Passive sampling techniques for monitoring pollutants in water

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We review the state of the art in using passive sampling technology for environmental monitoring of waterborne organic and inorganic pollutants. We discuss strategies for sampler design, calibration, *in situ* sampling and quality-control issues, and advantages and challenges associated with passive sampling in aqueous environments. We then review typical applications of passive samplers in assessing the aquatic environment.
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Abbreviations: ASV, Anodic stripping voltammetry; BTEX, Benzene, toluene, ethyl benzene and xylene; DET, Diffusion equilibrium in thin films; DGT, Diffusive gradient in thin films; GC, Gas chromatography; HPLC, High-performance liquid chromatography; LDPE, Low-density polyethylene; MESCO, Membrane-enclosed sorptive coating; nd-SPME; Negligible depletion solid-phase microextraction; NOM, Natural organic matter; OSPAR, The Convention for the Protection of the Marine Environment of the North-East Atlantic; PAH, Polycyclic aromatic hydrocarbon; PCB, Polychlorinated biphenyl; PCDD, Polychlorinated dibenzo[p]dioxin; PCDF, Polychlorinated dibenzo[p]furan; PDB, Polyethylene diffusion bag; PDBS, Passive diffusion bag sampler; PIMS, Passive integrative mercury sampler; PLM, Permeation liquid membrane; POCIS, Polar organic chemical integrative sampler; PRC, Performance reference compound; QA, Quality assurance; QC, Quality control; SBSE, Stir-bar sorptive extraction; SLM, Supported liquid membrane; SLMD, Stabilised liquid-membrane device; SPATT, Solid-phase adsorption toxin tracking; SPMD, Semi-permeable membrane device; SPME, Solid-phase microextraction; SVOC, Semi-volatile organic compound; TLC, Thin-layer chromatography; TRIMPS, Trimethylpentane-containing passive sampler; TWA, Time-weighted average; VOC, Volatile organic compound

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1. Introduction

It is necessary to monitor pollutants in the aquatic environment to satisfy the requirements of legislative frameworks and directives, as many of these compounds can pose a threat to both human health and ecosystems. A number of toxic compounds have been designated priority pollutants [e.g., those on lists of the US Environmental Protection Agency (EPA) and the Water Framework Directive of the European Union (EU)] and their measurement is necessary to ensure that water-quality standards are maintained. Sampling and analysis of such a broad range of organic (e.g., chlorophenols, organo- chlorine pesticides, polyaromatic hydrocarbons, polychlorinated biphenyls) and inorganic (e.g., heavy metals and some of their organo-metallic species) compounds represents an ongoing challenge to the environmental chemist.

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Most aquatic monitoring programmes rely on collecting discrete grab, spot or bottle samples of water at a given time. Often, where pollutants are present at only trace levels, large volumes of water need to be collected. The subsequent laboratory analysis of the sample provides only a snapshot of the levels of pollutants at the time of sampling. However, there are drawbacks to this approach in environments where contaminant concentrations vary over time, and episodic pollution events can be missed. One solution to this problem is to increase the frequency of sampling or to install automatic sampling systems that can take numerous water samples over a given time period. This is costly and in many cases impractical, since a secure site and significant pre-treatment of water are required. Such systems are rarely used in widespread monitoring campaigns. Spot sampling yields different apparent concentrations of pollutants depending on the pre-treatment applied (e.g., filtering) and does not provide information on the truly dissolved, bioavailable fraction of the contaminants.

Another approach that yields information on biologically relevant concentrations of pollutants uses biota. A number of test species can be used, depending on the water body being investigated. These organisms can be deployed for extended periods of time, during which they passively bioaccumulate pollutants in the surrounding water. Analysis of the tissues or lipid extracts of the test organism(s) can give an indication of the equilibrium level of waterborne contamination. A number of factors can influence the results – metabolism, depuration rates, excretion, stress, viability and condition of test organism. Furthermore, extraction of analytes from the tissue of animals prior to instrumental analysis is complex.

Estimates of pollutant concentrations in water can also be made by measuring concentrations in benthic sediments and then using equilibrium distribution coefficients to derive levels of dissolved analytes. This approach is limited by the assumption of equilibrium between the sediments and the water column, and the potential effects of organic carbon quality differences among sediments or the formation of non-extractable, sediment-bound residues that are not accounted for in current equilibrium-partition models.

In the last two decades, alternatives have been sought to overcome some of these difficulties. Of these, passive sampling methods have shown much promise as tools for measuring aqueous concentrations of a wide range of priority pollutants. Passive samplers avoid many of the problems outlined above, since they collect the target analyte *in situ* and without affecting the bulk solution. Depending on sampler design, the mass of pollutant accumulated by a sampler should reflect either the concentration with which the device is at equilibrium or the time-averaged concentration to which the sampler was exposed. Such devices have been available for monitoring air quality since the early 1970s. These diffusion-based dosimeters have been employed extensively by industry to measure toxic chemicals in workplace air.

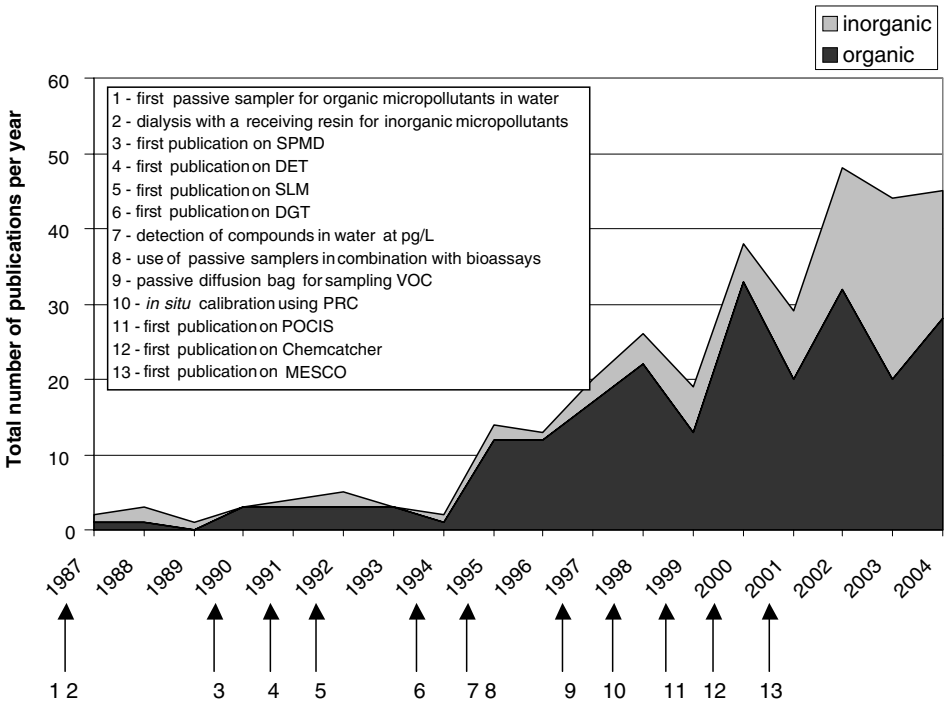

Figure 1. Milestones in the development of passive sampling techniques. The figure shows the annual number of peer-reviewed publications on the development and the application of passive samplers for monitoring of organic contaminants in water.

Later, the principles of passive dosimetry were applied in monitoring in aqueous environments. Milestones in the development of passive sampling devices for monitoring of water pollutants are shown in Fig. 1.

This article reviews the state of the art of different passive sampling methods that have been developed to measure both organic and inorganic pollutants in water and highlights their range of applicability. Their potential for use in monitoring programmes is considered alongside other issues, such as quality control and detection limits. We discuss recent developments to extend their use (e.g., extracts from the devices being incorporated into bioassay-based ecotoxicology tests), challenges and limitations of the technology.

2. Principles

Passive sampling can be defined in its broadest sense as any sampling technique based on free flow of analyte molecules from the sampled medium to a receiving phase in a sampling device, as a result of a difference between the chemical potentials of the analyte in the two media. The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling period is stopped [1]. Sampling proceeds without the need for any energy sources other than this chemical potential difference.

