

Linking organic pollutant (bio)availability with geosorbent properties and biomimetic methodology: A review of geosorbent characterisation and (bio)availability prediction

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Hydrophobic organic pollutant retention in geosorbent matrices, soil and sediment characteristics, biomimetic techniques is reviewed.

Abstract

The interdependent link between structure and physico-chemical properties of geosorbents and sorption activity of hydrophobic organic pollutants (HOC) upon interaction with solid matrices has been established. The conclusions derived from these investigations have not been actively incorporated into risk assessment and remediation protocols since legislators prefer to adopt a conservative approach when the potential of contaminants to be released from soil matrices are evaluated. With the advent of spectroscopic techniques, it is possible to determine the molecular properties of the geosorbent organic matter which play a pivotal role in HOC retention. Physical–chemical and biological methods are employed to predict the potential for HOC release from sorbent matrices. This article serves as a review discussing the literature and reports the progress that has been made in these particular areas. The implication of employing molecular descriptor factors correlated with a biomimetic method to assess availability and risk is also considered.

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1. Introduction

The ability to accurately determine the effects of contaminants on individual species, populations, communities and on ecosystems is curbed by an uncertainty in the quantification of receptor exposure (Quinones-Rivera et al., 2003). Due to this uncertainty, a conservative approach in exposure assessment as stipulated in legislation assumes that the total concentration of a contaminant present in a given soil or sediment is available for uptake by possible receptors. Numerous laboratory and field studies, however, have shown that this is not the

case. Organisms exposed to contaminants present in sorbents are mainly affected by the freely available fraction, therefore, the concentration bioavailable at a given time and at prevailing soil conditions. Uptake by ingestion and passive diffusion (skin contact with contaminated sorbents) are also potential routes of exposure (Jager et al., 2003). Contaminant fractions, upon interaction with soil matter, become progressively less available due to transport into soil aggregates and microsites that could be inaccessible to microorganisms, and through adsorption (binding of contaminant to mineral and organic matter). This could be a reversible process with contaminants released over time due to a change in sorbent properties, the slow migration of compounds to accessible sites or when the contaminant changes into an available form (Alexander, 2000).

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1.1. Definition and types of availability

Various viewpoints and conceptual definitions for bioavailability exist and have been reported and this has created ambiguity and miscommunication amongst interested parties of related scientific disciplines. This issue was recently raised by Semple et al. (2004). The authors state that “given the legal and regulatory implications of the bioavailability concept as part of the risk assessment framework, the term must be clearly understood”. Bioavailability is “those chemicals in the soil that are present in forms and amounts that plants (or other organisms) can take up during the time they are growing”, according to Warrington and Skogley (1997). Rockne et al. (1999) defined bioavailability as the rate at which a chemical compound can be transported to a specific biological population to induce toxic effects. It was also defined as a measure of the rate of mass transfer to organisms relative to their degradation capabilities (Bosma et al., 1997), or as the proportion of contaminants that are available for rapid transfer to the aqueous phase (Cornelissen et al., 1998a). Finally, the accessibility of contaminants to, or their absorptivity by, living organisms was considered an applicable explanation for bioavailability by Hrudey et al. (1995). These definitions can be grouped with respect to quantity of pollutants and the rate (flux) of transfer to organisms able to degrade and mineralize, accumulate and represent some inhibitory or ecotoxic effect from an environmental science and toxicology viewpoint.

Semple et al. (2004) distinguished between bioavailability and bioaccessibility. The authors proposed working definitions in relation to the literal applications of the words *available* and *accessible*. Bioavailability is a bioavailable chemical which is freely available to cross a microorganism’s membrane from the medium in which the organism exists. A bioaccessible compound, on the other hand, is defined as “that which is available to cross an organism’s cellular membrane from the environment, if the organism has access to the chemical”. The authors go on to say that the bioaccessible compound may also be unattainable due to physical separation (e.g. adsorption to sorbent organic matter) and only available to biota after desorption, therefore, it includes the compound fraction that is available at present in addition to what could become available.

Availability depends on sorbent characteristics, environmental conditions and pollutant properties and is dependent on the contact time between contaminant and sorbent. Due to changing conditions over time, the sorbed fraction is not fixed. With this in mind, various types of availability should be identified and defined. Escher and Hermens (2002) stipulated that only the freely dissolved concentration is available biologically in aquatic systems. Also, in more complex environmental systems where pollutant concentrations are reduced by partitioning and adsorption to solids, dissolved organic matter and sorbent organic matter, availability is associated with the freely dissolved concentrations in pore water (Harmsen et al., 2003). Fig. 1 presents a schematic representation of the pollutant fractions which are available and could potentially become (bio)available in a complex

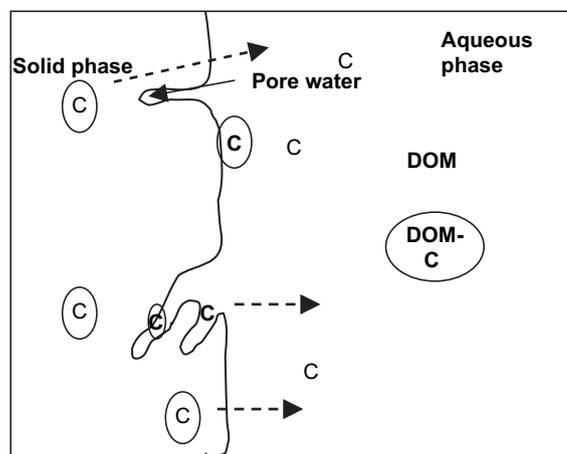


Fig. 1. Diagram representing the various contaminant fractions that are (bio)available in a complex environmental system: the freely dissolved concentration (C) which is bioavailable in the aqueous phase (including pore water volume) to biota and available to potentially leach out; the dissolved organic matter (DOM)-associated concentration (DOM-C); and solid surface-associated and pore-diffused adsorbed concentration (C) which could potentially become (bio)available (→) in the freely dissolved fraction (rapidly desorbing fraction).

environmental system. The International Organization for Standardization (ISO) Committee for Soil and Site Assessment specified that a simple approach would be to define an actual available fraction, a potential available fraction and a non-available fraction (ISO, 2004). The potentially available fraction includes the actual available fraction but cannot exceed the total concentration. To determine the potential available concentration, one must consider the sorbent, organisms and environmental conditions that impact fate and behaviour of pollutants.

Bioavailability categories should be considered with regard to the receptor, the organism for which the availability is relevant. The ISO, therefore, defines different availabilities in terms of dissimilar but defined target organisms or biotopes: availability to organisms able to degrade the contaminant, availability to organisms able to ingest the contaminant through gut uptake and passive diffusion processes, for plant uptake, for human exposure (by ingestion, inhalation and dermal contact) and for leaching processes (ISO, 2003). Depending on the use of contaminated land (agriculture, nature conservation, recreation, pasture), protection goals may differ and depending on the specific organism or entity that requires protection (human, wildlife, invertebrate, microorganism, ground or surface water body), one could define different bioavailabilities. The evaluation and appraisal of contamination for the purpose of remediation or ecotoxicological impact assessment would also render different bioavailabilities: (1) the fraction available to degrading or mineralizing bacteria (e.g. in a land farming operation), therefore, the biodegradable availability (Harmsen et al., 2003), and (2) the fraction available for bioaccumulation and which exerts toxicity towards biota, therefore, the ecotoxic availability.

The adsorption and release of hydrophobic organic compounds (HOC) from soils and sediments continue to be an

obstacle in remediation efforts and effect insecurity with respect to cleanup standards and risk assessments. The possible mobilisation of sorbed contaminant concentrations to subsequently become available and exposed to biota is uncertain and numerous studies have shown it to be difficult to evaluate and predict. To assist elucidation of this vital aspect of soil/sediment remediation and risk assessment, it is important to investigate structural and molecular properties of the soil matrix and fundamental mechanisms involved in the binding of HOC.

