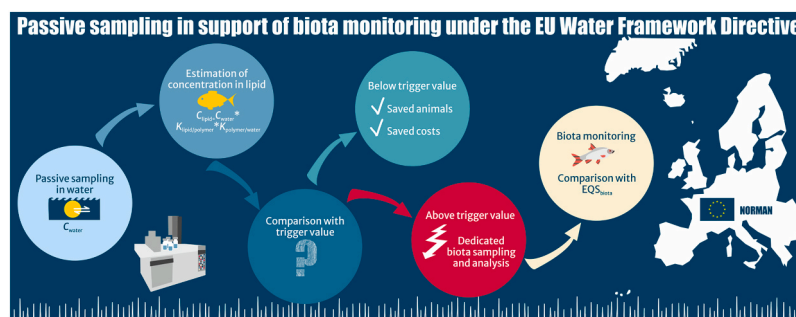
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### HIGHLIGHTS

- Chemical activities of contaminants are commonly higher in water than fish.
- PS as a conservative proxy for hydrophobic contaminant concentrations in fish.
- WFD compliance assessment for chemicals with  $EQS_{biota}$  can be done with PS.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Passive sampling  
Biota monitoring

### ABSTRACT

This paper presents an approach to apply aquatic passive sampling (PS) in regulatory chemical water quality monitoring in Europe. Absorption-based passive sampling is well developed and suitable for the sampling of hydrophobic chemicals, some of which are European Water Framework Directive priority substances with

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<https://doi.org/10.1016/j.jhazmat.2024.136672>

Received 28 September 2024; Received in revised form 19 November 2024; Accepted 25 November 2024

Available online 26 November 2024

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EQS  
Silicone rubber  
Tiered approach  
Priority substances

Environmental Quality Standards (EQS) derived for biota. Considering a chemical activity approach to chemical risk assessment, we propose equilibrium concentration in lipids (from passive water sampling) as a reference value for measured concentrations in biota. Through existing PS-fish datasets, we show a growing body of evidence supporting the use of lipid-based contaminant concentrations at equilibrium with water derived from PS as a conservative proxy of levels of these chemicals in fish. We propose a procedure that includes PS as a first, animal-free screening step of a tiered approach, followed by more conventional fish analyses when PS indicates these are needed to confirm EQS<sub>biota</sub> exceedance. This paper reviews fish-passive sampler datasets, provides a reasoning for the proposed procedure and discusses how to broadly put it into monitoring practice. PS offers the possibility of well-defined standardised monitoring approaches that can help overcome the natural variability challenges associated with measurements in biota across member states and simplify EQS<sub>biota</sub> compliance.

## 1. Introduction

Passive sampling (PS) methods have been developed and used for the monitoring of contaminants in water for three decades [1–4]. A variety of passive sampling devices at different stages of maturity regarding routine use in chemical monitoring are available for the sampling of contaminants with a wide range of physico-chemical properties. Many studies have been conducted on the calibration of passive samplers to characterise mass transfer and partitioning phenomena that govern chemical uptake from water into passive samplers [3,5,6].

The Water Framework Directive 2000/60/EC (WFD) was adopted in 2000 as a framework for the protection of all surface waters across Europe and defines a strategy against chemical pollution of surface water bodies [7]. One key objective of the WFD is to achieve good chemical status of all surface waters, defined as concentrations of priority substances and priority hazardous substances below their respective environmental quality standards (EQS). While the scope here is European, this work is likely relevant to other parts of the world and legislation.

A growing number of studies have investigated the applicability of PS in regulatory chemical monitoring programmes [2,3,8–10]. Milestones in the progress towards a more generalised use of PS include establishment of a global aquatic passive sampling network [11–13], the publication of an ISO standard on PS in water [14], the completion of several interlaboratory comparison studies [11,15–18], the reference to PS in various guidance documents published within the WFD common implementation strategy [19,20].

In this context, the NORMAN network has been a driving force bringing together experts, practitioners and environmental managers in an open discussion forum [2] and organising PS intercomparison studies or the application of PS in the field [17,21]. A first expert group meeting held in Brno (Czech Republic) in 2013 was dedicated to establishing links between WFD EQS and water monitoring data obtained by PS. This was followed by a joint NORMAN network-AQUAREF workshop in Lyon (France) in 2014, presenting the state-of-the-art and defining a roadmap and recommendations for further NORMAN actions to help with the implementation of PS in environmental monitoring [2]. In 2016, the NORMAN cross-working group on PS organised a workshop to initiate discussions about a common data repository for PS, to explore alternatives and stimulate research projects to combine PS and biota monitoring for substances with EQS in biota (EQS<sub>biota</sub>, Table 1). NORMAN activities have been a key contribution towards the use of passive sampling in regulatory settings and an outcome of this work is our proposal for the implementation of PS in the application of biota monitoring, initially as a first animal-free screening step in a tiered approach.

In this paper, we briefly review European regulatory monitoring in biota, focusing on the reasons for using biota and compliance assessment against EQS<sub>biota</sub>. Next, we introduce an approach to use passive samplers in water in support of chemical monitoring in biota. This is followed by presenting concrete examples for WFD priority substances where PS was conducted alongside chemical monitoring in fish. Finally, we discuss and demonstrate the application of the proposed tiered approach and consider the next step in its implementation.

We focus on a subgroup of hydrophobic pollutants (Table 1) which account for the majority of priority and river basin-specific WFD-regulated substances for which an EQS<sub>biota</sub> has been defined. In organisms, these compounds are known to accumulate by partitioning in all hydrophobic areas of cells as lipid bilayers and in lipid-rich organs such as liver and adipose tissues. The main driving force for a spontaneous accumulation of these compounds in both biota and in PS is the same, namely compound hydrophobicity. Mimicking the physical accumulation of contaminants in organism lipids by partitioning into PS presents the foundation for PS application in support of regulatory chemical monitoring in biota. Although EQS<sub>biota</sub> have also been set for perfluorooctanesulfonate (PFOS) and mercury, these two compounds do not accumulate in biota via hydrophobic partitioning into lipids, therefore they are outside the remit of this paper.

**Table 1**

Water Framework Directive priority substances with EQS<sub>biota</sub> [22], the protection goal, the matrix to be used and the related EQS<sub>biota</sub> ( $\mu\text{g kg}^{-1}$  wet weight (ww)). Note: Mercury and PFOS are not included in this table as they bioaccumulate by more complex mechanisms than hydrophobicity-driven partitioning.

