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S Supporting Information

**ABSTRACT:** We reviewed compliance monitoring requirements in the European Union, the United States, and the Oslo-Paris Convention for the protection of the marine environment of the North-East Atlantic, and evaluated if these are met by passive sampling methods for nonpolar compounds. The strengths and shortcomings of passive sampling are assessed for water, sediments, and biota. Passive water sampling is a suitable technique for measuring concentrations of freely dissolved compounds. This method yields results that are incompatible with the EU's quality standard definition in terms of total concentrations in water, but this definition has little scientific basis. Insufficient quality control is a present weakness of passive sampling in water. Laboratory performance studies and the development of standardized methods are needed to improve data quality and to encourage the use of passive sampling by commercial laboratories and monitoring agencies. Successful prediction of bioaccumulation based on passive sampling is well documented for organisms at the lower trophic levels, but requires more research for higher levels. Despite the existence of several knowledge gaps, passive sampling presently is the best available technology for chemical monitoring of nonpolar organic compounds. Key issues to be addressed by scientists and environmental managers are outlined.
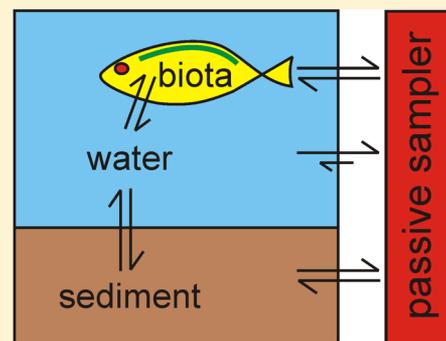
INTRODUCTION

Great progress has been made over the past few decades in the field of passive sampling of nonpolar organic compounds (log octanol−water partition coefficients (log K_{ow}) > 4) in the aquatic environment. With such methods, a sorption phase is exposed in a medium (e.g., water, sediment), where it samples the target compounds at a rate that is proportional to the difference in chemical activity between sampler and medium, and where the uptake kinetics are controlled by passive processes (diffusion and ambient convection), until equilibrium is attained. By contrast, grab sampling methods aim to quantitatively extract compounds from a distinct water volume (e.g., solid phase extraction, liquid−liquid extraction). Passive sampling allows measurement of the concentrations of freely dissolved compounds (C_{free}), while grab sampling yields total dissolved concentrations (freely dissolved + colloidally bound) or total concentrations (total dissolved + particulate).

Various passive sampler designs have been proposed for nonpolar organic compounds since the early 1980s (Supporting Information, Table S1),[1−7] of which solid phase microextraction (SPME)[8] and semipermeable membrane devices (SPMDs)[9] were the first designs that were used on a wider scale by multiple research and monitoring groups. Passive sampling devices (PSDs) can be broadly categorized as single-phase samplers, which only consist of a single polymer (e.g., low-density polyethylene) and dual-phase samplers, which consist of a sorption phase that is enclosed by a polymeric membrane (e.g., SPMDs, nonpolar version of the Chemcatcher).

The recognition of the added value of passive sampling by regulators is rather limited. PSDs are considered by European Union (EU) regulators to be useful but complementary tools for assessing environmental contamination under the EU Water Framework Directive.[10] The recent European Chemical Agency workshop on contaminated sediment risk assessments noted the utility of passive sampling for performing these assessments.[11] Environmental authorities in the U.S. actively support the use of passive sampling in environmental assessments.[12−15] For example, the U.S. Environmental Protection Agency's (U.S. EPA) Superfund program for the remediation of contaminated sites has encouraged the application of passive sampling at their sites around the country.[14] The Oslo-Paris Convention for the protection of the marine environment of the North-East Atlantic (OSPAR) recognizes the potential of passive sampling for the

risk assessment of nonpolar compounds in sediments and water, based on a trial survey in the OSPAR area.[16−18]

In January 2013, the International Council for the Exploration of the Sea (ICES) organized a workshop that aimed to 1. review the state of the knowledge on the applicability of passive sampling in relation to compliance monitoring, 2. review the links between passive sampling and chemical monitoring in biota, and 3. identify the research needs to further apply passive sampling in marine monitoring assessments.[19] The present review builds upon the findings of this workshop with respect to the monitoring of nonpolar compounds in water, sediment, and biota, considering that passive sampling of metals, polar organic compounds, and volatile molecules require separate evaluation. The United States perspective and experience with passive sampling in environmental monitoring was included in what started as primarily a European exercise in order to provide greater scientific and regulatory robustness to this review's analysis. In addition, inclusion of both the European and United States approaches provides interesting opportunities for contrasting the ways in which two of the largest political entities have applied passive sampling toward a specific aspect of environmental regulation. The aim of this review was 1. to evaluate the differences in perspective between environmental managers and passive sampling scientists with respect to the risk assessment of nonpolar compounds in the aquatic environment, and 2. to critically address the achievements and shortcomings of passive sampling research in relation to the needs of environmental managers, based on documented evidence.

REQUIREMENTS OF COMPLIANCE MONITORING

A major focus of chemical monitoring in the aquatic environment is to assess compliance with water quality thresholds that aim to protect aquatic organisms and humans from the adverse effects of chemicals.[20,21] Additional purposes are the assessment of the effectiveness of emission control policies (temporal trends) and source identification (geographical trends). The general approach is to set concentration thresholds in environmental matrices that offer adequate protection, and to set performance requirements for the methods that are used to measure actual concentrations in the environment.

The basis for monitoring programs can be national legislation (e.g., U.S. Clean Water Act), supra-national legislation (e.g., EU Water Framework Directive, WFD), or international treaties (e.g., regional seas conventions, such as OSPAR, and the

Canadian and United States International Joint Commission for the protection of transboundary waters). In this review, we take chemical monitoring in the U.S., EU, and the North-East Atlantic as examples to discuss the performance of passive sampling for demonstrating compliance with legally defined concentration thresholds. We selected these three regions because the status of chemical monitoring is sufficiently similar to identify general requirements, yet sufficiently different to illustrate that various approaches toward compliance monitoring are possible.