Analytes are trapped or retained in a suitable medium within the passive sampler, known as a reference or receiving phase. This can be a solvent, chemical reagent or a porous adsorbent. The receiving phase is exposed to the water phase, but without the aim of quantitatively extracting the dissolved contaminants. Pollutant adsorption or absorption from water into most passive sampling systems generally follows the pattern shown in Fig. 2. The exchange kinetics between a passive sampler and water phase can be described by a first-order, one-compartment mathematical model:

$$C_S(t) = C_W \frac{k_1}{k_2}(1 - e^{-k_2 t}), \quad (1)$$

where $C_S(t)$ is the concentration of the analyte in the sampler at exposure time t, C_W is the analyte concentration in the aqueous environment, and k_1 and k_2 are the uptake and offload rate constants, respectively. Two main accumulation regimes, either kinetic or equilibrium, can be distinguished in the operation of a sampler during field deployment.

2.1. Equilibrium-passive samplers

In equilibrium sampling, the exposure time is sufficiently long to permit the establishment of thermodynamic equilibrium between the water and reference phases. In this situation, equation (1) reduces to:

$$C_S = C_W \frac{k_1}{k_2} = C_W K. \quad (2)$$

Knowledge of the phase-water partition coefficient (K) allows estimation of dissolved analyte concentration. An overview of equilibrium-passive sampling devices has been published by Mayer et al. [2]. The basic requirements of the equilibrium-sampling approach are that stable concentrations are reached after a known response time, the sampler capacity is kept well below that of the sample to avoid depletion during extraction and the device response time needs to be shorter than any fluctuations in the environmental medium. Passive diffusion bag samplers (PDBSs) have been used extensively for monitoring volatile organic compounds (VOCs) in water [3,4].

2.2. Kinetic passive samplers

With kinetic sampling, it is assumed that the rate of mass transfer to the reference/receiving phase is linearly

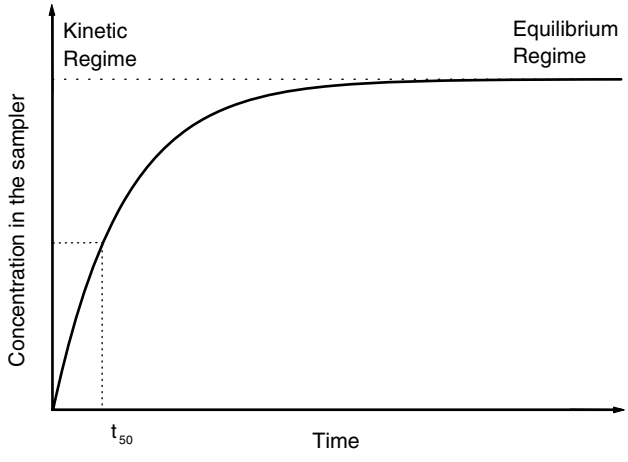

Figure 2. Passive sampling devices operate in two main regimes (kinetic and equilibrium).

proportional to the difference between the chemical activity of the contaminant in the water phase and that in the reference phase. In the initial phase of sampler exposure, the rate of desorption of analyte from the receiving phase to water is negligible, the sampler works in the linear uptake regime, and equation (1) reduces to:

$$C_S(t) = C_W k_1 t. \quad (3)$$

Equation (3) can be rearranged to an equivalent relationship:

$$M_S(t) = C_W R_S t, \quad (4)$$

where $M_S(t)$ is the mass of analyte accumulated in the receiving phase after an exposure time (t) and R_S is the proportionality constant (sampling rate), which is the product of the first-order rate constant for uptake of pollutant (k_1) and the volume of water that gives the same chemical activity as the volume of receiving phase. R_S may be interpreted as the volume of water cleared of analyte per unit of exposure time by the device.

When R_S is known, C_W [the time-weighted average (TWA) concentration of a pollutant in the water phase] may be calculated from the sampling rate (R_S), exposure time (t) and the amount ($M_S(t)$) of the analyte trapped by the receiving phase. For most devices operating in the kinetic mode, R_S does not vary with C_W, but is often affected by water flow or turbulence, temperature and biofouling. The advantages of kinetic or integrative sampling are that they sequester contaminants from episodic events commonly not detected with spot sampling, and can be used where water concentrations are variable. They permit measurement of ultra-trace, yet toxicologically relevant, contaminant concentrations over extended time periods.

2.3. Sampler design

Although many different types of kinetic passive sampler exist, nearly all share common design characteristics, the most important being the presence of a barrier between the sampled medium and the receiving phase. The barrier should determine the rate at which analyte molecules are collected at a given concentration. The barrier may also define the selectivity of the sampler and restrict certain classes of analyte or species sampled. Based on the properties of the barrier, samplers fall into one of the two categories – diffusion-based or permeation-based devices [1]. The sampling process is similar for both. Once exposed to water, they collect analyte molecules reaching the receiving phase by diffusion through a static layer of water contained in well-defined opening(s) in the sampler (diffusion samplers), or by permeation through a porous or non-porous membrane (permeation samplers).

The uptake rate of analytes depends on the sampler design, physicochemical properties of the analytes and environmental variables (i.e., water turbulence, water temperature and fouling). Passive samplers are designed to maximise the amount of analyte sampled in order to detect the generally low levels of analytes present in water, whilst ensuring a quantitative correlation between the mass of chemical separated and its concentration in the sampled medium.

Diffusional kinetic samplers mostly use a ''tube'' design, where the receiving phase is located inside a long, narrow inert tube or a capillary. The space between the edge of the sampler and the surface of the receiving phase, characterised by a diffusion distance (L), is filled with a stagnant layer of the sampled medium, and this defines the sampling rate. To avoid fluctuations in L, caused by the disturbance of the stagnant diffusion layer by facial water velocity/turbulence, tube-type diffusion samplers are characterised by a relatively low ratio of surface area of the receiving phase A to L. Since the amount of analyte sampled is directly proportional to the surface area of the sampler, tube-type samplers are generally less sensitive than so-called badge-type samplers, characterised by a high A/L ratio. The tube design is usually used in air monitoring. However, sampling kinetics in flat badge-type samplers with a large surface area are more affected by fluctuations in water velocity. To alleviate the impact of these fluctuations, a diffusion-limiting membrane is generally used to separate the receiving phase from the sampled medium and to control the mass transfer of analyte to the receiving phase. In water monitoring, badge-type samplers predominate.

2.4. Calibration of passive samplers

The theoretical background of passive sampling in water has been described previously [1,5–7]. The substance-specific kinetic constants, k_1 and k_2, and the distribution coefficient, K, can be determined in two ways. In theory, kinetic parameters characterising the uptake of analytes can be estimated using semi-empirical correlations between mass-transfer coefficients, physicochemical properties (mainly diffusivities in various media) and hydrodynamic parameters [8]. However, because of the complexity of the water flow around passive sampling devices during exposure (usually non-streamlined objects), it is often difficult to estimate uptake parameters from first principles. For K, which characterises the affinity of a pollutant to the receiving phase relative to water, more substance-specific information is usually available from the literature.

In a practical approach, calibration of passive sampling exchange kinetics is performed in the laboratory at known exposure concentrations [9–12]. To predict TWA water concentrations of contaminants from levels accumulated in passive samplers, extensive calibration studies are necessary to characterise the uptake of chemicals under various exposure conditions. Uptake kinetics of chemicals depends upon not only the physicochemical properties of the diffusand, but also the sampler

design and environmental variables, such as temperature, water turbulence and biofouling of the sampler surface [13,14].

2.5. Environmental factors affecting passive sampling

It is important to consider the mechanisms of the exchange process between the aqueous phase and the sampler components. The rate-limiting step in the uptake to the receiving phase (in the absence of fouling) may be controlled by diffusion in the diffusion-limiting membrane or across the aqueous diffusive boundary layer at the membrane–water interface [15]. Water turbulence affects the thickness of the unstirred layer of water that forms part of the diffusion-limiting barrier near the sampler surface, and consequently also affects the mass transfer of the analytes. The rate-limiting step depends on the type and properties of the membrane, the environmental conditions prevailing during sampling and the properties of the compound being sampled.

A number of methods have been developed to compensate for the effect of environmental variables on the sampler performance. Booij et al. [16,17] described a method to estimate the uptake kinetics in both laboratory and field situations by spiking devices prior to exposure with a number of performance reference compounds (PRCs) that do not occur in the environment. Where factors influencing uptake kinetics affect the offloading kinetics of PRCs in an identical manner, the release rate of these compounds is a measure of the exchange kinetics between the sampler and water, and can be used in field exposures to compensate for variations in environmental conditions.

