CEFIC-LRI ECO22

Final Report

Advancing the use of passive sampling in risk assessment and management of contaminated sediments: an inter-laboratory comparison study on measurements of freely dissolved (bioavailable) concentrations using different passive sampling formats

Michiel T.O. Jonker

Stephan A. van der Heijden

Institute for Risk Assessment Sciences, Utrecht University, Utrecht, the Netherlands

October, 2017

Executive Summary

The main objective of the CEFIC-LRI ECO22 project was to advance the use of passive sampling in risk assessment and management of contaminated sediments, through the performance of an inter-laboratory comparison study. Passive sampling methods (i.e., partitioning-based, non-depletive extractions with polymers) are used to determine freely dissolved concentrations (C_{free}) of organic chemicals in surface water and pore water of sediments and soils, and represent the most widely-used and well-characterized methods for assessing bioavailable concentrations in sediments. While there has been some progress in regulatory acceptance of passive sampling for sediment risk assessment, adoption has been slow, partly due to a lack of consensus among scientists on the best approach and validation across laboratories on the methods. Therefore, an international inter-laboratory comparison study on different passive sampling formats was performed in the CEFIC-LRI ECO22 project, in order to (1) map the state of the science in determining C_{free} in sediments with (*ex situ*) passive sampling; (2) identify the sources of variability by means of tiered experiments; (3) provide recommendations and practical guidance for standardized C_{free} determinations; and (4) increase confidence in the use of passive sampling and to advance its use outside the scientific domain. The inter-laboratory comparison study was performed by a consortium of 11 research laboratories with a track record in passive sampling, and included experiments with 14 passive sampling formats (different polymers, suppliers, shapes, thicknesses) on 3 sediments and 25 target chemicals (PAHs and PCBs). The resulting overall inter-laboratory variability was large; the averaged (all chemicals, samplers, and sediments) variation factor measured 10, but for certain chemicals the reported concentrations varied over more than 2 orders of magnitude. Standardization of methods halved the observed variability. The remaining variability was mostly due to factors that were not related to passive sampling itself, i.e., sediment heterogeneity and analytical chemistry (identification, integration, and calibration of the target compounds). Excluding the latter source of variability by performing all analyses in one laboratory showed that C_{free} can be determined with high precision, having a very low inter-method (i.e., passive sampler) variability (< factor of 1.7). It is concluded that passive sampling, irrespective of the specific method used, is fit for implementation in risk assessment and management of contaminated sediments, provided that chemical analyses are quality-controlled and standard protocols are being followed. As a follow-up of the CEFIC LRI ECO22 project, practical guidance (a proposed standard protocol) will be prepared jointly by the participants of the inter-laboratory comparison study.

Table of Contents

Acknowledgements

The authors of this report are very grateful for the financial support from the CEFIC-LRI program, as facilitated by Dr. Bruno Hubesch; the financial support from ILSI-HESI, as provided by Dr. Michelle Embry; and the support of ECETOC, as given by Dr. Malyka Galay Burgos. We also would like to thank the project scientific officer Dr. Mark Lampi (Exxon Mobil) for this continued support and input in the project. The (telecom) discussions were highly appreciated. Prof. Emmanuel Naffrechoux and Nathalie Cottin are kindly acknowledged for sampling a testing sediment in France. Theo Sinnige is thanked for his technical and analytical assistance.

List of Participants

The project described in this report concerned an international inter-laboratory comparison study (ring test; round robin study) on passive sampling measurements in sediments. The project was initiated and coordinated by the authors of this report, who also did most of the practical work and all the data analyses. However, the project also involved external partners, who participated in the ring test. These concerned eleven research laboratories, from three additional countries; they are listed below.

	Institute/research group	**Scientists involved**
1	Graduate School of Oceanography, University of Rhode Island, South Frry Road, URI Bay Campus, Narragansett, RI 02882, USA	**Rainer Lohmann** Dave Adelman Mohammed Khairy
2	RM Parsons Laboratory, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA	**Philip M. Gschwend** Jennifer N. Apell
3	Atlantic Ecology Division, Office of Research and Development, U.S. Environmental Protection Agency, Narragansett, RI, USA	**Robert M. Burgess**
4	Department of Civil and Environmental Engineering, Stanford University, 473 Via Ortega, Stanford, CA 94305, USA	**Yongju Choi** Yanwen Wu
5	Department of Civil and Environmental Engineering, Northeastern University, 473 Snell Engineering, 360 Huntington Avenue, Boston, MA 02115, USA	**Loretta A. Fernandez** Geanna M. Flavett
6	Department of Chemical, Biochemical, and Environmental Engineering, University of Maryland Baltimore County, 1000 Hilltop Circle, Baltimore, MD 21250, USA	**Upal Ghosh** Mehregan Jalalizadeh
7	Norwegian Geotechnical Institute. Environmental Technology. Sognsveien 72, 0806 Oslo, Norway	**Amy M.P. Oen** Sarah E. Hale
8	Southern California Coastal Water Research Project Authority. 3535 Harbor Blvd. Suite 110, Costa Mesa, CA 92626, USA	**Keith A. Maruya** Wenjian Lao
9	Center for Fisheries, Aquaculture and Aquatic Sciences, and Department of Zoology, Southern Illinois University, Carbondale, IL 62901, USA	**Michael J. Lydy** Samuel A. Nutile
10	Civil, Environmental and Construction Engineering, Texas Tech University, Box 41023, Lubbock, TX 79409-1023, USA	**Danny Reible** Magdalena I. Rakowska
11	Masaryk University, Faculty of Science, Research Centre for Toxic Compounds in the Environment (RECETOX), Kamenice 753/5, 62500, Brno, Czech Republic - and - Deltares, P.O. Box 85467, 3508 AL Utrecht, the Netherlands	**Foppe Smedes** Tatsiana P. Rusina

1. Introduction

Background

Traditional methods for assessing risks and managing contaminated sediments are based on total, solvent-extractable concentrations of sediment-associated chemicals.[1] Within the environmental scientific community it is generally accepted that this approach does not lead to a realistic assessment of actual risks.[2] Therefore, several methods for estimating the 'bioavailable' concentration or fraction of chemicals have been developed during the past decades. These methods aim at determining the concentration or fraction that is available for causing ecotoxicological effects and more closely reflects actual or potential exposure. Among these methods, partitioning-based, non-depletive extractions with polymers (colloquially referred to as "passive sampling methods") are considered the best developed and have the most solid scientific basis.[3] Through passive sampling, the freely dissolved concentration (C_{free}) of a chemical in sediment pore water is determined, which is a good metric of the driving force behind accumulation and toxicological effects in organisms.[4] The technique involves direct exposure of a polymer phase to sediment, either *in situ* or *ex situ*. Chemicals present in the sediment system partition into the polymer and the resulting polymer-sorbed equilibrium concentration is used to calculate C_{free}. Several different polymers have been applied as a sampling phase, including polydimethylsiloxane (PDMS), polyethylene (PE), polyoxymethylene (POM), polyacrylate, and silicone rubber, with the polymers coming in different formats.[5]

Despite the multitude of sampler formats and application possibilities, passive sampling is currently mostly used for scientific purposes and as an indicator of sediment remediation performance, rather than to define sediment management approaches. Acceptance in the risk assessment and regulatory community has been slow, among other things because of the fact that so many different types of passive samplers are available. There is a perception outside the scientific community that no scientific consensus exists on which is the best method to use.[2] Although guidelines for selection of specific polymers have been proposed,[5] and the application of different passive samplers and (calculation and analysis) methods should theoretically yield identical C_{free} values, it is currently unknown if this actually holds true and what the inter-method

variability is. This information is crucial however when aiming to implement passive sampling in risk assessment practices for contaminated sediments.

In November 2012, a SETAC workshop on passive sampling in sediments was held in Costa Mesa (CA, USA), with the goal of advancing the application of passive sampling in the risk assessment and management of contaminated sediments.[2] During the workshop, several research needs and bottlenecks for implementation were identified, including the above-mentioned issue and the necessity for a round-robin, inter-laboratory study; standardization of methods; and characterization of sources of uncertainty.[2,5] In response, an international inter-laboratory comparison study was initiated, of which the results are described in this report.

Project Research Objectives

The main objectives of the CEFIC ECO22 project were to:

- map the state of the science in *ex situ* passive sampling in sediments, and the inter-laboratory and inter-method variability in experimental C_{free} determinations;
- identify the sources of variability in C_{free} as determined with passive sampling;
- propose measures to reduce variability and to provide practical guidance (standardized methods); and,
- increase the overall confidence in passive sampling in order to advance its use outside the scientific domain.

Structure and Evolution of the Project

The work in the ECO22 project did not consist of specific work packages, but was set-up in a tiered fashion. First, participants were invited for the inter-laboratory project and sediments were selected and characterized (Sept. 2013 - May 2014). Then, the ring test was initiated and the overall inter-laboratory variability in passive sampling was mapped, after which dedicated experiments were performed in order to identify and evaluate specific sources of variability. One of the potential sources of variability was related to the polymer-water partition coefficients that are needed for calculating C_{free}. In order to be able to use consistent data from one source, the

coefficients for all passive sampling formats applied in the ring test were determined by the authors of this report in the ECO22.2 (extension) project (Dec. 2015).

Although the project was coordinated by the first author of this report, who also performed the data interpretation and most of the practical work together with the second author, the project involved external partners, who voluntarily participated in the ring test, without receiving funding. As such, data delivery entirely relied on the agenda and goodwill of the participants. This unfortunately resulted in the fact that the last data were finally received in February 2017, more than a year later than the agreed end date of the project (Dec. 2015). In the meantime, the research group of the authors of this report had also been discontinued. However, the scientific quality of the project and its resulting products were not affected in any way by the serious delay: all participants, all being international experts in the field of passive sampling, are very content with the final outcomes of the study, which have the potential to move forward passive sampling as a tool in the risk assessment and management of contaminated sediments.

Deliverables of the ECO22 Project

Deliverable	**Description**	**Date**
D1	Final study design ECO22	November 2013
D2	Sediment selection	March 2014
D2a	Sediment characterization	May 2014
D3	Final report	October 2017
D4	Submission of scientific manuscript on ECO22	Planned October 2017
D5	Submission of scientific manuscript on ECO22.2	Planned January 2018

2. Study design

Eleven laboratories from four different countries (USA, The Netherlands, Norway, and the Czech Republic) participated in the study. The Dutch laboratory (Utrecht University) acted as coordinating laboratory. Each participating laboratory had a proven track record in passive sampling in sediments and contributed to the study by applying their own passive sampling procedures (i.e., format, experimental setup), previously published in the peer-reviewed literature. In total, 14 passive sampling formats were included, which differed in polymer material, source, form (i.e., polymer sheet vs. coating on a glass (SPME) fiber), or thickness. Five of the 11 laboratories applied multiple formats. Passive sampling experiments were performed with three sediments, including two field-contaminated sediments and one unpolluted sediment that was spiked in the coordinating laboratory. Target chemicals included 12 polychlorinated biphenyls (PCBs) and 13 polycyclic aromatic hydrocarbons (PAHs). C_{free} values of these chemicals were determined in five-fold for each sediment in the following set of tiered experiments. In the first experiment, each laboratory followed its own procedure(s). The resulting C_{free} values were reported to the coordinating laboratory, along with the K_{pw} values used in the calculations and a description of the methods applied. This experiment mapped the overall variability in passive sampling methods. In the second experiment, participants were asked to redo the measurements, but to strictly apply a 'standard' protocol that was prepared by the coordinating laboratory. This experiment was performed in duplicate: one set of sample extracts was analyzed by the respective participant, to quantify the contribution of employing different protocols to the overall variability; the other set was shipped to, and analyzed by the coordinating laboratory, in order to evaluate the contribution of analytical chemistry to the overall variability. All participants were also provided with a standard solution of the target chemicals, of which the reported concentrations yielded a direct measure of the analytical variability. In the third experiment, the coordinating laboratory applied the 'standard' protocol to all 14 passive sampling formats (as shared by the participants) in order to identify the inter-method variability. Finally, supplementary tests were performed to map any additional sources of variation in C_{free}, including polymer mass determination, sediment heterogeneity, and sediment storage time.

3. Material and methods

Passive Sampler formats

An overview of the applied passive sampling formats (polymer types, thicknesses, suppliers) is given in Table 1.

Table 1. *Passive sampling formats applied during the inter-laboratory comparison study: codes, polymer types, thicknesses, and suppliers.*

Code	Polymer type	Polymer thickness	Supplier
Sheets			
PE-1	Polyethylene	25 µm	Ace Hardware Corporation, Oak Brook, IL, USA
PE-2	Polyethylene	25 µm	Berry Plastics Corporation, Evansville, IN, USA
PE-3	Polyethylene	51 µm	Brentwood Plastics, St. Louis, MO, USA
PE-4	Polyethylene	25 µm	Covalence Plastics, Minneapolis, MN, USA
PE-5	Polyethylene	25 µm	Berry Plastics Corporation (Film Gard sheeting)
PE-6	Polyethylene	26 µm	VWR International Ltd., Leicestershire, UK
POM	Polyoxymethylene	77 µm	CS Hyde Company, Lake Villa, IL, USA
SSP	Silicone rubber	100 µm	Shielding Solutions Ltd., Great Notley Essex, UK
SPME fibers [a]			
S10-1	Polydimethylsiloxane	10 µm	Poly Micro Industries, Phoenix, AZ, USA
S10-2	Polydimethylsiloxane	10 µm	Fiberguide, Stirling, NJ, USA
S30-1 [b]	Polydimethylsiloxane	30 µm	Poly Micro Industries, Phoenix, AZ, USA
S30-2 [b]	Polydimethylsiloxane	30 µm	Poly Micro Industries, Phoenix, AZ, USA
S100	Polydimethylsiloxane	100 µm	Fiberguide, Stirling, NJ, USA
PAc	Polyacrylate	30 µm	Poly Micro Industries, Phoenix, AZ, USA

[a] Actual (measured) polymer coating volumes are listed in Appendix 3.
[b] Core thickness of the S30-1 fiber was about 100 µm; of the S30-2 fiber it was about 500 µm.

Target Chemicals

Target chemicals were the PAHs phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, dibenz[*ah*]anthracene, and indeno[123,*cd*]pyrene; and PCB congeners 18, 28, 52, 66, 77, 101, 118, 138, 153, 170, 180, and 187.

Analytical Standard Solution

A standard solution was prepared for each participant, by adding 50 µL of an acetone spike containing the 25 target chemicals to 950 µL of the participant-specific injection solvent applied during chemical analyses by the respective laboratory (either *n*-hexane, *n*-heptane, *n*-hexane/acetone (1:1), dichloromethane, or acetonitrile). Nominal concentrations (not shared with the participants) were about 50 µg/L for PCBs and 100 µg/L for PAHs.