Priority substance	Protection goal of EQS <sub>biota</sub>	Matrix for EQS <sub>biota</sub>	EQS <sub>biota</sub> ( $\mu\text{g kg}^{-1}$ ww)
Hexachlorobenzene (HCB)	Human health via consumption of fish and fishery products	Fish fillet	10
Hexachlorobutadiene (HCBd)	Predators (birds and mammals) vulnerable to secondary poisoning	Whole fish	55
Polybrominated diphenyl ethers (PBDEs) (Sum BDE-28, 47, 99, 100, 153, 154)	Human health via consumption of fish and fishery products	Fish fillet	0.0085
Fluoranthene	Human health via consumption of fish and fishery products	Crustaceans Molluscs	30
5-,6-ring polycyclic aromatic hydrocarbons (PAHs) (Benzo[a]pyrene as a marker)	Human health via consumption of fish and fishery products	Crustaceans Molluscs	5
Hexabromocyclododecane (HBCDD) (sum of three isomers)	Predators (birds and mammals) vulnerable to secondary poisoning	Whole fish	167*
Dioxins and dioxin-like compounds	Human health via consumption of fish and fishery products	Fish fillet Crustaceans Molluscs	0.0065 TEQ <sub>2005</sub>
Heptachlor and heptachlor epoxide	Human health via consumption of fish and fishery products	Fish fillet	0.0067
Dicofol	Predators (birds and mammals) vulnerable to secondary poisoning	Whole fish	33

\* A reduction of EQS<sub>biota</sub> to 90  $\mu\text{g kg}^{-1}$  ww has been proposed [23].

## 2. Regulatory monitoring in biota

### 2.1. Biota monitoring for compliance assessment under the Water Framework Directive

Although the majority of EQS values are set for water, Directive 2013/39/EU, which amended the Directive 2008/105/EC, also includes EQS that apply to biota for a number of bioaccumulative chemicals that may pose a threat to aquatic wildlife and/or human health through the ingestion of contaminated prey or the consumption of contaminated food. Chemical monitoring in biota and especially fish is particularly relevant for substances that are persistent and likely to remain in the aquatic environment for a long time or for substances continuously emitted to the aquatic environment resulting in a wide distribution and continuous exposure of aquatic biota.

EQS<sub>biota</sub> should generally be reported as tissue concentrations in prey organisms, mainly fish, or, in some cases, where fish can biotransform some less persistent compounds such as polycyclic aromatic hydrocarbons (PAHs), lower trophic level (TL) monitoring is completed in organisms such as molluscs and crustaceans (see Table 1).

In order to achieve representative sampling, multiple individuals of a selected biota species must be collected and analysed. The time-integrative character of biota samples allows reduction of sampling frequency to once per year, in contrast to spot sampling of water, which needs to be performed 12 times per year, due to the more variable concentrations. Annual biota monitoring is also a consistent option to minimise the effects of seasonality-induced variations in contaminant levels in biota. Another aspect of the priority substance integration and resulting bioaccumulation is that concentrations in biota are much higher than in water, thus simplifying the sampling and chemical analysis with limited need of analyte concentration before analysis.

### 2.2. Compliance monitoring with biota: gaps and challenges

The publication of the EQS Directive 2013/39/EU implied that greater harmonisation of biota monitoring strategies and procedures among member states was needed. Besides decisions on the selection of species and tissue (see Table 1), biota sampling strategies need to take into account biological aspects such as sex, fish size or age, sampling period, etc., robust species abundance over time (to avoid effects on populations), species mobility, local or regional environmental hydrological and climate characteristics of water bodies and the representativeness of sampling sites for diffuse or point source pollution. Ultimately, variations in local conditions and selected species will limit comparability at large spatial scales, in addition to changes in habitats that might be related to climate change or other pressures [24].

The European Union published guidance documents under the Common Implementation Strategy of WFD (CIS-WFD) initiative to support the harmonisation of sampling and analytical protocols [25], monitoring strategies and compliance checking. The choice of species is intentionally kept flexible to account for diversity of habitats, the wide variety of freshwater species across Europe and the need to protect endangered species [19]. According to the EQS Directive 2013/39/EU, contaminant concentrations may be monitored in an alternative, lower-TL biota taxon or another matrix instead of the specified taxon (usually a fish) (Table 1). This situation may occur when target fish species are absent at a sampling location or found at very low abundance or cannot be sampled for ethical reasons (repeated sacrifice of vertebrate species). Furthermore, lower TL aquatic invertebrates (wild-caught or caged animals) can provide different information than fish in that they are less mobile, so their contaminant burdens are typically more representative of a specific area. They often display lower metabolic activity and resulting elimination rates, and owing to their smaller size, steady-state accumulation can be reached relatively rapidly [26], albeit being less explicit with regards biomagnification. The use of invertebrates or molluscs as monitoring matrices instead of fish

mandatory for PAHs and is a permitted option for polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (PCBs) (Table 1) [22].

There are multiple sources of natural variability that affect contaminant concentrations in the fish, including biological parameters as well as factors such as seasonality, feeding and health status of the fish. In fact, size-dependent concentration variability within a fish species can be even higher than intra species variability collected at the same site, this being particularly relevant for some biomagnifying substances [27]. The variability in contaminant concentrations is sought to be minimised through normalisation strategies referring to a standard “European fish” with 5% lipids and a trophic level of 4 [28]. The most common normalisation procedure for hydrophobic substances is the normalisation of the contaminant concentrations to the lipid content of the sample [19]. Fish monitoring data of the German Danube showed that normalisation to lipids was able to reduce inter-species and intra-species variability for some hydrophobic bioaccumulative compounds, such as PCDD/Fs, PCBs, hexachlorobenzene (HCB) and polybrominated diphenyl ethers (PBDEs) [29].

Another source of variability is the choice of the tissue to be analysed (e.g. fillet or whole fish). The choice of the matrix should be completed according to the protection goal, i.e. whole fish if the goal is the protection of predators (via secondary poisoning) and fish fillet if the goal is the protection of humans (via fish consumption) (Table 1). For example, hexachlorobutadiene (HCB), hexabromocyclododecane (HBCDD) and dicofol should be analysed in whole fish, while HCB, PBDEs, dioxins and heptachlor should be measured in the fish fillet. The guidance document on biota suggests that analysing contaminants in fillets and then converting data to whole fish concentrations by using conversion factors from fillet to whole fish which have been recently proposed for some priority substances [29–32] may be feasible. However, recent studies for HBCDD showed that the conversion can introduce substantial uncertainty [33]. The option of using human health-based EQS for environmental assessment is particularly pointed out by OSPAR’s Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment [34]. The Joint Research Centre of the European Union published various recommendations to improve contaminant assessment within the Marine Strategy Framework Directive (MSFD) [35]. One example under discussion is the adoption of the EQS<sub>secondary poisoning</sub> for HCB, HBCDD, and dioxins.