Concentration Thresholds. Compliance monitoring of European inland surface waters, estuaries, groundwater, coastal waters, and territorial waters is regulated by the WFD,[22] the directive on Environmental Quality Standards (EQSs),[23] and the directive on Technical Specifications for Chemical Analysis and Monitoring of Water Status.[24] Alongside these legally binding directives, technical guidance documents have been published for the implementation of the WFD. These documents provide guidance for defining quality standards (QS) for the protection of freshwater and saltwater pelagic and benthic communities, top predators, and humans, proposing to adopt the most protective QS as overall EQS.[20] To compare biota QSs ($\mu g\ kg^{-1}$wet weight) with those derived for the protection of pelagic communities ($\mu g\ L^{-1}$) the former have to be converted to equivalent water concentrations using appropriate bioaccumulation factors (BAFs).

For nonpolar organic compounds, the EQS guidance document states that laboratory toxicity and bioconcentration tests usually contain low levels of total organic carbon (TOC) in the test system, and that the resulting EQSs for water therefore refer to concentrations of dissolved compounds.[20] However, the EQS directive 2013/39/EU stipulates that the EQS for organic compounds refer to "total concentrations in the whole water sample", for unspecified reasons.[23]

Technical guidance documents on chemical monitoring of surface waters[10] and sediments/biota[25] state that passive sampling can be used as a complementary method. The WFD allows member states to use alternative matrices for compliance monitoring if they define and use EQS values that are at least as protective as those specified in the EQS directive. However, the legally binding definition of organic contaminant EQSs in terms of total concentrations remains an obstacle for the use of passive sampling in compliance checking in the EU.

The key drivers in compliance monitoring of marine, coastal and transitional waters in the North-East Atlantic Ocean and its adjacent seas are the OSPAR Coordinated Environmental Monitoring Program (CEMP),[26,27] the EU Marine Strategy Framework Directive (MSFD; coastal and marine waters only),[28] and the WFD with its daughter directive on EQSs (transitional, coastal, and territorial waters).[23] Regulations for chemical monitoring under the MSFD are still under discussion, but it is assumed that they will be based on those already established for the WFD, merged with the monitoring approaches by OSPAR and other regional seas conventions in the European area. Thresholds for the protection of marine systems are named Environmental Assessment Criteria (EAC) within OSPAR. These EACs are primarily based on aqueous toxicity data that have been recalculated to concentrations in sediments and biota using equilibrium partitioning (EqP) models.[29] OSPAR recognizes the relevance of C_{free} of nonpolar compounds for toxicity assessment, but requires contracting parties to monitor these compounds in biota and sediment, because these compounds cannot easily be measured in seawater due to their low concentrations.[30] EACs are not legally binding, but instead are based

on consensus among contracting parties, and can be adapted when additional knowledge becomes available.[31]

Chemical monitoring for checking compliance with National Pollutant Discharge Elimination System (NPDES) permit limits and for monitoring of ambient waters in the U.S. are regulated by the Clean Water Act (CWA). The CWA requires States to define Water Quality Standards (WQSs), which describe the designated uses of a water body, narrative and/or numerical Water Quality Criteria (WQC) that protect these uses, and antidegradation policies. Under Section 304(a) of the CWA, U.S. EPA publishes recommendations for WQC. States can either adopt these recommendations, modify them to account for site specific conditions, or use other scientifically defensible methods to develop their own WQC. State-adopted WQSs should be reviewed every three years, and are subject to approval by the federal EPA.[32] In some cases the EPA can promulgate WQC for the states. WQC aim to protect sensitive species, similar to EQSs under the WFD.[21] States monitor to assess attainment of WQS and identify impaired waters. If a waterbody is impaired, discharges are restricted to a total maximum daily load (TMDL).

Method Requirements. In the U.S., acceptable chemical analysis methods for compliance monitoring of effluents under the NPDES are listed in the Code of Federal Regulations, title 40, part 136, but a permitting authority may specify the use of alternative methods.[33] Passive sampling may not be the first method of choice for this type of compliance monitoring, because discharge permits are defined as TMDLs (i.e., concentrations in total effluent, multiplied by the daily effluent discharge volume). By contrast, method requirements for ambient water monitoring by the States are essentially unregulated by federal law, but instead result from the interaction between the U.S. EPA and a given State's department of environmental quality on how to assess water quality in relation to the WQC, using the best available practices. The Consolidated Assessment and Listing Methodology (CALM)[34] aims to continuously improve the quality of ambient water monitoring, using chemical, biological, and toxicological data, among others.

OSPAR and EU prescribe a number of criteria for chemical analysis and sampling to ensure that valid and comparable data are generated within monitoring programs (Table 1).[24,27] Methods have to be documented and validated, and a quality assurance and control system needs to be in place to monitor and control data quality. WFD related methods have to be in accordance with EN/ISO/IEC 17025. Reference materials should be used, and laboratories must participate in proficiency testing schemes for the analytes of interest. Legally binding minimum performance requirements for chemical methods used in WFD monitoring are that the measurement uncertainty be ≤50% at the level of the EQS, and the limit of quantification ≤30% of the EQS.[24] OSPAR does not specify quantitative requirements for these parameters, but requires that background assessment concentrations (BACs) for the target analytes in the sampled matrix be available. These BACs are derived from the mean and variance of long-term (10-year) concentration data for remote areas, as reported by participating laboratories. Measured concentration values are considered to be above background unless there is statistical evidence showing that it is near background.[24,27]

Method requirements for the application of PSDs in chemical monitoring of nonpolar compounds in a regulatory context are fulfilled to varying degrees (Table 1). Detailed guidelines for the use of PSDs are available for silicone sheet samplers[35] and semipermeable membrane devices.[2,36,37] ASTM International

