

ENVIRONMENTAL OCCURRENCE AND CONCERNS OF ANTIFOULING BIOCIDES

Passive sampling of antifouling compounds in compliance with the Water Framework Directive

The utilization of passive sampling allows the quantification of extremely low pollution levels and gives information concerning time-weighted average concentrations of the pollutants. These characteristics are fundamental for the employment of these systems as complementary methods in the design of monitoring programmes, in compliance with WFD

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■ Paolo Massaniso, Caterina Marcoaldi, Elisa Nardi

Introduction

Passive sampling, widely used to monitor air pollutants, has been gaining acceptance for monitoring organic contaminants in water [1-7]. More than 50% of the total number of publications over the last decade describes the use of passive samplers to monitor water environmental quality condition [8]. Contrary to grab sampling, passive sampling is less sensitive to extreme fast variations of the organic pollutant concentration in natural waters, and is suited to determining time-weighted average concentrations of pollutants.

A potential risk for the marine environment comes from the gradual release of biocides by antifouling paints, used to protect the boat hulls from the undesirable accumulation of micro-organisms, plants, and animals (marine biological fouling) and, consequently, to reduce the negative effects of fouling (slower speed, increased fuel consumption and maintenance costs, etc...) [9]. European legislation has established the Environmental Quality Standards (EQS) for a list of substances, including antifouling biocides: tributyltin (TBT) and diuron (Water Framework Directive WFD; Directive 2000/60/EC, annex X list of priority substances). These are subject to bioaccumulation and bioma-

gnification processes and therefore create a potential risk to human health and ecosystems. Limited data and information are available on the environmental occurrence, fate, toxicity, and persistence of these biocides; hence, any system able to improve the information concerning the environmental presence of these compounds is of great interest [5,10]. In the present work the utilization of passive sampling for the evaluation of antifouling agents in the seawater and the possible utilization of this new system of sampling in compliance with the WFD will be examined.

Passive sampling: principle of operation

Passive sampling is based on free flow (according to the Fick's first law of diffusion) of analyte molecules from the sampled medium to a collecting medium. The diffusion driving forces and separation mechanisms

■ Paolo Massaniso, Caterina Marcoaldi, Elisa Nardi
ENEA, Technical Unit for Environmental Characterization,
Prevention, and Remediation - Laboratory of environmental
biogeochemistry

depend on the different chemical potentials of trapped and non-trapped (remaining in the sample) analytes. Therefore, passive samplers are able to measure only the freely dissolved (bio-available) amount of these compounds.

The sort of analytical data obtained as a consequence of the utilization of passive sampling system depends, to a great extent, on the accumulation regimes in which passive samplers operate during field exposure: two main accumulation regimes (linear and equilibrium, Figure 1) can be distinguished in the operation of a sampler during field deployment, and the exchange kinetics between a passive device and the water phase can be described by a first-order, one-compartment mathematical model [11]:

$$C_s(t) = C_w \frac{k_1}{k_2} (1 - e^{-k_2 t}) \quad (\text{Eq. 1}),$$

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 water phase, and k_1 and k_2 are the uptake and offload rate constants, respectively.

The passive samplers can operate using these two different regimes [8]:

- 1) In the linear uptake, passive samplers and/or non-equilibrium passive samplers, the rate of mass transfer to the receiving phase is linearly proportional to the difference in the chemical potential of the contaminant in the receiving phase for the compounds to be analysed (kinetic and time-integrative uptake phase). Based on the application of this type of passive sampler, average contaminant concentrations present in the monitored part of the environment over the entire sampling period can be obtained.
- 2) In equilibrium passive sampling, the regime is described by a partition coefficient between the receiving phase and the sample matrix. When equilibrium passive sampling is used for sample collection the sampler should be deployed long enough to ensure that the thermodynamic equilibrium is reached between the environmental media and the receiving phase.

The most useful utilization of the passive sampler in monitoring is the linear uptake design [12]. Indeed, the main advantage of using an integrative sampler is that

