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Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances

Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives
Position Paper

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This document has been written as a follow-up to the expert group meeting organised by the NORMAN association on 27th May 2009 in Prague. It reflects the position of the NORMAN association experts and invited speakers on the topic of passive sampling and its application in the monitoring of emerging pollutants in aquatic environment.

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Executive Summary

Passive samplers represent an innovative monitoring tool for the time-integrated measurement of bioavailable contaminants in water and sediment. Passive sampling technology is proving to be a reliable, robust and cost-effective tool that could be used in monitoring programmes across Europe. These devices are now being considered as a part of an emerging strategy for monitoring a range of priority and emerging pollutants.

Passive sampling is based on the deployment *in-situ*, or use in the laboratory, of non-mechanical devices of simple construction capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs via diffusion, typically over periods of days to weeks. Contaminants accumulated in exposed samplers are subsequently extracted and their concentration levels measured, allowing the quantification of time-weighted average (TWA) concentrations in water or equilibrium pore water concentrations in sediment. These devices can be deployed in most aquatic conditions (fresh and saline) and associated water treatment facilities, thus making them ideal for monitoring across the entire water cycle and even in remote areas with minimal infrastructure. Passive sampling can also be employed in batch sediment extractions to provide estimates of contaminant concentrations in pore water or assessment of bioavailable concentrations of contaminants in sediment.

In 2009, the NORMAN association organised a meeting of experts in the field of passive sampling. As a result of this meeting a position paper was produced, which reflects the view of the experts on the topic of passive sampling and its application in the monitoring of emerging pollutants in the aquatic environment and indicates future research and development needs in this area.

The position paper discusses functional principles of passive samplers and problems associated with the effects of environmental variables (temperature, water turbulence and sampler fouling) on their performance. Further, it lists the established or expected/potential performance of passive samplers for monitoring of the most discussed groups of emerging substances (such as cyanobacterial toxins, antifouling agents, brominated flame retardants, endocrine disrupting compounds, fluorinated surfactants, organosiloxanes, pharmaceuticals, polar pesticides, sunscreen filters etc.) and availability of calibration data that enable estimation of TWA concentrations. The document also shows the applicability of the passive sampling concept in risk-oriented monitoring of emerging substances in sediments and in determination of the bioaccumulative exposure of organisms. The great potential of this technology in combination with toxicological assays to determine the biological relevance of mixtures of toxicants with specific modes of action, and present at low concentrations, is also demonstrated.

If passive sampling is to become accepted and used in a regulatory context for monitoring water quality across Europe, then there is a need for the development of improved validation methods and setting-up of the appropriate quality control and quality assurance schemes for the technology. Successful demonstration of the performance of passive samplers alongside conventional sampling schemes, and inter-laboratory studies that demonstrate reproducibility of data produced by different designs of passive samplers, are urgently needed to facilitate the acceptance of passive sampling in routine regulatory monitoring programmes in the future.

I. Introduction

Improvements in analytical methods, primarily the introduction of more sensitive and specific mass spectrometry techniques, have increased awareness of the presence of emerging substances from many sources at trace levels (low ng L^{-1}) in the aquatic environment [1]. These substances include industrial chemicals and products, consumer products such as pharmaceuticals (both prescription and non-prescription drugs) and personal-care products, pesticides, natural bioactive compounds such as cyanotoxins and hormones, and metabolites of all these chemicals. Previous research focused mainly on non-polar and mono-polar compounds such as PCBs (polychlorinated biphenyls), PAHs (polycyclic aromatic hydrocarbons), chlorinated solvents, or chlorinated pesticides such as DDT or lindane. More recently attention has turned to the modern polyfunctional and often ionisable pesticides, biocides, drugs and personal care products. Currently there is a lack of knowledge regarding the fate and effects of many chemicals released into the environment either as products or accidentally. Although most of these compounds are present in the environment at low concentrations, many of them raise considerable toxicological concerns, particularly when present as components of complex mixtures [2].

Exposure assessment in the aquatic environment is based primarily on analytical measurements of chemical compounds in samples from various environmental compartments – water, sediments, soils, air – as well as from organisms from different trophic levels within a food chain [2]. Understanding and quantification of processes which emerging compounds can undergo in the environment, such as adsorption and partitioning between solid and aqueous phases, formation of complexes in solution as well as abiotic and biological transformation, are also urgently required. Both effective sampling and analytical methods are therefore essential to obtain reliable data on the concentrations, speciation and fate of these compounds in the aquatic environment.

While a lot of effort has been put into research and development of increasingly sensitive instrumental analytical methods for the measurement of emerging substances in various matrices in the aquatic environment, less interest has been paid to the development of suitable sampling techniques. Until recently, sampling methods for emerging substances were the same as those routinely used for monitoring priority pollutants in the aquatic environment. These are based on periodic collection of spot or grab bottle samples of water. The subsequent laboratory analysis of the sample provides a snapshot of the levels of pollutants at the time of sampling. There are, however, drawbacks to this approach in environments where contaminant concentrations vary over time, and where episodic pollution events such as spills or storm water runoff can easily be missed. This problem is particularly relevant to polar (hydrophilic) emerging substances. The residence times of these compounds in aquatic systems are generally lower than those of hydrophobic organic compounds. However, the presence of these more hydrophilic compounds in these systems (wastewater, surface water) may occur as a result of relatively episodic events (frequent, short duration and high concentration peaks). Thus, there is an urgent need for the development of suitable sampling and analytical methods capable of detecting and identifying contaminants in an integrative manner for an adequate assessment of the environmental risk posed by emerging substances.

One solution to this problem is to increase the frequency of sampling or to install automatic sampling systems that can collect numerous water samples over a given period. For example, the pooling of samples collected hourly into a 24 h composite sample, or continuous on-line monitoring for specific sets of compounds can be used to provide representative data. These methods are both costly and in many cases impractical, since a secure site and additional infrastructure or personnel are required to protect, operate and maintain the mechanical automatic sampling devices. Over the last decade alternative

methods for monitoring water quality have been sought to overcome some of the difficulties. A developing alternative strategy to these traditional sampling methods is to employ passive sampling devices that can be deployed over extended time periods (days to weeks) to provide time-weighted average (TWA) concentrations [3,4].

Passive sampling is a relatively easily applied sampling technique, based on the use of non-mechanical samplers of simple construction, often consisting of a single polymeric sorbing phase. In most cases these samplers do not require any external energy source to function. These devices can be deployed in most aquatic conditions (fresh and saline) and associated water treatment facilities, thus making them ideal for monitoring across the entire water cycle and even in remote areas with minimal infrastructure. Furthermore, these samplers assist with the sensitivity of subsequent analytical methods as they pre-concentrate and preserve chemicals sampled within these polymeric receiving phases. This enables improved sensitivity for a greater range of compounds and improved stability of chemicals within the sample without additional treatment (e.g. pH adjustment) unlike more traditional grab sampling techniques. In some cases, the use of passive samplers can also help to reduce or even eliminate the use of excessive volumes of toxic extraction solvents.

Passive samplers have been used for environmental monitoring since the 1970s, when the first samplers for the assessment of ambient air quality and workplace exposures to potentially hazardous air pollutants were developed and applied. To date, a number of sampler designs are commercially available and there are now established standards and official methods (e.g. ASTM, EPA, NIOSH, CEN and ISO protocols) for the use of these devices, which form part of legal frameworks. More recently, worldwide monitoring networks have been set up using passive air samplers to monitor persistent organic pollutants on a global scale [5,6].

In contrast, the application of passive samplers in monitoring water quality is some way behind the situation for air, and the technologies available for monitoring soils and sediments are even further from recognition. Since the introduction of the semi-permeable membrane device (SPMD), designed at USGS by Huckins et al. [7] in the early 1990s, passive samplers have become widely used for monitoring persistent organic pollutants and other non-polar organic compounds in the aquatic environment. Nearly ten years later, the passive sampling technology suitable for sampling hydrophilic organic compounds including modern pesticides, pharmaceuticals and personal care products has been reported in the work of Alvarez (POCIS sampler) [8] and Kingston et al. (Chemcatcher concept) [9]. Since then, the number of publications on development, performance optimisation and field application of passive samplers for emerging substances has grown rapidly.

A number of recent reviews have been published describing the design, calibration procedures, figures of merit and applications of the different devices for monitoring the aquatic environment [3,10,11,12]. Booij summarised in a report for the ICES Marine Chemistry Working Group the established or expected/potential performance of various passive samplers of compounds that are listed under WFD and other directives or conventions [13]. Recently, several review papers addressing passive sampling of emerging pollutants have been published [14,15]. In addition, a book describing the SPMD [16] and a general text describing many passive sampling techniques for environmental monitoring [17] are available.

II. Concept of passive sampling

Passive sampling is based on the deployment *in-situ* or use in the laboratory of devices capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs via diffusion, typically over periods of days to weeks. Contaminants accumulated in exposed samplers are subsequently extracted and their concentration levels measured, allowing the quantification of TWA concentrations in water or equilibrium pore water concentrations in sediment. It enables temporally-representative sampling or sampling of the truly dissolved concentration of contaminants in water or aquatic sediments. Even for those chemicals that are present at extremely low concentrations in the dissolved phase and are primarily accumulated in biota via the dietary uptake, passive samplers generally extract sufficient amounts of residues for analysis. Passive sampling can also be employed in batch sediment extractions under laboratory conditions to provide estimates of contaminant concentrations in pore water or assessment of bioavailable fraction of contaminant in sediment [18,19].
Passive sampling is based on the diffusion of analyte molecules from the sampled environmental medium (water or sediment pore water) to a receiving phase in the sampling device. The diffusion occurs as a result of a difference between chemical potentials of the analyte in the two media (Figure 1). The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling is stopped. The mass of chemical sorbed in the sampler following a given exposure period is initially proportional to the TWA concentration in the environmental medium to which the sampler was exposed (integrative samplers) and subsequently once equilibrium is achieved to the concentration in the environmental medium with which the device is at thermodynamic equilibrium (equilibrium samplers). The main advantage of kinetic or **integrative sampling** is that even contaminants from episodic events commonly not detected with spot sampling are collected by the sampler. This permits the measurement of time weighted average (TWA) contaminant concentrations over extended time periods using a single sample (extract from the passive sampler). This gives a more representative picture of contaminant levels than that obtained with the use of infrequent spot samples. To achieve **equilibrium sampling**, for a given sampler the sampling period needs to be sufficiently long to establish thermodynamic equilibrium between the water and the sorbent phase of the sampler. To achieve equilibrium within reasonable sampling periods samplers of relatively low capacity for the analytes of interest or with modified surface area to volume ratios may be required [20]. Application of the sampler-water distribution coefficient then enables the calculation of the analyte concentration in the sampled medium.

