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Demonstration and Evaluation of Solid Phase Microextraction For the Assessment of Bioavailability and Contaminant Mobility

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This method is an operating procedure for in-situ measurement of sediment pore water concentrations with solid phase microextraction using polydimethyl siloxane as the extractant. The method is used to assess the mobile and available contaminants in the pore water. Included in this description are procedures for preparation, deployment, retrieval, processing and interpretation of the collected pore water concentrations. The method is applicable to hydrophobic organic contaminants (HOCs) and the focus herein is on polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Because the method detection limits as well as potential losses are related to compound hydrophobicity, the method must be used with caution when analyzing relatively volatile constituents which exhibit greater losses and relatively poor detection limits.

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Table of Contents

1 Scope and Application 3
2 Summary of Method 3
3 Supplies 3
3.1 Solid phase micro-extraction fibers 3
3.2 Sampler or fiber holder 4
4 Procedures 5
4.1 Predeployment preparation 5
4.2 Deployment 5
4.3 Retrieval 5
4.4 Analysis of samples to get the accumulated uptake in the fiber 8
4.5 Determination of pore water concentrations from PDMS 8
4.6 Evaluation of equilibrium uptake onto the PDMS fiber 10
4.6.1 Use of impregnated performance reference compounds 10
4.6.2 Compare fibers of the same size collected at two different times or use of two different size fibers 11
4.6.3 Direct use of the transient uptake model (diffusion only) 12
4.7 Assessing bioavailability with pore water concentrations measured by SPME 12
5 Quality Control 12
5.1 Field blanks 12
5.2 Field solvent blanks 12
5.3 Field control samples 13
5.4 Field internal standards 13
5.5 QC samples for chemical analysis 13
6 References 17

1 Scope and Application

This method is an operating procedure for in-situ measurement of sediment pore water concentrations with solid phase microextraction using polydimethyl siloxane as the extractant. The method is used to assess the mobile and available contaminants in the pore water. Included in this description are procedures for preparation, deployment, retrieval, processing and interpretation of the collected pore water concentrations. The method is applicable to hydrophobic organic contaminants (HOCs) and the focus herein is on polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Because the method detection limits as well as potential losses are related to compound hydrophobicity, the method must be used with caution when analyzing relatively volatile constituents which exhibit greater losses and relatively poor detection limits. The procedure discussed herein is focused on the analysis of priority pollutant PAHs with HPLC and PCBs with GC-ECD. Details of the chemical analysis are not included in this description but standard methods are referenced. Other analytical methods may be used if capable of analyzing the concentrated extract from the SPME fibers.

2 Summary of Method

In-situ solid-phase microextraction (SPME) is a passive sampling approach for measuring hydrophobic organic contaminants in sediment pore water. It involves the insertion of a polymer sorbent with a sampler or fiber holder into the sediments, withdrawal after a period of time, preferably after achievement of equilibrium, and measuring the contaminants sorbed to the polymer. The contaminant concentration that accumulates in the polymer sorbent at equilibrium is directly proportional to the dissolved contaminant concentration in the pore water. Pore water concentration can be inferred from the concentration in the sorbent, here as the concentration in a polymer-coated fiber, C_f , and a polymer sorbent-water partition coefficient, K_{fw}

$$C_w = \frac{C_f}{K_{fw}} \tag{0}$$

Non-equilibrium exposures must be corrected for the kinetics of uptake. The measured pore water concentration is an indicator of the mobile and available fraction of contaminants. The measured pore water can be used to infer lipid normalized bioaccumulation with the product of measured pore water concentrations and the octanol-water partition coefficients[1].

$$C_{t,\text{predict}} = K_{OW} * C_{\text{pw}} \tag{2}$$

Pore water concentrations can also be measured with high spatial resolution providing insight into mobility and the performance of in-situ remedial approaches such as capping[2].

