Measuring laboratory performance in the analysis of passive sampling devices

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Acknowledgements

We would like to acknowledge Undine Baatz and Andreas Sven Høgfeldt for their contribution in the laboratory and in the field. Erik Bjerknes is thanked for help with the fieldwork.

Sammendrag

"Kvalitetssikring i laboratoriet ved analyse av passive prøvetakere". Passiv prøvetaking er en metode som brukes i økende grad for overvåking av upolare organiske miljøgifter slik som polysykliske aromatiske hydrokarboner (PAH), polyklorerte bifenyler (PCB), klorerte pesticider og polybromerte difenylethere (PBDE) i overflatevann. Den økende bruken og etterspørselen etter disse målingene, samt publiseringen av en ISO standard for passiv prøvetaking i overflatevann tidligere i år (ISO 5667-23) medfører behov for utvikling og anvendelse av prosedyrer for å sikre kvaliteten til laboratoriene som er involvert i ekstraksjon og analyse av passive prøvetakere. For å oppnå dette er det behov for å produsere et egnet referansemateriale i rimelige mengder for videre sammenlikning mellom laboratoriene. I denne artikkelen har vi vurdert to mulige tilnærminger for å tilsette PAH i semipermeable membranenheter (SPMDs). Potensialet for bruk av disse prosedyrene til sammenliknende laboratorieprøvinger/referansemateriale vil bli diskutert.

Summary

Passive sampling is a strategy that is increasingly being used for the monitoring of nonpolar organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides or polybrominated diphenyl ether (PBDEs) in surface waters. This increase in the use and demand for these measurements together with the publication earlier this year of an ISO

standard on passive sampling in surface waters (ISO 5667-23) require the development and application of procedures for testing the performance of laboratories involved in the extraction and analysis of these passive sampling devices. To this end, production at a reasonable scale of suitable reference materials is required for future intercomparison testing of laboratories. Here we evaluated two procedures for the spiking of PAHs into semipermeable membrane devices (SPMDs). The potential for these procedures to be used for laboratory intercomparison studies/reference materials is discussed.

Introduction

Passive sampling is increasingly being used for the monitoring of trace levels of nonpolar organic pollutants in water. The use of passive sampling devices presents many advantages over more standard bottle sampling and these include significantly lower limits of detection for compounds dissolved in water and the ability to undertake time-integrated sampling (Vrana et al. 2005). Passive sampling is based on the exposure of a device able to accumulate chemicals present in water by diffusion. This diffusion process is driven by a gradient of concentration between chemicals dissolved in water and that in the sampler initially free of the chemical of interest. Passive samplers available for the monitoring of non-ionic hydrophobic compounds include semipermeable membrane devices (SPMDs), low density polyethylene membranes (LDPE) or silicone strips (Allan et al. 2010).

The application of passive sampling for regulatory monitoring such as for the measurement of priority substances under the European Union's Water Framework Directive (WFD) requires that data obtained across Europe are comparable. This signifies that quality assurance procedures must be in place throughout the process from sampler production to the data treatment and interpretation to ensure the quality of the data is acceptable. To this end, an ISO standard, ISO 5667-23 (2011) setting guidelines for passive sampling in surface waters was recently published.

Various possibilities exist to evaluate the performance of each step of the passive sampling process. Some passive sampler intercomparisons have already been undertaken (Allan et al. 2010; Miege et al. 2011). Despite these studies encompassing many types of samplers, data was shown to be relatively consistent (Allan et al. 2009a). Standard interlaboratory comparisons are conducted specifically to evaluate the performance of the overall analytical procedure consisting of sample processing, extraction and analysis in participating laboratories. To this end, production of reliable reference materials analogous to real samples that can easily be distributed to the different laboratories is needed. This is already a common practise in the quality assurance for sediment and biota samples and a requirement for accredited laboratories. For passive sampling, different strategies can be used to prepare these reference materials. For SPMDs, for example, the spike of analytes of inte-

rest can be incorporated into the triolein added to each of the samplers while for silicone strips or LDPE membrane where no triolein is added, spiking of the samplers can be done using a methanol/water solution (Booij et al. 2002). Such procedures enable the production of relatively large batches of samplers with variability likely to be well below 10 %. Alternatively, batches of samplers can be prepared by exposing them to chemicals spiked in water such as in laboratory-based calibrations experiments (Vrana et al. 2006) or to natural waters in the field. If near-to-identical samplers are deployed under very similar water turbulences, similar sampling rates are generally observed and the variability in contaminant masses accumulated can also be below 10 % (Allan et al. 2010).

