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Ex situ determination of freely dissolved concentrations of hydrophobic organic chemicals in sediments and soils: basis for interpreting toxicity and assessing bioavailability, risks and remediation necessity

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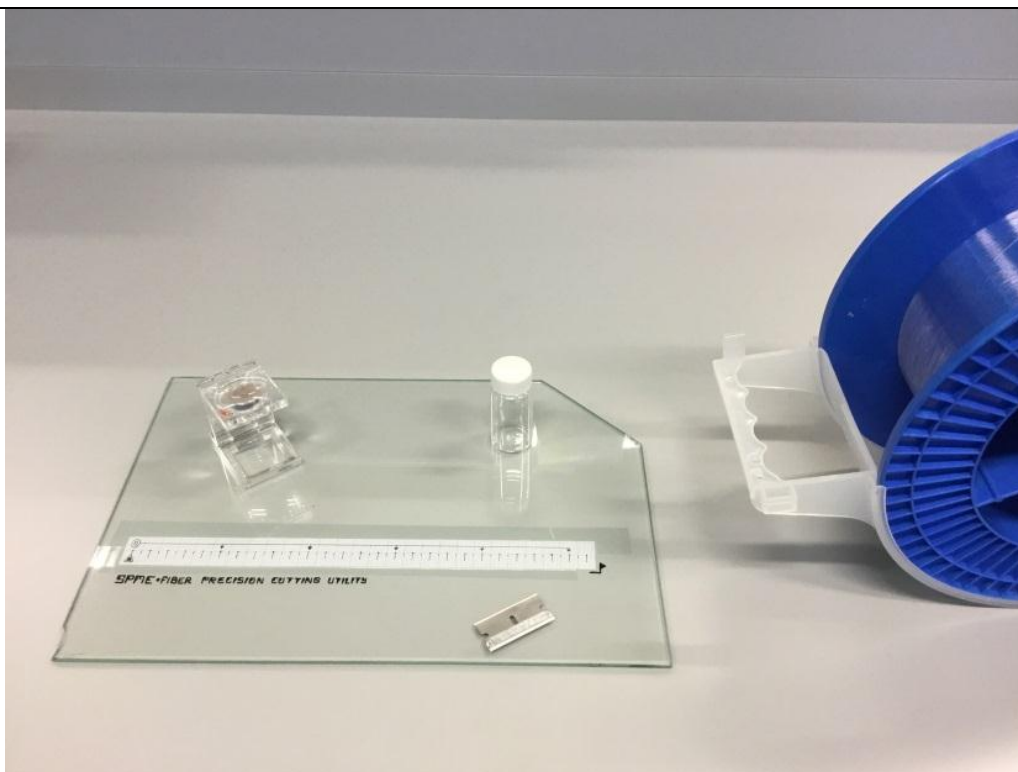
¹Institute for Risk Assessment Sciences, Utrecht University, Utrecht, the Netherlands. ²Atlantic Coastal Environmental Science Division, Office of Research and Development, U.S. Environmental Protection Agency, Narragansett, RI, USA. ³Department of Chemical, Biochemical, and Environmental Engineering, University of Maryland, Baltimore County, Baltimore, MD, USA. ⁴RM Parsons Laboratory, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA. ⁵Geotechnics and Environment, Norwegian Geotechnical Institute, Oslo, Norway. ⁶Graduate School of Oceanography, University of Rhode Island, Narragansett, RI, USA. ⁷Center for Fisheries, Aquaculture and Aquatic Sciences, and Department of Zoology, Southern Illinois University, Carbondale, IL, USA. ⁸Chemistry Department, Southern California Coastal Water Research Project Authority, Costa Mesa, CA, USA. ⁹Civil, Environmental and Construction Engineering, Texas Tech University, Lubbock, TX, USA. ¹⁰Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Brno, Czech Republic. ✉e-mail: m.t.o.jonker@uu.nl



Supplementary Figure 1

Weighing polymer strips.