3 Supplies

3.1 Solid phase micro-extraction fibers

The term solid phase microextraction (SPME) has been most often applied to the use of the sorbent polydimethylsiloxane (PDMS). PDMS is used herein in that it is available as a thin coating (10-35 µm) on a variety glass capillaries of various sizes (110-1000 µm). The cylindrical shape is convenient for insertion into sediments and the availability of thin layers with modest sorption capacity speeds equilibration kinetics (compared to POM and PE which are

slightly more sorbing and therefore slower, even with identical sorbent thickness). The length can be segmented to achieve the desired vertical resolution or to provide sufficient sorbent volume to meet detection limit requirements. Costs of fabricating the PDMS coated glass fibers ranges from approximately $1/m (for commercial available optical fibers) to $10-25/m (for specially fabricated coated fibers). Only 1-5 cm of this fiber is necessary for detection of HOCs at sub-ng/L concentrations and therefore the cost of the PDMS is negligible compared to the chemical analysis. Although fibers are available at different dimensions, thin fibers are usually fragile, which limits their use in coarse sediments. Fiber with 30 to 35 µm thickness of coating on 1000 µm glass are easy to handle and robust and exhibit low detection limits (pg/L to ng/L in 1 cm lengths) although they exhibit slower uptake kinetics than thinner fibers. Fibers with customized dimensions can be obtained from Polymicro Technologies (Phoenix, AZ) and Fiberguide Industries (Stirling, NJ).

3.2 Sampler or fiber holder

For in-situ application of SPME, the fiber should be placed in a holder to protect from breakage. In coarse sediments (gravel, rocky or filled with debris) the holder should include an external sheath. The holder or sampler used herein is modified from a hand-held piezometer (Henry Sampler). Modifications include adding perforations in the outer sheath to allow water exchange, incorporation of a slit into the inner sheath to hold the SPME fiber and adding a washer to mark the cap (or sediment) water interface (Figure 1a). Fibers can be left unshielded for short lengths (up to 30 cm) in soft sediments (Figure 1b). Fibers require neither holder nor protective sheath if used in short lengths in laboratory samples or laboratory slurries although some form of holder (e.g. a Teflon septum or wire mesh bag) is useful for locating and retrieving the fiber in such applications. Other types of samplers or fiber holders are acceptable as long as they can protect fiber from breakage, not interfere with water and fiber exchange, and can be easily deployed.

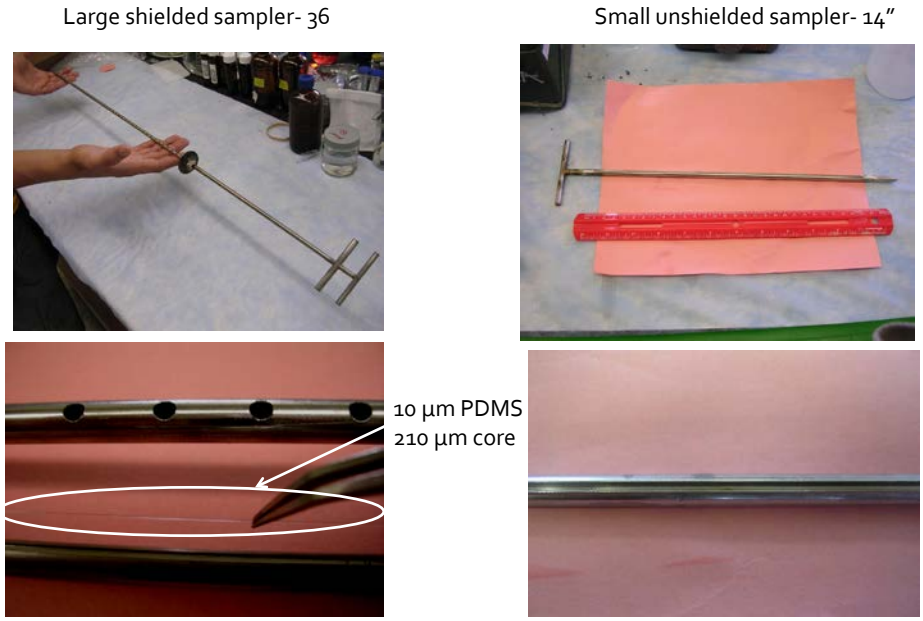

Figure 1- Shielded and unshielded holders for SPME fiber (a, left- holder with shielding, a modified Henry's type sampler and b, right- unshielded holder)

4 Procedures

4.1 Predeployment preparation

Before loading the SPME fibers, the sampling devices are disassembled and washed with detergent and hot water, and then rinsed sequentially by rinsing with hexane, acetonitrile and distilled water, and then dried in an oven. For PCBs, methanol is used instead of acetonitrile. The solvents used in cleaning were selected based upon their use in the extraction from the exposed fibers and to ensure that anything extractible by the solvent is removed from the sampling equipment prior to use. After cleaning, 3 ml of clean acetonitrile for PAHs or Hexane for PCBs is introduced into the inner rod of an assembled sampler. The test solvent is collected at the bottom of the sampler and analytically checked for PAH or PCB peaks. As necessary, the cleaning procedure is repeated until no contaminants of concerns are detected in the eluting solvent.

