Comparison of five integrative samplers in laboratory for the monitoring of indicator and dioxin-like polychlorinated biphenyls in water

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HIGHLIGHTS

- We compare uptake kinetics for five integrative samplers applied for PCB in water.
- The method to calculate TWA concentrations strongly influences results.
- SPMD, SR and LDPE strip are the most efficient to accumulate PCB.

ARTICLE INFO

ABSTRACT

This study aimed at evaluating and comparing five integrative samplers for the monitoring of indicator and dioxin-like polychlorinated biphenyls (PCBs) in water: semi-permeable membrane device (SPMD), silicone rubber, low-density polyethylene (LDPE) strip, Chemcatcher and a continuous-flow integrative sampler (CFIS). These samplers were spiked with performance reference compounds (PRCs) and then simultaneously exposed under constant agitation and temperature in a 200 L stainless steel tank for periods ranging from one day to three months. A constant PCB concentration of about 1 ng·L^{-1} was achieved by immersing a large amount of silicone rubber sheets ("dosing sheets") spiked with the target PCBs. The uptake of PCBs in the five samplers showed overall good repeatability and their accumulation was linear with time. The samplers SPMD, silicone rubber and LDPE strip were the most promising in terms of achieving low limits of quantification. Time-weighted average (TWA) concentrations of PCBs in water were estimated from uptake of PCBs using the sampling rates calculated from the release of PRCs. Except for Chemcatcher, a good agreement was found between the different samplers and TWA concentrations ranged between 0.4 and 2.8 times the nominal water concentration. Finally, the influence of calculation methods (sampler-water partition coefficients, selected PRCs, models) on final TWA concentrations was studied.

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1. Introduction

Like many other hydrophobic organic contaminants, polychlorinated biphenyls (PCBs) have toxic effects on living organisms, including human beings (Carpenter, 2006). In aquatic environments, PCBs are principally adsorbed on particulate matter due to their hydrophobicity ($\log K_{OW} > 4.5$); hence, their concentration in the dissolved phase is therefore very low, typically in the ng·L^{-1} to pg·L^{-1} range. Monitoring such low concentrations with traditional bottle (or grab) sampling is challenging and requires sophisticated analytical methods such as isotopic dilution mass spectrometry. Furthermore, grab sampling only provides a snapshot of the contaminant concentration at a particular time without taking temporal variations into account.

Since two decades, several integrative sampling devices have been developed for the monitoring of organic contaminants in aquatic environments (Greenwood et al., 2009; Söderström et al., 2009; Lohmann et al., 2012). These samplers enable the improvement of

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limits of quantification (LOQ) by accumulation and concentration of contaminants over long-term exposure. Moreover, when they are used in the integrative phase of uptake (i.e. integrative samplers), time-weighted average (TWA) concentrations over the exposure period can be calculated, leading to a better representativeness of measurements.

Several integrative samplers, at different stages of development, are now available for monitoring non-polar organic contaminants. The semi-permeable membrane device (SPMD) is one of the most comprehensively studied integrative sampler; it consists of a low-density polyethylene (LDPE) lay-flat tubing filled with a small quantity of triolein. It was designed to sequester and concentrate freely dissolved organic contaminants with $\log K_{OW}$ ranging from three to eight and has already been extensively used for the monitoring of PCBs in water (Huckins et al., 2006). Next to biphasic sampling devices like SPMD, single-phase integrative samplers, such as LDPE strip and silicone rubber (SR), are gaining interest due to simpler modeling of contaminant transport processes and easier sample processing. Numerous studies have shown the suitability of LDPE strips for the monitoring of hydrophobic organic contaminants, such as polyaromatic hydrocarbons (PAHs) or PCBs in various water bodies (Booij et al., 2003; Carls et al., 2004; Adams et al., 2007; Anderson et al., 2008). Silicone rubber was also found to be a suitable alternative to SPMD for the monitoring of hydrophobic contaminants (Rusina et al., 2007). Indeed, SR sheets have been successfully used for the monitoring of PAHs and PCBs from 2002 in The Netherlands (Smedes, 2007). Chemcatcher can house different combinations of receiving phases and membranes as appropriate for polar or non-polar contaminants monitoring (Greenwood et al., 2007). The first non-polar version of Chemcatcher, made of a C18 Empore disk and a LDPE membrane, aimed at sampling contaminants with $\log K_{OW}$ greater than three (Kingston et al., 2000). A recent optimization of the sampler, by adding a small volume of octanol between the receiving phase and the membrane, was proposed to decrease the internal sampler resistance to mass transfer of hydrophobic compounds with $\log K_{OW}$ above five (Vrana et al., 2005). Chemcatcher has already been used during field campaigns for the monitoring of PAH and organochlorine pesticides (Vrana et al., 2010). Finally, developed since 2008, CFIS (Continuous Integrative Flow Sampler) is a new active (i.e. using a pump) sampler designed for the determination of TWA concentrations of organic compounds in water (Llorca et al., 2009). Briefly, CFIS is a fully immersible device consisting of a small peristaltic pump powered by batteries and producing a constant water flow through the glass cell containing a PDMS sorbent. The main advantage of CFIS is that sampling rates are unaffected by water turbulence or velocity and thus, the use of performance reference compounds (PRCs) is not required. It has already been used for the monitoring of PAH and organochlorine pesticides in wastewater treatment plant effluent (Llorca et al., 2009).

