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Methods to Assess Bioavailability of Hydrophobic Organic Contaminants: Principles, Operations, and Limitations

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Abstract

Many important environmental contaminants are hydrophobic organic contaminants (HOCs), which include PCBs, PAHs, PBDEs, DDT and other chlorinated insecticides, among others. Owing to their strong hydrophobicity, HOCs have their final destination in soil or sediment, where their ecotoxicological effects are closely regulated by sorption and thus bioavailability. The last two decades has seen a dramatic increase in research efforts in developing and applying partitioning based methods and biomimetic extractions for measuring HOC bioavailability. However, the many variations of both analytical methods and associated measurement endpoints are often a source of confusion for users. In this review, we distinguish the most commonly used analytical approaches based on their measurement objectives, and illustrate their practical operational steps, strengths and limitations using simple flowcharts. This review may serve as guidance for new users on the selection and use of established methods, and a reference for experienced investigators to identify potential topics for further research.

Keywords

bioavailability; hydrophobic organic compounds; bioaccessibility; passive sampling; SPME

1. Introduction

Sediment and soil contamination from historical and current use of hydrophobic organic contaminants (HOCs) is spread throughout the world. Sediment and soil-borne HOCs are a concern for ecosystems and human health because of their persistence, bioaccumulation potential and toxicity (Weber et al., 2008). The hydrophobicity of HOCs underlines that their phase distribution is closely influenced by factors such as sediment (or soil) properties and contact time (i.e., aging). Such influences dictate that the exposure and effects of HOCs are not directly related to the commonly measured bulk chemical concentration. Thus, predicting bioavailability has been recognized as a critical step in risk assessment of HOC-contaminated sediments or soils (Alexander, 2000; Cornelissen et al., 2005; Reid et al., 2000).

Over the last two decades, tremendous efforts have been devoted to developing chemical methods capable of predicting HOC bioavailability (Cuypers et al., 2002; Doick et al., 2005;

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Kelsey et al., 1997; Reichenberg and Mayer, 2006). Some of these techniques aim at "mimicking" the uptake into various organisms and can then be termed "biomimetic" methods, whereas other methods aim at measuring chemically defined exposure parameters. All these methods roughly fall into two types. The first type involves partial removal of sorbed HOCs using a mild chemical extractant, a sorbent (e.g., Tenax, XAD resin), or a complexing agent (e.g., cyclodextrin). The second set of methods work on the principle of equilibrium sampling, which include passive samplers such as polyethylene devices (PEDs), semi-permeable membrane devices (SPMDs), polyoxymethylene (POM) sampler, thin ethylene vinyl acetate (EVA) or polydimethylsiloxane (PDMS) coatings, and fiber samplers, e.g., solid phase microextraction (SPME).

This review provides an up-to-date discussion with a focus on the principles, operational steps, and limitations of some of the most commonly used analytical extraction and sampling methods that are directed at measuring bioavailability parameters. For each method, we provide a practical operational protocol that a new user may easily follow, and outline method limitations that may serve as topics for further research.

2. What is bioavailability?

In a paper published in *Science*, Schwarzenbach and colleagues (2006) stated that a major issue in understanding the environmental fate and risk of HOCs in aquatic environments is bioavailability. Although the term "bioavailability" has been widely used in ecotoxicology and risk assessment arena, its definition seems to vary with discipline-specific designations (Alexander, 2000; Bosma et al., 1997; Reichenberg and Mayer, 2006; Semple et al., 2004). In a comprehensive National Research Council report, instead of giving an explicit definition of bioavailability, the authors describe "bioavailability processes" as "individual physical, chemical, and biological interactions that determine the exposure of organisms to chemicals associated with soils and sediments" (Ehlers and Luthy, 2003).

The concept of bioavailability may be better inferred from the methods used for its measurement. Reichenberg and Mayer (2006) summarized that there are two end points that researchers try to measure for bioavailability, i.e., *bioaccessibility* - the measurement of the HOC fraction that is weakly or reversibly sorbed and can undergo rapid desorption from the solid phase to the aqueous phase, and *chemical activity* - the potential of HOCs to partition into organisms at equilibrium according to the Equilibrium Partitioning Theory (EqP) (Di Toro et al., 1991).

2.1 Bioaccessibility and the rapid desorption fraction

Conceptually, as an organism moves through or digests soil or sediment, it is exposed to the freely dissolved HOCs in the aqueous phase. As bio-uptake occurs, the freely dissolved concentration is lowered and replenished relatively quickly by the HOC fraction that is weakly or reversibly sorbed (Ehlers and Luthy, 2003; Lanno et al., 2004). Similarly, it is believed that to be degraded by bacteria, HOCs must first enter the water phase, and that degradation drives the continuous desorption of the reversibly sorbed HOCs from the solid matrix. Thus, the desorbable fraction, or bioaccessibility, may best represent that quantity that is accessible to organisms over a relevant time scale (Cornelissen et al., 2005; Reichenberg and Mayer, 2006).

2.2 Chemical activity and the equilibrium partition theory

Chemical activity depicts the potential for a chemical to undergo spontaneous processes such as diffusion and partitioning (Reichenberg and Mayer, 2006). At equilibrium, chemical activity is the same in each matrix compartment (e.g., solid phase, dissolved organic matter,

water, biota) (Di Toro et al., 1991; Reichenberg and Mayer, 2006). Consequently, at equilibrium, the HOC concentration in one compartment is proportional to that in another. When the relationship between two phases is known, the HOC concentration in one phase can be used along with a partition coefficient (e.g., K_{oc}, BSAF) to predict the concentration in another phase. This is the basis of the Equilibrium Partition theory (EqP) that was originally proposed as a method for predicting bioavailability and benthic bioaccumulation by Di Torro et al. (1991) and Shea (1988). For HOCs present at environmentally relevant levels, chemical activity is represented by the freely dissolved concentration C_{free} (Reichenberg and Mayer, 2006). Many methods have been proposed for measuring C_{free}, most of which fall under the category of equilibrium passive samplers.

2.3 Difference and relationship between bioaccessibility and chemical activity

According to Reichenberg and Mayer (2006), bioaccessibility and chemical activity are two fundamentally different parameters. Bioaccessibility indicates the amount or portion of contaminant that is or can become available within a given time span, and can be measured by partial extraction methods (such as mild solvent extraction or Tenax desorption), while chemical activity refers to the energetic state of a chemical and quantifies the potential for spontaneous physicochemical processes. Chemical activity is theoretically related to C_{free} and can be measured by equilibrium samplers. It should be noted that bioaccessibility is operationally defined, and dependent on the specific scenario (e.g., target organisms, sample matrix, or properties of HOCs) or desorption time and /conditions (e.g., solvent, temperature, shaking velocity) selected during the measurement process. In contrast, chemical activity should be a singular value in a given sample.