The aim of the present work was to evaluate two procedures for the preparation of SPMD passive samplers to be used as reference materials for future intercomparison studies for the monitoring of polycyclic aromatic hydrocarbons (PAHs) in water. The first procedure was based on spiking of triolein lipids with a reference solution of PAHs, while the second procedure involved deploying samplers in the sea (Aker Brygge, inner Oslofjord) in order to accumulate PAHs from water under natural conditions.

Material and methods

Preparation of laboratory-spiked SPMDs

SPMDs are made of 2.5 cm wide lay-flat low density polyethylene (LDPE) tubing filled with ultrapure triolein lipids. The LDPE tubing purchased from Brentwoods Plastics (US) was cut into 55 cm long strips and cleaned by soaking in pentane then in n-hexane (both HPLC grade and from Rathburn, UK) for 24 hours. The length of the strips was adjusted to 50 cm. While, the preparation of SPMDs generally includes an additional clean-up step for the triolein, here the triolein (> 99 %, Sigma-Aldrich, Norway) was used without further clean-up. The triolein (6 ml) was spiked with 110 µl of a stock solution containing the 16 US EPA priority PAHs s (EPA method 610) prepared in cyclohexane (5000 ng ml^{-1}). The solution was thoroughly mixed and the solvent was allowed to dry off before the solution was stored at -20 °C until use. A total of 8 spiked SPMDs were prepared from heat-sealed LDPE tubing filled with 500 µl of PAH-spiked triolein. Two SPMD blanks were made by adding 500 µl of un-spiked triolein. Samplers were stored in freezer at -20 °C until extraction.

Field deployment of SPMDs

A second batch of standard-size SPMDs (92cm long and 2,5 cm wide) was purchased from Exposmeter AB (Sweden) and samplers were deployed for 28 days in harbour waters (Aker Brygge, Oslo, Norway) using stainless steel cages. Eight samplers were mounted onto spider holders and cages were kept horizontally at a depth of approximately 15 m in the water to ensure similar exposure of all samplers. Two trip control samplers were used to assess possible contamination

during deployment and retrieval procedures and storage. When not deployed, samplers were kept in the freezer at -20 °C or on ice during transportation to the field site. These samplers were spiked with performance reference compounds during their preparation. The dissipation of these compounds (deuterated PAHs) during field exposures allows the estimation of sampling rates.

SPMD extraction and analysis

Procedures for the extraction and analysis of SPMDs have previously been published elsewhere (Allan et al. 2010; Harman et al. 2008). In short, the surface of all controls and exposed samplers was cleaned with ultra pure water and wiped with a clean tissue. Samplers were dialysed twice with 100 mL with *n*-hexane or pentane for 24 hours and the extracts combined. Internal standards were added at the dialysis stage. Extracts were reduced and the solvent exchanged to dichloromethane prior to clean-up with gel permeation chromatography. Extracts were reduced under nitrogen prior to analysis. Extracts were analysed used a HP-6890N gas chromatograph (GC) equipped with a HP 5973 Mass Selective Detector (MS) (Agilent Technologies, USA). Operational details are given elsewhere (Harman et al. 2008).

Results and discussion

PAH masses in lab-spiked and field-exposed samplers

Two procedures were evaluated to obtain SPMD passive samplers spiked with a series of PAHs. The first method involved adding a series of PAHs to triolein lipids that were subsequently inserted into clean LDPE tubing. The second procedure involved exposing samplers to seawater at a harbour site (Aker Brygge, Oslo) for a period of 28 days. As shown on Figure 1, masses measured in laboratory-spiked SPMDs are generally similar for most PAHs and are close to the nominal value of ~ 63 ng $SPMD^{-1}$. In comparison, contaminant masses absorbed in field-exposed samplers vary considerably with highest masses absorbed observed for phenanthrene, fluoranthene and pyrene, Figure 1. Masses of larger molecular weight PAHs are lower and close to or below limits of detection (~ 5 ng $SPMD^{-1}$). A longer exposure may have enabled absorption of sufficient amounts of these compounds for their quantification. The pattern of masses of PAHs accumulated in field-exposed SPMDs is similar to that generally observed for exposures in water and is the result of differences in dissolved PAH concentrations in water and in sampling rates for compounds with different hydrophobicity (Huckins et al. 2006).