2.6. Biofouling

Unprotected surfaces submersed in water eventually become colonised by bacteria and various flora and fauna that may ultimately form a biofilm. The thickness of this biofilm varies from not only exposure to exposure but also spot to spot on the same diffusion-limiting membrane. The composition of biofilms varies significantly depending on the aquatic system. Biofouling can affect the overall resistance to mass transfer by increasing the thickness of the barrier and by blocking any water-filled pores in the diffusion-limiting membranes. Colonising organisms may damage the surface of membranes, if made of a degradable material. Huckins et al. [18] reported 20–70% impedance in uptake of polyaromatic hydrocarbons (PAHs) in severe cases, but also showed that, for biofouled semi-permeable membrane devices (SPMDs), PRCs can be applied to correct for biofouling during deployment. Their model describing the mass transfer in a biofilm indicates that, ideally, it behaves like an immobilised water layer, with a resistance independent of the biofilm/water partition coefficient, which would mean a similar mobility of compounds in biofilm, independent of their hydrophobicity [18]. The problem of sampler fouling may be reduced by selecting suitable construction materials. For example, polyethersulphone used in one design of the Chemcatcher and in the polar organic chemical integrative sampler (POCIS) is less prone to fouling than polyethylene used in SPMDs [19]. In addition, certain solvent-filled membrane devices are protected from fouling by slow seeping of the fouling-inhibiting solvent (e.g., *n*-hexane) from the sampler during exposure. Protective screens made of copper or bronze mesh have also been shown to inhibit biofouling; however, their use is restricted when monitoring for heavy metals.

3. Passive sampling devices

Passive samplers usually combine sampling, selective analyte isolation, pre-concentration and, in some cases, speciation preservation in one step. They simplify the operations performed at the sampling site. They eliminate the need for an energy/power supply and allow the entire sampling set-up to be simplified and miniaturised. Once the sample is collected, further steps in its processing are usually the same as for other sampling/sample pre-concentration methods in analysis. They include extraction/desorption of the analytes, final instrumental analysis and processing the data.

A review of passive samplers used for monitoring pollutants in various media has been published by Namiesnik et al. [20]. Tables 1 and 2 present an overview of devices used to measure organic and inorganic contaminants in water. In the following sub-sections, we present in detail several (but not all) samplers with a potential for use in environmental monitoring programmes to illustrate the manifold applications of this technology.

3.1. Passive samplers for organic pollutants

3.1.1. Semi-permeable membrane devices. SPMDs comprise lay-flat tubing made of low-density polyethylene (LDPE) filled with a high-molecular weight lipid, typically high-purity synthetic triolein. LDPE is a non-porous material with no fixed pores, only transient cavities with a typical size of 1 nm. This solute size limitation excludes large molecules as well as those that are adsorbed on colloids or humic acids. Only truly dissolved and non-ionised contaminants diffuse through the LDPE membrane and can be separated by the sampler. Triolein represents a receiving phase with a high capacity for compounds with octanol/water partition coefficients $\log K_{OW} > 3$ [21]. The design of the SPMD was first published in 1990. Since then, nearly 200 studies have been reported, and this is the most mature technique for sampling organic pollutants [22]. Several reviews and one monograph have been published on this technology [18,23–25].

Table 1. Overview of passive sampling devices for organic contaminants

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment	Advantages	Drawbacks	Sample preparation for chemical analysis	Ref.
Ceramic dosimeter	Ceramic dosimeter and toximeter	Ceramic tube (5 × 1 cm) filled with a solid-phase sorbent material, closed with PTFE lids	PAHs, BTEX, chlorinated hydrocarbons	Integrative sampling in ground-water	Up to 1 year	No need for extensive laboratory calibrations. Robust design, suitable for long-term monitoring. Sorbent material of the ''Toximeter'' variant can be tested in contact bioassays	Low sensitivity	Solvent extraction or thermal desorption	[32]
Chemcatcher	Universal passive sampler using Empore disk	A housing made of inert plastic (e.g., PTFE), containing a disk of solid receiving phase bound in a porous polymer, and a disk of diffusion-modulating membrane.	Polar and non-polar organics	Integrative	14 days –1 month	Selectivity of the sampler can be adjusted using appropriate combination of membrane and Empore disks. Calibration data available for many chemicals		Solvent extraction	[27]
Dosimeter		Activated carbon receiving phase in a perforated acrylic housing	BTEX and atrazine	Integrative	Up to 2 months			Solvent extraction	[72]
Ecoscope	A sampler based on solvent-filled dialysis membranes and chelating sorbent discs	A plastic housing containing a chelating sorbent disc for sampling metals and dialysis membrane filled with solvents	Non-polar organics	Qualitative screening					[73]
Gaiasafe		Paper or fabric strips impregnated with a solution of binding agent	Metals, anions, organic compounds	Screening	2 days –2 months			Solvent extraction	[74]
Gore-Sorber		Various sorbent materials filled in a carrier hose made of Gore-Tex	BTEX, MTBE, PAHs, VOCs, SVOCs	Equilibrium	14 days			Thermal desorption	[75]

LDPE and silicone strips		Low-density polyethylene or silicone strips	Hydrophobic organic compounds	Integrative	1 month	Simple construction, inexpensive, simple sample processing, and calibration data available for many analyte classes	Smaller sampling capacity than SPMDs	Solvent extraction	[76]
MESCO	Membrane–enclosed sorptive coating	PDMS-coated stir bar used in SBSE or a PDMS rod enclosed in a membrane made of regenerated cellulose or low-density polyethylene	PAHs, PCBs, organochlorine pesticides	Integrative	2 weeks	Miniaturised sampler, non-depletive matrix extraction, solventless sample processing, and both non-polar and polar analytes are accumulated in the sampler equipped with a cellulose membrane	Low membrane stability of the sampler variant with cellulose dialysis membrane	Thermal desorption	[31]
nd-SPME	Negligible depletion-solid phase microextraction	A fibre coated with a liquid (polymer), a solid (sorbent), or a combination of both	Hydrophobic chemicals, including PAHs, PCBs, petroleum hydrocarbons, organochlorine pesticides, aniline, phenols	Equilibrium	Hours	Negligible depletion extraction, a cheap, disposable device	Low sensitivity	Thermal desorption in GC inlet	[30]
Passive	Sampler according to Lee and Hardy	Silicone polycarbonate permeation membrane and an adsorbent receiving phase	Chlorobenzenes, nitrobenzenes and nitrotoluenes	Integrative	Up to 1 day			Solvent extraction	[77]
PDB	Passive diffusion bag samplers	Dialysis membrane or a low-density polyethylene bag filled with distilled water	Polar organic compounds, VOCs, metals, trace elements	Equilibrium sampling in groundwater	2 weeks	Relatively inexpensive, and sample recovery is rapid	Not suitable for sampling semi-volatile organic compounds	Conventional analysis of the receiving water phase	[35]
PISCES	Passive *in situ* concentration-extraction sampler	Hexane in a polyethylene membrane	PCB	Integrative	2 weeks			Volume reduction of the receiving phase	[78]
POCIS	Polar organic chemical integrative sampler	Solid sorbent receiving phase material enclosed in a polyethersulphone membrane	Herbicides and pharmaceuticals with $\log K_{Ow} < 3$	Integrative	Up to 2 months	High sensitivity; capacity of the sampler can be adjusted using appropriate sorbent materials, membrane has low susceptibility to biofouling, and calibration data available for many chemicals		Solvent extraction	[26]

(*continued on next page*)

Table 1 (*continued*)

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment	Advantages	Drawbacks	Sample preparation for chemical analysis	Ref.
Porous	Sampler according to De Jonge and Rothenberg	A water permeable porous sampler that acts as a semi-infinitive adsorptive sink	Wide range of contaminants	Flux-proportional sampling in soil and ground-water	1 month	Tracers integrated in the sampler store information of water volume that passed the sampler during deployment		Solvent extraction	[79]
Stainless steel housing	Sampler according to Kot-Wasik	A stainless steel housing, containing organic solvent in a chamber separated from water by a membrane	Phenols, acid herbicides, triazines	Integrative	1 month	A sample of the receiving phase solvent can be taken without affecting the integrity of the sampler	Low-sensitivity, receiving phase solvent may diffuse out of the sampler during field deployment	Analysis of a sub-sample of solvent is taken and analysed without further clean-up steps	[80]
Solvent-filled dialysis membranes		Non-polar solvent immiscible with water filled in a cellulose dialysis membrane	Hydrophobic organic compounds	Integrative	1 month	Not prone to biofouling	Low sensitivity for very hydrophobic compounds, and solvent diffuses out of the sampler during deployment	Volume reduction of the receiving phase	[81]
SPATT	Solid-phase adsorption toxin tracking	Porous synthetic resin filled polyester fabric sachets	Polar phytotoxins	Integrative	1 week			Solvent extraction	[82]