The difference between bioaccessibility and C_{free} may be further reflected in their roles in various environmental processes. For example, bioavailability in processes such as biodegradation is more closely dependent on bioaccessibility (Cornelissen et al., 1997; Cuypers et al., 2002; Reid et al., 2000), while in other processes (e.g., baseline and acute aquatic toxicity), it is regulated by chemical activity such as C_{free} (Leslie et al., 2002a; Xu et al., 2007). However, both parameters have been used to describe bioaccumulation of HOCs into invertebrates, often with similar successes (Jonker et al., 2007; Kraaij et al., 2003; Leppänen et al., 2003; Trimble et al., 2008; Yang et al., 2008; You et al., 2007b, 2011). The validity in using C_{free} to predict bioaccumulation may be attributed to the fact that small organisms such as aquatic invertebrates accumulate HOCs passively via diffusion – a process driven by chemical activity gradient (Recheinberg and Mayer, 2006). The overlapping applications, nevertheless, may have contributed to the ambiguity or confusion in bioavailability measurement.

3. Partial extraction methods for measuring bioaccessibility

Several partial extraction techniques, including mild solvent extraction, cyclodextrin (e.g., hydroxypropyl-β-cyclodextrin or HPCD) extraction and Tenax extraction, are commonly used to measure bioaccessibility. Table 1 outlines the working principles of some of the most commonly used methods for measuring bioaccessibility, along with notable advantages and limitations for each method.

3.1 Mild solvent extraction

The general procedure of the mild solvent extraction approach is depicted in Fig. 1, as modified from Kelsey et al. (1997) and Liste and Alexander (2002). The mild solvent extraction presented here includes adding solvent or mixture of solvent and water to a sediment or soil sample, and then agitating the mixture for a period of time prior to analysis of HOCs extracted into the solvent. Mild solvent extraction has been used extensively to

assess the bioaccessibility of HOCs in solid matrices. A wide range of solvents, typically polar solvents, alone or with water, have been tested and in most cases, the measurement was shown to be proportional to biological endpoints such as bioaccumulation and biodegradation (Chung and Alexander, 1998; Dean, 2007; Kelsey et al., 1997; Lei et al., 2006; National Research Council, 2003; Sakai et al., 2009; Tao et al., 2006). For instance, Lei et al. (2006) found that extraction with 70% ethanol for 1 d resulted in 1:1 relationships between the amount of PAHs extracted in the solvent and that biodegraded in field-aged sediments. However, studies show that the "best" method may depend on the matrix, the chemical of interest, as well as the biological endpoint under consideration. For example, methanol-water at the ratio of 9:1 (v/v) resulted in good correlation of atrazine uptake by earthworms, methanol-water at the ratio of 1:1 was found to be better for correlating atrazine mineralization by bacteria, whereas *n*-butanol gave the best estimate of phenanthrene availability to earthworms (Kelsey et al., 1997). Chung and Alexander (1998) in a study involving aged pyrene in soils with different physical and chemical characteristics did not find a strong correlation between the amount assimilated by earthworm and that extracted by *n*-butanol across different concentrations. Therefore, while it has the advantage of being practical and simple, mild solvent extraction has its limitation in its intrinsic dependence on operational conditions such as solvent type, soil-to-water ratio, agitation level and extraction time.

3.2 Cyclodextrin (CD) extraction

Cyclodextrin is a cyclic oligosaccharide with a hydrophilic shell and a toroidal-shaped non-polar cavity that can capture HOC molecules desorbed from a solid matrix. HPCD is the most commonly used CD for bioavailability measurement (Dean, 2007). Fig. 2 displays a flow chart (modified from Cuypers et al., 2002; Reid et al., 2000) showing the general steps of partial extraction using HPCD. The procedure involves adding HPCD solution into a soil or sediment sample, mixing for a predetermined time interval (e.g., 20 h) and then centrifugation to obtain the supernatant to be used for analysis. HPCD extraction has mainly been used to study and predict the biodegradation of PAHs (Cuypers et al., 2002; Doick et al., 2006; Reid et al., 2000; Rhodes et al., 2008, 2010; Stroud et al., 2009; van der Heijden and Jonker, 2009), organochlorines (Wong and Bidleman, 2010), PCBs (Puglisi et al., 2007; Wong and Bidleman, 2010), linear alkylbenzenes (Dew et al., 2005), and aliphatic hydrocarbons (Stroud et al., 2008, 2009) in soils or sediments. Reid et al. (2000) used an excess of HPCD in aqueous solutions to extract soil-associated ^{14}C phenanthrene. The amount of ^{14}C phenanthrene that could be rapidly (20 h) exchanged into HPCD solution provided close to 1:1 correlation with the amount of phenanthrene degraded by catabolically active microorganisms. In another study, extractability of ^{14}C phenanthrene by HPCD solution (50 mM) was compared with microbial mineralization in activated carbon-amended soils. A significant relationship ($p < 0.01$) between HPCD extractability and mineralization was observed in soils with or without activated carbon amendment at 0.1% (Rhodes et al., 2008). It has been suggested that HPCD extraction was a good mimic of the mass transfer processes that limit contaminant availability to microorganisms (Reid et al., 2000). However, the predictability of HPCD extraction decreased for higher organisms such as earthworms (Barthe and Pelletier, 2007; Hartnik et al., 2008; Hickman and Reid, 2005). For instance, no relationship between earthworm accumulation and phenanthrene extractability by HPCD was observed ($r^2 = 0.07$) (Hickman and Reid, 2005). Similarly, HPCD extraction was observed to be a poor indicator of PAH accumulation in benthic invertebrates (Barthe and Pelletier, 2007). The main advantages of HPCD are the ease in sample handling and that no additional device is needed, while the major weaknesses are the species-dependent performance and the limited extraction capacity of HPCD that can lead to underestimations of bioaccessibility (Hartnik et al., 2008). Very recently, "sorptive bioaccessibility extraction (SBE)" has been developed as an approach to avoid such underestimations. SBE integrates a

high capacity absorptive polymer within the bioaccessibility extraction for the continuous removal of analytes from the HPCD solution (Gouliarmou and Mayer, 2012). The SBE approach resulted in higher bioaccessibility estimates for PAHs in wood soot and facilitated also the instrumental analysis by GC-MS.

3.3 Tenax extraction

It is generally believed that microbes or small animals can only access the desorbable portion of the sorbed HOC (Miller and Alexander, 1991), which may be limited by mass transfer kinetics (Bosma et al., 1997). To this end, researchers have used water to desorb soil or sediment-associated HOCs in combination with a compound-scavenging resin, such as Tenax TA. The general operational and data analysis steps are outlined in Fig. 3 for the sequential Tenax extraction method (modified from Xu et al., 2008). The extraction depicted here is initiated by mixing Tenax beads with the sediment slurry in centrifuge tubes, followed by harvesting the Tenax beads by centrifugation and repeating the same step multiple times using clean Tenax beads. The desorbed fraction of HOCs is obtained by analyzing the recovered Tenax beads using solvent extraction and cleanup (if necessary). Tenax TA is a porous polymer having a high affinity for HOCs (Cornelissen et al., 1997; Pignatello et al., 1990a, b). Tenax beads have a density lower than water, making them float to the surface after centrifugation and easy to be recovered from the supernatant (e.g., by filtration). This property, when coupled with its hydrophobic nature for trapping HOCs, simplifies the measurement of HOC desorption. Desorption kinetics derived from sequential Tenax extractions of the same soil or sediment sample can be described with a three-compartment model (Eq. 1), assuming first-order kinetics for each of the three compartments, namely, rapid desorption fraction (F_{rapid}), slow desorption fraction (F_{slow}), and very slow desorption fraction (F_{vslow}) (Cornelissen et al., 1997):