Sediments

The three testing sediments differed in degree of complexity by passive sampling application. The 'least complex' sediment was an unpolluted, sandy sediment, sampled from the small river 'Kromme Rijn', near Werkhoven, the Netherlands. It was sieved through a 1 mm sieve, yielding a 20-kg dry weight (dw) sample, which was intensively mixed for 30 min with a mechanical mixer. Ten 2 kg (dw) portions of the wet sediment were successively spiked in 5 L glass beakers with relatively high levels of the target chemicals, by adding drop-wise 4 mL of an acetone solution containing the target chemicals, while intensively mechanically stirring (30 min). All portions were finally pooled in a 110 L concrete mixer, which subsequently mixed this spiked "SP sediment" continuously for 4.5 weeks. The sediment of 'intermediate complexity' originated from the "Biesbosch", a Dutch sedimentation area. This "BB sediment" had been used in a previous study in outdoor ditches,[6] from which the material for the present study was sampled. It contained relatively low native concentrations of the target chemicals, but was known to be homogeneous. Therefore, it was mixed in a concrete mixer for a shorter period of time, i.e., 1.5 week. The most complex sediment ("FD sediment") was a sediment composed by combining (2:1) a French and a Dutch sediment. The French sediment was sampled from the river Tillet (Aix les Bains, Savoie), was very sandy, and contained hardly any PAHs. PCBs were however present at high concentrations, and originated from a former electric transformer manufacturing

facility 2 km upstream. The Dutch sediment was sampled from the river Hollandsche IJssel and had been previously studied.[7] It contained no detectable PCBs, but PAHs were present at intermediate concentrations, mostly originating from an upstream diesel-powered water pumping station. This sediment also contained non-aqueous phase liquids (NAPLs; diesel). The composited sediment was mixed in a concrete mixer for 4 weeks nonstop. Before mixing, all sediments received sodium azide (NaN_3) as a biocide, at a final concentration of 100 mg/L water. After mixing, the sediments were divided among amber-colored glass jars in portions sufficient to meet each participant's requirement to complete the tests (different procedures by different participants required different sediment masses). All jars were closed with aluminum foil-lined lids and shipped in cooled containers to the participants, along with the standard solution and coded autosampler vials and glassware for the standardized experiments. Dry weight and organic carbon content, as well as total concentrations of the target chemicals in the sediments were determined as previously described.[8] The results are provided in Appendix 1. This information was shared with the participants before initiating the experiments.

Determination of C_{free} Based on the Participants' Own Procedures

In this first experiment, all participants performed C_{free} determinations according to their own procedure(s) and analyzed the resulting extracts themselves. Each measurement was performed five-fold. A summary of the material used and methods applied by all 11 participants is (anonymously) listed in Appendix 2. Procedures clearly differed in terms of type of exposure (i.e., static vs. dynamic), exposure duration, verification of equilibrium conditions (i.e., use of performance reference compounds (PRCs), multiple sampler thicknesses, or multiple time points), sampler mass, sampler/sediment/water ratio, washing and extraction of samplers, and solvents used.

Determination of C_{free} Based on Standardized Procedures

After completing the above experiment, participants received a standardized protocol and were asked to repeat the five-fold C_{free} determinations, strictly adhering to the prescribed procedure. Two protocols had been prepared; one for polymer sheets and one for SPME fibers. In the protocols, all aspects and steps (except the chemical analysis) were standardized, including sampler/sediment and sediment/water ratio, sampler washing, glassware, composition of the

added water (Millipore containing 100 mg/L NaN_3), exposure duration (6 weeks), method of shaking and shaking speed, and sampler cleaning and extraction procedures after finishing the exposures. The sampler/sediment ratio was dependent on the sediment and the polymer used; and the sampler washing and extraction procedures were different for different polymers. Furthermore, the sampler extraction was tuned to the solvent used during chemical analysis by the particular participant. As outlined in Chapter 2, this experiment was performed in duplicate. One set of extracts was analyzed by the participant, the other set was shipped in a cooled container to the coordinating laboratory, where internal standards were added and the extracts analyzed. The standardized protocol was also applied by the coordinating laboratory to all 14 sampler formats (as shared by the participants), in order to quantify the inter-method variability.

Supplementary Tests

Supplementary tests focused on additional sources of variation in C_{free} (polymer mass determination, sediment heterogeneity, and sediment storage time). Participants using polymer sheets (n = 10) received 6 or 9 (i.e., 2 or 3 triplicate) pieces of POM, having a weight similar to the polymer weights prescribed in their standardized protocol (2.5, 6, 10, and/or 30 mg). All pieces had been cut, coded and weighed on two different, recently serviced/calibrated analytical balances by the coordinating laboratory. Participants reported back the weights of their pieces and the results were used to evaluate any contribution of sampler mass determination to the variability in C_{free}. Likewise, the accuracy of nominal coating volumes, as applied by participants using SPME fibers, was evaluated by determining the actual coating thickness of all fibers by microscopic measurements (methods described in Appendix 3).

To investigate the possible contribution of sediment heterogeneity to the overall C_{free} variability, 10 batches of each sediment were randomly sampled from the concrete mixers directly after finishing the mixing. C_{free} in all batches was determined by the coordinating laboratory, according to the standardized protocol with POM as the sampler.

Because it was impossible to synchronize the measurements by all participants, sediments were stored in refrigerators in different laboratories for different lengths of time. The time between starting the first and the last measurement was 4 months. The coordinating laboratory investigated any effects of sediment storage time by performing the measurements first and last

(two time points, 4.5 months apart). Measurements were performed according to the standardized protocol with POM and SPME (S30-1) as the samplers.

Chemical and Data analysis

Target chemicals were analyzed by the participants as described in Appendix 2. GC-MS or GC-ECD was used for PCB quantification, whereas PAHs were analysed by either GC-MS or HPLC-FLD. Concentrations in the sampler extracts were converted to concentrations in the sampler material (C_s), using the sampler mass (sheets) or volume (SPME fibers). C_{free} was then obtained by dividing C_s by a polymer- and chemical-specific K_{pw}. In the first experiment (participants' own procedures), participants applied their own K_{pw}s (measured themselves or taken from the literature) and some used PRCs in their calculations. In the standardized experiment, a fixed set of K_{pw} values as measured by the coordinating laboratory was applied. Variability in each experiment was quantified by averaging the five-fold C_{free} measurements of each participant and by subsequently calculating a variation factor (*VF*) for each target chemical. This factor was calculated by dividing the 95th percentile (*PCTL*) value of the averaged C_{free} values per target chemical, by the 5th percentile value:

$$VF = \frac{95th\ PCTL}{5th\ PCTL}$$

Using this statistic, the range in C_{free} was quantified and expressed intuitively as a factor, while excluding outliers. In order to compare experiments and sediments in a simple way, the chemical-specific *VF* values were averaged per sediment for each experiment (VF_{av}).

4. Results and discussion

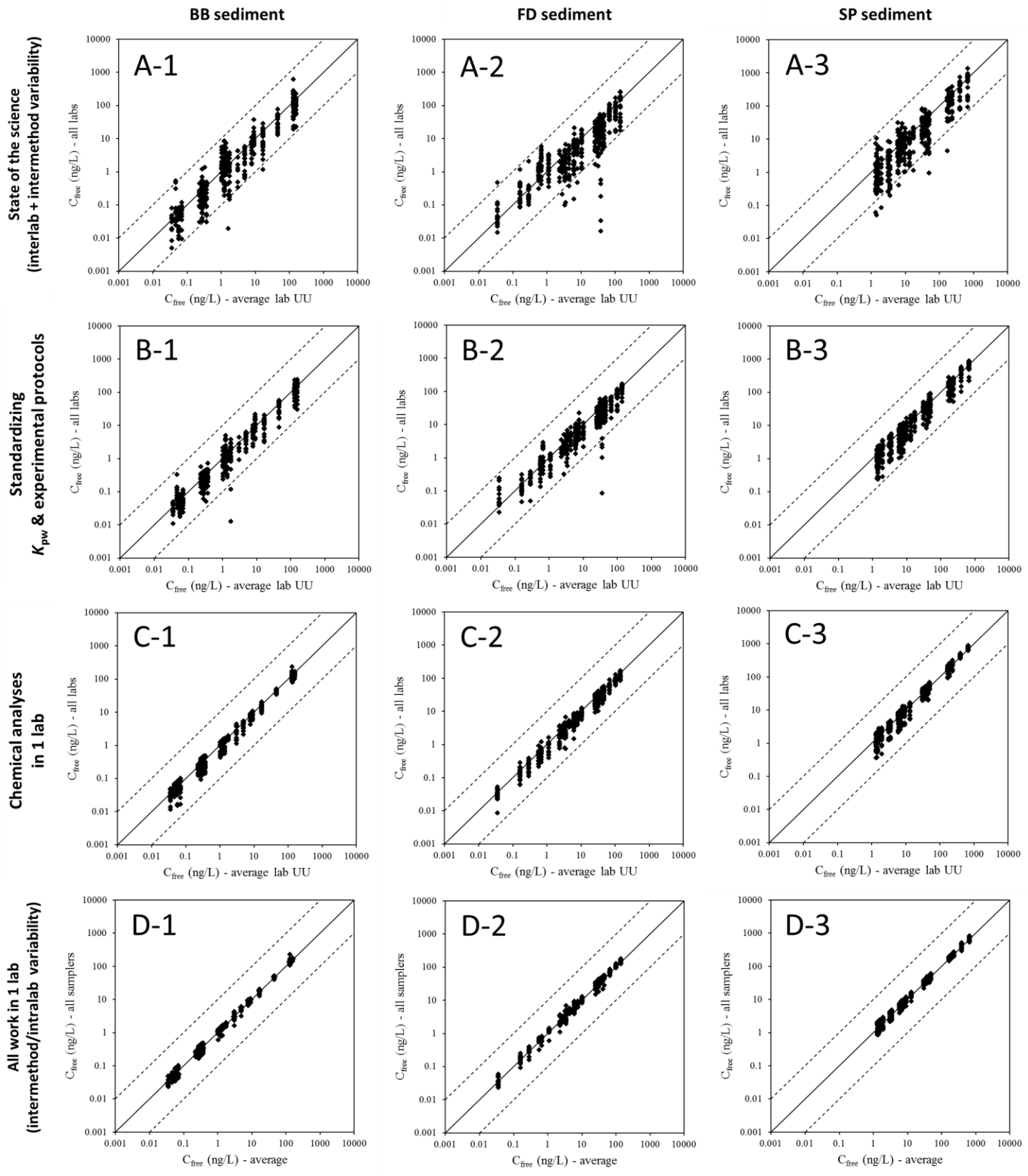


Figure 1. *Variability in freely dissolved concentrations (C_{free}) determined in three sediments as measured with passive sampling methods (A) when the participants of the inter-laboratory comparison followed their own protocols, (B) after standardization of K_{pw}s and experimental protocols, (C) when, in addition to B, all chemical analyses were performed in one laboratory, and (D) when both experiments and analyses with all samplers were performed in one laboratory. Solid lines represent the 1:1 relationships; dashed lines indicate ± a factor of ten.*

State of the Science in Passive Sampling Sediment Pore Water

The results of the first experiment, in which all participants performed C_{free} determinations according to their own procedures, are presented in sub figures A1-3 of Figure 1. In these three figures (one for each sediment), the averaged C_{free} data for all target chemicals are plotted against C_{free} values obtained by averaging all chemical-specific data produced by the coordinating laboratory (Lab UU; all passive sampling formats; standardized protocol). This way, the data are presented in a straightforward and understandable manner, without any data manipulation, yet clearly demonstrating the data variability. It should be stressed, though, that using the averaged coordinating laboratory data as independent variables does not imply these values are the target or actual values; they are solely used as reference values. Nearly all data points fall within the 10:1 and 1:10 interval, but there is a clear tendency towards under predicting the averaged data of the coordinating laboratory. Overall, the observed inter-laboratory variation is quite large; larger than the variability reported for a previous small-scale inter-laboratory passive sampling comparison.[9] Note however that in ref *9* fewer samplers and target analytes (3 and 8, respectively) were tested using a single sediment. Figure 1 may be also somewhat misleading as the apparent concentration ranges in some cases seem to cover a factor of 100, whereas they are actually composed of data for more than one chemical. The largest variation in the present study was observed for PCB-77 in the BB and FD sediments, where the concentration ranges did indeed span a factor of 100 and even 2400, respectively (see Appendix 4, in which ranges for all chemicals are presented). The cause for the deviating behavior of this particular chemical is as follows. Although PCB-77 was a target chemical, which was added to the SP sediment, it was not present at detectable concentrations in the field-contaminated BB and FD sediments. Nevertheless, several participants reported false positive C_{free} values for the chemical in these sediments. The large concentration ranges observed can thus be explained by the different detection (MS; ECD) and separation (GC columns) approaches applied by different participants,

which will have resulted in inconsistencies in interfering/mis-identified peaks. Because the data for PCB-77 in the BB and FD sediments obscure the average variability, they were excluded from the data analysis when calculating VF_{av} values (averaged variation factors). These VF_{av} values are listed in Table 2. Values for the first experiment are 10, 9, and 11 for the BB, FD, and SP sediment, respectively. Apparently, when omitting the PCB-77 data, there are no obvious differences in variability among the three sediments, even though they were selected/composed based on differences in complexity for passive sampling. This either implies that passive sampling is a robust technique that produces results that are independent of the type of sediment studied, or that the overall variability is so large that it obscures more subtle differences between results for the various sediments. Note that the variation observed in Figures 1 A1-3 includes variability as introduced by (i) different laboratories, applying different protocols carried out by different people (inter-laboratory variability), (ii) the use of different K_{pw} values by different participants, (iii) different ways of analyzing the chemicals, (iv) sediment heterogeneity and instability; and, (v) the use of different passive sampling approaches (inter-method variability). The contribution of each of these sources will be discussed in a semi-quantitative manner in the subsequent sections.

***Table 2**. Averaged Variation Factors (VF_{av}; ± standard deviations) per sediment and per experiment.*[a]

	BB sediment[b]	FD sediment[b]	SP sediment
Measurements based on own protocols	9.7 ± 4.1	9.4 ± 6.3	10.8 ± 4.5
Standardizing K_{pw} values	8.9 ± 3.6	9.3 ± 4.6	10.8 ± 5.6
Standardizing protocols & K_{pw} values	4.4 ± 1.4	4.6 ± 2.2	4.5 ± 1.2
Standardizing & chemical analyses in one lab	2.4 ± 0.89	2.4 ± 0.72	2.6 ± 0.82
All work in one lab	1.6 ± 0.35	1.7 ± 0.42	1.7 ± 0.32

[a] The VF_{av} values are calculated by averaging the *VF* values of all chemicals for one sediment in a specific experiment.
[b] Data for PCB-77 are excluded (see text for explanation).

Impact of Standardizing K_{pw} values

Since most of the measurements performed by the participants concerned equilibrium passive sampling, and inaccuracies in the K_{pw} of target analytes under equilibrium conditions are considered "a major source of concern",[10] one would expect a clear contribution to reducing the overall variability by standardizing the K_{pw}s used for calculating C_{free} values. After all, the participants applied K_{pw} values measured in their own laboratory or values taken from the literature. As such, there were considerable differences between the values that were used. For PDMS, the difference between the lowest and the highest chemical-specific K_{pw} values increased up to a factor of 7; whereas for PE the maximum difference was a factor of 13 and for POM it was even a factor of 20 (1.3 log units). The impact of standardizing K_{pw}s was investigated by using K_{pw} values that had been determined for each sampler/chemical by the coordinating laboratory, as part of the project (see Appendix 5). Remarkably, the impact of using K_{pw} values from a single source on the overall variability was negligible, as shown in Appendix 6. The VF_{av} values (excluding the PCB-77 data) basically remained the same after recalculating the C_{free} data as reported by the participants, using K_{pw} values from the single source (see Table 2). The position of the data points, however did change in many cases, which makes sense, as K_{pw} values determine the absolute value for C_{free}. In other words, standardizing K_{pw}s does not reduce the variability of C_{free} measurements, but it is of utmost importance for the accuracy of C_{free} data. Using inaccurate K_{pw}s will yield erroneous C_{free} data, which is an unwanted situation when applying passive sampling for assessing risks of contaminated sediments. Therefore, it is recommended that high-quality, standardized (consensus) K_{pw} values be used by the passive sampling community.[5] This will be discussed further in an upcoming paper on the ECO22.2 results.