Over the past 20 years, a variety of models has been developed to better describe the transfer kinetics of hydrophobic contaminants into integrative samplers (Booij et al., 2007). Whatever the integrative sampler and model considered, the calculation of TWA concentrations of contaminants in water from amounts accumulated in the sampler requires the knowledge of sampling rate (R_S) and sampler-water partition coefficient (K_{SW}) for each compound. Sampling rates are determined by laboratory calibration under controlled exposure conditions. *In situ* R_s calibration is needed to take into account differences between laboratory versus *in situ* exposure conditions (i.e. flow velocity, biofouling or temperature); it is achieved by the use of internal surrogates (performance reference compounds, PRCs), spiked in samplers prior to exposure (Huckins et al., 2002). K_{SW} can be determined experimentally (Smedes et al., 2009 for LDPE and SR) or estimated via empirical relationships as a function of $\log K_{OW}$ (Huckins et al., 2006 for

SPMD, Vrana et al., 2006 for Chemcatcher, Booij et al., 2003; Adams et al., 2007 and Lohmann and Muir, 2010 for LDPE). Concerning CFIS, that is an "active" sampler, the use of PRC and K_{SW} is not necessary. Indeed, a pump enables to control the water flow during exposure and the temperature effect is known by previous calibration in laboratory (from 5 °C to 35 °C). By this way, R_s estimated in laboratory for each PCB is corrected according to the average temperature encountered during *in situ* exposure, to be directly used for the determination of TWA concentrations (Llorca et al., 2009).

Very few intercomparison exercises on integrative samplers have been performed until now. Allan et al. (2009) or Miège et al. (2012) tested *in situ* the performance of several PSs (including non-polar Chemcatcher, LDPE, membrane enclosed sorptive coating – MESCO, SR and SPMD) for the monitoring of hydrophobic compounds (among PAHs, PCBs or organochlorine pesticides) in the river Meuse (The Netherlands) (Allan et al., 2009) or the river Rhône (France) (Miège et al., 2012) respectively. Although different integrative samplers and methods of calculation were used, relatively consistent TWA concentrations were obtained (variation by a factor up to two). Allan et al. (2010) compared under laboratory conditions the performances of six different integrative samplers (non-polar Chemcatcher, SPMD, silicone rod and strip and two modified versions of MESCO), exposed in a flow-through calibration system with Meuse river water spiked with PAHs, PCBs and organochlorine pesticides (concentrations ranging from 20 to 700 ng·L^{-1}). This laboratory experiment only lasting five days showed that the mass of contaminant absorbed normalized to the sampler surface area was comparable if uptake was controlled by diffusion through the water boundary layer.

In the context of the ECLIPSE project (2009–2011),[1] we have studied five integrative samplers that well represent the various types used nowadays for PCBs in term of receiving phase and configuration (dimensions, holders): SPMD, SR, LDPE strip, Chemcatcher (apolar version) and CFIS. After PRC spiking or not, samplers were exposed under constant agitation and temperature in water contaminated with 19 indicator and dioxin-like PCBs for periods ranging from one day to three months. A constant PCB concentration of about 1 ng·L^{-1} was achieved by immersing a large amount of spiked silicone rubber sheets (Rusina et al., 2010). Using these five samplers allows comparing different strategies for integrative sampling: passive versus active (with pump) sampling, use of PRC or not, use of different models and equations to assess TWA concentration. By exposing these five integrative samplers into the same experimental calibration system, a first objective was to compare their performances in accumulating PCBs (uptake, repeatability and linearity). Moreover, since there is no detailed guideline on integrative sampling, a second objective was to compare different methods of calculation of TWA concentrations (models, partition coefficients values and selected PRCs).

2. Materials and methods

2.1. Integrative samplers

The main characteristics of the studied integrative samplers as well as the PRCs tested and main steps of their processing are summarized in Table 1. Further details on their characteristics, pretreatment and analysis are given in Supplementary data (S1).

2.2. Target molecules

The exposure of samplers was performed with 19 PCBs: PCB 18, indicator PCBs (PCB 28, 52, 101, 118, 138, 153 and 180) and

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[1] **EC**hantil**L**onneurs **I**ntégratifs pour la mesure de **P**CB dans la phase dis**S**oute de mili**E**ux aqueux, 2009–2011, coord. Irstea (C. Miège), funded by the French Axelera cluster.