Analytes are accumulated in a suitable sorbent material within the passive sampler, known as a receiving phase. This can be a solvent, chemical reagent, absorbent polymer or a porous adsorbent material. Whereas most samplers of hydrophobic compounds are based on diffusion and absorption in non-porous polymers, most samplers of polar organic compounds (i.e. majority of emerging compounds) and metals are based on diffusion through porous membranes and sorption to selective **adsorbent materials**. The difference in selection of materials applied in sampler construction results in different sorption phenomena that define the driving force of the sampling process (Figure 2). In general, accumulation of hydrophilic organic compounds to porous adsorbents is more complex than absorption and dissolution of hydrophobic chemicals in non-porous polymers (polyethylene or polydimethylsiloxane). This is because adsorption distribution coefficients (unlike partition coefficients in solvents and sub-cooled liquid polymers) described by sorption isotherms can be concentration-dependent. Competitive adsorption of analytes and possible interferences are also possible. The polar organic compounds are mainly retained by specific interactions with functional groups at the surface of the adsorbent. Although the use of adsorptive polymers with specific interactions is preferred in certain cases, the risk always exists of saturating the fixed number of superficial bonding sites when these polymers are applied to a

complex sample matrix. Finally, many compounds may speciate into multiple forms depending on their pK_a parameters and the pH of the sampled medium. Where a sorbent phase only accumulates a single form of a specific compound such as the neutral species, these phenomena will also influence the observed uptake. Sampling description is thereby complicated by the presence of several species with different diffusion and sorption properties that may dynamically change during the sampling process, depending on a milieu of properties of both the sampled medium, the receiving phase and of the individual compound.

Recently, a novel absorptive equilibirum passive sampler for polar organic compounds has been reported by Magnér et al. [21]. This is based on a plastic material, polyethylene-co-vinyl acetate-co-carbon monoxide (PEVAC). This receiving phase operates as a homogenous, non-porous liquid in which the analytes are retained by dissolution rather than by specific interactions with the surface of the polymer. The PEVAC material showed enhanced sorption of several polar pesticides and pharmaceuticals compared to the silicone material. Identification of suitable absorbent polymer materials with high retention capacity of polar compounds presents a promising approach in future development of passive sampling technology and may replace currently used complex adsorption-based samplers for which data conversion into aqueous concentrations is often difficult.

For devices that operate in the kinetic or integrative mode, the sampling rate is given by the product of the overall analyte mass transfer coefficient and the active surface area of the sampler (R_S = k_o A). Sampling rate may be interpreted as the volume of water cleared of analyte per unit of exposure time (e.g. mL h^{-1} or L day^{-1}) by the device and is independent of the analyte concentration in the sampled medium. It can be affected and modulated by the analyte diffusion and partition properties in the media along the diffusional path, and is determined in laboratory calibration studies.

Often the main barrier to mass transfer is the water boundary layer (WBL) located at the external surface of the sampler. In such a case the sampling rate is significantly affected by environmental variables such as water temperature, turbulence and biofouling. If laboratory calibration data is to be used for calculation of TWA concentrations, the effect of these variables has to be either controlled or quantified. For samplers used to measure concentrations of non-polar organic analytes, one method of overcoming some of the problems associated with the impact of fluctuating *in situ* environmental conditions (temperature and turbulence) on sampling rate is the use of performance reference compounds (PRCs) [22]. These are analytically non-interfering compounds (typically deuterium or ^{13}C labelled analogues of the compounds to be measured) and are loaded onto the receiving phase of the sampler prior to deployment. These PRCs are eliminated from the receiving phase during the deployment period. Where the kinetics of uptake and elimination are isotropic, that is the rate constants for the elimination of the PRCs are affected by environmental variables in a manner similar to the uptake rates of pollutants, these elimination rate constants can be used to correct the sampling rates of pollutants in field deployments. There is also some evidence that the elimination rate constants of PRCs can be used to compensate for the impact of biofouling on uptake; however, more work is needed in this area [23,24,25].

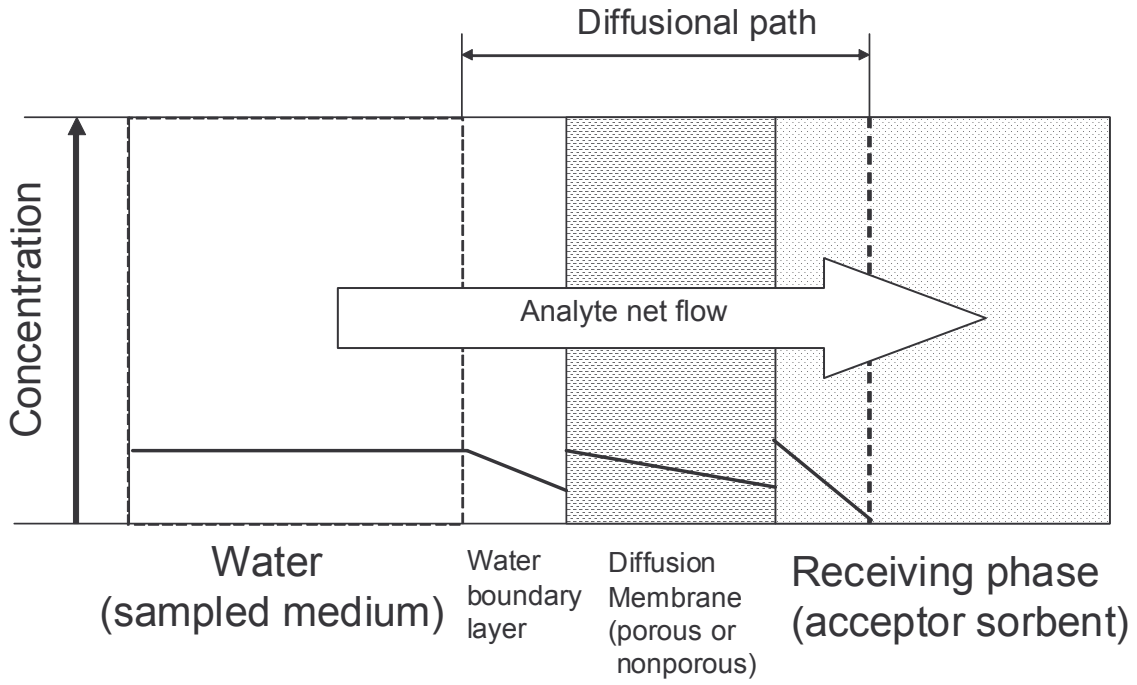

Figure1. *Functional principle of a passive sampling device, showing the concentration profile of a compound during diffusion and accumulation from bulk of the sampled medium to the sorbent (receiving phase) through a permeable (porous or non-porous) membrane. High affinity to the sorbent inside the sampler drives the diffusion of analyte molecules from the sampled medium into the sampler until the thermodynamic equilibrium is established. (adapted from Mills et al. [14]).*

The correction for the effect of environmental variables in samplers where the sequestration process depends on adsorption of the analyte presents one of the major challenges in the development of the technology. In many cases, uptake of analytes (polar organic compounds and metals) into these devices is WBL-controlled and thus sensitive to changes in flow turbulence. The PRC concept cannot, however, be generally used to correct calibration data for changes in field conditions because of the complex character of the desorption kinetics that may not be isotropic with the adsorption [26]. Mazzella et al. [27] and Budzinski et al. [28] have recently demonstrated isotropic exchange in certain exposure scenarios, but this concept still remains to be fully explored. In cases where PRC loss is not isotropic with uptake of target analytes, an alternative *in situ* calibration approach is to load PRCs into co-deployed sampling phases from which elimination is observed and which may subsequently be related to uptake. An *in situ* calibration technique, using PRC-loaded absorbent polydimethylsiloxane (PDMS) disks deployed alongside the Empore^{TM} adsorbent disk samplers as a surrogate calibration phase, has been proposed by Shaw et al. [26] and shows promise for future applications. Alternatively a passive flow monitor based on dissolution gypsum has been developed which may predict the sampling rate in response to *in situ* flow conditions [29]. Differences in mass transfer in absorption- and adsorption-based samplers are illustrated in Figure 3.

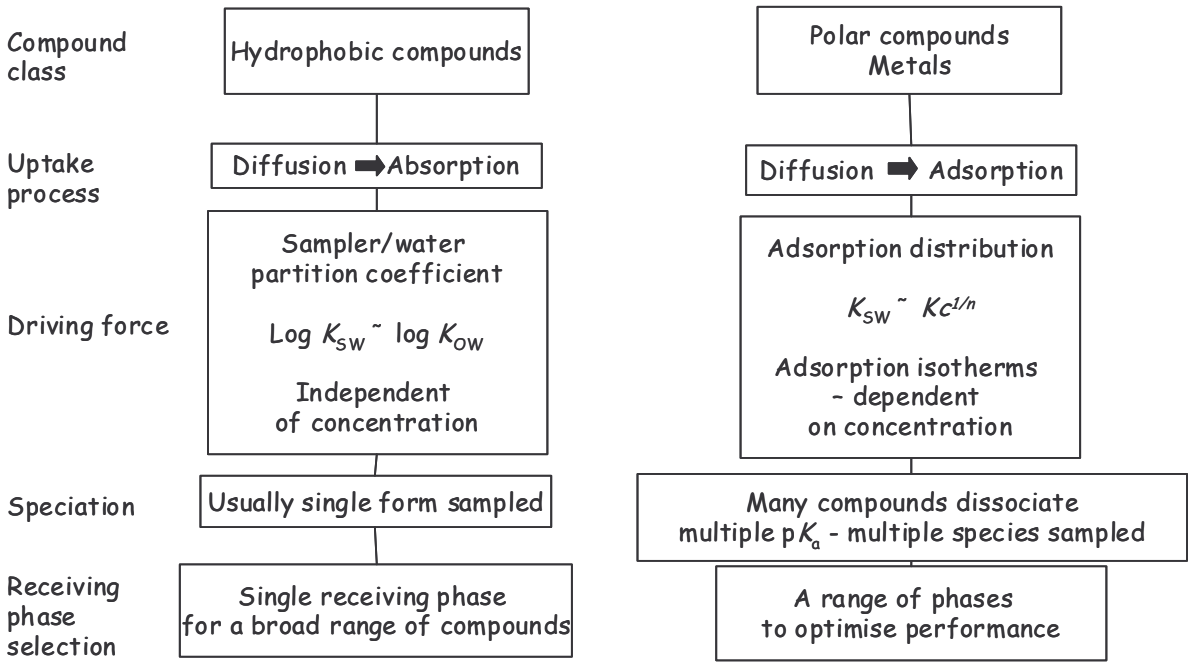

Figure 2. *Differences in passive sampling in (left) absorption- and (right) adsorption- based samplers. The majority of emerging substances are polar or semi-hydrophobic. Thus, the use of adsorbent-based samplers presents the most suitable sampling approach for these compounds.*