Table 1. Formal Requirements for Methods Used in Chemical Monitoring of Nonpolar Compounds in Water, for the Coordinated Environmental Monitoring Programme (CEMP) of the Oslo-Paris Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR), the EU Water Framework Directive (WFD), and the U.S. Clean Water Act (CWA)

	required by			
requirements	OSPAR	WFD	CWA[a]	present status for passive sampling
guidelines for passive sampling in water	yes	yes	yes	available for silicone samplers[35] and SPMDs[2]
				insufficiently available for low-density polyethylene, poly(oxymethylene), and other PSDs
proficiency testing schemes (PTS) and interlaboratory studies (ILS)	yes (PTS)	yes (PTS)	yes (ILS)	PTS for silicone samplers is operational (www.quasimeme.org)
				some interlaboratory comparisons available[49−51]
certified reference materials	yes	yes	no	no CRMs available
accuracy assessment	yes	yes	yes	general considerations available for nonpolar samplers[52]
background assessment concentrations	yes	no	no	available for PAHs, PCBs, HCB, DDE[53]
water quality standards	yes (EAC)	yes (EQS)	yes (WQC)	OSPAR: in development (to be defined as C_{free})
				EU: defined as C_{total}
				USA: defined as C_{free} and C_{total}
ISO standard	yes	yes	no	ISO 5667−23:2011(E)[46]
QA/QC system	yes	yes (ISO 17025)	yes (EPA guide-lines)[b]	QA/QC considerations available in the guidelines above, and in ISO 5667−23:2011(E)

[a]Ambient water monitoring. [b]www.epa.gov/quality/qa_docs.html.

developed a standard method for SPME of polycyclic aromatic hydrocarbons (PAHs) in pore waters.[38] Several interlaboratory studies that demonstrate method consistency are available, and are discussed below. A proficiency testing scheme organized by QUASIMEME is operational (www.quasimeme.org). Certified reference materials (CRMs) are presently not available, but CRM preparation for passive sampling could be easier than for batch water sampling.[39] Data quality can be assessed from repeated analysis of CRMs (when available) or reference materials prepared by laboratories in-house, similar to current practice for the analysis of sediment and biota samples. Although Table 1 is focused on passive sampling in water, it can be envisioned that similar requirements exist for passive sampling in sediments.

In the U.S. context, ambient WQC for the protection of aquatic life against nonpolar compounds are based on toxicity tests with low organic carbon concentrations in the test water, and hence are essentially based on C_{free}, albeit implicitly.[40] WQC for the protection of human health are derived from chemical uptake by consumption (drinking water, fish/shellfish). Concentrations in fish/shellfish that are considered to be sufficiently protective are converted to aqueous concentrations using (preferably field derived) BAFs that are based on C_{free}.[41] However, for use in WQC development, to be consistent with water quality monitoring data, these BAFs are converted back to values based on the total concentration.[42,43] Thus, human health WQC cannot be directly compared with passive sampling results. Consequently, while regulators in the U.S. recognize the importance of C_{free}, the actual water quality monitoring regulations do not yet use this parameter. OSPAR also aims to define water standards on a C_{free} basis.[30] Quality standards in the EU are commonly defined as C_{total}, but EU regulations allow the use of standards for other matrices if these offer an equal level of protection. Generic suspended particulate matter (SPM)

contents of 15 mg L^{-1} (fresh waters) and 3 mg L^{-1} (marine waters) are recommended to convert between C_{free}, C_{total} and concentrations in SPM.[20,44,45] An ISO standard for the deployment, retrieval, and analysis of passive samplers is available,[46] but guidance that is specific to particular sampler types and contaminant groups (e.g., polychlorinated biphenyls - PCBs, PAHs, polychlorinated dibenzo-p-dioxins/furans - PCDD/Fs) may have to be added in the future. This ISO standard also includes quality control measures to assess recoveries, precision, and method detection limits. Guidance for the selection, validation (QA/QC) and deployment of PSDs for contaminated sediments is also available.[47]

Differences in the monitoring approaches between the U.S. and OSPAR on one hand, and the EU on the other, will likely affect the further application of passive sampling in a regulatory context. In the U.S. context, States, U.S. EPA, and the research community cooperate in the CALM approach, to generate monitoring data that are best fit for a given purpose.[34] Also OSPAR promotes the use of new technologies to amend existing methods for chemical monitoring.[48] By contrast, monitoring in the EU is strongly regulated in legally binding directives that define EU-wide EQSs and specify method requirements for compliance checking with these EQSs.

To promote adoption of passive sampling into the implementation of compliance monitoring regulations, there is a critical need to get beyond passive sampling as a purely scientific endeavor and begin to standardize PSD type selection, deployment, chemical analysis, and data reporting. For example, in the United States, the lack of standardized methods has impeded greater acceptance of passive sampling in regulations. The following discussion reviews the progress made with passive sampling with regard to use in water, sediments, and biota. The discussion also emphasizes the areas in which passive sampling needs more work before standardizing can be successfully initiated.

■ PASSIVE SAMPLING IN WATER

Target Compounds. The capability of PSDs for measuring aqueous concentrations of most nonpolar compounds ($\log K_{ow} > 4$) that are listed by OSPAR, U.S., and EU has been demonstrated, with detection levels in the low picogram per liter range.[54] While most studies have focused on PAHs and globally regulated contaminants such as hexachlorobenzene (HCB), PCBs, organochlorine pesticides, PCDD/Fs, and polybrominated diphenyl ethers (PBDEs),[55−58] a number of hydrophobic compounds of emerging concern have also been sampled by PSDs, including triclosan,[57,59] alkylphenols,[59] pyrethroids,[60−62] cyclic methylsiloxanes,[63] and organophosphates.[58]

Kinetic and Equilibrium Sampling Stages. Understanding the difference between the kinetic and the equilibrium sampling stage is important for a proper evaluation of the information that PSDs can and cannot provide. During the initial (kinetic) sampling stage, PSDs can be regarded as an infinite sink, and accumulated amounts of target compounds reflect the time weighted average concentrations over the deployment period. During prolonged exposure, the compounds gradually attain their equilibrium concentrations. All samplers go through a kinetic sampling stage, but equilibrium is not always reached on practical time scales for compounds with high sampler-water partition coefficients (K_{sw}), particularly for passive sampling in the water column, where the sampling rates (R_s) are usually smaller than for passive sampling in pore waters or biota.[64−68] Equilibration times are generally shorter at higher water flow rates, lower K_{sw}, and higher area/volume ratios of the sampler,[2,69] and typically range from days (e.g., endosulfan, $\log K_{ow} = 4$) to years (e.g., benzo[ghi]perylene, $\log K_{ow} = 6.5$) and beyond.[54] Whether or not fast equilibration is desirable depends on the research question: long equilibration time scales may be desirable when a time-weighted average concentration is aimed for. Fast equilibration may be desired when studying the extent of equilibrium between pore waters and overlying waters, because equilibrium concentrations in the samplers can be directly compared (i.e., require no knowledge of the sampling kinetics). The options for optimizing equilibration time scales are limited to manipulation of the area/volume ratio, the choice of sampler material (higher or lower K_{sw} for a particular compound), and flow rate.[70,71]

