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Critical Review

CALIBRATION AND USE OF THE POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER—A CRITICAL REVIEW

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Abstract—The implementation of strict environmental quality standards for polar organic priority pollutants poses a challenge for monitoring programs. The polar organic chemical integrative sampler (POCIS) may help to address the challenge of measuring low and fluctuating trace concentrations of such organic contaminants, offering significant advantages over traditional sampling. In the present review, the authors evaluate POCIS calibration methods and factors affecting sampling rates together with reported environmental applications. Over 300 compounds have been shown to accumulate in POCIS, including pesticides, pharmaceuticals, hormones, and industrial chemicals. Polar organic chemical integrative sampler extracts have been used for both chemical and biological analyses. Several different calibration methods have been described, which makes it difficult to directly compare sampling rates. In addition, despite the fact that some attempts to correlate sampling rates with the properties of target compounds such as log K_{OW} have been met with varying success, an overall model that can predict uptake is lacking. Furthermore, temperature, water flow rates, salinity, pH, and fouling have all been shown to affect uptake; however, there is currently no robust method available for adjusting for these differences. Overall, POCIS has been applied to a wide range of sampling environments and scenarios and has been proven to be a useful screening tool. However, based on the existing literature, a more mechanistic approach is required to increase understanding and thus improve the quantitative nature of the measurements. Environ. Toxicol. Chem. 2012;31:2724–2738. © 2012 SETAC

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INTRODUCTION

The need for polar passive samplers

Within environmental science there is an increasing focus toward so-called emerging contaminants. Many of these compounds are polar or semipolar, such as pharmaceuticals and personal care products (PPCPs), and thus, their behavior and fate in the environment can be very different from more traditionally studied persistent organic pollutants. These compounds are just beginning to be included in legislation, for example, in the amended list of priority substances for the European Water Framework Directive. Due to their potency at low concentrations, several of these additions to the priority list have environmental quality standard values set at extremely low levels (e.g., 0.035 ng/L for the pharmaceutical 17α-ethinylestradiol [EE2] and 0.65 ng/L for the industrial chemical perfluorooctane sulfonic acid) [1]. The measurement of polar compounds in environmental matrices and at such trace concentrations represents a significant challenge and has become possible only in recent years due to significant improvements in analytical techniques. In this regard, passive sampling devices (PSDs) may have much to offer the analytical process by providing a time-integrated sample with low detection limits and in situ extraction of analytes (http://www.norman-network.net/public_docs/slides_prague/norman_position_paper_pas_sampling.pdf). Such PSDs are fairly well developed for hydrophobic compounds such as polychlorinated biphenyls, for example, the semipermeable membrane device (SPMD), low-density polyethylene (LDPE), and silicone rubbers. However, although samplers suitable for polar compounds have been available for some years, they remain more poorly characterized in terms of modeling uptake rates and the effects of environmental factors. In the present study, we provide a critical review of the calibration and use of the most popular of these samplers, the polar organic chemical integrative sampler (POCIS).

Polar organic chemical integrative sampler

The polar organic chemical integrative sampler consists of a receiving phase (sorbent) sandwiched between two polyethersulfone (PES) microporous (usually with 0.1 μm pore size) membranes [2]. The sampler is generally compressed together using two stainless steel rings (interior diameter usually 51–54 mm), which expose a surface area of 41 to 46 cm^2. In the original description of POCIS the exposed membrane was 3.3 cm in diameter, giving a surface area of 17 cm^2 and a recommended membrane to sorbent ratio of 180 cm^2/g [2]. The two commercial versions are POCIS "pharmaceuticals," which contain the widely used Oasis hydrophilic–lipophilic balance (HLB) sorbent, and POCIS "pesticides," which contain a triphasic sorbent admixture 80:20 (wt:wt) of hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+) and a carbonaceous sorbent (Ambersorb 1500), dispersed on S-X3 biobeads. This second configuration provided superior uptake and recovery for certain classes of polar compounds including pesticides and hormones [2]. Several deviations from these standard configurations are reported, including sizes, types, and amounts of sorbents, membranes, and so forth, which are presented in the following text where appropriate.

Basic POCIS theory and modeling

A comprehensive analysis of relevant uptake theory and modeling applicable to POCIS is not the purpose of the present review and is covered in detail elsewhere [2,3]. In addition,

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comprehensive descriptions of general passive sampling theory, including different types of calibration experiments, are also provided elsewhere [4,5]. Thus, we limit the following section to several fundamental issues that facilitate an understanding of the subsequent text.

Accumulation in the sampler is driven by a difference in chemical activity of the substance dissolved in water and in the receiving phase of the sampler, initially free of the contaminant of interest. Accumulation of polar contaminants into POCIS devices is the result of successive processes occurring at the surface of the membrane and within the device. First, analytes dissolved in water have to cross (by diffusion) the water boundary layer (WBL), a retarded layer of water that develops due to friction and results in increased viscosity at the surface of the sampler [6]. The thickness of this boundary layer is dependent on water flow/turbulence around the sampler and can affect accumulation rates significantly as observed for samplers for nonpolar substances [6,7]. Second, analyte transport across the PES membrane can be through water-filled pores of the microporous PES membrane or via the polymer itself. The average thickness of the hydrated PES membrane is 130 μm, while the estimated water-filled pore volume is 76.5% of the total membrane volume [3]. Finally, compounds transfer from the PES membranes to the sorbent material mainly through adsorption. These last two steps render the understanding, modeling, and prediction of accumulation of the wide range of possible chemicals by POCIS challenging. As opposed to the absorption process that governs nonpolar contaminant accumulation, adsorption is a concentration-dependent phenomenon in nonporous polymeric samplers [5]. Sorption isotherm experiments are needed to understand the distribution of polar substances between sorbent and water over a range of concentrations. These can be undertaken for individual compounds or as mixtures because competition between analytes for the same sorption sites on the sorbent is possible. For extended exposures, biofouling of the surface of the membrane needs to be accounted for.

Though they are assumed to be additives, very little is known for any chemical of the relative resistances to mass transfer in each of these compartments. In addition, there may be WBLs on the inside of the POCIS associated with both the membrane and the sorbent particles [3]. For nonporous sorbents, analytes will usually bind with the active site at a rate which is too fast for this step to become limiting. For porous sorbents (such as Oasis HLB), analytes have to diffuse first through the pores to reach the binding site, although considering the other resistances potentially influencing uptake, such as multiple WBLs, it seems unlikely that this is the rate-limiting step. Boundary-layer control of the uptake in POCIS is generally exemplified by increases in observed sampling rates with increases in water turbulence [2,3]. When water turbulences are high enough for the resistance to mass transfer in the boundary layer to be negligible, transport across the PES membrane dominates the overall resistance and becomes the rate-limiting factor in contaminant uptake by POCIS. However, a comprehensive determination of the range of water turbulences that will affect sampling rates significantly is lacking. Experiments dedicated solely to the measurement of analyte mass transfer coefficients in the membrane are yet to be conducted in detail, but some water–membrane partitioning coefficients are provided by Vermeirssen et al. [8]. In that study, compounds with log $K_{OW} > 2$ clearly showed a lag phase in uptake due to accumulation in the PES membrane. The importance of the PES membrane is also exemplified for Empore disk–based samplers, where its addition slows sampling rates considerably compared with using naked discs, suggesting the introduction of a degree of membrane control into the uptake process [9–12]. Detailed information on the effects of environmental parameters on sampling rates is also required to obtain quantitative data.

Previous reviews

Several reviews cover the use of PSDs for environmental monitoring in general [13–15] and in the aquatic environment [16,17], or consider specific types of hydrophobic passive sampler such as SPMDs [18,19]. Additionally, polar passive samplers (including POCIS) are mentioned as part of several reviews considering the measurement of specific groups of compounds such as PPCPs [20–22], emerging polar contaminants in general [23,24], or in relation to wastewater [25]. The focus of the present review is on critically evaluating several aspects of the use of POCIS, particularly its calibration and the effects of environmental conditions on the uptake process.