Priority substance concentrations in fish at TL 4 are selected as the basis for assessing compliance with the EQS<sub>biota</sub> [28]. Data obtained for fish of lower TLs as well as in crustaceans and molluscs can be corrected by using trophic magnification factors (TMFs). This conversion also enables to include molluscs in WFD monitoring, for which monitoring programmes are already in place in some coastal areas (e.g. Mussel Watch Programmes). The TMF correction requires ecosystem-relevant contaminant-specific TMF values. Much work has been conducted to estimate TMFs in aquatic environments. A robust TMF determination ought to (i) be based on the selection of species with a minimum TL range of 2.0 (e.g. 2.0–4.0), (ii) ideally use a balance of lower-TL versus higher-TL organisms that are linked by diet through the food web, (iii) make use of determination of the  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  stable isotopes, (iv) detect the target compounds in all samples above the detection limit and ensure that all organisms are collected within an appropriate sampling period (e.g. one season) [36]. In practice, this approach needs experimental determinations of stable isotopes of nitrogen and carbon for site-specific TL derivation, because the use of literature-based TL is often not realistic [37]. Further uncertainty arises from the choice of the correct trophic web baseline species (e.g. pelagic, littoral or benthic) in the experimental derivation of TL from stable isotope analysis in biota species from water-body characteristic trophic webs [38]. Moreover, the 3.4 ‰, commonly used  $\Delta^{15}\text{N}$  representing the shift in  $\delta^{15}\text{N}$  typical for one TL, is also a consensual value, and it is estimated to be associated with a variance of approximately 1 ‰ [39], and alternative values have been suggested [40]. As a pragmatic compromise that avoids extensive

chemical analyses, Rüdél and coworkers reviewed available TMFs and selected generic TMF values valid for all water bodies [41]. Overall, the application of site-specific or generic TMFs remains vague. The determination of water-body specific TMFs is laborious, time-consuming and hence not financially realistic within regular monitoring activities. Thus, accepting a high uncertainty in TMFs will undoubtedly affect decision processes regarding EQS exceedances. In order to interpret the concentrations of priority substances against quantitative criteria, Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) developed Environmental Assessment Criteria (EACs) for a limited list of contaminants in biota (shellfish and fish). EACs can be considered analogous to WFD EQS, but some EQS<sub>biota</sub> are recognized as too restrictive and not fully adapted to the marine environment [42].

### 3. Passive sampling in support of chemical monitoring in biota under the WFD

#### 3.1. Theoretical aspects

PS for hydrophobic chemicals is based on partitioning into polymeric materials such as silicone rubber or low-density polyethylene which have a high capacity to sorb the chemicals of interest [3]. For these substances, polymer-water partition coefficients ( $K_{pw}$ ), defined as the equilibrium partitioning concentration in the polymer over that in water, are high which implies a spontaneous pre-concentration of these chemicals from water to the polymer. During exposure, contaminants diffuse into the polymer and accumulate in the sampler by absorption. Initially, this accumulation is linear and proportional to the freely dissolved concentration in water through a substance-specific sampling rate  $R_s$ , which expresses the equivalent volume of water extracted by the sampler per unit of time. If samplers are left in water for a sufficiently long period of time, the concentration of the chemical in the sampler with enough exposure time, reaches equilibrium partitioning with that in water. This equilibration time increases with hydrophobicity of the chemicals of interest, and for very hydrophobic contaminants, equilibration is not expected for reasonable PS exposure timeframes (days to months). The dissipation of performance reference compounds (PRCs) that follow the same mass transfer and partitioning mechanism as the target compounds but are not present in the environment and are loaded into the samplers prior to exposure, enables the estimation of contaminant exchange kinetics between water and the polymer and the extent to which equilibrium is reached [43,44]. Factors that influence this uptake include (a) compound physicochemical properties (mainly hydrophobicity and diffusivity), (b) environmental conditions such as water turbulence, temperature, salinity, fouling, and (c) sampler configuration such as polymer type, sampler mass and surface area [4,45–51].

A crucial aspect, particularly for compounds that can potentially reach equilibrium, is the availability and quality of  $K_{pw}$  values for chemicals of interest [52–59]. Likewise, it has to be ensured that diffusion coefficients in the polymer are sufficiently high to minimise the formation of concentration gradients inside the polymer and to assure that transfer across the water-boundary layer controls chemical uptake, which in turn allows using PRCs for simple uptake modelling [44]. For compounds in the linear phase of uptake, knowledge of their accurate partition coefficients  $K_{pw}$  is less critical than that of the PRCs used for estimating  $R_s$ . This is because the calculation of  $C_w$  for these compounds relies on the estimation of  $R_s$  and the exposure time and much less on the sampler's sorption capacity, i.e.  $K_{pw} \times$  sampler mass [3]. Guidelines for the determination of  $K_{pw}$  values have been published [52] and can be followed to obtain measurements with adequate quality assessment. Once  $K_{pw}$  values have been derived accurately for one polymer, cross calibration of other polymers with this reference polymer facilitates the estimation of  $K_{pw}$  for other polymers [54]. Nowadays, the most comprehensive database of  $K_{pw}$  is for silicone polymers such as AlteSil™ (Altec, UK, though production has been phased out) or SSP (Specialty

Silicone Products, Inc., USA) with values available for close to 100 different compounds [53–56,58,60]. However, experimental  $K_{pw}$  values are not available for all substances amenable to biota monitoring (Table 1), i.e. PCDD/Fs and HBCDD. Most recently,  $K_{pw}$  values were obtained for chlorinated paraffins [61].

#### 3.2. PS in support of EQS<sub>biota</sub> compliance

PS for nonpolar substances has the potential to be used for compliance monitoring and ultimately for comparison with WFD EQS. While passive samplers have been mentioned as complementary tools in guidance documents of the WFD Common Implementation Strategy [19, 20,25], an approach for use in a compliance assessment context is needed.

Given the challenges with natural variability of biota matrices, the use of a well-defined standardised PS matrix to sample these chemicals will have some advantages. The repeatability associated with the estimation of freely dissolved concentrations from co-deployed passive samplers in water is generally high (with variations under 10 %, [62]). The variability exhibited by different laboratories involved in the analysis of hydrophobic organic compounds in silicone rubber extracts during the QUASIMEME intercomparison (DE-13) was not higher than that achieved during the analysis of the same contaminants in biota samples [63,64].