The supplied fiber is cleaned by soaking in acetonitrile solvent, rinsing with distilled water, and blotting dry with Kimwipes™. The cleaned fibers are laid into the groove of the inner rod of the modified sampler and affixed with approximately 1 cm of waterproof caulk (hydrocarbon-free silicon) at both ends. Caulk serves to hold the fiber in place, and can also be used to fill any gaps at the ends of the insertion tool to eliminate any water movement vertically. Care should be taken to avoid any placement of silicon on the screened length or active measurement portion of the insertion tool or to place so much silicon that cured silicon will hinder insertion tool separation after field exposure. To make sure the fiber is securely in place, a finger should be run along the groove. After the caulk dries, the inner rod with the fiber is then inserted into the outer sheath with groove and fiber aligned with the screened side of the sheath. The handles on both inner grooved rod and sheath are then wrapped together to maintain orientation of the fiber to the screened section of the outer sheath. The length of fiber that was loaded into each of the insertion tools is documented. The samplers are labeled via a waterproof marker.

4.2 Deployment

The assembled SPME insertion devices are driven perpendicular to the sediment surface by divers at locations not accessible by foot although alternative approaches exist (e.g. by using a long sleeved pipe to insert the sampler into the sediment from the surface. Samples can also be collected by conventional cylindrical or box corer and placed in the laboratory before insertion of the sampler. Sampling in the laboratory is identical to the field except the effects of field-related processes such as groundwater upwelling will not be measured. All SPME insertion devices are connected via nylon cords to surface-deployed buoys served as markers for their retrieval. The samplers can be pushed into sediment by hand at easily accessible sites, e.g. onshore locations at low tide and shallow water creeks. Deployment blanks can be shipped to the field but not deployed to assess possible airborne contribution to the samples on-site or during shipping. The deployment blank should be processed at the time of deployment. A deployment blank can also be used for retrieval although no deployment blank is needed if the samples are processed on site immediately after retrieval.

4.3 Retrieval

All fibers are typically equilibrated in situ for 7 to 28 days before retrieval. The equilibration time is chosen as a balance between using short times to minimize sample disturbance or vandalism and the time required to achieve a significant fraction of equilibration. Full equilibration involves the initial depletion of the pore water surrounding the fiber and then a

slow re-equilibration with the surrounding media. The time required to achieve full equilibration depends upon the hydrophobicity of the compound being analyzed, the dimensions of the PDMS sorbent, and the mixing characteristics within the sediment. A highly hydrophobic contaminant (e.g. a tetrachloro or higher biphenyl), with a little sorptive capacity (e.g. sand) under conditions of limited transport (e.g. diffusion controlled conditions) may require well in excess of 28 days to achieve full equilibrium whereas a less hydrophobic (3 or 4 ring PAH) may reach equilibrium within a period of days in a typical fine-grained organic-rich sediment. Performance reference compounds (the use of which is described in section 4.6.1) or placement of co-located samples retrieved in a time series are recommended to know the extent of equilibrium, particularly with highly hydrophobic contaminants.

During retrieval, the SPME fibers are withdrawn from the sediment by diver or pulled out by hand from the surface at easily accessible sites. It is generally convenient to immediately process the fibers on site by segmenting and placing the individual segments in solvent. Processing on-site maximizes retention of any volatile contaminants and also provides samples that are much easier to transport to the laboratory for chemical analysis. Contaminants more volatile (generally lower in molecular weight) than phenanthrene will be unstable if processing is not conducted immediately. Phenanthrene and less volatile contaminants (i.e. phenanthrene and generally higher molecular weight) are stable on the fibers with transport to a laboratory for processing via overnight courier while maintaining a temperature of 4 ºC. Low molecular weight contaminants such as naphthalene can be retained more effectively on thicker fibers and by using stronger sorbents. These measures would increase the required equilibration time, however, for the compounds of primary interest here, higher molecular weight PAHs and PCBs.

The segmentation depends on the objectives of the project. Samples might be segmented in the biologically active zone (e.g. 0-10 cm) to compare to benthic criteria then at deeper segments (e.g. 10-20, 20-30, etc.) to evaluate deeper contamination or potential migration into the biologically active zone. Adjacent samples, for example, 3-5 and 5-7 cm could be used to effectively represent duplicate samples under most environmental conditions. Under some conditions (e.g. diffusion dominated conditions), these adjacent segments would not represent a duplicate but instead indicate small scale gradients and, in such conditions, a separate fiber can be deployed at the same location to serve as a duplicate, if desired.