Impact of Standardizing Experimental Protocols

Standardizing the experimental protocols, in addition to the K_{pw} values, had a clear impact on the C_{free} variability. Figures 1 B1-3 and Table 2 demonstrate that the variability roughly halved, with the VF_{av} values being reduced to about 4-5 for all tested sediments. This obviously implies that the methodology of passive sampling measurements influences the outcomes and that standardization of passive sampling methods is definitely desirable. Because multiple issues and steps were standardized in the protocols, it is not possible to attribute the variation reductions to

a specific aspect of the protocols; there are several likely candidates. The most important aspects that were standardized (thus changed for certain participants) included the sampler/sediment and sediment/water ratios, sampler washing procedure, applied glassware, composition of the water added, exposure duration, way of shaking and shaking speed, and the sampler cleaning and extraction procedure after finishing the exposures. Smedes et al.[11] showed that the sampler/sediment ratio may influence the equilibrium concentration in the sampler (and thereby the calculated C_{free}), as it was observed to be inversely related to this metric, due to depletion of the system. In the standardized protocol, the ratio was designed such that chemical depletion from the three sediments was always below 2% for all chemicals and samplers.[11] However, when performing the measurements according to their own procedure(s), some participants applied (much) higher ratios, which will have resulted in higher depletion ratios (theoretically up to about 70%). Therefore, standardization of this step may have contributed to the variation reduction. Likewise, Smedes et al.[11] demonstrated that the sediment/water ratio can affect the system's kinetics. Higher ratios were observed to yield faster equilibration. Standardization of this ratio, together with a fixed equilibration time and shaking regime, assured (near) equilibrium in all cases during the standardized experiment, as illustrated in Appendix 7. In the first experiment in which the participants followed their own procedures, several participants (presumably) did not achieve full equilibrium for all chemicals. PRCs were used to correct for this in several cases, following different calculation approaches, but such a correction may introduce uncertainties and inaccuracies.[12-13] This particularly applies to the more hydrophobic chemicals, for which the correction by some participants was based on extrapolation from released fractions of less hydrophobic PRCs only. It should be stressed though that correction for the degree of non-equilibrium based on PRCs does not necessarily introduce substantial error, as demonstrated by the experiments from one participant. Whereas the standardized protocol prescribed thorough mixing and no PRCs, the own procedures of this participant involved static exposures and included PRC corrections. The figure in Appendix 8 shows that the results of both approaches agreed within a factor of about 2 for all chemicals and sediments.

Standardization of some of the other aspects of the protocols may also have contributed to the variability reduction, but their contribution is probably less substantial. Sampler extraction procedure after finishing the exposures may be an exception, as specific solvent use or handling

of samplers/extracts (e.g. cleanup or evaporation steps) by participants may have introduced variability through, for instance, variable extraction recoveries or losses of chemicals.

Contribution of Analytical Chemistry to the Variability

Even after standardizing K_{pw} values and experimental protocols, considerable variability in the inter-laboratory C_{free} data remained (Figures 1 B1 to B-3). This variability, however, again roughly halved when all passive sampling extracts were analyzed in one laboratory (see Figures 1 C-1 to C-3). VF_{av} values decreased to about 2.5 for all three sediments. As such, chemical analyses appear to have an important contribution to the overall variability. This conclusion was also drawn for other inter-laboratory comparison studies on passive sampling in surface waters,[14-15] but certainly is not restricted to passive sampling measurements. Each experiment involving chemical analyses will suffer from errors introduced through inaccuracies in the identification, integration, and calibration of compounds. The case of PCB-77, as discussed above, already demonstrated that identification is the first crucial step and, if not performed correctly, can result in huge variability. Integration of chromatograms generally will not be considered as the step that contributes most to the overall variability introduced through chemical analysis, but poor integrations may add a few percent of error to the results, up to perhaps a factor of 2 or more in the case of complex chromatograms with co-eluting peaks. Any error will strongly depend on the sediment, the chemical, the analytical separation power, the selectivity of identification, the integration approach (i.e., quantification based on peak area or height), and the efficacy of any clean-up procedure. The major and most general source of error introduced by analytical chemistry, causing variability in accuracy, most probably is calibration. Apart from correct application of internal standards, calibration standards straightforwardly determine the final concentration quantified in the analyzed extracts. Errors in the weight/volume of neat compounds used for the preparation of calibration standards or in standard dilutions may cause inaccuracies in calibration curves. Even for PAHs and PCBs, i.e., compounds that are very frequently and often routinely analyzed, these inaccuracies may be considerable. The analysis of the standard solution in the present study demonstrated that the variation in PCB concentrations was quantified by a *VF* of 2 - 3, while for PAHs it was 3 - 4.5 (see Figure 2). From Figure 2 and the difference between Figures 1B and 1C it can thus be concluded that a major part of the variability in the present inter-laboratory C_{free} data originates from a step that basically has

nothing to do with passive sampling measurements, but is part of every experiment involving chemical analysis, and is often not even considered as a source of error in experimental results. Therefore, it is strongly recommended to include a standard solution in inter-laboratory comparison studies involving chemical quantification. Note that the present inter-laboratory study was performed by research laboratories, where (analytical) quality assurance often is less developed than at commercial laboratories. Data variability may therefore be lower for inter-laboratory studies performed by the latter laboratories.

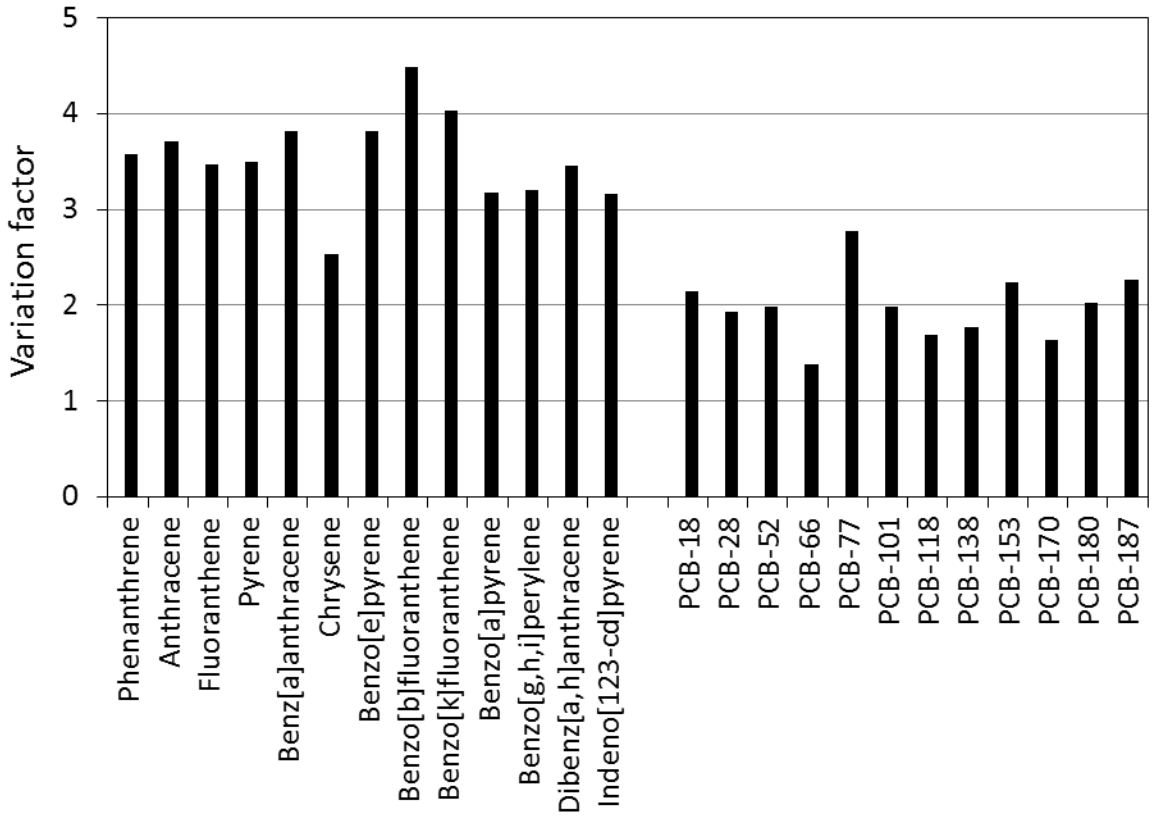


Figure 2*. Variation factors (95th PCTL/5th PCTL) calculated based on the (range of) concentrations of the target chemicals in the analytical standard, as reported by the participants of the inter-laboratory comparison.*

Other Sources of Variability

Figure 1 C expresses the variability of experiments that were standardized and of which the extracts were analysed by one laboratory. The observed variability will therefore be caused by (i)

inter-method variability, which will be discussed below, and (ii) other sources of variability. Two other sources of variability were investigated in the present study, i.e., the accuracy of sampler mass and fiber coating volume (i.e., analytical weighing and the use of nominal fiber coating thickness) and sediment heterogeneity (originating from insufficient mixing and different storage times). Generally, sheet samplers are weighed on a balance and concentrations quantified in polymers are expressed on a sampler mass basis. Samplers for C_{free} measurements in sediment pore water usually have a mass in the mg range. Since this is a delicate range on a balance, an inaccurate balance or weighing procedure may introduce error and consequently increase data variability. The results of the weighing test however demonstrated that sampler weights generally were within 1% of the weights recorded by the coordinating laboratory. Only one participant reported weights deviating up to 4.7%. These differences are small and consequently it can be concluded that weighing did not contribute significantly to the experimental variability in the present study. Needless to say, in order to prevent weighing being a significant contributing factor to the accuracy and precision of future passive sampling work, it is recommended to frequently calibrate and periodically service analytical balances used for weighing samplers.

When deriving the coating volume of a SPME fiber, product specifications provided by the manufacturer are rarely questioned, although it often remains obscure how these were established. A comparison of coating volumes calculated based on nominal, manufacturer-provided thicknesses and actually measured ones (see Appendix 3) demonstrated obvious differences, which amounted up to 16%. As such, in contrast to sheet masses, fiber coating volumes may be a potential source of variability in C_{free}. However, two of the fibers showing the largest deviations (S30-1 and PAc) were applied by the coordinating laboratory only, which used actual volumes throughout the different experiments. Therefore, in the present study, the use of nominal coating volumes may only have been a potential source of variability for the S10-1 fiber, albeit not in the experiments where the chemical analyses (and subsequent calculations) were performed by the coordinating laboratory.

The sediment heterogeneity experiment showed that even after mixing for several weeks, sediment heterogeneity may also have contributed to the observed overall variability in C_{free}. VF_{av} values of 1.1 to 1.4 for the field-contaminated BB and FD sediments and 1.2 to even 2.4 for the spiked SP sediment were calculated (see Appendix 9). The *VF* values are rather chemical-

independent for the BB and FD sediments, but for the SP sediment, they increase with chemical hydrophobicity (see Appendix 9). Apparently, mixing this spiked sediment for up to 4.5 weeks in a concrete mixer was insufficient to allow full chemical homogenization of, in particular, the most hydrophobic compounds. Note that the results presented here concern the heterogeneity applying to a series of samples (n=10) taken directly from the concrete mixer. These samples do not necessarily perfectly represent the sediment samples as received by the participants, considering the large sediment volume in the mixers. After filling all the jars with sediment required by the participants, excess sediment was placed in spare jars. The VF_{av} values thus do not *per se* exactly quantify the actual variability caused by sediment heterogeneity in the experiments, and cannot directly be deducted from the values in Table 2. They do indicate, however, that sediment heterogeneity potentially may have contributed to the variability observed in Figures 1A-C. Apart from that, sediment heterogeneity within a single sediment batch as received by a participant is expected to be much smaller, as will be discussed below (intra-method variability).

Measurements performed with sediments stored for 4.5 months in the refrigerator, as compared to measurements initiated directly after sampling from the concrete mixers demonstrated that C_{free} of the target PAHs and PCBs decreased to about 80 % in the FD sediment and 90 % in the BB and SP sediments. This suggests that storage time also cannot be excluded as a source of variability. However, the time between the first participant starting the first experiment and the last participant starting this experiment, was only one month. Therefore, it is not very likely that storage time contributed to the variability in Figure 1 A. The first and last started standardized experiments were, however, three months apart and storage time thus may have been an additional source of variability in Figure 1 B. It should be stressed though that the two measurements (i.e., before and after storage) were performed with two different sediment batches (jars); as such, sediment heterogeneity may also have caused (part of) the difference in C_{free}. If the concentration decrease is a real phenomenon, it is unclear what the exact underlying mechanism would be: degradation is unlikely in all cases (chemicals, sediments) and progressive sorption is improbable for the BB sediment.

Intra-method and Inter-method Variability

The last experiment included C_{free} measurements with all sampler formats by the coordinating laboratory. From this experiment, both the intra- and inter-method variability could be deduced. As observed before,[16] the intra-method variability appeared very low. For sheet samplers (PE, POM, SR), relative standard deviations (RSDs) of the five-fold measurements generally were < 5% and for the (homogeneous) BB sediment, RSDs were often < 2 or even 1 %, indicating very high repeatability. Requisite for low RSDs is that the measurements are being performed by skilled personnel, trained to work with passive samplers and to do high-quality chemical analyses (including highly consistent integrations). For SPME fibers, RSDs of the five-fold measurements by the coordinating laboratory were somewhat higher, with the values increasing with decreasing coating thickness: RSDs S10 > S30 > S100 > sheets (see Appendix 10). The cause of this order most probably relates to the facts that (i) the uncertainty in the sampling phase volume increases with decreasing coating thickness (because of increased uncertainties in the actual coating thickness, inaccurate cutting of the fibers, or coating wear during equilibration) and (ii) the thinner the coating, the higher the probability for artifacts to occur through 'fouling', i.e., particles or NAPLs sticking to the coating, potentially causing over estimation of the polymer-sorbed concentration.[7]

Because of the high method precision, it was possible to accurately quantify the inter-method variability. The resulting VF_{av} values (see Table 2, last row) demonstrate that on average the results of all 14 passive sampling formats (both sheets and SPME fibers of different polymers, sources, and thicknesses) match within a factor of 1.7. Thus, differences in C_{free} determined with a suite of passive samplers are very small. The underlying *VF* values do slightly increase with target chemical hydrophobicity, in particular for the PCBs (see Appendix 11). This increase is probably caused by the fact that K_{pw} values become more uncertain for very hydrophobic chemicals, due to increasing experimental difficulties related to slow kinetics and reduced solubilities,[17] which may cause somewhat increased data variability. Lower C_{free} values for the more hydrophobic chemicals cannot explain the observation, as the underlying measured concentrations in the extracts were not related to chemical hydrophobicity.

Similar to the previous experiments, the data variability is practically identical for the different sediments, here indicating that passive sampling is a robust technique, with which freely dissolved (bioavailable) concentrations can be determined precisely, irrespective of the sediment

under study. A comparison of the results of the different samplers shows that the highest C_{free} values generally were measured with the S100, S30-2, and S10 SPME fibers, whereas the lowest values generally were determined with POM, PE-6, and SSP. Because the differences are so small, in particular relative to the average, it can be concluded however, that there are no specific polymers that are behaving substantially differently and that their usage should be avoided. Different methods do have their specific 'pros' and 'cons' though (e.g., practicability of handling, ease of K_{pw} determination, detection limits, etc.). A detailed discussion of these factors is beyond the scope of the present report, and will be presented in a future scientific paper.