Uptake Rate Control. Uptake rates of nonpolar compounds by PSDs can be limited by transport through the water boundary layer (WBL) or by the polymer, and the relative importance of these transport steps can be estimated from the polymer−water partition coefficient K_{pw} and the mass transfer coefficients of the WBL (k_w) and the polymer (k_p). Specifically, $k_w/(K_{pw}k_p) \ll 1$ is indicative of WBL controlled uptake and values $\gg 1$ indicate polymer control.[2,69,72] Uptake rates of highly hydrophobic chemicals are usually limited by transport through the WBL, and weakly decrease with increasing molecular size. Polymer-controlled uptake is characterized by a strong decrease of R_s with decreasing hydrophobicity.[2,73−75] Models for k_p in single-phase PSDs typically rely on the assumption that k_p equals the diffusion coefficient of the chemical in the membrane divided by the half-thickness of the polymer.[76−78] However, these models are approximate, because k_p decreases with time as the analytes diffuse further into the polymer, until a steady state value is attained.[69,79] The compounds that show polymer controlled uptake typically have low K_{sw} values, and reach equilibrium relatively quickly. Models for partial and full polymer-controlled uptake are available,[80] but are usually not needed for passive

sampling of the water column, possibly with the exception of short-term exposures,[81] very high water flow rates[71] and in the case of polyoxymethylene (POM) samplers, for which diffusion coefficients in the polymer are more than an order of magnitude smaller than in low density polyethylene (LDPE) and 3 orders of magnitude smaller than in silicone.[77,79,82,83] In addition, a comparison of silicone and LDPE samplers suggests that the uptake of PBDEs by LDPE may be polymer controlled to some extent.[58]

For WBL controlled uptake, hydrodynamic theory predicts k_w to be proportional to aqueous diffusion coefficient (D_w) to the power 2/3.[84,85] D_w has been correlated with molar volume, molecular weight, K_{ow}, and K_{sw}, and all of these models predict a similar decrease of R_s with increasing molecular size.[78] For example, the R_s of PCB180 is expected to be 1.2−1.5 times smaller than the R_s of pyrene, depending on the model.[86] The weak dependency of R_s on molecular size was experimentally confirmed in some studies,[75,78] but in other studies a stronger dependency was observed, which was modeled empirically as a polynomial regression of $\log R_s$ versus $\log K_{ow}$.[2,87] The stronger-than-expected decrease in R_s with increasing K_{ow} has been attributed to experimental artifacts due to sorption of analytes to dissolved organic matter in calibration setups,[88] and the use of these models is therefore not recommended.

A value of $\log K_{ow} = 4.5$ is often used as a reference for the transition from polymer-controlled to >50% WBL-controlled uptake.[2,81,89,90] However, this is an approximate value only, because the transition value depends on the hydrodynamic conditions, the diffusion coefficient in the polymer, and the polymer thickness. Thus, the transition to WBL-controlled uptake has been observed for SPMDs at $\log K_{ow} = 5.5$ at flow rates of 90 cm s^{-1},[75] and for uptake by LDPE samplers in sediment slurries at $\log K_{ow} = 6.5$.[91] The >100 times higher diffusion coefficients in silicone compared with LDPE may explain WBL-controlled uptake by silicone samplers for all compounds with $\log K_{ow}$ values >3.[78,82]

In Situ Calibration. The dependency of R_s on water flow velocity makes it necessary to either control the flow rate near the sampler[5,92,93] or to calibrate the in situ uptake kinetics using the dissipation rates of performance reference compounds (PRCs).[52,94−96] The PRC method is based on the consideration that the magnitude of R_s results from exposure-specific effects (flow, temperature, biofouling) and compound-specific effects (diffusion coefficients, K_{sw}). In the original application of the PRC method, R_s were calculated for individual PRCs that show sufficient (e.g., > 20%), yet not complete dissipation, in order to determine the exposure-specific effect. An R_s model was used to calculate the R_s of compounds in the high-hydrophobicity range, for which PRCs show insufficient dissipation.[2] In a later application, the exposure-specific effect was determined by nonlinear least-squares regression based on all PRC dissipation data, including PRCs that show insignificant or complete dissipation,[52] thus allowing to determine uncertainties in R_s. The PRC method requires the use of an R_s model for calculating the R_s for compounds in the hydrophobicity range where PRCs show insignificant dissipation. These models can be empirical,[2,87] semiempirical,[75] or mechanistic.[2,52,78] The use of mechanistic R_s models is recommended, because the empirical models likely suffer from experimental artifacts, and semiempirical models must first be calibrated for particular contaminant classes. In a special application of PRCs, the degree of equilibrium for target analytes is calculated directly (i.e., without the use of any model) from the fractional dissipation of isotopically labeled analogues.[93]

In a modification of the latter approach, equilibrium attainment of target analytes is estimated from an empirical linear correlation of 100 minus the percentage of retained PRCs versus log K_{ow}.[97] This approach may not be ideal, because the degree of equilibrium is not a linear function of log K_{ow}, and because log K_{sw} - log K_{ow} correlations may be compound class dependent.[98,99] A relatively widespread idea is that PRCs must be mass-labeled analogues of the target analytes,[100] but although this criterion is sufficient, it is too restrictive. Instead, the only requirement is that the PRCs should follow the same R_s model as the target analytes.[101]

In situ calibration is not necessary for sampler designs in which the mass transfer resistance of the membrane is much larger than that of the water boundary layer; for example, membrane-enclosed sorptive coating (MESCO)[102] and ceramic dosimeters.[103] This approach inevitably reduces the R_s and increases the detection limits, and therefore restricts the use of these samplers to highly contaminated sites.