2. Binding and immobilisation by solid matrices

There is a need to clarify and define the terminology that is relevant to the bioavailability research sphere and associated with the introduction of HOC into complex environments, retardation of pollutant release from sorbent matrices and (bio)availability prediction. The terms *partitioning*, *sorption* including *adsorption* and *absorption* and *diffusion* are regularly used to describe the behaviour of contaminants at and inside sorbents. Chiou (2002) and Pignatello and Xing (1996) employed the term *sorption* to denote the uptake of a pollutant by a sorbent without reference to a specific process. Schwarzenbach et al. (2003) described *sorption* as the process in which chemicals become associated with solid-phases. *Sorption*, therefore, includes all the relevant processes which are involved when the pollutants come into contact with solid matrices. It is *adsorption* if the compounds attach to a two-dimensional surface. *Absorption*, on the other hand, is used to define the penetration of molecules into a three-dimensional matrix (Schwarzenbach et al., 2003).

Traditionally, *partitioning* is the distribution of a molecule between two phases (e.g. gaseous and solid, or aqueous and solid) governed by equilibrium. For contaminated soils, *partitioning* can be considered as an umbrella term that comprises various processes that result in the distribution of HOC between aqueous and non-polar phases. Sorption, therefore, can be considered as one type of partitioning process since it involves the distribution of organic pollutants between pore water and geosorbent matrices.

Diffusion is more a process of the transport of pollutants inside the soil matrix to reach potential adsorption sites. Diffusion processes include intraorganic matter diffusion (IOMD), film diffusion, intraparticulate diffusion (IPD) and diffusion within pores (intrapore diffusion) (Luthy et al., 1997; Northcott and Jones, 2000; Pignatello and Xing, 1996).

Consequently, it is possible to group the terms into two categories: transport and binding-related processes (Brusseau et al., 1991). While diffusion is considered a transport-related process, adsorption is a binding process. When soils are considered, the term *absorption* might be misconstrued as it would encompass both transport and binding processes depending on the perspective from which one assesses it. Following the definition given by Schwarzenbach et al. (2003), one can assess absorption from a closer angle: penetration may comprise diffusion into a matrix and binding to internal surfaces. Fig. 2 shows a schematic representation of the relevant processes involved.

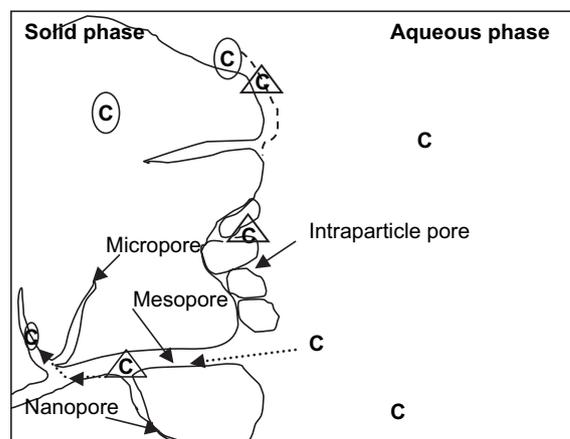


Fig. 2. Schematic of sorbent particle aggregate showing the transport and binding-related processes involved when an HOC is introduced into a complex environmental system: diffusion (film diffusion, intraparticle diffusion, intrapore diffusion) (\triangle), partitioning ($\dots\blacktriangleright$) of the freely dissolved contaminant concentration (C) between the aqueous phase and the soil matrix to become associated with the solid phase through adsorption (\odot) when the contaminant binds to surfaces and inside pores.

As a result of the processes outlined above, *sequestration* may occur and *bound residues* may be formed. Pignatello and Xing (1996) described *bound residue* formation as any organic carbon remaining after exhaustive extraction. Northcott and Jones (2000) differentiated between free and bound residues as the concentration of a compound that can be extracted from soil and without modification of the compound or the structure of the matrix, and the non-extractable portion. The authors acknowledge the potential for misinterpretation of these residues as a wide range of methods with different extractability yields have been employed to determine distribution of contaminants in sorbents. HOC can undergo *sequestration* after prolonged residence times in soils (aging). A pollutant is considered sequestered when the desorbing rate as reflected by mass-transfer of the chemical is very slow (Gevao et al., 2000; Schwarzenbach et al., 2003).

The transport, binding and desorption of HOC in soils and sediments depend on the nature, morphology and macro- and microscopic properties of the solid matrix. Environmental factors such as temperature, pH and moisture content (Luthy et al., 1997; Park et al., 2003; Pignatello and Xing, 1996; Weber et al., 1992; Xing et al., 1994) also play a major role in conjunction with the pollutant's physico-chemical properties, molecular structure and concentration (Braida et al., 2002; Huuskonen, 2002; Schwarzenbach et al., 2003; Van Noort et al., 2003). Soil/sediment structure, particularly sorbent constituents which play major roles in the immobilisation of HOC, as well as mechanisms and molecular characteristics pertaining to sorption are considered.

2.1. Geosorbents

Soils, sediments and aquifer solids, collectively termed geosorbents, are heterogeneous at various particle, aggregate and sample scales which vary temporally as well as spatially

(Luthy et al., 1997). The interaction of HOC with geosorbents is governed by structurally different and specific chemical properties of geosorbent constituents. When inclination towards sorption to mineral constituents is low where sorbent organic carbon content is present above >0.01 – 0.2% , overall transport and binding reactions are dominated by sorbent organic matter (SOM) (Chiou et al., 1998; Huang et al., 2003; Mader et al., 1997). Sorbent organic matter has been described as the total of the organic material in soils and sediments, including litter, microbial biomass, water-soluble organics, humic substances and plant residues in various stages of decomposition (Cuypers et al., 2002a). The existing physical apprehension of SOM is one of a polymer-mesh phase which can be visualized as a three-dimensional entanglement of macromolecules that is perfused with water (Pignatello, 1998). SOM comprises several domains or constituents that ultimately effect different sorption activities (Cuypers et al., 2002a). In addition to these defined spheres within soils and sediments, sorbent heterogeneity may be amplified due to the presence of anthropogenic organic substances such as oils, soot or surfactants (Luthy et al., 1997).

2.2. Geosorbent characteristics and impact on transport and binding processes

It is not intended for an exhaustive review of the chemical and physical characteristics of mineral and organic geosorbent fractions to be documented here, for an extensive summary refer to Huang et al. (2003) and Schwarzenbach et al. (2003).

2.2.1. Organic fraction

Sorbent organic matter is generally grouped in an amorphous or expanded “soft rubbery” carbon phase such as humic matter and a condensed or “hard glassy” carbon phase such as kerogen and char materials (Carroll et al., 1994; Huang et al., 2003; Luthy et al., 1997; Weber et al., 1992; Weber and Huang, 1996). These two phases constitute the major domains that are found within sorbent matrices and are primarily responsible for the transport and binding of HOC (Huang and Weber, 1997). Table 1 shows the organic materials that comprise the two phases of SOM. It has been stated that the amorphous carbon phase is primarily responsible for partitioning of HOC while condensed carbon, including combustion produced matter such as char and soot, and kerogen may serve as adsorption medium (Luo and Farrell, 2003). Strong adsorption

sites as represented by rigid condensed carbon moieties in SOM effect adsorption and possible bound residue formation of HOC. Condensed SOM is less polar and considered more aromatic than the amorphous SOM domains when elemental molar ratios (e.g. $[O + N]/C$, C/H) are interpreted (Cuypers et al., 2002a; Huang and Weber, 1997; Kile et al., 1999; Rutherford et al., 1992; Stuer-Lauridsen and Pedersen, 1997; Xing et al., 1994). Spectroscopic studies have shown that condensed domains are mainly constructed from rigid aromatic moieties (Gunasekara and Xing, 2003; Perminova et al., 1999; Xing and Chen, 1999). The origin and nature of SOM, however, seem to affect the composition of condensed and amorphous domains. It was found that condensed domains in non-decomposed soil were enriched in aliphatic carbon, whereas, weathered SOM was enriched in aromatic carbon (Cuypers et al., 2002a).