$$S_t/S_0 = F_{rapid}e^{-K_{rapid}t} + F_{slow}e^{-k_{slow}t} + F_{vslow}e^{-k_{vslow}t} \quad (1)$$

where S_0 and S_t are the HOC concentrations in the sample at the beginning (i.e., prior to desorption) and time t, respectively, and k_{rapid}, k_{slow}, and k_{vslow} are the corresponding rate constants for the three desorption pools. However, it should be noted that desorption of HOCs from sediment is a continuum, and the parameters, such as F_{rapid}, F_{slow}, and F_{vslow}, are operationally defined to simplify the model application (Cornelissen et al., 1997; You et al., 2011). Tenax extraction has been often used for determining F_{rapid} of soil or sediment samples (e.g., (Cornelissen et al., 1997; Kukkonen et al., 2003). Many studies show that F_{rapid} is positively related with bioaccumulation or microbial degradation (Braida et al., 2004; Cornelissen et al., 1998; Cui et al., 2010; Kraaij et al., 2002; Landrum et al., 2007; Leppänen et al., 2003; Moermond et al., 2004; White et al., 1999). A significant drawback of Tenax extraction is that a lengthy series of extractions must be carried out to construct desorption kinetics for deriving F_{rapid}, which is both time consuming and laborious. In light of this disadvantage, Cornelissen et al. (2001) and others (Landrum et al., 2007; Moermond et al., 2004; Ten Hulscher et al., 2003) explored the use of a single time-interval desorption (e.g., 6 h, or F_{6h}) in place of F_{rapid}. However, studies show that the ratio of F_{6h} to F_{rapid} may vary greatly, ranging from 0.38 ± 0.25 to 10.26 ± 5.15 for PCBs, PAHs, chlorinated benzenes, and DDTs (Cornelissen et al., 2001; Ten Hulscher et al., 2003). For instance, Yang et al. (2008) observed that for sediment-sorbed pyrethroids, F_{6h} was more similar to C_{free} and was much smaller than F_{rapid}. Such variations may be attributed to different sediment and HOC properties, but nevertheless limit the broad applicability of Tenax extraction for bioavailability evaluation.

4. Passive samplers for measuring freely dissolved concentration

Table 2 lists some of the most commonly used methods for measuring C_{free}, along with their operational principles, notable advantages and limitations. Many different types of equilibrium or passive samplers have been explored for environmental monitoring and these devices can, for practical reasons, be used under non-equilibrium conditions. In non-equilibrium applications, the large capacity of some passive samplers allows the accumulation of HOCs to proceed in the linear range over a long time. Consequently, an average contaminant concentration over a given sampling period can be obtained, which is the so-called time-weighted average (TWA) concentration. Passive samplers in most environmental monitoring studies have been employed as non-equilibrium samplers for the reason of practicality (Petty et al., 2000). However, when passive samplers are applied to sediments and soil (slurries), it is desirable to operate them in the equilibrium partitioning regime, which allows the determination of C_{free}, fugacity and chemical activity without the need for kinetic input variables (Mayer et al., 2000, 2003).

The overarching principle of equilibrium samplers is to measure the analyte concentration in a sampler ($C_{sampler}$) at equilibrium and then use a sampler-to-sample partition coefficient (K_s) to derive C_{free}:

$$C_{free}=\frac{C_{sampler}}{K_s} \quad (2)$$

In the following sections, several passive samplers, i.e., PEDs, POMs, and SPMDs, as well as SPME fibers, are described and discussed. SPMDs are a deviation from true membrane samplers in that a sorbent, usually a lipid-like substance, is enclosed between two layers of membrane, where the membrane plays the role of a holder but may be considered as part of the sorbent phase out of convenience for analyzing the whole SPMD (Huckins et al., 1990, 1999). In addition, in-vial coating with a polymer sorbent (e.g., ethylene vinyl acetate, Wilcockson and Gobas, 2001; PDMS, Reichenberg et al., 2008) represents a recent advancement since it achieves very short equilibration times due to very thin coating thicknesses. Both SPMDs and in-vial coating are included herein to provide an up-to-date and comprehensive review of partitioning based methods.

4.1 Semi-permeable membrane devices (SPMDs)

Semi-permeable membrane devices (SPMDs), originally introduced by Huckins et al. (1990), usually consist of low-density polyethylene (LDPE) membrane, filled with either natural lipids or the model lipid triolein [1,2,3-tri(*cis*-9-octadecenoyl)glycerol]. When placed in samples or in the environment, SPMDs passively accumulate HOCs driven by membrane lipid-sample partitioning. HOCs can cross the polyethylene membrane because random thermal motion of polymers creates transient cavities. The maximal cavity diameter in the membrane is about 10 Å, and therefore only truly dissolved HOCs are expected to be accumulated in SPMDs. A typical operational procedure of SPMD is given in Fig. 4. Similar to the other passive samplers, the operation procedure starts with exposure of SPMDs to the HOC-contaminated sediments. Even though HOCs concentrated in SPMDs can be easily recovered by dialysis into organic solvents (e.g. hexane), the extract often needs to be further cleaned up because of impurity from triolein and polyethylene. The cleaned extract is then measured by GC to derive the HOC concentration on SPMD, and hence C_{free}. Several studies have demonstrated the ability of SPMDs for predicting bioavailability of HOCs (Baussant et al., 2001; Cho et al., 2009; Hofelt and Shea, 1997; Leppänen and Kukkonen, 2006; Tomaszewski et al., 2007; Zimmerman et al., 2004). In Hofelt and Shea (1997), SPMDs were deployed concurrently with blue mussels in a marine harbor contaminated

with PCBs and organochlorine pesticides. A good correlation was observed between HOC accumulation in SPMDs and mussels (r^2 = 0.57-0.85 for individual pesticides; r^2 = 0.81-0.96 for PCB congeners). More recently, SPMDs were deployed under field conditions to investigate the effect of active carbon on bioavailability of PCBs. About 50% reduction in PCB accumulation in the SPMD sampler was seen when the sediment was amended with 2% active carbon, which mimicked the effect on the uptake of PCBs by clams (Cho et al., 2009). A significant advantage of SPMDs is its commercialization and standard operation protocols (Huckins et al., 1990). However, sample depletion caused by the high extraction capacity of SPMDs similarly limits their use for measuring bioavailability, especially for samples with limited volumes. The outside of exposed SPMDs is often biofouled by particles or small organisms from the sample matrix and must be cleaned by dilute acid and water before analysis. Moreover, the operation of SPMDs is not straightforward (e.g., potential loss of triolein, extra clean-up steps before analysis as mentioned above), and the time to equilibrium is often very long (Hofelt and Shea, 1997; Leppänen and Kukkonen, 2006).