The chemical activity approach has been proposed before as a common metric linking risk assessment and management, exposure analysis, toxicity or hazard assessment [65,66]. Relationships between equilibrium concentrations in passive samplers, water and fish are illustrated in Fig. 1. Here, chemical activity ( $a$ ) is defined as the concentration of the chemical in a matrix divided by its solubility  $S$  in that matrix:

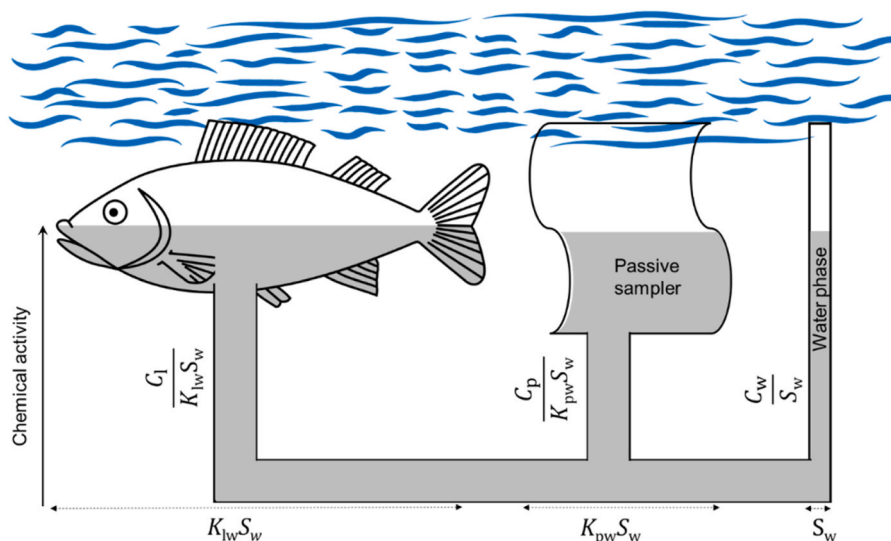
$$a = \frac{C_p}{K_{pw}S_w} = \frac{C_l}{K_{lw}S_w} = \frac{C_w}{S_w} \quad (1)$$

with  $C_p$ ,  $C_l$ ,  $C_w$  the concentration in the polymer ( $\text{ng g}^{-1}$ ), in lipids ( $\text{ng g}^{-1}$ ) and freely dissolved in water ( $\text{ng L}^{-1}$ ),  $K_{pw}$  and  $K_{lw}$ , the polymer-water and lipid-water partition coefficients ( $\text{L kg}^{-1}$ ), respectively and  $S_w$  the solubility of the chemicals in water ( $\text{ng L}^{-1}$ ).  $K_{lw}$  is calculated from  $K_{pw}$  and Eq. (1) uses liquid state concentrations and solubilities therefore refer to subcooled liquid solubilities for solid chemicals.

Over the last decade, there has also been a focus on measuring lipid-polymer partition coefficients  $K_{lp}$ , for a variety of combinations of polymer, chemicals and lipid types [54,56,67–69]. Overall, because of similar solubility of nonpolar chemicals in neutral lipids and polymers such as silicone or LDPE, the range of  $K_{lp}$  is rather narrow. As an example,  $K_{lp}$  for AlteSil™ silicone rubber (SR) ranged from 1.9 for hexachloro-1,3-butadiene to 33 for PCB169 or  $65 \text{ g g}^{-1}$  for benzo[ghi]perylene [68]. For PCB congeners,  $K_{lp}$  values spanned a factor of 5 while  $K_{ow}$  values span over three orders of magnitude for the different congeners. In addition, most persistent organic pollutants (POPs) such as PCBs only show minor differences in  $K_{lp}$  for different types of neutral lipids. At present,  $K_{pw}$  and  $K_{lp}$  are not available for all WFD priority substances with EQS<sub>biota</sub>. In general,  $K_{lp}$  are available for PCBs and other chlorinated compounds such as pentachlorobenzene (PeCB) and HCB, dichlorodiphenyltrichloroethane (DDTs), hexachlorocyclohexanes (HCHs), PAHs and PBDEs [56,68–70]. Minor differences in  $K_{lp}$  observed are unlikely to explain differences in bioaccumulation in different organisms caused by the capacity of these lipids [70] but do support the use of a consensus chemical-specific  $K_{lp}$  in our proposed methodology.

Multiplying  $K_{lp}$  and  $K_{pw}$  results in a lipid-water partition coefficient,  $K_{lw}$ . This  $K_{lw}$  also represents an abiotic predictor of a bioconcentration factor. The product of  $K_{lw}$  and  $C_w$  estimated from PS with the polymer used to derive  $K_{lw}$  enables the calculation of a contaminant concentration in (biota) lipids at equilibrium with the concentration in water [71], ( $C_{l=w}$ ), that can be used to compare contaminant levels in abiotic





**Fig. 1.** Chemical activity of organic pollutants in various compartments (fish, absorption-based passive sampler and water) at equilibrium. The meaning of symbols is explained in the Section 3.2.

environmental compartments with those in biota:

$$C_{l=w} = K_{lw}C_w = K_{lp}K_{pw}C_w \quad (2)$$

Comparing the level of a chemical in biota (chemical activity expressed as a concentration on a lipid basis,  $C_{l-biota}$ ) with  $C_{l=w}$  (Eq. (2)) can be done through an activity ratio ( $a_{biota}/a_{water}$ ):

$$\frac{a_{biota}}{a_{water}} = \frac{C_{l-biota}}{C_{l=w}} = \frac{C_{l-fish}}{K_{lp}K_{pw}C_w} \quad (3)$$

An activity ratio below 1 indicates a contaminant level in biota lower than what could be expected from equilibrium partitioning with the media the organism is living in, and vice versa.