SOM often contains a range of physically and chemically different organic materials consisting of biopolymers such as lignin, polysaccharides, lipids and proteins, humic substances derived from biopolymers to diagenetically matured kerogen and black carbon (Huang et al., 2003; Song et al., 2002). Humic substances are dominant organic components in geosorbents (Stevenson, 1994). Piccolo (2002) argued that the traditional view of humic substances as biopolymers has not been substantiated by direct evidence. Recent work has presented a different understanding of the configurational nature of humic substances as a supramolecular conformation of self-assembling heterogeneous molecules derived from the degradation of dead biological material. Depending on their extractability in dilute base solutions and solubility in dilute acid solutions, three humic fractions are defined: humic acid, fulvic acid and humin (Rutherford et al., 1992; Stevenson, 1994). In studies where these humic components were extracted and separately investigated for their sorption reactivity, different trends were observed which may be related to the molecular characteristics of the components. Humic acid has a lower carboxylic and phenolic group content and lower H-to-C and O-to-C molar ratios which make it less polar compared to fulvic acid and also more condensed (De Paolis and Kukkonen, 1997; Perminova et al., 1999). The physical and chemical properties of humin are less understood probably due to its nonextractability in alkaline solution. It has been suggested that humin may include unchanged or transformed lignin and polysaccharides, humic acid-like materials and black carbon (Rice and MacCarthy, 1990; Song et al., 2002). Humin has also been considered as precursors of kerogen and macromolecules with molecular weights greater than humic acids (Huang et al., 2003).

The relative content of particulate kerogen and black carbon materials in sorbents may range from a few percent to more than half the total organic carbon (TOC) (Song et al., 2002). Major input of kerogen in soils is from the natural weathering processes of sedimentary rocks and from coal since coal comprising mainly kerogen is dispersed during mining operations (Ghosh et al., 2000). Kerogen, typically, has a three-dimensional structure with aromatic nuclei cross-linked by aliphatic chain-like bridges. The nuclei consist of

Table 1
The organic materials that comprise the two phases of SOM

Amorphous/expanded “soft rubbery” phase	Condensed “hard glassy” phase
Humic acid	Soot (black carbon)
Fulvic acid	Char (black carbon)
Humin	Humin
Polysaccharides	Kerogen
Lipids	
Proteins	
Lignin	

aromatic sheets separated by voids with an average width of 30–40 nm. The aliphatic bridges contain linear or branched chains, and/or S- or O-containing functional groups (Engel and Macko, 1993; Huang et al., 2003).

Depending on the origin, black carbon produced from the complete combustion of liquid fuel may be highly aromatic and reduced and is often called soot (Huang et al., 2003). Incomplete combustion products often show morphologies and structure characteristics which resemble parental materials and are referred to as char (Schmidt and Noack, 2000). Black carbon sources include forest fires and anthropogenic activities (e.g. coal and smelter-derived combustion) through surface run-off and atmospheric circulation (Ghosh et al., 2000; Mitra et al., 2002). Physical and chemical properties of black carbon may vary extensively depending on the source and combustion conditions (Jonker and Koelmans, 2002). Typically, it has three-dimensional structures with stacked aromatic sheets as back-bones. It appears to have specific condensed moieties which exhibit high affinity for especially planar HOC (Accardi-Dey and Gschwend, 2002; Chiou et al., 2000; Næs et al., 1998; Ran et al., 2002).

2.2.2. Inorganic fraction

The sorption of HOC by natural inorganic surfaces can be an important uptake route where the organic carbon content is relatively low (<0.1%) in a variety of situations from air or aqueous solution (Cuypers et al., 2002a). Various mechanisms by which organic chemicals may sorb to inorganic solids include: adsorption from air to surfaces with minimal water presence, adsorption to specific surface sites due to electron donor–acceptor interaction, or adsorption of charged molecules from the aqueous phase to complementary charged surfaces by electrostatic interaction. Where the organic chemical participates in a bond-breaking and bond-making surface reaction, especially where inorganic surfaces expose metals like iron and aluminum that utilize the sorbate as a supplement of ligands, it is termed chemisorption (Schwarzenbach et al., 2003). Inorganic surfaces associated with geosorbent mineral components include internal pore surfaces, external surfaces and internal interlayer surfaces (Luthy et al., 1997). These surface areas yield different sorption behaviours which appear to result from differences in their relative accessibility to the sorbate, as affected by pore geometry and by preferential sorption of water molecules (Huang et al., 1996; Rutherford et al., 1992). Many common minerals expose a surface to the exterior which consists of hydroxyl groups protruding into the medium from a plane of electron-deficient metals (i.e. Si, Al, Fe) and electron-rich ligands (i.e. hydroxyl, carbonate). The role of inorganic surfaces on sorption affinity for HOC has not been investigated systematically. It has been established that mineral surfaces can alter the ability of humic substances to bind HOC (Gunasekara and Xing, 2003; Hur and Schlautman, 2004). Interaction between amorphous-condensed aliphatic organic matter and mineral surfaces was shown to rearrange the amorphous region to take on a more condensed structure thereby facilitating non-linear adsorption. This condensed arrangement contributed to enhanced HOC immobilisation.

3. Retardation and immobilisation of HOC in relation to micro- and macroscopic geosorbent character

Interaction processes between HOC and geosorbents are distributed across the mineral and SOM fractions (Luthy et al., 1997). It is generally accepted that a rapid desorption stage is followed by a slower release (Cornelissen et al., 1997a,b; Huang and Weber, 1997; Pignatello and Xing, 1996; Xing and Pignatello, 1997). Cornelissen et al. (2000) and Ten Hulscher et al. (1999) showed the slow phase to comprise two parts: slow and very slow desorption, which differ in their first-order constants for desorption of PCB, PAH and chlorobenzenes from sediments by about two orders of magnitude. It is envisaged that two kinds of retarded diffusion which are responsible for the slow and very slow desorption from and transport through the geosorbent matrix are present: (1) diffusion through the organic matter with the distinction between amorphous and condensed domains within SOM (IOMD), the latter effecting strong retardation (Pignatello and Xing, 1996; Ran et al., 2002); and (2) diffusion through and along meso-, micro- and nanopores (intrapore diffusion) (Nam and Alexander, 1998). The entry and deposition of organic compounds into nanopores with voids in the diameter range of 0.3–1.0 nm, the size range of toxicological significant organics, would make it inaccessible to bacteria (Alexander, 2000). However, the sorbed compound could diffuse out of the nanopores to an area where it is accessible to microbes. If adsorption and the formation of bound residues are a factor given hydrophobic surfaces within soil pores, the diffusion of the sorbed chemical to a site which is accessible to microbes may be retarded (Cornelissen et al., 1998b; Nam and Alexander, 1998). In addition, the entrapment of HOC in spaces that exist in organic matter that behaves like a glassy polymer in that it has a semi-permanent internal nanopore structure has also been proposed for the retardation of sorbed compounds (Luthy et al., 1997; Xing, 1997; Xing and Pignatello, 1997). This is supported by Ran et al. (2002) who established that transient nanoporosity in the condensed domain of SOM is important for the HOC sorption capacity of sediments and peat.

3.1. Techniques for studying SOM and deriving molecular descriptor factors

The binding affinity of geosorbents for HOC has been related to the composition and structure of SOM (Perminova et al., 1999). Various constitutional descriptors such as H/C and (O + N)/C atomic ratios, molecular weight, molar absorptivity and aromaticity have been employed to evaluate correlation relationships between partitioning coefficients and molecular characteristics of sorbents (Gunasekara and Xing, 2003; Kile et al., 1999; Perminova et al., 1999, 2001; Rutherford et al., 1992; Stuer-Lauridsen and Pedersen, 1997; Xing et al., 1994). The use of molecular descriptors in these studies has garnered great variance to predict HOC binding affinity. This could have resulted from the use of different SOM material, extracted and fractionated humic matter, dissolved organic carbon and bulk soil. Also, the origin and degree of humification of SOM

and choice of compounds could have effected variability in the outcome of these studies.