CALIBRATION METHODS USED FOR POCIS

Rationale for calibration

Passive sampler calibration generally involves exposing samplers to water spiked with a known concentration of analytes of interest under controlled conditions in the laboratory [5,16]. This way a sampling rate (R_s) can be estimated, which is the equivalent volume of water extracted by the sampler per unit of time (typically given as liters per day). These experiments can also be designed to establish exposure times during which contaminant accumulation remains in the linear phase of uptake or whether contaminant uptake is concentration-independent (prerequisites for quantitative use). An understanding of the effects of environmental variables on POCIS sampling rates is required to ensure quantitative information can be obtained from field deployments [16]. Calibration can, however, also be synonymous with experiments specifically designed to understand processes governing solute–sampler interactions. For passive samplers of nonpolar organic pollutants, these have focused on the measurement of polymer–water partition coefficients [26,27] or of contaminant diffusion coefficients in polymers [28,29]. These supporting data often help to explain the mechanisms of analyte uptake into passive samplers and experimental sampling rates and their modeling [4]. Over the last decade, numerous POCIS calibration studies have been conducted to derive R_s estimates for herbicides such as triazines, polar pesticides such as phenyl ureas, a wide range of PPCPs, endocrine-disrupting chemicals (EDCs), natural/synthetic hormones, and illicit drugs (see *Reported sampling rates* and *Reported Applications and Use* below). Different procedures varying in their level of complexity and resources needed have been applied to determine POCIS sampling rates [2,30,31].

Static renewal

The first POCIS calibration experiments were undertaken using a static renewal design, where samplers were exposed to a relatively small volume of exposure water (1–3 L) refreshed periodically [2]. The POCIS was then removed at intervals, and the mass of analytes sorbed was measured in POCIS extracts. Such a procedure has been used in several instances since [32–35]. The frequency for refreshing the test water should be high enough to minimize the decrease (ideally <10% per refreshment period) in analyte concentration caused by uptake into the sampler(s) during each batch exposure and allows for a

more straightforward modeling of sampling rates. Ideally, the exposure concentration should be measured at least at the start and end of each batch renewal [5]. Often, daily renewals are necessary, which results in an intensive sampling of the water phase for calibrations typically running for up to one month. Despite this, static renewal procedures are convenient. They are generally conducted in 1- to 3-L beakers, although volumes of up to 80 L are also reported [36]; and replicate exposures can easily be prepared using different types of water. Larger tank volumes may appear to allow a static calibration where exposure water depletion is negligible and, thus, renewal not needed [30], although careful attention must still be paid to the water concentrations and additional spikes may be required [36].

Static depletion

The design of static depletion experiments revolves around a single spike of a chemical to the water, following which the drop in analyte concentration in the exposure solution, often covering some orders of magnitude, is monitored. Temporal changes in analyte concentration in water are used to estimate R_s [37–42]. First-order dissipation kinetics are in general subsequently fitted to decreases in solute concentration in water observed with time. High initial analyte concentrations are often used (i.e., >5–10 $\mu g\,L^{-1}$) because they allow the decrease in analyte concentration in the exposure solution to be followed over three to four orders of magnitude [37]. Positive controls are often needed for such calibrations to assess analyte losses due to processes other than sampler accumulation (e.g., volatilization, photodegradation, or hydrolysis). For example, a short half-life for omeprazole (antiulcerative) of 2 d was observed in POCIS calibration experiments by MacLeod et al. [38], and a significant decrease in concentration of ketoprofen was observed over 50 h in experiments by Togola and Budzinski [43]. These authors noted the importance of relying on analyte masses sorbed to the POCIS sorbent for R_s estimation rather than only the drop in analyte concentration in water. The importance of using adequate positive controls in these calibrations should not be underestimated, especially in the light of evidence that a significant amount of some analytes may be contained within the membrane [8,44], which is usually not analyzed or included in the calculations. Despite this, some authors do not appear to have conducted any such control [42] or describe them as "fortified water" [40] or exposure water with either "no POCIS" [38] or just the steel rings without any membranes [41]. Static depletion designs have proved useful to investigate the effects of dissolved organic matter (DOM) or pH on R_s, for example Vrana et al. [39], covered in more detail below (*Factors Affecting POCIS Sampling Rates*).

Flow-through systems

Flow-through experiments are designed with the aim of maintaining a constant analyte concentration in water. This is achieved with a continuous supply of fortified water to the exposure tank where multiple samplers are deployed under identical hydrodynamic conditions [45]. Constant concentrations can be obtained if the flushing rate is able to compensate for analyte losses and removal from solution by the samplers [5]. Importantly, all samplers are in principle exposed to the exact same analyte concentration in water in this experimental design. Samplers are removed from the exposure tank over time, and the sorbent is analyzed to assess the uptake of analytes by POCIS. Relatively high exposure concentrations are reported (e.g., 1 μg/L) [2] for static/static renewal exposures as this enables the collection of small enough aliquots of exposure solution without influencing the test. However, for flow-through exposures, lower exposure concentrations (<100 ng/L) can be used because the collection of larger water samples will not affect the calibration as spiked water is being added continuously. Analytes in acetone or methanol can be injected directly into the calibration tank or mixed in water before it is pumped into the calibration tank. In addition, it is worth noting that flow-through systems avoid the positive control requirements of the static experiments. Flow-through calibrations have been undertaken for alkylphenols [46,47] and EDCs [48], for example.

In situ calibration

In situ calibration is a procedure that can be used to measure sampling rates in the field at the exact location where measurements are to later take place and has successfully been carried out for hydrophobic PSDs [49]. Samplers deployed in the field are calibrated by comparing analyte accumulation with time-averaged concentrations in water obtained from high-frequency grab sampling [31]. While simple models can be used to calculate R_s in cases where analyte concentrations are relatively constant, models also exist for when analyte concentrations in exposure water are more variable [5]. In a recent study by Harman et al. [31] an in situ calibration of POCIS devices was undertaken in a sedimentation overflow channel of a sewage-treatment plant. The channel provided a system with relatively stable conditions of flow and temperature. Samplers were exposed for periods of 3, 7, 14, 21, and 31 d over a five-week-long calibration during which high-resolution automatic sampling (6-h time proportional samples) was conducted for a range of illicit drugs. Sampling rates were then used to interpret data for a year-long consecutive 14-d POCIS exposure [31].

In the absence of a performance reference compound (PRC)–based system (see below, *Development of a PRC approach for POCIS*), which can link lab-based R_s to those occurring in field deployments, in situ calibration is the technique that will provide the best possible approximation of time-weighted average concentrations from POCIS deployments, if this is of great importance to the study. This is due to deployment factors such as the chemical composition of the matrix, pH, dissolved organic carbon, competitive sorption, temperature, and flow rates, likely being more similar to those during actual field deployments compared to those under laboratory calibration conditions. This appears to be confirmed by Zhang et al. [48], who found much higher sampling rates for a suite of EDCs when calibrated in situ compared to laboratory-derived values. Although a considerable amount of effort is required to perform such calibrations, which may appear prohibitory, the need for positive controls and maintaining an experimental laboratory setup is removed.

Outlook for POCIS calibrations

Which calibration method is most appropriate depends on the question to be answered. Thus, in situ calibration should be considered where the accuracy of estimated water concentrations is imperative or when sampling is carried out over long time periods. Conversely, where a simple, cost-effective estimation of sampling rates is required, static renewal experiments might be sufficient. In the absence of any evidence in the literature to the contrary, it appears convenient to standardize static renewal calibrations to that originally described by Alvarez et al. [2]. A summary of the advantages and disadvantages of the various POCIS calibration methods is given in Table 1.