Sampler-Water Partition Coefficients. The accuracy of K_{sw} values is a key issue for compounds that reach the equilibrium sampling stage, since the errors in the estimated C_{free} are linearly proportional to the errors in K_{sw}. For compounds that remain in the kinetic sampling stage, R_s is the critical factor, and errors in C_{free} measurements depend strongly on the errors in the K_{sw} of the PRCs, and not on the K_{sw} of the target analytes themselves.[52] Dissolved salts cause log K_{sw} to be higher in seawater (ionic strength = 0.72 mol L^{-1}) than in fresh water by about 0.1−0.2 log units, and a temperature decrease from 25 to 5 °C causes an increase in log K_{sw} by about 0.1−0.7 log units.[76,104] Hydrostatic pressure may have an effect on log K_{sw} that becomes noticeable below a few hundred meters water depth.[105]

The experimental determination of K_{sw} values of nonpolar compounds is not a trivial task, as is evidenced by the high interlaboratory variability of 0.2−0.5 log units.[76,90,106] This gives rise to errors in the estimated C_{free} by factors of 1.6−3. We recommend to use stricter protocols for the determination of K_{sw} and, for quality control purposes, to include a limited number of compounds with well-established K_{sw} values for new K_{sw} experiments. The selection and use of reference polymers can also be considered for documenting the accuracy of K_{sw} determinations. Further, considering that polymer−polymer partition coefficients are within 1 order of magnitude from unity, and therefore easier to measure than K_{sw}, the use of a reference polymer may help to harmonize K_{sw} values for different polymers, and may help to better address between-manufacturer and between-batch variability of the polymers used. Application of this approach showed that the manufacturer effect on K_{sw} for five silicone sheets ranged between 0.2 and 0.6 log units, and that the K_{sw} for three batches from the same manufacturer differed less than 0.09 log units[98]

Due to the difficulty of measuring K_{sw}, several authors have suggested to report equilibrium concentrations in a reference polymer (e.g., poly(dimethylsiloxane) - PDMS) or reference lipid as target parameters in addition to C_{free}, because these concentrations are also linearly proportional to chemical activity.[107−109] In this approach, K_{sw} is not needed since the monitoring results are reported as concentrations in the reference polymer or the reference lipid. Concentrations in the reference lipid are calculated from concentrations in the polymer and the polymer−lipid partition coefficients. The latter are easier to measure than K_{sw} due to their lower values. The conversion of aquatic toxicity thresholds from C_{free} to equilibrium concentrations in a reference polymer allows the use of these

concentrations within a regulatory context. Although this approach is scientifically sound, it requires a change of paradigm that is not easily accomplished, and accurate K_{sw} values are still needed for the conversion of toxicity data that have been published as total dissolved concentrations or C_{free}. Further, practical difficulties with reference polymers or lipids are that the scientific community has to agree on phases for which all target analytes reach equilibrium within a reasonable time frame. Rapid equilibrium attainment can be accomplished for passive sampling in sediments and in lipid-rich phases, but generally not for passive sampling in the water column, where equilibrium attainment for compounds with log K_{ow} values >5.5 is not often observed.

Uncertainties. The EU's directive on technical specifications for chemical analysis and monitoring of water status requires a measurement uncertainty of ≤50% ($k = 2$) at the level of the EQS.[24] It should be noted that the main error source for C_{free} is not in the chemical analysis of the PSD matrix, but in the K_{sw} values used in the calculations thereafter (see above). Further, the uncertainty in C_{free} remains fairly constant down to the level where the amounts in exposed PSDs approach the amounts that are present in the field control samplers (i.e., ~ 10 pg L^{-1} or lower).[54] In addition, several water EQS values for nonpolar compounds are set at the pg L^{-1} level (e.g., cypermethrin) or below, and it is difficult to imagine how compliance with these EQS can be demonstrated without PSDs. Moreover, the time-integrative nature of passive sampling makes this method less sensitive to short-term temporal variation than batch sampling. Finally, it should be considered that QA/QC measures that are typically taken for the chemical analysis of other matrices can also be applied to PSDs, including the determination of recoveries, procedure blanks, quantitation and detection limits, the analysis of CRMs and the participation in laboratory performance studies.[46]

The accuracy of PSD based C_{free} determinations can be assessed from PSD comparisons, which should all yield the same values. A field deployment of seven PSDs in the river Meuse showed that C_{free} estimates from SPMDs, silicone, and LDPE strips were in agreement within a factor of 2, with somewhat larger deviations for Chemcatcher, MESCO and silicone rods.[49] In a PSD comparison in the laboratory, the calculated C_{free} agreed with nominal concentrations within a factor of 2 for SPMDs, silicone, and LPDE strips, with low values for LDPE and high values for silicone, on average.[110] Results for POM and thin-film PDMS samplers that were exposed in a Norwegian Fjord agreed within a factor of 2−3.[111] Calculated C_{free} of PAHs were 3 times higher for POM than for LDPE samplers exposed in Narragansett Bay, while the reverse was found for PCBs.[97] Concentrations of o,p'-DDE and p,p'-DDE derived from LDPE samplers were about 3 times higher than SPME based concentrations.[112] Results from an interlaboratory study for PAH passive sampling that included 22 laboratories using five sampler types, showed a coefficient of variation (CV) in C_{free} of 90%, and mean PSD based concentrations that were two times higher than results based on batch sampling.[51] No relationship between C_{free} and sampler type was observed in this study, suggesting that the chemical analysis of the sampler and/or the chosen method of C_{free} calculation are important sources of variability. Results from the NORMAN interlaboratory study on passive sampling (www.norman-network.net) showed that R_s estimation is a major error source (~factor 25) for the reported C_{free} of PBDEs (14 laboratories), followed by the chemical analysis of target compounds and PRCs in the sampler (~factor 4).[50] The ICES Passive Sampling Trial Survey identified chemical analysis