SPMD	Semi-permeable membrane devices	Flat tube of LDPE filled with triolein	Hydrophobic semi-volatile organic compounds	Integrative	1 month	Widely used method, commercially available, well-established standard operation procedures, and calibration data available for many analyte classes, and high sensitivity	Complicated sample clean-up, susceptible to biofouling	Dialysis in organic solvents, size exclusion chromato-graphy	[21]
TLC plate	Thin-layer chromatography plate		Organo-phosphates	Screening	1 month	Good sensitivity because of a large surface area		Solvent extraction	[83]
TRIMPS	Trimethyl-pentane-containing passive sampler	2,2,3-Trimethylpentane filled in a low density polyethylene membrane	Pesticides	Integrative	1 month	Simple sample clean-up and analysis	Receiving phase solvent diffuses out of the sampler during field deployment	Direct analysis of the receiving phase solvent	[84,85]
TWA-SPME	Solid-phase microextraction applied for determination of TWA concentrations	A fibre coated with a liquid (polymer), a solid (sorbent), or a combination of both	BTEX	Integrative	A few minutes	No need for extensive laboratory calibrations, and sampling rates can be estimated using empirical mass-transfer models	Short-term sampling only, and fibre susceptible to damage or fouling in the field	Thermal desorption in GC inlet	[86]

Table 2. Overview of passive sampling devices for inorganic contaminants

Sampler	Full name	Construction	Analytes	Sampling purpose	Typical deployment period	Advantages	Drawbacks	Sample preparation for chemical analysis	Ref.
Chemcatcher		Comprises an immobilized chelating acceptor resin on a PTFE base and a cellulose acetate membrane filter acting as a thin diffusion layer	Cd, Cu, Ni, Pb and Zn	*In situ* sampling, integrative, speciation	14 days –1 month	Selectivity of the sampler can be adjusted using appropriate combination of membrane and Empore disks, and calibration data available for many chemicals		Acid extraction	[53]
DGT	Diffusion gradients in thin films	Two layers of acrylamide gel mounted in a holder device, one containing an acceptor phase, the other acting as a thin diffusion layer	55 metallic elements including the common heavy metals, phosphorous, sulphide and ^{99}Tc	Integrative, speciation, screening, mimicking biological uptake	1 week	Versatile, well documented	Complicated preparation of device	Acid extraction	[87]
PIMS	Passive integrative mercury sampler	LDPE lay-flat tubing	Neutral Hg species	Pre-concentration, screening	Weeks–months	Membrane characteristics may be altered for control of sampling rates	Further development necessary for aquatic conditions	Direct analysis of the receiving phase	[52]
PLM	Permeation liquid membrane	Microporous hydrophobic support separating test solution from receiving solution	Cu, Pb	Bioavailable metal species	Hours	Selectivity of the sampler can be adjusted using appropriate combination of carrier media and receiving phase	Complicated preparation of device	Solvent extraction	[88]
SLM	Supported liquid membrane	A strip solution with strong complexing agent is separated from the test solution by a macro-porous hydrophobic membrane	Doubly charged cations	Integrative field sampling, pre-concentration of trace elements, mimicking biological membranes	Days	Versatile, selectivity of the sampler can be adjusted		Direct analysis, can be coupled on-line for real-time monitoring	[89]
SLMD	Stabilized liquid membrane device	LDPE lay-flat tubing containing an acidic solution with high affinity for the target elements	Divalent metal ions	Pre-concentration, *in situ* sampling, determination of labile metal ions in grab samples	Days–weeks		Early development stage	Acid extraction	[47]

3.1.2. Polar organic chemical integrative sampler. The POCIS is used to monitor hydrophilic contaminants, such as pesticides, prescription and over-the-counter drugs, steroids, hormones, antibiotics and personal-care products [26]. Such compounds are entering water and ecosystems on a global scale and some have been linked with chronic toxicities. POCIS samples from the dissolved phase and thereby enables the biologically available fraction to be estimated. This sampler permits determination of TWA concentration in water over extended periods (several weeks).

The POCIS comprises a solid receiving phase material (sorbent) sandwiched between two microporous polyethersulphone diffusion-limiting membranes. The type of sorbent used can be changed to target specifically certain compounds or chemical classes. Two configurations are commonly used:

- a 'generic' configuration contains a mixture of three solid-phase sorbents (Isolute ENV+ polystyrene divinylbenzene and Ambersorb 1500 carbon dispersed on S-X3 Biobeads); it is used to monitor most pesticides, natural and synthetic hormones, many wastewater-related chemicals, and other water-soluble organic chemicals and
- the 'pharmaceutical' configuration contains a single (Oasis HLB) solid-phase sorbent and is designed for drug residues [26].

3.1.3. Chemcatcher (organic version). This system uses a diffusion-limiting membrane and a bound, solid-phase receiving phase. Accumulation rates and selectivity are regulated by the choice of both the diffusion-limiting membrane and the solid-phase receiving material; both are supported and sealed in place by an inert plastic housing. For a range of priority pollutant classes, a number of designs are available with different combinations of receiving phase and diffusion-limiting membrane [27].

One design is used for the sampling of non-polar organic compounds with $\log K_{OW}$ values greater than 4 [27]. This uses a 47-mm C_{18} Empore disk as receiving phase and an LDPE diffusion-limiting membrane. The C_{18} Empore disk has a high affinity and capacity for non-polar organic pollutants. Another design used for the sampling more polar organic contaminants combines a 47-mm C_{18} Empore disk as the receiving phase with a polyethersulphone diffusion-limiting membrane [27]. Other devices are being developed for a range of emerging pollutants, including alkylphenols, anti-inflammatory drugs and other pharmaceuticals, polybrominated flame retardants, steroids, sulphonamides and metals (e.g., mercury, tin and their organometallic species) [28].

3.1.4. Negligible depletion-solid-phase microextraction. Solid-phase microextraction (SPME) was developed by Pawliszyn et al. [29] as a simple extraction method with several advantages over liquid–liquid extraction and solid-phase extraction. The use of organic solvents is diminished and the SPME technique is simple, precise, and it may be automated easily, and the apparatus is inexpensive. The extraction medium is a thin layer of a polymer coating on an optical silica fibre, with a typical volume of 10–150 nL. Extraction equilibrium may generally be reached in 30 min. The mass of analyte on the fibre can be measured by either gas chromatography (GC) or high-performance liquid chromatography (HPLC). While most applications of SPME aim at the highest possible extraction efficiency, negligible depletion SPME (nd-SPME) represents a specific application to measure free concentrations based on negligible analyte extraction from the sampled matrix. In addition to the advantages of SPME, existing equilibria within the sample remain undisturbed during nd-SPME. The disadvantage of nd-SPME is the small amount of analyte that is available for analysis (typically only a few percent of the total amount in the sample), and this may lead to quantification problems. A review of nd-SPME has been published by Heringa and Hermens [30].

3.1.5. Membrane-enclosed sorptive coating. This adaptation of the SPME technique to enable integrative passive sampling of hydrophobic organic pollutants has been reported. The device, referred to as the MESCO (membrane-enclosed sorptive coating), comprises a Gerstel Twister stir bar used for stir-bar sorptive extraction (SBSE) or a silicone polymer rod enclosed in a membrane made of regenerated cellulose. The receiving phases may be surrounded by air or water within the bag [31]. The miniature MESCO sampling system combines sampling with solventless pre-concentration. The sampler enables direct analysis of the accumulated contaminants by thermodesorption coupled on-line to GC, thereby avoiding time-consuming sample preparation and clean-up. Despite the small surface area and volume of the sampler, its sensitivity is comparable with other passive sampling systems, since the entire amount of analyte contained in the receiving phase is introduced into GC and subsequently detected.