Table 1. Main characteristics, advantages, and disadvantages of different polar organic chemical integrative sampler calibration procedures available (based on a typical four-week calibration)

Method	Main characteristics	Advantages	Disadvantages
Static depletion	1- to 3-L exposures in beakers High initial solute concentration in water Measurement of solute concentration in water (at least five or more time points) R_s calculation: First-order dissipation model fitted to changes in concentration in water	Simple procedure Many replicates can be prepared Ability to test many types of waters (e.g., tap water, seawater, freshwater) Ability to vary certain environmental variables Small number of samples that require chemical analysis Low cost	Inability to systematically test the impact of water turbulences Inability to evaluate concentration dependence of sampling rates Unrealistically high starting exposure concentrations Inability to assess linearity of solute accumulation with time Issues with positive controls
Static renewal	1- to 3-L exposures in beakers Daily–several days renewal frequency of exposure solution Measurement of solute concentration in water at least as often as renewed and accumulation in samplers (at least four time points)	Simple procedure Many replicates can be prepared Ability to test many types of waters (e.g., tap water, seawater, freshwater) Ability to vary certain environmental variables	Intensive exposure water sampling and analysis Relatively complex R_s calculation when exposure concentration drops significantly Inability to systematically test the impact of water turbulences Labor-intensive
Flow-through	>20-L exposure tank Constant flow-through of fortified exposure solution Measurement and analysis of exposure solution and of samplers (four or more time points)	Possibility to systematically test effects of a wide range of environmental variables Ability to obtain constant exposure concentrations Collection of water samples is simple Long-term calibrations are possible Many samplers exposed to identical water and solute concentrations	Biofouling is possible for long exposures (e.g., one month) Difficulty in setting up a system in a temperature-controlled room Relatively large volumes of water and amount of solute needed Generation of large amounts of wastewater Expensive
In situ calibration	In situ exposure Dedicated on-site sampling cells or channels Measurement and analysis of exposure solution and of samplers Sampler deployment in an identical housing, and position to when measurement is needed R_s calculation: From the kinetics of solute accumulation in the samplers and time-weighted average exposure solution concentration	Simple Sampling rates are obtained for conditions that are very similar to future field deployments No positive controls required Focus on relevant compounds	Requires very intensive/high frequency water measurements to account for fluctuations (Autosampler may be used) Compounds need to be in the exposure medium without spiking Challenge with the measurement of the truly dissolved fraction Potentially complex modeling

It is desirable that future calibration studies focus on a more systematic testing of changes in sampling rates with changes in important environmental variables. While a large number of calibration experiments have been conducted using static exposure designs, it is important that the sampling rates generated can be related to those from other designs. A first step in this process may be to include widely studied compounds in all calibration experiments where possible (suitable compounds suggested below in *Reported Applications and Use*) as well as some interlaboratory studies to determine variability between calibrations. Future calibrations should also focus on gaining a more detailed functional understanding of solute–sorbent interactions for POCIS, along the lines of recent work by Bauerlein et al. [50], who examined which function groups govern sorption for Oasis HLB. This will help in developing models to predict which compounds will be retained on POCIS sorbents and hopefully reduce the use of resource-intensive calibration experiments for this purpose (solid phase extraction–type method development may also be used instead, see below in *Types of POCIS used*).

The processes of sorption and desorption that have been observed in several studies [30,31,47,51] and their dependence on exposure concentration or the presence of multiple substances competing for the same sorption sites need to be examined. In addition, the water concentrations of many compounds that are sampled by POCIS can vary over orders of magnitude very rapidly, for example, in wastewater [52]. Thus, understanding sampler reaction to varying solute concentrations in water is vital if an accurate interpretation of masses accumulated in the samplers is to be achieved. While modeling of sampler reaction to varying concentrations has been undertaken for nonpolar substances [53–55] and for medium polar herbicides using SDB-RPS Empore disks [56], limited data are available for POCIS [57]. Calibration experiments simulating variable water concentrations should therefore be undertaken to develop and validate models that can describe how accurately POCIS integrates peaks in analyte concentrations.

FACTORS AFFECTING POCIS SAMPLING RATES

Water flow rates

At least five studies have compared POCIS sampling rates under conditions of differing water turbulences (Table 2). These have largely been carried out using static- or static renewal–type calibrations where the exposure water is still or stirred using a magnetic stirrer [2,34,40] or stirred at different rates [38]. All these studies report severalfold increases in R_s (Table 2). However, making generalizations about these reported effects is difficult due to other factors also being different between studies (e.g., temperature) and the fact that flow rates are seldom measured with any accuracy and/or that they may represent poorly what is actually happening at the sampler surface. For example, the flow rate of 4.5 m/s in a 2-L beaker stated by Bartelt-Hunt et al. [37] seems highly unlikely to provide the same flow regime as 4.5 m/s in a river. Thus, while such experiments are simple to perform, they are not representative of conditions found in the environment. However, Charlestra et al. [58] recently showed similar uptake of pesticides when comparing stirred (magnetic stirrer at 40 rpm in a 1-L exposure vessel) batch experiments with those gained from a flow-through system (flow ~0.32 cm/s). Both showed higher uptake (generally $<\times 2$) than quiescent experiments that were also carried out. In a more comprehensive study, Li et al. [59] studied uptake of PPCPs from municipal wastewater at four different flow rates (2.6, 5.5, 15, and 37 cm/s) using a system of channels [9]. Sampling rates were not calculated, but the authors describe a less than twofold increase in accumulated amounts between 2.6 and 37 cm/s, with a few exceptions (e.g., trimethoprim and triclosan, 3.5- and sevenfold increases, respectively). These generally small differences ($<\times 2$, Table 2)

Table 2. Reported effects of environmental factors on polar organic chemical integrative sampler (POCIS) sampling rates (irrespective of POCIS configuration)

Factor	Range	Effects on R_s	Target compounds (*n*)	References
Temperature	10–20°C	Increase $<\times 1.5$	Hormone (1)	[41]
	15–21°C	Increase $\times 1$–2[a]	Pharmaceuticals (12)	[43]
	5–25°C	Increase $<\times 2$ (generally)	Pharmaceuticals/PCPs/EDCs (29)	[42]
Water turbulence	Static-stirred	Increase $\times 4$–9	Pharmaceuticals/pesticides (6)	[2]
	Static-stirred	Increase $\times 4$–5	Natural toxins (2)	[34]
	2.6–37 cm s^{-1}	Increase $<\times 2$[b] (generally)	Pharmaceuticals/PCPs/EDCs (24)	[59]
	Static-stirred[c]	Increase $<\times 3$ (generally)	Pharmaceuticals/PCPs/EDCs (29)	[40]
	3–12 cm s^{-1}[d]	Increase $<\times 7$ (generally)	Pharmaceuticals/PCPs (25)	[38]
Fouling	0.2–1.5 vs 0.5–2.4 g dm^{2-1}	Increase $<\times 1.5$ (generally)	Alkylphenols (21)	[47]
pH	3.7–9	Dependent on species (increase $<\times 3$ with increasing pH for basic compounds and decreased for acidic compounds)	Pharmaceuticals/PCPs/EDCs (21)	[39]
	4–10	Similar	EE2 BPA + 2 not given (4)	[48]
Salinity	0–35 PSU	Decrease similar $<\times 0.4$	Pharmaceuticals (13)	[43]
	0–35 PSU	Similar	Not given (4)	[48]
DOM	3–5 mg/L	No significant effect	Pharmaceuticals/PCPs/EDCs (21)	[39]
NOM[e]	0.5–5 mg/L	No significant effect	Pesticides (5)	[58]

[a] No replication.
[b] As nanograms $POCIS^{-1}$, not sampling rate.
[c] Static condition also "slightly stirred."
[d] Estimated flow rates.
[e] Reported as total organic carbon concentrations.
PCP = personal care product; EDC = endocrine-disrupting chemical; EE2 = 17α-ethinylestradiol; DOM = dissolved organic matter; NOM = natural organic matter; PSU = practical salinity units; BPA = Bisphenol A.

led those authors to conclude that flow correction may not be necessary in studies where water flow rates vary over the range studied. Similar flow effects were observed when using a PES membrane but with an Empore disk receiving phase [60].