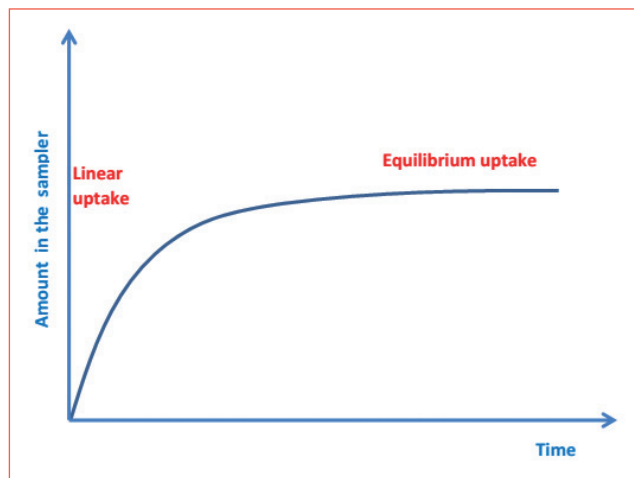


FIGURE 1 Mass uptake in passive sampler: two main accumulation regimes can be considered

episodic events (surface runoff, spills, and other unpredictable sources of contamination) can be sampled without the cost of trained staff and challenges of trying to catch the events; however, because of the sampling nature of the devices, it is impossible to determine when the event occurred during the deployment period, nor to know the maximum concentration of a chemical related to the event. Integrative samplers provide data of C_w as a time-weighted average concentration of a chemical within the whole exposure period.

Equation 1 can be rearranged to an equivalent relationship [11] $C_w = \frac{M_s}{R_s \cdot t}$ (Eq. 2), where M_s 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 the receiving phase. The sampling rate (R_s) can be stated as the number of litres of water per day that are sampled 'through' the sampler during the exposure time. The higher C_w , the higher the amount of the substance obtained from that volume of water that goes through the sampler. When R_s is known, C_w (the time-weighted average (TWA) concentration of a pollutant in the water phase) may be calculated since the exposure time is also known, and the amount of the analyte trapped by the

receiving phase can be measured after extraction from the receiving phase.

The measurement of R_s is defined as the calibration of the passive sampling device and it is performed in laboratory or in field with the utilization of performance reference compounds [13]. To predict accurately TWA water concentrations of contaminants from the levels accumulated in passive samplers, extensive calibration studies, aimed at characterizing the uptake of chemicals under various exposure conditions, are necessary. Uptake kinetics of chemicals depends not only on the physicochemical properties of the compound to be measured, but also on the sampler design and environmental variables, such as temperature, water turbulence and biofouling presence on samplers. The R_s typically falls in the range of 0.5 to 5 l/day, with the most hydrophobic compounds having the higher value [7].

The devices used for passive sampling are usually based on diffusion through a well-defined diffusion barrier or permeation through a membrane. Several designs of passive samplers have been proposed, where the main characteristic is the collecting medium utilized in the system. The most commonly used sampler structures can be separated into two categories [7]:

- “solvent”-filled (semipermeable membrane devices (SPMDs));
- “sorbent”-filled (POCIS and Chemcatcher)

In the SPMD, a tubular low-density polyethylene (LDPE) lay-flat membrane is filled with a high-molecular-weight lipid-usually high purity synthetic triolein 1,2,3-

tri-[cis-9-octacenoil] glycerol (>95%) and usually they are used to monitor lipophilic compounds with octanol/water partition coefficients $\log K_{OW} > 3$ (hydrophobic pollutants, PAH, PCBs, etc.) [14].

The POCIS comprises a solid receiving phase material (non-polar sorbent), sandwiched between two microporous polyethersulphone diffusion-limiting membranes. They are used to sample hydrophilic compounds with octanol/water partition coefficients $\log K_{OW} < 3$ (polar organic pollutants, drug residues, pesticides, etc.). In the chemcatcher passive sampler the receiving phase is typically a C18 Empore disk and it is suitable for monitoring organic compounds with $\log K_{OW}$ between 2 and 4 [15, 16].

Up to now, few data have been published on antifouling compounds occurrence in the seawater sampled with passive devices, and the results are reported in Table 1. The significant point to be highlighted is the extremely low concentration (sub ng/L), that is possible to quantify with all the passive sampling devices employed in the selected studies.

Passive sampling with respect to WFD

For priority pollutants, annual average and maximum acceptable concentration environmental quality standards (AA-EQS and MAC-EQS, respectively) are to be used in compliance with the WFD (Directive on Environmental Quality Standards - Directive 2008/105/EC, EQSD).