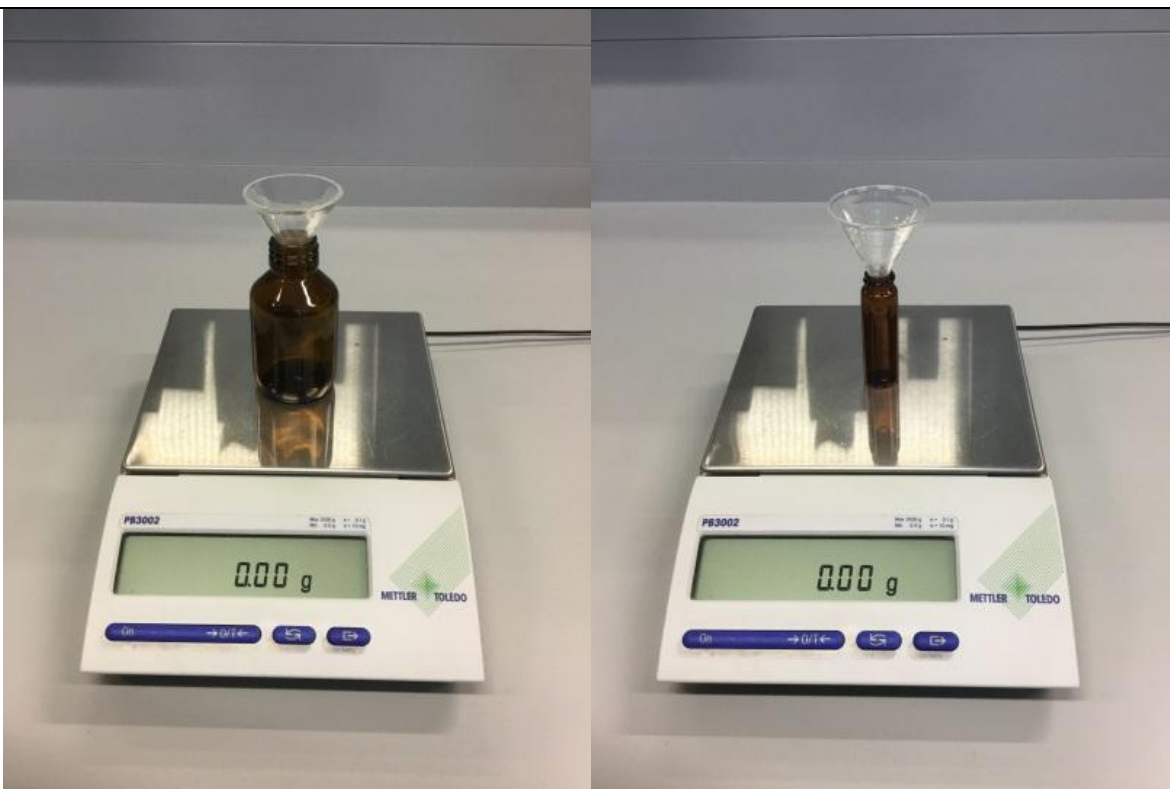
Weighing of polymer strips is most convenient when using a (cleaned) support device (e.g., an upside down aluminum cryotube, as shown). This prevents the sampler from contacting the possibly contaminated surface of the balance and facilitates picking-up the sampler with tweezers.



Supplementary Figure 2

Cutting SPME fibers.

Cutting SPME fibers can be performed using a glass plate, underneath which a ruler is fixed. The image also shows a magnifying glass, a razor blade, a 20 mL vial for the fibers, and a fiber roll.



Supplementary Figure 3

Adding sample to the equilibration system.

Use a glass funnel placed in the mouth of either the bottle (polymer strips) or 15 mL vial (SPME fibers) when adding the sediment or soil sample.



Supplementary Figure 4

Application of aluminum foil on 120 mL bottles.

When using 120 mL equilibration bottles, apply a 5x5 cm piece of thick acetone-cleaned laboratory aluminum foil in order not to expose the sample to the plastic cap. Place the foil on the mouth of the bottle, with the dull side facing the inside of the bottle. Carefully crimp the foil around the neck, making sure that the foil touches the bottle mouth completely, showing no creases.



Supplementary Figure 5

Overall setup for collecting polymer strips.

Overview of needed materials and setup for collecting and cleaning polymer strips.



Supplementary Figure 6

Overall setup for collecting SPME fibers.

Overview of needed materials and setup for collecting and cleaning SPME fibers.



Supplementary Figure 7

Collecting a sampler from a sediment or soil suspension.