An increase in sampling rates due to an increase in water flow rates or turbulences is due to WBL control of uptake in hydrophobic passive samplers [6,7,45,55,61]. As similar observations are made for POCIS, WBL control of uptake has been assumed for POCIS as well. Thus, it is also assumed that eventually the WBL will be reduced to a thickness at which further increasing turbulences will no longer affect R_s as the membrane matrix and/or water-filled pores will dominate the overall uptake resistance [3]. From the literature available it is apparent that increases in water flow rates increase POCIS sampling rates generally by a factor of <2. However, while this suggests WBL control of uptake, the situation may be more complicated for POCIS than for hydrophobic samplers. It is interesting to note that the effect appears to be compound-specific, for example, largest for more hydrophobic compounds in the study by Li et al. [59]. This may be due to hydrophobic compounds being hindered more by the WBL than polar ones and due to increasing affinity for the PES membrane with hydrophobicity [8]. In such cases, the question arises as to what extent WBL controls uptake into the membrane or whether the membrane itself influences accumulations within the sorbent. In conclusion, future work should focus on elucidating the uptake pathways taken by individual compounds and to what extent these may be affected differently by changes in exposure conditions.

Temperature

Several studies have examined the effects of water temperature on POCIS sampling rates (Table 2). In a comprehensive analysis, Li et al. [40] found relatively small differences in sampling rates with increasing temperature (twofold increase or less, from 5 to 25°C) for a range of nearly 30 PPCPs and EDCs. This is similar to the results of Togola and Budzinski [43], who found an increase in R_s of up to twofold (and a corresponding difference in estimated water concentrations) for most compounds over a temperature range of 15 to 21°C. Carbamazepine was an exception, where the increase of 6% was within the variation of the data. These results coincide closely with the twofold increase in diffusion coefficients over a temperature range of 20°C, which was predicted to cause a 50% increase in R_s by Alvarez et al. [2].

Fouling

It is generally stated that the PES membrane used in POCIS is less susceptible to fouling than those used in hydrophobic samplers such as SPMDs [2,3]. Polyethersulfone is, however, not immune to fouling, the level of fouling instead being dependent on the exposure environment (Fig. 1). In a comparison of fouling for SPMDs and POCIS, the polar sampler actually showed more fouling overall (0.2–2.8 vs 0.1–1.4 g dry wt/dm^2 membrane area) [47]. However, it is difficult to know how such results from controlled laboratory experiments relate to actual environmental exposures. A further interesting finding in that study was that sampling rates actually increased up to 55% for some alkylphenols in fouled compared to nonfouled samplers.

For hydrophobic samplers, the problem of a reduction in sampling rates due to fouling is assumed to be corrected by using the PRC approach, and several studies show both reduced dissipation of PRCs and uptake of target compounds due to

Fig. 1. Differences in polar organic chemical integrative samplers (POCIS) fouling from different deployment environments. Very lightly fouled POCIS (upper picture) deployed in the Norwegian Sea (~200 km offshore) for 42 d and moderately fouled POCIS (bottom picture) from wastewater treatment works after 14 d exposure. [Color figure can be seen in the online version of this article, available at wileyonlinelibrary.com.]

fouling [47,62,63]. It is likely that the effect of fouling on the sampling rates of POCIS will be compound-dependent, which may simply represent differences in the affinity of different target compounds to the fouling layer. As the fouling layer will largely consist of organic material, it will be reasonable to assume that the effect will be more significant for less polar compounds, although there is no overall trend toward that effect in the three studies mentioned above. In either case such differences mean that fouling may be difficult to correct for and, as such, should be taken into account for deployments where it is a significant issue, for example, if sampling rates used are from calibrations conducted in pure water and sampling takes place in wastewater. Additional experiments testing uptake in fouled and nonfouled samplers for a range of target compounds, preferably carried out in the environment, are required to determine the importance of fouling on POCIS uptake. Fouling has also been suggested as an issue for other configurations of PSDs suitable for sampling polar compounds, for example, when Empore disk–based receiving phases are exposed without membranes [10,64].

Salinity, pH, and DOM

The effect of salinity on POCIS sampling rates will be highly compound-specific according to the various chemical groups that make up the compound. For example, Togola and Budzinski [43] found that acidic compounds showed no significant change in R_s with increasing salinity, whereas basic compounds

including several tricyclic antidepressants showed reductions of up to 64%. Increasing salinity increases the energy required for a solute molecule cavity to form and increases the partitioning of neutral compounds toward nonaqueous phases, the so-called salting-out effect. This effect increases with the size and decreases with the polarity of the solute molecule [65] and, thus, should not be significant for most POCIS target compounds. Nevertheless, the application of freshwater-derived sampling rates to the marine environment should therefore be carried out with caution, despite suggestions to the contrary [48]. Similarly, pH will affect sampling rates dependent on the species, with up to threefold increases for basic compounds with increasing alkalinity (pH 3–9) and decreases for acidic compounds, shown by Li et al. [39]. Sampling rates for the neutral drug carbamazepine and the phenolic compounds studied (p*K*a values >10) were not affected [39]. The same study also showed little advantage of replacing HLB with ion-exchange sorbents, in neutral waters, and no statistical difference in sampling rates with increases in DOM, albeit over a narrow range of DOM concentrations (3–5 mg/L). Furthermore, in a recent study, Charlestra et al. [58] also noted no apparent effect of natural organic matter concentrations (0.1–5 mg/L as total organic carbon) on POCIS R_s.

Properties of target compounds and sampler configurations

As well as the environmental conditions during sampler deployment listed above that affect uptake in POCIS, the physicochemical properties of individual compounds obviously will determine whether they accumulate or not and, if so, to what extent. In stark contrast to apolar passive samplers, where uptake has successfully been related to hydrophobicity [5] and molecular weight or volume [5], there are currently no such models to describe uptake in POCIS. This is due to the diversity of functional groups that polar compounds may possess and, therefore, the associated complexity of solute–solvent–sorbent interactions that are possible [50,66].

Several attempts have been made to correlate observed sampling rates with some property of target compounds in the hope of being able to predict them for similar compounds, for example, using polynomial-type relationships similar to those observed for hydrophobic samplers to describe sampling rates for pesticides in terms of their log K_{OW} [30,35]. However, other studies have found no such observable trend for alkylated phenols [46] or for a range of EDCs in either the pesticide or pharmaceutical version of POCIS [32]. MacLeod et al. [38] found no overall trend for their studied target compounds based on log K_{OW}, although improvements were apparent when compounds were separated based on charge speciation, where gaussian trends were fitted to anions and zwitterions and either a linear or curvilinear trend to cations depending on flow conditions. Gaussian trends were also fitted to a very limited number of sampling rates of beta-blockers and nonsteroidal anti-inflammatory drugs [38]. Togola and Budzinski [43] reported a positive trend with log K_{OW} for neutral and basic pharmaceuticals in freshwater but not for acidic compounds or in saline waters. Similarly, Li et al. [40] described a linear relationship with log K_{OW} for a range of PPCPs and EDCs, when acidic and phenolic compounds were excluded. A linear relationship was also observed between R_s and chromatographic retention times on a C18 reversed-phase column in that study and subsequently when log K_{OW} was normalized to the fraction of the neutral species, log D [39]. Several of these results appear to be substantiated by recent work describing the predominance of apolar interactions for sorption of neutral compounds to Oasis HLB [50]. Bartelt-Hunt et al. [39] hypothesized that if uptake is controlled by diffusion across the boundary layer, then it should be able to be modeled using the molecular weight of the compound, although no discernible trend was observed in the study. Due to lack of data, we have not discussed the relationship between sampling rates and target compound properties in terms of the two different types of POCIS available. Thus, it is important to note that such relationships may be specific to each sorbent, for example, where highly polar compounds have poor affinity for HLB but are retained by pesticide POCIS.