(20−40%) and R_s estimation (30%) to be the main sources of interlaboratory variability of reported C_{free} values of PAHs and PCBs.[113] Between-laboratory CVs for the chemical analysis of PSDs are at the lower end of CVs for the analysis of PCBs in biological materials (14−117%), PCBs in sediments (21−59%), and PAHs in sediment and mussel (23−62%).[114−116] The results from interlaboratory studies imply that standardization of R_s estimation methods, improvement of analytical techniques, and the selection of consensus values for K_{sw} may greatly reduce interlaboratory variability of passive sampling results. It can therefore be expected that participation in laboratory performance studies that focus on chemical analysis of PSDs and on calculation methods will reduce between-laboratory variability for two reasons. First, such studies will force laboratories to continuously and critically assess their analytical methods. Second, a comparison of calculation methods will reveal if any inappropriate C_{free} calculation methods are being used. The observed differences in C_{free} estimates are not surprising in view of the inaccuracies in K_{sw} values and the occasional use of empirical R_s models.[49,117] This stresses the importance of improving the experimental determination and theoretical evaluation of K_{sw} and R_s as well as developing robust guidelines for not only chemical analysis but also C_{free} calculation.

Comparisons of passive sampling with batch water sampling followed by filtration and extraction provide additional information about passive sampling accuracy. However, results from these studies are difficult to interpret, because of the differences of the targeted concentrations (freely dissolved versus total dissolved), the time-integrative nature of passive sampling data, and because filtration/extraction methods have their own difficulties, such as contaminant adsorption to equipment surfaces, and filtration efficiencies that vary with the extent of filter clogging.[118,119]

Results from passive sampling with SPMDs, POM, and silicones generally agree within a factor of 3 with results from batch sampling[119−125] although differences by a factor of ~10 have also been observed.[111,126] In some cases, differences increased with hydrophobicity, which could be attributed to the contribution of dissolved organic carbon (DOC) bound compounds to batch sampling based results.[121,123,125]

PASSIVE SAMPLING IN SEDIMENTS

The 2012 SETAC technical workshop "Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments" reviewed the knowledge on passive sampling of nonpolar organic compounds and trace metals in sediments.[127,128] There was general agreement that C_{free} of nonpolar compounds is a better proxy of sediment toxicity and bioaccumulation in benthic invertebrates than total concentrations in the sediment,[12,129−132] and that passive sampling is a better method for obtaining C_{free} than EqP calculations utilizing sorption to amorphous and black carbon.[130,133] The SETAC workshop also noted that the uncertainties in C_{free} span several orders of magnitude for EqP calculations, and 1 order of magnitude for direct measurement with PSDs.[127,130] The preferred strategy for obtaining C_{free} from ex situ passive sampling in sediments was to allow compounds to reach equilibrium with the sampler, because C_{free} can then be directly calculated from K_{sw}.[47,127,129,130] It was also noted that equilibrium may be difficult to attain at reasonable time scales for some very hydrophobic compounds at least when sampling in situ, and that kinetic models may be needed in those cases.[129] With passive sampling in stirred sediments (ex situ) the same first-order kinetic uptake models that are used in passive

water sampling may be applied[47,91,129,134] while more complex models are needed for sampling in unstirred (in situ) sediments.[91,130,135−137] Parallel sampling with multiple coating thicknesses are increasingly used to confirm attainment of equilibrium, while at the same time checking for additional quality assurance criteria (negligible depletion, absence of surface related artifacts).[109,138] The SETAC workshop noted further that the main sources of error for passive sampling in sediments are the inaccuracies in the K_{sw} values, and the possible underestimation of equilibration times, particularly for in situ applications.[130] Practical guidance on the use of PSDs for measuring C_{free} in sediments was summarized, including the choice of sampler type, in situ versus ex situ application, sampler calibration, experimental design, assessment of equilibrium attainment, QA/QC issues, and the use of passive sampling in tiered risk assessments.[47]

Bioaccessibility and Chemical Activity. Passive sampling can be used as a depletive method for measuring the (readily) desorbing contaminant fraction of the sediment as a measure of bioaccessibility, or as a negligible-depletion method for C_{free} as a measure of chemical activity.[139,140] The 2012 SETAC workshop focused for practical reasons on C_{free} but also recognized the relevance of passive sampling for evaluating bioaccessibility. Depletive sampling of sediment slurries with poly(2,6-diphenyl-p-phenylene oxide) (Tenax) has been used to separate contaminant fractions that show rapid, slow, and very slow desorption rates.[141,142] It has been suggested that high organic carbon−water partitioning coefficients can be quantitatively explained by the occurrence of a (very) slowly desorbing contaminant fraction.[142,143] Further, the available evidence suggests that contaminant toxicity and body burden for benthic organisms are linked both to concentrations in SPME fibers at equilibrium and to the rapidly desorbing fraction as determined with the Tenax method.[144] Tenax and SPME performed equally well in explaining bifenthrin toxicity to chironomids and crustaceans for three sediments that spanned a 5 fold difference in organic carbon content.[145] Smedes et al. developed a passive sampling approach for measuring both accessibility and C_{free} by incubating sediments and silicone sheets at multiple polymer/sediment mass ratios.[66] At low ratios, this method yielded C_{free} (no depletion of the sediment phase). At high ratios the accessible contaminant pool in the sediment phase could be quantified (maximum depletion).

LINKING PASSIVE SAMPLING TO CONCENTRATIONS IN BIOTA

Maximum protection of aquatic species, humans, and predators is achieved by monitoring all relevant matrices (water, food, prey organisms, respectively) but this would be very costly. It is therefore common practice to limit the number of matrices that are monitored, and to establish relationships between concentrations in water and in biota in order to compare quality standards derived for the protection targets (aquatic organisms, predators and humans).[20] Whether passive sampling or biota monitoring is the preferred method therefore depends on their respective relevance for the species that is to be protected and on the uncertainties involved in estimating concentration levels in water from those in biota and vice versa. Below, we will discuss established biota-PSD relationships and the performance of PSDs and biota monitoring for assessing C_{free}, spatial and temporal trends, and predator diet.