In some cases the EQS are extremely low, under ng/L

Analyte	Range of concentrations	Notes
TBT	32 - 220 ng Sn/mL SPMD	SPMD, Oslofjord Harbour (Norway) [17]
TBT	0.4 - 10 ng/L	SPMD, Seawater Oslofjord (Norway). Reference in [18]
TBT	<1 ng Sn/mL SPMD	SPMD, Pacific Ocean. [19]
TBT	8.3 ng/L	Chemcatcher, Alicante Harbour (Spain) [16]
Diuron	0.06 - 2.5 ng/L	SPMD, Great Barrier Reef (Australia). Reference in [18]
Diuron	50 - 1400 ng/L	Chemcatcher, Portsmouth Harbour (Portsmouth, UK) [20]
Diuron	0.4 - 2.5 ng/L	POCIS, Mediterranean Sea (Spain) [21]
Irgarol	0.02 - 0.7 ng/L	POCIS, Mediterranean Sea (Spain) [21]
Irgarol	10 - 230 ng/L	Chemcatcher, Portsmouth Harbour (Portsmouth, UK) [20]
Chlorothalonil	2.7 - 48 ng/L	SPMD, Estuarine ecosystems (FL,USA). Reference in [18]

TABLE 1 Concentration of antifouling biocides worldwide using passive sampling devices



(AA-EQS for TBT 0.08 ng/L as tin) and the utilization of the conventional method of spot sampling do not permit to reach the limit of quantification (LOQ) of the most advanced methods of analysis. Passive samplers have been validated and provide high sampling rates (litre/day) for various contaminants, thus allowing to quantify extremely low pollution levels in water using the same methods of analysis [22]. In addition, since one of the primary objectives of WFD is the assessment of the average concentrations of pollutants in water bodies, the determination of time-integrated concentrations using passive samplers seems to be a promising approach [23].

The Commission Directive 2009/90/EC on technical specifications for chemical analysis and monitoring of water status (pursuant to Directive 2000/60/EC of the European Parliament and of the Council) sets out the technical specifications for chemical analysis and monitoring of water. The objective of this Directive is to establish common quality rules for chemical analysis and monitoring of water, sediment and biota carried out by Member States.

In this technical specifications, minimum performance criteria have been defined for the LOQ and the measurement uncertainty “U” (expanded uncertainty of measurement). They are, wherever possible, linked to the EQS.

If no suitable analytical method is available that meets these minimum performance criteria for a particular priority substance, e.g., TBT, monitoring has to be carried out using the best available techniques not entailing excessive costs. Passive sampling may be the best available technique for evidencing very low concentrations not detectable in water samples collected in the traditional way (using spot sample). Furthermore, passive sampling can also be used in parallel with spot sampling in order to confirm or refute the results for water samples taken in the traditional way, particularly in situations in which contaminant concentrations fluctuate considerably over time [24, 25].

Recently, a monitoring campaign on TBT has been carried out by ENEA in the Gulf of La Spezia with the utilization of grab sample and SPMD devices. The results (Table 2) show that the data obtained are comparable in the Port and confirm that only SPMD allows to measu-

	SPMD	Grab samples
Port of La Spezia	1.6 ± 0.1	1.3 ± 0.4
Cinque Terre Marine Protected Area	0.2 ± 0.05	n.d

TABLE 2 TBT (as Sn, ng/L) concentration in the Gulf of La Spezia using SPMD devices and the classical sampling method (n.d, non-detected) [26]

re TBT levels in the protected area (< 1 ng/L), reaching quantification limits similar to the requested EQS for this contaminant [26].

Conclusion

The main benefit of the passive approach over grab sampling and/or extraction is that only one device is necessary at a given sampling location for the duration of sampling. In grab sampling, where the sample represents the conditions at the sampling site at a given moment in time, the number of samples collected over the duration of the sampling survey can be larger if the same time-averaged information is obtained. Passive sampling requires only a few analyses over the monitoring period, hence analytical costs can be substantially reduced. Passive sampling devices might be useful for identifying pollution sources, in particular, if extremely low levels have to be detected or when the pollution source is not constant. Moreover, the use of passive sampling for measuring the time-weighted average concentration is in compliance with the EQS (annual average in particular) defined by the WFD.

The debate on the issue of passive sampling for the WFD has been developed in the guidance document on surface water chemical monitoring [24], where passive sampling is indicated as one of the complementary methods that can be used for both monitoring network design and surveillance monitoring. An ongoing issue is that the compliance checking of water quality under WFD, with respect to organic compounds, is based on total water concentrations, and that passive sampling only measures the concentration of freely dissolved (bio-available) fractions. However, total concentrations in water can be calculated using averaged measured

DOC concentrations, concentrations of suspended matter and total organic matter levels in the suspended matter with equilibrium partitioning, on the basis of the freely dissolved concentration determined with passive sampling. Finally, another interesting possible

development in the field of passive sampling is the use of these devices (the extracts), in combination with biological tests to measure toxicity and genotoxicity for a better definition of the EQS in compliance with the WFD [23].

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