4.2 Polyethylene devices (PEDs)

Another kind of passive sampler, similar to SPMDs, but without the triolein filling, employs polyethylene as sorbent phase and is thus termed polyethylene devices (PEDs). A number of studies have used PEDs to measure HOC concentrations in water (Adams et al., 2007; Booij et al., 2003), C_{free} in sediment porewater (Cornelissen et al., 2008; Friedman et al., 2009), and bioavailability as affected by carbon amendment or sediment resuspension (Hale et al., 2010; Tomaszewski et a., 2008; Tomaszewski and Luthy, 2008; Vinturella et al., 2004; Wang et al., 2011). In Tomaszewski et al. (2008), *Mytilus edulis* accumulated significantly less DDT in sediments amended with virgin and reactivated carbon as compared to non-amendment sediment. The tissue concentrations correlated well with concentrations in PEDs placed in the same sediments. Similarly, the bioavailability of PCBs in resuspended sediments was assessed by both PEDs and bioaccumulation in a polychaete. A nearly 1:1 relationship (r^2 = 0.87) was observed between PCB concentration in PEDs and polychaete lipid (Friedman et al., 2009). PEDs are inexpensive, easily deployable, and adoptable to various sensitivity needs. Compared with SPMDs, the operation of PEDs is more straightforward because of the absence of a second sorbent phase and the omission of extra clean-up for lipid removal as in SPMDs. In the same vein with SPMDs, a large size of sample is needed for PEDs to prevent depletion and equilibration times are generally very long since PE is generally rather thick and characterized by high K values. In recent years, a performance reference compound (PRC)-based kinetic calibration approach has been proposed to mitigate the problem of unreasonably long equilibrium time. As an isotope-labeled analogue (referred as PRC) and the target analyte have nearly identical properties, the desorption rate constant of PRC may be used to approximate the absorption or extraction rate constant of the target analyte, and therefore long sampling time (to attain equilibrium) is no longer a prerequisite for passive samplers. The PRC-based calibration has been applied for passive samplers, like PEDs or SPMD, to calibrate sampling rate and compensate the effect of environmental factors for *in situ* sampling (Adams et al., 2007; Allan et al., 2009; Booij et al., 2006; Tomaszewski and Luthy, 2008).

4.3 Polyoxymethylene (POM) samplers

POM was initially introduced by Jonker and Koelmans (2001) to determine partitioning of PAHs and PCBs in soot-water and sediment-water systems. POM-based equilibrium samplers were later deployed in both marine and freshwater sediments (Cornelissen et al., 2008; Hawthorne et al., 2009; Oen et al., 2011). Unlike the other polymer materials frequently used for equilibrium sampling, POM contains a repeating polar group (-CH_2-O-H_2-). It is therefore expected that POM also has an improved sensitivity for detecting polar

compounds (Endo et al., 2011). The feasibility of POM in predicting bioavailability has been evaluated in a number of recent studies (Gomez-Eyles et al., 2012; Gschwend et al., 2011; Muijs and Jonker, 2011, 2012; Sormunen et al., 2008). For example, the bioconcentration of petroleum hydrocarbon mixtures in aquatic worms exposed to oil-contaminated sediments was well predicted using POM-based samplers under laboratory conditions (Muijs and Jonker, 2011). POM has good physical and chemical stability and is resistant to organic solvents under harsh extraction conditions (Jonker and Koelmans, 2001). The smooth and hard surface of POM also makes it less susceptible to the trapping of particles or biofouling, as compared to some other samplers (van der Heijden and Jonker, 2009). Like PEDs or SPMDs, sampling with POM also requires long time to attain equilibrium and large sample sizes to avoid disruption of phase equilibrium. Compared to other passive sampling materials and particularly the silicone PDMS, POM provides very low diffusion coefficients for both analytes and potential impurities (Rusina et al., 2007). This has the advantage of leading to very clean solvent extracts and the disadvantage of leading to slow sampling kinetics when diffusive mass transfer within the polymer becomes rate limiting. Compared to other passive samplers, development of POM for sampling under field conditions is still limited.

4.4 In-vial coating samplers

Wilcockson and Gobas (2001) introduced the in-vial coating concept by depositing ethylene vinyl acetate (EVA) on the internal wall of glass vials to form a thin sorbent layer of μm-thickness. Reichenberg et al. (2008) extended this approach to vials with PDMS coatings of multiple coating thicknesses (e.g., 3-12 μm thickness). The sampling procedure generally follows: (1) equilibrating the coated vials with the investigated soil or sediment; (2) extracting the empty vial and analyzing the HOC to determine $C_{polymer}$; and (3) calculating C_{free} from $C_{polymer}$ and a pre-determined partition coefficient. The general advantages of coated vials and coated jars are the combination of (1) very thin coating thicknesses that provide short equilibration times, (2) a sufficiently large polymer volume to provide good method sensitivity and (3) practical and simple sampling and extraction. Commercialization of coated vials or jars in the future would assure uniformity of samplers and may help promote the adoption of this method. An apparent general limitation of coated vials is that they might be difficult to apply for *in situ* sampling.

The multiple coating approach has some important general features (Reichenberg et al., 2008), and allows, for instance, equilibrium sampling to be confirmed without tedious time series measurements (Bartkow et al., 2004; Mayer et al., 2003). The extracted mass of analyte is plotted against the mass of polymer coating, and proportionality then indicates that the sampling is characterized by (1) equilibrium sampling, (2) real phase partitioning into the polymer rather than adsorption and (3) the absence of biofouling or polymer abrasion artifacts (Reichenberg et al., 2008). A relatively large surface area to volume (A/V) ratio in the in-vial coating method accelerates equilibration. For example, the A/V ratio of SPME fiber with 100 μm coating is 15.4 mm^{-1}(Wilcockson and Gobas, 2001), while the A/V ratio for a coated vial with 2 μm coating is 500 mm^{-1}. Mäenpää et al. (2001) demonstrated that equilibrium could be reached within 2 weeks for PCB congeners, including PCB-209, when contaminated sediments were equilibrated with PDMS coated jars under agitated conditions. Equilibrium may be further sped up by decreasing the thickness of polymer coating (Minhas et al., 2006; Wilcockson and Gobas, 2001). Due to the relatively large polymer volume in PDMS-coated glass jars, PCBs in Baltic Sea sediments were detected at levels as low as fg/L and pg/L in a recent study (Jahnke et al., in press).

4.5 Solid phase microextraction (SPME) fibers

Solid-phase micro-extraction (SPME), originally introduced by Arthur and Pawliszyn (1990), employs a fiber that usually contains a glass or steel rod coated with a thin film of polymer (e.g., PDMS, polyacrylate). When in contact with sample, HOCs are absorbed via diffusion into the polymer phase. Because of the minute amount of polymer on the thin fiber, SPME sampling is usually non-depletive and thus does not appreciably disturb phase equilibrium in the sampled matrix, which makes it highly compatible with bench-scale bioassay tests using small exposure vessels or even biological samples (Jonker et al., 2007; Leslie et al., 2002ab; Mayer et al., 2000, 2003; Potter and Pawliszyn, 1994; Ramos et al., 1998; Trimble et al., 2008; You et al., 2007a; Zhang et al., 2010). In addition, SPME, as compared with SPMDs or PEDs, requires little or no solvent in sample preparation. Depending on the configuration, there are two general types of SPME applications, i.e., injector-type SPME and disposable SPME.