Affinity for the sorbent is not the only consideration, however; interactions with the PES membrane, which is normally discarded and not analyzed, are also apparent. These interactions have been reported several times for explaining a lag phase in uptake, which in general appears to be related to hydrophobicity [46,60]. This has been confirmed in more comprehensive studies where the membrane was also analyzed during calibration experiments [8]. Thus, a three-compartment model (water–membrane–sorbent) might be sufficient to explain overall uptake in POCIS, similar to that proposed for SPMDs [8,55]. What is clear is that trying to extract general trends in uptake rates in relation to the physicochemical properties of target compounds based on the available data is not straightforward. This is not least due to differences between the calibration techniques used. For example, the apparent positive correlation between R_s and log K_{OW} in some static depletion experiments mentioned above is likely due to overestimation of sampling rates for less polar compounds which have affinity for PES. In this regard, water–PES diffusion coefficients should also be determined as part of the calibration process (see also recommendations for calibrations above, *Outlook for POCIS calibrations*). A further unanswered issue is that of competitive sorption, whether compounds weakly retained by POCIS sorbents can be replaced by more strongly binding ones. In such situations, uptake could be under "matrix control" rather than WBL or membrane control. Thus, uptake experiments also need to be conducted with different concentrations of interfering substances present.

The surface area of a passive sampler is a crucial factor in the amount of analyte accumulated [16]. As sampling rates for POCIS tend to be given as liters per day for a "standard" configuration, which has been defined as 41 cm^2 [3], deviations from this surface area will result in different sampling rates. Apart from the original descriptions of POCIS, which used a smaller sampler with a surface area of 18 cm^2 [2,67], some studies report 42 cm^2 [68] and some 46 cm^2 [25,69], which is a difference of up to 10% from the proposed standard configuration. Zhang et al. [48] found a positive relationship between POCIS exposure area (~6–23 cm^2) and R_s, although its effect appeared to be compound-specific ($n = 4$). The effects on uptake of the POCIS membrane surface area and the amount of sorbent used warrant further investigation for a range of target compounds.

Reported sampling rates

It is apparent, based on the above discussions, that there are many different experimental, compound-specific, and exposure-specific factors that affect the published sampling rates. Thus, sampling rates available in the literature should be treated as approximations and not applied as definitive numbers to other studies at different locations under different exposure conditions without adequate examination of those differences. For these reasons a comprehensive listing of all published R_s values

is of little value to the current review (for reference purposes, they are provided in Supplemental Data, Table S1). Sampling rates reported in the literature for stagnant or near stagnant calibration conditions range from 0.001 L/d for malachite green [33] to 1.34 L/d for the antifungicide triclosan [39], whereas for turbulent conditions they range from 0.003 L/d for the pharmaceutical metabolite metroprolol acid [31] to 2.46 L/d for the antiulcerative drug omeprazole [38]. The median values for all reported R_s values are 0.18 and 0.19 L/d (stagnant and turbulent exposures, respectively). At the lower end of the reported range are compounds that are not suited to be sampled by standard configurations of POCIS, with poor affinity for the sorbent. Rates of several liters per day may appear erroneous compared to most studies (Fig. 2); however, omeprazole was not the only compound which displayed high sampling rates in the study by MacLeod et al. [38], with both triclosan and the antidepressive drug fluoxetine having R_s values >1 L/d. The stability of these and similar compounds in the exposure system is of critical importance, especially when static depletion–type calibrations are used with sampling rates derived from reductions in water concentrations. Additionally, based on recent evidence of increasing affinity with the PES membrane with increasing log K_{OW} [8], sampling rates for relatively hydrophobic compounds are likely to have been overestimated in several of these depletion-type calibrations. To address this issue, side-by-side calibrations using the different methods would need to be carried out with identical exposure parameters for the same compounds. As such studies are lacking, it is difficult to know to what extent differences in reported sampling rates are influenced by interactions with the membrane in depletion experiments. However, Figure 2 clearly shows a tendency of higher sampling rates in studies using static depletion. Triclosan sampling rates have also been shown to be relatively high in two other studies using the static depletion calibration method, for example, 0.753 to 1.929 L/d (quiescent and turbulent, respectively) [40] and 1.01 to 1.34 L/d under static conditions with a range of pH and DOM concentrations [38]. Unfortunately, no other calibration method has been used to determine POCIS sampling rates for triclosan. However, for both omeprazole and fluoxetine sampling rates of 0.007 to 0.03 and 0.012 to 0.086 L/d (18 cm^2 surface area) were reported by Alvarez et al. [2] from renewal-type calibrations compared to 2.47 and 0.223 to 1.37 L/d given by MacLeod et al. [38] from depletion-type calibrations. Similarly, differences in literature sampling rates for some alkylphenols have recently been shown to vary by a factor of between 10 and 100, which seems unlikely to be explained purely by exposure differences in calibration studies [25]. Conversely, some pesticides, such as atrazine, which have been calibrated in several different studies [8,30,33,35–37], show very similar sampling rates, 0.25 ± 0.03 L/d (mean $\pm$ standard deviation, $n = 6$). This illustrates the problem with POCIS sampling rates, where the variation apparent in published values (Fig. 2) is as likely to come from study artifacts or exposure differences as it is due to differing physicochemical properties of target analytes without being able to discern between the two aspects.

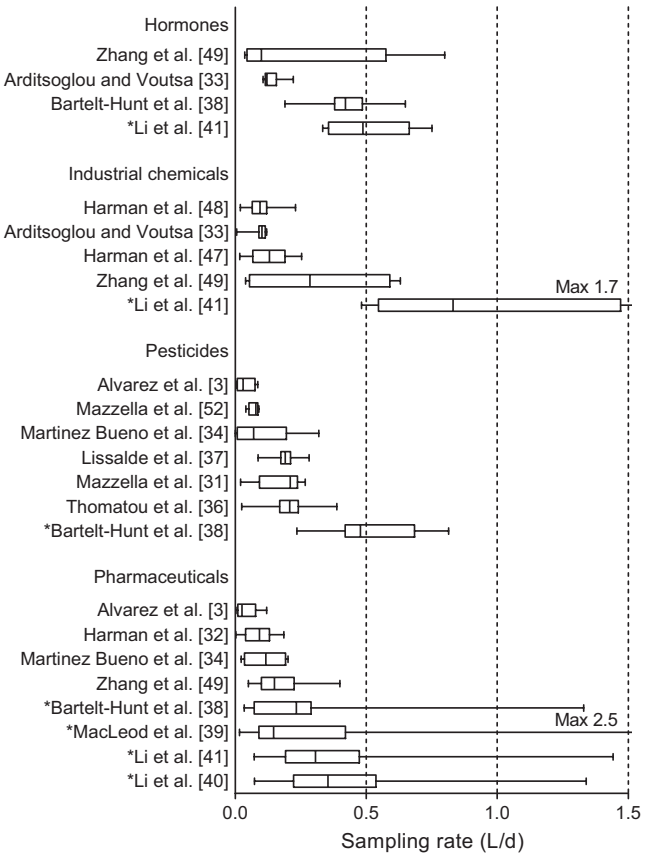

Fig. 2. Range of sampling rates reported in selected literature for hormones, industrial chemicals, pesticides, and pharmaceuticals. Whiskers show minimum and maximum values. No differentiation between types of polar organic chemical integrative samplers (POCIS) used or calibration conditions (temperature, etc.). Asterisk (*) indicates studies using the static depletion calibration method. Data from Alvarez et al. [2] are reported for POCIS with a surface area of 18 cm^2.