The elemental content of carbon, hydrogen, oxygen and nitrogen of bulk or fractionated soil/sediment has been used to derive molar or weight ratios. The most prominent ratios established to characterise organic matter and correlate with partitioning coefficients are (O + N)/C (approximate polar-to-nonpolar balance, also termed the polarity index) (Rutherford et al., 1992; Stuer-Lauridsen and Pedersen, 1997; Xing et al., 1994) and H/C (degree of aromaticity) (Haitzer et al., 1999; Kukkonen and Oikari, 1991; Thomsen et al., 2002).

In general, a relative increase of solute partitioning coefficient with a decrease of polar SOM content is found which suggests that K_{oc} of soils might vary if they differ in age and humification of the organic content. Employing the atomic H/C ratio to establish correlation between the partitioning coefficient and aromaticity of organic matter should be approached with circumspection as observed by Haitzer et al. (1999). Generally, a negative correlation between K_{oc} (or K_{doc} if dissolved organic carbon partitioning relationships are considered) and the H/C ratio is found. However, it was pointed out that both COOH and $-\text{CH}=\text{CH}-$ groups have the same H/C ratio and, therefore, the presence of a high concentration of COOH groups can adversely affect the use of H/C as a measure of $-\text{HC}=\text{CH}-$ groups (Gauthier et al., 1987). Adsorption of HOC is assumed to be promoted by aromaticity and impeded by hydrophilic carboxylic groups, therefore, correlations of HOC sorption with the atomic H/C ratio could be ambiguous.

The use of ^1H , ^{15}N or ^{13}C nuclear magnetic resonance (NMR) spectroscopy has contributed greatly to characterisation of the structure of SOM on a molecular level and in conjunction with site-specific labelled isotopes has assisted to determine positions responsible for particular bonding mechanisms (Käcker et al., 2002 and references therein). Solid-state ^{13}C NMR is recognized as the best analytical tool for determining the gross chemical composition of complex organic matrices (Kögel-Knaber, 2000). NMR is potentially quantitative as it can provide a complete and unbiased average chemical structure because, in principle, each ^{13}C nucleus gives rise to the same quantity of signal, regardless of its chemical environment (Smernik and Oades, 2003).

Solid-state ^{13}C cross-polarization with magic angle spinning (CPMAS) has been used to characterise soil organic matter in a number of studies (Ahmad et al., 2001; Carter et al., 2002; Gunasekara and Xing, 2003; Käcker et al., 2002; Kile et al., 1999; Perminova et al., 1999; Ran et al., 2002). NMR data are used to derive molecular descriptors according to the quantification of carbon range in chemical shift bands on NMR spectra. Molecular expressions are concluded to reveal interaction activity with SOM structure such as the prevalence of aromatic core over aliphatic periphery (lipophilic–lipophobic balance), the degree of oxidation of aromatic carbon (Perminova et al., 1999) and aromaticity of organic C (Ahmad et al., 2001). The lipophilic–lipophobic balance is indicated by the $\sum\text{C}_{\text{AR}}/\sum\text{C}_{\text{ALK}}$ ratio, where $\sum\text{C}_{\text{AR}}$ = aromatic C atoms (aryl C plus O-aryl C); and $\sum\text{C}_{\text{ALK}}$ = aliphatic C atoms

(alkyl C plus O-alkyl C). The degree of aromatic-C oxidation would be estimated as O-aryl C/ $\sum\text{C}_{\text{AR}}$ and aromaticity of organic C by dividing $\sum\text{C}_{\text{AR}}$ by the sum of the fractions of all carbon components. In agreement with observations where the polarity index was used, strong correlations between K_{oc} and $\sum\text{C}_{\text{AR}}/\sum\text{C}_{\text{ALK}}$ ratio was found by Perminova et al. (1999, 2001). They suggested that the $\sum\text{C}_{\text{AR}}/\sum\text{C}_{\text{ALK}}$ ratio could reflect the lipophilic–lipophobic balance of extracted humic material with the highest binding affinity for PAH in the least sterically hindered aromatic structures which, at the same time, are the most hydrophobic.

A major limitation of CPMAS is its inability to accurately detect combustion-produced char materials and other adsorption sites which include kerogen and other less well defined condensed phases in soils and sediments (Smernik et al., 2000; Smernik, 2004). Aryl C signals in structures such as lignin also occur at similar chemical shifts, therefore, charcoal content cannot be determined accurately from a CPMAS ^{13}C spectrum. A solid-state NMR spectral editing technique, proton spin relaxation editing (PSRE), has recently been investigated to distinguish and detect highly distinct organic domains in SOM and sewage sludge (Smernik, 2004; Smernik et al., 2000, 2003; Smernik and Oades, 2003). Smernik (2004) proposed PSRE to be a highly effective technique to characterise and quantify domains within organic phases which have been typed as highly sorptive. It could be used in conjunction with radiolabeled isotopes to enable easy identification of adsorption sites.

Other spectroscopic methods employed for the investigation of immobilized or sequestered fractions include infrared (IR) absorption spectroscopy, electron spin resonance spectroscopy and fluorescence spectroscopy (Northcott and Jones, 2000 and references therein). IR spectroscopy provides evidence for the binding of contaminants to soil by measuring the relative intensity of the compound's IR absorption bands. Shifts in specific functional group IR absorption bands, particularly those with hydrogen bonding transfer ability, can be measured and compared to the pure compound and compound-model conjugates to provide information on specific functional group interactions with a sorbent (Northcott and Jones, 2000; Käcker et al., 2002; Singh, 2002). Synchrotron radiation-based Fourier transform infra-red (SR-FTIR) spectroscopy is an extension of conventional IR systems which enables a superior signal-to-noise ratio. It produces unique infra-red signatures for each component involved in sorption and biotransformation of HOC at spatial resolutions smaller than 10 μm (Holman et al., 2002). This is quite a novel technique useful to follow in real time in situ interaction with, and biodegradation of, HOC on mineral surfaces although it has not been extensively employed for this purpose (Sparks, 2004). Holman et al. (2002) were the first to elucidate the potential solubilising role of humic acid on the biodegradation of sorbed pyrene in real time by a bacterial colony immobilized on a magnetite surface utilizing an IR spectroscope and synchrotron photon source.

In addition to elemental analysis and spectroscopy, specific absorptivity and molecular weight (by size-exclusion

chromatography) have been considered to characterise mostly aquatic humic substances and dissolved organic matter (DOM) (Chin et al., 1994, 1997; Haitzer et al., 1999; Thomsen et al., 2002). The reduced bioavailability of contaminants in the presence of DOM has been attributed to the formation of DOM-contaminant aggregates that are too large, too polar, or both to cross-biological membranes at an appreciable rate (Haitzer et al., 1999). The specific absorptivity at wavelength between 250 and 280 nm may yield information regarding degree of aromaticity and degree of humification.

Pyrolysis and thermal desorption methods coupled with gas chromatography–mass spectrometry (MS) have also been employed as a method to characterise the chemical structure of SOM and suspended and dissolved matter in various studies (Cotrim da Cunha et al., 2000 and references therein). Pyrolysis and thermal desorption are useful tools to study natural organic matter, during which generated products can give information about the original mixture of polymers that compose SOM and show differences in binding mechanisms. Combined with MS they can determine the structure of bound fractions and differentiate between parent compound and the bound fractions (Schulten and Leinweber, 1996). The main difference between the two methods is the manner in which the sorbent samples are heated. During thermal desorption, heating is under isothermal conditions at lower temperatures and operated over longer time frames than pyrolysis where a range of sample heating options including high rate temperature ramping and flash pyrolysis are employed (Northcott and Jones, 2000).