Upon retrieval, any color changes in the sampler should be documented. These may be due to changes in sediment biogeochemistry or indicate the potential that the fiber may have been in contact with nonaqueous phase liquids (NAPL). It should be noted that contact with NAPL may change the validity of the fiber measurements of pore water concentration since the fiber may directly absorb the NAPL. During processing, the insertion tools are dismantled and the fibers are removed from the inner rod and wiped with damp tissue to remove sediment particles and sampled from top to bottom. The SPME fiber should be located and carefully removed and placed on a clean, high contrast surface with the position of the sediment-water interface noted. If the fiber is broken during removal, care should be taken to maintain the relative position of the pieces. Any missing pieces or length, if any, should be documented and the overall length of fiber recovered should be documented. The fibers are sampled at the planned depths and with enough length to insure detectable levels.

Detection limits for individual compounds are discussed in the Cost and Performance Report[3] or Final Project Report[4]. Due to the strong sorption by PDMS, the corresponding detection limits by SPME are orders of magnitude lower than by conventional methods. The

detection limits by SPME depends on the fiber-water partition coefficients of the compound, volume of the PDMS and the volume of the solvent used to extract fiber.

$$C_{\det\ water\ by\ SPME} = \frac{C_{\det\ \mathrm{SPME}}}{K_{PDMS-w}} = \frac{n_{\mathrm{detection}}}{V_{PDMS} * K_{PDMS-w}} = \frac{C_{\det} * V_{solvent}}{V_{PDMS} * K_{PDMS-w}} \quad (3)$$

$C_{\mathrm{det,\ water\ by\ SPME}}$ =the detection limit of water by SPME

$C_{\mathrm{det,SPME}}$ =the detection limit of fiber concentration

$K_{\mathrm{PDMS\text{-}w}}$ = fiber-water partition coefficient

$n_{\mathrm{detection}}$ = the mass of contaminant detected

V_{PDMS} = the volume of PDMS coating

V_{PDMS} =PDMS coating concentration (µL/m) * length of fiber (cm)

Table 4.1 summarizes the detection limits by SPME-PDMS for selected PAHs and PCBs. The detection limits are based upon 1 cm of fiber (210/230 and 1000/1060) extracted with 100 µL solvent.

Table 4.1 Detection limits by SPME-PDMS for selected PAHs and PCB congeners

Compounds	Log K_{ow}	MDL direct injection (µg/L)	MDL SPME (210/230) (µg/L)	MDL SPME (1000/1060) (µg/L)
Naphthalene	3.37	0.07	1.15E-01	8.19E-03
Dibenzofuran	4.30	0.14	3.82E-02	2.72E-03
2-Methylnaphthylene	3.90	0.19	1.12E-01	7.99E-03
Fluorene	4.18	0.81	2.79E-01	1.98E-02
Acenaphthene	3.92	0.32	1.82E-01	1.29E-02
Phenanthrene	4.57	0.33	5.34E-02	3.80E-03
Anthracene	4.54	0.23	3.95E-02	2.81E-03
Fluoranthene	5.22	0.21	9.69E-03	6.89E-04
Pyrene	5.18	0.21	1.05E-02	7.45E-04
Chrysene	5.86	0.07	9.38E-04	6.67E-05
Benz[a]anthracene	5.91	0.027	3.28E-04	2.34E-05
Benzo[b]Fluoranthene	5.80	0.037	5.57E-04	3.96E-05
Benzo[k]Fluoranthene	6.00	0.065	6.64E-04	4.73E-05
Benzo[a]pyrene	6.04	0.018	1.70E-04	1.21E-05
Dibenz[a,h]anthracene	6.75	0.026	6.24E-05	4.44E-06
Benzo[ghi]perylene + Indenopyrene	6.72	0.045	1.14E-04	8.15E-06
PCB10	4.84	0.030	3.85E-03	2.74E-06
PCB28	5.67	0.023	4.12E-04	2.93E-07
PCB52	5.84	0.025	3.04E-04	2.17E-07
PCB153	6.92	0.018	1.72E-05	1.22E-08
PCB138	6.83	0.020	2.36E-05	1.68E-08
PCB180	7.36	0.035	1.14E-05	8.14E-09