CORRECTION OF SAMPLING RATES FOR EXPOSURE CONDITIONS

Development of a PRC approach for POCIS

Although POCIS has already been shown to be a good tool for investigative monitoring and offers advantages over grab sampling, it is clear from the above discussion that the issues of uptake modeling and exposure correction are central to the development of POCIS as a quantitative technique. This second issue has been resolved for hydrophobic passive samplers by the use of PRCs [6]. These substances, which must not interfere with analytical procedures, are spiked into samplers prior to deployment; and as their dissipation shows isotropic kinetics analogous to uptake, they are used to estimate R_s values of target compounds in situ. Thus, investigations have been undertaken to develop a PRC approach for POCIS, built around the observation that some compounds could be released again after spiking them into the sorbent [30]. The release of compounds after initial uptake has been found in both laboratory and field calibration studies [31,47], although the reasons remain unexplained. In a later study, Mazzella et al. [51] reported that a compound with relatively high fugacity (deuterium-labeled atrazine-desisopropyl) from the Oasis HLB sorbent showed promise as a PRC, narrowing the gap between POCIS water concentration estimates and those made by automatic sampling methods. Based on these results, Lissalde et al. [36] used the same compound to provide "quite acceptable" in situ sampling rates by adjusting those gained from laboratory calibrations using the environmental adjustment factor approach. However, no quantitative analysis of the applicability of these sampling rates was provided. Such an approach may be problematic if there is a discrepancy between the factors controlling the release of deuterium-labeled atrazine-desisopropyl and those controlling the uptake of target compounds. Conversely, the pesticides

studied displayed fairly similar laboratory sampling rates, 0.195 ± 0.039 L/d (average $\pm$ standard deviation, $n = 32$), which may reduce such differences [36]. Other compounds have subsequently been suggested as potential PRCs based on observational losses, although there were no attempts to apply them for sampling rate correction [25]. Dias and Poole [66] demonstrated in an earlier mechanistic study of Oasis HLB that it showed both the properties of an adsorbent as well as a contribution of some partitioning mechanism, which may increase the likelihood of usable PRCs. It is interesting to note that in both of the available studies to examine the PRC approach in POCIS [30,51] the Oasis containing pharmaceuticals POCIS version was used. Despite the triphasic pesticides POCIS configuration being considered the generic version, it has been shown to have a tendency to bind certain compounds very strongly due to the carbonaceous component, resulting in poor recoveries [3]. Thus, it appears logical that the PRC approach may have limited applicability for the POCIS pesticides version. When using a different type of polar passive sampler based on Empore disks, Shaw et al. [71] attempted a PRC approach but found differences between the uptake stage of target compounds and the dissipation of the PRCs tested (linear vs nonlinear) and poor reproducibility.

Due to the range of conceivable interactions and based on the available calibration data, an all-encompassing PRC approach for POCIS may not be possible [72]. Despite both the need for such a solution and some encouraging initial results, a more appropriate way forward is to first understand the processes governing uptake. Only then can an evaluation of the application of the PRC approach to POCIS be carried out adequately.

Surrogate PRC systems based around hydrophobic samplers

The codeployment of PRC-spiked hydrophobic samplers alongside POCIS has been suggested as a surrogate method for sensing sampling rate changes [3]. Although there are many studies which codeploy samplers with different selectivity to measure a broad range of target compounds (see below, *Reported Applications and Use*), few have specifically corrected sampling rates of polar samplers with PRC data from hydrophobic ones. This is in part due to the need for cocalibration of both samplers, which is problematic for static-type experiments due to the high sampling rates of hydrophobic samplers. Harman et al. [46] calibrated POCIS and SPMDs together for alkylated phenols and polycyclic aromatic hydrocarbons, respectively, using a large flow-through system. Subsequently, both sampler types were exposed to measure the concentrations of those compounds in the receiving waters of discharges from the offshore oil industry [68,73]. Thus, the dissipation of PRCs in SPMDs during the calibration study could be compared to that during the environmental exposure. In this way, an environmental adjustment factor [70] was obtained, which was then used to correct POCIS R_s values from the calibration study. However, a suite of such calibration studies under a range of exposure conditions is required to validate this approach. One significant problem here is that dissipation of PRCs from nonpolar samplers is likely to be under WBL control, whereas the uptake of certain compounds in POCIS may be controlled by interactions with the membrane and/or the WBL [8]. A further issue is likely to be physical differences between the currently available hydrophobic samplers and POCIS. Differences in the configuration of the same sampler (i.e., varying the depth of the sampler body) have been shown to affect R_s by as much as twofold for hydrophobic compounds [74]. This approach may therefore be most easily realized when using the Chemcatcher passive sampling device as the deployment equipment and, thus, the exposure surface areas are the same for both hydrophobic and hydrophilic samplers [45,75]. Shaw et al. [76] used sampling rates from SPMDs and silicone rubber samplers to confirm similar sampling rates for pesticides between exposure stations for codeployed Chemcatcher samplers (SDB-RPS Empore disks covered with a PES membrane). However, no correction of the laboratory-derived sampling rates for environmental conditions was possible.

Novel approaches for POCIS performance reference systems

Another external correction method that has been proposed to correct for temperature and flow effects is based on studying the dissolution of a cast of calcium sulfate decahydrate, which is deployed alongside samplers. This approach has been applied to other passive sampling devices [77–79] and, thus, may offer some potential for use with POCIS, although this remains to be tested. Similar to using surrogate hydrophobic samplers, this method requires the plaster casts to be cocalibrated with the samplers, under a range of exposure conditions.

Instead of constructing a sampler with a rate-limiting membrane, a gel-based layer similar to that applied in diffusive gradient in thin film (DGT) samplers [80] widely used to measure inorganic compounds, may be used along with a suitable receiving phase [44]. As in a DGT, the resistance to uptake is dominated by the gel layer so that uptake is much less affected by changes in water flow rates, reducing the need for exposure correction. Such an approach was recently reported as suitable for sampling the antibiotic sulfamethoxazole under a range of water pH values and ionic strengths [81]. The sampling rate provided by this new organic-DGT was low (0.011 L/d) when compared to those reported for the same compound in POCIS (0.210–0.348 L/d) [40,82], although this can likely be improved by increasing the surface area of the organic-DGT [81]. The use of other materials for sampling polar compounds is possible, for example, silicone rubber, which has been shown to be able to sample several groups of medium polar compounds [83]. However, the problem of sampling very hydrophilic compounds is likely to remain. Polyoxymethylene has also been claimed to be suitable for use as a passive sampler for many polar organic compounds [84]. However, the usefulness of applying equilibrium passive sampling for the measurement of highly fluctuating concentrations of polar compounds, for example, in wastewater, appears limited. In summary, all these approaches may at least help toward uptake correction for certain applications. However, the overall inability to adjust uptake rates of polar passive samplers for differing environmental conditions during deployment means that estimations of time-integrated water concentrations of target compounds remain currently semiquantitative. If a custom solution is required for each study and suits only a limited group of similar compounds, then the overall applicability of polar samplers may be reduced. Thus, this issue requires considerable attention in future research if the full potential of the technique is to be realized. As mentioned previously, the first step of this process should be to focus on gaining an understanding of the processes governing uptake and how these are affected by exposure conditions.