Biota-PSD Relationships. Passive sampling research has shown that BAFs and K_{ow} follow a log−log linear relationship when the BAFs are based on C_{free} rather than on total dissolved

concentrations, and that the frequently reported nonlinearity in log BAF at high log K_{ow} is in fact artificial.[146,147] Passive sampling based linear log BAF- log K_{ow} relationships have been observed for bioaccumulation of nonpolar compounds (3 < log K_{ow} < 7.5) by oligochaetes,[146,148,149] midge larvae,[150] and blue mussels.[151]

Many studies show correlations between measured concentrations in PSDs and aquatic animals. Strong correlations have, for instance, been observed between lipid-based concentrations of organochlorine pesticides, PAHs and PCBs in biota and equilibrium concentrations in thin (<0.05−0.5 μm) films of poly(ethylene-*co*-vinyl acetate) (EVA) for earthworms,[152] bivalves,[153] and amphipods.[154] Lipid-EVA concentration ratios ranged between 0.1 and 0.8, and similar ratios (~0.5) were observed with in vitro sampling of rainbow trout homogenates with EVA.[155] Lipid normalized PCB concentrations in polychaetes were also strongly correlated with equilibrium concentrations in LDPE, with polychaete/PSD concentration ratios ranging from about 1 to 20.[156,157] Weaker correlations (log−log slope of 0.6) and site-specific concentration ratios were observed for PAHs in polychaetes and LDPE.[158] Concentrations of PAHs and organochlorine pesticides in mussels were positively correlated with C_{free} that were obtained from SPME and LDPE samplers, but correlations for PCBs were much weaker.[60]

It is also possible to predict EqP concentrations in biota. One approach is to predict lipid based biota concentrations as the product of C_{free} and BAF values,[149,159−161] where some studies used K_{ow} as surrogate for BAF.[162−165] This approach yielded predicted lipid based concentrations of PCBs and PAHs in earthworms and oligochaetes that were generally within a factor of 3 of measured lipid normalized concentrations. This is a surprisingly good agreement, considering that uncertainties in BAF, K_{ow}, and K_{sw} all contribute to the error in the predicted EqP concentrations. Another approach is to determine EqP concentrations in lipids from the product of measured equilibrium concentrations in the passive sampling polymer and lipid to polymer partition coefficients.[138,166,167] This approach resulted in EqP concentrations in lipids, which were either near or higher than actually measured concentrations in biota. This was observed for benthic worms,[138] mussels, and several fish species.[109,167−169] A close correspondence between passive sampling based C_{free} and concentrations in mussels for PAHs and PCBs was observed in a monitoring study over four years, two sampling seasons, and eight estuarine and coastal stations.[151] Calculated log BAF values showed a scatter of ~0.2 log units, indicating that concentrations in mussels can be predicted from PSD based C_{free} with a similar precision.

Chemical Activity. It is widely recognized that C_{free} is a valuable proxy for chemical activity, because knowledge of these concentrations allows estimation of the equilibrium concentrations in other environmental compartments (sediments, air, biota).[12,20,90,132,170] Measured chemical activities in sediment and overlaying water allow a direct assessment of whether the sediment acts as a diffusive source or sink, since diffusive mass transfer always goes from high to low chemical activity. Chemical activity can be measured with passive sampling, either as ratio of C_{free} and subcooled liquid solubility or as product of C_{free} and activity coefficient. Witt et al. have for instance used ex situ passive sampling with silicone coated glass fibers to determine depth profiles of chemical activity for PAHs at three locations in the Baltic Sea.[171] For equilibrium sampling, ratios of chemical activity can be determined very easily as concentration ratios on a polymer basis.

Passive sampling of biota tissue and extracted lipids is a recent application that allows for a direct assessment of chemical activity in biota.[67,68,138,166,172,173] With this method, a polymer is equilibrated with biota tissue, tissue homogenate, or lipid extract, by immersion or via a headspace. Typical equilibration times are in the order of hours for PCBs and PAHs in fat-rich tissues.[67,172,173] Contaminant concentrations in the polymer are directly proportional to the chemical activity, and comparison of these concentrations therefore allows for directly comparing chemical activities. For instance, Jahnke et al. applied equilibrium sampling to sediment and eel tissue from a Swedish lake, and showed the eel to be under-equilibrated relative to the sediment.[168] Allan et al. compared equilibrium concentrations in silicone samplers that were exposed to water with samplers that were exposed to fish tissue in vivo.[68] Concentration ratios were ~1 for hexachlorobenzene and PCBs as well as for some three-ring PAHs, reflecting a significant degree of fish-water equilibrium for these compounds.

Biota monitoring is less suitable for estimating C_{free} and chemical activity, because the required BAFs show a high variability among studies, even for the same species.[45,174] Furthermore, a review of >7000 BAF values showed that 45% of the data suffered from one or more major sources of uncertainty.[175]

Spatial and Temporal Trends. Biota monitoring has been used extensively to assess spatial and temporal trends of contamination by nonpolar compounds and trace metals.[176−179]

The limitations of using sentinel organisms for comparing contamination levels in time and space are generally recognized. Multiple species may be needed for obtaining a good geographical coverage (e.g., oysters, blue mussels, green mussels, zebra mussels), and sometimes may not be available (e.g., off-shore environments, deep sea, anoxic or toxic locations), and several biotic and abiotic factors have to be accounted for.[180,181] These issues do not exist for PSDs when results are expressed as C_{free} (rather than as an accumulated amount per unit sampler mass). When a transition from biota to PSD-based trend monitoring is considered, it is important to determine appropriate biota-PSD conversion factors, in order to ensure data continuity. An evaluation of nine mussel-SPMD comparison studies suggested that BAF values were the major source of variability of SPMD/mussel concentration ratios, and that site-specific repetitive parallel exposures are needed to convert historical biomonitoring data to current passive sampling data.[174] The 4-y mussel-PSD comparison study mentioned above showed that the transition of biota monitoring time series (using bivalves) to passive sampler based time series is feasible.[151]

