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CRITICAL REVIEW

Chemical techniques for assessing bioavailability of sediment-associated contaminants: SPME *versus* Tenax extraction†

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The traditional approach for predicting the risk of hydrophobic organic contaminants (HOCs) in sediment is to relate organic carbon normalized sediment concentrations to body residues or toxic effects to organisms. However, due to the multiple variables controlling bioavailability, this method has limitations. A matrix independent method of predicting bioavailability needs to be used in order to be universally applicable. Both chemical activity (freely dissolved chemical concentrations) measured by solid-phase microextraction (SPME) and bioaccessibility (rapidly desorbing fraction) estimated by Tenax extraction have been developed to predict bioavailability of sediment-associated HOCs. The objectives of this review are to summarize a number of studies using matrix-SPME or Tenax extraction to estimate bioavailability and/or toxicity of different classes of HOCs and evaluate the strengths and weakness of these two techniques. Although the two chemical techniques assess different components of the matrix, estimates obtained from both techniques have been correlated to organism body residues. The advantages of SPME fibers are their applicability for use *in situ* and their potential usage for a wide array of contaminants by selection of appropriate coatings. Single time-point Tenax extraction, however, is more time- and labor-effective. Tenax extraction also has lower detection limits, making it more applicable for highly toxic contaminants. This review also calls for additional research to evaluate the role of sequestrated contaminants and ingestion of sediment particles by organisms on HOC bioavailability. The use of performance reference compounds to reduce SPME sampling time and linking chemical based bioavailability estimates to toxicological endpoints are essential to expand the applications of these methods.

Introduction

Aquatic systems are often severely impacted by a variety of contaminants, and various approaches including bioaccumulation and toxicity testing have been developed to assess the risks of this contamination. Bioaccumulation is defined as the total accumulation of contaminants in an organism from all uptake routes[1] and the most straightforward method of determining bioaccumulation potential is by directly measuring chemical residues in organisms exposed to the contaminated matrices. The importance of this concept is that bioaccumulation of a compound in an organism beyond a specific threshold can

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Environmental impact

For more accurate evaluation of the risks of hydrophobic organic contaminants in sediment, a matrix independent method of predicting bioavailability needs to be developed. For this purpose both chemical activity, measured by solid-phase microextraction (SPME), and bioaccessibility estimated by Tenax extraction have been developed. This review summarizes a number of studies using matrix-SPME or Tenax extraction to estimate bioavailability and toxicity of various classes of contaminants, evaluates the strengths and weakness of these two techniques, and provides information for the future applications of these two techniques in sediment risk assessment.

subsequently lead to adverse effects. Traditionally bulk sediment concentrations (C_s) determined from exhaustive extractions have been used for predicting bioaccumulation and toxicity of hydrophobic organic contaminants (HOCs) in sediment. The accuracy of this prediction has been improved by organic carbon (OC) normalization. Organic carbon is the most important factor in determining partitioning of sediment-associated HOCs and bioaccumulation could be estimated by equilibrium partitioning theory (EqP).[2] The EqP theory assumes that an equilibrium exists among sediment OC, porewater, and the lipids of organisms exposed to the sediment, and that the chemical activity (fugacity) of a contaminant in each phase is equal.[2] Therefore, a biota sediment accumulation factor was proposed to represent the accumulation potential of chemicals by organisms.[2]

Other sediment characteristics, however, such as particle size[3] and types of OC, *e.g.* black carbon and pigments,[4–6] can also play a critical role in the bioaccumulation of sediment-associated HOCs. As a result, simply normalizing HOC concentrations to sediment OC may not fully compensate for the differences among sediments. This makes the use of C_s, despite OC-normalization, a flawed method to predict bioaccumulation and toxicity. To better quantify the risk of sediment-associated HOCs, it is necessary to incorporate the concept of bioavailability into the assessment and develop matrix-independent methods for estimating bioavailability.

Generally speaking, bioavailability is a measure of the amount of a chemical available for uptake by an organism and can be highly variable and dependent upon factors within the exposure media (*e.g.* sediment composition), organism characteristics (*e.g.* feeding rates, behaviors, and niche occupied), chemical properties (*e.g.* hydrophobicity and planarity), and/or environmental parameters (*e.g.* temperature and pH).[7] Due to the potential array of variables, differences in bioavailability among species

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may be simultaneously driven by multiple variables. Therefore, a better understanding of the influence of these factors on bioavailability is needed and this would aid in the development of more accurate methods to estimate bioavailability.