REPORTED APPLICATIONS AND USE

Types of compounds

Over 300 individual compounds have been detected in POCIS (Fig. 2; Supplemental Data, Table S1), either in

laboratory calibrations, in environmental exposures, or in both (note not all calibrated compounds have been detected in the environment). Of these, four of the most commonly measured compound groups are pesticides (>100 individual compounds in ≥26 studies), pharmaceuticals (>90 individual compounds in ≥21 studies), industrial chemicals (>30 individual compounds in ≥23 studies), and hormones (>15 individual compounds in ≥18 studies; see Supplemental Data, Table S1 for compound groups). Within these four groups, the most commonly measured compounds are the herbicide atrazine (20 studies), the stimulant caffeine (15 studies), the plastics production chemical bisphenol A (12 studies), and estrone (a metabolite of the hormone 17β-estradiol, 15 studies). Therefore, these four compounds appear well suited to be included in all future calibrations, which would facilitate the comparison of sampling rates between studies. The inclusion of compounds that are representative of specific chemical groups, for example, based on charge or interaction with the PES membrane, should also be considered.

Another significant compound group measured in POCIS is alkylated phenols (>60 individual compounds) both discharged in production waters in offshore oil and gas extraction [46,47,68,73] and present in the environment from other sources [85]. The latter also includes various nonyl and octylphenol ethoxylates and or their degradation products [32,86–92], which are both included in the group industrial compounds above. Numerous compounds which are additives in a variety of PCPs have also been detected in POCIS extracts, for example, musks such as galaxolide and tonalide [85,87,93,94], various UV filters [95,96], and the insect repellent *N,N*-diethyl-meta-toluamide [82,86–88,93,97,98]. Additionally, several hydrophobic compounds which are outside of the range of log K_{OW} (<3–4) to which POCIS is normally applied [3] are reported to accumulate, such as polycyclic aromatic hydrocarbons [88,99] and even polybrominated diphenylethers [99]. If such compounds are targets to be measured, then much lower detection limits are likely to be reached by using hydrophobic PSDs with a larger surface area such as SPMDs, LDPE, or silicone rubber. Finally, several naturally occurring compounds have been measured in POCIS, notably cyanobacterial toxins microcystins [34,100] and various natural fragrances or odors [87,88].

Types of POCIS used

Consideration should be given before the start of a new study regarding which type of POCIS is to be used. For general screening, it is recommended to deploy both types to increase the range of compounds accumulated [3]. The importance of carrying out some preliminary work considering POCIS sorbents and target compounds should not be underestimated. For example, at least half of studies concerning pesticide measurements are made using the pharmaceutical version of POCIS, for example, herbicides measured by Mazzella and coworkers [30,51]. Conversely, sampling rates for some pharmaceuticals have been shown to be higher in pesticide POCIS [59]. Although those authors argue that there are practical reasons for choosing the pharmaceutical POCIS version based on the OASIS sorbent, not least where POCIS is constructed in house because the procedure for the pesticides POCIS version is more complicated (triphasic adsorbent mixture). Equally, consideration must be given to the suitability of the elution solvents used to extract POCIS sorbents. For example, Harman et al. [99] failed to measure mono- and dibutyltin when eluting Oasis with methanol, whereas recovery would have been improved by acidifying the solvent, facilitating calibration [101]. A few studies report such preliminary work, for example, Arditsoglou and Voutsa [32], who improved recovery of EDCs from Oasis by using acetone instead of methanol. It is recommended that one should check the suitability of POCIS sorbents (and existing elution solvents) for target compounds before calibration/exposure. This can be carried out relatively easily using standard solid-phase extraction method development but is generally overlooked.

Other sorbents that have been tried in versions of POCIS include the polymeric reverse phase Strata X [102]. Those authors claim this sorbent was applicable to a wider range of compounds than was Oasis HLB in preliminary trials, although they do not provide the data. Li and coworkers [39] calibrated POCIS containing the Oasis MAX and MCX (mixed mode anion exchange, and mixed mode cation exchange, respectively), as described previously. They concluded that the MAX and MCX versions showed little advantage over HLB in natural waters. Kaserzon et al. [103] used a weak anion exchange sorbent (Strata XAW) for sampling perfluorinated alkyl carboxylates and sulfonates, based on its superiority for sequestering the shorter-chain compounds. Other types of membrane-covered, sorbent-based samplers for polar compounds are also described in the literature, for example, coconut charcoal in teabag filter papers for nitrosamines [104] and sorbent-based samplers to target microalgal biotoxins [105–107].

Types of aquatic environments sampled

The majority of published POCIS studies making measurements in the environment are from a variety of lotic and lentic freshwater systems, with only a few studies considering purely marine sites [33,68,73,108,109]. Interestingly, several studies report contamination in cave streams [88,98] and even a coastal aquifer system [110]. Dougherty et al. [97] also deployed POCIS in wells to consider pollution of groundwater. For studies carried out in the marine environment, consideration should be given where freshwater-derived sampling rates are used to estimate water concentrations in the marine environment as sampling rates may differ considerably between the two, as mentioned previously [43]. In fact, sampling rates from laboratory conditions using tap or nanopure water have been used to estimate water concentrations in marine environments, without considering the effects of salinity [32]. POCIS has also been applied to various measurement scenarios inside and around wastewater-treatment systems. Some examples are as follows: examination of the loadings, trends, comparisons, and fate of achiral and chiral pharmaceuticals [69]; measuring steroidal estrogens and their removal [42]; attempts to link chemical analysis with bioassay toxicity results from over 20 treated sewage effluents [111]; calibration-type studies [31,59]; evaluating the presence of endocrine-disrupting substances posttreatment along with freshwater mussels [90]; and studying the occurrence of illicit and therapeutic pharmaceuticals in wastewater effluent and surface waters [82].

Deployment times

In general, POCIS deployments tend to be for a period of several weeks, with the shortest reported deployments being 7 d [32,82,112]. Such a time period is desirable to provide a reasonable time integrative window and secondly to aid detection at typical environmental concentrations. However, detection of illicit drugs in wastewater by POCIS was shown to be possible after just 3 d [31]. Many environmental studies refer to the original POCIS work, where linear uptake was shown in the

laboratory over a 56-d period at concentrations of 1 μg L/d, as evidence that field exposures where deployments are typically two to four weeks will also have experienced linear uptake. While this may appear logical, assuming environmental concentrations of typical target compounds are well below the 1 μg L/d level used for calibration, many other compounds (matrix) will accumulate during environmental exposures when compared to the laboratory. These additional compounds are not analyzed but may affect uptake in terms of competitive sorption processes. Care must thus be taken when assuming linearity of uptake during long deployments as this remains to be tested. For example, equilibrium or some kind of sorbent capacity may well have been reached for various estrogenic compounds during deployments of up to 169 d in Lake Thun in Switzerland [113]. Fouling may also become an increasing problem during long deployments, although its effects on uptake remain poorly described for polar samplers. Where such long-term data are required, consecutive deployments of POCIS are likely to be more appropriate, although both the sampling and analysis burden are inherently increased. At least three such studies exist, two sampling wastewater continuously for 367 and 271 d [31,69] and one year-long study of micropollutants from a Spanish fish farm [33,108], allowing tends in contaminant concentrations to be elucidated.