Overall, it can be concluded from this study that passive sampling is ready for implementation in actual risk assessment and the management practices of contaminated sediments. The technique is robust, as it produces results that are independent of the sediment under study and sampling polymer or format used. However, standard protocols should be applied (most importantly ensuring non-depletion, equilibrium conditions, and full sampler extraction) and the analytical chemistry carefully be quality-controlled, e.g., by means of (certified) external standards. The use of a passive sampling reference sediment is also highly recommended. This material is currently under development. Based on the standardized procedure, a standard protocol for passive sampling in sediments will be prepared and presented in a future scientific paper.

5. Project Dissemination

Presentations:

Michiel T.O. Jonker, Stephan A. van der Heijden, Yongju Choi, Yanwen Wu, Loretta A. Fernandez, Robert M. Burgess, Upal Ghosh, Mehregan Jalalizadeh, Philip M. Gschwend, Jennifer N. Apell, Rainer Lohmann, Mohammed Khairy, Dave Adelman, Michael J. Lydy, Samuel A. Nutile, Keith A. Maruya, Wenjian Lao, Amy M.P. Oen, Sarah E. Hale, Danny Reible, Magdalena I. Rakowska, Foppe Smedes, Mark A. Lampi. Advancing the use of passive sampling in risk assessment and management of contaminated sediments: Results of an international passive sampling inter-laboratory comparison. Platform presentation at SETAC Europe (Nantes), May 22–26, 2016.

Manuscripts (in preparation):

Michiel T.O. Jonker, Stephan A. van der Heijden, Dave Adelman, Jennifer N. Apell, Robert M. Burgess, Yongju Choi, Loretta A. Fernandez, Geanna M. Flavetta, Upal Ghosh, Philip M. Gschwend, Sarah E. Hale, Mehregan Jalalizadeh, Mohammed Khairy, Mark A. Lampi, Wenjian Lao, Rainer Lohmann, Michael J. Lydy, Keith A. Maruya, Samuel A. Nutile, Amy M.P. Oen, Magdalena I. Rakowska, Danny Reible, Tatsiana P. Rusina, Foppe Smedes, and Yanwen Wu. Advancing the use of passive sampling in risk assessment and management of contaminated sediments: Results of an international passive sampling inter-laboratory comparison. In preparation for submission to *Environmental Science and Technology*.

Michiel T.O. Jonker, Stephan A. van der Heijden. Towards standard PAH and PCB polymer-water partition coefficients for commonly used passive sampling materials. *In preparation.*

Michiel T.O. Jonker, Stephan A. van der Heijden, Jennifer N. Apell, Robert M. Burgess, Yongju Choi, Loretta A. Fernandez, Upal Ghosh, Philip M. Gschwend, Rainer Lohmann, Michael J. Lydy, Keith A. Maruya, Amy M.P. Oen, Danny Reible, Foppe Smedes. A proposed standard protocol for determining the freely dissolved, bioavailable concentration of hydrophobic organic chemicals in sediments with passive sampling. *Preparation planned for 2018.*

Literature cited

(1) Di Toro, D. M.; Zarba, C. S.; Hansen, D. J.; Berry, W. J.; Swartz, R. C.; Cowan, C. E.; Pavlou, S. P.; Allen, H. E.; Thomas, N. A.; Paquin, P. R. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* **1991,** *10* (12), 1541-1583.

(2) Parkerton, T. F.; Maruya, K. A. Passive sampling in contaminated sediment assessment: building consensus to improve decision making. *Integr. Environ. Assess. Manag.* **2014,** *10* (2), 163-166.

(3) Mayer, P.; Parkerton, T. F.; Adams, R. G.; Cargill, J. G.; Gan, J.; Gouin, T.; Gschwend, P. M.; Hawthorne, S. B.; Helm, P.; Witt, G.; You, J.; Escher, B. I. Passive sampling methods for contaminated sediments: scientific rationale supporting use of freely dissolved concentrations. *Integr. Environ. Assess. Manag.* **2014,** *10* (2), 197-209.

(4) Lydy, M. J.; Landrum, P. F.; Oen, A. M.; Allinson, M.; Smedes, F.; Harwood, A. D.; Li, H.; Maruya, K. A.; Liu, J. Passive sampling methods for contaminated sediments: state of the science for organic contaminants. *Integr. Environ. Assess. Manag.* **2014,** *10* (2), 167-178.

(5) Ghosh, U.; Kane Driscoll, S.; Burgess, R. M.; Jonker, M. T.; Reible, D.; Gobas, F.; Choi, Y.; Apitz, S. E.; Maruya, K. A.; Gala, W. R.; Mortimer, M.; Beegan, C. Passive sampling methods for contaminated sediments: practical guidance for selection, calibration, and implementation. *Integr. Environ. Assess. Manag.* **2014,** *10* (2), 210-223.

(6) Kupryianchyk, D.; Rakowska, M. I.; Roessink, I.; Reichman, E. P.; Grotenhuis, J. T. C.; Koelmans, A. A. In situ treatment with activated carbon reduces bioaccumulation in aquatic food chains. *Environ. Sci. Technol.* **2013,** *47* (9), 4563-4571.

(7) Van der Heijden, S. A.; Jonker, M. T. O. PAH bioavailability in field sediments: Comparing different methods for predicting in situ bioaccumulation. *Environ. Sci. Technol.* **2009,** *43* (10), 3757-3763.

(8) Jonker, M. T. O.; Smedes, F. Preferential sorption of planar contaminants in sediments from Lake Ketelmeer, The Netherlands. *Environ. Sci. Technol.* **2000,** *34* (9), 1620-1626.

(9) Gschwend, P. M.; Macfarlane, J. K.; Reible, D. D.; Lu, X.; Hawthorne, S. B.; Nakles, D. V.; Thompson, T. Comparison of polymeric samplers for accurately assessing PCBs in pore waters. *Environ. Tox. Chem.* **2011,** *30* (6), 1288-1296.

(10) Booij, K.; Robinson, C. D.; Burgess, R. M.; Mayer, P.; Roberts, C. A.; Ahrens, L.; Allan, I. J.; Brant, J.; Jones, L.; Kraus, U. R.; Larsen, M. M.; Lepom, P.; Petersen, J.; Pröfrock, D.; Roose, P.; Schäfer, S.; Smedes, F.; Tixier, C.; Vorkamp, K.; Whitehouse, P. Passive Sampling in Regulatory Chemical Monitoring of Nonpolar Organic Compounds in the Aquatic Environment. *Environ. Sci. Technol.* **2016,** *50* (1), 3-17.

(11) Smedes, F.; Van Vliet, L. A.; Booij, K. Multi-ratio equilibrium passive sampling method to estimate accessible and pore water concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in sediment. *Environ. Sci. Technol.* **2013,** *47* (1), 510-517.

(12) Apell, J. N.; Gschwend, P. M. Validating the use of performance reference compounds in passive samplers to assess porewater concentrations in sediment beds. **2014,** *48* (17), 10301-10307.

(13) Fernandez, L. A.; Harvey, C. F.; Gschwend, P. M. Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals. **2009,** *43* (23), 8888-8894.

(14) Vrana, B.; Smedes, F.; Prokeš, R.; Loos, R.; Mazzella, N.; Miege, C.; Budzinski, H.; Vermeirssen, E.; Ocelka, T.; Gravell, A.; Kaserzon, S. An interlaboratory study on passive sampling of emerging water pollutants. *TrAC, Trends Anal. Chem.* **2016,** *76*, 153-165.

(15) Booij, K.; Smedes, F.; Crum, S. Laboratory performance study for passive sampling of nonpolar chemicals in water. *Environ. Tox. Chem.* **2017,** *36* (5), 1156-1161.

(16) Hawthorne, S. B.; Jonker, M. T. O.; Van Der Heijden, S. A.; Grabanski, C. B.; Azzolina, N. A.; Miller, D. J. Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Environ. Sci. Technol.* **2011,** *83* (17), 6754-6761.

(17) Jonker, M. T. O.; Van Der Heijden, S. A.; Kotte, M.; Smedes, F. Quantifying the effects of temperature and salinity on partitioning of hydrophobic organic chemicals to silicone rubber passive samplers. *Environ. Sci. Technol.* **2015,** *49* (11), 6791-6799.

Appendices

Appendix 1:

Physico-chemical characteristics of the test sediments.[a]

	BB sediment	FD sediment	SP sediment
Dry weight (%)	53.5 ± 0.03	52.2 ± 0.05	55.0 ± 0.18
f_{oc} (fraction organic carbon) [b]	4.29 ± 0.07	2.31 ± 0.14	1.40 ± 0.10
Phenanthrene	1507 ± 68	590 ± 213	505 ± 10
Anthracene	918 ± 9	204 ± 32	333 ± 4
Fluoranthene	2888 ± 139	1821 ± 493	812 ± 32
Pyrene	2236 ± 118	1338 ± 330	698 ± 24
Benz[a]anthracene	1884 ± 87	1006 ± 133	654 ± 21
Chrysene	1474 ± 67	803 ± 97	605 ± 21
Benzo[*e*]pyrene	1286 ± 41	835 ± 88	636 ± 9
Benzo[*b*]fluoranthene	1579 ± 58	1044 ± 102	642 ± 10
Benzo[*k*]fluoranthene	747 ± 33	507 ± 54	536 ± 6
Benzo[*a*]pyrene	1399 ± 65	1004 ± 126	579 ± 19
Benzo[*g,h,i*]perylene	1079 ± 35	837 ± 113	591 ± 8
Dibenz[*a,h*]anthracene	142 ± 6	105 ± 8	443 ± 6
Indeno[123-*cd*]pyrene	996 ± 67	687 ± 75	560 ± 8
PCB-18	34 ± 1	10 ± 1	266 ± 5
PCB-28	61 ± 4	44 ± 4	265 ± 6
PCB-52	66 ± 1	489 ± 28	276 ± 6
PCB-66	*n.d.*	*n.d.*	290 ± 12
PCB-77	*n.d.*	*n.d.*	277 ± 12
PCB-101	66 ± 1	1902 ± 115	301 ± 12
PCB-118	37 ± 0	678 ± 55	294 ± 14
PCB-138	58 ± 0	5913 ± 895	279 ± 14
PCB-153	64 ± 1	6274 ± 966	271 ± 13
PCB-170	19 ± 0	2315 ± 558	281 ± 14
PCB-180	26 ± 1	4204 ± 915	275 ± 14
PCB-187	21 ± 0	1454 ± 282	271 ± 13

[a] *Concentrations of target chemicals are in µg/kg;* [b] *Values are multiplied by 100; n.d.: not detected.*

Appendix 2:

Material and methods applied by the 11 participants of the inter-laboratory comparison study *in the first experiment* (C_{free} determinations according to own procedures); presented in an anonymous way (participant A-K).

Participant A	
Equilibration:	
Equilibration system	Jar, amber, 250 mL, Teflon-lined stopper
Mass of sediment per system (g)	100
Aqueous solution added (Y/N)	Y
Composition of aqueous solution (biocide, salts)	1 g/L NaN_3 solution (100 mL per sample)
Pre-cleaning procedure sampler	Wash the samplers by rolling in a bottle (@ 2 rpm) with hexanes (mixture of isomers) – 24 hr, then acetone – 30 min, then water – 30 min. Remove moisture using Kimwipes and further dry at 60°C for 4 hr.
Mass (or length for SPME; cm) of sampler (mg) for each sediment	two pieces of approx. 30 mg PE per jar (ca. 60 mg per jar)
Equilibration: static or dynamic	Dynamic
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	1D shaker
Speed of shaker (rpm)	150
Equilibration time (days)	125
PRCs added (Y/N). If yes, which ones	Y; For PCBs: PCB 29, 69, 103, 155, 192. For PAHs: d10-flurene, d10-fluoranthene, d12-perylene.
Time series to confirm equilibration (Y/N). If yes: which time points	N
Equilibration temperature (°C ± ..)	20±2
Precautions taken against exposure to light	Used amber glasswares throughout the experiment for PAH samples
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	In a 40 mL amber vial, added 40 mL hexane (mixture of isomers) & rolled @ 2 rpm for 24 hrs. Repeated the procedure once and combined the extracts. The remaining vial and PSM were rinsed twice with hexane.
Clean-up (Y/N)	Y
If clean-up: brief description (sorbent material, solvent, etc)	i) For PAHs (EPA Method 3630C) – the extract in hexane was concentrated and exchanged to cyclohexane (~ 2 mL). The cyclohexane extract was introduced to an activated silica gel column, and after flushing the column with pentane, the PAHs attached to the silica gel were eluted using 3:2 pentane/methylene chloride. ii) For PCBs (EPA Method 3660B & 3630C) –

	the extract in hexane was concentrated to ~2 mL. Activated copper was added to each sample to remove sulfur species. The extract was introduced to a 3% deactivated silica gel column and hexane was used to elute the PCBs from the column.
If clean-up: recoveries and blanks determined (Y/N) and how	Y Spiked surrogate standards at the beginning of the extraction procedure. The recoveries were checked for all samples. Data were accepted when the surrogate recovery was 50-120%. Surrogate standards used: 2-fluorobiphenyl & d-terphenyl for PAHs; PCB 14 & 65 for PCBs.
Data corrected for blanks and recoveries (Y/N)	N
Final solvent after clean-up (injection solvent)	PAHs: methylene chloride PCBs: hexane (mixture of isomers)
Volume of final extract (solvent) (mL)	1
Type of autosampler vial (volume; clear, amber)	2 mL; amber for PAHs & clear for PCBs
Analysis/calculation:	
Internal standard(s) used (Y/N)	Y
If internal standard(s): specify	PAHs: d8-naphthalene, d10-acenaphthene, d10-anthracene, d10-pyrene, d12-chrysene, d12-benzo[a]pyrene; PCBs: PCB 30 & 204
Analysis technique used for PAHs (+ detection)	GC-MS (selective ion monitoring mode)
Brief description of column, injection technique, temperature program/gradient, length of run, etc	Column: HP-5MS, 30 m x 0.25 mm ID, 0.25 μm film thickness. Injection: splitless, 1.0 μL. Temperature: Hold @ 60°C for 2 min, ramp @ 6°C/min to 258°C, ramp @ 2°C/min to 300°C, hold @ 300°C for 4 min. Length of run: 60 min.
Analysis technique used for PCBs (+ detection)	GC (+ μECD)
Brief description of column, injection technique, temperature program, length of run, etc	Column: DB-5MS, 60 m x 0.25 mm ID, 0.25 μm film thickness. Injection: splitless, 2.0 μL. Temperature: Start @ 100°C, ramp @ 1.5°C/min to 270°C, ramp @ 15°C to 280°C, Hold @ 280°C for 15 min. Length of run: 129 min.
Automatic or manual integration of chromatograms	PAHs – manual PCBs – automatic with full review of the chromatograms (manual integration if needed)
PRC data used for calculation of C_{free} (Y/N)	N
Reference for PRC calculation method	NA

Participant B	
Equilibration:	
Equilibration system	Jar, amber, 120 mL, aluminum foil lined cap