Bioavailability and its role in sediment risk assessments

Despite acknowledgement of the importance of incorporating bioavailability into sediment risk assessments, the practice is hindered by the lack of a universally accepted definition of bioavailability. For example, Hamelink *et al.*[8] defined bioavailability as the fraction of a chemical that can be taken up by an organism within a given period of time, while Spacie *et al.*[9] considered bioavailability as the amount of chemical which can be utilized by an organism. In addition to the aforementioned content-based definitions, bioavailability was defined on the basis of flux or kinetic rates as well. Shor and Kosson[10] suggested that bioavailability is the transfer rate (flux) of a chemical into an organism. Currently, the content-based concept is the preferred definition of bioavailability because it is easier to quantify the body residues than the flux or rates of chemicals into organisms. In 2004, Semple *et al.*[11] separated the definition of bioavailability into two concepts: bioavailability and bioaccessibility. Bioavailability is the fraction of chemical readily available for uptake by an organism, whereas bioaccessibility represents the fraction of chemical potentially available to an organism. This definition implies that the bioaccesible fraction is greater than the bioavailable fraction.

In addition to clarifying the definition of bioavailability, developing practical methods to measure bioavailability is another limitation to incorporate bioavailability into sediment risk assessments. Reichenberg and Mayer[12] used chemical activity and accessibility to replace the terms bioavailability and bioaccessibility proposed by Semple *et al.*,[11] and separated the commonly used chemical techniques for bioavailability measurements into two groups according to the two theoretical concepts. Chemical activity (or fugacity) describes the energy state of contaminants and is closely related to the freely dissolved concentration in sediment porewater (C_{free}) and can be estimated by EqP[2] or measured by passive sampling techniques, such as semi-permeable membrane devices,[13] solid-phase microextraction (SPME),[14] polyoxymethylene solid phase extraction,[15] and polyethylene devices.[16] On the other hand, accessibility is an operational parameter describing the mass quantity of contaminants, and could be measured by non-exhaustive extractions, such as mild solvent extraction,[17] supercritical fluid extraction,[18] and sorbent-assisted desorption methods (*e.g.* Tenax extraction).[19]

Based on the concept that the bioavailable concentration is a better metric of risk than bulk sediment concentration, various techniques have been developed to simplify the process of estimating bioavailability. Recent studies have demonstrated that chemical techniques including SPME and Tenax extraction, can adequately predict HOC body residues in organisms. Although the two techniques measure different components of the matrix,[12,20] estimates obtained from both methods have been shown to be equally effective in predicting HOC body residues.[3,21–23]

The objective of this review is to summarize the applications of these two chemical techniques for evaluating bioavailability and/or toxicity of sediment-associated HOCs as well as outline the advantages and limitations of each technique. Additionally, future perspectives of the application of these techniques in sediment risk assessments are discussed. Although this review focuses only on SPME and Tenax extraction, the theories are applicable to other chemical techniques which measure bioavailability of HOCs in sediment.[13,15–18]

Solid-phase microextraction

Theoretical considerations and methodologies

The SPME fibers are considered a passive sampling technique, which is defined as "any sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potential of the analytes between the two media".[24] A SPME fiber usually consists of a silica core with a thin polymer coating, such as polydimethylsiloxane or polyacrylate. During exposure, the analytes are sorbed to the coating and a thermodynamic equilibrium is established between the coating and the freely dissolved analytes. This technique, proposed by Arthur and Pawliszyn,[25] was later modified by Mayer *et al.*[14] to estimate the freely dissolved contaminant concentration (C_{free}) in sediment porewater using the whole sediment matrix as the source for the reduction of chemicals sorbed by the fibers. For this reason, the modified method is referred to as matrix-SPME. One of the fundamental principles of matrix-SPME is that it is non-depletive in nature, implying that only a minor portion of the analyte is removed from the matrix by the SPME fibers.[14] The non-depletive nature of SPMEs is necessary, since if the chemical in the matrix is depleted, the equilibrium would be shifted, which would reduce the accuracy of the SPME estimates of C_{free} under the original conditions. The non-depletive condition requires keeping the sorption capacity of the fiber substantially less than 5% of the analytes.[26] However, it is difficult to keep the non-depletive condition in porewater alone for highly hydrophobic contaminants due to the low C_{free}, so the non-depletive requirement is extended to the entire sediment matrix.[14]

Since only the freely dissolved component is considered bioavailable, C_{free} is a better metric for assessing bioavailability and subsequent toxic effects than the traditionally used C_s. The exchange kinetics of a chemical between the fiber and porewater can be expressed by a first-order-one-compartment model (eqn (1)).

$$C_{f,t} = C_{free}\frac{k_1}{k_2}(1 - e^{-k_2 t}) \quad (1)$$

Where, $C_{f,t}$ is the chemical concentration in the fiber at exposure time t, C_{free} is the concentration of the freely-dissolved chemical in sediment porewater, while k_1 and k_2 are the uptake and desorption rate coefficients, respectively.