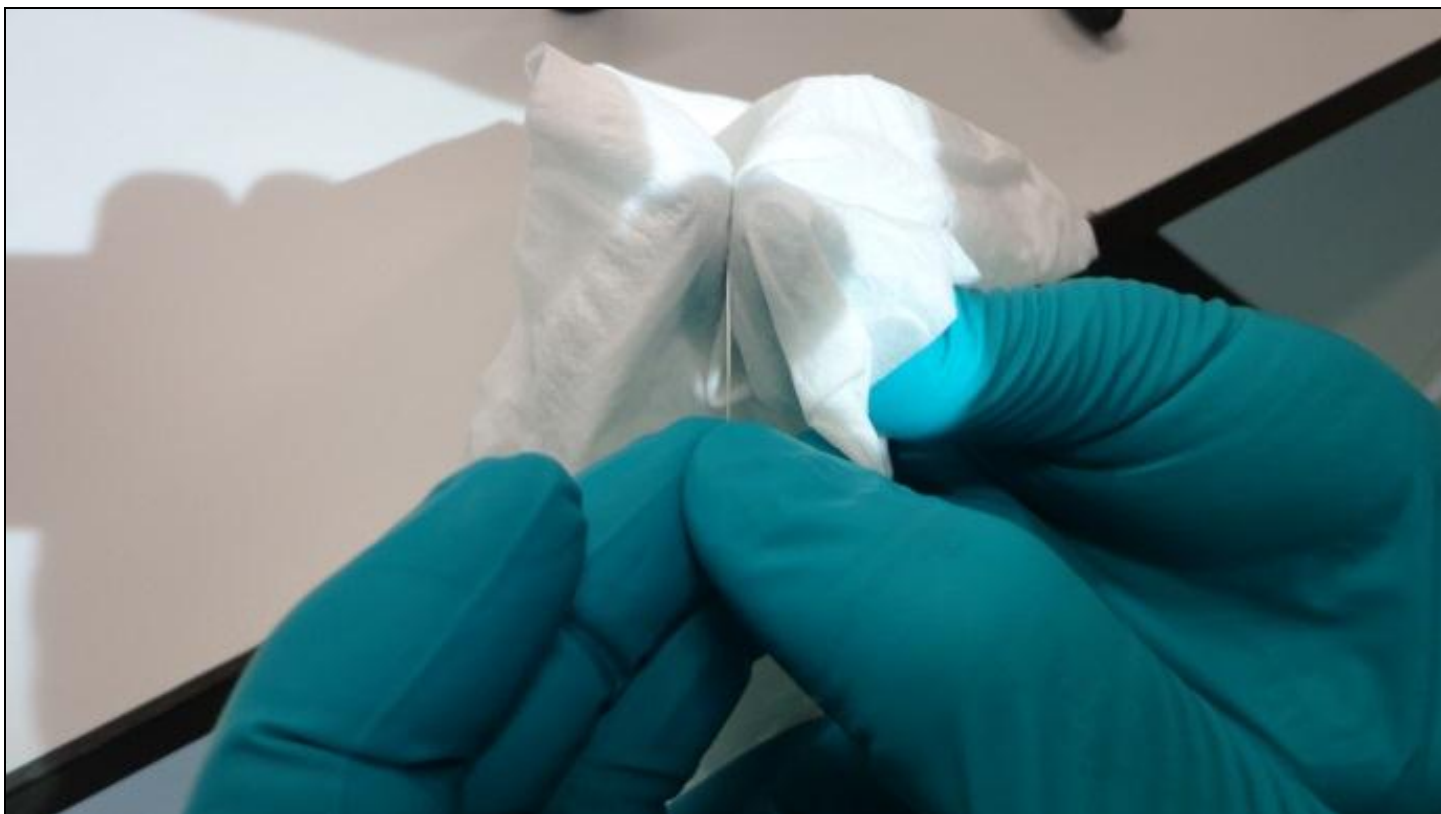
Using a tea sieve placed on a beaker is a convenient way of collecting a polymer strip or short SPME fiber from an equilibration bottle/vial.



Supplementary Figure 8

Placing polymer strips in extraction vials.