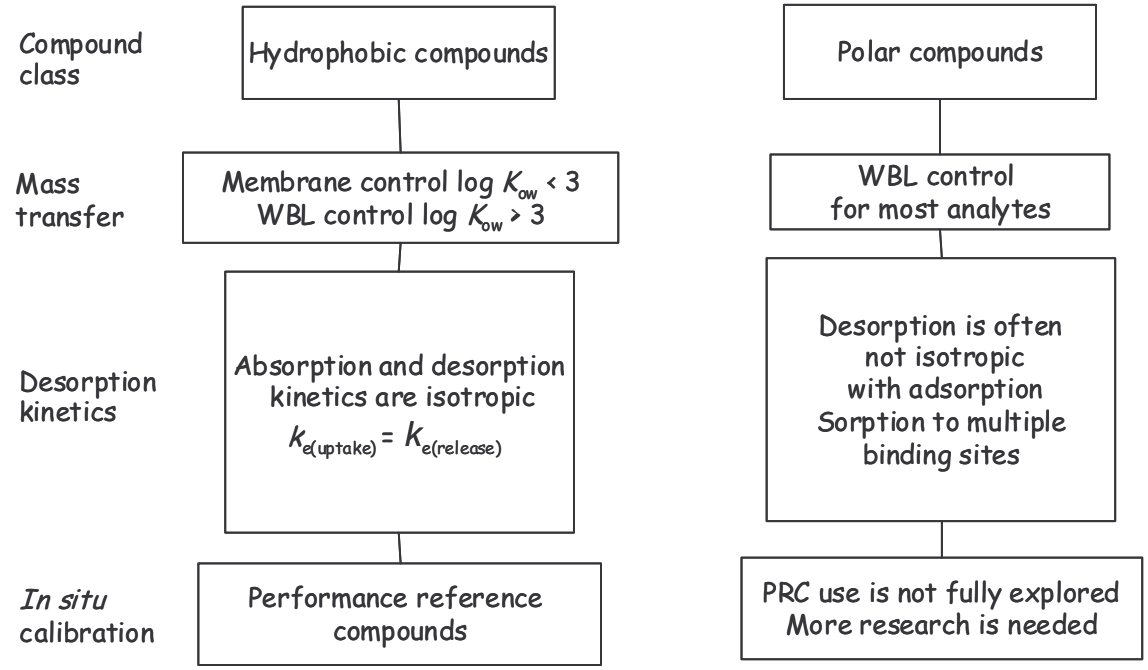

Figure 3. *Differences in mass transfer in (left) absorption- and (right) adsorption-based samplers*

III. Applications in aquatic monitoring of emerging compounds

A detailed description of sampler designs available for monitoring emerging polar organic compounds has recently been published by Söderström et al. [15]. Applications of passive samplers for some important groups of emerging substances are discussed in the following section. Table 1 lists the most discussed emerging pollutants in the aquatic environment, the established or expected/potential performance of passive samplers of these compounds and availability of calibration data that enable calculation of TWA concentrations.

III.1. Algal toxins

Algal toxins are a group of natural products which may occur in fresh, brackish and marine waters. However, possibly because of anthropogenic eutrophication and global climate changes, and subsequent blooms of potentially toxin-producing cyanobacteria, the incidence of contamination of water bodies with these compounds seems to have increased over recent years[30]. Algal toxins are structurally, functionally and phylogenetically diverse group of compounds with variable chemical and toxicological characteristics. These pollutants may cause serious health problems as documented by cases of human and animal intoxications as well as by the results of laboratory studies [30]. Based on the toxicity data, the World Health Organization (WHO) suggested the tolerable daily intake (TDI) value for microcystin-LR (a widespread hepatotoxin produced by cyanobacteria) is 0.04 μg kg^{-1} body weight, and corresponding safety guideline value 1.0 μg L^{-1} is recommended for drinking waters. There are no obligatory guidelines for other cyanobacterial and algal toxins. However the presence of these compounds in water is highly undesirable and tools for proper monitoring are necessary.

Owing to the quite high spatial and temporal variability of the occurrence and subsequent development of algal blooms, and hence potentially of co-occurring toxin production, passive samplers may prove to be a useful tool for monitoring of natural toxins. The first use of integrative passive sampling for algal toxins was described in the work of MacKenzie et al. They developed a passive sampler (SPATT bag) based on synthetic resin enclosed in porous sachets and used it for monitoring a group of marine toxins known as paralytic shellfish poisons [31]. The device was designed as an early warning of developing cyanobacterial blooms to protect consumers and prevent the harvesting of contaminated seafood products. This work was continued by other authors. Fux et al. evaluated various sorbents in the SPATT system [32]. Rundberget et al. redesigned the device and used it for monitoring of various natural toxins on the southern coast of Norway [33]. Shea et al. described the development of a monophasic device for monitoring of brevetoxins, highly toxic compounds produce during red tide events. Devices constructed of polydimethylsiloxane sheets were successfully used for integrative sampling [34]. Kohoutek et al. employed POCIS for the monitoring of microcystins in freshwater. The study was focused on evaluation of various configurations of the sampling device [35], and described calibration procedures and monitoring of the toxins under conditions of natural algal blooms. Concentrations of toxins obtained by passive sampling correlated well with the overall concentration of dissolved microcystins, demonstrating the suitability of passive sampling for the determination of TWA concentrations [35].

III.2.Antifouling compounds – organotins

Due to their bioaccumulation potential and toxicity, organo-metallic substances are considered as emerging pollutants of concern. In some cases organo-metallic compounds (e.g. some organic forms of tin) are more toxic than inorganic complexes or free forms of the parent metal. Passive sampling devices have been used to measure a number of organo-metallic species, including those of lead, mercury and tin.

Følsvik et al. [36,37] reported the use of SPMDs for monitoring organotin compounds using SPMDs. Both dibutyl- and tributyltin were accumulated by the devices, but no accumulation of monobutyltin was observed during several weeks of SPMD exposure in a Norwegian fjord. Using this method, it was possible to identify concentration gradients of organotin compounds at the sampling site. Later, a variant of the Chemcatcher® sampler was developed and calibrated for the measurement of the TWA concentration of organotin compounds. [38,39]. Using gas chromatography (GC) with either ICP-MS or flame photometric detection, favourable limits of quantification for the device (14-day deployment) for the different organotin compounds in water were in the range of 0.8–25 ng L^{-1}, and once accumulated in the receiving phase the compounds were stable over prolonged periods [39].

III.3. Brominated flame retardants

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in products such as furniture, textiles, plastics, paints and electronic appliances. Due to their extreme hydrophobicity (log K_{ow} values 4–10), these compounds are dissolved in the aqueous phase at extremely low (sub-ppb) concentrations. Nevertheless, because of their possible environmental risks due to their persistence and bioaccumulation, the inclusion of certain PBDE congeners in monitoring programmes is justified. Booij et al. [40] used SPMDs for sampling and *in situ* pre-concentration of PBDEs from water at several sampling stations in the Scheldt estuary and the North Sea along the Dutch coast. The application of integrative sampling enabled the back-calculation of extremely low concentrations (in range 0.1-5 pg L^{-1}) of PBDE congeners in water from SPMD-accumulated amounts. Rayne and Ikonomou [41] employed SPMDs for sampling PBDEs in water in the Fraser River near Vancouver, Canada. The concentrations of PBDE found in SPMDs, their physicochemical properties, and their SPMD uptake parameters were used in an aquatic transport model to reconstruct the patterns of PBDE in pollution sources. The reconstructed patterns of accumulation in SPMDs closely approximated the composition of known technical mixtures of PBDEs.

III.4. Endocrine disrupting compounds

Over the last two decades the presence in the environment of endocrine disrupting compounds, such as those which mimic or block the action of endogenous hormones on steroid (oestrogen and androgen) receptors and subsequently alter the normal functioning of the endocrine system in wildlife and humans, has emerged as a major environmental issue [42,43]. Natural oestrogens (such as oestrone, E1, and 17-β oestradiol, E2) and synthetic oestrogens (e.g. 17-α-ethinyloestradiol, EE2, the active component of oral contraceptives) are very powerful endocrine disruptors. They derive mainly from excreta of humans and livestock [44]. Anthropogenic industrial chemicals such as nonylphenol (NP), bisphenol A (BPA) and phtalates are, however also known to influence the hormonal system of aquatic organisms. Wastewater treatment plants are important sources of pollution, since many endocrine disrupting compounds are not fully removed by the treatment processes. Several studies have demonstrated applicability of passive samplers for integrative sampling of these compounds during exposure periods up to several weeks [126,128,129,142]. For many compounds, calibration data that enable quantitative translation of amounts accumulated by the sampler into TWA concentrations are available (Table 1).

III.5. Fluorinated *surfactants*

Fluorinated surfactants (also referred to as poly- and perfluoroalkyl compounds, including perfluoroalkyl carboxylic acids, perfluoroalkyl sulfonates, fluorotelomeric acids, alcohols, etc.) have been used for decades to make stain repellents that are widely applied to fabrics, carpets and paper. They are still used in the manufacture of paints, adhesives, waxes, polishes, metal coatings, electronics and caulks. Due to concern over their persistence and global occurrence in humans and wildlife, two of these fluorinated surfactants,

perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) are within the family of compounds currently attracting the greatest attention as emerging pollutants.[45] It is difficult to identify the origin of pollution by fluorinated surfactants found in wastewater. Although no quantitative studies aimed at monitoring of these substances with passive sampling methods have been reported, Casey et al. [46] reported identification of these compounds in POCIS extracts at levels above associated controls. Recently, Günther et al. described the application of a passive sampler based on active carbon adsorbent [47]. Further research in development of passive samplers suitable for monitoring of these compounds in water is needed.

III.6. Organosiloxanes

Another important class of emerging pollutants is the organosiloxanes. These polymers comprise a backbone of alternating silicon-oxygen units with organic side chains attached to each silicon atom. Over the last 30 years organosiloxanes (silicones), both cyclic and linear forms, have been extensively used in a number of consumer products. These include for example anti-perspirants, and hair and skin care items. It has been estimated that in the USA adult women are exposed to up to 307 mg of organosiloxanes daily [48]. The most commonly used organosiloxane is decamethylcyclopentasiloxane (abbreviated to D_5) although others such as octamethylcyclotetrasiloxane (D_4) and their linear versions can be used in products [48]. These compounds have unusual physico-chemical properties combining high hydrophobicity (e.g. D_5 has a log K_{ow} of 6-8, depending on the literature reference used)) with a high Henry's Law constant and low water solubility [49]. Owing to these properties, most (c. 90%) of the organosiloxanes used in personal protection products are expected to be evaporated to the atmosphere during and after use, with the remainder being discharged into the wastewater. Several organosiloxanes are under assessment for classification as very persistent and very bioaccumulative in the environment. Hence there is an urgent need for monitoring levels of these compounds in different environmental compartments.

Analytically, siloxanes are difficult to measure at trace levels as they are ubiquitous atmospheric environmental contaminants, they are contained in sample vial caps, septa, gas chromatographic columns and they give problems of cross-contamination by laboratory workers using personal care products containing these substances. The maintenance of good procedural blanks and rigorous quality assurance and quality control measures are needed to ensure confidence in any quantitative results. For these reasons reliable environmental monitoring data are sparse. Most analytical methods for both cyclic and linear siloxanes employ headspace gas chromatography/mass spectrometry techniques [49], although large volume direct injection methods using *n*-hexane have also proved to be useful [50]. Sparham et al. [49] have recently analysed D_5 in the Rivers Great Ouse and Nene, UK (concentration range < 10-29 ng L^{-1}) and in treated wastewater (concentration range 31-400 ng L^{-1}). There are few other quantitative studies for D_5 and the other organosiloxanes of environmental concern.