3.1.6. Ceramic dosimeter. The ceramic dosimeter [32] uses a ceramic tube as the diffusion-limiting barrier to enclose a receiving phase comprising solid sorbent beads. Recently, the utility of the ceramic dosimeter as a robust groundwater-sampling device was demonstrated for benzene, toluene, ethyl benzenes, xylenes (BTEX) and naphthalenes, using Dowex Optipore L-493 as the receiving phase [33]. In up to 90 days of sampling in a contaminated aquifer, the ceramic dosimeter showed an excellent performance, as judged by comparing TWA contaminant concentrations derived from dosimeters with average aqueous concentrations determined by

frequent conventional spot-sampling methods. Based on the same principle, researchers proposed using Amberlite IRA-743 as a solid receiving phase for the measurement of PAHs [32,34].

3.1.7. Polyethylene diffusion bags. There is potential for loss of volatiles during the collection of VOCs from groundwater. Polyethylene diffusion bag (PDB) samplers help to eliminate this problem [35,36]. The sampler comprises a membrane sealed in the form of a long cylindrical bag, filled with deionised water. The bag is made of LDPE and acts as a semi-permeable membrane allowing the passage of most chlorinated VOCs. VOCs in groundwater diffuse across the membrane into the de-ionised water in the bag until equilibrium is reached. Typically, PDBs take about 2 weeks to equilibrate in an aquifer [37]. Once this equilibration has occurred, sample recovery takes place.

3.2. Passive samplers for inorganic pollutants

3.2.1. Dialysis in situ. Equilibrium dialysis is a simple, size-based separation method applicable to the study of trace-metal speciation [38]. Sampling with a dialysis cell is based on a diffusive flux of species able to pass through the cell membrane towards a small volume of water as the acceptor solution, until equilibrium is reached. Metals associated with colloids and humic acid complexes, which are larger than the pores of the membrane, are excluded [39].

3.2.2. Dialysis with receiving resins. An alternative configuration to the above is to add a receiving phase (e.g., a chelating resin) with a high affinity for the species being measured in the cell. Under these conditions, the diffusion rate is theoretically directly proportional to the metal concentration in the water being sampled [40]. If a suitable chelating resin is selected, the bioavailable metal species can be separated. In this case, diffusion across the dialysis membrane may simulate metal-transport processes across biological barriers. The use of the chelating resin, Chelex 100, showed a measurable, reproducible uptake of the soluble fraction of Cd, Pb and Zn at low ambient water concentrations [41]. Coefficients of variations were lower than for mussels, making this resin a promising acceptor phase for the measurement of dissolved metal species in sea-water. These devices have also been deployed in storm-water run-off and variations in the uptake rates of metals could be correlated to hydrological/hydrochemical parameters, such as rainfall volume and pH [42].

3.2.3. Liquid membrane devices. Supported liquid membranes (SLMs) pre-concentrate trace elements from water and have been developed to mimic uptake across biological membranes. This system comprises an organic solvent with a complexing agent that is selective for the target element and is immobilised on a thin macroporous hydrophobic membrane (either as a flat sheet or as a hollow fibre with a small lumen) [43,44]. One side of the membrane is exposed to the aqueous environment, while the other is in contact with a strip solution containing a complexing agent with a higher affinity towards the metals being separated than the one immobilised in the membrane. A proton, an anion or a metal-ion counter gradient drives the transport across the device. The device can be tailored to separate specific metal species by a careful selection of complexing agents or by altering the lipophilicity of the diffusion membrane [45,46]. SLM devices have been used to measure Cd, Co, Cu, Ni, Pb and Zn in natural waters. Effects of turbulence, pH and concentration variations on the performance of SLM devices have been reported [47].

The permeation liquid membrane (PLM) device is the result of further development of the SLM. This technique is based on carrier-mediated transport of metals across a hydrophobic membrane. The microporous support is impregnated with a hydrophobic organic solvent and placed between the sample and a receiving solution [48]. The transport of Cu and Pb complexes through a PLM with a neutral macrocyclic carrier has been described [49].

3.2.4. Diffusive gradient in thin films. The diffusive gradient in thin-films (DGT) device is a development of a similar sampler – the diffusion equilibrium in thin-films (DET) device – initially suggested by Davison and co-workers in 1991 [50]. The first reported use of the improved DGT device was in 1994 for measuring Zn in sea-water. The DGT device comprises a gel-layer incorporating a binding agent (which acts as a solute sink) and a hydrated acrylamide diffusion gel separating it from the water column. This creates a diffusion layer of well-defined thickness. The initial design of the DGT utilised an ion-exchange resin as the receiving phase. Later, Zhang and co-workers [51] demonstrated the applicability of the technique to determination of trace metals (Cd, Cu, Fe and Mn) in sea-water. With a chelating resin embedded in the gel layer, metals could be quantified as low as 4 pmol/L after deployment for 1 h.

The subsequent refinement of the design and the extended range of inorganic pollutants that may be sampled indicate the versatility and the widespread use of the DGT device. In principle, it is possible to sample any labile species for which a suitable binding agent can be embedded into the receiving phase gel.

3.2.5. Passive integrative mercury sampler. Attempts have been made to use the passive integrative mercury sampler (PIMS), originally designed for air sampling, to sample neutral Hg species in water [52]. The device comprises lay-flat LDPE tubing containing a reagent mixture of nitric acid and gold stock solution.

Experiments were performed in simulated freshwater and sea-water environments. The uptake rates remained linear for 2 weeks and preliminary results indicate that sampling of neutral Hg species from water is feasible. Sampling in freshwater was more effective than in sea-water, likely to be because a larger fraction of the total Hg in sea-water was present as charged chloro-anion complexes that could not readily permeate through the membrane.

3.2.6. Chemcatcher (inorganic version). An alternative configuration of the Chemcatcher (see Section 3.1.3) has been developed for the separation of metals. The device comprises a commercially available 47 mm diameter chelating extraction disk as receiving phase and a cellulose acetate diffusion-limiting membrane [53]. The sampler has been used to monitor Cd, Cu, Ni, Pb and Zn, in various aquatic environments, such as a storm-water pond, where the uptake of metals was compared with flow-weighted bottle samples. Results indicated a good correlation with the electro-available Cu fraction but were somewhat less clear for Zn [53].

The diffusion-limiting membrane can be treated with a low surface-energy coating (e.g., polyfluorinated sulphonic acid polymer (Nafion)) to reduce biofouling on the surface of the membrane. The diffusion characteristics of the membrane, the influences of water turbulence and the radius of metal ions monitored have been investigated [54].

4. Applications of samplers

The first publications on the use of passive samplers to monitor aquatic contaminants were in 1980s (Fig. 1) and these devices have since received widespread recognition as effective tools in environmental research. Passive sampling technology is widely applicable in monitoring studies and the results obtained can be interpreted at different levels of complexity. Passive samplers have been employed in field studies aimed at:

(a) screening for the presence and absence of pollutants;
(b) investigating temporal trends in levels of waterborne contaminants;
(c) monitoring spatial contaminant distribution and tracing point and diffusive pollution sources;
(d) speciation of contaminants;
(e) assessing pollutant fate and distribution between environmental compartments;
(f) measuring TWA concentrations of waterborne pollutants;
(g) comparing contaminant patterns in biota and passive samplers – biomimetic sampling to estimate organism exposure; and,
(h) assessing toxicity of bioavailable pollutants in extracts from the receiving phase of passive samplers.

Tables 3 and 4 illustrate the different field applications. These tables are not intended to be comprehensive, but rather to give the reader an overview of the variety of applications. A detailed review of the organic contaminant classes and aqueous matrices that can be sampled by passive samplers was recently published by Stuer-Lauridsen [55].

4.1. Use in chemical monitoring

There are several advantages in using passive samplers for monitoring pollutants in water including:

(a) non-mechanical or passive operation;
(b) ability to sample large volumes of water and
(c) reduced effort required for deployment and sample processing compared to other commonly used methods.

Currently available passive sampling devices are applicable to monitoring chemicals with a broad range of physicochemical properties (Fig. 3) and the detection limits obtained or the lowest measured concentrations (Fig. 4) suggest that passive samplers may find application in monitoring programmes.