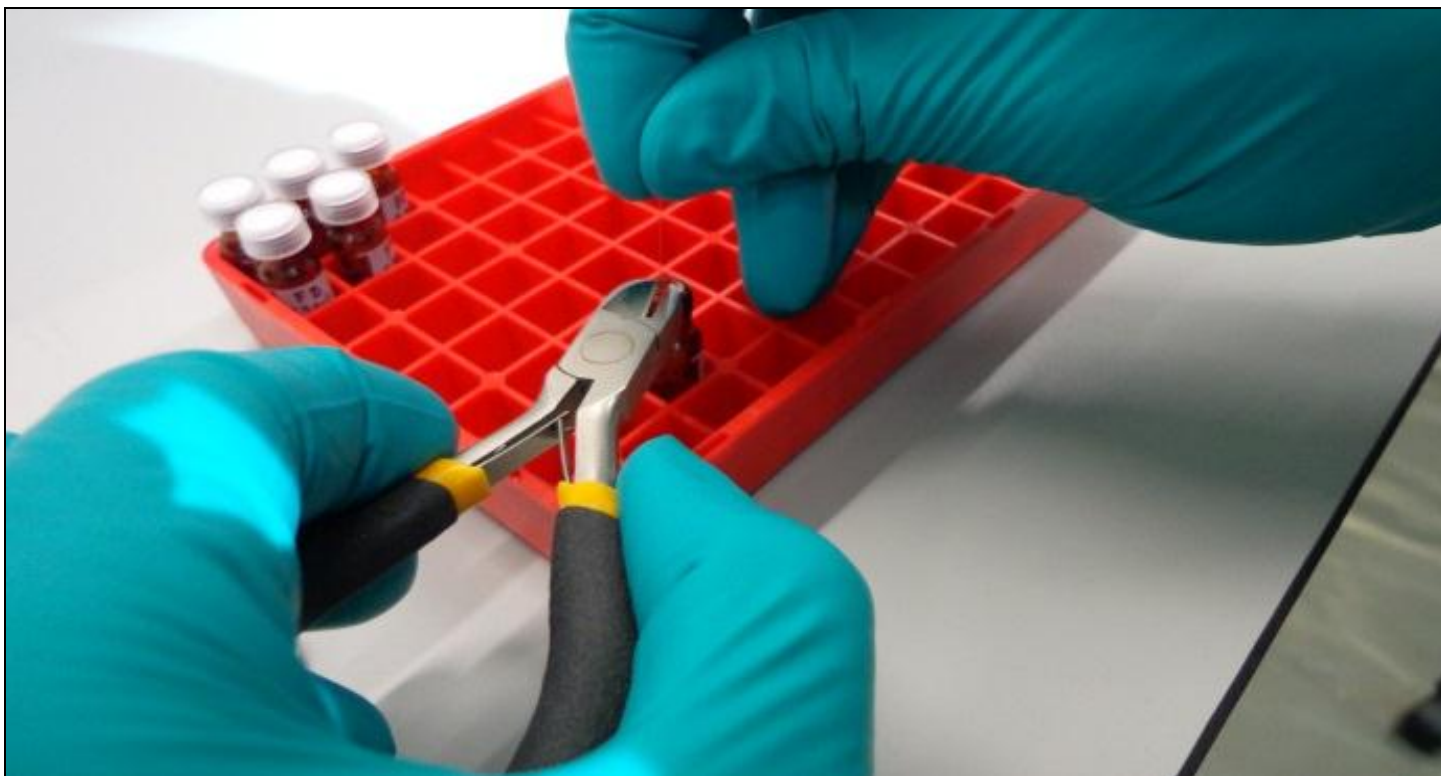
Stick the cleaned polymer strip in the mouth of the corresponding autosampler vial and cut into multiple pieces of ≤ 7 mm, such that the pieces will fit in the flat position at the bottom of the vial.



Supplementary Figure 9

Cleaning SPME fibers.

Hold the SPME fiber between the fore/middle finger and thumb and wipe with a damp tissue, held in the other hand.



Supplementary Figure 10

Cutting SPME fibers.

Stick the fiber into the mouth of the corresponding autosampler vial and cut with a clean wire cutter into pieces with such a length that these will be submerged in the solvent (e.g., ≤ 1.3 cm pieces in the case 300 μ L inserts are used).

SUPPLEMENTARY METHODS

Alternative procedures for passive sampling with POM sheet samplers and polyacrylate-coated SPME fibers.

POM sheet samplers

When using strips cut from POM sheets (77 μm ; CS Hyde Company, Lake Villa, IL, USA), most of the steps described in the main protocol for PE and PDMS/SR sheets can be followed in their entirety. Exceptions are:

1. **Reagents.**

Additional reagents needed for sampling with POM strips include:

- Acetonitrile (GC-MS grade) (Merck, cat. no. 1006651000 or equivalent)

! CAUTION Flammable; avoid inhalation, ingestion and skin contact.

- Dichloromethane (GC grade for residue analysis) (Merck, cat. no. 1006681000 or equivalent)

! CAUTION Flammable; avoid inhalation, ingestion and skin contact.

2. **Preconditioning.**

(i) Wash the POM samplers in 20 mL vials as follows: Twice with acetonitrile (2x 30 min), twice with dichloromethane (DCM; 2x 30 min), and twice with *n*-hexane (2x 30 min), sequentially.

▲ CRITICAL STEP The use of these specific solvents and their order is critical.

(ii) Air-dry the samplers in a fume hood. To this end, use clean (wiped with acetone) tweezers without ribs to place the polymer strips on 4 layers of thick lint-free laboratory tissue in a clean fume hood. Separate clotted strips in order to optimally expose them to air. Make sure that the air flow is sufficiently gentle, such that no strips are blown away (if this does happen and strips land on a dirty surface, open the fume hood window further and wash the respective strip(s) once more with *n*-hexane for 30 min and restart the drying period).