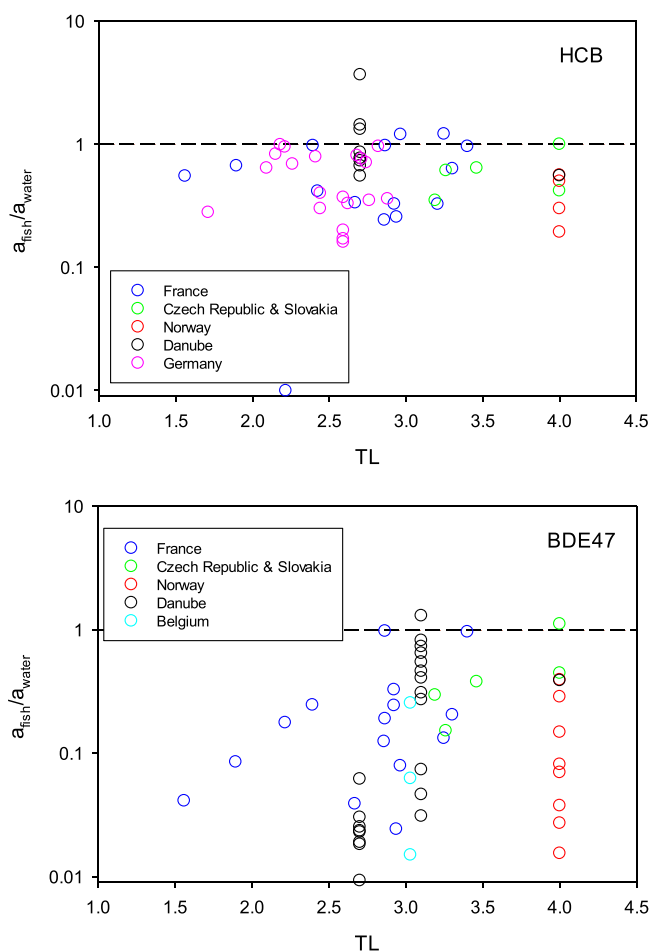
The earliest comparisons of this kind were made between levels of PCBs in sediments with those in fish living above these sediments [71–75]. These comparisons consistently indicated that levels (or chemical activities) of contaminants were higher in sediments than those in fish. An advantage of comparing  $C_{l=sed}$  from sediments is that the PS in sediments can be done at equilibrium for most chemicals and therefore does not require knowledge of  $K_{pw}$  values since  $C_p$  at equilibrium is directly available. A disadvantage is that sediment is generally less relevant for the exposure of many (pelagic) species. In the last decade, bioaccumulation of selected contaminants in biota and particularly in fish has been interpreted with the help of PS in water [27, 76–78]. The chemical activity of the chemical in fish on a lipid basis can be compared with the chemical activity in water expressed as an equivalent contaminant concentration in lipids at equilibrium with that in water, with the same units to facilitate comparison (Fig. 1 and Eq. (3)). The uncertainty of the PS-based estimates of  $C_{l=w}$  will be the result of the uncertainty in  $K_{pw}$  values,  $K_{lp}$  values (Eq. (2)). Ideally, the chemical activity in fish tissues may best be derived from direct PS exposure to intact fish tissues such as muscle [49,73,79–82]. However, this is a relatively laborious procedure, and the available data indicate that the use of robust  $K_{lp}$  values enables accurate calculation of  $C_l$  from  $C_p$  at equilibrium with fish tissues and vice versa [27,49,73,79–82].

This means activity ratios based on PS in abiotic media like water, suspended particulate matter or sediments, and either biota monitoring (with concentrations reported on a lipid basis) or “in tissue” biota can be used. A comparison was made of chemical activity in water and in a variety of fish at two sites in the Czech Republic [27]. Surprisingly, for most chemicals under investigation, activities in biota generally were lower than those in water, despite the observation of biomagnification for some compounds [27]. For certain compounds such as PeCB, the

chemical activity in fish, regardless of its trophic position, was very close to that in water, indicating equilibrium or steady state, with no indication of biomagnification. For the BDE congener 154, the activity was orders of magnitude below that in water for fish at the lowest trophic positions and increasing to activity levels under one order of magnitude below that in water for fish at TL = 3.5–4.0. Despite these data indicating biomagnification, activities in fish remained below those in water. Plankton and algae at the lowest trophic levels are being ingested before they have reached equilibrium with the surrounding water.

#### 4. Highlights from studies of PS in support of biota monitoring in practice at national level

Studies involving the measurement of pollutant levels in water with PS alongside measurements in biota are undertaken with increasing frequency at the local to national level. The fish-PS comparison by Smedes et al. [27] showed for three freshwater sites in the Czech Republic and Slovakia with different levels of pollution that the chemical activity in 11 fish species of different TL (up to a TL of 4) only in exceptional cases exceeded the chemical activity in water. The study also showed that for fish at TL < 4 the chemical activity of hydrophobic substances with  $\log K_{ow} > 6$  progressively decreased in fish relative to the water phase. Assembling the results from other fish-PS studies can provide further evidence that justifies the implementation of PS for compliance assessment for pollutants with  $EQS_{biota}$ . Allan et al. [77] showed that no biomagnification of the WFD priority substance HCB could be observed for freshwater fish (e.g. Arctic char (*Salvelinus alpinus*), brown trout (*Salmo trutta*), European perch (*Perca fluviatilis*) or salmon (*Salmo salar*)) and the marine fish cod (*Gadus morhua*) and salmon (*Salmo salar*) used for chemical monitoring of surface waters in Norway. In addition, concentrations of HCB and PCB congeners in cod liver lipids from five sites along the Norwegian coast and in the North Atlantic Ocean [83–86] did not exceed concentrations in neutral lipids at equilibrium with the water, estimated from silicone PS (Fig. 2). This equilibrium status and lack of biomagnification were also apparent for HCB when comparing  $C_{l=sed}$  and  $C_{l-fish}$  in a Swedish lake [73]. Similar results were found for the Joint Danube Surveys in 2013 and 2019 [87–89] and are included in Fig. 2. In this case, common bleak (*Alburnus alburnus*), asp (*Aspius aspius*) and common bream (*Abramis brama*) were sampled and analysed at multiple sites in the Danube River where also PS was conducted. Ratios are presented for the WFD priority substances HCB and 2,2',4,4'-tetrabromodiphenyl ether (BDE47) which are



**Fig. 2.** Fish-water activity ratios for hexachlorobenzene (HCB) and brominated diphenyl ether BDE47, plotted as a function of the trophic level of the fish (TL) and calculated from lipid-based concentrations in fish and in model lipid at equilibrium with the water phase  $C_{l-fish}/C_{l-w}$ . A ratio above one (above the broken line indicates a higher chemical activity in the fish than in water while a ratio below one is indicative of a lower chemical activity in the fish than in water. Data are from field studies where PS and chemical monitoring of fish were conducted alongside [27,77,83,85,88–93]. Each data point may represent a different fish species (freshwater or marine), a different sampling location or sampling event. It further represents the average of measurements in multiple, composite fish or fish fillet/liver samples and replicate PS. TL values were either estimated from stable isotope analysis or from reference values for that species ([www.fishbase.se](http://www.fishbase.se)).

representative of hydrophobic neutral priority pollutants with no (HCB) or significant (BDE47) trophic magnification. Additional BDE47 data-points were obtained from a pilot study in Belgian rivers [90] and included in Fig. 2, together with HCB data from German rivers where PS was conducted alongside monitoring in eel (*Anguilla anguilla*), ide (*Leuciscus idus*), European perch, chub (*Squalius cephalus*), pike (*Esox lucius*) and asp [91]. Finally, a study was undertaken in France in 2018 with multiple PS exposures conducted at 15 freshwater monitoring sites in several river catchments where fish sampling was carried out with the same timeline [92]. For most of these sites and monitored fish species, the chemical activity of pollutants in fish were well below those in water (Fig. 2), similar as the observations considering sediment as discussed above. The data in Fig. 2 demonstrate that the chemical activity represented by  $C_{l-w}$  estimated from aqueous PS can be considered a conservative proxy for hydrophobic pollutant concentrations in fish used for chemical monitoring in European waters.