Stuer-Lauridsen [55] indicated that passive sampling devices can be used to monitor more than 75% of the organic micropollutants listed in water-quality criteria of the EU and US, the EU Water Framework Directive and the recommendations of The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR).

4.2. Contaminant speciation

Speciation of environmental contaminants includes not only physicochemical speciation of the forms in which analytes are present in the sampled matrix (e.g., freely dissolved, colloidal and particle-bound forms), but also chemical speciation (e.g., the valency state of metals in the sampled water). Trace metals are present in water in various forms (hydrated ions, and inorganic and organic complexes) together with species associated with heterogeneous colloidal dispersions. The particulate phase also contains elements in a range of chemical associations, from weak adsorption to binding in the mineral matrix. These species coexist, although they may not necessarily be in thermodynamic equilibrium.

The difficulty in differentiating the various forms arises from the low levels present in natural waters. The fractionation of species is recognised as an essential step in assessing bioavailability and toxicity in water. A problem is that solution equilibria may change after sample collection through adsorption or desorption of analytes to particulate and colloidal surfaces. A representative

Table 3. Examples of field applications of passive sampling devices for monitoring organic contaminants

Application	Sampler	Environment	Analytes	Short description	Ref.
Screening of contaminant for presence or absence	*n*-Hexane-filled dialysis membranes	Lake water	Organochlorine compounds	Detection of contaminants in passive samplers and mussels	[90]
	POCIS	Wastewater effluents	Polar wastewater-related contaminants and pharmaceuticals	Screening of contaminants	[19]
	SPMD	River	Hydrophobic organic contaminants	Screening of contaminants	[91,92]
Speciation of contaminants	SPMD	Seawater	PAHs	Distribution of particulate, dissolved, and colloidal PAHs in the water column	[57]
	nd-SPME	River water	PCBs, chlorobenzenes	Determination of freely dissolved contaminant fraction in presence of humic acids	[58]
	SPMD	River	PAHs	Relationship between freely dissolved contaminant levels and the quality of dissolved organic matter	[59]
Monitoring of temporal pollution trends	SPMD	Seawater	Organochlorine compounds	Temporal trend in sea-water pollution by outflow of contaminated freshwater following a flood episode	[93]
	SPMD	Seawater	PCBs and hexachloro-benzene	Time evolution in air, sea-water, and at the sea-air boundary layer	[94]
Monitoring of spatial distribution and tracing pollution sources	SPMDs	River	PCBs	Identification and contribution of point and diffusive sources to the total contaminant flux	[95]
	SPMD	River	PCDDs, PCDFs and PCBs	Spatial distribution of contaminants in a river basin	[96]
	SPMD	River and sea-water	PAHs	Spatial distribution of contaminants	[97]
	SPMD	Surface water	UV filter compounds	A regional mass-balance study	[98]
	PISCES	Surface water and effluent wastewater	PCBs	Tracing a point source of pollution	[99]
	SPMD	Discharge from wastewater-treatment plants	Alkylphenol ethoxylates	Spatial distribution of contaminants and their degradation products in the aqueous phase and their distribution between sediment and water column	[100]
	SPMD	River	PBDEs	Assessment of spatial contaminant levels and contaminant-pattern profiles and their relation to contaminant sources	[101, 102]
	SPMD	Seawater contaminated by discharged oilfield-produced water	PAHs	Spatial levels and patterns of bioavailable contaminant fraction	[103]

Table 3 (*continued*)

Application	Sampler	Environment	Analytes	Short description	Ref.
	SPMD	Seawater	Organotin compounds	Spatial levels and patterns of contaminants sampled by passive samplers and mussels compared to those with water samples	[104]
Assessment of contaminant fate and distribution between environmental compartments	SPMD	Irrigation water canal	PAHs	Measuring the residence times (or persistence) of analytes in the dissolved phase water	[105]
	SPMD	Discharge from an industrial source to sea-water	PCBs, chlorophenols, chlorobenzenes	Comparison of contaminant levels in SPMD, mussel and sediment	[106]
	SPMD	Freshwater, wastewater-treatment plants	Triclosan	Fate of a bactericide in the aquatic environment	[107,108]
	Low-density polyethy-lene strips	Seawater	PCBs, PAHs and hexachloro-benzene	Distribution of dissolved contaminants between sediment, pore-water and overlying water column	[109]
	SPMD	River	PCBs, PAHs, PCDDs, PCDFs and substituted benzenes	Comparison of dissolved contaminant levels and patterns estimated using sediment, fish and SPMD	[110–113]
	SPMD	River	Petroleum hydrocarbons	Pre-concentration of sub-part per billion levels for studying source, transport, and bioremediation using carbon- and hydrogen-isotope analysis	[114]
Measurement of time-weighted average aqueous concentrations	SPMDs	River	PCDDs, PCDFs	Comparison of levels and congener profiles of extremely hydrophobic compounds in SPMDs and water	[115,116]
	Ceramic dosimeter	Groundwater	PAHs	Comparison of passive samplers with spot sampling	[34]
	SPMD	Groundwater	PAHs	Comparison of passive samplers with spot sampling	[70]
	POCIS	Effluent of wastewater-treatment plants	Polar pharmaceuticals	Assessment of prescription and illicit drugs in treated sewage effluents	[117]
	Chem-catcher	Harbour	Antifouling agents	Comparison of passive samplers with spot sampling	[27]
Estimate of organism exposure	SPMD	Harbour	Organochlorine pesticides	Comparison of contaminant levels and patterns in mussels and SPMDs	[118]
	SPMD	Seawater	PAHs	Assessment of contaminant accumulation in mussels, fish and SPMDs exposed to dispersed crude oil	[119]
	SPMD	Laboratory exposure in groundwater spiked with contaminant	PCBs and Organochlorine pesticides	Comparison of uptake kinetics in SPMDs and fish	[120,121]

(*continued on next page*)

Table 3 (*continued*)

Application	Sampler	Environment	Analytes	Short description	Ref.
	SPMD	Seawater	PAHs	Assessment of chemical exposure in a side-by-side deployment of SPMD and bivalves	[122,123]
	TRIMPS	River polluted by field run-off by pesticides	Endosulfan	Correlation of contaminant levels in passive samplers with population densities of macroinvertebrates	[124]
	SPMD	Wastewater-treatment plant	Synthetic musks	Comparison contaminant levels and patterns in fish, mussels and SPMDs	[125]
	SPATT	Seawater	Algal toxins	Assessment of shellfish contamination by toxins using samplers and mussels deployed side by side	[82]
Biomimetic extraction for toxicity assessment of aqueous contaminants	Equilibrium sampling using Empore disk (sampling is not performed *in situ*)	Effluents and surface water	A complex mixture of hydrophobic chemicals	Estimate of total body residues in biota after exposure to complex chemical mixtures	[126,127]
	SPME	A methodical study	A complex mixture of hydrophobic chemicals	Estimate of total body residues in biota after exposure to complex chemical mixtures	[65]
	SPMD	Effluents of wastewater-treatment plant	Organochlorine pesticides, PCBs, PAHs	Instrumental analysis and bioindicator tests to determine toxic potential of bioavailable contaminants	[128]
	SPMD	River	A complex mixture of hydrophobic chemicals	Bioassay-directed fractionation to identify bioavailable and toxic chemicals	[129]
	SPMD	Urban stream	PAHs	Assessment of toxic potency of compounds collected by SPMDs using an *in vitro* bioassay	[130]

value is particularly difficult to identify through conventional sampling procedures in environments where concentrations fluctuate [56].

4.2.1. Organic contaminants. Passive samplers can be applied to characterise the distribution of organic contaminants between particulate, dissolved and colloidal phases in the water column [57–59]. The selectivity of devices may be adjusted to sample a desired fraction of an analyte present by choosing membrane materials with desired properties (e.g., pore size and charge on the surface).

Most passive samplers collect only the truly dissolved fraction of chemicals, since: (a) the truly dissolved molecules become separated from colloids and particles during their diffusion across the membrane that separates water from the receiving phase [21]; and, (b) only dissolved molecules are sorbed by the receiving phase [30].

4.2.2. Inorganic contaminants. Passive samplers have been used to gain understanding of the species of metals in the aquatic environment. Speciation of metals with the DGT device relies on two effects: the relative difference in diffusion coefficients; and, the relative difference in affinity to the binding agent between the species to be characterized. It is possible to differentiate between inorganic labile species and organic labile species by employing a systematic variation of diffusion gel pore sizes, resulting in a size-discriminating uptake in a similar fashion to voltammetry. However, diffusion coefficients of the model species have to be determined individually to make accurate measurements of the concentration of the labile species [60].