At equilibrium, the chemical activity of a contaminant is the same in the fiber, porewater, and sediment, and C_{free} could be derived from the fiber concentration at equilibrium (C_f) and the partitioning coefficients between the fiber and water (K_{fw}) using eqn (2):

$$K_{fw} = \frac{C_f}{C_{free}} = \frac{k1}{k2} \quad (2)$$

The K_{fw} values are generally determined using water-only exposures, and their accuracy is critical for accurate measurements of C_{free}.[27]

Depending on the sampling design, SPME methodologies to estimate C_{free} of contaminants are generally grouped into two categories, equilibrium- or kinetically-controlled samplings. As indicated by its name equilibrium-controlled sampling requires equilibrium to be reached before ending the test. Both separate exposures using serial sampling and concurrent exposures with organisms have been conducted for equilibrium-controlled SPME sampling. Generally it takes a long time for HOCs to reach equilibrium between the fiber and the matrix, thus serial sampling is required to ensure equilibrium is reached. Gentle shaking has been applied to the samples to increase the movement of the porewater and shorten the time to reach equilibrium.[14] On the other hand, concurrent exposure of the fibers in experimental chambers with the organisms is theoretically more representative of organism exposure.[28] However, it is difficult to guarantee that equilibrium is reached for all contaminants using the latter method in which only a single-point sampling is used. After exposure, the sorbed compound can be recovered from the fiber either using solvent extraction or direct thermal desorption into an analytical instrument.

Although equilibrium-controlled SPME is the common practice for matrix-SPME, equilibrium of the chemicals between the fiber and the matrix is not always reached within a reasonable time frame, especially for highly hydrophobic contaminants, limiting the practicality of the equilibrium sampling method.[29] In order to shorten the sampling time, kinetically-controlled sampling was introduced. Instead of terminating the SPME sampling after reaching equilibrium, the fiber was manually retrieved from the exposed media at pre-determined sampling time-points prior to equilibrium. Kinetically-controlled equilibrium assumed that the concentration gradient was stable and the rate of mass transfer was linearly related to the difference in fugacity between the phases,[24] and that the partitioning process followed Fisk's first law (eqn (3)):

$$J = -D\left(\frac{\mathrm{d}C}{\mathrm{d}z}\right) \quad (3)$$

Where, J is the flux of the analyte, D is the diffusion coefficient, and $\mathrm{d}C/\mathrm{d}z$ is the concentration gradient of a chemical.

Because SPME uptake processes may be influenced by various environmental factors, such as temperature and salinity, calibration of kinetic coefficients in the laboratory was generally conducted before employing kinetically-controlled SPME sampling to measure C_{free} in sediment porewater. Various calibration methods for kinetically-controlled SPME sampling have been developed and reviewed by Ouyang and Pawliszyn.[30]

Applications of SPME in sediment risk assessment

Since the concentration of contaminants on the fibers (C_f) is proportional to C_{free} which dictates bioavailability, C_f may correlate to chemical residues in organisms and subsequently toxic effects. Studies using the matrix-SPME technique to estimate bioavailability and/or toxicity of HOCs in sediment are summarized in Table 1. The accuracy of using C_f to predict bioavailability has been examined for different classes of sediment-associated HOCs, including polycyclic aromatic hydrocarbons (PAHs),[6,31–33] polychlorinated biphenyls (PCBs),[3,6,21–23,31] polybrominated diphenyl ethers (PBDEs),[3] 2,4,6-trinitrotoluene (TNT) and its metabolites,[28,34] and insecticides.[3,6,21,35,36] In the majority of these studies, a direct relationship has been established between lipid-normalized organism tissue residues and SPME fiber concentrations (Table 1). Several studies also suggested organism body residues could be directly calculated by multiplying the SPME measured C_{free} with the bioconcentration factor (BCF) from water-only exposures.[22,23,31]

As previously discussed, the fibers could be exposed simultaneously with organisms in the same experimental chambers.[21,28,35,36] In this case, exposure duration is particularly important because equilibrium of the contaminant may not have been reached between the matrix and either the fiber or organism because the rates at which the contaminant absorbs to the fiber and is taken up by the organism are likely to be quite different.[37] If the equilibrium condition is not fulfilled, the SPME fibers concurrently exposed with the organisms should not be considered as a passive sampler, but rather an operational non-exhaustive extraction technique for bioavailability estimation.[21] Conversely, other studies have compared C_f to chemical residues in organisms at the completion of exposure when the fiber and the organism have reached equilibrium and steady state, respectively.[3,6,22,23,31] Due to the different uptake rates for the fibers and organisms, relationships established at equilibrium are more likely to be consistent. Nevertheless, a longer exposure time and serial sampling were usually required to ensure equilibrium conditions. Collectively, it has been demonstrated that the SPME technique could adequately indicate bioavailability for a variety of sediment-associated HOCs, however, which methodology (concurrent exposure or equilibrium exposure with serial sampling) provides a better prediction of body residues has not been established.