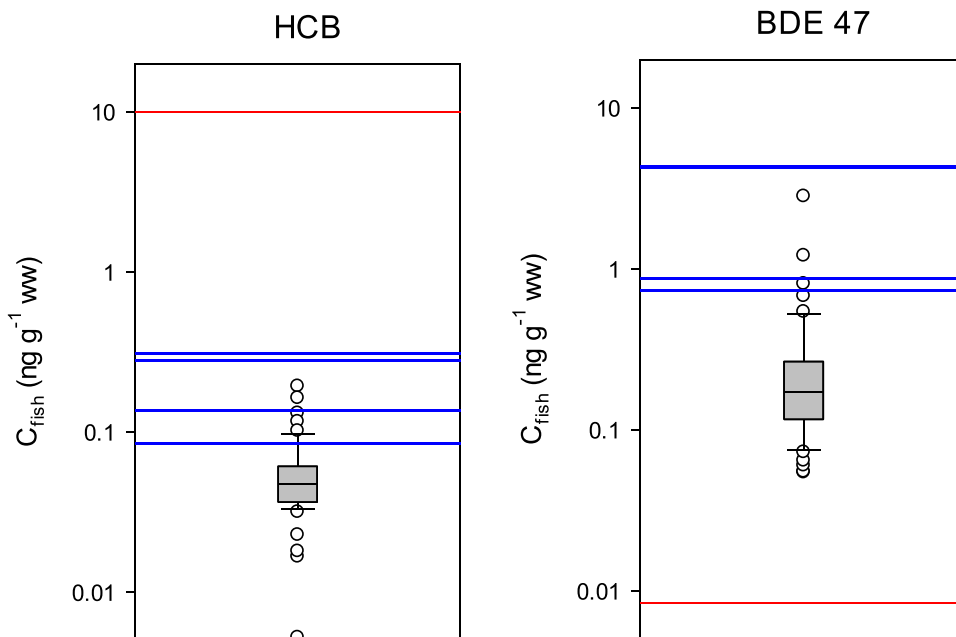
## 5. Tiered approach in practice

A regulatory use of PS-derived concentrations in water of hydrophobic substances for compliance testing against  $EQS_{water}$  is challenging since the latter have not been derived for freely dissolved concentrations measured with PS.  $EQS_{water}$  refers to the concentration in whole-water which differs from the dissolved concentration. Divergence between whole-water and dissolved concentrations will become more substantial with increasing contaminant hydrophobicity due to increasing sorption to suspended and dissolved organic matter [94]. Here we build upon a previous proposal for a tiered approach to incorporate PS into regulatory WFD monitoring [2]. For priority substances with  $EQS_{biota}$ , we propose a first, animal-free step for screening for absence/presence of chemicals of interest in water with PS. Based on these results, which include comparisons with relevant threshold values, water bodies can be identified where it is necessary to conduct biota monitoring. A similar approach was proposed based on PS in sediments [71] as well as in EU guidance documents to identify major problem areas or sources of exposure before implementation of biota monitoring [19]. This way, fish sampling would only be conducted at sites at risk of exceeding the  $EQS_{biota}$ . Only  $EQS$  exceedance in the first tier should trigger the sampling and analysis of fish.

A practical application of this tiered approach is given in Fig. 3 for the passive sampling/cod dataset of the inner Oslofjord (2012–2016) for HCB and BDE47. Yearly exposures of silicone rubber yielded the four blue lines. Freely dissolved concentrations were expressed as concentrations in lipids at equilibrium with the water phase,  $C_{l=w}$ . A cod fillet concentration on a ww basis was then estimated assuming a mean lipid content of the fillet of 0.34 %. This procedure recommended by ICES/OSPAR was also employed to estimate fillet concentrations from those measured in the liver of fish sampled in the inner Oslofjord as part of national monitoring programmes over this same 4-year period (boxplot on Fig. 3). Passive sampler-derived fillet concentrations were 50–100 times lower than human health-based  $EQS_{biota}$  of  $10 \text{ ng g}^{-1} \text{ ww}$  for HCB (red line on Fig. 3). PS hence indicated that actual HCB concentrations in fillet were likely to be well below  $EQS_{biota}$ . Considering that direct measurement in fillet was not possible, the boxplot of fillet concentrations calculated from liver data shows that PS-derived data are a suitable conservative proxy for fish data. PS-derived fish fillet concentrations of BDE47 indicated a clear exceedance of human health-based  $EQS_{biota}$  for this chemical. As shown in Fig. 3, the PS-derived concentrations also represented a suitable conservative proxy for liver-derived fillet concentrations that also exceeded  $EQS_{biota}$ . This case study demonstrates that a PS measurement as a first step in a tiered approach could avoid fish monitoring for HCB but imply the need to measure the levels in fish fillet for BDE47. Despite the  $EQS_{biota}$  for PBDEs being for the sum of six congeners, the comparison made here remains valid since already the concentration of a single congener (BDE47) clearly exceeded the threshold.

The empirical data shown here (Figs. 2 and 3) and published elsewhere [27,77] show:

- Since PS is based on a simple process of partitioning, measured chemical levels are not affected by biological variability, e.g. associated with feeding, reproduction, metabolism or active depuration that occurs in biota. No detection of a chemical in organism tissue does not automatically imply it was not exposed to it. In that context, PS-based measurements of contaminants in abiotic media are more straightforward for the assessment of external exposure of aquatic biota to chemicals and translating them into internal exposure data. This holds true especially since compliance monitoring currently focuses on priority substances, but not on their metabolites.
- The interpretation of pollutant levels in biota can be improved through chemical activity-based investigation of pollutant levels in the abiotic environment biota lives in using PS.