Table 4. Examples of field applications of passive sampling devices for monitoring inorganic contaminants

Application	Sampler	Environment	Analytes	Short description	Ref.
In situ metal speciation	SLM	Natural waters	Cd, Cu and Pb	The transport mechanisms through supported liquid membrane devices for metal-ion separation and pre-concentration were studied and optimised	[45,46,131]
	SLMD	Natural waters	Cd, Co, Cu, Ni, Pb, Zn	Effects of environmental conditions on the sampling of metals were investigated	[47]
	Chem-catcher	Natural waters	Cd, Cu, Ni, Pb, Zn	Integrative metal sampling was compared with spot sampling and attempts made to reduce biofouling	[53,54]
	DGT and DET	Natural waters	Cr	Simultaneous application of DGT and DET to determine Cr(III) and Cr(III)/Cr(VI) fractions in resin layer and diffusive equilibrium layer, respectively	[132]
	DGT	Lake water	Cu, Fe, Mn and Zn	Study of DGT performance in five different lakes (pH 4.7–7.5) and comparison between dialysis and predictions of a speciation model	[133]
	DGT	Natural freshwater	Cu and Zn	Comparison of DGT, competitive ligand exchange and voltammetric measurements, as well as examining the agreement of the results with predictions made by several speciation models	[134]
	DGT	Synthetic freshwater	Cd	Examination of DGT lability of Cd in solutions containing various synthetic (nitrilo-triacetic acid (NTA) and diglycolic acid) and natural (extracted fulvic acid) ligands. Diffusion gel of reduced pore size used to estimate portion of Cd complexed by fulvic acid	[135]
	DGT	Natural water	Ni and Zn	*In situ* determination of Zn and Ni speciation between humic and fulvic acid complexes through the use of diffusive gel layers with different pore sizes. Comparison with ASV results and predictions of speciation model	[136]
Mimics bioavailability	DGT	Ion-poor water	Cu	Comparison of Cu binding to trout gills and results for ion-selective electrode and DGT measurements. Examination of the influence of NOM on Cu bioavailability	[137]
	DGT	Freshwater	Cu	Investigation of the performance of DGT in the evaluation of toxic fraction of Cu to *Daphnia magna*, using synthetic ligands (EDTA, NTA, glycine and humic acids)	[138]

(*continued on next page*)

Table 4 (*continued*)

Application	Sampler	Environment	Analytes	Short description	Ref.
	DGT	Seawater	Cd, Cu, Pb and Zn	Parallel use of DGT devices and transplanted mussels to assess metal levels in marine environment	[139]
	DGT	Freshwater	Al	Comparison of the relevance of DGT performance to the observed bioavailability of Al with trout (*Salmo trutta* L.) compared with a pyrocatechol violet fractionation procedure	[140]
	PLM	Natural waters	Cu, Pb	Transport of metal complexes through the permeation liquid membrane depends on the lipophilicity of the complexes	[88,141]
Determination of radionuclides	DGT	Freshwater	^{134}Cs	Use of ammonium molybdophosphate binding agent to collect and determine ^{134}Cs in laboratory tests and applied to a natural freshwater lake	[142]
Determination of metal remobilization	DGT	Freshwater	Al, Ba, Co, Cu, Fe, Mn and Ni	A novel sediment trap device was used together with a DGT device to determine the metal remobilization from settling particles in a well-mixed lake	[143]

4.3. Quantification of concentrations in water

Passive sampling methods can be used to calculate the concentrations of compounds in the aqueous phase, using the principles described in Section 2. Fig. 5 illustrates the way in which integrative passive samplers can provide representative information on TWA contaminant concentrations over a long period of time with a sampling frequency lower than in spot sampling. However, it is important to recognise that, in most cases, the aqueous concentration estimated using passive samplers reflects only the truly dissolved contaminant fraction and is not necessarily equal to the concentration measured in spot samples, particularly in very hydrophobic compounds in the presence of elevated levels of dissolved organic matter. Nevertheless, the comparison is possible, if all species and fractions of contaminants present in the sampled matrix are characterised (see Section 1).

In many aquatic systems, contaminant concentrations are not constant, but fluctuate or occur in the form of unpredictable pulses. Concentrations reflected by integrative passive samplers are TWAs over the exposure period, but more research is needed to quantitate the uptake in passive samplers in scenarios involving pulsed and discontinuous exposure. Such research will provide sufficient evidence of realistic concentration estimates using passive samplers and convince the regulators of the application of passive samplers in monitoring programmes.

4.4. Estimate of organism exposure

Sijm et al. [61] reviewed biomimetic passive sampling methods to study the bioavailability of chemicals in soil or sediment. Biomimetic equilibrium sampling approaches using SPME [29] and Empore disks can mimic partitioning of contaminants between the pore water and the organism. Both approaches assume that the freely dissolved contaminant concentrations will represent bioavailability. However, for substances that may be biotransformed in the organism, the methods will overestimate the concentration in the organism. For organisms that have several routes of uptake (in addition to via the water phase), the biomimetic method will underestimate the concentration in the organisms.

Biomimetic sampling devices have been applied to sense dissolved sediment pore-water concentrations

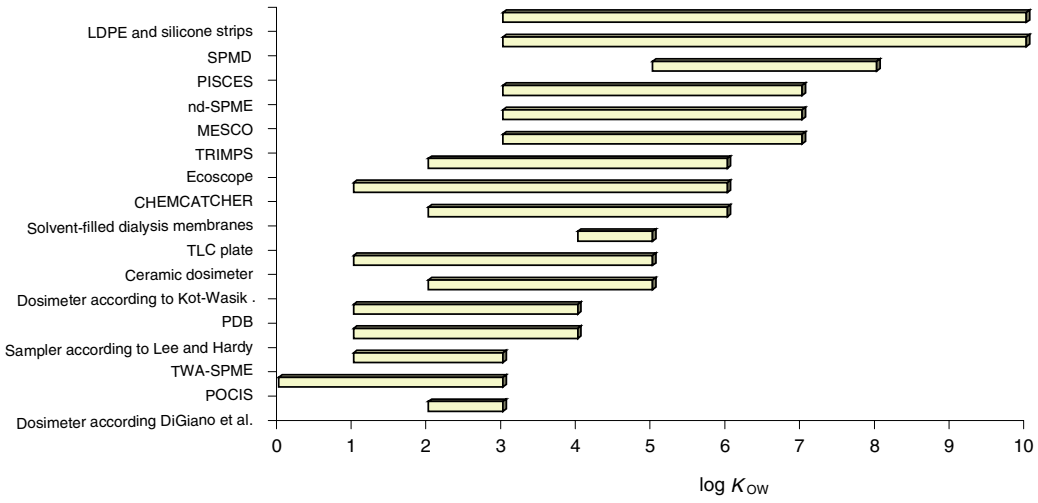

Figure 3. Typical hydrophobicity range of organic compounds sampled by selected passive sampling devices (characterised by the value of octanol/water partition coefficient, log K_{OW}).

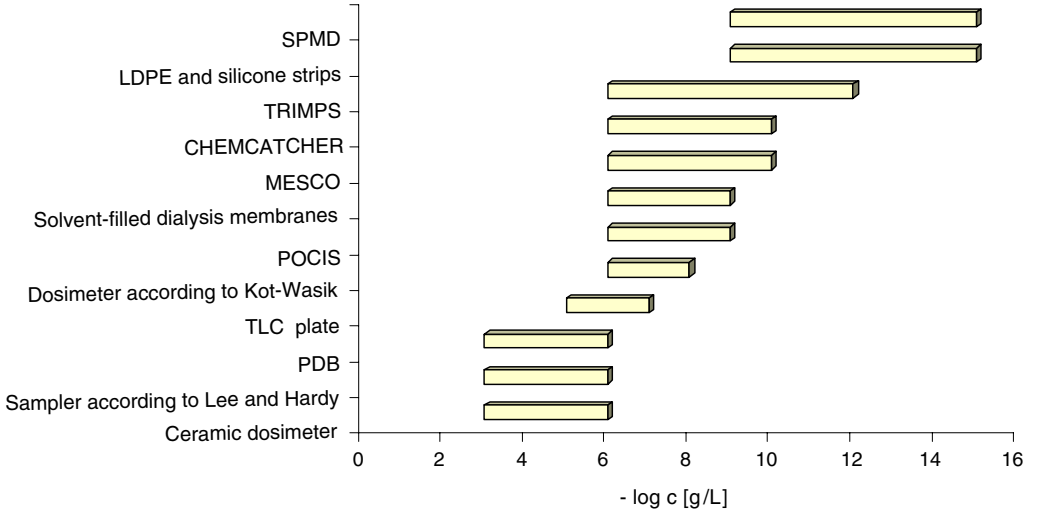

Figure 4. Typical detectable concentrations of organic compounds by selected passive sampling devices.

of contaminants [62,63] and to estimate the bioaccumulation potential in effluents and surface waters [64,65].