In addition to measuring C_{free} and organism body residues, SPME measurements have also been used to assess sediment toxicity induced by PAHs,[38–40] TNT,[41,42] and insecticides.[43,44] Five metrics, including C_s, OC-normalized C_s, porewater concentration (including chemicals binding to dissolved OC (DOC)), DOC-normalized porewater concentration, and SPME-measured C_{free} were used as metrics for sediment toxicity caused by pyrethroid insecticides, and results showed that C_{free} was the best way to express pyrethroid toxicity across sediments.[43] The potential effect of degradation of the insecticide fipronil on sediment toxicity was also evaluated by measuring C_{free} of fipronil and its metabolites by matrix-SPME.[44] Overall, SPME measurements have successfully predicted bioavailability and toxicity of sediment-associated HOCs.

Tenax extraction

Theoretical considerations and methodologies

Tenax beads are porous polymer resins and originally were used as column packing materials. Having a strong sorption affinity for a variety of HOCs, Tenax can be used to measure desorption of HOCs by serving as an "infinite" sink for the desorbed HOCs from the sediment particles.[45] The use of Tenax beads to predict bioavailability relies on the principle that HOCs are not uniformly distributed in sediment particles, but instead are in different compartments with distinct desorption rates.[19] Although the desorption of HOCs from sediment is a continuum,

two or three compartments were operationally defined to simplify the modeling of the desorption process.[19] Since they have a faster desorption rate, contaminants in the rapidly desorbing fraction (F_{rap}) contribute more to the sediment porewater concentration. Therefore, while all compartments of the sediment may contribute, the main source of C_{free} is F_{rap} rather than the whole sediment OC suggested by EqP theory (Fig. 1).[20,31,46,47] Using serial sampling, consecutive Tenax extraction can be used to measure desorption kinetics of a contaminant from sediment by fitting the data to a desorption model as shown in eqn (4) and 5 (a triphasic model is shown).

$$\frac{S_t}{S_0} = F_{rap}(e^{-k_{rap}\cdot t}) + F_s(e^{-k_s\cdot t}) + F_{vs}(e^{-k_{vs}\cdot t}) \quad (4)$$

$$F_{rap} + F_s + F_{vs} = 1 \quad (5)$$

Where, S_t and S_0 represent the amount of sediment-sorbed contaminant at time t and time zero, respectively. The F_{rap}, F_s, and F_{vs} are the fraction of chemical in the rapidly, slowly, and very slowly desorbing fractions at time zero and k_{rap}, k_s, and k_{vs} are the corresponding desorption rate constants, respectively. It is important to note that these compartments are operationally defined as mentioned previously and that in reality the desorption rates represent a continuum of values.

In contrast to the SPME, which measures the chemical activity of sediment-associated HOCs at equilibrium, Tenax extraction estimates the fraction of contaminants that are potentially available to an organism (bioaccessibility). Due to the relative sequestration of the other compartments, it is hypothesized that F_{rap} is the most bioavailable portion of contaminants. Previous studies have shown that chemical residues in organisms directly correlated with the chemical concentrations in F_{rap}.[3,22,23,31,48–50] The amounts of HOCs desorbed are dependent on the exposure time of the sorbent to the sediment slurry, correlations between F_{rap} and desorption fraction at the single time-point were observed.[51] As a result, Cornelissen *et al.*[51] suggested that a simplified Tenax extraction at a single time-point, representative of F_{rap}, could also be correlated to organism tissue residues.