Injector-type SPME—The injector-type SPME, which was first developed as a solvent-free analytical tool by Arthur and Pawlizsyn (1990) for headspace or aqueous phase analysis, streamlines sampling and analysis as the exposed fiber is directly inserted into a GC or HPLC inlet for elution. Since the entire amount on the SPME fiber is introduced into the GC or HPLC column, good sensitivity is attained. The use of injector-type SPME to measure C_{free} and related parameters is an extension of the originally intended application (Leslie et al., 2002ab; Maruya et al., 2009; Ramos et al., 1998; Xu et al., 2007; Yang et al., 2006, 2007; Zeng et al., 2005). Due to its assembly configuration, the operation of injector-SPME can be operated with an autosampler, which maximizes sample throughput and precision, but also restricts the sampling time to be within the range of minutes and up to one hour. Such sampling times are generally not sufficient for the equilibrium sampling of HOCs and injector-SPME is thus often operated in the linear kinetic mode, i.e., under non-equilibrium conditions. For instance, Xu et al. (2007) used injector-type SPME with fixed sampling conditions (e.g., sampling time of 25 min and consistent mixing rate) to measure C_{free} of pyrethroid insecticides in sediment porewater. Compared to four other estimation methods, i.e., bulk sediment concentration, OC-normalized sediment concentration, total porewater concentration, and porewater concentration normalized over dissolved OC, C_{free} given by SPME yielded the best correlation with mortality of *Chironomus tentans* in sediments. In addition to bench-scale applications, Zeng et al. (2005) and Maruya et al. (2009) expanded the use of injector-type SPME to *in situ* monitoring, under non-equilibrium conditions (Zeng et al., 2005) and equilibrium conditions (Maruya et al., 2009), in the open environment. The SPME fiber assembly was protected from damage or biofouling by being secured inside a perforated copper housing. After deployment in coastal ocean water for weeks, parts-pertrillion concentrations of DDT were detected by the sampler, which was in close agreement with independently measured values (Zeng et al., 2005).

Non-equilibrium or kinetic SPME is the most commonly used style for injector-type SPME sampling, but the influence of matrix effects on the accuracy of C_{free} analysis need to be carefully evaluated. The diffusive uptake into the fiber was found to be enhanced by various media constituents, such as humic acid, digestive fluid, or plant exudates (Kramer et al., 2007; Mayer et al., 2005, 2007). However, the overestimation, based on the results in Oomen et al. (2000), could be observed only if diffusion through the boundary layer was the rate-limiting step. Ramos et al. (1998) showed that the matrix did not interfere with C_{free} determination of PCB 77 by PDMS fibers in samples containing 20 mg/L of humic acid. Oomen et al. (2000) suggested that significant matrix influences may occur only under extreme conditions (e.g., a solution containing proteins at 3.7 g/L).

Disposable SPME—Fibers in the injector-type SPME are some of the same optical fibers used in telecommunication. Disposable type-SPME makes use of the SPME fibers but without the accessories, lending much increased flexibility and feasibility. Disposable fibers can be thermally desorbed manually in the injector of conventional GCs (Mayer et al., 2000), which however is not very time efficient. A more practical approach is the extraction with a small amount of solvent before analysis, which then can be measured not only by GC but also by HPLC (Ter Laak et al., 2006). Mayer et al. (2000) introduced equilibrium sampling with polydimethylsiloxane (PDMS)-coated fibers to measure C_{free} by placing short fibers directly in a sediment matrix, and termed the method "matrix-SPME". In matrix-SPME, the fiber is equilibrated within the sediment (or soil) and C_{free} is calculated from the concentration in the fiber coating (C_{fiber}) using a predetermined fiber-to-water partition coefficient (K_{SPME}). The validity of matrix-SPME for estimating bioavailability has been demonstrated for different classes of HOCs under various environmental conditions. In many cases, a direct relationship has been observed between organism body residues, bioaccumulation factor (BCF), or biota sediment accumulation factor (BSAF) and fiber concentrations (Cui et al., 2011; Heringa and Hermens, 2003; Kraaij et al., 2003; Mayer et al., 2000; van der Wal et al., 2004; Yang et al., 2009ab). For instance, steady-state concentrations of chlorobenzenes in earthworms were linearly related to concentrations on PDMS fibers when both the organisms and fibers were simultaneously exposed in spiked Organization for Economic Cooperation and Development (OECD) soils containing various chlorobenzenes (van der Wal et al., 2004). In addition to the qualitative relationship observed between C_{fiber} and endpoint of bioassays, C_{free} derived from SPME has also been used to predict body residues of HOCs by multiplying with bioconcentration factor (BCF) (Hunter et al., 2008; Jonker et al., 2007; Kraaij et al., 2003; Lu et al., 2011; Trimble et al., 2008; van der Wal et al., 2004). For example, in Jonker et al. (2007), SPME-predicted bioaccumulation generally was within a factor of 10 of the measured body residue in earthworms, while the currently used risk assessment model over-predicted bioaccumulation by 10-10000 times. PCBs and PAHs accumulated in the deposit-feeding oligochaete *Ilyodrilus templetoni* was accurately predicted via a linear relationship (slope = 1.08, r^2 = 0.76) using C_{free} derived from PDMS fibers and BCFs, which were derived from K_{ow} of HOCs (Lu et al., 2011). However, such predictions have the drawback of requiring several input parameters, i.e., BCF and K_{SPME}, each with its associated error. In a recent study, bioconcentration into organism lipids was predicted as the product of equilibrium concentration in PDMS coating and PDMS to lipid partition ratio (Mäenpää et al., 2011). The estimation of equilibrium partitioning concentrations in organisms via lipid to PDMS partition coefficients is a promising strategy to circumvent some of the errors introduced with input parameters.

A unique advantage of disposable SPME is its compatibility with bench-scale bioassays, largely because of the small size and flexibility of disposable fibers. The concurrent exposure of disposable fibers and organisms in the same bioassay chambers are considered to be more representative of organism exposure (Trimble et al., 2008; van der Heijden and Jonker, 2009; You et al., 2006, 2007a). The typical operational procedures of disposable SPME involving coexposure with organisms are depicted in Fig. 5 (modified from Hunter et al., 2008, 2009). After a thermodynamic equilibrium among fiber, biota, and sediment is established during the co-exposure, C_{free} may be calculated from C_{fiber} measured after solvent extraction and instrumental analysis. When radio-labeled HOCs are used, the fiber may be placed directly in scintillation cocktail for measurement (Heringa et al., 2003). For non-labeled HOCs, the fiber may either be thermally desorbed or extracted with a small volume of solvent (e.g., 100 μL) before routine instrumental analysis (e.g. HPLC or GC) for quantitative analysis (Hunter et al., 2009).

The use of biomimetic tools such as SPME has contributed to a better understanding of how sediment or soil geochemistry influences contaminant bioavailability. For example, carbonaceous materials in sediments or soils are considered super sorbents for HOCs and have the ability to markedly alter the bioavailability of HOCs (Cornelissen et al., 2005). The effect of different types of black carbon on the bioavailability of HOCs has been investigated with the aid of disposable SPME fibers (Conder and La Point, 2005; Jonker et al., 2007; Pehkonen et al., 2010; Yang et al., 2009ab). In the case of carbon nanomaterials, the availability of HOCs has also been found to correlate closely with C_{free} measured by SPME fibers (Cui et al., 2011, Hu et al., 2008), but exceptions exist. For instance, Hu et al. (2008) used SPME fibers to measure C_{free} in fullerene suspensions and the correlation between organochlorine concentrations in medaka (*Oryzias latipes*) and that on the SPME fiber deteriorated in the presence of fullerene (p = 0.073-0.081, r^2 = 0.42-0.44). The poor correlation was attributed to the different uptake mechanisms of organochlorine by the organism and the fiber, i.e., only the freely dissolved form was available for accumulation on the SPME fiber, while both the freely dissolved and the fullerene-associated forms were involved in medaka accumulation.