Owing to the low concentrations of organosiloxanes found in the aquatic environment, the use of passive samplers in monitoring campaigns may offer the opportunity to pre-concentrate these compounds prior to instrumental analysis. To date, however, there is little experience of their use with this class of pollutants. Work in this area is being undertaken by researchers (Mills and Greenwood) at the University of Portsmouth, Portsmouth, UK. Preliminary findings show that pre-cleaned thin sheets of low density polyethylene (LDPE) membrane can be effectively used as passive samplers for D_4 and D_5. Work is currently being undertaken to identify PRCs that are suitable for use with the samplers and that are appropriate for the organosiloxanes of major environmental concern. Polydimethylsiloxane (PDMS) sheets cannot be used for this purpose because of background contamination with these smaller siloxane polymers. This makes it difficult to obtain good procedural blanks. Even with extensive washing it is still hard to remove all traces of D_4 and D_5 from these

materials. Other polymers such as polyethylene terephthalate (PET), polyoxymethylene (POM), polytetrafluoroethylene (PTFE) and polycarbonate could potentially be used as either equilibrium or kinetic samplers for these compounds. Because the organosiloxanes are volatile, care must be taken during field deployments not to lose the sequestered analytes during retrieval and transport of samplers and in subsequent laboratory processing. Extensive QA and QC procedures must also be employed. Data from the Portsmouth group on the initial field use of the LDPE samplers for measuring this class of compounds are expected in 2011.

III.7. Pharmaceuticals

Concern over pharmaceutical residues (and personal care products) entering the aquatic environment has been growing since the mid-1990s. Both classes of compounds enter the environment largely as a result of human use, although some come from veterinary use. Several studies have reported the presence of a wide range of these chemicals at ng L^{-1} and sub ng L^{-1} concentrations in various water bodies. A complex mixture of chemicals is often present comprising the parent molecule, associated metabolites and environmental degradation products. Some of these substances may subsequently enter the food chain. The biological effects of pharmaceutical residues on aquatic organisms have been reviewed recently [51].

Effluent from wastewater treatment works is the most common source of pharmaceutical residues in streams and rivers. Some of these chemicals are resistant to treatment. Often the treatment process can break down conjugated drug metabolites to release the parent molecule back into the environment. A range of tertiary treatment processes (e.g. chlorination, ozonation and UV light) can be employed to reduce these levels, but these are expensive to operate continuously at the treatment plant.

Pharmaceuticals have a wide range of physico-chemical properties and concentrations in the aquatic environment and this can make their measurement challenging. Many drugs are either weak acids or bases with pK_a values in the range 4-10. The degree of ionisation will therefore differ in different water bodies that have pH values typically over the range 5.5-8.4 (i.e. from soft to hard fresh water and sea water). Likewise, these substances have a range of log K_{ow} values, but most are considered polar compounds. In some cases the chirality of the drug molecule also needs to be considered. Most compounds of environmental concern can be analysed using LC/MS/MS instrumental methods after extraction and concentration. Typically a wide range of analytes can be separated and quantified at the trace level in a single analysis.

There is a need to obtain reliable data on the fate of pharmaceuticals in the aquatic environment. These data can then be used to develop appropriate models and assist in the risk assessment process. As most discharges of these substances are sporadic and seasonal it is difficult to obtain such information using spot or grab sampling alone. Passive sampling therefore offers a number of opportunities in this area and this has been summarised by Mills et al. [14]. Recently, Söderström et al. [15] reviewed performance characteristics of samplers suitable for monitoring pharmaceuticals and other polar organic pollutants in the aquatic environment.

Two types of passive sampler (polar version of the Chemcatcher and POCIS) have been used for measuring TWA concentrations of pharmaceuticals (and some personal care products). The devices use either an immobilised (Chemcatcher) or loose (POCIS) receiving phase. The Chemcatcher uses a 47 mm Empore™ disk, usually based on divinylbenzene co-polymer chemistry, although ion-exchange (both anion and cation) receiving phases can be used for certain classes of analyte. The POCIS uses a commercially available solid-phase extraction adsorbent (typically c. 200 mg Oasis HLB) that is specially designed to sequester

pharmaceuticals. The same diffusion-limiting membrane (polyethersulphone) is used in both devices. This membrane has a low surface energy and this can limit biofouling of its surface during field use. The uptake rates of the two devices for these more polar analytes are low (typically less than 1 L d^{-1}) compared with the sampling of non-polar compounds by, for example, SPMDs. This can limit their usefulness in some applications, but – unlike non-polar compounds – polar compounds are usually present at higher concentrations, so that sampling rates below 1 L d^{-1} are not an obstacle.

Although a number of laboratory and field studies have been carried out using the POCIS, there is an urgent need for reliable calibration data (Table 1). In many cases different calibration systems (e.g. flow through and static with renewal) [52] and different water turbulences and temperatures have been used and this increased the variation in the data obtained. Much of the field data reported is therefore either qualitative (presence or absence of a pollutant) or semi-quantitative (amount extracted from the receiving phase) rather than using uptake rates to calculate actual water concentrations (ng L^{-1}).

III.8. Polar pesticides

Use of pesticides can have unintended effects on the environment. Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water, bottom sediments, and food [53]. There are four major routes through which pesticides reach water, including: spray-drift outside of the intended application area, percolation, or leaching, through soil column, with water runoff or concomitant soil erosion, or through accidental or negligent releases [54]. There is an increased demand for environmental monitoring of pesticides because some of them are either already identified as priority substances under the Water Framework Directive (e.g. atrazine, simazine, diuron, isoproturon), or may become priority substances in the future or are relevant as river basin-specific pollutants in selected European regions [55]. An EU "Thematic Strategy on the Sustainable Use of Pesticides" calls for environmental monitoring to be done for other new pesticides in order to verify whether the concentrations in the aquatic environment are "safe" [56].

The first passive sampler reported for this chemical class was the POCIS [57,58]. Typically, for sampling of polar pesticides POCIS remains in the time-integrative mode for exposure periods of up to several weeks. This sampler has found application in integrative sampling of a wide range of polar pesticides and, for many of them, calibration data are available that enable quantitative translation of amounts accumulated by the sampler into TWA concentrations (Table 1).

Polar pesticides are often released at high concentrations into streams and rivers in episodic events. These events usually last only a few hours and for these compounds to be detected by passive samplers, a device with a short response time is required. But passive sampling devices fitted with microporous membranes (e.g. polyethersulphone membrane in POCIS), although ideal for long-term monitoring [59], have a lag-phase of several hours which represents the time necessary for the analytes to diffuse through the membrane to reach the receiving phase [24]. In situations where detection of short pollution events in the monitored water body is required, a long lag-phase of the sampling device presents a potential disadvantage. Shaw and Mueller [60] suggested the use of a device fitted with an Empore™ disk bonded polymeric sorbent as receiving phase (without a diffusion limiting membrane) to reduce the response time and make the sampler more reactive to sudden pollution events [61]. The disadvantage of such devices is a fast equilibration of the sampling devices with the water phase, which restricts to a few days the time over which the samplers operate in time-integrative mode. Comparison of the performance of two different types of Empore™ disks as passive samplers showed that the styrene-divinylbenzene-reverse phase sulfonated (SDB-

RPS) Empore™ disk had better performance as sorbent phase for very polar compounds compared to C18 [62].

III.9. Sunscreen and ultra-violet filters

The analysis of sunscreens/organic ultra-violet (UV) filters in water has increased substantially in the last two years. Due to their use in a variety of personal care products, these compounds can enter the aquatic environment indirectly from showering, washing clothes, via wastewater treatment plants and also directly from recreational activities.

In one of the first studies, Poiger et al. [63] detected four organic UV filters (80-950 ng $SPMD^{-1}$) in SPMDs deployed at Lakes Zurich and Greifensee, Switzerland. SPMD-derived water concentrations were in the range of 1-10 ng L^{-1} and corresponded well with those determined in spot samples of water. In a later study, Balmer et al. [64] investigated the occurrence of four important organic UV filter compounds in water, wastewater and fish from various Swiss lakes. Data from passive sampling using SPMDs supported the presence of these UV filters in lakes and rivers and suggested some potential for accumulation of these compounds in biota. Recently, Fent and Zenker et al. [65,66] demonstrated the applicability of the POCIS sampler for monitoring oestrogenic UV filters in surface water. They found that processing of POCIS samples with subsequent instrumental measurements was much less time consuming than processing of fish samples for environmental monitoring. Hydrophilic compounds like benzophenone-4 which do not accumulate in fish lipids could also easily be determined using the POCIS sampler.

IV. Application in sediment monitoring

Until recently sediment monitoring has relied on the determination of total or normalised contaminant concentrations. This approach, however, does not distinguish between freely dissolved and bound molecules and aims to assess the presence of chemicals rather than their activity and availability [67]. Since many laboratory and field studies have demonstrated that biological effects in benthic organisms are not generally related to the total concentration of contaminants in sediments, alternative and more representative measures of the bioavailable fraction of contaminants in sediments are required [68]. In addition, it has been shown that traditional empirical models tend to overestimate pore water concentrations.

Application of passive sampling to sediment monitoring can be undertaken *in situ* with buried passive samplers or in batch experiments in the laboratory following grab sampling or coring (and sectioning). Passive samplers can be used to:

- Determine freely dissolved contaminant concentrations in pore water;
- Estimate sediment-pore water partition coefficients for contaminants of interest;
- Measure contaminant desorption rates;
- Estimate the fraction of contaminants available for desorption within a relatively short time scale or fraction effectively contributing to the partitioning with pore water and/or biota;
- Measure surface water/pore water activity or fugacity ratios to estimate whether sediments act as a source or sink for contamination in the overlying water;
- Measure the total contaminant amount in sediment that is available for release to the aqueous phase within a given time.

The most commonly used passive sampling approach is based on the principle that the passive sampler is exposed to a sediment sample until a thermodynamic equilibrium between the two phases is established. According to partition theory, the concentration of a compound in the sampler is directly proportional (by the equilibrium partitioning coefficient

between sampler and water) to the freely dissolved concentration of sampled compounds in pore water. Because this concentration is considered to be the driving force for the uptake of the contaminants by aquatic organisms, the bioavailability of a substance can be directly assessed using passive samplers. However, depending on sampler characteristics (e.g. surface area and volume), equilibrium may not be established for the most hydrophobic compounds during exposure and therefore performance reference compounds (such as used for surface water deployments) can be used to quantify sampler-pore water exchange kinetics and dissolved concentrations in such situations [67,69].

In all cases it is absolutely crucial to select an appropriate combination of sampler and sediment volumes in order to avoid significant depletion of the pore water phase. The true freely dissolved concentration of contaminant in pore water can be determined when the sampler's sorption capacity is kept well below that of the sediment sample to avoid depletion during the extraction [20,70,71]. When the sorption capacity of sampler to sediment is kept high, samplers can be used to measure the total contaminant amount in sediment that is available for release to the aqueous phase within a given time. This represents the fraction available to take part in partitioning with sediment organisms. The contaminants remaining in the sediment following such extraction can be considered effectively unavailable [72]. This fraction can also be estimated by repeated/successive extractions of the sediment with an adsorbent phase such as Tenax [73,74]. Such procedures also enable the quantification of contaminant desorption rates.