The variability in measured PAH masses in replicate laboratory-spiked samplers was very low, see Figure 2. On average it was less than 2 % relative standard deviation (RSD) for these laboratory-spiked samplers. The variability in masses absorbed *in situ* during the 28 day-exposure in the field was generally substantially higher than for spiked samplers (RSD = 11.4 %,). This is in agreement with previous work where the variability in PAH masses absorbed in replicate

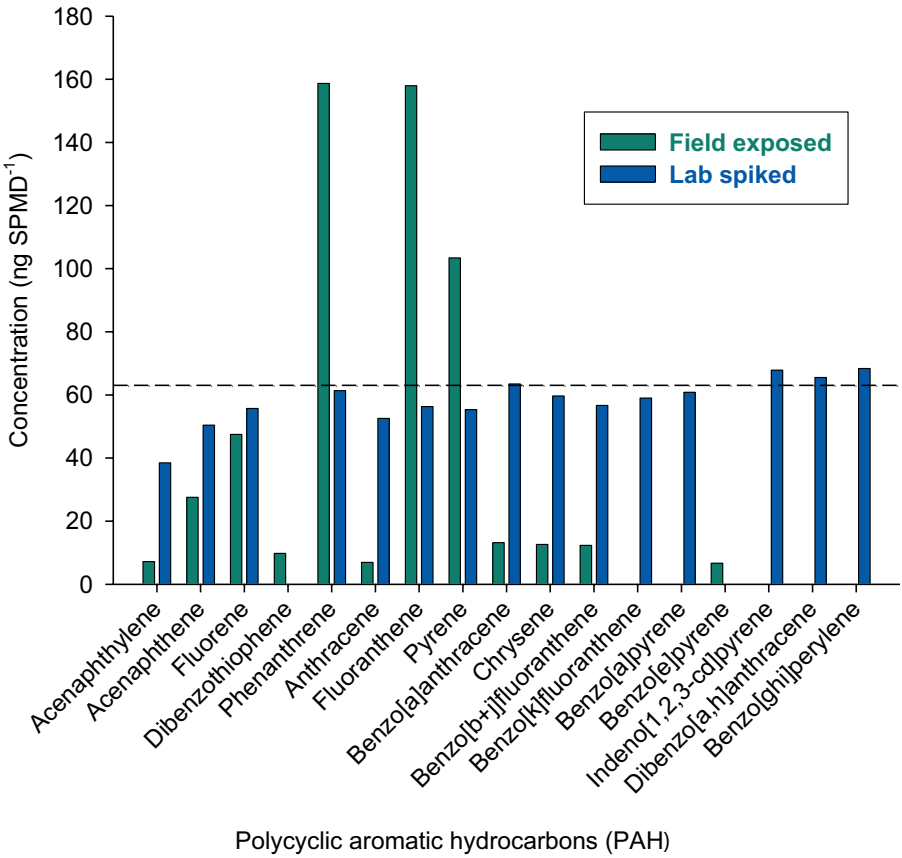

Figure 1. Mean concentrations of polycyclic aromatic hydrocarbons measured in semipermeable membrane devices (SPMDs) exposed in the harbour (Aker Brygge, Oslo, Norway) or spiked in the laboratory. The dashed line represents the nominal concentrations expected for laboratory-spiked samplers.

SPMDs and silicone strips deployed in the Drammen River for up to 51 days was well below 10 % RSD (Allan et al. 2010).