For thick fibers (e.g. 1000/1060), 1 to 2 cm of fiber are usually all that is needed and two adjacent 1 to 2-cm fiber sections are sampled at each depth as replicates; while for thin fiber (e.g. 210/230), 5 to 10 cm fiber may be needed to get detectable concentrations. The fibers are cut with ceramic column cutter (thick fiber) or single edged razor (thin fiber). The sectioned fibers are added to 2-ml amber auto-sampling vials with inserts prefilled with 100-250 µL of acetonitrile for PAHs and hexane for PCBs. If 5-10 cm of fiber length is used, these should be cut to 1-2 cm segments then placed together in a single sampling vial. The type of solvent and volume can be modified depending upon contaminant of interest and chemical analysis method. An internal standard can be added if desired. Deuterated PAHs are a convenient internal standard for hydrophobic organic compounds. Sectioned samples are shipped overnight to the laboratory at 4ºC and are subsequent stored in a freezer at -17ºC until analysis. Temperature is not significant to the stability of the samples although any loss of solvent volume will affect quantitation unless an internal standard is used. All samples should be analyzed within one month after receipt because there will be a slow loss in solvent volume. If samples are analyzed after a longer time period, any change in solvent volume should be noted.

4.4 Analysis of samples to get the accumulated uptake in the fiber

The solvent extract can be transferred from the extraction vial before analysis or the fiber removed from the extraction vial if needed to avoid interference with sample injection needles. Priority pollutant listed PAHs can be analyzed by EPA Method 8310 (SW-846 3rd edition, 1986)[5] and PCB congeners were analyzed by EPA Method 8082[6]. Although these two standard methods are more frequently used by researchers and commercial labs, any method appropriate for the contaminants of concern capable of analyzing a concentrated sample of extract can also be successfully employed.

4.5 Determination of pore water concentrations from PDMS

The freely-dissolved pore water concentrations can be calculated from the accumulated uptake in the fiber and the fiber-water partition coefficients as shown in the following equation:

$$C_W = \frac{C_{PDMS}}{K_{PDMS-W}} = \frac{A*RSF*V_{solvent}}{L_{fiber}*V_{fiber}*K_{PDMS-W}} \quad (4)$$

where:

A = Areas of chromatography peaks
RSF = response factor from calibration curve unique to each HOCs
$V_{solvent}$ = volume of solvent used to extract fiber
L_{fiber} = length of fiber sample
V_{fiber} = specific volume of fiber
K_{PDMS-W} = fiber-water partition coefficient unique to each HOCs

The fiber-water partition coefficient should correlate with the hydrophobicity of the compound and thus can be correlated with K_{ow} as shown in Equations (5) and (6). A potential source of error is uncertainty in the values of the K_{ow} with values from different sources often differing by a factor of 2 (0.3 log units). Thus the source of K_{ow} should be defined when developing a correlation and the same source should be employed in the analysis of pore water

concentrations. In this method, fiber-water partition coefficients of PAHs and PCBs as measured by Reible et al (2010)[7] and Mayer et al (2000)[8] are employed to correlate with a consistent set of K_{ow} values, Mackay et al. (1992)[9] for PAHs and Hawker and Connell (1988)[10] for PCBs. The fiber-water partition coefficients of selected PAHs and PCBs from the correlations with K_{ow} (Eqn 5&6) are listed in Table 4.2. Note that the fiber-water partition coefficients depend on the hydrophobicity of the compounds and the sorbent material (e.g., PDMS, POM or PE) but are independent of the volume of the sorbent or dimension of the fiber (e.g. 210/230 or 1000/1060).

The correlation for PAHs is:

$$LogK_{fw} = 0.839(\pm 0.048)LogK_{ow} + 0.117(\pm 0.21) \qquad R^2 = 0.97 \tag{5}$$

The correlation for PCBs is:

$$LogK_{fw} = 1.03(\pm 0.068)LogK_{ow} - 0.938(\pm 0.427) \qquad R^2 = 0.94 \tag{6}$$

Table 4.2 Fiber-water partition coefficients of selected PAHs and PCB congeners from correlations with K_{ow}s