The concentration difference between the *in situ* deployed samplers from the sediment and those from the overlying water give direct information on the fugacity difference between sediment and water, and on the direction of the contaminant diffusion at the sediment−water interface as well [20,71,75]. This enables identification of sites where remedial treatment of sediment may be appropriate. Other parameters, such as sedimentation rates and the spatial resolution of sediment sampling close to the sediment-water interface, are crucial for such measurements.

For metals, the technique of diffusive gradients in thin films (DGT) provides an important contribution to understanding processes that metals undergo in sediments. DGT provide measurements in sediments that can be reported either as the mean flux of labile metal species to the device during the deployment time, or as the mean interfacial concentration in pore water. For a given device and deployment time, the interfacial concentration can be related directly to the effective concentration of labile metal [76]. This concentration represents the supply of metal to any sink, be it DGT or an organism that comes from both diffusion in solution and release from the solid phase. The primary use of DGT in sediments has been to investigate the distribution of solutes (metals) at high spatial resolution and to interpret the dynamics of the pollutant release from sediment [76]. Pore water concentration profiles with a fine resolution can be obtained by deploying DGT probes vertically in sediment and across the sediment–water interface. Modelling of metal accumulation in DGT with increasing exposure time can allow the estimation of sediment–water partition coefficients for metals of interest.

It is crucial that the risk assessments of contaminants in sediment are as reliable as possible. It is widely accepted that it is the dissolved fraction of pollutants that is available for interaction with biological tissues and that can thereby cause bioaccumulation and/or biological effects. Several studies have shown that biota concentrations, calculated from partition coefficients based on classical equilibrium partition theory, are often orders of magnitude higher than the actual measured concentration in the sediment-dwelling organisms. But, using the freely dissolved concentration derived from passive samplers, the calculated concentrations in biota are in good agreement with the actual measured values [77].The methodology using passive sampling is leading to a much better understanding of how hydrophobic contaminants interact with sediment. This will allow a better estimation of

(bio)availability, as can be validated through comparison with uptake by organisms. Data obtained with passive samplers can be used in risk calculations for sediment-bound contaminants with regard to any need for remedial measures for contaminated sediments and these studies would be an important input with regard to environmental quality standards for contaminants in water proposed in the EU Water Framework Directive.

So far, the methodology of passive sampling in sediment has been tested and successfully validated in studies focused mainly on priority groups of contaminants that cause major environmental problems, such as polycyclic aromatic hydrocarbons or polychlorinated biphenyls. Nevertheless, this concept can also be successfully applied in risk-oriented monitoring of other groups of contaminants in sediments, including emerging substances. Further research is needed to develop novel solid phases with strong affinity to a broad range of compounds that may be found in sediments. These sampler materials should allow an easy extraction and analysis of accumulated substances [68].

V. Application in monitoring of contaminants in biota

Knowledge of dissolved phase chemical concentrations is a critical part of understanding how aqueous exposure levels relate to the concentrations of residues measured in organisms in various trophic levels of aquatic ecosystems. The freely dissolved concentrations of pollutants represent the driving force for bioconcentration. Thus, passive samplers enable *in situ* determination of the bioaccumulative exposure of organisms at the lowest trophic level (filter feeders, e.g. mussels), in nearly all food chains, to hydrophobic organic compounds [78,79]. The estimation of bioaccumulation factors (BAFs) in certain species of concern (e.g. mussels) has also been demonstrated [79,80]. Moreover, since the contribution of dietary uptake for organic compounds with log K_{ow}s < 5.5 is generally very small, organism exposure assessment can be potentially extended to higher trophic levels for less hydrophobic compounds.

Bayen et al. [81] recently reviewed kinetic studies of the uptake of neutral non-polar chemicals from the aqueous phase into organisms (fish, bivalve, crustacean, insect, worm, algae, and protozoan) and passive samplers. They demonstrated that passive samplers are biomimetic when diffusional partitioning processes mediate concentrations in organisms of concern (i.e., when residue accumulation in organism tissues follows equilibrium partitioning theory). Huckins et al. [78] discussed in detail accumulation into the SPMD sampler compared with that into biomonitoring organisms.

The large number of variables, which potentially affects the accumulation of hydrophobic organic compounds in biota, suggests that it is unrealistic to expect any single passive sampler to be biomimetic of all biomonitoring organisms. Also, it is similarly unrealistic to expect that one or two species of biota mimic bioaccumulation in all organisms of concern. Variables affecting pollutant accumulation in passive samplers are limited to the sampler properties, physicochemical properties of the sampled chemical, exposure site conditions (e.g. temperature and turbulence, and exposure scenario factors such as the constancy of chemical concentrations during the exposure period). The ability to generate chemical-specific calibration data and then adjust these values to site-specific conditions (e.g. using PRCs) [22] means that analyte concentrations obtained using passive samplers are directly comparable across sampling sites.

There are some fundamental similarities in the characteristics and processes affecting the accumulation in biota and passive samplers, especially for hydrophobic organic compounds. Diffusion of non-polar compounds through non-porous polymers used in passive sampler construction mimics the diffusion across bio-membranes. Also, partitioning between the

polymers, organism lipids and the exposure water is similar and can be described by the equilibrium partitioning theory. Finally, the surface-to-volume ratio appears to be a critical parameter for the uptake rate of the more hydrophobic chemicals, both for samplers and organisms.

Monitoring by passive samplers has some advantages over the use of biota. Passive samplers can be prepared to a standardised quality characterised by low initial concentration of contaminants, uniform composition, diffusion and sorption properties. In contrast, test organisms often contain background contamination levels and they are naturally variable in composition. As a result, variability of chemical analysis of biota or sediment is in most cases higher than that associated with analysis of passive samplers. Moreover, the simple polymeric matrix composition of passive samplers provides sample extracts that contain much less matrix interference in comparison with extracts from biota and sediment. Samplers can be applied in almost any environment with a broad range of water quality properties and even in very polluted sites where biomonitoring organisms may not survive. In contrast, biomonitoring organisms can be applied only within a certain geographical range and they do not tolerate extreme exposure conditions (e.g. temperature, pH, pollution, and salinity). The uptake process of pollutants in passive samplers is simple (by diffusion and sorption), whereas it is more complex in organisms since it includes bioconcentration, bioaccumulation and metabolism. The complexity of these processes is increased by behavioural, physiological and anatomical characteristics of biomonitoring organisms.

The uptake capacity of polar organic compounds in biomonitoring organisms is in most cases low. Also, these compounds reach steady state within a short period of time, so that biological sampling of polar organic compounds has a very limited applicability [82]. In comparison with biomonitoring organisms, passive samplers demonstrate better retention of contaminants that are absorbed during peak exposure events. The amount of chemicals accumulated in passive samplers in most cases reflects the dissolved, readily bioavailable, concentration in sampled water, whereas the estimation of contaminant bioavailability from total amount found in an organism body may be difficult, owing to the presence of a non-incorporated portion of the pollutant in its intestines.

For metals, the DGT technique measures directly the variables needed to assess water quality. Uptake of trace metals across living membranes is determined by free ion concentrations when membrane transport is slow and by the total concentration of labile species when membrane transport is fast. Deployment of twin DGT devices with different diffusive gel layers can provide an *in situ* measurement of both labile inorganic and total labile species. Free ion activities can be calculated from labile (free and/or kinetically-labile species in solution) inorganic concentrations.

VI. Application in ecotoxicity assessment

Ecotoxicity assessments are an invaluable tool for the evaluation of water quality and in some countries ecotoxicity assessments are compulsory, for example, with direct toxicity assessments of effluents released to the environment [83]. One of the main advantages of ecotoxicity assessments is that they give an integrated picture of the total toxic burden of the complex mix of chemicals that are present in environmental samples. It is often the case that toxic substances cannot be identified and chemical monitoring methods cannot be targeted, but ecotoxicity assessments can still measure the effect of these unknowns in environmental samples. Such samples can be tested, either at the level of organisms (e.g. daphnids or fish embryos [83],[84]), at the level of cells (e.g. fish cell lines) [84] or at the sub-cellular level (e.g. specific binding of chemicals to receptors using reporter gene assays). An example of such a reporter assay comes from research on endocrine disruptors, where cells have been modified to express oestrogen receptors ([85],[86]). The binding of oestrogens – or

oestrogen-like compounds – to the receptors leads to the production of an enzyme which in turn induces a colour change in the medium (or light emission) that can be quantified easily. Commonly, bioassays are applied to whole water samples, extracts of water samples or extracts of organism tissues. Applying the same bioassays to extracts of passive samplers is straightforward and an increasing number of studies have explored this.

VI.1. Passive samplers as mimics for bioconcentration

Combining bioassays with (grab) water samples has the same limitations (or advantages) as compared to combining chemical analyses with water samples. Grab samples give an accurate picture of the total concentration only at a certain point in time. Grab samples again provide data on toxic effects that relate only to the time of sampling. As an alternative, combining ecotoxicity assessments with monitoring of chemicals in biota, for example by analysing extracts of aquatic organisms, is certainly feasible, and produces more representative results than analysing grab samples, but has the same limitations associated with monitoring of contaminants in biota as discussed in the previous section (i.e. section V.). Combining bioassays with passive sampling circumvents the limitations that are associated with grab samples and chemical monitoring in biota. Furthermore, a passive sampler mimics bioconcentration of freely dissolved chemicals over cell walls, membranes or a filter feeding apparatus or gills. Thus, testing passive sampler extracts in bioassays has a high relevance as this reflects exposure scenarios in the aquatic environment.

VI.2. Which passive sampler suits which bioassay?

Numerous biological assays have already been used successfully in combination with passive samplers. Many studies deal with quantification of environmental oestrogens with reporter gene assays in extracts from SPMDs ([87,88]), POCIS ([89],[90],[91],[92],[93],[94]) and Chemcatchers ([95]). An assay that covers compounds such as PAHs and dioxin-like compounds, the EROD assay, has been used with extracts from SPMDs ([87]) and in combination with the Toximeter ([96]). Several studies describe the use of Chemcatchers and POCIS to measure photosystem II (PS-II) inhibitors ([97],[98],[99],[100]). Microtox, a bacterial whole cell assay that is used to measure baseline toxicity, has also been used in combination with POCIS ([94],[100]), Chemcatcher ([98]) and SPMD ([101]) extracts. Muller et al. tested Chemcatchers extracts in the umuC assay, which is used to assess genotoxic effects in response to the presence of DNA-damaging chemicals within the sampled mixture. [98]. Mutagenicity has been assessed in extracts from SPMDs by Rastall et al. [87]. Shaw et al. used Chemcatchers in combination with two invertebrate bioassays, coral larval settlement and sea urchin larval development, in addition to bacterial luminescence and microalgal photosynthesis [102].