There are several important considerations in the use of SPME for bioavailability assessment, including fiber surface fouling, matrix effects, and sample equilibrium time. As with other passive samplers, there is a potential for surface fouling from particles, humic matter and bacteria adhering to the fiber surface. Surface fouling may cause an overestimation if HOCs are contained in high concentrations in the adhering particles or underestimation if the particles prevent HOCs from diffusing into the SPME polymer (Heringa and Hermens, 2003). Although a few studies have shown variations in measurements caused by protein coating on the fiber surface (e.g., Poon et al., 1999), most published studies have demonstrated the absence of a significant effect from fiber fouling in diverse environmental matrices (Heringa and Hermens, 2003; Oomen et al., 2000) or even biological tissues with high fat content (Ossiander et al., 2008). However, when applied in complex matrices like sediments or digestive fluids, it can be difficult to control the sampling kinetics of fibers because various sample constituents may affect the diffusive mass transfer into the sampler (Mayer et al., 2007; Oomen et al., 2000). For instance, the presence of high levels of DOC in the matrix increased the diffusive mass flux into the fiber polymer phase and shortened the equilibrium time (Heringa and Hermens, 2003; Mayer et al., 2007; Oomen et al., 2000; ter Laak et al., 2009). In Mayer et al. (2007), the diffusive mass transfer of 12 PAHs was much faster in the tested media with humic acid or digestive fluid than that in water. It is generally accepted that the matrix effect in SPME applications is not an issue if the operation is in the equilibrium sampling mode (Mayer et al., 2003), since the partitioning properties of the PDMS remain unchanged (Jahnke and Mayer, 2010).

Although equilibrium sampling is the preferred approach in matrix-SPME applications, it is often difficult if not infeasible to attain equilibrium between the fiber and the matrix within a reasonable time for many HOCs. The time to equilibrium increases linearly as the thickness of polymer coating or the hydrophobicity (K_{ow}) of HOCs increases (Mayer et al., 2003; ter Laak et al., 2008). Meanwhile, long equilibration times make separate validation experiments costly and labor-demanding. Therefore, the long time to equilibrium is a significant limitation in the use of SPME for C_{free} measurement. Solutions to circumvent this limitation will almost certainly increase the versatility and hence the adoption of SPME in bioavailability assessment.

5. Conclusion and recommendation

Traditional methods for assessing ecological risks of organic contaminants that utilize bulk concentrations often contain matrix-specific biases or artifacts in risk predictions. Over the

last two decades, a range of biomimetic methods have been explored for measuring bioavailability of HOCs, and many successful applications have been found in such matrices as sediments, soils, water and even biological samples (e.g., serum, fluids, tissues). However, these biomimetic methods, measuring either bioaccessibility (e.g., mild solvent extraction, Tenax, cyclodextrin) or chemical activity (e.g., SPMDs, POMs, PEDs, SPME), aim to provide a better exposure basis to study and predict different biological end-points. Therefore, careful consideration should be given to method selection o match measurement objectives.

In most studies to date, spiked sediments or soils were used in the evaluation of biomimetic methods. Further investigations should involve field-contaminated sediments or soils, including samples from actual remediation sites to further expand the scope of method utility. In addition, most method evaluations have employed small benthos or terrestrial invertebrates and relatively stable legacy HOCs (e.g., PCBs, PAHs). Future studies should consider the use of such methods on HOCs that are readily metabolized or to address HOC biomagnification through food webs.

Research on bioavailability and biomimetic methods, although has increased substantially when gauged with the sheer number of published studies, is still rather discorded at the moment. Most studies stopped at the state of method development or validation. In the scenario where a method was validated, researchers frequently stopped at finding a positive correlation, rather than evaluating the slope of regression or testing the predictive power of the measured bioavailability in various risk assessment paradigms. The broader adoption of biomimetic methods will also depend on method standardization or commercialization. At present, various versions of these methods are being used, which often hinders direct data comparisons because of inconsistencies in the operational protocols, materials used, or even means of data interpretation. For conventional methods, benchmarks such as recovery, method detection limit, accuracy, precision, are clearly defined and the procedures for testing these benchmarks have been clearly spelled out in guidelines published by the U.S. EPA or OECD. While the performance evaluation criteria may be different for biomimetic methods, publication of standard methods and adherence to clear QA/QC criteria will be critical for assuring data quality and hence increased the acceptance of biomimetic methods.

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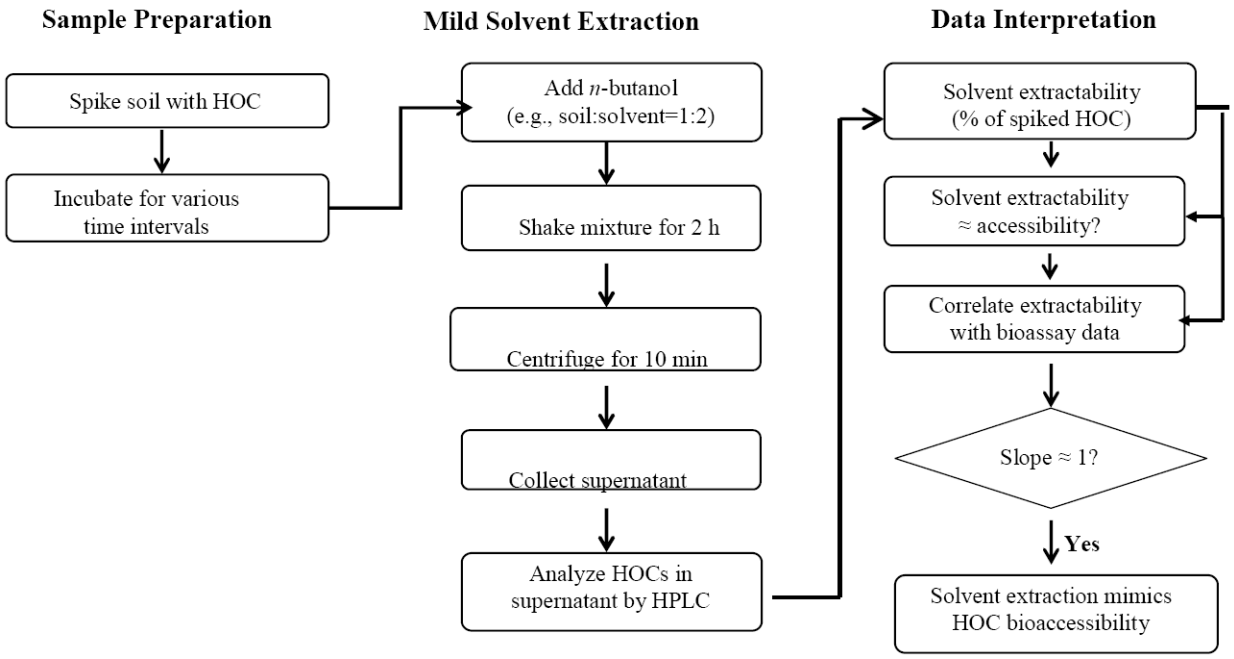