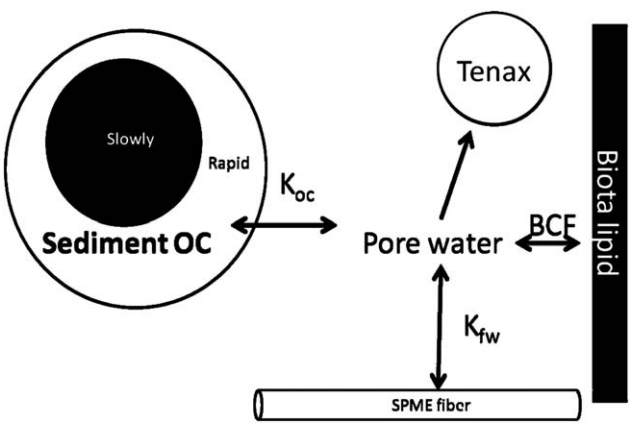

Fig. 1 Equilibrium between the sediment, porewater, and organism with the consideration of multiple desorption compartments within sediment, partitioning between the sediment and porewater (K_{oc}) and bioconcentration (BCF). Equilibrium is also established between the SPME fiber with partitioning based on the partitioning coefficient between the fiber and porewater (K_{fw}).

Either 6 or 24 h Tenax extraction has been applied to predict HOC bioavailability from sediment.[21,52,53] Therefore, either F_{rap} estimated by consecutive Tenax extraction or Tenax extractable chemicals at a single time-point, could be used in bioavailability estimates for sediment-associated HOCs.

The Tenax extraction process is initiated by adding Tenax beads to a sediment slurry in glass tubes, with the tubes being continuously rotated. At each predetermined time, Tenax is separated from the sediment by centrifugation, and this process is simplified, since Tenax beads float on the water. The target analytes sorbed by Tenax are then analyzed after solvent extraction and cleanup. For consecutive Tenax extractions, fresh Tenax is added to resume the desorption process.

Applications in sediment risk assessment

As the chemicals desorbing from sediments are the most accessible portions to organisms, they also represent what is potentially available to have a toxicological effect (bioaccessibility). The applications of Tenax extraction for measuring bioavailability and toxicity of HOCs in sediments are summarized in Table 1.

As shown in Table 1, different classes of HOCs in the F_{rap} phase have been found to be directly related to organism body residues, including PAHs,[46,48,54–56] PCBs,[3,21–23,46,48,49,57] PBDEs,[3,56,58] dioxins,[58] and insecticides.[3,50] Single time-point Tenax extraction has also been used to estimate bioavailability. Relationships between single time-point Tenax extractable chemical concentrations and organism tissue residues have been determined for PAHs,[21,52,53] PCBs,[21,52,53] and insecticides.[21] Landrum *et al.*[53] showed that a single regression line between the 6 h Tenax extractable contaminants and the organism body residues established using laboratory-spiked sediments[21] successfully described the accumulation of HOCs in organisms exposed to field-contaminated sediments as well as field-collected organisms. This implies that this method is adequate for predicting the bioavailability of a range of HOCs across sediment types and species.

Compared to the SPME method, there are fewer studies using Tenax extraction to estimate sediment toxicity.[59,60] You *et al.*[59] reported the bioavailable toxic unit estimated by Tenax extraction better explained sediment toxicity due to pyrethroid insecticides than the toxic unit measured by exhaustive extraction because it considered bioavailability. Moreover, Tenax extraction has been used as a bioaccessibility-directed extraction in effect-directed analysis to identify the potential cause of sediment toxicity.[61] In summary, Tenax extraction estimates the bioaccessibility of HOCs in sediment and has successfully predicted organism body residues, in addition this data also could be used for toxicity assessment and identification.

Relationship between the SPME and Tenax extraction measurements

In this review, two chemical techniques are compared to estimate bioavailability and toxicity of HOCs in sediment. Matrix-SPME directly measures C_{free} of HOCs in sediment porewater which is a reflection of chemical activity or the proportion of chemical involved in equilibrium partitioning, whereas Tenax extraction

Table 1 Summary of studies using solid-phase microextraction (SPME) and Tenax extraction techniques to predict organism body residues or toxicity of sediment-associated hydrophobic organic contaminants (HOCs). The relationship between chemical measurements and organism body residues is presented as r^2[a]