The use of sorbent characteristics for deriving molecular descriptor factors as a predictive tool to evaluate contaminant mobility and availability has been drawn into question. This was disclosed in a number of studies (Alexander and Alexander, 2000; Chefetz et al., 2000; Hawthorne et al., 2002) where specifically the proposed advantages of SOM aromaticity as HOC sorption predictor were shown to be misleading through investigations by Mao et al. (2002), Salloum et al. (2002) and Gunasekara and Xing (2003).

4. Biomimetic methodology

Biomimetic extraction differs from conventional extraction in that the objective is not a complete removal of analytes from the sorbent. It allows for selective partitioning and adsorption of analytes to a surrogate phase in order to simulate desorption from soil and sediment surfaces to estimate available concentrations (Parkerton et al., 2000). (Bio)availability can be studied from two different perspectives: physical–chemical and biological. The predictive power can be grouped according to the goal of availability testing (remediation or toxicity evaluation) which, by employing a specific biomimetic method, can measure particular fractions such as the freely dissolved concentration and rapidly desorbing fraction. Physical–chemical assays usually involve non-exhaustive removal of sorbed contaminants from sorbent matrices, employing water, a mild chemical extractant or supercritical carbon dioxide. It can also be accomplished by applying passive samplers

(i.e. semi-permeable membrane devices or solid-phase micro-extraction) or surrogate phases that bind the freely dissolved concentration which will result in the establishment of a concentration gradient between solid and aqueous phases (i.e. Tenax TA[®], XAD resins). Since a particular biomimetic method tests for a specific availability type, whether it is the freely dissolved concentration and/or rapidly desorbing fraction, the selection of a method should depend on the purpose (e.g. bioremediation, leaching, bioaccumulation or toxicity) of (bio)availability prediction.

4.1. Bioavailability by physical–chemical assessment

4.1.1. Chemical extractants

The use of harsh chemical extractants and vigorous extraction procedures, such as Soxhlet extraction, have been promulgated by governmental regulations to assess potential future release and dissipation of organic contaminants into ground-water bodies and to establish goals for remediation of contaminated soils (Kelsey et al., 1997; US EPA, 1992). Harsh, vigorous extraction procedures, however, remove a large percentage of the contaminant from the soil and, therefore, do not represent the fraction available to biota and bear little relevance to availability prediction (Bosma et al., 1997; Reid et al., 2000a; Tang et al., 2002). Data to support this have been gathered in numerous studies employing different test organisms and HOC. The availability of PAH to microorganisms (Erickson et al., 1993; Tang et al., 1998), uptake of chlorinated insecticides such as [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] (DDT), [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane] (DDE), [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene] (DDD) and dieldrin (Morrison et al., 2000), and PAH (Kelsey and Alexander, 1997) by earthworms, as well as toxicity of DDT and dieldrin to insect species (Robertson and Alexander, 1998) have shown overestimation of available quantities to test species due to exhaustive extraction. Kelsey et al. (1997) and others (Reid et al., 2000a; Tang et al., 1999; Tang and Alexander, 1999; Wahle and Kördel, 1997) proposed the use of mild and selective extractants (alcohols, alcohol–water mixtures or organic acids) which may mimic bioavailable release and exposure more competently.

Relative bioavailability of atrazine and phenanthrene from spiked and aged soil to two test organisms was determined by the use of various organic solvents and solvent combinations (Kelsey et al., 1997). Bacteria and earthworms (*Eisenia foetida*) were used as test organisms. Results showed vigorous extraction did not correlate with the bioavailability of the two compounds to the test organisms, whereas the use of gentle and selective extractants (methanol–water, *n*-butanol, ethanol, hexane) was capable to predict bioavailability. The authors found that extraction by a single solvent could not predict availability to both species. For atrazine, methanol–water (9:1) and methanol–water (1:1) were the best predictors for uptake by earthworms and mineralization by bacteria, respectively, whereas for phenanthrene, *n*-butanol functioned as the best predictor for availability to the test organisms. The availability to earthworms and bacteria and the amounts of

phenanthrene and atrazine that were recovered by the extractants declined with residence time in the soil, albeit availability rates varied with test species and solvents. Importantly, the findings did not provide a 1:1 relationship between extractability and bioavailability. Similar declines in extractability with increased residence time in soil have been reported for pyrene, simazine and phenanthrene (Hatzinger and Alexander, 1995; Kelsey et al., 1997).

Following on this investigation, Chung and Alexander (1998) conducted an investigation into the bioavailability of phenanthrene and atrazine aged in 16 soils with different physico-chemical properties using mild extractants. Diluted ethanol (71% and 95% v/v in water for phenanthrene and atrazine, respectively) was used as extraction chemical followed by vigorous extraction (two 6-h Soxhlet extractions using 100% methanol). The results showed that greatest reduction in bioavailability to phenanthrene and atrazine-degrading bacterial strains were evident in soils which produced the greatest reduction in extractability, however, correlation among the soils was not observed. The authors concluded that the mild extractants used in the study are not appropriate surrogates to predict bioavailability.

Unaged and aged PAH (anthracene, fluoranthene and pyrene) in soil were assessed for their availability to *E. foetida*, wheat or barley plants and degradation (anthracene) by a bacterial culture (Tang and Alexander, 1999). The amount of compound available at specific time intervals determined by short extraction times and mild chemical extractants (*n*-butanol, propanol, ethyl acetate and methanol) was correlated by the amount of compound accumulated in earthworms and plants or biodegraded by bacteria. No single organism or combination of organisms removed the entire fraction that was extracted by the mild alcohols and solvents, although bacteria removed the greatest percentage. Relationships were determined by regression analysis and correlation factors (r^2) calculated were in the range 0.91–0.99. The interdependence was evident as extractability and bioavailability of the PAH changed as a result of aging.

The use of a single chemical extractant to predict (bio-)availability for a variety of sorbents, for different pollutants and conditions is unlikely (Alexander, 2000; Reid et al., 2000a). Advanced solvent extraction technologies such as ultrasonication and accelerated solvent extraction (ASE), considered to enhance extraction kinetics of organic compounds (Northcott and Jones, 2000), have only recently been examined and suggested as potential bioavailability predictive tools (Tao et al., 2004).

4.1.2. Solid-phase extraction

It is generally accepted that microorganisms can only take up pollutants that are present in the aqueous phase and this is influenced by the mass transfer kinetics from the solid phase (Bosma et al., 1997; Miller and Alexander, 1991; Reid et al., 2000a). Therefore, water has been used as solvent in many studies to extract soil-adsorbed pollutants in combination with a solid-phase extractant usually involving a surrogate phase such as Tenax TA (Cornelissen et al., 1997a,b, 1998a,

2001; Macrae and Hall, 1998; Morrison et al., 2000; Ten Hulscher et al., 2003), or XAD (styrene–divinylbenzene copolymer) (Carroll et al., 1994; Hawthorne et al., 2002; Huesemann et al., 2003). Semi-permeable membrane devices (SPMD) containing triolein and octadecyl-modified silica impregnated into Teflon (e.g. C₁₈ membrane disks) have been proposed as surrogate lipid phases (Krauss and Wilcke, 2001; Macrae and Hall, 1998; Parkerton et al., 2000; Tang et al., 1999; Verhaar et al., 1995) into which analytes in the aqueous phase selectively partitions to simulate availability.