Figure 1.
A typical operational protocol of the mild solvent extraction method (modified from Kelsey et al., 1997; Liste and Alexander, 2002). (Sample preparation optional)

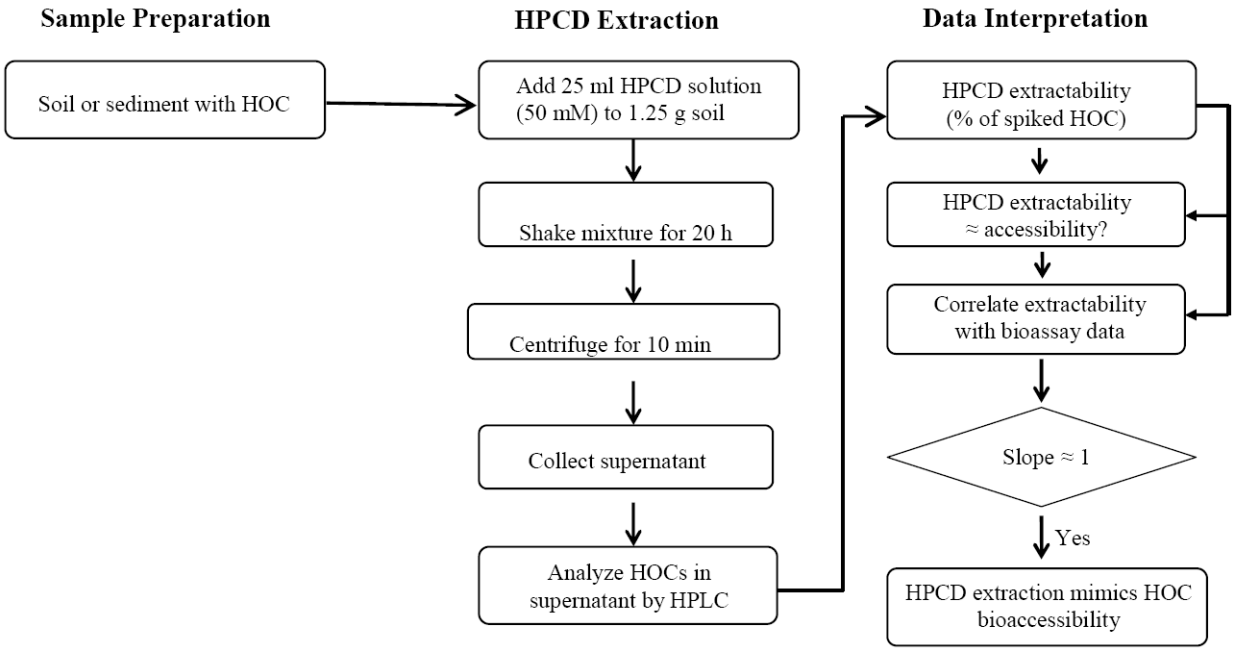

Figure 2.
A typical operational protocol of the hydroxypropyl-β-cyclodextrin (HPCD) extraction method (modified from Cuypers et al., 2002; Reid et al., 2000).

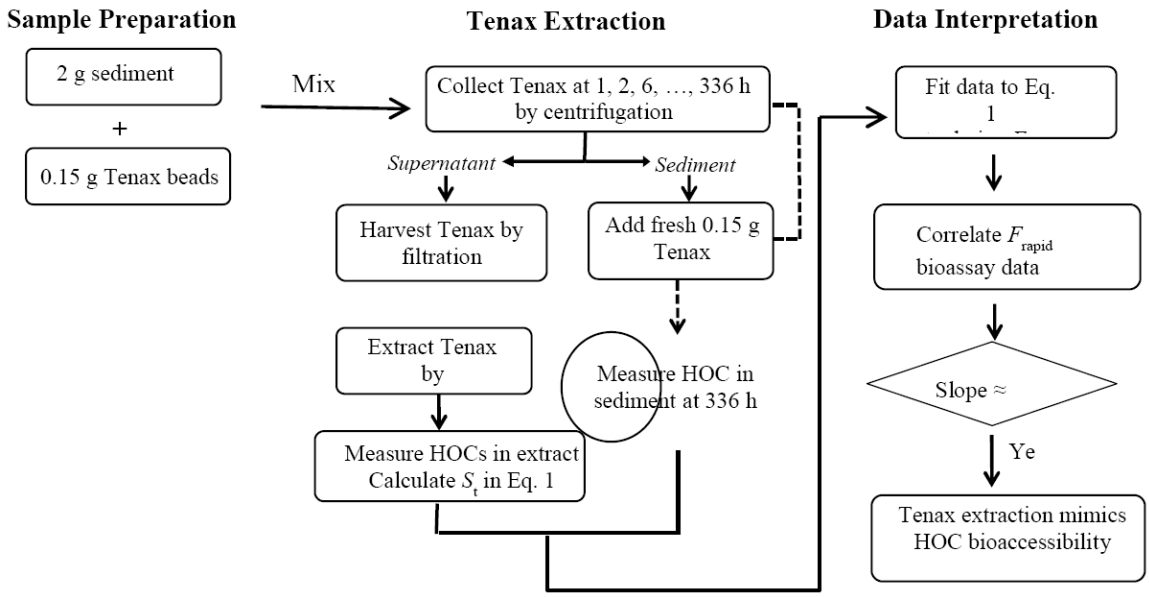

Figure 3.
A typical operational protocol of the Tenax extraction method (modified from Xu et al., 2008).

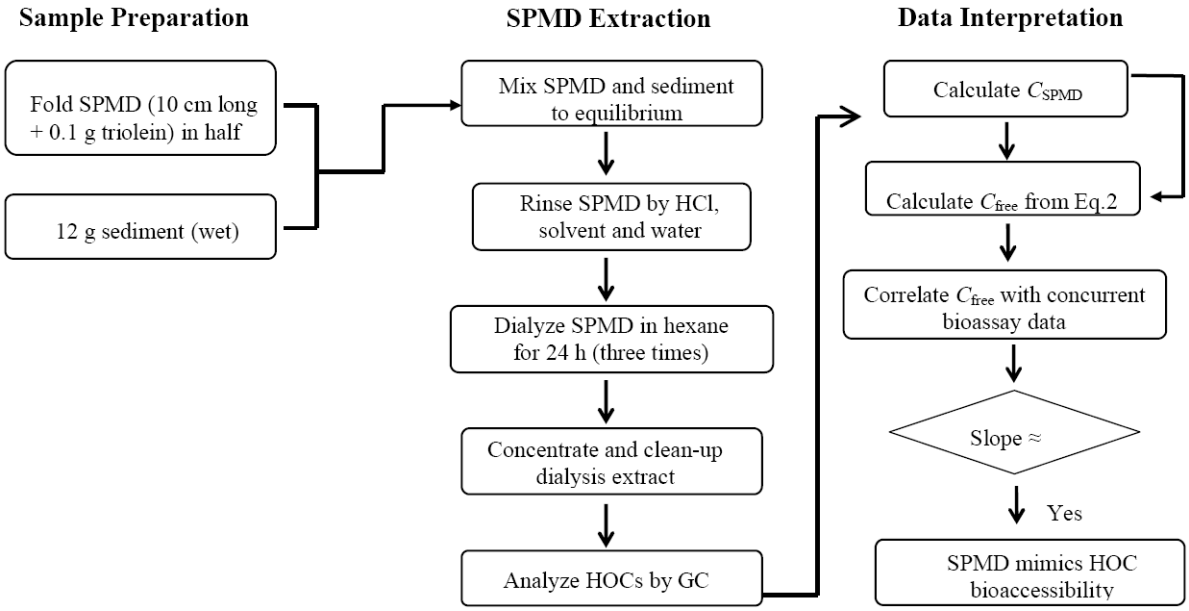

Figure 4.