It is generally not surprising to observe a higher variability for samplers exposed in the field than for those spiked in the laboratory. While the variability obtained with the laboratory-spiking procedures relies on the reproducibility of the volume of triolein added to the different samplers, it is independent of the size of the sampler. For samplers exposed in the field however, the surface area of the sampler and sampler volume directly affect masses absorbed for compounds under integrative uptake and for those for which the concentration in the sam-

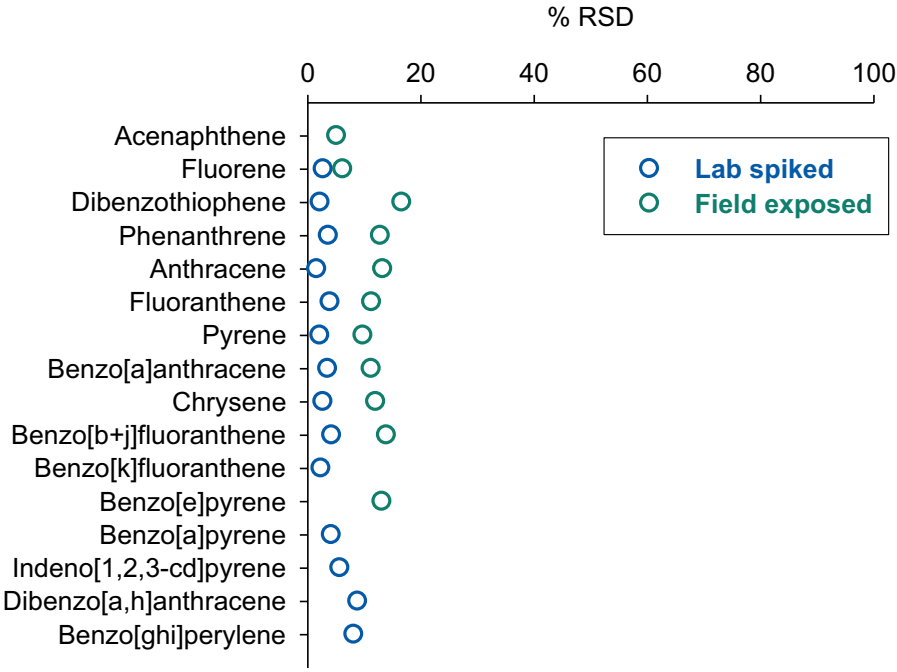

Figure 2. Variability (expressed as % relative standard deviation, RSD) of masses of PAHs spiked into SPMDs in the laboratory (n=6) and for those absorbed during exposure in the field (n=5), with samplers extracted using both n-hexane and pentane.

plers has reached equilibrium with the concentrations in water, respectively (Allan et al. 2010). While the actual length of SPMDs used here varied between 93.6 and 94.0 cm, a considerably higher variation in the width of SPMDs could be observed (2.5 and 3.2 cm wide) and this may affect the surface area of the sampling surface and the resulting contaminant masses accumulated. Differences in variability of PAH masses accumulated if samplers are exposed to freshwater (Allan et al. 2010) or seawater (this study) are expected to be small. The main difference may be the result of uptake of sulphur compounds in seawater that might require additional clean up due to interference with some organic pollutants.

Sampling rates for SPMDs exposed at Aker Brygge

Part of the variability in PAH masses accumulated in replicate samplers exposed in the field at Aker Brygge is likely to result from differences in sampling rates (equivalent volumes of water extracted by the sampler per unit of time) for the various samplers. These differences can be due to variable sizes of the samplers

but also to differences in environmental conditions during exposure. Water turbulences around the samplers as well biofouling of the surface of the membrane are two processes that have been shown to influence sampling rates to a high extent (Booij et al. 2003). It is possible to use performance reference compounds (PRCs), non-naturally occurring (and non-analytically interfering) analogues of compounds of interest that are spiked in the samplers prior to exposure to estimate in situ sampling rates. Due to the isotropic nature of the exchange of chemicals between water and the sampler, 1st-order PRC dissipation rates enable us to estimate sampling rates for analytes of interest (Booij et al. 1998).