Compounds	Log K_{ow}	log $K_{f\text{-}w}$	Compounds	Log K_{ow}	log $K_{f\text{-}w}$
Naphthalene	3.37	2.94	PCB 10	4.84	4.05
Dibenzofuran	4.30	3.72	PCB 15	5.3	4.52
2-Methylnaphthylene	3.90	3.39	PCB28	5.67	4.90
Fluorene	4.18	3.62	PCB49	5.85	5.09
Acenaphthene	3.92	3.41	PCB52	5.84	5.08
Phenanthrene	4.57	3.95	PCB65	5.86	5.10
Anthracene	4.54	3.93	PCB101	6.2	5.45
Fluoranthene	5.22	4.50	PCB105	6.65	5.91
Pyrene	5.18	4.46	PCB112	6.45	5.71
Chrysene	5.86	5.03	PCB118	6.74	6.00
Benz[a]anthracene	5.91	5.08	PCB138	6.83	6.10
Benzo[b]Fluoranthene	5.80	4.98	PCB153	6.92	6.19
Benzo[k]Fluoranthene	6.00	5.15	PCB154	6.76	6.02
Benzo[a]pyrene	6.04	5.18	PCB155	6.41	5.66
Dibenz[a,h]anthracene	6.75	5.78	PCB156	7.18	6.46
Benzo[ghi]perylene + Indenopyrene	6.72	5.76	PCB180	7.36	6.64

4.6 Evaluation of equilibrium uptake onto the PDMS fiber

The accurate measurement of pore water concentration depends upon the ability to achieve equilibrium uptake in the PDMS fiber or to be able to extrapolate from the actual uptake given a known fractional extent of equilibrium. In sediments, equilibrium can take far longer and may be more difficult to establish, particularly in the field, due to uncertain transport processes, heterogeneity and time requirements. The kinetics of uptake is dependent upon the sediment and external transport processes and is difficult to predict under field conditions. A practical means of estimating the kinetics or estimating equilibrium uptake is required. There are several ways that can be applied to evaluate the uptake kinetics and determine the fraction of equilibrium. The actual pore water concentrations is equal to the concentration measured on the PDMS divided by the fiber –water partition coefficients and the fraction of equilibrium estimated by one of the methods described below.

$$C_w = \frac{C_{PDMS}}{K_{f-w} * f_{ss}} \tag{7}$$

Where f_{ss} is the fraction of equilibrium or steady state. The fractional approach to steady state is determined for specific compounds using either the performance reference compound approach (Section 4.6.1) or via different size or different exposure periods (Section 4.6.2) and then extrapolated to other compounds based upon a model.

4.6.1 Use of impregnated performance reference compounds

With this approach (Huckins et al., 2002)[11], the passive sampling device is initially equilibrated with an innocuous species that is not native to the sediment. At equilibrium, the performance reference compounds (PRC) concentration on the fiber will approach zero so measurement of the remaining PRC to its initial concentration provides a direct indication of the fractional extent of equilibrium. Difficulties with this approach include appropriate identification of a compound not present or present in very low concentrations that can be used as a PRC. In addition, the hydrophobicities (and therefore kinetics of uptake) of the PRCs should be similar to the compounds of interest and equilibrium must be achieved during pre-equilibration prior to use of the passive sampler. Finally sorption and desorption must be linear, first order and reversible processes (generally valid at low concentrations but may not be valid at high concentrations or in the presence of strongly sorbing phases such as activated carbon). Deuterated PAHs (d10-Fluoranthene, d12-chrysene, d12-benzo[b]fluoranthene and d14-dibenz[a]anthracene) satisfy these requirements and have been successfully used as PRCs[12]. By fitting the fractional approach to steady state for these deuterated PAHs to a model of sorption onto the passive sampler (as described below), the fractional approach to steady state for any compound could be estimated. Decachlorobiphenyl or PCB congeners that are absent from field samples are good internal standards for PCBs

The uptake kinetics model used to calibrate the data is described in Lampert (2010)[13]. Assuming external mass transfer resistances control uptake in a thin film (locally two dimensional) surrounding by static sediment (diffusion controlled transport), the mass uptake into a sorbent fiber is given by

$$M(t) = K_{fw} C_{pw} L \left[1 - \exp\left(\frac{RDt}{L^2 K_{fw}^2} \right) \mathrm{erfc}\left(\frac{\sqrt{RDt}}{LK_{fw}} \right) \right] \quad \text{for uptake of contaminants}$$

$$M(t) = M_0 \left[\exp\left(\frac{RDt}{L^2 K_{fw}^2} \right) \mathrm{erfc}\left(\frac{\sqrt{RDt}}{LK_{fw}} \right) \right] \quad \text{for desorption of PRCs} \tag{8}$$