Tang et al. (1999) used C₁₈ membranes to assess bioavailability of DDT, DDE and DDD in freshly spiked and aged soils from a historically contaminated site. They employed earthworm uptake as bioassay to correlate with physical–chemical extractability. Liquid-phase extraction with an aqueous solution containing tetrahydrofuran (THF) (25% v/v in water) was also undertaken as parallel study to the solid-phase extraction (SPE). The amounts of DDT, DDE and DDD sorbed by the C₁₈ membranes and extracted by THF–water mixture correlated with *E. foetida* uptake and accumulation. Linear-regression analysis between the chemical assays and bioassay was used to assess correlation. Correlation coefficients were >0.92 for the C₁₈ disk study and between 0.83 and 0.94 for the solvent extraction assay in relation to the bioassay. Consequently, Tang et al. (2002) assessed non-exhaustive extraction by 25% v/v THF, 95% v/v ethanol and C₁₈ membranes to predict availability of PAH in soil to earthworms. Correlation coefficients for THF extraction and earthworm accumulation for anthracene, chrysene, pyrene and benzo[*a*]pyrene, added as a mixture in unaged and aged model soils, exceeded 0.85. Correlations were also good with the C₁₈ membrane assay (≥ 0.77) and ethanol (>0.87). Contamination of soil usually occurs as mixtures of hydrocarbons and other compound classes, therefore, the physical–chemical assays examined by Tang et al. (2002) exhibit potential for use in the field.

Krauss and Wilcke (2001) related uptake of PAH and PCB by a benthic soil dwelling organism (*Lumbricus terrestris* L.) from historically contaminated soil to extraction with C₁₈ disks. Regression equations involving log BSAF (biota-to-soil accumulation factor) and log C₁₈ disk-soil partitioning coefficients (K_{disk}) were used to calculate the correlation coefficient ($0.47 \leq r^2 \leq 0.87$). The results showed that BSAF of high molecular weight PAH and PCB were higher than the corresponding K_{disk} suggesting enhanced uptake and ingestion by increased PAH and PCB partitioning between soil and earthworms. Indeed, significance of the feeding behaviour of benthic organisms that affects uptake and accumulation of hydrophobic pollutants was shown by Leppänen and Kukkonen (2000). The amounts of ingested pyrene and benzo[*a*]pyrene-spiked sediment varied between exposure periods which was contributed to combined effects of variable ingestion rates by *Lumbricus variegatus* and decreasing bioavailable fractions of the chemicals. SPMD (low density polyethylene layflat tubing filled with triolein, heat sealed and frozen) were employed to mimic the available and accumulated PAH fraction in relation to residence time in the sediment which was shown to decrease with increasing contact time. Ultimately, it was

concluded that uptake of sediment-associated PAH by SPMD appeared to simulate uptake by non-feeding worms.

Tang et al. (1999) stated that correlation between biological and physical–chemical assays is essential for any bioavailability predictive procedure to be ultimately accepted for risk assessment purposes, however, implicit details regarding experimental protocol (e.g. soil:water ratio, length of time for assays and best solvent systems) still need to be elucidated. In addition, SPMD pose operational difficulties: sorption kinetics are relatively slow which may take weeks to reach equilibrium plus large sample volumes may be required to obtain acceptable analytical sensitivity (Parkerton et al., 2000; Sijm et al., 2000), and more research to compare uptake by surrogate devices to biota needs to be undertaken (Leppänen and Kukkonen, 2000).

Macrae and Hall (1998) employed SPMD, Tenax TA and polyethylene tube dialysis (PTD) to assess bioavailability of PAH from historically contaminated sediment. The SPMD (layflat polyethylene tubing with triolein) were exposed to wet sediment in sea salts medium (24 h) followed by rinsing and dialysis in pentane. Tenax is a partially crystalline glassy polymer synthesized by oxidative coupling and is not cross-linked (Zhao and Pignatello, 2004). The PTD method involved sediment and sea salts solution heat-sealed in polyethylene tubing. The three methods showed that PAH associated with spiked sediment were more available than endogenous (not spiked) PAH. This was to be expected since aged contaminants tend to be more strongly adsorbed to sediments (Huang et al., 2003; Pignatello and Xing, 1996). Generally, the PTD method was more effective than the other two which, according to Macrae and Hall (1998), could make it useful when the object of an availability assay is to assess potential risk associated with exposure to contaminated sediments. Comparing results of the SPMD and Tenax extractions, SPMD gave slightly higher recoveries. This was not applicable to five- and six-ring compounds which was likely due to a slow transfer of large PAH across polyethylene tubing which may simulate the biomembrane protective effect. The authors conceded that transfer of pollutants is not always by passive diffusion. Tenax TA might provide a more accurate measure of availability and would be more reflective of the freely dissolved and fast desorbing pollutant fractions plus all dissolved and colloidal organic matter, not only those passing through biomembranes. This study, however, did not employ bioassays and thus no assessment of the potential predictive power of the physical–chemical assays could be undertaken.

Cornelissen et al. (1997a,b, 1998a, 2001) and Van Noort et al. (2003) employed Tenax TA beads to calculate desorption kinetics of chlorinated benzenes, PCB and PAH from laboratory-contaminated sediment and historically contaminated harbour sediment. These studies did not categorically link the use of the organic compound-scavenging material and its potential for mimicking bioavailability with parallel bioassays per se. The study in which aged contaminated sediment was employed for desorption studies, however, did feature slurry bioreactor and land farming remediation activities (Cornelissen et al., 1998a). Desorption kinetics were used to show the so-called biphasic and triphasic desorption: an initial rapid

desorption phase followed by a slower release (biphasic) and much slower release (triphasic) (Carroll et al., 1994; Cornelissen et al., 1997a; Leppänen et al., 2003; Pignatello and Xing, 1996). It was shown that initial rapid desorption fractions were smaller after bioremediation than before treatment, therefore, mainly rapidly desorbing PAH were biodegraded during remediation. In general, the data indicated a 1:1 relationship between extractability and biodegradability before remedial action. It was suggested that the Tenax extraction method is also theoretically sound as predictor of the extent of biodegradation ability because the beads are similar to degrading microorganisms in the sense that both Tenax and microbes increase the sorbent-aqueous phase concentration gradient. Microbial activity steepens the concentration gradient between sorbent and water and, therefore, according to Rijnaarts et al. (1990), accelerated desorption occurs.

The hypothesis that the amount of HOC sorbed to Tenax in 6 h (Cornelissen et al., 1997b) from the freely dissolved and sorbent-associated fractions represents the concentration that can potentially accumulate in test organisms was studied by Ten Hulscher et al. (2003). The organic compounds investigated were PCB, PAH, chlorinated benzenes, DDD and DDE and test organisms, oligochaetes (*Limnodrilus* sp.) and earthworms (*Lumbricus rubellus*), for bioaccumulation experiments. The data showed that accumulation of organic compounds in test organisms can be estimated to be five times the amount sorbed to Tenax in 6 h. The ratio between concentrations in biota and Tenax-extractable concentrations showed some variation between sediment and compound class.

Morrison et al. (2000) conducted a study to determine availability of DDT, DDE, DDD and dieldrin in historically contaminated and spiked soils to earthworms. This study was complimentary to the Tang et al. (1999) investigation which employed C₁₈ membranes to predict bioavailability of the insecticides. Morrison et al. (2000) performed adsorption to Tenax TA beads to simulate the bioavailable fraction and correlated the data to accumulation in *E. foetida*. The data from this investigation showed that values for uptake by worms from soil with high (>9.2–15.2%) or low (<1.75%) bioavailable percentages of DDT, DDE and DDD correlated with retention on Tenax, however, strong correlation was not evident at intermediate (2.3–7.8%) bioavailable percentages. The authors speculated that Tenax might be useful to distinguish among soils with high or low bioavailable fractions.