Correlation with spot sampling

Many studies report comparisons between POCIS-generated water concentrations and those shown with spot sampling [36]. Although this appears a logical step in the validation of (especially) sampling rates [2], it is difficult to know what information can be gained by comparing a three- to four-week POCIS deployment to a single grab sample. The accuracy of the water concentrations derived from POCIS will depend on the sampling rates applied (differences in exposure conditions, *Factors Affecting POCIS Sampling Rates*) and the ability of POCIS to integrate concentration changes adequately, as examined by Mazzella et al. [57] in controlled laboratory conditions. The verification of this time-integrated measurement by water analysis may require a sampling frequency beyond that which is practically feasible for certain scenarios such as wastewater-treatment systems [52]. This potential variation in water concentrations which may be gained from spot sampling, one of the fundamental reasons for proposing passive sampling in the first place, means that for studies using a single or very few water samples the comparison would likely give different results if another sampling time point was used. Thus, comparisons will be poorest where the water-sampling interval is large and the water concentrations change rapidly [52,57]. As mentioned previously, detailed studies concerning the response time of POCIS to changes in water concentrations are lacking, and efforts should be focused on tackling this issue in a systematic way instead of ad hoc comparisons. This may be carried out in the laboratory or in situ where accumulations in samplers during overlapping exposures are statistically compared to frequent grab samples, under a range of fluctuating concentration scenarios.

Use of POCIS extracts in bioassays

Passive sampling devices, including POCIS, were initially developed for time-integrative monitoring of individual compounds measured by means of chemical analysis. However, PSD extracts have also been applied to biological testing, in both in vitro and in vivo assays [114]. One of the first published POCIS studies [91] already covered the evaluation of POCIS extracts in a yeast-based assay to measure environmental estrogens. This study clearly established the potential of the use of POCIS in combination with bioassays. A large number of studies have now been performed where POCIS was combined with bioassays, many of them having dealt with endocrine disruptors, particularly the environmental estrogens [41,90,92,102,115–120]. Other bioassays that have been used in combination with POCIS extracts have end points such as the inhibition of bacterial bioluminescence (i.e., an indicator of general toxicity [111,115]) and the inhibition of photosynthetic yield in algae or biofilms (i.e., an indicator of photosystem II inhibitors such as diuron and atrazine [111,121]).

Testing POCIS extracts in biological assays is useful for a number of reasons. First, POCIS continuously samples chemicals over the deployment period, and biologically active compounds that occur at varying concentrations can be more effectively monitored with POCIS than by means of grab sampling. Second, bioassays often require replication and dose–response curves for proper data evaluation [121]. Therefore, a substantial original sample is needed to reach effective doses in the media used in bioassays. The fact that POCIS has sampling rates of one liter or more per week is thus an advantage, and POCIS can provide large enough samples for bioassays. In fact, samples from POCIS are often large enough to be used for more than one bioassay and multiple chemical analyses [111,115]. Third, it can be argued that the use of POCIS, rather than relying on traditional water sampling, is more relevant from an ecotoxicological perspective in that a passive sampler mimics uptake of compounds by organisms. For example, it was shown that the amounts of estrogenic activity in POCIS extracts correlated with the amounts of estrogenic activity found in the bile of fish [118]. Therefore, using the time-integrative aspect of POCIS and combining POCIS extracts with multiple biological and chemical analyses provides for an efficient tool for investigative monitoring [92,111].

One major strength of using bioassays to test environmental samples is that they can provide an integrative measure of the toxic potential of a group of compounds including unknown toxicants. This has been shown to be valid also when testing POCIS extracts in bioassays. Examples are (1) herbicides whose mode of action is to inhibit photosystem II [111] and (2) compounds that can bind to receptors in vertebrate cells [92]. Unfortunately, the fact that a bioassay result comprises the toxicity of a range of compounds, each with its own toxic potency and its own sampling rate, thwarts the possibility of calculating an accurate time-weighted average (TWA) concentration for the measured toxicity in a PSD. For example, a toxic potential of 100 ng per POCIS may equate to 1 L of sampled water containing a potent chemical (i.e., a TWA of 100 ng/L) or it may equate to 20 L of sampled water containing a 10-fold less potent chemical with a twofold lower sampling rate (a TWA of 5 ng/L). Thus, it is not possible to calibrate POCIS to provide TWA concentrations for toxicity assessments. The issue also highlights a major critical question that emerges when combining a POCIS extract with a bioassay: How well does the mixture of chemicals in the extract resemble the mixture of chemicals present in the water during deployment? For the purpose of quantifying individual compounds, it is not a problem when each compound has a different sampling rate. As long as the sampling rate of a compound is known, a TWA concentration may be calculated. However, when a number of compounds with the same mode of action have different sampling rates this causes problems. A compound may dominate the toxicity in a

water body, but because of its low sampling rate, it will be underrepresented in a POCIS extract to the extent where it may no longer dominate toxicity. Given the observed variability in sampling rates (Fig. 2), it is thus inevitable that the mixture of toxicants in the POCIS extract will differ from that in the water where the POCIS was deployed and, thus, is not a fully representative sample. Although this issue also applies to an enrichment technique such as solid-phase extraction, it is easier to optimize, standardize, and control the enrichment step with solid-phase extraction, at least for known toxicants.

This critical issue of shifting toxicity profiles between the sampled water and POCIS extracts has not yet been examined, to our knowledge, but can be illustrated for a well-studied class of compounds like the environmental estrogens. Zhang et al. [48] found that POCIS sampled four steroidal estrogens in a narrow range of 0.04 to 0.05 L/d (for a 27-mm POCIS). This suggests that the estrogenic toxicity profile would be preserved when going from the sampled water to the POCIS extract (see also Rujiralai et al. [42]). However, Arditsoglou and Voutsa [32] looked at a broader range of endocrine disruptors and found that the potent steroidal EE2 had an almost twofold higher sampling rate than five other steroidal estrogens. Furthermore, the endocrine disruptor 4-octylphenol had a 30-fold lower sampling rate than EE2. Going by these sampling rate data [32], the toxic potential of a POCIS extract would contain an overrepresentation of the pharmaceutical EE2 and would largely miss the contribution of the industrial chemical 4-octylphenol. Currently, there is no way around this problem. Consequently, when combining POCIS with biological analysis, it is advisable to be aware of the issue and to check if sampling rates of know toxicants are in a similar range.

CONCLUSIONS AND RECOMMENDATIONS

Polar organic chemical integrative sampler has been applied to a wide variety of over 300 target compounds, different environments, and sampling scenarios. In several of these studies it is difficult to see how the samples could have been taken otherwise. However, the results have been examined at different levels of complexity. Despite the advantages over traditional spot sampling offered by POCIS, the two interrelated issues of modeling uptake and exposure correction remain unresolved. These questions will require considerable attention before we can approach quantitative measurements for polar passive samplers. Although POCIS already serves as a versatile, economic, and robust tool for investigative monitoring studies and for observing spatial and temporal trends, sampling rates are not yet robust enough to supply reliable TWA concentrations, particularly for the monitoring of environmental quality standards. We make the following recommendations based on our review of the literature. First, preliminary studies considering sorbents and extraction methods/solvents for the target compounds should be carried out before sampler calibration and/or environmental exposure; this should include examining partitioning to PES. In addition, laboratory calibrations need standardizing, including methods for measuring and reporting as well as the calculation of sampling rates and the frequency of sampling for water concentrations. Furthermore, though static calibrations are very economical, flow-through calibrations are methodologically better approximations of POCIS deployments in the field. Static depletion calibration should be used only with adequate consideration of uptake by the PES membrane, and where possible, widely studied compounds should be added to all calibration experiments (e.g., atrazine). Next, more mechanistic-type studies are required to understand the adsorption process and transport through/into the membranes and which factors are controlling uptake. This should also include examination of competitive sorption by interfering substances: sampling rates should be seen as a guide, rather than a definite number. Finally, providing a TWA for toxicity measurements made in POCIS extracts should not be attempted as toxicity involves mixtures of compounds with different toxic potencies and different sampling rates. When interpreting bioassay results from POCIS extracts it has to be kept in mind that POCIS will not provide a one-to-one mirror image of the cocktail of toxicants in the sampled water.

SUPPLEMENTAL DATA

Table S1. Selected chemicals measured by POCIS and their sampling rates reported in the literature. (233 KB DOC).

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