4.5. Bioassays

The pre-concentrated extracts obtained from the elution of receiving phases of passive samplers (particularly those used to measure organic pollutants) can subsequently be combined with a variety of bioassay procedures to assess both the level and the biological effects of water contaminants [66]. In some *in vitro* bioassays used to assess the health of an ecosystem, problems can occur due to the difficulty of obtaining suitable water samples for testing. For example, most hydrophobic organic contaminants are present in aquatic environment only at trace levels (i.e., <1 μg/L). The extraction of several litres of water would be required to yield sufficient amounts of analyte for subsequent bioassay.

The use of ''bio-mimetically'' separated extracts from passive samplers can overcome this problem [67].

It has been shown that the baseline toxicity of chemicals can be predicted (based on total body residue estimates) from the concentration of contaminants separated by passive samplers [68].

5. Quality control

The level of quality control (QC) applied to passive sampling varies with project goals and analytical procedures

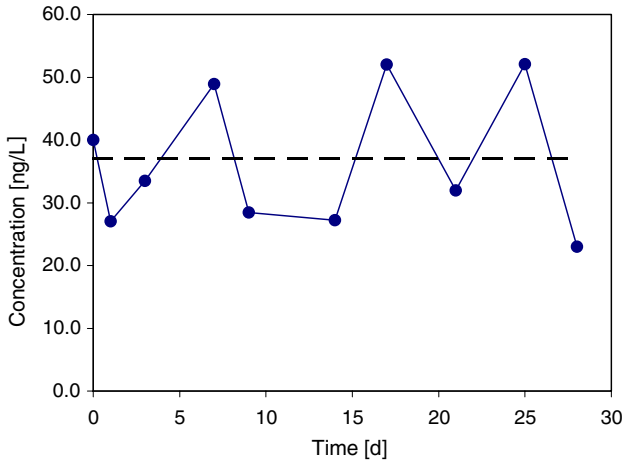

Figure 5. Comparison of a 28-day TWA concentration of simazine obtained using passive sampling (dashed line; the Chemcatcher integrative sampler variant for polar organic chemicals) with the concentrations determined in filtered spot samples (circles) from the Meuse River, The Netherlands, in Spring 2004 [144].

involved. The application of appropriate QC procedures and parameters is a mandatory consideration in both sampler deployment and subsequent analysis. QC samples should address issues of purity of materials used to construct a device, and potential contamination during transport, deployment, retrieval and subsequent storage. QC protocols are also required for analyte recovery and further processing (enrichment and fractionation operations). Control charts are recommended for monitoring analyte recoveries throughout a project. The QC samples relevant to passive sampler studies include fabrication blanks, process blanks, reagent blanks, field blanks and sampler spikes.

DeVita and Crunkilton [69] examined the QC issues associated with using SPMDs for monitoring PAHs in water. Their results showed that QC measures applied to SPMDs met or surpassed conventional guidelines (EPA method 610 for PAHs in water) for precision and accuracy.

However, assessing the accuracy and the trueness of determinations made by passive samplers may prove difficult, as the results may not be directly comparable with total concentrations found in spot samples or by other sampling techniques. This is because only very few methods, other than passive samplers, can truly measure dissolved contaminant fractions.

When environmental conditions at an exposure site differ from laboratory calibration conditions or calibration data are not available, samplers spiked with PRCs serve as a special type of QC sample. These provide information about *in situ* uptake kinetics [16,17].

QC samples involved in using passive sampling devices are shown in Fig. 6.

Stuer-Lauridsen [55] discussed the quality assurance (QA) that would be required for passive samplers to be accepted in water-quality-monitoring programmes.

6. Future trends

There are several major trends in the future development of passive sampling technology.

The first is towards miniaturisation of devices. Small devices offer the advantages of inexpensive transportation to and from the sampling site, the requirement for small deployment devices and a low consumption of solvents and reagents during their subsequent processing. Moreover, miniaturised devices allow application in situations with limited space and volume of water (e.g., in groundwater boreholes [70]). Miniaturisation goes hand in hand with the trend to develop solventless sample-preparation techniques. Passive samplers based on *in situ* analyte preconcentration using SPME or similar techniques allow sample processing (following exposure) using thermal desorption GC [31] or solvent microextraction followed by HPLC [71]. However, the practical application of SPME-based techniques in *in situ* passive sampling of aqueous trace contaminants will require their robustness and sensitivity to be further enhanced.

The second trend is the development of passive sampling technology to monitor a wider range of chemicals. Recently, attention has been focused on compounds with medium-to-high polarity (e.g., polar pesticides and drugs [26]).

Precise calibration of passive sampling devices for monitoring trace metals is essential for quantifying the various metal species and complexes found in water.

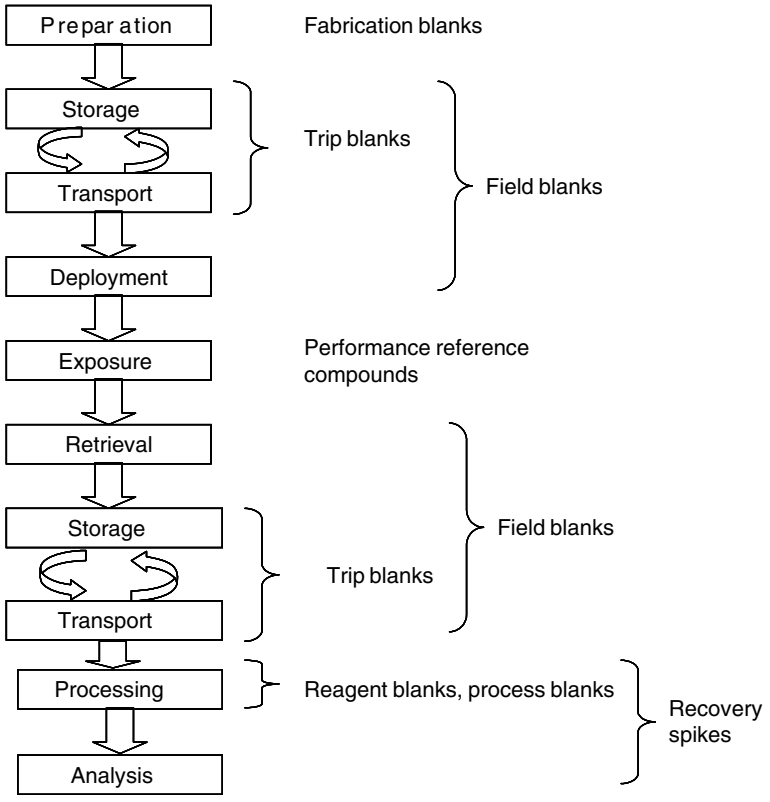

Figure 6. Quality control samples involved in passive sampling.

This requires knowledge of the uptake kinetics of different metal moieties. Configuration of specific devices for monitoring well-defined fractions of metals will increase their potential as regulatory tools.

A further challenge is to improve robustness by reducing or controlling the impacts of environmental conditions and biofouling on the sampler performance. Internal and external PRCs are being tested for improving the accuracy of TWA concentrations of contaminants.

Another trend is the coupling of chemical and biological analysis of samples collected using passive samplers, with detection and identification of toxicologically relevant compounds. The marriage of passive samplers and bio-marker and bio-indicator tests offers many avenues of investigation to provide information concerning the relative toxicological significance of waterborne contaminants.

Finally, the development of efficient QA, QC and method-validation schemes for passive sampling techniques is essential to gain broader acceptance for the technology in regulatory programmes.

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