4.1.3. Solid-phase micro-extraction

Solid-phase micro-extraction with negligible depletion (nd-SPME) employs a fiber that contains a silica backbone that is coated with a thin film of organic phase (e.g. poly(dimethylsiloxane) and polyacrylate) and extracts HOC from the aqueous phase in a non-exhaustive manner (Parkerton et al., 2000; Sijm et al., 2000; Van der Wal et al., 2004; Verbruggen et al., 2000). It, therefore, measures the freely dissolved fraction of the pollutant and mimics the accumulation of contaminants in biota (Leslie et al., 2002b). Once equilibrated with the sample matrix, the SPME fiber can be directly inserted into a GC where contaminants are thermally desorbed and subsequently

quantified. It has the advantage that only the freely dissolved contaminants will partition between the aqueous phase and the fiber, therefore, functions as a surrogate surface for the freely dissolved and bioavailable concentration in the interstitial water (Sijm et al., 2000). SPME with negligible depletion is a passive process; organic compounds are not adsorbed, but absorbed into the organic layer so that there is neither competition between compounds nor saturation of the layer (Mayer et al., 2000). A number of studies evaluated the potential use of SPME as an indicator of water contamination and toxicity of PAH, PCB and chlorinated and petroleum hydrocarbon mixtures (Leslie et al., 2002a,b; Parkerton et al., 2000; Potter and Pawliszyn, 1994; Van der Wal et al., 2004), soil contamination by creosote employing headspace SPME analysis (Eriksson et al., 2001), to monitor biodegradation of diesel in water and soil (Eriksson et al., 1998), to investigate the effects of salinity and humic acids on the availability of freely dissolved DDT and chlorpyrifos (Mezin and Hale, 2004) and as a measurement of 2,4,6-trinitrotoluene (TNT) and metabolites at historically contaminated military sites (Conder et al., 2003).

Other advantages of using SPME include fast sorption kinetics and only small sample volumes are required. SPME fibers are also regenerated by the thermal desorption step and can therefore be used cost-effectively for availability and toxicity assessment (Parkerton et al., 2000). SPME measurements were correlated with toxicity tests for rainbow trout (Parkerton et al., 2000) and uptake and accumulation by earthworms (*Eisania andrei* and *Aporrectodea caliginosa*) (Van der Wal et al., 2004) and midge larvae (*Chironomus riparius*) (Leslie et al., 2002a,b). Steady-state concentrations in both earthworm species were linearly related to concentrations in poly(dimethylsiloxane) (PDMS) fibers. Moreover, freely dissolved concentrations of the pollutants in pore water, derived from SPME measurements, were used to calculate levels in earthworms. The measured accumulated concentrations in the earthworms were close to calculated concentrations from the fibers. Leslie et al. (2002b) found that PDMS fibers had higher uptake rate constants than larvae and accumulated the chemicals five times faster. It was concluded that SPME represents a simple tool to estimate internal concentrations of contaminants in biota though the incorporation of a factor could be a necessity to translate fiber concentrations to biota concentrations depending on the test organism.

4.1.4. Supercritical fluid extraction

Recently, supercritical fluid extraction (SFE) with pure carbon dioxide has been actively considered as a tool to characterize sorption–desorption behaviour of organics in natural solids and to predict the bioavailable fraction of soil- and sediment-bound organic contaminants (Björklund et al., 1999, 2000; Hawthorne et al., 2002; Hawthorne and Grabanski, 2000; Hawthorne and Miller, 2003; Loibner et al., 1997, 2000; Nilsson et al., 2002, 2003; Szolar et al., 2004; Young and Weber, 1997), and SFE followed by GC–MS has been used for fingerprinting volatile and semi-volatile hydrocarbon

fractions in light non-aqueous phase liquids in soil, though not for bioavailability prediction (Lundegaard et al., 2003).

Cited advantages of SFE include the possibility to adapt the strength of the extraction procedure by changing fluid temperature and density and allowing to alter desorption kinetics by sequential extraction to represent the range of “fast” to “slow” desorption sites (Hawthorne and Grabanski, 2000). Also, employing SFE with pure CO₂ as extractant seems to have minimal affect on the bulk matrix of the organic material in contrast to organic solvent use (Björklund et al., 1999). Moreover, supercritical CO₂ is relatively lipophilic and can, therefore, displace HOC from nonpolar matrices compared to water which is a poor extractant to disturb associations between hydrophobic fractions and sorbent surfaces (Hawthorne et al., 2002). However, it has been suggested that SFE may introduce an artefact as swelling of the organic matter during the extraction procedure, which enhances extraction rates, may change the structure of SOM and thereby affecting the sorption properties of the material investigated (Xing and Pignatello, 1997).

The use of SFE to predict desorption behaviour and bioavailability of sediment-bound PCB was investigated by Björklund et al. (1999, 2000) and Nilsson et al. (2002, 2003). In a preliminary investigation, Björklund et al. (1999) studied the uptake of 11 PCB congeners into the benthic larvae *Chironimus pallidivittatus* in conjunction with selective SFE to assess possible correlation in predicted available and accumulated fractions. Two sediment batches contaminated with PCB were used. One of the batches was pre-extracted by the initial (weakest of four) SFE condition (60 min at 120 bar, 40 °C) which allowed for 45% of total PCB to be removed. Results showed larvae exposed to the pre-extracted sediment accumulated on an average 22% less PCB compared to larvae in the untreated batch. The authors suggested that the difference in uptake, albeit small, gives an indication that SFE has the potential to preferentially extract bioavailable analytes. Following this, the selective SFE method was simplified by collection of single and not multiple fractions during each of the four extraction conditions for the two sediments (Nilsson et al., 2002). For both sediments it was shown that major fractions of the analytes (58% and 65% for the two sediments, respectively) were situated on the most easily extractable sites (weak SFE conditions), whereas about 10% were tightly bound (slow desorption) with harshest SFE conditions (60 min at 400 bar, 150 °C) required to desorb these fractions. Consequently, Nilsson et al. (2003) employed chironomid larvae to establish BSAF in selectively extracted and untreated sediment substrates. The BSAF for 11 PCB congeners decreased by about 40% for pre-extracted sediment samples in contrast to accumulation factors for larvae in untreated batches, which was concluded as an indication that selective SFE preferentially has removed bioavailable PCB fractions from soil.

Similarly, BTEX and PAH availability was estimated in historically polluted soils by employing sequential SFE correlated with biodegradation experiments and remediation behaviour (Hawthorne et al., 2002; Hawthorne and Grabanski,

2000; Hawthorne and Miller, 2003; Loibner et al., 1997, 2000; Szolar et al., 2004). Hawthorne and Grabanski (2000) and Hawthorne et al. (2002) assessed SFE behaviour of PAH from gas manufacturing plant soils in untreated and soils collected after 6 and 12 months of bioremediation. Sequentially, stronger SFE conditions gave selective extraction of PAH associated with rapidly desorbing (“fast”), “moderate”, “slow” and “very slow” sites on the soil collected before and during bioremediation. The researchers found approximately 80–90% of each low molecular weight PAH in the “fast” (weakest SFE condition: 30 min at 120 bar, 50 °C) fraction and that bioremediation removed PAH molecules which was found in the “fast” fraction by SFE. Correlation coefficients for each individual PAH removed by bioremediation and extracted by the weakest SFE condition were 0.93 and 0.92 for 6 and 12 months, respectively. Hawthorne et al. (2002) correlated prediction of PAH release from gas plant soils and sediments, using SFE and SPE (XAD-2) taking into consideration basic soil parameters (carbon content, elemental composition, condensed and amorphous organic carbon). Rapidly released fractions correlated with SFE desorption and XAD uptake with sorbents rich in amorphous carbon, however, higher yields with supercritical CO₂ extraction were obtained which was attributed to the stronger ability of carbon dioxide to desorb PAH compared to water from condensed aromatic carbon in sorbent matrices.

Five sequential SFE phases of increasing strength were applied to eight historically contaminated soils with the aim to elucidate sorption–desorption behaviour of high molecular weight PAH (Szolar et al., 2004). Two groups of soils were identified based on rapidly desorbing PAH fractions under weakest extraction conditions (rapidly desorbing fractions varied between the soils, ranging from <10% to >90%). Extracted fractions strongly correlated with molecular weight showing decreasing PAH availability with increasing molecular weight. Degradation and toxicity tests were also undertaken. Biodegradation did show good correlation with recovered PAH fraction employing the two mildest SFE extraction conditions, though quantitative relationships could only be established with three soils since the remainder (including soils with the lowest fraction of readily desorbing PAH) showed little or no degradation. A major conclusion from this study was that compound mass transfer is a major requirement for degradation, though not an absolute requirement since one soil which showed high toxicity to *Vibrio fischeri* did not match the pattern showing no or little PAH degradation, although, large fractions of mobile PAH were detected using SFE.