Mass of sediment per system (g)	Approximately 90 mL (~80 g)
Aqueous solution added (Y/N)	N
Composition of aqueous solution (biocide, salts)	-
Pre-cleaning procedure sampler	Samplers were rinsed in DCM twice, Methanol twice, and Milli-Q water twice for at least 24 hours in each rinse. The samplers were stored in Milli-Q water afterward.
Mass (or length for SPME; cm) of sampler (mg) for each sediment	~25 mg PE; ~100 mg POM
Equilibration: static or dynamic	Static
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	-
Speed of shaker (rpm)	-
Equilibration time (days)	42 days
PRCs added (Y/N). If yes, which ones	Y (PCBs – 28, 52, 118, 128; PAHs – d10 pyrene, d10 phenanthrene, d12 chrysene).
Time series to confirm equilibration (Y/N). If yes: which time points	N
Equilibration temperature (°C ± ..)	20.6°C
Precautions taken against exposure to light	Stored in dark (cardboard boxes); hood light left off.
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	Samplers were removed from sediment with DCM-cleaned tweezers and rinsed with millipore water. Then they were wiped with a kimwipe and place in a cleaned (DCM and methanol rinsed x3) foiled amber vial. Recovery compounds (100 ng of d10-anthracene, d10-fluoranthene, and d12-benz(a)anthracene in 100 µL of DCM) we added to the PE in the vial and allowed to dry. High purity DCM was then added to cover sampler (~15 mL). Samplers were placed on an orbital shaker (80 rpm) for 3 days. Vials were removed and DCM was transferred to cleaned and foiled amber vials. The original sampler vials were filled again with high purity DCM to cover sampler and returned to the shaker. The combined extracts were blown down with ultra high purity nitrogen. The process was repeated twice more with at least a 24 hour wait time in between. The vials with DCM were blown down to approximately 1 mL. The solution was then transferred to amber 2 mL autosampler vial using glass pipettes. The autosampler vials were labelled and placed in the freezer.
Clean-up (Y/N)	N
If clean-up: brief description (sorbent material, solvent, etc)	-

If clean-up: recoveries and blanks determined (Y/N) and how	-
Data corrected for blanks and recoveries (Y/N)	Y; Surrogate Standards (PCBs 8, 77, 153; PAHs d10 anthracene, d12 fluoranthene, d12 benz[a]anthracene).
Final solvent after clean-up (injection solvent)	DCM
Volume of final extract (solvent) (mL)	1 mL nominally
Type of autosampler vial (volume; clear, amber)	Amber, 2 mL, PTFE Septum
Analysis/calculation:	
Internal standard(s) used (Y/N)	Y
If internal standard(s): specify	p-terphenyl-d14
Analysis technique used for PAHs (+ detection)	GC/MS/MS
Brief description of column, injection technique, temperature program/gradient, length of run, etc	Column – Thermo Scientific TG – 5MS, L 30M, ID 0.25 mM, Film 0.25 um; Splitless, PTV injector; Oven temperature program: initial temp: 70ºC, raised 20ºC/min to 180ºC, then 6ºC/min to 300ºC and held for 7.5 min.
Analysis technique used for PCBs (+ detection)	GC/MS/MS
Brief description of column, injection technique, temperature program, length of run, etc	Column – Thermo Scientific TG – 5MS, L 30M, ID 0.25 mm, Film 0.25 um; Splitless, PTV injector; Oven temperature program: initial temp: 70ºC, raised 20ºC/min to 180ºC, then 6ºC/min to 300ºC and held for 7.5 min.
Automatic or manual integration of chromatograms	Manual
PRC data used for calculation of C_{free} (Y/N)	Y
Reference for PRC calculation method	Fernandez et al., *ES&T*, 43, 8888-8894.

Participant C	
Equilibration:	
Equilibration system	Jar, amber, 250 mL, PTFE-lined lid
Mass of sediment per system (g)	100
Aqueous solution added (Y/N)	Y
Composition of aqueous solution (biocide, salts)	Sodium azide
Pre-cleaning procedure sampler	Soaking in hexane-acetone over night
Mass (or length for SPME; cm) of sampler (mg) for each sediment	40 mg POM
Equilibration: static or dynamic	dynamic
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	TCLP
Speed of shaker (rpm)	28
Equilibration time (days)	32 days
PRCs added (Y/N). If yes, which ones	Y. pyrene-d10
Time series to confirm equilibration (Y/N). If yes: which time points	N
Equilibration temperature (°C ± ..)	25°C

Precautions taken against exposure to light	Dark room. Amber glass.
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	Passive samplers were extracted with 1:1 hexane and acetone mixtures (3 × 24 h, with sequential extracts pooled). Prior to extraction phenanthrene-d10 surrogate was added to assess the effectiveness of sample processing. The final extraction volume was concentrated to 10mL. 1mL of this volume was analyzed for PCBs. The rest was concentrated to 1mL and analyzed for PAHs
Clean-up (Y/N)	N
If clean-up: brief description (sorbent material, solvent, etc)	-
If clean-up: recoveries and blanks determined (Y/N) and how	-
Data corrected for blanks and recoveries (Y/N)	Y
Final solvent after clean-up (injection solvent)	Hexane-acetone
Volume of final extract (solvent) (mL)	1 mL
Type of autosampler vial (volume; clear, amber)	clear
Analysis/calculation:	
Internal standard(s) used (Y/N)	Y
If internal standard(s): specify	Fluoronaphthalene, p-terphenyl-d14, Benzo(a)pyrene-d12, Dibenz(a,h)anthracene-d14.
Analysis technique used for PAHs (+ detection)	gas chromatography with mass detection (Agilent 6890 gas chromatograph coupled to an Agilent 5973N MS detector)
Brief description of column, injection technique, temperature program/gradient, length of run, etc	GC-MS is equipped with a fused silica capillary column (HP-5, 60m x 250µm x 0.25µm). Oven temperature remains at 35 °C for 1 minute. Then it increases from 35 °C to 300 °C at 6°C /min, and maintains at 300°C for 20 minutes. The MS temperature is 300 ° C. Sample total run time is 65 minutes.
Analysis technique used for PCBs (+ detection)	gas chromatography with electron capture detection (an Agilent 6890N).
Brief description of column, injection technique, temperature program, length of run, etc	GC-ECD is equipped with a fused silica capillary column (HP-5, 60m x 250µm x 0.25µm). Oven temperature remains at 100 °C for 1 minute. Then it increases from 100 °C to 280 °C at 2°C /min, and then rises from 280 °C to 300°C at 10°C /min. The temperature is maintained at 300°C for 6 minutes. The detector temperature is 300 ° C. Sample total run time is 98 minutes.

Automatic or manual integration of chromatograms	manual
PRC data used for calculation of C_{free} (Y/N)	N
Reference for PRC calculation method	Although only %50 loss of PRCs was observed in samplers, no PRC correction was performed to calculate C_{free}. This is because the values of K_{POM} from Hawthorne et al., 2011 were obtained by shaking 76µm POM strips in contaminated sediments for 28 days (very similar condition to own experiment). Thus, K_{POM} values that are used here already account for the possible non-equilibration.

Participant D	
Equilibration:	
Equilibration system	Jar, amber, 125 mL, aluminum foil-lined Teflon
Mass of sediment per system (g)	mass sent by coordinating lab split into 5
Aqueous solution added (Y/N)	N
Composition of aqueous solution (biocide, salts)	n/a
Pre-cleaning procedure sampler	Soak (24 h) twice with DCM, twice with methanol, soaked (>2 weeks) in methanol:water PRC solution, and soaked (24 h) twice with pure water
Mass (or length for SPME; cm) of sampler (mg) for each sediment	~20 mg PE for PCBs and ~15 mg for PAHs
Equilibration: static or dynamic	static
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	n/a
Speed of shaker (rpm)	n/a
Equilibration time (days)	56 days
PRCs added (Y/N). If yes, which ones	Yes, labelled PCBs (13C 28, 47, 54, 97, 111, 153, and 178) or PAHs (phenanthrene-d10, pyrene-d10, chrysene-d12)
Time series to confirm equilibration (Y/N). If yes: which time points	no
Equilibration temperature (°C ± ..)	Room temperature, usually about 21 °C
Precautions taken against exposure to light	In amber jars, placed in container covered with foil while experiment was going on
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	Wipe PE with kimwipe, place in amber vial, spike with surrogate standard, extract 3 times with DCM, combine extract in combusted round bottom flask, evaporate to 1 mL by heating solvent and allowing vapor go through a chilled condenser column while under vacuum, quantitative transfer to 4 mL vial, evaporate under N2 line to 0.1 mL and solvent exchange

	to hexane, quantitative transfer to small volume insert of autosampler, spike with injection standards
Clean-up (Y/N)	no
If clean-up: brief description (sorbent material, solvent, etc)	n/a
If clean-up: recoveries and blanks determined (Y/N) and how	n/a
Data corrected for blanks and recoveries (Y/N)	yes
Final solvent after clean-up (injection solvent)	hexane
Volume of final extract (solvent) (mL)	~ 0.05-0.3 mL, calculated using injection standards
Type of autosampler vial (volume; clear, amber)	2 mL amber, Agilent brand with Teflon septa screw caps
Analysis/calculation:	
Internal standard(s) used (Y/N)	yes
If internal standard(s): specify	PCBs (non-labelled 39, 55, 104, 150, 188) and PAHs (acenaphthene-d10, m-terphenyl, perylene-d12)
Analysis technique used for PAHs (+ detection)	High res GC, low res MS
Brief description of column, injection technique, temperature program/gradient, length of run, etc	60 m DB-5MS, splitless; operated in 'selected ion monitoring'. Injection port: 305 C; Program: 67C, ramp at 15C to 180C, ramp at 4C to 315C, hold for 5.7 min; total run time 47 min. Flow: 2 mL/min.
Analysis technique used for PCBs (+ detection)	Same as above
Brief description of column, injection technique, temperature program, length of run, etc	Injection port: 280 C; Program: 67C, ramp at 25C to 188C, ramp at 1.5C to 276C, ramp at 25C to 300C, hold for 1 min. Flow: 1 mL/min
Automatic or manual integration of chromatograms	Automatic integration by program, manual selection of peak area to integrate
PRC data used for calculation of C_{free} (Y/N)	Yes. Only PRCs with 10-90% remaining in the PE were used. Generally, I could use 5 PCB congeners – except for the SP samples that went dry during nitrogen blowdown (PCB 28 could not be used). There were only 3 PRCs for the PAHs (imitating earlier work like Fernandez & Gschwend 2009). Phenanthrene always had <10% remaining, so only 2 PRCs were used to correct PAHs – this leads to more variability in PRC corrections than were seen for the PCBs.
Reference for PRC calculation method	Apell and Gschwend 2014 (ES&T) – used the GUI for PRC correction.

Participant E	
Equilibration:	
Equilibration system	Vial, amber, 15 mL for SPME; bottle, amber,

	120 mL for sheets
Mass of sediment per system (g)	Approx. 8 for SPME and 60 for sheets (ww)
Aqueous solution added (Y/N)	Y
Composition of aqueous solution (biocide, salts)	100 mg/L NaN3
Pre-cleaning procedure sampler	Shake with different solvents (depending on polymer) successively and store in water (fibers) or air-dry (sheets)
Mass (or length for SPME; cm) of sampler (mg) for each sediment	2-30 cm fiber (depending on sediment and coating); 2.5-30 mg sheet (depending on sediment and polymer)
Equilibration: static or dynamic	Dynamic
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	Rock & Roller for SPME, 1-D shaker for sheets
Speed of shaker (rpm)	60 for SPME; 150 for sheets
Equilibration time (days)	42
PRCs added (Y/N). If yes, which ones	N
Time series to confirm equilibration (Y/N). If yes: which time points	2, 4, 6, 9, 12 weeks
Equilibration temperature (°C ± ..)	20 ± 1 °C
Precautions taken against exposure to light	Amber glassware, dark room, covered box
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	Samplers were removed from the sediment slurry, cleaned with wet tissue, cut, and placed in autosampler vials containing acetonitrile. Internal standards were added and the vials were placed in the freezer. Prior to analysis, they were left at room temperature for several hours and vortexed for 1-4 min (depending on the sampler)
Clean-up (Y/N)	N
If clean-up: brief description (sorbent material, solvent, etc)	-
If clean-up: recoveries and blanks determined (Y/N) and how	-
Data corrected for blanks and recoveries (Y/N)	Y (blanks)
Final solvent after clean-up (injection solvent)	Acetonitrile
Volume of final extract (solvent) (mL)	0.2-0.5 (SPME), 1.0 for sheets
Type of autosampler vial (volume; clear, amber)	Amber, 1.8 mL (with 200 µL insert for SPME if necessary)
Analysis/calculation:	
Internal standard(s) used (Y/N)	Y
If internal standard(s): specify	PCB-209 and 2-methylchrysene
Analysis technique used for PAHs (+ detection)	HPLC-FLD
Brief description of column, injection technique, temperature program/gradient, length of run, etc	Twenty µL of sample were injected by a Varian Prostar 420 autosampler on a Vydac 201TP54 C_{18} column (25 cm; d.i. 4.2 mm; d.f. 5 µm; kept at 27.0 °C). The mobile phase consisted of

	methanol and water (mixture changing from 30:70 to 100:0; degassed by a Grace 590 degasser), and was pumped at a flow increasing from 0.7 to 1.5 mL/min by a Gynkotec P680HPG HPLC pump. Detection was performed by a Jasco FP-2020 Plus fluorescence detector (programmed to measure at different excitation/emission wavelength combinations and detector gain for different PAHs)
Analysis technique used for PCBs (+ detection)	GC-ECD
Brief description of column, injection technique, temperature program, length of run, etc	One μL of sample was injected in the split mode (split ratio 12) by a TriPlus autosampler on a Zebron ZB-5MSi column (Phenomenex; 30 m, 0.25 mm i.d., 0.25 μm f.t.). Temperature program of the Thermo Trace GC Ultra: 185 °C (0 min); 2.5 °/min to 240 (0 min); 15 °/min to 300 (3 min). Carrier gas: He, at a rate of 1.2 mL/min. Detector temp of the ECD: 365 °C.
Automatic or manual integration of chromatograms	Manual
PRC data used for calculation of C_{free} (Y/N)	N
Reference for PRC calculation method	-

Participant F	
Equilibration:	
Equilibration system	Jar, tin foil wrapped, 500 mL, Teflon lid
Mass of sediment per system (g)	50 g dry basis
Aqueous solution added (Y/N)	Y
Composition of aqueous solution (biocide, salts)	NaN3
Pre-cleaning procedure sampler	In acetone and n-hexane for 24 hours each
Mass (or length for SPME; cm) of sampler (mg) for each sediment	400-1200 mg PE
Equilibration: static or dynamic	dynamic
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	Orbital table shaker
Speed of shaker (rpm)	120
Equilibration time (days)	90 days
PRCs added (Y/N). If yes, which ones	Yes, three. Fluorene-d10, pyrene-d10, benzo(a)pyrene-d12, Dibromobiphenyl, tetrabromobiphenyl, pentabromobiphenyl, octachloronaphthalene
Time series to confirm equilibration (Y/N). If yes: which time points	no
Equilibration temperature (°C ± ..)	20
Precautions taken against exposure to light	Jars covered with tin foil

Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	Cold extraction using n-hexane for 24 hours, then solvent reduction using a turbovap (set at 30 ^{0}C and the nitrogen at 5 psi)
Clean-up (Y/N)	yes
If clean-up: brief description (sorbent material, solvent, etc)	SPE cartridge (1 g silica gel), elution with n-hexane/DCM (70:30)
If clean-up: recoveries and blanks determined (Y/N) and how	yes
Data corrected for blanks and recoveries (Y/N)	yes
Final solvent after clean-up (injection solvent)	n-hexane/nonane
Volume of final extract (solvent) (mL)	0.05
Type of autosampler vial (volume; clear, amber)	(2.0 mL amber vials and samples were in glass inserts 50 uL volume)
Analysis/calculation:	
Internal standard(s) used (Y/N)	Y
If internal standard(s): specify	p-terphenyl-d14 for PAHs and 2,4,6-tribromobiphenyl for PCBs (those are injection standards), $^{13}C_{12}$ PCB 8, 18, 52, 118, 138, 180, 209. Acenaphthene-d10; Phenanthrene-d10; Chrysene-d12 and perylene-d12. The labeled PCBs and deuterated PAHs were used as surrogates in the own experiment only,
Analysis technique used for PAHs (+ detection)	GC/MS in the SIM mode
Brief description of column, injection technique, temperature program/gradient, length of run, etc	DB5-MS 30 m x 0.25 x 0.25, autoinjection of 1 uL in the splitless mode
Analysis technique used for PCBs (+ detection)	Same as PAHs
Brief description of column, injection technique, temperature program, length of run, etc	Same as PAHs but with a different temperature program
Automatic or manual integration of chromatograms	Manual integration
PRC data used for calculation of C_{free} (Y/N)	Y
Reference for PRC calculation method	An improved method for estimating in situ sampling rates of nonpolar passive samplers. ES&T 44, 2010, 6789-6794.