Technique	Contaminant	Endpoint	r^2	Organism	Matrix	Reference
SPME/Tenax	Various HOCs	CR	0.92/0.94	*Lumbriculus variegatus*	Spiked and field sediments	21
SPME/Tenax	Various HOCs	CR	0.86/0.89	*L. variegatus* [b]	Spiked sediment	3
SPME/Tenax	Various HOCs	CR	NP	Tubificidae	Spiked sediment	31
SPME/Tenax	PCBs	CR	0.30/0.95	*L. variegatus*	Field sediment	22
SPME/Tenax	PCBs	CR	0.86/0.91	*L. variegatus*	Field sediment	23
SPME/Tenax	PAHs	CR	0.62/0.67	*L. variegatus*[d]	Field sediment	33
SPME	TNT	B	NP	NA	Spiked and field sediments	28
SPME	TNT	Toxicity	NP	*Tubifex tubifex*	Spiked sediment	41
SPME	TNT and metabolites	Toxicity	NP	*T. tubifex* & *Chironomus dilutus*	Spiked sediment	42
SPME	TNT	CR	0.79	*T. tubifex*	Spiked sediment	34
SPME	2ADNT	CR	0.83	*T. tubifex*	Spiked sediment	34
SPME	4ADNT	CR	0.78	*T. tubifex*	Spiked sediment	34
SPME	PAHs	Toxicity	NP	NA	Field sediment	38
SPME	PAHs	Toxicity	NP	*Hyalella azteca*	Field sediment	39
SPME	Pesticides	Toxicity	NP	*C. dilutus*	Spiked sediment	43
SPME	Permethrin	CR	0.86	*C. dilutus*	Amended field sediment	35
SPME	Permethrin	CR	0.38	*C. dilutus*	Amended field sediment	35
SPME	PAHs	Toxicity	NP	*L. variegatus*	Spiked sediment	35
SPME	Fipronil	Toxicity	NP	*C. dilutus*	Spiked sediment	44
SPME	Permethrin	CR	0.91	*C. dilutus*	Field sediment	36
SPME	PAHs	CBSAF	NP	*L. variegatus*	Spiked cellulose	32
SPME	Various HOCs	CBSAF	NP	*L. variegatus*	Spiked sediment	6
Tenax	Various HOCs	B	NP	NA	Field sediment	51
Tenax	PAHs & PCBs	CBSAF	NP	Tubificidae	Spiked sediment	46
Tenax	PAHs	CBSAF	0.96	*Limnodrilus* sp.	Field sediment	52
Tenax	PCB	CR	NP	*H. azteca*, *C. dilutus*, & *L. variegatus*	Spiked sediment	58
Tenax	PAHs	CR	0.66	*Diporeia* sp.	Spiked sediment	48
Tenax	PAHs	CR	0.67	*L. variegatus*	Spiked sediment	48
Tenax	PAHs	CBSAF	NP	*L. variegatus*	Spiked sediment	54
Tenax	PAHs	CBSAF	NP	*Hinia reticulata*	Field sediment	55
Tenax	Various HOCs	CR	0.84	*L. variegatus*	Spiked sediment	21
Tenax	PCBs and PAHs	CR	0.63	*Diporeia* sp.[b,c]	Field sediment	53
Tenax	PCBs and PAHs	CR	0.63	Oligochaetes[b,c]	Field sediment	53
Tenax	Various HOCs	CR	0.89	Oligochaetes	Spiked and field sediments	53
Tenax	Various HOCs	CR	0.89	Oligochaetes	Spiked and field sediments	53
Tenax	PCB-77	CR	0.80	*L. variegatus*	Spiked sediment	49
Tenax	Nonylphenol	B	NP	NA	Field sediment	60
Tenax	Pyrethroids	Toxicity	NP	*H. azteca*	Field sediment	59
Tenax	PBDE-99 & TCDD	CBSAF	NP	*L. variegatus*	Spiked sediment	57
Tenax	PBDE-47 & B*a*P	CBSAF	NP	*L. variegatus*	Spiked sediment	56
Tenax	Permethrin	CR	NP	*L. variegatus*	Spiked sediment	50

[a] CR = correlation to residues, CBSAF = correlation to BSAF, B = bioavailability in general, PCBs = polychlorinated biphenyls, PAHs = polycyclic aromatic hydrocarbons, TNT = 2,4,6-trinitrotoluene, 2ADNT = 2-amino-2,6-dinitrotoluene, 4ADNT = 4-amino-2,6-dinitrotoluene, PBDE = polybrominated diphenyl ether, TCDD = tetrachlorodibenzo-*p*-dioxin, B*a*P = benzo[*a*]pyrene, NP = Not Presented, NA = Not Applicable. [b] Includes data from other studies. [c] Field-collected organisms. [d] Field-deployed organisms.

assesses desorption kinetics of HOCs from sediment, and represents the proportion of HOCs which could be desorbed and potentially available to organisms (bioaccessibility).[12,20] While each method measures a different component of the matrix, previous studies have shown the amount of contaminants accumulated by organisms were equally predicted from either SPME fiber or Tenax extractable concentrations. A question has arisen, however, about the relationship between the two terms, the bioavailable concentration measured by SPME and the bioaccesible fraction of contaminant measured by Tenax extraction.

The EqP theory suggests equal chemical activity of HOCs among the phases at equilibrium, and was the first attempt to predict bioavailability of HOCs in sediments.[2] However, when sequestration of HOCs in sediment was considered, EqP could be modified to include multiple desorption compartments.[20,31] As shown in Fig. 1, when an organism is exposed to sediment-associated HOCs, an equilibrium is established among the F_{rap} of sediment, porewater, and biota lipids.