Where L is the surface volume to area ratio of the fiber (the thickness if a rectangular film with a single side exposed or the half thickness if both sides are exposed), *erfc* represents the complementary error function and the other parameters are as defined previously. The complementary error function is a tabulated function that can be found in standard mathematical reference texts but it also an available function within the mathematical library of excel and most other numerical evaluation languages. The bracketed term is the fractional approach to steady state or equilibrium for uptake of contaminants (or loss of PRCs). Key simplifications that lead to this solution are locally flat coordinates and control by external mass transfer resistances. Both of these assumptions are typically valid even for cylindrical PDMS fibers placed in a static environment. The assumption of diffusion controlled transport can be relaxed by interpreting the value of D as an effective diffusion/dispersion coefficient.

Use of this approach involves measurement of the value of $M(t)/M_0$ for each PRC. This is simply the ratio of the concentration in the fiber divided by its initial concentration for each PRC. The product RD consistent with this ratio for the specific exposure time t, fiber thickness L and PRC K_{fw} (as estimated with K_{ow}) can then be determined directly. Values for each PRC can then be plotted against a measure of hydrophobicity, such as K_{ow}. The retardation factor, R, is normally expected to be linearly dependent upon K_{ow}, while the effective diffusivity, D, is only a weak function of compound and therefore RD is normally expected to be linearly dependent upon K_{ow}. Thus a plot of RD vs. K_{ow} should be linear and the linear best fit curve can be used to estimate RD for any other compound based upon its K_{ow}. The estimated value of RD can then be used in the first equation of Equation (8) using that compounds K_{fw} (also correlated with K_{ow}) and the fiber dimension L and exposure time t.

4.6.2 Compare fibers of the same size collected at two different times or use of two different size fibers

In this approach the accumulation of the contaminant of interest in the PDMS at two different times or with two different size fibers can be used in conjunction with a kinetic model to estimate the fractional achievement of steady state. The ratio of the concentrations measured in the two different size fibers or at two different times provides an equation from which RD can be estimated using a nonlinear root finding function (e.g. in Excel) or via trial and error.

$$\frac{M_1(L_1,t_1)}{M_2(L_2,t_2)} = \frac{L_1}{L_2} \frac{\left[1 - \exp\left(\frac{(RD)t_1}{L_1^2 K_{fw}^2} \right) \mathrm{erfc}\left(\frac{(RD)^{1/2} t_1^{1/2}}{L_1 K_{fw}} \right) \right]}{\left[1 - \exp\left(\frac{(RD)t_2}{L_2^2 K_{fw}^2} \right) \mathrm{erfc}\left(\frac{(RD)^{1/2} t_2^{1/2}}{L_2 K_{fw}} \right) \right]} \tag{9}$$

One advantage of this approach is that there is no additional analytical complexity. In addition, data from all compounds, i.e. over the entire range of hydrophobicities, can be used to

calibrate the model and yield higher accuracy estimates of the required non-equilibrium corrections.

4.6.3 Direct use of the transient uptake model (diffusion only)

The model of transient uptake could also be used directly to estimate the fractional approach to equilibrium by using predictive estimates of retardation factor and effective diffusivity. Details of this method are described by Lampert (2010)[13].

Active mixing of pore waters by tidal mixing, groundwater upwelling, bioturbation or hyporheic exchange will speed transport and can be incorporated into Equation (8) by considering an effective diffusion coefficient. In general, however, this is difficult to estimate *a priori* in field sediments and the use of performance reference compounds (e.g. deuterated compounds), time series measurements, or two different size sorbent fibers is recommended to fit uptake kinetics model to observations as outlined above.

4.7 Assessing bioavailability with pore water concentrations measured by SPME

Lu et al (2011)[1]demonstrated that bioaccumulation of PAHs and PCBs in deposit-feeding organism can be predicted from the pore water concentrations measured as outlined above. At equilibrium, the potential for bioaccumulation of non-metabolizing hydrophobic organics is given by a lipid-water partition coefficient usually estimated asK_{ow}[14]. Therefore, site-specific bioaccumulation of HOCs (i.e. lipid normalized tissue concentration) can be estimated from the in-situ pore water concentrations measured by passive sampling devices as shown by Eqn 10

$$C_{t,\text{predict(site)}} = K_{OW} * C_{pw}(site) \qquad (10)$$

It should be emphasized that because bioaccumulation may correlate well with water concentrations does not mean that the route of uptake is through the water. It is more likely that the sediment, pore water and benthic organisms are in a state of quasi-equilibrium and the pore water concentration is simply an indicator of that equilibrium.