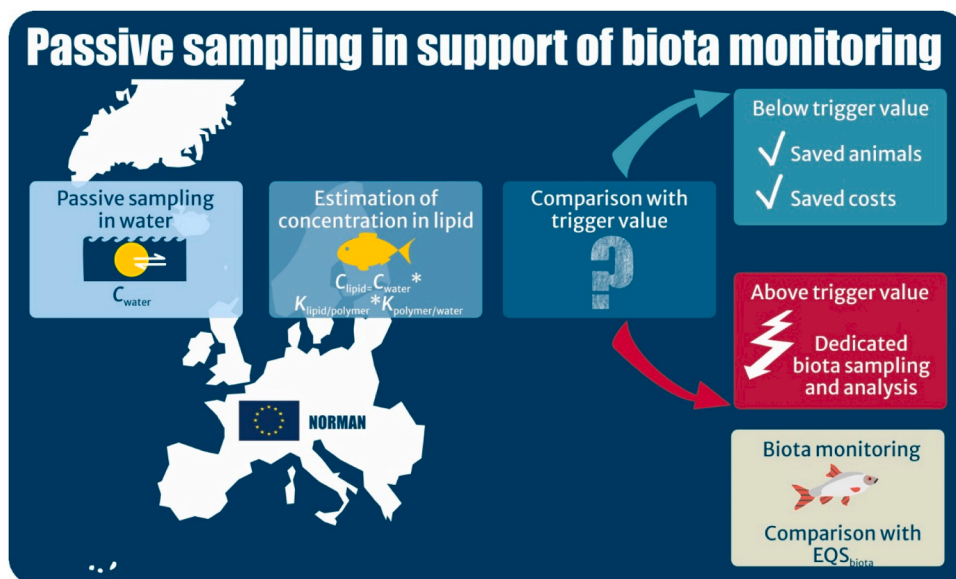


**Fig. 3.** Comparison of cod fillet concentrations of HCB and BDE47 ( $\text{ng g}^{-1} \text{ ww}$ ) estimated from silicone rubber passive sampling (blue lines) and measurement in cod liver (box plot) with human health-based WFD  $\text{EQS}_{\text{biota}}$  (red line) for the inner Oslofjord (Norway). Red lines represent  $\text{EQS}_{\text{biota}}$  values of 10 and  $0.0085 \text{ ng g}^{-1} \text{ ww}$  for HCB and BDE47, respectively. Blue lines represent yearly measurements with replicate silicone rubber samplers in the period 2012–2016. Boxplots are made from  $n = 58$  and  $55$  individual cod liver measurements of HCB and BDE47, respectively, over the period 2013–2016 [77,85].

- A direct comparison of chemical data from monitoring in the two matrices (i.e., biota and water) is feasible after conversion to the same units, namely to lipid-based concentrations. The differences in lipid-based concentrations in matrices under comparison quantifies the difference in pollutant level on a thermodynamic basis.
- Evidence from multiple field studies shows that PS-based  $C_{l \rightleftharpoons w}$  of hydrophobic chemicals are largely higher than or equal to  $C_l$  in freshwater or marine fish species. This observation may be used for chemical monitoring of the WFD for species with TL up to 4. Certain less hydrophobic substances such as PeCB and HCB tend to exhibit equilibrium conditions between water and fish, but in the case of most other investigated substances, despite apparent

- biomagnification, concentrations in fish with TL < 4 only rarely exceeded the abiotic  $C_{l \rightleftharpoons w}$  from PS.
- Some fundamental processes, likely occurring at the base of the food chain, hamper contaminants in species at the base of the food chain from reaching equilibrium with the water [27]. This lower-than-expected bioconcentration translates into contaminant levels at higher trophic levels (fish) that at most reach the activity in abiotic media like water or sediment. This lack of (understanding of the) connection between levels in biota and in water also challenges the use of biota to infer a chemical quality status for a water body.

Based on the information above, we suggest to further refine the tiered approach proposed previously [2] by including PS as the initial



**Fig. 4.** A proposed tiered approach including a PS step for compliance testing for hydrophobic non-ionised priority substances against WFD  $\text{EQS}_{\text{biota}}$ .

step, followed by a calculation of the equilibrium partitioning concentration of the contaminant in lipids with the water phase (Fig. 1). This approach facilitates a comparison with an  $EQS_{biota}$  expressed on a lipid basis or with a related trigger value. Setting this trigger value should consider the uncertainty in the PS-derived data and the safety factors already used to establish  $EQS_{biota}$  values. Considering the robustness of the empirical PS data, this step is expected to be sufficient to validate that pollutant levels expected in fish at an appropriate trophic level are below  $EQS_{biota}$ . If the conservative data from PS indicates exceedance of the trigger value, and therefore a risk that levels in biota may exceed  $EQS_{biota}$ , then biota monitoring can be conducted as the second tier (Fig. 4).

For compounds for which  $C_{l=w}$  are expected to be consistently above  $C_l$  in fish at a TL for which  $EQS_{biota}$  have been derived, a direct comparison of  $C_{l=w}$  and  $EQS_{biota}$  on a lipid basis is feasible. It is always possible to apply a safety factor by re-calculating  $C_{l=w}$  assuming that these data are representative of a TL lower than that for which  $EQS_{biota}$  has been derived. For example,  $C_{l=w}$  could be given a TL of 3.5 instead of 4.0 in the equation below if an appropriate TMF was known:

$$\log C_{l=w}^{TL(x)} = \log C_{l=w}^{TL(y)} + \{TL(x) - TL(y)\} \log TMF \quad (4)$$

In that case the safety factor will be equivalent to  $0.5 \log TMF$ . This could be done the opposite way, with no correction to  $C_{l=w}$  but an adjustment of the lipid-based  $EQS_{biota}$  instead, by substituting  $C_{l=w}$  in Eq. (4) by lipid-based  $EQS_{biota}$ . The challenge of this procedure is to select an appropriate TMF when considerable uncertainty is associated with literature TMFs and when acknowledging that TMFs are always ecosystem- or trophic foodweb-specific. Considering that underestimating the existing risk must be avoided, the proposed tiered approach may require the use of the highest published TMF values to consider the worst case of highest trophic magnification. In any case, the uncertainty in the inclusion of a safety factor in this proposed tiered approach does not exceed the uncertainty in the selection of TMF value.

## 6. Next steps

The last two decades of research and implementation of absorption-based PS with polymers such as SR have demonstrated the robustness of the PS-based measurements for hydrophobic non-ionised bio-accumulative substances [3]. The ability to calculate a contaminant concentration in lipids ( $C_{l=w}$ ) at equilibrium with the water is a powerful way to predict worse case scenarios of contaminant concentrations in fish. This comparison so far indicates that  $C_{l=w}$  can be used as conservative proxy [95] for the concentration of these chemicals in fish, regardless of their trophic levels. Further work should aim to expand this PS-fish dataset to further consolidate the use of PS-derived  $C_{l=w}$  as a conservative proxy for fish concentrations. This strategy is ready for implementation and considering the timeline for updating river basin management plans, targeting an implementation in 2027, appears feasible. In case more data are needed to support these relationships, we suggest conducting further PS-biota comparisons to increase the basis of the chemical activity ratio approach across Europe and increase the breadth of the chemicals. Expanding the dataset should consider including a wider variety of chemicals, e.g. by considering river basin-specific substances, additional fish species, lower and higher trophic level organisms or freshwater and marine monitoring locations. Extending this work to new chemicals may require laboratory-based measurement of  $K_{pw}$  and  $K_{lp}$  [56–58] or robust estimates if these are not available [96–98]. A further aspect to discuss in the application of a tiered approach is whether to use the (i) wet weight or lipid-based  $EQS_{biota}$ , and (ii) a TMF-based trigger value, as reference for comparison with  $C_{l=w}$ .