Predator Diet. Under the WFD, EQS values in biota (EQS$_{biota}$) are defined for hydrophobic and other substances (e.g., Hg) where risks of secondary poisoning and risk for human health via fish consumption cannot be excluded.[20] In the most current revision of the EQS directive most of these substances have to be monitored in fish, except for PAHs (crustaceans and molluscs), and dioxins as well as dioxin-like PCBs (fish, crustaceans and molluscs), but other organisms can be used if EQSs for these alternative organisms offer the same level of protection.[23] Some promising relationships have been established for legacy contaminants between equilibrium concentrations in PSDs and biota, including fish (see above). However, the WFD requires monitoring of other substances in fish (e.g., Hg, hexachlorobutadiene - HCBD, dicofol, hexabromocyclododecane -HBCDD), and the suitability of PSDs to predict concentrations of these compounds in fish is still unclear. Bioaccumulation

models for aquatic species at trophic levels up to and including predatory fish provide a mechanistic link between the concentrations in biota and concentrations in the water phase,[170] although reliable species- and compound- specific BAF values are required. These can be scarce or even absent.[175] These considerations imply that setting water based thresholds for the protection of predators is in principle valid, but direct monitoring of prey organisms may still be required because of the uncertainties in the BAF values that are used. We recommend that biota based monitoring be supplemented by passive sampling, because this allows the generation of valuable field-based BAF values that would improve modeling of contaminant transfer to the higher trophic levels. Such data would also be helpful for establishing biota-PSD relationships for pelagic species, which are presently scarce.[182]

■ THE WAY FORWARD

Much progress has been made in the field of passive sampling for environmental monitoring of nonpolar compounds in the aquatic environment, since the introduction of passive sampling in the early 1990s. This is notably the case for the risk assessment of contaminated sediments, where passive sampling based C_{free} has proven superior to the use of concentrations in whole sediment or partitioning based modeling approaches for the various organic carbon pools, both with respect to sediment toxicity and bioaccumulation. Significant progress has also been made for passive water sampling, with the development of mechanistic sampler-water exchange models and improved in situ calibration. Yet, not all claims that have been made by the passive sampling community with respect to accuracy, have been demonstrated beyond doubt. Insufficient quality control presently appears to be a dominant weakness of passive sampling, and progress can be expected from laboratory performance studies that include a detailed assessment of the sources of variability in the reported results. Inaccuracies in the K_{sw} of target analytes (in the case of equilibrium passive sampling) and PRCs (kinetic sampling) are a major source of concern. The determination of these partition coefficients is more difficult than generally assumed, and scientific journals could be less permissive in admitting data obtained from single experiments, even when these are carried out in triplicate. Researchers should carefully consider this issue before introducing new passive sampling matrices for nonpolar compounds.

The tight connection between PSD-based C_{free} and lipid-normalized concentrations in biota suggests that passive sampling can be used to predict C_{biota} to a fair or good degree for organisms at lower trophic levels. More research is needed to assess how passive sampling measurements can best be linked to concentrations at higher levels of the aquatic food web. The combination of passive sampling and bioaccumulation models seems then the most effective approach for assessing and predicting bioaccumulation.

Passive sampling inside biota, or in biota homogenates and lipid extracts, is a promising method for assessing the degree of equilibrium between biota and their environment. More research in this field is required, particularly with respect to passive sampling in biota with low lipid content, and for compounds other than PCBs and PAHs.

The capabilities of passive sampling are not fully utilized in a regulatory context by environmental managers, particularly in the EU. This is partly due to the scientific community, which may have overrated the achievements of passive sampling research in the past, and may have shown insufficient concern for the legal and practical context in which environmental managers operate, including quality control procedures. The community of environmental managers on its part could make more efforts in comparing the pros and cons of passive sampling based monitoring with the pros and cons of current approaches, with respect to scientific justification, uncertainty (including sampling uncertainty), and relevance for environmental risk assessment.

In Europe, the strict monitoring requirements laid down in the EU WFD and its daughter directives impede the implementation of passive sampling for regulatory purposes, whereas environmental managers in the United States and in OSPAR have more freedom to adapt management approaches to current scientific insights.

Specifically, in the United States, the use of passive sampling in the implementation of ambient water monitoring and remediation processes for contaminated sediments has been encouraged by regulators. This encouragement is based on the recognition that passive sampling-based C_{free} data provides a better scientific basis for risk assessment, compared with conventional sampling and monitoring procedures. The actual use of passive sampling is limited by the current lack of commercial laboratories performing passive sampler deployments, chemical analyses, and data reporting. Hesitancy by many commercial laboratories is linked to the current lack of standardized methods and procedures for using PSDs. In the near future, the scientific community will be crucial in providing guidance on the standardization of passive sampling methods. We expect that an open and critical communication between scientists and environmental managers will be beneficial for both.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b04050.

Types and configurations of passive samplers for nonpolar organic compounds (PDF)

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Notes

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GLOSSARY

BAC	Background Assessment Concentration, threshold concentration that is considered to indicate that measured concentrations represent natural background levels (OSPAR)
BAF	Bioaccumulation factor, concentration in biota divided by concentration in water at steady state, resulting from all uptake and elimination processes, including bioconcentration, biomagnification, biotransformation, and growth dilution
C_{free}	concentration of freely dissolved compounds in the water phase
C_{total}	total concentration of compounds, including freely dissolved compounds and compounds that are bound to particles and colloids
CWA	Clean Water Act (U.S.)
EAC	Environmental Assessment Criteria, threshold concentrations that are considered to cause no unacceptable adverse effects on biota or human health (OSPAR)
EQS	Environmental Quality Standard, threshold concentration that is considered to cause no unacceptable adverse effects on biota or human health (EU)
k_w	mass transfer coefficient of the water boundary layer at the PSD-water interface
k_p	mass transfer coefficient in the polymer
k_o	overall mass transfer coefficient of the water boundary layer
K_{ow}	1-octanol - water partition coefficient
K_{pw}	polymer - water partition coefficient
K_{sw}	sampler - water partition coefficient
MSFD	Marine Strategy Framework Directive (EU)
OSPAR	Oslo-Paris Convention for the protection of the marine environment of the North-East Atlantic
R_s	water sampling rate
PSD	passive sampling device
WQC	Water Quality Criteria, narrative and/or numerical indicator of water quality that is considered to cause no unacceptable adverse effects on biota or human health (U.S.)
WQS	Water Quality Standard, description of designated uses of a water body, WQC that protect these uses, and antidegradation policies (U.S.)
WFD	Water Framework Directive (EU)

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