Similar to F_{rap} which represents bioaccessibility estimated by Tenax extraction, bioavailability measured by matrix-SPME can also be described by the fraction of HOCs in sediment readily available for equilibrium partitioning (F_{AEP}). The F_{AEP} is directly related to C_{free} and can be calculated from C_{free} through eqn (6)

$$F_{AEP} = \frac{C_{free} \times K_{oc}}{C_{s\text{-}oc}} \quad (6)$$

Where, K_{oc} is the partitioning coefficient between sediment OC and water and is available in the literature for the majority of compounds or derived from K_{ow} values, while $C_{s\text{-}oc}$ is the OC

normalized bulk sediment concentration. Fig. 2 shows a relationship between F_{AEP} and F_{rap} derived from the data in a previous study.[20] The regression equation, $F_{AEP} = 0.47F_{rap}$ ($r^2 = 0.77$) indicates approximately half of the HOCs in the F_{rap} phase (accessible fraction), measured by Tenax extraction, was readily available for equilibrium partitioning to the porewater as suggested by matrix-SPME and the two chemical measurements correlate well to each other.

Strengths and weakness of each technique

While both SPME and Tenax extraction are viable means of predicting bioavailability, there are advantages to each of these methods. While Tenax extraction is limited to measuring HOCs, SPME fiber coatings could be chosen to target a wide range of compounds including relatively polar compounds. Ideally, differing sorbents other than Tenax might be used for compounds with different polarity, but the authors are unaware of any research completed in this area except of the use of XAD-2 absorbents.[62,63] Conversely there are more choices of the SPME fibers and suites of coatings in polarity have been commercialized[30] and theoretically more selective and specific SPME coatings could be developed. Additionally, SPME fibers can be exposed simultaneously with the organisms in the laboratory or may be used *in situ* which may better mimic organism exposure in the field. This may increase the accuracy of SPME fibers in predicting bioaccumulation and toxicity in the environment.

Conversely, estimating the potential bioavailability using Tenax extraction could be achieved with a single 6 or 24 h measurement, whereas estimating C_{free} using SPMEs generally requires the fibers to reach equilibrium, a process that could take weeks to months and serial sampling is often required to assure that equilibrium has been reached. As a result, the SPME technique is more time- and labor-intensive. The equilibrium

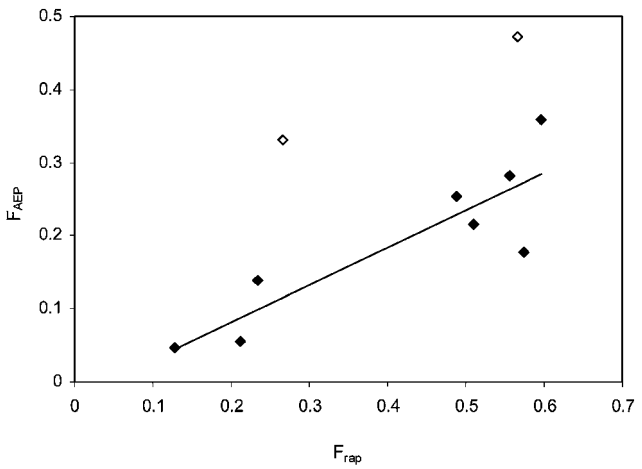

Fig. 2 The relationship between the rapidly desorbing fraction (F_{rap}), measured by Tenax extraction, and the fraction available for equilibrium partitioning (F_{AEP}), measured by matrix solid-phase microextraction, for 2,2′,4,4′,5,5′-hexachlorobiphenyl, 4,4′-dichlorodiphenyldichloroethylene, permethrin, chlorpyrifos and phenathrene in two types of sediments. The solid line represents the relationship between F_{AEP} and F_{rap} ($F_{AEP} = 0.47(0.042)F_{rap}$, $r^2 = 0.77$). Open symbols represent chlorpyrifos in the two sediments and solid symbols represent the other compounds. The Figure was created by data from You *et al.*[20]

requirement may also limit the applicability of SPME fibers for rapidly degrading compounds, since current SPME methods typically require a long-term, constant concentration.[44] Development of kinetically-controlled SPME sampling methods may resolve the problem of requiring extremely long exposure times in matrix-SPME applications. Pre-exposure of passive samplers, including SPME fibers, to performance reference compounds (PRCs) has been successfully used to estimate sampling rates of the target HOCs in sediment through the dissipation rates of the PRCs from the passive samplers.[30,64–66]

Furthermore, the extractable concentration using Tenax beads is also potentially much greater than that with SPME fibers. This is because Tenax serves as an "infinite" sink to remove the entire pool of HOCs that have desorbed from sediment during a given time frame. The SPME fibers, however, must not deplete the system as it would shift the equilibrium, inhibiting an accurate estimation of the chemical activity in the porewater. So, Tenax extraction may be a better choice than the SPME fibers for sediments that contain much lower contaminant concentrations or for contaminants that rapidly degrade. This feature of Tenax extraction may also make it more applicable for highly toxic compounds whose ecologically relevant concentrations are typically low and may not be easily detected in the porewater with SPMEs.