A series of deuterated PAHs spiked in SPMDs were used as PRCs here. Amounts of PRCs remaining in the samplers following the 28 day exposure at Aker Brygge and resulting estimates of sampling rates for samplers extracted are given in Table 1. As shown in Table 1, substantial dissipation of acenaphthene-d_{10} and fluorene-d_{10} was observed (~ 20 % remaining in the samplers). Over 60 % of phenanthrene-d_{10} was left in the samplers following exposure, indicating that compounds with logK_{ow} > 4.5 remained in the linear mode of uptake throughout the exposure. No dissipation of higher molecular weight PRCs was observed. Sampling rates were calculated from PRC dissipation rates, sampler-water partition coefficients and the volume of the samplers and are given in Table 1. Mean sampling rates calculated from the three PRCs were consistent and in the range 3.2-4.6 L d^{-1}. An effort was made during this study to expose SPMDs in a similar way to ensure identical sampling rates for all replicate SPMDs. As shown in Table 1, this resulted in a low variability in PRC amount remaining in the

	LogK_{ow} [a]	Dissipation[b]	Sampling rate (L d^{-1})
Acenaphthene-d_{10}	3.92	15.8 (2.2)[c]	3.3 (0.3)
Fluorene-d_{10}	4.18	23.7 (3.3)	4.7 (0.4)
Phenanthrene-d_{10}	4.57	59.9 (3.8)	3.8 (0.5)
Chrysene-d_{12}	5.86	98.7 (5.1)	-
Benzo[*e*]pyrene-d_{10}	6.05	97.2 (2.0)	-

[a] Octanol-water partition coefficients
[b] Level of PRC remaining in samplers following 28d exposure relative to initial levels (%)
[c] Standard deviation (n=6) provided in brackets

Table 1. Levels of performance reference compound measured in field-exposed samplers relative to initial levels (%) and estimates of sampling rates calculated from PRC dissipation rates. Data are given for samplers extracted with n-hexane and pentane (n=6).

samplers following exposure and therefore similar sampling rates. This variability is influenced by the variability in the size of replicate samplers and by environmental conditions affecting each of the deployed samplers.

PAH concentrations in water at Aker Brygge

Dissolved PAH concentrations in water were calculated using PRC-based sampling rates and the model as described in (Huckins et al. 2006). PAH concentrations in water, C_w were calculated from PAH masses absorbed (m), the exposure time (t) for each single SPMD from its own PRC-based sampling rates, R_s ($C_w = m/[R_s\, t]$). Dissolved PAH concentrations ranged between values of 0.06 ng l^{-1} for benzo[*e*]pyrene to values of 1.4 ng l^{-1} for phenanthrene. These concentrations are generally higher than those measured in relatively clean riverine environments such as the Drammen River (Allan et al. 2009b).

The variability in measured PAH concentrations in water by replicate SPMDs exposed alongside is given in Figure 3 and is compared with the variability in masses accumulated in exposed samplers. Relative standard deviations varied between 1.2 and 13 % and were on average 5.5 % for PAHs above limits of detection. This is a factor of 2.7 lower than devia-