Participant G	
Equilibration:	
Equilibration system	Scintillation vial, clear, 20 mL, plastic-lined cap
Mass of sediment per system (g)	~10 g (wet weight)
Aqueous solution added (Y/N)	Y
Composition of aqueous solution (biocide, salts)	10 mL moderately hard water, 3 mL, 3 mg/mL $HgCl_2$
Pre-cleaning procedure sampler	none

Mass (or length for SPME; cm) of sampler (mg) for each sediment	30 cm fiber
Equilibration: static or dynamic	Dynamic
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	Rock & Roller
Speed of shaker (rpm)	100 rpm
Equilibration time (days)	42 d
PRCs added (Y/N). If yes, which ones	N
Time series to confirm equilibration (Y/N). If yes: which time points	Y, 21, 28, 42 d
Equilibration temperature (°C ± ..)	25 ± 1°C
Precautions taken against exposure to light	Covered the vials in foil
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	Fibers were held in 4 mL of hexane for 48 h, the hexane was removed, concentrated to 0.75 mL, transferred to GC vials for analysis
Clean-up (Y/N)	Y
If clean-up: brief description (sorbent material, solvent, etc)	Hexane
If clean-up: recoveries and blanks determined (Y/N) and how	Surrogates, 50 ng of 4,4'-dibromooctafluoro-biphenyl (DBOFB) and decachlorobiphenyl (DCBP) were added prior to concentration of hexane used to extract SPME fibers
Data corrected for blanks and recoveries (Y/N)	N
Final solvent after clean-up (injection solvent)	Hexane
Volume of final extract (solvent) (mL)	1 mL
Type of autosampler vial (volume; clear, amber)	1.5 mL amber GC vial
Analysis/calculation:	
Internal standard(s) used (Y/N)	Y
If internal standard(s): specify	Chrysene d12, Perylene d12
Analysis technique used for PAHs (+ detection)	GC-MS
Brief description of column, injection technique, temperature program/gradient, length of run, etc	HP-5MS 5% Phenyl Methyl Siloxane 30 m Column, 0.25 µm film thickness, pulsed splitless injection, 100°C (hold 1 min) to 205°C at 10°C/min, 205°C to 230°C at 2°C/min, 230°C to 270°C 5°C/min (hold 13.5 min); 45.50 minute run
Analysis technique used for PCBs (+ detection)	GC-MS
Brief description of column, injection technique, temperature program, length of run, etc	Same as PAHs
Automatic or manual integration of chromatograms	Manual
PRC data used for calculation of C_{free} (Y/N)	N
Reference for PRC calculation method	N/A

Participant H	
Equilibration:	
Equilibration system	Scintillation vial, amber, 20 mL, Teflon-lined cap
Mass of sediment per system (g)	20 wet weight
Aqueous solution added (Y/N)	N
Composition of aqueous solution (biocide, salts)	N
Pre-cleaning procedure sampler	pre-cleaned by sonication with methylene chloride, methanol, and deionized water for 15 min in each solvent.
Mass (or length for SPME; cm) of sampler (mg) for each sediment	5 mg PE
Equilibration: static or dynamic	dynamic
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	Barnstead Thermolyne M49235 Bigger Bill orbital platform shaker
Speed of shaker (rpm)	175
Equilibration time (days)	15
PRCs added (Y/N). If yes, which ones	Y. 13C PCB28, 13C PCB52, 13C PCB118, 13C PCB128, 13C p,p'-DDE, 13C p,p'-DDD
Time series to confirm equilibration (Y/N). If yes: which time points	Y. 3, 12, and 15 d
Equilibration temperature (°C ± ..)	22°C ±1
Precautions taken against exposure to light	No, due to the amber vial.
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	The PED is extracted by dichloromethane (DCM). Before extraction, spike surrogate solution on each piece of PED. The PED is extracted three times in DCM by sonication for 15 min. Combine the extracts, concentrate and exchange solvent into hexane. The volume of the extract was blown down to 0.2mL, add internal standard for GC/EI-MS analysis.
Clean-up (Y/N)	N
If clean-up: brief description (sorbent material, solvent, etc)	NA
If clean-up: recoveries and blanks determined (Y/N) and how	NA
Data corrected for blanks and recoveries (Y/N)	N
Final solvent after clean-up (injection solvent)	Hexane
Volume of final extract (solvent) (mL)	0.2
Type of autosampler vial (volume; clear, amber)	1.5 mL clear vial with 200 uL insert
Analysis/calculation:	
Internal standard(s) used (Y/N)	Y
If internal standard(s): specify	2-Fluorobiphenyl-d14(PAH2 IS 1) p-Terphenyl-d14 (PAHs IS2) PCB30 (IS1-PCB)

	PCB205 (IS2-PCB)
Analysis technique used for PAHs (+ detection)	GC/EI-MS. PAHs and PCBs are analyzed together in one injection.
Brief description of column, injection technique, temperature program/gradient, length of run, etc	DB-XLB column (30m × 0.25mm × 0.25 μm, Agilent J&W Scientific, Santa Clara, CA, USA); The split/splitless inlet is operated isothermally at 300ºC in 1-min splitless mode for the PE analysis. Injection volume is 1 uL. The oven temperature is programmed from 80°C held for 1 min to 190°C at 5°C/min, to 260 °C at 4°C/min, to 290°C at 20°C/min, and to 300°C at 50°C/min held for 20 min. The running time is 67 min.
Analysis technique used for PCBs (+ detection)	See above
Brief description of column, injection technique, temperature program, length of run, etc	See above
Automatic or manual integration of chromatograms	manual integration
PRC data used for calculation of C_{free} (Y/N)	Y
Reference for PRC calculation method	Own method (to be published).

Participant I	
Equilibration:	
Equilibration system	Glass flask, clear, 50 mL, glass stopper
Mass of sediment per system (g)	5
Aqueous solution added (Y/N)	Y
Composition of aqueous solution (biocide, salts)	40 ml water spiked with sodium azide, amount of sodium azide added 1% by water volume from a 20 g/L stock
Pre-cleaning procedure sampler	Submerging the materials 24 h in each solvent (hexane, methanol, deionized water) and then allowed to dry at 20 °C for 12 h between each solvent rinse. After last 24 h rinse in deionized water, 4 x rinse in smaller volumes of deionized water.
Mass (or length for SPME; cm) of sampler (mg) for each sediment	100 mg
Equilibration: static or dynamic	Dynamic
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	End-over-end
Speed of shaker (rpm)	7-10 rpm
Equilibration time (days)	28
PRCs added (Y/N). If yes, which ones	N
Time series to confirm equilibration (Y/N). If yes: which time points	N
Equilibration temperature (°C ± ..)	22-23 °C
Precautions taken against exposure to light	Flasks wrapped and packed in box during

	equilibration
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	Place the clean PE or POM in a 50 ml glass flask with glass stopper for extraction, add 20 ml of an 80:20 mixture of heptane:acetone. Add surrogate standard, shake for 2 days (orbital shaker at 100 rpm). Remove sampler from the solvent. Reduce the volume of solvent with evaporation until approximately 1 ml.
Clean-up (Y/N)	Y
If clean-up: brief description (sorbent material, solvent, etc)	Silica gel clean up (modified Silica gel clean-up method 3630C (USEPA)). Preclean the silica column with heptane. After the sample has completely entered the silica column (achieved by pipetting the approximately 1 ml from the above extraction method), elute the column with 10 ml heptane. Rinse the glass vial that contained the sample with a few ml of heptane in order that the entire sample is transferred to the column
If clean-up: recoveries and blanks determined (Y/N) and how	Y, using blank samples and by spiking internal standard (PCB77) in order to look at the recovery of the process.
Data corrected for blanks and recoveries (Y/N)	Y
Final solvent after clean-up (injection solvent)	heptane
Volume of final extract (solvent) (mL)	0.7 ml
Type of autosampler vial (volume; clear, amber)	1.5 ml clear glass
Analysis/calculation:	
Internal standard(s) used (Y/N)	Y
If internal standard(s): specify	PCB77
Analysis technique used for PAHs (+ detection)	GCMS to 0,001 ug/ml
Brief description of column, injection technique, temperature program/gradient, length of run, etc	Agilent 6850 Gas Chromatograph equipped with a Agilent DB-XLB Column (length 30 m, 0.25 mm id and 0.1 lm film thickness, TeknoLab, Kolbotn, Norway) with a flow of 1 mL min_1 and the following temperature program: 2 min at 50 °C, to 150 °C at 10 °C min-1, to 280 °C at 5°C min-1, 9 min at 280 °C, to 310 °C with 40°C min-1, at 310 °C for 8 min. Detection was performed with an Agilent 5973 mass spectrometer in the electron impact mode with a 70 eV ionisation energy and a dwelling time of 25 ms. Identification of the PAH was assured by using two compound-specific ions: a quantifier ion corresponding to the respective molecular weight (m/z=M+) and a qualifier ion ([M_2H]+ for analytes and [M_2D]+ for internal

	standards) with a mass ratio similar to the one determined in the calibration
Analysis technique used for PCBs (+ detection)	GCMS 0,0001 ug/ml
Brief description of column, injection technique, temperature program, length of run, etc	As above
Automatic or manual integration of chromatograms	Manual
PRC data used for calculation of C_{free} (Y/N)	N
Reference for PRC calculation method	-

Participant J	
Equilibration:	
Equilibration system	Jar, amber, 20 or 40 mL, Teflon-lined cap
Mass of sediment per system (g)	Approx 20 (SPME) or 10 (POM) g
Aqueous solution added (Y/N)	N for SPME; Y for POM
Composition of aqueous solution (biocide, salts)	POM: Sodium azide 100 mg/L + 0.01 M calcium chloride
Pre-cleaning procedure sampler	SPME: Soak in hexane for 1 hour, soak in acetonitrile for 1 hour, soak in Millipore water for 1 hour, blot dry with lint free tissue. POM: 1× n-hexane + 3 × methanol wash
Mass (or length for SPME; cm) of sampler (mg) for each sediment	2 cm fibers; 5 mg POM for PAH and 40 mg for PCBs
Equilibration: static or dynamic	Dynamic
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	2D Shaker
Speed of shaker (rpm)	60 rpm for SPME; 160 for POM
Equilibration time (days)	20 days for SPME; 32 days for POM
PRCs added (Y/N). If yes, which ones	Y (fluoranthene-d10, chrysene-d12, benzo(b)fluoranthene-d12, dibenz(a,h)anthracene-d14, PCB 209)
Time series to confirm equilibration (Y/N). If yes: which time points	N
Equilibration temperature (°C ± ..)	Approx 25°C for SPME, 20 °C for POM
Precautions taken against exposure to light	Amber vials and aluminum foil on top of batch box for POM
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	Fibers were removed from sediment and wiped with a damp lint free tissue, cut with a ceramic column cutter into 1 cm segments, and placed in 150 µL of solvent (acetonitrile for PAH analysis/hexane for PCB analysis). The fibers were left in the solvent for 1 day (previous time series shows that desorption of the compounds from the PDMS layer occurs in less than a minute) before analysis.

	POM strips approx. 5 mg each for PAH analysis were removed from sediment, rinsed with MiliQ water and wiped with a damp lint free tissue, and placed in 250 µL of acetonitrile (in inserts). The samples were placed on a 2D shaker and mixed @ 160 rpm for 3 h. The POM strips were withdrawn from the inserts and the extracts were analyzed for PAHs using HPLC. POM strips for PCB analysis (40 mg) were removed from sediment, rinsed with MiliQ water and wiped with a damp lint free tissue. The samplers were placed in 40 mL vials containing 20 mL of hexane/acetone (1:1) and mixed @ 160 rpm for 3 h using the 2D shaker. Following this procedure the extracts were transferred to small volumetric flasks and reduced to 200 µL under gentle flow of nitrogen. The final extracts were transferred to 2 ml amber vials with 250 µL glass inserts and analyzed for PCB-12 using GC- µECD.
Clean-up (Y/N)	N
If clean-up: brief description (sorbent material, solvent, etc)	-
If clean-up: recoveries and blanks determined (Y/N) and how	-
Data corrected for blanks and recoveries (Y/N)	N
Final solvent after clean-up (injection solvent)	Acetonitrile for PAHs, hexane for PCBs
Volume of final extract (solvent) (mL)	0.15- 0.25 mL
Type of autosampler vial (volume; clear, amber)	2 ml amber vial with 250 µL glass insert
Analysis/calculation:	
Internal standard(s) used (Y/N)	N
If internal standard(s): specify	-
Analysis technique used for PAHs (+ detection)	LC with fluorescence
Brief description of column, injection technique, temperature program/gradient, length of run, etc	Column: Phenomenex; Temperature: Constant 40°C; Length of run: 42 min; Solvent: 70% Acetonitrile 30% Water @ 1 ml/min
Analysis technique used for PCBs (+ detection)	GC µECD
Brief description of column, injection technique, temperature program, length of run, etc	Agilent Technologies, HP-5, 30m x 0.320 mm x 0.25 micron, injection volume = 2 µL, mode: splitless, run time = 48 min, He@ 100 °C oven. Analysis of standards in hexane
Automatic or manual integration of chromatograms	Manual
PRC data used for calculation of C_{free} (Y/N)	Y
Reference for PRC calculation method	Lampert, D.J., Thomas, C., Reible, D.D., 2015. Internal and external transport significance for predicting contaminant uptake rates in passive samplers. Chemosphere 119, 910-916.