(iii) Place the open 20 mL vial(s) next to the polymer pieces with the mouth facing the fume hood window (the cap can be put on the tissue too).

(iv) After 45 min, turn the strips upside down with clean tweezers.

(v) After another 45 min, use tweezers to transfer the dry strips to the dry 20 mL vial and cap it.

■ PAUSE POINT Washed polymer strips can be stored in tightly closed vials in the dark at room temperature for up to about six months.

3. **Equilibration.**

In particular for POM, the intensive mixing prescribed in the main protocol is crucial. Shaking should be performed at 150-180 rpm on a one-dimensional (reciprocal) shaker for at least 6 weeks. A time series (the use of PRCs with POM is controversial) should be included when trying to assess equilibrium conditions.

4. **Extraction.**

POM passive samplers can only be (cold) extracted in acetonitrile, DCM or *n*-hexane:acetone (1:1). Other solvents, such as *n*-hexane, heptane, iso-octane, and methanol are not capable of fully recovering HOCs from POM through soaking/shaking. Recovery percentages may be as low as 10 % (e.g., for the more hydrophobic PCBs (MTO Jonker, unpublished results)). Using the prescribed solvents, maximally 50 mg of POM (preferably 30 mg max) can be extracted in 0.5 mL of solvent. Sufficient time should be allowed for the extraction: at least (but preferably longer) the 24 h soaking step, as described in the main protocol. While soaking, shaking the vials placed vertically on a small rotation table shaker is recommended.

Polyacrylate-coated SPME fibers

When using polyacrylate-coated SPME fibers (30 µm; Poly Micro Industries, Phoenix, AZ, USA), most of the steps described in the main protocol for PDMS-coated SPME fibers can be followed in their entirety. Exceptions are:

1. **Reagents.**

Additional reagents needed for sampling with polyacrylate-coated SPME fibers include: Methanol (GC-MS grade for residue analysis) (Merck, cat. no. 1008371000 or equivalent)
! CAUTION Flammable; avoid inhalation, ingestion and skin contact.
Acetonitrile (GC-MS grade) (Merck, cat. no. 1006651000 or equivalent)
! CAUTION Flammable; avoid inhalation, ingestion and skin contact.

2. **Preconditioning.**

The fibers should be washed as described, but using 50:50 (w/w) methanol:Millipore water as the washing solvent (using 100% organic solvent may cause the coating to come off the core). Wash the fibers in the 20 mL vial twice for 1 h with this mixture. Then, wash the fibers twice for 30 min with Millipore water and finally store the fibers in Millipore water.

3. **Equilibration.**

Equilibration should be performed on a Rock and Roller apparatus, as described in the main protocol for at least 6 weeks. It is recommended to include a time series (the applicability of PRCs with these fibers is unevaluated) when trying to assess equilibrium conditions.

4. **Extraction.**

The fibers can be extracted in acetonitrile. Other solvents should be tested first to investigate if they are capable of fully recovering polymer-associated target chemicals.

SUPPLEMENTARY TABLE

Supplementary Table 1: Indicative polymer - methanol/water (80:20) partition coefficients (L/kg) for a series of PRCs ^a

	PE	PDMS
Naphthalene-D ₈	2.0	0.8
Acenaphthene-D ₁₀	4.0	1.4
Fluorene-D ₁₀	3.5	1.0
Phenanthrene-D ₁₀	4.5	0.8
Anthracene-D ₁₀	4.7	0.9
Fluoranthene-D ₁₀	7.1	0.9
Pyrene-D ₁₀	9.0	0.9
Chrysene-D ₁₂	14	0.9
Perylene-D ₁₂	56	0.9
Benzo[<i>e</i>]pyrene-D ₁₂	27	0.9
Coronene-D ₁₂	135	1.2
PCB-4	1.7	1.2
PCB-10	2.2	1.4
PCB-14	8.8	3.3
PCB-21	6.5	2.7
PCB-29	10	3.4
PCB-30	7.4	3.0
PCB-50	5.3	2.5
PCB-55	9.2	3.3
PCB-78	18	4.3
PCB-104	4.9	2.6
PCB-145	7.3	3.7
PCB-155	18	6.0
PCB-204	61	16

^a Collected from underlying data in: Smedes, F., Geertsma, R. W., Van Der Zande, T. & Booij, K. Polymer-water partition coefficients of hydrophobic compounds for passive sampling: Application of cosolvent models for validation. *Environ. Sci. Technol.* **43**, 7047-7054 (2009).