A typical operational protocol of measuring C_{free} by using semi-permeable membrane devices (SPMDs) (modified from Zimmerman et al., 2004) (Sample preparation step optional)

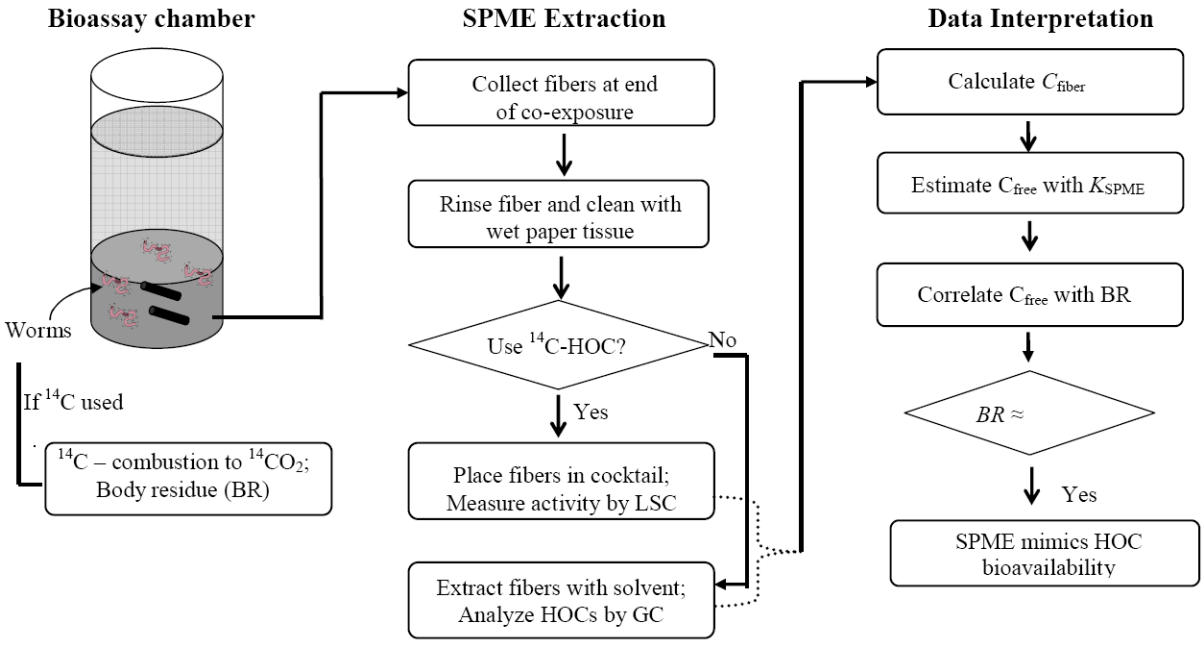

Figure 5.

A typical operational protocol for measuring C_{free} using disposable solid-phase microextraction (SPME) fiber (modified from Hunter et al., 2008, 2009; Kraiij et al., 2003) (LSC: liquid scintillation counting).

Table 1

An overview of biomimetic methods for measuring hydrophobic organic contaminant (HOC) bioaccessibility: Principles, strengths and weaknesses

Method	Working principle	Strengths	Weaknesses
Mild solvent extraction (Kelsey et al., 1997; Liste and Alexander, 2002)	• Analyze HOC in mild solvent after extraction • Partial extraction measuring rapid desorption fraction	• Easy operation	• Results vary with solvent, matrix and organisms • Not applicable for *in-situ* measurement
HPCD extraction (Cuypers et al., 2002 ; Reid et al., 2000)	• Analyze HOC in HPCD after extraction • Partial extraction measuring rapid desorption fraction	• Fast and easy operation	• Species-dependent performance and limited extraction capacity • Not applicable for *in-situ* measurement
Sequential Tenax extraction (Cornelissen et al., 1997; Xu et al., 2008)	• Consecutive desorption with Tenax as HOC trap • Use regression model to estimate various desorption fractions • Use F_{rapid} to indicate bioaccessibility	• Tenax reused and economical • Understanding of desorption kinetics	• Time consuming and laborious • Not applicable for *in-situ* measurement
6-h Tenax extraction (Cornelissen et al., 2001)	• Single-step desorption with Tenax as HOC trap Use F_{6h} to approximate bioaccessibility	• Fast and easy operation	• F_{6h} may not equal to F_{rapid} • Not applicable for *in-situ* measurement

Table 2

An overview of partitioning based methods for measuring hydrophobic organic contaminant (HOC) freely dissolved concentration (C_{free}): Principles, strengths and weaknesses

Method	Working principle	Strengths	Weaknesses
SPMD (Semi-permeable membrane device) (Huckins et al., 1990; Zimmerman et al., 2004)	• Expose sampler in sample matrix • Analysis of HOC in sampler after solvent extraction • Derive C_{free} and use C_{free} to indicate bioavailability	• Good sensitivity due to large sampler volume • Commercially available • Applicable for *in-situ* measurement	• Extensive post-sample processing • Require large sample size • Very long equilibration times • Not compatible with bench-scale bioassays
PED (Polyethylene device) (Cho et al., 2009)	• Expose sampler in sample matrix • Analysis of HOC in sampler after solvent extraction • Derive C_{free} and use C_{free} to indicate bioavailability	• Good sensitivity due to large sampler volume • Inexpensive • Applicable for *in-situ* measurement	• Require large sample size • Very long equilibration times • Not compatible with bench-scale bioassays
Injector-type SPME (Arthur and Pawliszyn, 1990; Xu et al., 2007)	• Expose sampler in sample matrix • Analyze HOC on fiber by direct injection • Derive C_{free} via external calibration and use C_{free} to indicate bioavailability	• Good sensitivity due to analysis of whole fiber • Less time consuming and solvent-free • Automation possible • Applicable for *in-situ* measurement	• Non-equilibrium sampling • Matrix effect • Not compatible with bench-scale bioassays
Disposable SPME (Mayer et al., 2000; Hunter et al., 2008)	• Expose fiber in sample matrix • Analyze HOC at equilibrium • Derive C_{free} via K_{SPME} and use C_{free} to indicate bioavailability	• Inexpensive and easy operation • Compatible with bench-scale bioassays and co-exposure • Applicable for *in-situ* measurements	• Sensitivity may be low • Long equilibrium times for HOCs with large K_{ow}