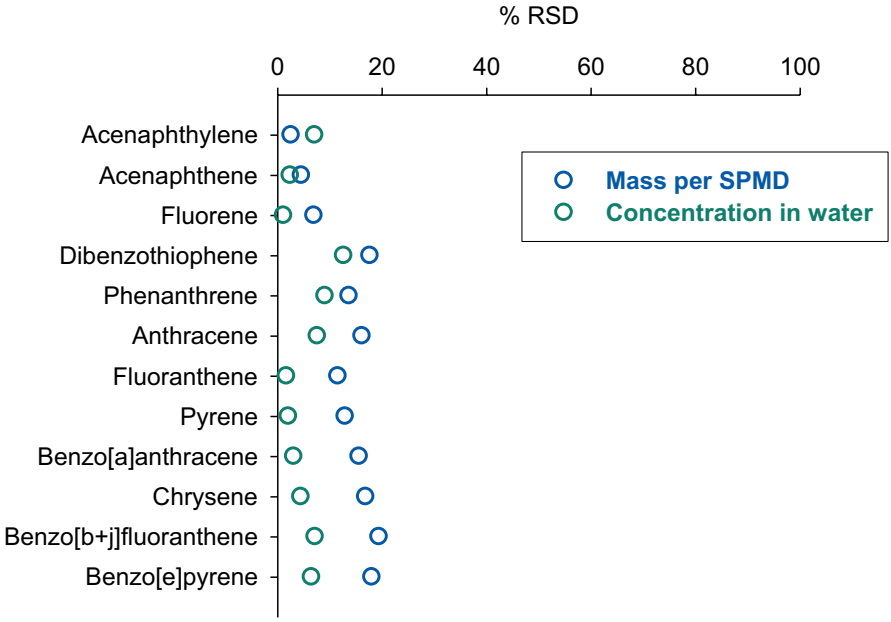

Figure 3. Variability (expressed as % relative standard deviation, RSD) of PAH masses absorbed into SPMDs during a 28 d exposure at in seawater in Aker Brygge (Oslo, Norway) and of estimates of dissolved PAH concentrations (n=5).

tions observed for PAH masses absorbed (see Figures 2 and 3). This means that replicate SPMDs with relatively higher PAH masses absorbed (for those in linear mode of uptake) also exhibited relatively higher sampling rates. In turn PRC dissipation from those with lowest masses absorbed were the lowest. Differences in sampling rates are clearly able to explain (at least partly) the variability in PAH masses absorbed. The application of the PRCs for the estimation of sampling rates is clearly able to reduce the variability observed when using replicate samplers deployed alongside.

Conclusions and implications

The application of the ISO standard 5667-23 on passive sampling in surface waters will in the future require evaluating the performance of laboratories and capability of the method itself to provide reliable data. To this end, reference materials will be needed to (i) compare the performance of laboratories in the extraction and analysis of passive samplers and (ii) monitor intra-laboratory consistency as part of quality assurance schemes. The two methods tested here are cost-effective yet fit-for-purpose. While the "spiking" alternative gives the possibility to obtain many compounds in detectable levels in the samplers with very low variability, the "exposure" alternative provide more realistic samples with more challenging analysis with regards matrix effects, interferences and low/undetectable levels for some compounds.

There are advantages to both methods and a possibility is to use one of the methods as standard reference material and the other method for intra laboratory testing. We showed here that we were able to produce laboratory-spiked with a variability not exceeding 9 % relative standard deviation (median for all PAHs of 4 % RSD). The field exposure of SPMDs alongside resulted in differences in masses absorbed for the various PAHs and with a variability generally higher than that observed for laboratory-spiked samplers. The profile of PAH masses accumulated in SPMD exposed at Aker Brygge was in line with generally observed masses (i.e. with higher masses absorbed for compounds with $\log K_{ow} \sim 5$).

The exposure of samplers in the environments results in a more complex matrix, with possible interferences, presence of sulphur compounds particularly when samplers are exposed to sea water and biofouling of sampler surfaces. This variability seen for masses accumulated was reduced by more than half by accounting for differences due to sampling rates as shown by PRC data from individual samplers. If such exposed samplers were to be used as reference material, the PRC data would provide a mean to confirm that sampling rates and masses accumulated following field exposure are in agreement with other samplers from that batch.

One has to bear in mind however that other types of samplers (some of which are in use at NIVA) do exist and reference materials for passive sampling may need to be produced for compounds that are not necessarily present in the environment in sufficiently high concentration

to obtain analyte masses high enough in exposed samplers. Single-phase samplers such as silicone rubber and low density polyethylene membranes may require the use of alternative procedures (e.g (Booij et al. 2002)) for spiking of analytes of interest. In this case, provided that analyte distribution within the sampler matrix is homogenous, a small amount of a single-phase sampler can be cut off and analysed to verify concentrations of analytes of interest prior to dispatching reference materials.

Samplers such as SPMDs have been used for the monitoring of PCBs and other organochlorines pesticides or more recently for the measurement of brominated flame retardants (e.g. PBDEs). Since these compounds are generally found at very low levels dissolved in water, masses absorbed into exposed samplers remain low and this may become problematic for the preparation of reference material. In this case spiking of the compounds in the laboratory may be desirable. Other methods based for example on passive sampler calibration set ups could be developed for spiking of samplers in the laboratory, however when the cost of production is taken into account such a method may prove too expensive.

Reliable production of reference materials and matrix spiked passive sampling devices will bring this technology a step closer to being used for regulatory purposes. From a financial perspective as well as for data comparability purposes, production of reference material may ultimately need to be restricted to only a few types of passive sampling devices.

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