Participant K	
Equilibration:	
Equilibration system	Bottles, amber, 30-250 mL, alu foil-lined caps
Mass of sediment per system (g)	30-40 dw.
Aqueous solution added (Y/N)	Y
Composition of aqueous solution (biocide, salts)	1ml per g dry sediment of 1g NaN3/L (1mg NaN3per gram sediment)
Pre-cleaning procedure sampler	Wet tissue
Mass (or length for SPME; cm) of sampler (mg) for each sediment	25-30 mg
Equilibration: static or dynamic	dynamic
If dynamic: type of 'shaker' (e.g. tumbler/1D shaker/2D shaker/Rock&Roller)	2D shaker
Speed of shaker (rpm)	130
Equilibration time (days)	90
PRCs added (Y/N). If yes, which ones	Yes
Time series to confirm equilibration (Y/N). If yes: which time points	N
Equilibration temperature (°C ± ..)	Ambient ~20°C
Precautions taken against exposure to light	Placed in box
Extraction/clean-up:	
Brief extraction procedure (extraction method, equipment, solvent, time, etc)	First extraction overnight with 10 methanol , second with 30mL 30% acetone/methanol
Clean-up (Y/N)	Y
If clean-up: brief description (sorbent material, solvent, etc)	Florisil and elution with 15 mL 20 diethylether/hexane
If clean-up: recoveries and blanks determined (Y/N) and how	Blanks and recovery standards
Data corrected for blanks and recoveries (Y/N)	Not for blanks (except solvent blank) but yes for recovery standards
Final solvent after clean-up (injection solvent)	hexane
Volume of final extract (solvent) (mL)	1 or 5 or 10mL
Type of autosampler vial (volume; clear, amber)	amber
Analysis/calculation:	
Internal standard(s) used (Y/N)	Yes
If internal standard(s): specify	C13-PCBs and ….
Analysis technique used for PAHs (+ detection)	GCMS-EI
Brief description of column, injection technique, temperature program/gradient, length of run, etc	2 µL, splitless injection at 300°C, AT-5MS column, 30 m length, 0.25 mm internal diameter and 0.25 µm film thickness (Grace, USA). The PAH temperature program applied starts with 60°C (1 min hold), 10 °C/min to 100 °C, 20°C/min to 320°C for 9 minutes hold
Analysis technique used for PCBs (+ detection)	GC MSMS
Brief description of column, injection	Two µL were splitless injected at 280°C on an

technique, temperature program, length of run, etc	AT-5MS column of 30 m length, 0.25 mm internal diameter and 0.25 µm film thickness (Grace, USA).
Automatic or manual integration of chromatograms	Automatic with manual inspection
PRC data used for calculation of C_{free} (Y/N)	No, only for quality assurance, i.e. confirm non depletion and indication of equilibrium.
Reference for PRC calculation method	-

Appendix 3:

Determination of the actual coating thickness/volume of SPME fibers.

Fiber	Manufacturer provided (nominal) volume (L/cm)	Actual (measured) volume (L/cm)	% deviation
S10-1 (10 µm)	$6.912 \cdot 10^{-8}$	$7.821 \cdot 10^{-8}$	11.6
S10-2 (10 µm)	$6.912 \cdot 10^{-8}$	$6.654 \cdot 10^{-8}$	3.9
S30-1 (30 µm)	$1.329 \cdot 10^{-7}$	$1.142 \cdot 10^{-7}$	16.4
S30-2 (30 µm)	$5.904 \cdot 10^{-7}$	$5.704 \cdot 10^{-7}$	3.5
S100 (100 µm)	$9.425 \cdot 10^{-7}$	$9.421 \cdot 10^{-7}$	0.04
PAc (30 µm)	$1.536 \cdot 10^{-7}$	$1.408 \cdot 10^{-7}$	9.1

The accuracy of the nominal coating volume of the fiber-bound polymers (PDMS on the S10-1, S10-2, S30-1, S30-2, and S100 fibers and polyacrylate on the PAc fiber) was evaluated by determining the exact coating thickness of all fibers by microscopic measurements. Five pieces of 3 cm were cut from different positions of the stock fibers. They were sampled from either end and, if possible, from the middle. The pieces were cleaned with solvents and water according to the methods prescribed in the standardized protocol. Next, the coating of one half of each fiber piece was stripped with a razorblade. Here, it should be noted that the razor stripping did not affect the glass core, as thorough scraping was found to have no effect on its thickness. Subsequently, the pieces were examined at the largest magnification possible (100 - 400 x). After pulling the maximal width of the object into focus, the diameter of the coated and stripped parts were measured at 10 positions each with the assistance of microscopy software. After subtraction of the core diameter from the total diameter, the coating thickness was derived. The error of the measurements is estimated to be about 0.5 µm (based on full width of the fibers) (i.e., < 0.5%).

Appendix 4:

Concentration ranges (expressed as factors) in C_{free} values in the first experiment (measurements based on own procedures); i.e., highest (averaged) C_{free} for the respective chemical measured by a specific participant / lowest (averaged) C_{free} for that chemical (measured by another participant). Outliers are not excluded.

	BB sediment	**FD sediment**	**SP sediment**
Phenanthrene	32	15	15
Anthracene	6	8	9
Fluoranthene	10	10	10
Pyrene	10	7	9
Benz[a]anthracene	24	15	21
Chrysene	11	11	11
Benzo[*e*]pyrene	13	8	14
Benzo[*b*]fluoranthene	11	14	13
Benzo[*k*]fluoranthene	10	5	9
Benzo[*a*]pyrene	18	10	34
Benzo[*g,h,i*]perylene	13	21	20
Dibenz[*a,h*]anthracene	22	32	19
Indeno[123-*cd*]pyrene	10	14	13
PCB-18	7	14	67
PCB-28	26	16	68
PCB-52	9	9	14
PCB-66	32	53	20
PCB-77	98	2371	20
PCB-101	7	11	10
PCB-118	15	19	31
PCB-138	12	20	35
PCB-153	16	27	41
PCB-170	16	45	120
PCB-180	9	57	204
PCB-187	13	56	59

Appendix 5:

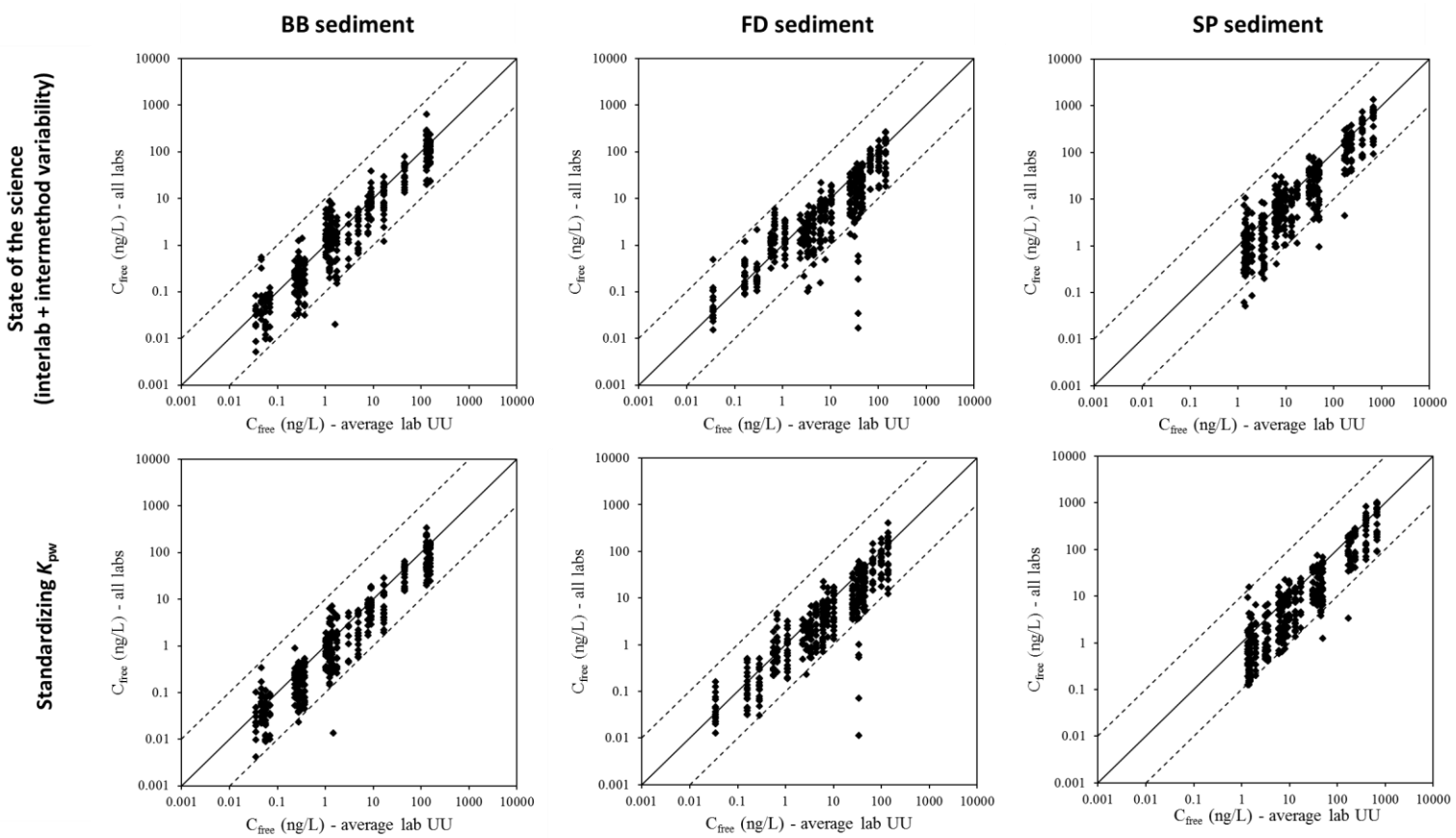
Summary of logarithmic polymer-water partition coefficients (logK_{pw}), as determined in the present project (ECO22.2).[a] Values are averages ± standard deviations for replicated measurements and pooled formats.

	PE	PDMS	POM	PAc
Phenanthrene	4.13 ± 0.03	3.78 ± 0.04	4.16 ± 0.01	4.93 ± 0.01
Anthracene	4.27 ± 0.03	3.88 ± 0.04	4.24 ± 0.01	5.01 ± 0.02
Fluoranthene	4.79 ± 0.03	4.23 ± 0.04	4.84 ± 0.01	5.59 ± 0.00
Pyrene	4.93 ± 0.03	4.30 ± 0.03	4.92 ± 0.01	5.67 ± 0.00
Benz[a]anthracene	5.60 ± 0.03	4.79 ± 0.04	5.65 ± 0.01	6.40 ± 0.01
Chrysene	5.60 ± 0.03	4.72 ± 0.04	5.68 ± 0.01	6.38 ± 0.01
Benzo[*e*]pyrene	6.26 ± 0.04	5.13 ± 0.04	6.12 ± 0.03	7.03 ± 0.05
Benzo[*b*]fluoranthene	6.33 ± 0.04	5.19 ± 0.05	6.26 ± 0.04	7.03 ± 0.05
Benzo[*k*]fluoranthene	6.44 ± 0.04	5.23 ± 0.04	6.39 ± 0.03	6.98 ± 0.03
Benzo[*a*]pyrene	6.47 ± 0.04	5.21 ± 0.04	6.39 ± 0.03	7.09 ± 0.04
Benzo[*g,h,i*]perylene	7.05 ± 0.06	5.51 ± 0.09	6.51 ± 0.11	7.65 ± 0.04
Dibenz[*a,h*]anthracene	7.00 ± 0.07	5.61 ± 0.08	6.47 ± 0.23	7.61 ± 0.16
Indeno[123-*cd*]pyrene	7.17 ± 0.07	5.54 ± 0.08	6.75 ± 0.10	7.60 ± 0.04
PCB-18	4.81 ± 0.03	4.99 ± 0.04	5.13 ± 0.02	5.72 ± 0.01
PCB-28	5.36 ± 0.03	5.22 ± 0.04	5.43 ± 0.01	6.01 ± 0.02
PCB-52	5.47 ± 0.04	5.50 ± 0.05	5.70 ± 0.02	6.32 ± 0.01
PCB-66	5.89 ± 0.05	5.66 ± 0.04	5.95 ± 0.01	6.56 ± 0.02
PCB-77	5.95 ± 0.04	5.54 ± 0.04	6.08 ± 0.02	6.70 ± 0.01
PCB-101	6.18 ± 0.05	5.98 ± 0.05	6.19 ± 0.03	6.81 ± 0.03
PCB-118	6.46 ± 0.06	6.05 ± 0.04	6.40 ± 0.03	6.98 ± 0.03
PCB-138	6.81 ± 0.08	6.43 ± 0.05	6.57 ± 0.06	7.30 ± 0.06
PCB-153	6.89 ± 0.08	6.43 ± 0.06	6.56 ± 0.06	7.21 ± 0.06
PCB-170	7.25 ± 0.12	6.72 ± 0.11	6.67 ± 0.11	7.46 ± 0.12
PCB-180	7.36 ± 0.12	6.73 ± 0.10	6.67 ± 0.11	7.40 ± 0.12
PCB-187	7.23 ± 0.12	6.76 ± 0.09	6.58 ± 0.08	7.40 ± 0.10

[a] Detailed methods and results will be presented in a future scientific paper (in preparation).

Appendix 6:

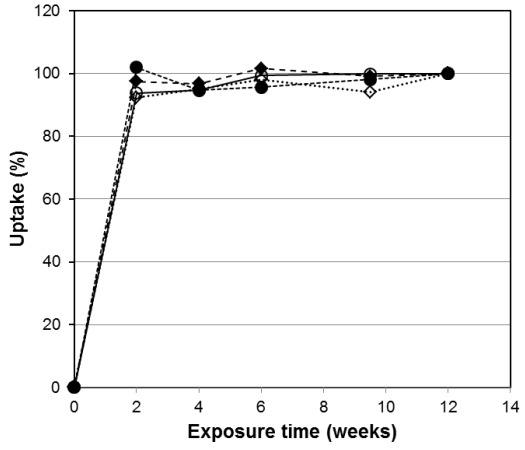
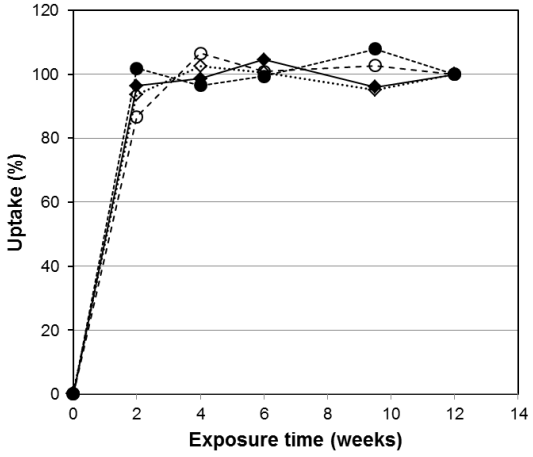
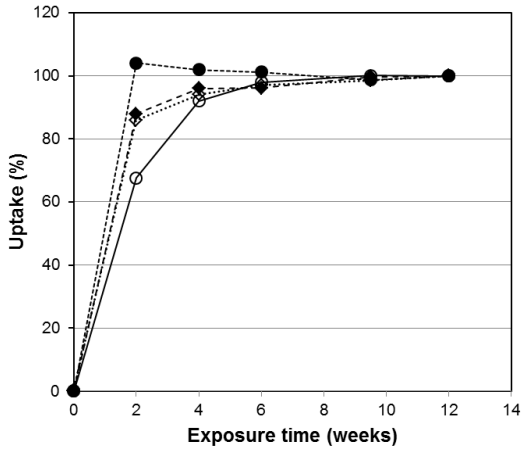
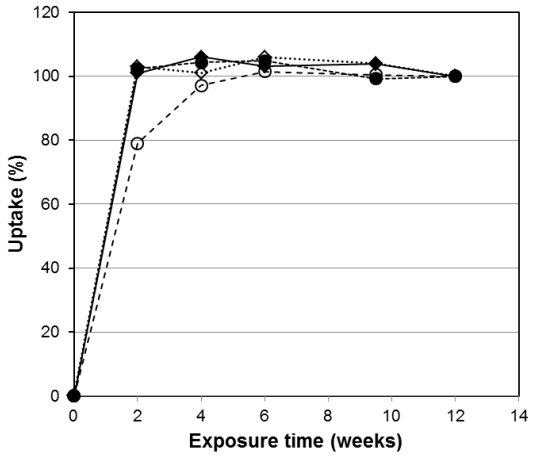
Effect of standardizing K_{pw} values on the inter-laboratory variability.