The above listing is certainly not complete but illustrates that the range of bioassays is very diverse, spans across organisational levels – from gene expression to whole organisms – and covers multiple modes of action. In addition, both relatively hydrophobic absorptive passive samplers and adsorptive samplers used to sample more polar chemicals have been used in combination with these multiple end-point bioassays. Although various combinations of passive sampler and bioassays have been explored, it is difficult to list fixed combinations for passive samplers and biotests. The reason for this is that the range of compounds that is targeted by bioassays is often very diverse and no single sampler can adequately target a set of chemicals with diverse physicochemical properties. This issue can be illustrated for an algal test that is used to quantify the effects of herbicides such as diuron and atrazine that inhibit PS-II. Log K_{ow} values for PS-II inhibitors range from below 1 (e.g. metamitron) to 4 (dipropetryn). Metabolites of these compounds can also be active PS-II inhibitors and may further extend the log K_{ow} range of possible PS-II inhibitors. Log K_{ow} ranges for compound classes targeted by other bioassays can be even larger; e.g. PCBs with log K_{ow} values up to 7 are oestrogenic whereas benzotriazole, with a log K_{ow} of 1.4, is anti-oestrogenic. As

passive samplers usually target a range of log K_{ow} values spanning 2 to 3 orders of magnitude [87], it is clear that not all compounds that are active in a bioassay will be sampled in a similar, integrative fashion. Some toxic compounds may reach equilibrium well before others. Thus, even when the concentration ratios of various toxicants in the environment are constant, different integrative sampling windows of individual compounds will cause their concentration ratios in a passive sampler to vary over the deployment time of the sampler. In addition, different compounds with the same mode of action may have very different diffusion coefficients within a given sampler (or over a membrane that envelops the sampling phase), and thus behave differently in response to changing environmental conditions.

Although no single passive sampler covers all compounds that act on a certain organism or have a certain mode of action, this does not negate the rationale of combining passive samplers with ecotoxicity assessments. The use of bioassays is a more holistic approach to assessing the risk associated with exposure, since the technique provides a functional integrative assessment of mixture toxicity for chemicals accumulated by passive samplers to levels sufficient to induce a biological response. So, by combining passive sampling with bioassays it is possible to avoid intensive chemical analyses. However, when using a specific bioassay in a sampling campaign, one has to attempt to identify the main possible toxicants that may be present at the sampling locations and select a sampler that best covers the log K_{ows} of those toxicants.

VI.3. The link between biological and chemical analysis

It is common to express the effect of water samples in ecotoxicity tests as a dilution factor, i.e. at what dilution the sample still leads to a certain effect level in the bioassay [83]. The same approach can be used for a passive sampler and one can express the toxic effect in terms of a certain portion of a sampler extract [89]. An alternative approach was developed by Koči et al., a toxicity measure corrected for the volume sampled by a passive sampler (vtox [103]). Although these approaches are clearly informative, and one can classify more or less polluted sites and derive water quality criteria on this basis, it is difficult to compare chemical and biological analyses directly.

Another system to evaluate effects in bioassays is the toxic equivalent (TEQ) concept. It was first established for effects caused by dioxins and PCBs on the arylhydrocarbon receptor [104]. Subsequently, the concept has been applied to oestrogenic activity, phytotoxicity and other types of toxicity. In essence the TEQ concept revolves around comparing the dose response curve induced by a sample to the dose response induced by a reference compound (see [105]). The biological response to the sample can then be expressed in terms of an amount or concentration of the reference compound. This approach can then be complemented by testing many individual compounds in the bioassay to establish their dose-response curves; from these one can derive their potencies relative to the reference. When a set of compounds has been quantified in an environmental sample by means of chemical analysis, concentrations of these compounds can be multiplied by the potencies of the compounds and added together (assuming concentration addition applies) [106]. The sum of the individual chemicals signifies the toxicity based on chemical analysis and the minimum expected response of the environmental sample in the biological test. This approach is well established and many legal TEQ limits are in place for dioxin-like compounds (e.g. the EU limit for fish = 4 pg WHO-PCDD/F-TEQ /g fresh weight) [107].

Being able to relate results from a bioassay directly to those obtained by chemical analyses has the main advantage that one can assess whether most of the toxicity has been accounted for by the chemical analyses, or whether major toxicants have been missed. In passive sampling, linking biological analyses to chemical analyses has been done in several

studies ([90],[92],[93],[97],[99]). Attention has focused on oestrogens, PAHs and herbicides and recently also on baseline toxicity ([100]).

VI.4. Identification of toxic compounds in passive samplers: effect-directed analysis

Effect-directed analysis (EDA) is another area where ecotoxicity assessments can be used [108]. In EDA, an environmental sample is fractionated chromatographically and next, the various fractions are tested individually for toxic effects. Once toxicity has been detected in a fraction, this fraction can be analysed chemically to identify possible toxicants. This is a very powerful method for identifying major toxicants in a complex environmental sample, particularly when the bioassay data are expressed as TEQ to allow for direct comparisons between data from chemical and biological analyses.

The EDA approach has been applied frequently in sediments [68,109]. As yet, only one example comes from passive sampling. Rastall et al. [110] fractionated SPMD extracts and tested these for activity in a reporter gene assay for oestrogen receptor agonists. They found that oestrogens sampled by SPMDs cover a wide log K_{OW} range, but individual oestrogens could not be identified. This area is one where much progress can be made.

In a recent field study where POCIS were deployed for five weeks in treated sewage effluents, a toxic spill occurred at one of 21 sites. The toxic spill caused a fish kill in the receiving river, and the POCIS from this site recorded the highest baseline toxicity in a bacterial test [100]. Using chemical analyses of water samples taken directly following the fish kill, the toxicant(s) causing fish mortality could not be identified (A. Stockli, personal communication). Although EDA was not attempted with these POCIS, it clearly points to an effective use for passive samplers as monitors for such peak toxic events.

VI.5. How does the bioassay response in passive sampler extracts relate to sampler exposure conditions?

The rate at which a compound is sampled by a passive sampler depends on the properties of the compound, the properties of the sampler and the environmental conditions at the deployment site. For individual chemicals it is fairly straightforward to establish relationships between compound properties, environmental conditions and sampling rates [111]. In contrast, the response in bioassays is the sum of the effects caused by contributions from at best a few (for highly specific endpoints) to a large number of individual compounds. As the composition of the mixtures and the relative abundance of the toxicants can vary widely across sites, and over time, this poses certain limitations on how bioassay results can be interpreted with respect to varying environmental conditions. Interpretation can be even harder when a sampler includes a membrane. For example, it was shown that more polar compounds (log $K_{OW} < 2$) move more rapidly over a polyethersulphone membrane than less polar compounds (log $K_{OW} > 3$) into the SDB sampler phase in the Chemcatcher [99]. For short sampling windows, less polar compounds may be under-represented in the mixture of toxicants which will skew results. Thus, when combining bioassays and passive sampling one has to appreciate the uncertainties caused by the fact that the suites of target chemicals cover a wide range of physicochemical properties. As a result, different mixtures of chemicals with the same mode of toxic action will respond differently to varying exposure conditions.

VII. Quality assurance, quality control and normation

If passive sampling is to become accepted and used in a regulatory context for monitoring water quality across Europe, then there is a need for the development of improved validation methods and setting up of the appropriate quality control and quality assurance schemes for the technology. This would involve a set of activities (e.g. development of standard certified reference materials, setting-up of round robin exercises and the publication of standard methods) as those have been established for the validation of analytical techniques for the measurement of various analytes of importance in different environmental matrices. There is also a need for associated accreditation schemes laboratories involved in passive sampler calibration measurements in the lab and those using passive samplers in the field.

The implementation of the above is not straightforward. For laboratory calibrations of the samplers, there is a need for large volumes of reference materials to be available. For field trials it may be possible to use reference sites that are well characterised and stable in chemical composition. An attempt to compare various water monitoring methods that could potentially be used in support of the Water Framework Directive was undertaken as part of a European Union-funded project [112] and the results of this activity have been summarized [113]. A number of field trials were undertaken in different water bodies across Europe and the results from these multiple comparisons indicated the potential utility of this approach. But these activities are expensive to develop and organize and therefore regulators and other end-users need to be convinced of the value of these alternative monitoring techniques so that they can support the provision of EU funding to enable this important research in support of policy and associated legislation.

Several interlaboratory field trials, where a range of passive sampling technologies will be evaluated at European riverine sites, are being set up in 2010. The first is being facilitated within the framework of AQUAREF (the organisation coordinating French laboratories involved in water monitoring) [114]. A call was made in early 2010 for the participation of research groups across Europe who are involved in either developing or using passive sampling technology. Several field sites were selected and include both surface water and a marine lagoon in France. This trial focuses on the monitoring of pesticides, PAHs and metals. The second exercise is being proposed by the NORMAN network, where the focus of this exercise will be on the application of passive sampling for monitoring pollutants of emerging concern. Further, an interlaboratory proficiency testing scheme aimed at the chemical analysis of a range of hydrophobic organic compounds and metals in two commercially available passive samplers has been launched recently in the Czech Republic. [115] The results of these exercises will be of value in demonstrating the future utility of the technology and will be helpful in the design of similar activities in the future.

Progress has been made on the normation of passive sampling methods. One of the deliverables of the European Union-funded project STAMPS [116] was the development of a British Standards Institution Publicly Available Specification [117]. This specification provides guidance for end-users on the preparation, deployment and associated quality assurance requirements for the use of passive samplers in surface waters. The specification is currently under consideration for development of a CEN/ISO standard [118].

VIII. Application of passive samplers in regulatory monitoring

"Emerging pollutants" can be defined as pollutants that are currently not included in routine monitoring programmes at the European level and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments. In many cases knowledge of their ambient and background levels in water,

sediments and biota is still limited and even less is known of the long-term ecotoxicological effects of these emerging contaminants. At such an early stage, it is difficult if not impossible to derive appropriate environmental quality standards (EQS) for these chemicals without the use of significant safety factors. Therefore compliance testing against EQS values is not often undertaken for these substances. Most monitoring programmes that include emerging pollutants are in general screening studies [119,120] aimed at obtaining additional information on the occurrence of these compounds in various aquatic environmental matrices, where they are likely to accumulate. Passive sampling may be favoured over matrices such as sediments and biota for such screening. It draws advantage from a simple matrix composition that enables simplified sample extraction, cleanup and the subsequent instrumental analysis. Moreover, field exposure of passive samplers in various matrices such as surface waters, wastewaters and sediment can be standardised. In addition, the use of, for example absorption-based samplers for the screening of non-ionic hydrophobic substances in water and sediments results in limits of detection which are generally substantially lower than those that can be achieved through bottle sampling [121]. Another factor to be taken into account in screening studies is the possible (mostly unknown) temporal variability in the concentration of emerging pollutants in water. Continuous monitoring possible with passive samplers can help in reducing the uncertainty associated with sampling when concentrations vary in time. For example, variable concentrations may be observed for emerging contaminants that are emitted in the urban environment and that can ultimately be released from sources such as landfill and wastewater effluents. This is, however, also valid for compliance monitoring of more conventional pollutants for which EQS have been derived and are in use (e.g. for the EU WFD). Despite the measurement of a different fraction of contaminants in water, passive samplers can be used to support data collected by infrequent bottle sampling [122,123] or through monitoring in biota. This allows continuous monitoring in conditions where this would not be feasible and improves the representativeness of the sampling. The integrative nature of passive sampling combined with extremely low limits of detection for non-ionic hydrophobic organic contaminants may represent the only acceptable way to monitor some of these substances in surface waters. Since passive sampling is based on the measurement of dissolved phase pollutants, further comparison with EQS based on “whole water” concentration values may require additional information to account for the fraction of contaminants associated with other phases such as dissolved organic carbon and suspended particulate matter. In the long term, such a strategy requires the development of water body-specific knowledge of contaminant speciation and partitioning. The additional information on non-dissolved fractions of compounds can be obtained in parallel representative measurements of these compounds in suspended particular matter or bottom sediments. The sum of the representative (e.g. TWA) contaminant concentration in the dissolved phase (provided by passive samplers) and that bound to colloids and particles (provided by sampling of suspended particulate matter) will provide the measure of total concentration that can be applied in compliance checking with EQS.