The application of chemical monitoring in fish across Europe for the WFD results in the need to sample several individuals of fish per monitoring location. Increasing the number of parameters or chemicals

that need to be investigated in turn requires more specimens to be sampled to obtain sufficient biomass for extraction and analysis. Partially replacing biota monitoring by PS can become a more standardised and legitimate alternative for ethical reasons and in a sustainability context.

In general, the risk of overlooking a chemical above  $EQS_{biota}$  level (risk of false negatives) can be limited with the application of appropriate and realistic safety factors in deriving trigger values. When considering the use of the tiered approach for compliance monitoring, the risk of false negative results, i.e. of judging a water body as unproblematic when it actually fails an  $EQS_{biota}$  needs to be assessed. In a tiered approach, potential false positives will be identified in a subsequent sampling of fish when PS has identified sites at risk of failing  $EQS_{biota}$ . The evidence so far shows that  $C_{l=w}$  is a conservative proxy for concentrations in fish (89 % and 96 % of chemical activity ratios plotted in Fig. 2 for HCB and BDE47, respectively are  $< 1$ ). Exceedances observed by Wernicke et al. [91,95] when comparing fish concentrations with  $C_{l=sed}$  from equilibration of PS with suspended riverine particulate matter (SPM) and with water were mostly for older fish, indicating that fish age/size likely plays a role in the ability of pollutant levels in fish to exceed levels in water for very hydrophobic compounds.

Aspects to consider with the application of PS as first step of a tiered approach include exposure times, seasonality and the number of deployment locations and depths needed to provide data of comparable spatial representativeness as for fish data. There are risks associated with the practical application of PS (such as losing the samplers), however recent large-scale projects such as under the AQUAREF umbrella in France have demonstrated that PS deployment on the scale of a European country is possible.

So far, we have addressed the use of PS-based  $C_{l=w}$  as a conservative proxy for levels in fish. However, we have not yet considered molluscs such as mussel that may be deemed suitable biota for the measurement of contaminants for which fish is not suitable [95,99,100]. Recently published data tend to support the SPM-based  $C_{l=sed}$  use as a conservative proxy for mussel concentrations as well for compounds such as PAHs [91]. PS-mussel datasets do exist [101] but a more global comparison of  $C_{l=w}$  and mussel concentrations has yet to be undertaken.

A practical strategy must be in place in order to bring PS to implementation in regulatory WFD monitoring in Europe. Considering that river basin management plans were updated in 2022 and require updating every 6 years, the next possibility for inclusion of PS in monitoring plans is in 2028. Steps that may be taken to enable PS implementation include drafting of PS guidance documents under the common implementation strategy of the European WFD, and a “one stop” shop assembling PS information, case studies, guidelines, reference/calibration values under the remit of NORMAN. Despite these obstacles, following a series of demonstration projects in France, a first concrete legislative advance at national level was made towards inclusion of PS into WFD monitoring [102]. It is also important to point out that the proposed methodology is likely applicable to other legislation that may require chemical monitoring in biota (e.g. MSFD in Europe) or other parts of the globe.

## 7. Conclusions

The use of fish for chemical monitoring in the aquatic environment is subject to natural variability, causing difficulties in standardising the monitoring and assessment methodology on a European scale. PS-based measurements offer a better possibility of standardization. They allow comparisons on a thermodynamic basis between the chemical activity in biota and water, which is the most important exposure medium of aquatic organisms. Results of field studies assembled here have shown that PS-based concentrations ( $C_{l=w}$ ) usually are higher than or equal to concentrations in fish at trophic levels less than four, supporting the use of PS measurements as a conservative proxy of the levels of hydrophobic chemicals in fish. PS can be applied in chemical monitoring in a tiered



approach, starting with PS for screening chemical levels in water as the first tier, which can help identify water bodies that require biota monitoring, reducing the need for extensive fish sampling. Expanding the PS-fish dataset and including a wider variety of chemicals and species will further validate this approach. Further comparisons between PS and biota data are suggested to strengthen the general validity of the proposed biota/water chemical activity ratio approach across Europe, considering priority substances, river basin-specific substances and various trophic levels of aquatic organisms.

#### CRediT authorship contribution statement

**Branislav vrana:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Katrin Vorkamp:** Writing – review & editing. **Cecile Kech:** Writing – review & editing, Investigation. **Stefano Polesello:** Writing – review & editing, Writing – original draft. **Olivier Perceval:** Writing – review & editing. **Kees Booij:** Writing – review & editing, Conceptualization. **Valeria Dulio:** Writing – review & editing. **Nicolas Estoppey:** Writing – review & editing. **Philipp Mayer:** Writing – review & editing, Conceptualization. **Ian Allan:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Brendan McHugh:** Writing – review & editing. **Cecile Miège:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Catherine Munsch:** Writing – review & editing. **Annika Jahnke:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Pierre-Francois Staub:** Writing – review & editing. **Elisa Rojo-Nieto:** Writing – review & editing, Investigation, Conceptualization.

#### Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ian Allan reports financial support was provided by Research Council of Norway. Annika Jahnke reports financial support was provided by European Union. Annika Jahnke reports financial support was provided by HGF. Cecile Kech reports financial support was provided by Walloon Public Service. Branislav Vrana reports financial support was provided by Ministry of Education Youth and Sports of the Czech Republic. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

The authors thank the NORMAN association for its contribution to this work over the years. The Norwegian Council of Research is thanked for financing part of this work through NIVA's Basic Research Funding (contract no. 342628/L10). For Belgium, fish data were financed by SPW (Service Public de Wallonie) - ARNE - Direction des Eaux de Surface and PS data was acquired through the ECHAPA project financed by ISSep. Part of the work was supported by the Projects CHEMO-RISK (ERC Grant agreement no. 715173), EXPOSO-METER (HGF W2/W3-126) and the UFZ PhD Colledge "Proxies of the Eco-Exposome". Authors thank the RECETOX Research Infrastructure (No. LM2023069) financed by the Ministry of Education, Youth and Sport for their supportive background. Foppe Smedes is thanked for his contribution to this work.

#### Data availability

Data will be made available on request.

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