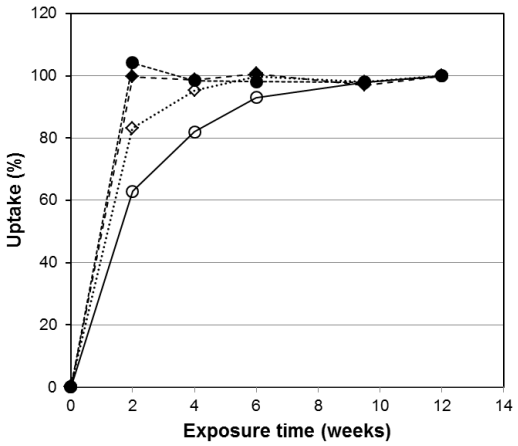
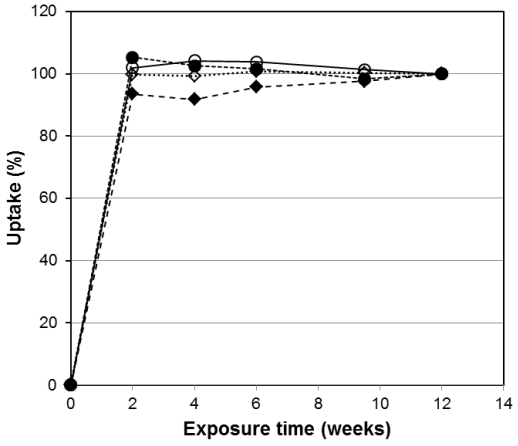
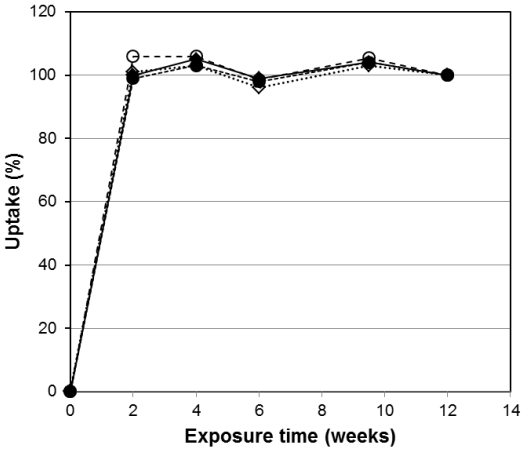
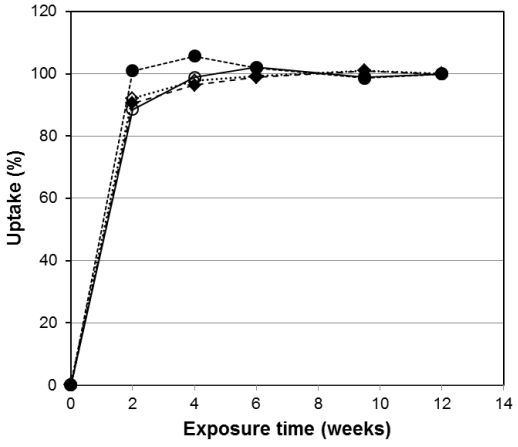
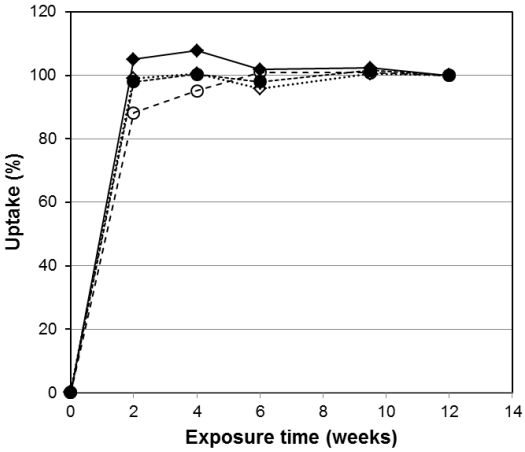


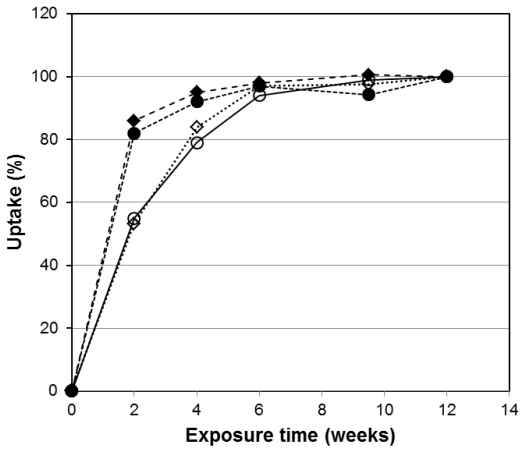
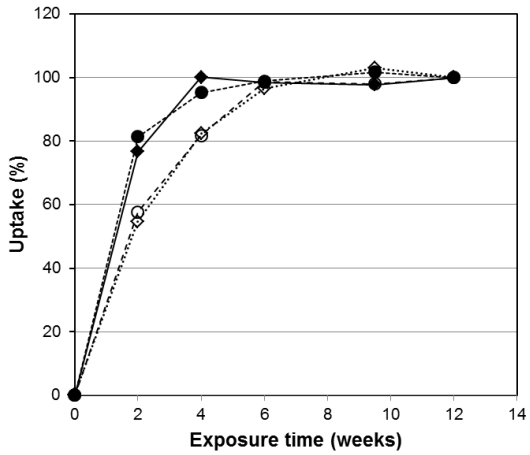
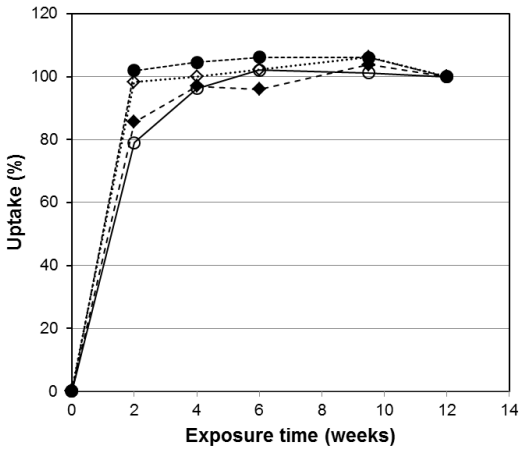
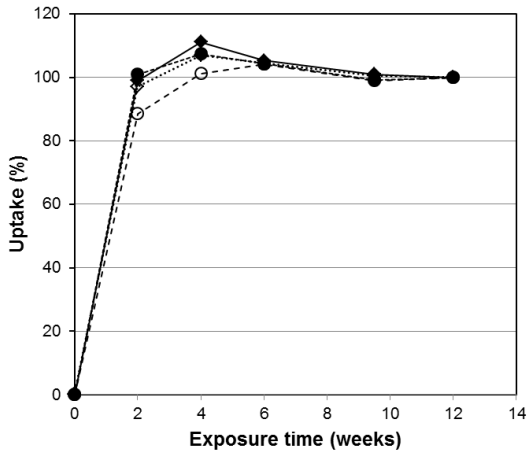
Appendix 7:

Uptake kinetics in different passive samplers.

Uptake kinetics were determined for 7 samplers, according to the standardized protocol: S30-1, S100, PAc, PE-2, PE-3, POM, and SSP (see Table S1 for explanation of abbreviations). Kinetics in the other PE samplers was assumed to be similar to uptake in PE-2. Likewise, S30-2 kinetics were assumed to be represented by kinetics in S30-1. Kinetics in S10-1 and S10-2 will be faster than for S30 and were therefore not quantified. Uptake was determined after exposure for 2, 4, 6, 9.5, and 12 weeks to the BB and the SP sediment. Uptake of chemicals in PAc from the SP sediment was not determined due to logistic reasons. Each measurement was performed in three-fold. For the graphical presentation below, four chemicals were selected, i.e., a moderately and very hydrophobic PAH and a moderately and very hydrophobic PCB: fluoranthene (♦), benzo[*g,h,i*]perylene (◊), PCB-52 (●), and PCB-180 (○).

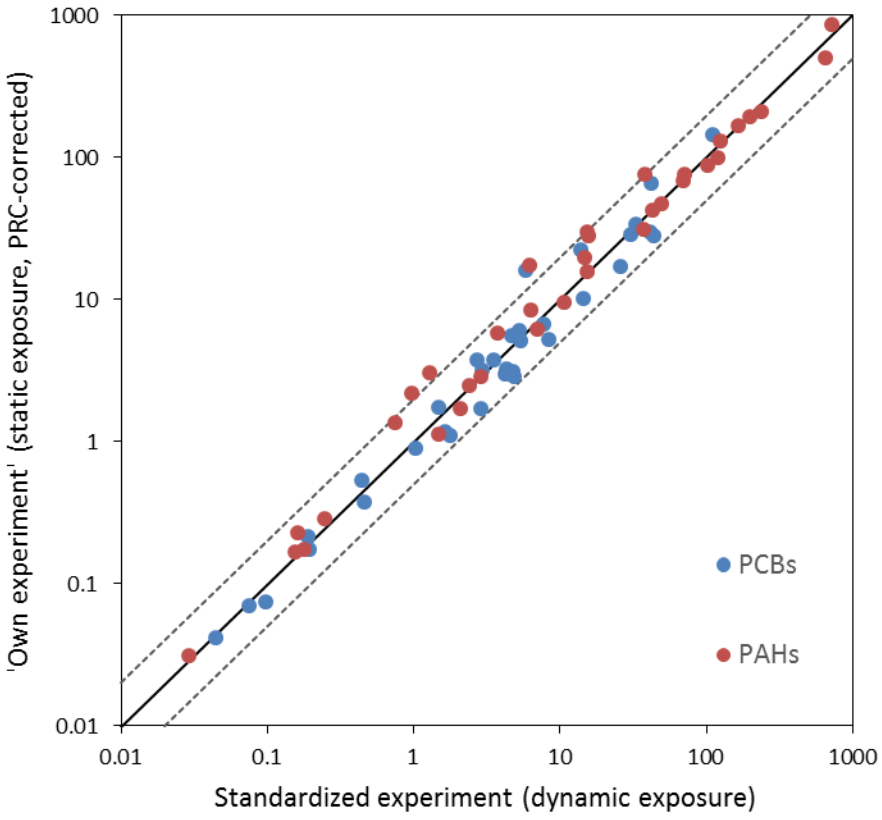
	BB sediment	**SP sediment**
S30-1 (SPME, 30 µm PDMS)		
S100 (SPME, 100 µm PDMS)		

	BB sediment	SP sediment
PAc (SPME, 30 µm polyacrylate)		
PE-2 (25 µm)		
PE-3 (51 µm)		

	BB sediment	SP sediment
POM (77 µm)		
SSP (100 µm silicone rubber)		

Appendix 8:

Relationship between C_{free} determined statically and well-mixed (dynamic) with PE (25 µm thickness) by one of the participants. The solid line represents the 1:1 relationship; the dashed lines the 1:2 and 2:1 relationships. Data concern C_{free} values determined in all three sediments.



Appendix 9:

Variation Factors (*VF*s) calculated for the sediment heterogeneity experiment.

	BB sediment	FD sediment	SP sediment
Phenanthrene	1.1	1.2	1.2
Anthracene	1.1	1.2	1.2
Fluoranthene	1.2	1.2	1.5
Pyrene	1.2	1.2	1.6
Benz[a]anthracene	1.2	1.2	1.8
Chrysene	1.2	1.2	1.9
Benzo[*e*]pyrene	1.2	1.2	1.9
Benzo[*b*]fluoranthene	1.2	1.2	2.1
Benzo[*k*]fluoranthene	1.2	1.2	2.1
Benzo[*a*]pyrene	1.2	1.2	2.1
Benzo[*g,h,i*]perylene	1.2	1.3	2.1
Dibenz[*a,h*]anthracene	1.4	1.4	2.4
Indeno[123-*cd*]pyrene	1.2	1.2	2.4
PCB-18	1.2	1.2	1.6
PCB-28	1.2	1.2	1.7
PCB-52	1.2	1.2	1.8
PCB-66	-	-	1.9
PCB-77	-	-	2.0
PCB-101	1.2	1.3	2.0
PCB-118	1.2	1.3	2.1
PCB-138	1.2	1.3	2.2
PCB-153	1.2	1.3	2.2
PCB-170	1.2	1.3	2.1
PCB-180	1.3	1.4	2.4
PCB-187	1.2	1.3	2.4

Appendix 10:

Averaged relative standard deviations (RSDs; **%**) calculated for replicated (n = 5) measurements by the coordinating laboratory, with different samplers, according to the standardized protocols (intra-method variability).

	BB sediment	**FD sediment**	**SP sediment**
Sheets			
PE-1	1.5	3.1	2.2
PE-2	2.3	4.8	7.6
PE-3	1.8	3.1	6.0
PE-4	2.4	4.8	1.5
PE-5	2.0	3.5	2.5
PE-6	2.2	4.7	4.3
POM	2.3	3.4	3.2
SSP	1.7	5.0	2.0
SPME fibers			
S10-1 (10 µm)	7.6	9.9	6.2
S10-2 (10 µm)	5.8	9.9	3.6
S30-1 (30 µm)	5.0	10.3	4.3
S30-2 (30 µm)	4.1	7.6	5.2
S100 (100 µm)	3.0	6.7	1.7
PAc (30 µm)	4.9	7.2	3.6

Appendix 11:

Variation Factors (*VF*s) calculated based on the (range of) concentrations obtained with all the different sampling formats (inter-method variability).

	BB sediment	FD sediment	SP sediment
Phenanthrene	1.7	1.4	1.4
Anthracene	1.2	1.3	1.5
Fluoranthene	1.2	1.3	1.3
Pyrene	1.3	1.3	1.3
Benz[a]anthracene	1.5	1.4	1.5
Chrysene	1.3	1.4	1.5
Benzo[*e*]pyrene	2.0	2.4	1.6
Benzo[*b*]fluoranthene	1.4	1.6	1.6
Benzo[*k*]fluoranthene	1.6	1.6	1.7
Benzo[*a*]pyrene	1.5	1.5	1.6
Benzo[*g,h,i*]perylene	2.1	2.1	1.8
Dibenz[*a,h*]anthracene	1.7	2.2	1.9
Indeno[123-*cd*]pyrene	2.1	2.1	1.9
PCB-18	1.3	1.3	1.3
PCB-28	1.2	1.4	1.5
PCB-52	1.4	1.5	1.4
PCB-66	-	-	1.4
PCB-77	-	-	1.6
PCB-101	1.4	1.6	1.6
PCB-118	1.5	1.4	1.6
PCB-138	1.8	1.9	1.9
PCB-153	1.9	1.9	1.9
PCB-170	2.0	2.1	2.3
PCB-180	2.3	2.2	2.4
PCB-187	2.2	2.7	2.3