Alternatively, the pore water concentration could be compared directly to water based criteria. Although not strictly applicable in pore waters, surface water quality standards such as National Recommended Water Quality Criteria (NRWQC) are often as a comparison tool for pore water concentrations. Water concentrations leading to toxicity are also often used as a comparison tool.

5 Quality Control

5.1 Field blanks

A deployment blank should be employed as a field blank. The deployment blank is a sampler that is shipped together with other samplers to the field but is shipped back without deployment. A retrieval blank is a sampler that is shipped together with other samplers upon retrieval but is not needed if the samples are processed immediately upon retrieval. The field blanks are used to assess possible contribution of airborne contamination during shipboard activities.

5.2 Field solvent blanks

Field solvent blanks will be analyzed at the time of filling of the vials for shipment, i.e. one at the start of filling and one at the end where the same solvent source has been used. If these

contain PAHs at significant levels, new vials will be filled with a separate source and the process will be repeated. In addition, solvent blanks should be shipped with the samples at a frequency of 1 per 20 samples.

5.3 Field control samples

Field control samples are used to track the solvent volume change or contamination during transition if on site processing samplers are needed. The field control samples can be calibration standards or other solution with known concentrations. The field control samples are treated identically with other samples. At least five field control samples are needed for each deployment. They can be five different concentrations or five replicates of the same concentration if estimation of field concentrations is available. The average of the concentration change for all compounds and in all field control samples should be within 15% to avoid solvent volume adjustment.

5.4 Field internal standards

Although field control samples indicate solvent stability during transition, internal standards are recommended for field samples to indicate any changes in solvent loss in individual samples. Deuterated PAHs and PCB congeners not present in the field are good choices for internal standards. If an internal standard is used it should be included in the extraction vials. It should not be present in the field in significant quantities and should not be used as a PRC. The average of the concentration change for all internal standards added in each sample should be within 15% to avoid solvent volume adjustment.

5.5 QC samples for chemical analysis

The QC samples for chemical analysis of PAHs and PCBs including initial calibration, second source standard check and continue calibration verification check etc should meet the acceptance criterion set in the analytical methods. A complete set of appropriate guidelines for QA-QC can be found in Table 5.1

Table 5.1 Quality guidelines for organic analysis by gas chromatography and high-performance liquid chromatography (method 8082&8310). From DoD QSM version 4.1[15].

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method	QC acceptance criteria published by DoD, if available; otherwise method-specific criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria	NA	This is a demonstration of analytical ability to generate acceptable precision and bias per the procedure in Appendix A. No analysis shall be allowed by analyst until successful demonstration of capability is complete
MDL study	At initial set-up and subsequently once per 12-month period; otherwise quarterly MDL verification checks shall be performed	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or re-conduct MDL study	NA	Samples cannot be analyzed without a valid MDL.
Minimum five-point initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	One of the options below: Option 1: RSD for each analyte ≤ 20%; Option 2: linear least squares regression: r ≥ 0.995; Option 3: non-linear regression: coefficient of determination (COD) r2 ≥ 0.99 (6 points shall be used for second order, 7 points shall be used for third order).	Correct problem then repeat initial calibration.	NA	Problem must be corrected. No samples may be run until ICAL has passed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Continuing calibration verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the analysis sequence.	All project analytes within established retention time windows. All project analytes within ± 15% of expected value from the ICAL	Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. Retention time windows are updated per the method.
Second source calibration verification (ICV)	Once after each initial calibration	All project analytes within established retention time windows. Value of second source for all analytes within ± 15% of expected value (ICAL)	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL	NA	Problem must be corrected. No samples may be run until calibration has been verified.
Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	NA	
Internal standards verification	In all field samples and standards	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL EICP area within -50% to + 100% of ICAL midpoint standard	Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria are not appropriate for failed standards.	Sample results are not acceptable without a valid IS verification.
Method blank	One per preparatory batch	No analytes detected > ½ RL. and > 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results	Correct problem, then, If required, re-prep and reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
LCS containing all analytes required to be reported	One LCS per preparatory batch	See Table 5 4-1. In-house control limits may not be greater than ± 3 times the standard deviation of the mean LCS recovery.	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Retention time window position establishment for each analyte	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA	NA	
Results reported between MDL and MRL	NA	NA	NA	Apply J-flag to all results between MDL and MRL.	

6 References

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