Therefore, SPME fibers would be ideal for situations in which *in situ* quantification is preferred or required. The SPME fibers have demonstrated success in predicting bioavailability with multiple compounds, and with the various fiber coatings available, can measure a greater range of compounds than Tenax. However, if a more rapid, less labor intensive method is preferred, then a single time-point Tenax extraction would be the choice. Tenax extraction would also be the preferred method for compounds at low concentrations and for those which are highly toxic for the aforementioned reasons. Ultimately, which method is best is chemical and situation dependant.

Conclusions and future perspectives

The traditional methods for predicting toxicological effects that utilize bulk sediment concentration often over-estimate risk. Newer chemical extraction methods that consider bioavailability may have greater predictive capacity. Both SPME and Tenax extraction have been developed for predicting bioavailability for several HOCs including PAHs, PCBs, PBDEs, and pesticides in laboratory and field sediments for a number of species. While each method measures a very different parameter, both are equally effective at predicting bioavailability and are correlated to each other. The advantages of SPME fibers are their applicability for use *in situ* and their potential greater range of compound selection. Tenax extraction, however, only requires a single time-point treatment, decreasing time and labor. This feature also makes it more effective for compounds with short environmental half-lives. Tenax extraction also has lower detection limits, making it more applicable for highly toxic contaminants.

Despite the multiple studies presented in this review, there is still significant research potential in this area. The SPME fibers can be further tested with different coating types and thicknesses to expand the variety of compounds that can be measured with

SPME. Comparisons between laboratory and *in situ* SPME fiber based bioavailability estimates need to be evaluated as well as comparisons among the different ways to use SPMEs within the laboratory. More studies on the kinetically-controlled SPME sampling methods are critical to expand the practical uses of matrix-SPME by reducing the exposure time. The applicability of estimating *in situ* sampling rates of sediment-associated HOCs by pre-exposing SPME fibers to the PRCs is required to be evaluated for more compound classes and SPME types. Furthermore, examination of additional sorbents with different characteristics than Tenax could expand the use of this methodology to more compounds.

Additionally, more comparisons between the two methods, particularly in field sediments, are required to substantiate under which circumstances either method may be preferable to predict bioavailability. However, the research area which may have the most impact on environmental assessments is expanding the link between the measurements of both methods and toxicity endpoints. While some of the aforementioned studies begin to address this issue by establishing a direct link between a SPME fiber or Tenax extractable concentration and a toxicological endpoint, additional studies linking chemical based bioavailability estimates to lethality or other toxicity estimates are essential to expand the applications of these methods. In order to establish the applicability of these methods for use in environmental risk assessments, more chemicals, species, and endpoints need to be tested.

Besides the development of the practical application of the two methodologies, more studies are required to better understanding their theoretical basis. It must be considered that these techniques rely on the idea that only the freely dissolved and rapidly desorbing concentrations contribute to HOC bioavailability. However, HOCs binding to the ingested sediment or in the slower desorbing fractions may contribute to chemical accumulation and toxic effects in an organism as well. Sormunen *et al.*[49] suggested greater accumulation of PCB was observed for *Lumbriculus variegatus* which were capable of ingesting sediment particles. Moreover, a recent study[47] claimed chemicals in the F_s phase became bioavailable after depleting F_{rap}. Therefore, the contribution of HOCs binding to the slowly desorbing fraction in sediment to bioavailability should also be better evaluated. Additionally, contaminant accumulation may not reach steady state levels in an organism, because toxic effects occur or environmental concentrations fluctuate. In these cases, kinetic rates may better describe sediment risk than the total amount of chemical accumulated in an organism. Thus, more research using chemical techniques, such as SPME and Tenax extraction, to measure flux- or rate-based bioavailability is required.

Overall, the degree of the accuracy of these predictions is organism and chemical dependent. While these simple and less-expensive chemical techniques show promise as a matrix independent, universally applicable means of predicting toxicity, more research is still needed to establish chemical based values for the plethora of contaminants and organisms in aquatic systems.

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