Moving towards an implementation of passive sampling for regulatory monitoring of emerging substances will require the identification of suitable material for accumulation of target compounds and an accurate characterisation and calibration of the devices. In this regulatory context, passive samplers may be applied to the monitoring of surface waters in both populated and remote areas and other aqueous matrices such as wastewaters and other effluents. Samplers can be deployed simultaneously in different media in order to detect gradients in chemical activity/concentration and understand fluxes of these emerging substances.

IX. Future trends

There are several future trends for the development of passive sampling techniques for emerging substances.

Novel materials will need to be tested as selective receiving phases (e.g. ionic liquids, molecularly imprinted polymers, and immuno-adsorbents), together with membrane materials that permit the selective diffusion of chemicals. Novel synthetic absorbent polymer materials with high retention capacity of polar organic compounds may enable the replacement of currently used adsorption-based samplers for which data conversion into aqueous concentrations is often difficult.

A major challenge in the future development of the technology is the calibration of devices to enable the quantification of the concentration of emerging substances present in water. In comparison with devices designed for sampling hydrophobic organic compounds, sampling of most emerging substances is more complex. In addition to the common factors (temperature, water turbulence and biofouling), other factors (e.g. salinity, DOC level, pH, and the presence of complex mixtures of contaminants) may significantly affect the performance of samplers of emerging substances and these need to be evaluated. There are several routes to reduce uncertainty associated with the passive sampler data. These include quantitative assessment, reduction or control of the known factors which impact on sampler performance. For samplers where analytes are accumulated in the receiving phase by absorption mechanisms, PRCs can be successfully employed for improving the accuracy of the measurement of TWA concentrations of contaminants in the field. However, further research is needed to understand accumulation kinetics in samplers fitted with adsorbent-type receiving phases. Mechanical control of constant water flow conditions around the receiving phase in the field enables sampling rates of WBL-controlled samplers that are unaffected by turbulence [124]. Such devices require an *in situ* use of rotors or pumps that force water motion around the sampling devices. Thus, they cannot be classified as true “passive samplers”. However, miniaturised devices that require only a low energy supply (e.g. batteries or solar cells) for the operation of pumps can be deployed in the same way as passive samplers.

Miniaturised devices present a further trend in technology development. Small samplers are usually less expensive to use because of the lower costs of materials needed for their preparation and the reduced equipment requirements for their deployment. Lower volumes of solvents and reagents are consumed during their subsequent processing. Small samplers also offer the advantage of easy transportation to and from the sampling site. As miniaturised devices should not deplete the bulk matrix, they can be used in situations where space, volume and the flow of water are limited; for example, in groundwater boreholes.

The ability to predict kinetic and thermodynamic uptake parameters for passive samplers using quantitative structure property relationship (QSPR) models describing interactions of sampled compounds with materials used in the construction of devices is also important. This may help to reduce the amount of required laboratory-based calibration experiments.

Development of biomimetic devices capable of simulating the accumulation of toxic chemicals in tissues of aquatic organisms will enable a reduction in the use of chemical monitoring in biota in routine monitoring programmes. It will also decrease the uncertainty associated with the data obtained, as this is based on highly variable samples of biological material.

The combination of the deployment of passive samplers followed by the biological testing of sampler extracts with the aim of detecting and subsequently identifying toxicologically

relevant compounds offers much potential. This approach can provide information concerning the relative toxicological significance of waterborne contaminants and hence help to improve risk assessments for different water bodies.

Finally, further development of QA/QC, method validation schemes, and standards for the use of passive sampling devices is urgently needed. Successful demonstration of the performance of passive samplers alongside conventional sampling schemes as well as inter-laboratory studies that demonstrate reproducibility of data produced by different designs of passive samplers will help to facilitate the acceptance of passive sampling in routine regulatory monitoring programmes in the future.

Table 1. List of most discussed emerging pollutants in the aquatic environment and the established or expected/potential performance of passive samplers of these compounds.

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
Natural products	Cyanotoxins	Microcystins	-	+	**d**	[125]
Antioxidants	Antioxidants	2,6-Di-tert-butylphenol	-	+		
		4-tert-Butylphenol	-	+		
		BHA	-	+		
		BHQ	-	+		
		BHT	-	+		
Antifouling compounds	Antifouling compounds	Irgarol	-	+	**d**	[9,99]
	Organotin compounds	Dibutyltin ion	-	+	**d**	[38,39]
		Monobutyltin ion	-	+	**d**	[38,39]
		Tetrabutyltin ion	-	+	**d**	[38,39]
		Diphenyltinion	-	+	**d**	[38,39]
		Triphenyltin ion	-	+	**d**	[38,39]
Detergents	Ethoxylates/ carboxylates of octyl/nonyl phenols	4-Nonylphenol di-ethoxylate (NPE2O)	-	+	**d**	[25,126, ,127]
		4-Nonylphenol mono-ethoxylate (NPE1O)	-	+	**d**	[25,126 ,127]
		4-Nonylphenoxy acetic acid (NPE1C)				
		4-Nonylphenoxyethoxy acetic acid (NPE2C)				
		4-Octylphenol di-ethoxylate (OPE2O)	-	+	**d**	[25,126,127]
		4-Octylphenol mono-ethoxylate (OPE1O)	-	+	**d**	[25,126,127]
		4-Octylphenoxy acetic acid (OPE1C)				

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		4-Octylphenoxyethoxy acetic acid (OPE2C)				
Disinfection by-products (drinking water)	Iodo-trihalomethanes		-			
	Bromoacids		-			
	Bromoacetonitriles		-			
	Bromoaldehydes		-			
	Haloacetic acids (chloro-, bromo-, iodo-)		-			
	Other disinfection by-products	Bromate				
		Cyanoformaldehyde				
		Decabromodiphenyl ethane				
		Hexabromocyclododecane (HBCD)	+	-		
		NDMA	+	-	**d**	
Plasticizers	Phthalates	Benzylbutylphthalate (BBP)	+	-		
		Diethylphthalate (DEP)	+	-		
		Dimetylphthalate (DMP)	+	-		
		Di-n-butylphthalate (DBP)	+	-		
		Di-n-octylphthalate (DOP)	+	-		
	Other	Bisphenol A	-	+	**d**	[25,128,142,129]
		Triphenyl phosphate			**d**	
	Benzophenone derivatives	2,4-Dihydroxybenzophenone	-	+	**d**	[65]
Flame retardants	Brominated flame retardants	1,2,5,6,9,10-Hexabromocyclododecane (HBCD)	+	-		
		Tetrabromo bisphenol A (TBBPA)	+	-		
		Tetrabromo bisphenol A bis (2,3 dibromopropylether)	+	-		
		Hexabromocyclododecane (isomers)	+	-		
		Decabromodiphenyl ethane	+	-		

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
	Polybrominated diphenylethers	2,2',3,4,4',5',6-Heptabromodiphenyl ether (BDE 183)	+	-	**d**	
		2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	+	-	**d**	
		2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE-154)	+	-	**d**	
		2,2',4,4',5-Pentabromodiphenyl ether (BDE-99)	+	-	**d**	
		2,2',4,4',6-Pentabromodiphenyl ether (BDE-100)	+	-	**d**	
		2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	+	-	**d**	
		2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether (BDE-209)	+	-	**d**	
		Technical Decabromodiphenyl ether	+	-	**d**	
		Technical Octabromodiphenyl ether	+	-	**d**	
		Technical Pentabromodiphenyl ether	+	-	**d**	
	Organo-phosphates	Tri-(dichlorisopropyl)-phosphate		+	p	[130]
		Triethylphosphate		+	p	
		Tri-n-butylphosphate		+	**d**	
		Triphenylphosphate		+	**d**	
		Tris(2-chloroethyl)-phosphate		+	p	
	Chlorinated paraffins	Long chain PCAs (lPCAs, C>17)	+	-	p	
		Medium chain PCAs (mPCAs, C14-17)	+	-	p	
		Technical PCA products	+	-	p	
Fragrances	Fragrances	Acetylcedrene		+	p	
		Benzylacetate		+	p	
		Benzylsalicylate		+	p	
		Camphor		+	p	
		g-Methylionone		+	p	
		Hexylcinnamaldehyde		+	p	
		Isoborneol		+	p	
		Isobornylacetate		+	p	
		Isoquinoline		+	p	
		d-Limonene		+	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Methyldihydrojasmonate		+	p	
		Methylsalicylate	-	+	**d**	
		p-t-Bucinal		+	p	
		Terpineol		+	p	
	Nitro musks	Muskketone	+	-	**d**	
		Muskxylene	+	-	**d**	
		Musk ambrette	+		p	
	Macrocyclic musks					
	Polycyclic musks	AHTN (Tonalide)	+	-	**d**	
		Galaxolide	+	-	**d**	
		OTNE	+	-	**d**	
		AHDI (Phantolide)	+	-	**d**	
		ADBI (Celestolide)	+	-	**d**	
		ATII (Traseolide)	+	-	**d**	
Gasoline additives	Dialkyl ethers	Methyl-tert-butyl ether (MTBE)	-	-		
Indus-trial chemi-cals	Industrial chemicals	TCEP				
		Triphenyl phosphine oxide				
Perfluoro-alkylated substances	Perfluoroalkylated substances	Perfluorooctane sulfonate (PFOS)		+	p	
		Perfluorooctanoic acid (PFOA)		+	p	
Personal care products	Sun-screen agents	4-Methylbenzylidene camphor	+	+	**d**	
		Benzophenone	-	+	**d**	
		Benzophenone-3	-	+	**d**	
		Butyl methoxydibenzoyl-methane			p	
		Ethylhexyl methoxycinnamate	+	+		
		Eusolex Homosalate				
		N,N-Diethyltoluamide	-	+	**d**	
		Octocrylene				
		Oxybenzone				
	Insect repellents	N,N-diethyl-m-toluamide (DEET)	-	+	**d**	
		Bayrepel				
	Carriers	Octamethylcyclotetrasiloxane (D4)	+	-	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Decamethylcyclopentasiloxane (D5)	+	-	p	
		Dodecamethylcyclohexasiloxane (D6)	+	-	p	
		Hexamethyldisiloxane (HM or HMDS)	+	-	p	
		Octamethyltrisiloxane (MDM)	+	-	p	
		Decamethyltetrasiloxane (MD2M)	+	-	p	
		Dodecamethylpentasiloxane (MD3M)	+	-	p	
	Parabens (hydroxybenzoic acid esters)	Methyl-paraben	-	+	p	
		Ethyl-paraben	-	+	p	
		Propyl-paraben	-	+	p	
		Isobutyl-paraben	-	+	p	
Pesticides	Polar pesticides and their degradation products	Acetochlor	-	+	**d**	[26,131, 132]
		Amitrole	-	+		
		Bentazone	-	+	**d**	
		Bromofos-ethyl	-	+		
		Carbazole	-	+		
		Carbendazim	-	+	**d**	[99]
		Carboxin	-	+		
		Glyphosate	-	+		
		Chloridazon	-	+	**d**	
		Clopyralid	-	+		
		Chlorpropham	-	+		
		Chlorpyrifos	-	+	**d**	[130]
		Chlorotoluron	-	+	**d**	
		2,4 D	-	+	**d**	[59]
		Dicamba	-	+	p	[59]
		Desethylterbutylazine	-	+	**d**	
		Desmedipham	-	+		
		Desmetryn	-	+		
		Diazinon	+	+	**d**	[99]
		Diclobenil	-	+		
		d-Dichlorvos	+	+	**d**	[57]
		Dinoterb	-	+		
		Endosulfan-sulfate	+	+	**d**	[133]
		Ethoprophos	-	+		
		Ethofumesate	-	+	**d**	
		Fluroxypyr	-	+		
		Heptenophos	-	+		
		Iodofenphos	-	+		
		Imidacloprid	-	+		
		MCPA	-	+	**d**	[59]
		MCPB	-	+	p	
		MCPP (Mecoprop)	-	+	p	[99]
		Metalaxyl	-	+	**d**	[27]

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Methomyl	-	+		
		Metamitron	-	+	**d**	
		Mevinphos	-	+		
		Phenmedipham	-	+		
		Prometryn	+	+	p	
		Prometon	-	+	**d**	
		Secbumeton	-	+		
		Terbutryn	+	+	p	[99]
		Terbutylazine	-	+	**d**	[134,99]
		Thiabendazyl	-	+	**d**	
		Triadimefon	-	+		
	Other pesticides	Cypermethrin	+	-	**d**	
		Deltamethrin	+	-	**d**	
		Permethrin	+	-	**d**	[135]
	New pesticides	Sulfonyl urea				
	Degradation products of pesticides	Desisopropylatrazine	-	+	**d**	[27]
		Desethylatrazine	-	+	**d**	[27,99]
Bio-cides	Biocides	Triclosan	+	+	**d**	[129,136]
		Methyltriclosan	+	+	**d**	[137]
Pharmaceuticals	Analgesic	Acetaminophen (paracetamol)	-	+	**d**	[129,138, 139]
		Codeine	-	+	p	
		Hydrocodone	-	+		
	Anorexic	Fenfluramine	-	+	p	
	Anthelmintic	Ivermectin	-	+	p	
	Antibacterial	Amoxicillin	-	+	p	
		Ampicillin	-	+	p	
		Azithromycin	-	+	**d**	[128,140]
		Chloramphenicol	-	+	p	
		Chlortetracycline	-	+	p	
		Ciprofloxacin	-	+	p	
		Clarithromycin	-	+	**d**	[95,141]
		Cloxacillin	-	+	p	
		Danofloxacin	-	+	p	
		Dicloxacillin	-	+	p	
		Doxycycline (anhydrous)	-	+	p	
		Doxycycline (monohydrate)	-	+	p	
		Enoxacin	-	+	p	
		Enrofloxacin	-	+	p	
		Erythromycin	-	+	**d**	[141]
		Flumequine	-	+	p	
		Josamycin	-	+	p	
		Lincomycin	-	+	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Methicillin	-	+	p	
		Minocycline	-	+	p	
		Norfloxacin	-	+	p	
		Novobiocin	-	+	p	
		Ofloxacin	-	+	p	
		Oleandomycin	-	+	p	
		Oxacillin	-	+	p	
		Oxytetracycline	-	+	**d**	
		Penicillin G	-	+	p	
		Penicillin V	-	+	p	
		Roxithromycin	-	+	**d**	[141]
		Spiramycin	-	+	p	
		Sulfadiazine	-	+	**d**	
		Sulfamerazine	-	+	**d**	[128]
		Sulfamethazine	-	+	**d**	[141]
	Anticonvulsant	Sulfamethoxazole	-	+	**d**	[99,129]
		Sulfapyridine	-	+	**d**	[129,138, 141]
		Carbamazepine	-	+	**d**	[95,129, 138,141]
		Primidone	-	+		
	Antidepressant	Tetracycline	-	+	**d**	
		Tiamulin	-	+		
		Citalopram	-	+		[129]
		Escitalopram	-	+		
		Sertraline	-	+	**d**	[129]
		Fluoxetine	-	+	**d**	[129,141, 140]
		Fluvoxamine	-	+		
		Paroxetine	-	+	**d**	[129]
	Antidiabetic	Glyburide (glibenclamid; glybenzcyclamide)	-	+		
		Metformin	-	+	p	
	Antiemetic	Diphenhydramine	-	+	**d**	
	Antihistaminic	Loratadine	-	+		
	Antihyperten-sive	Nadolol	-	+		
		Verapamil	-	+		
	Anti-inflammatory	Aceclofenac	-	+		
		Acemetacin	-	+		
		Acetylsalicylic acid (aspirin)	-	+	**d**	[138]
		Alclofenac	-	+		
		Diclofenac	-	+	**d**	[99,138, 141]
		Fenoprofen	-	+	**d**	[141]
		Fenoprofen calcium salt dihydrate	-	+		

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Ibuprofen	-	+	**d**	[129,138]
		Indomethacin	-	+	**d**	
		Ketoprofen	-	+	**d**	[138,141]
		Meclofenamic acid	-	+		
		Mefenamic acid	-	+		
		Naproxen	-	+	**d**	[129,138, 141]
		Phenylbutazone	-	+		
		Phenazone	-	+		
		Propyphenazone	-	+		
		Tolfenamic acid	-	+		
	Antimicrobial agent	Clotrimazole	-	+		
	Antineoplastic	Cyclophosphamide	-	+	p	
		Cyclophosphamide (anhydrous form)	-	+		
		Daunorubicin	-	+		
		Doxorubicin	-	+		
		Epirubicin	-	+		
		Fluorouracil	-	+		
		Ifosfamide	-	+	p	
	Antiulcerative	Famotidine	-	+		
		Lansoprazole	-	+		
		Omeprazole	-	+	**d**	[141,140]
		Ranitidine	-	+	p	
	Anxiolytic	Alprazolam	-	+	**d**	
		Bromazepam	-	+	**d**	
		Diazepam	-	+	**d**	[138]
		Lorazepam	-	+	p	
		Medazepam	-	+	p	
		Meprobamate	-	+	p	
		Nordiazepam	-	+	p	[138]
		Oxazepam	-	+	p	
		Temazepam	-	+	**d**	[141]
	Beta-Blockers	Acebutolol	-	+	p	
		Atenolol	-	+	**d**	[129,141]
		Betaxolol	-	+	p	
		Bisoprolol	-	+	p	
		Carazolol	-	+	p	
		Metoprolol	-	+	p	[129]
		Oxprenolol	-	+	p	
		Pindolol	-	+	p	
		Propranolol	-	+	**d**	[129,141]
		Sotalol	-	+	p	[129]
		Timolol	-	+	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
	Blood viscosity agents	Pentoxifylline	-	+		
	Bronchodilators	Albuterol	-	+		
		Albuterol sulfate	-	+		
		Clenbuterol	-	+	**d**	[138]
		Fenoterol	-	+		
		Salbutamol	-	+	**d**	[138]
		Terbutaline	-	+	**d**	[138]
	Diuretic	Caffeine	-	+	**d**	[128, 129,138]
		Furosemide	-	+	p	
		Hydrochlorothiazide	-	+	**d**	[141]
	Lipid regulators	Bezafibrate	-	+		
		Clofibric acid	-	+	**d**	[141]
		Etofibrate	-	+		
		Fenofibrate	-	+		
		Fenofibric acid	-	+		
		Gemfibrozil	-	+	**d**	[129,138,141]
		Lovastatin	-	+		
		Mevastatin	-	+		
		Pravastatin	-	+		
		Simvastatin	-	+	p	
	Sedatives, hypnotics	Acecarbromal	-	+		
		Allobarbital	-	+		
		Amobarbital	-	+		
		Butalbital	-	+		
		Hexobarbital	-	+		
		Pentobarbital	-	+		
		Aprobarbital	-	+		
		Secobarbital sodium	-	+		
	Steroids and hormones	17-alpha-Oestradiol	-	+	**d**	[25,128,129,142]
		17-alpha-Ethinyloestradiol	-	+	**d**	[25,128]
		17-beta-Oestradiol	-	+	**d**	[25,128,129, ,142]
		Beta-sitosterol	-	+	**d**	
		Cholesterol	-	+	**d**	
		Diethylstilbestrol	-	+	p	
		Oestriol	-	+	**d**	[142]
		Oestrone	-	+	**d**	[25,128,129]
		Oestrone 3-sulphate	-	+	p	
		Prednisolone	-	+	p	
		Dexamethasone	-	+	p	
		Bethametasone	-	+	p	
		Mestranol	-	+	**d**	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
	Psychiatric drugs	Amitryptiline	-	+	**d**	[138]
		Doxepine	-	+	**d**	[138]
		Imapramine	-	+		
		Nordiazepam	-	+	**d**	[138]
		Zolpidem	-	+		
	X-ray contrast media	Diatrizoate	-	+		
		Iohexol	-	+		
		Iomeprol	-	+		
		Iopamidol	-	+		
		Iopromide	-	+		
Trace metals	Trace metals and their compounds	Tetramethyllead	+	-		
		Tetraethyllead	+	-		
	Benzotriazoles	4-Methyl-1H-benzotriazole	-	+	p	
		5-Methyl-1H-benzotriazole	-	+	**d**	
		5,6-Dimethyl-1-H-benzotriazole	-	+	p	
	Tolyltriazoles (TT)	Tolyltriazole				
		4-/5-Tolyltriazole (TTri)				
Wood preserva-tives	Phenols	para-Cresol	-	+	**d**	
Other	Drugs of abuse	Cocaine	-	+	p	
		Codeine	-	+	**d**	[141]
		Dihydrocodeine	-	+	p	
		Heroin	-	+	p	
		Hydrocodone	-	+	p	
		Morphine	-	+	p	
		Oxycodone	-	+	p	
	Benzothiazoles (BT)	Benzothiazole	-	+	**d**	
		2-Mercapto-benzothiazole	-	+	**d**	
		Benzothiazole sulfonic acid	-	+	p	
	Nicotine metabolite	Cotinine	-	+	**d**	[128]

The following considerations apply.

[a]potential of non-polar samplers: (e.g. SPMD, LDPE, silicone, non-polar Chemcatcher)

+ = log K_{ow} > 4; - = log K_{ow} < 3

[b]potential of hydrophilic samplers (POCIS, the hydrophilic version of Chemcatcher, Empore™ disks and others)

+ = log K_{ow} < 3 ; - = log K_{ow} >4

[c]stage of development:

d = performance has been demonstrated in the laboratory and/or in the field;

p = performance is likely to be good, but experimental evidence is not available.

[d]selected references are given to publications containing sampler calibration data

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