4.1.5. Solubilising agents and surfactants

The utilization of solubilising agents such as β -cyclodextrin (Bardi et al., 2000; Reid et al., 1999, 2000a,b, 2004) and surfactants (Cuypers et al., 2002b; Volkering et al., 1998) have been employed for the prediction of bioavailability of HOC. Reid et al. (1999, 2000b, 2004) proposed the use of a hydroxypropyl- β -cyclodextrin (HPCD) solution to extract soil-sorbed PAH. HPCD is a cyclic oligosaccharide with a hydrophilic shell and a toroidal-shaped apolar cavity. It can form

water-soluble inclusion complexes by incorporating PAH in its cavities (Cuypers et al., 2002b). Nonionic surfactants (i.e. Triton X-100) form micelles above their critical micelle concentration. Hydrophobic compounds can be included in these micelles which lead to an increase in solubility (Volkering et al., 1998). In general, there has been some contradiction with respect to the use of solubilising agents and surfactants as predictors of availability and to improve bioavailability (such as in studies by Bardi et al., 2000; Boopathy and Manning, 1999; Fava and Di Gioia, 1998; Fava and Ciccotosto, 2002; Fava et al., 1998, 2003; Wang et al., 1998).

Fava and Di Gioia (1998), Fava and Ciccotosto (2002), Fava et al. (1998, 2003) showed that the supplementation of PCB-contaminated soils with methyl- β -cyclodextrin, Triton X-100 and Quillaya Saponin (a biogenic glycoside with surfactant properties) could potentially enhance bioremediation by increasing bioavailability of the contaminants. Bardi et al. (2000) measured accelerated biodegradation of paraffinic and aromatic compounds by introducing β -cyclodextrin, therefore, higher biomass yields and increased utilization of the hydrocarbons as sole carbon and energy sources was shown. Reid et al. (1999, 2000b, 2004) showed good correlation (1:1) between the amount of soil-sorbed phenanthrene (spiked and aged soils), which could be rapidly exchanged (showed to be optimum in 20 h) into an HPCD solution, and the amount mineralized. This amount was also correlated with dichloromethane (Soxhlet extraction)- and butanol-extractable concentrations. Both these methods overestimated bioavailability to the microorganisms. This, according to the authors, offers a feasible method of assessing bioavailability, at least to degrading microorganisms. SPE (Tenax TA) and biodegradation were used as reference methods to assess which fraction of PAH (16 US EPA) could be degraded and to what extent biodegradation was governed by availability limitation in conjunction with HPCD and Triton X-100 extractions of historically contaminated sediments (Cuypers et al., 2002b). Overall, correlation was found between HPCD and SPE extraction to remove readily (fast desorbing) bioavailable PAH, whereas Triton X-100 removed readily available and more tightly bound PAH. It was also shown that Triton X-100 enhanced biodegradation of low molecular weight PAH, while HPCD did not affect degradation.

4.1.6. Other methods

Other methods employed to predict bioavailability of HOC include the soil/sediment availability ratio (SARA), thermodesorption and persulphate oxidation. SARA uses organisms to estimate bioavailable concentrations and can be employed to measure available contaminant fractions of aged pollution by exposing test organisms to contaminated soil to which a ‘like’ chemical which is usually a structural isomer of the already present pollutant is spiked (Sijm et al., 2000). The ratio of the concentration of a contaminant in a test organism divided by the concentration in soil or sediment of the aged contaminant is related to that of the ‘like’ chemical which reveals the bioavailable fraction. SARA has been employed to measure

bioavailability of hydrophobic pollutants including PAH (Belfroid et al., 1995; Kraaij et al., 1998).

Persulphate ($S_2O_8^{2-}$) oxidation was used as a tool to predict PAH and petroleum hydrocarbon availability in historically contaminated model soils and sediments (Cuypers et al., 2000, 2001). Results showed that after a 3-h persulphate oxidation period ($S_2O_8^{2-}$:SOM, 12 g g^{-1} ; $70\text{ }^\circ\text{C}$) residual PAH concentrations corresponded with biodegradation after 21 days, while persulphate oxidation of samples that were first subjected to degradation yielded only limited additional PAH oxidation. It was concluded that $S_2O_8^{2-}$ oxidation and biodegradation removed approximately the same PAH fraction. Though proposed as a rapid and effective method to predict PAH availability, it was unfit for the prediction of total petroleum hydrocarbon availability probably due to the inability of persulphate to oxidize hydrocarbons with a high ionization potential.

Thermodesorption and microwave extraction have also been considered. During thermodesorption, an amount of soil is deposited in a quartz tube and heated under an increasing temperature range. Usually the volatile compounds are then transported into a GC–MS. Ghosh et al. (2001), Löser et al. (1999) and Uzgiris et al. (1995) employed this technique to evaluate the mobilisation of PAH, petroleum hydrocarbons and PCB from geosorbents, respectively, though this method has not been validated by employing a bioassay for comparative purposes. Microwave extraction has recently only been considered as availability predictive tool and has only been examined to evaluate heavy metal immobilisation (Anxiang et al., 2003; Zhang et al., 2002).

4.2. Bioavailability by biological assessment

A comprehensive overview of biological assays is not reported here. The full scope of bioassays available is reported in Loibner et al. (2003). Bioassays have been widely used for the evaluation of potentially contaminated sites with varying degrees of success. The application and success of bioassays have been shown when employed in conjunction with a physical–chemical assay since correlating, for example, an SPE extraction with biodegradation performance or accumulation and toxicity is vital to substantiate the predictive power of the physical–chemical assay. The particular application and outcome of a bioassay should be considered carefully. A reduction in bioluminescence or plant growth will not be considered an indication for remediation potential, however, it could be regarded as an indicator of toxicity and pollution and whether physical–chemical testing would be a necessity.

5. Implications and consideration of a geosorbent molecular descriptor–biomimetic relationship for assessing availability

The experimental work documenting the outcome of physical–chemical biomimetic strategies reviewed in this article is often complimentary but also contradictory. Evidence to

support the use of a particular method which outperformed other methods in laboratory studies in terms of its predictive capacity is, therefore, lacking. This is partly due to the fact that comparison and correlation of results among biomimetic studies from different laboratories are implausible since laboratory and field conditions, selection of compounds and field samples vary greatly. Table 2 presents the principal studies which applied physical–chemical biomimetic methods. It also documents bioassay correlation, sorbent source and considers the fraction and type of availability each method measures. Hawthorne et al. (2002) noted that interpretation of predictive assays is limited by the lack of data of common field samples since representative sorbents are largely unavailable to multiple investigators. Considering this, no representative physical–chemical or biological test that is all encompassing is as yet available, and the research and development of such a test is probably infeasible since accurate availability prediction would require acknowledgment and inclusion of diverse parameters and conditions. There is, therefore, justification for considering the availability of contaminants and assessing contaminated sites on a case-by-case basis and accordingly site-specific assays would probably be needed for determining availability of contaminants. Reid et al. (2000a) suggested that a “middle ground” approach be followed, therefore, a move towards developing standardised and validated physical–chemical and biological assays performed under controlled conditions.

The type of (bio)availability to be evaluated is an important aspect to recognize when assessment is to be undertaken. The prediction of bioremediation potential is one application that can be considered for testing the availability of contaminants, at present and for future scenarios, to microorganisms able to catabolize the contaminants. This would mostly represent the freely dissolved (in the pore water volume) plus rapidly desorbing concentrations which would be available over a relatively short period. Biomimetic methodology that can be employed to measure the freely dissolved concentration includes passive samplers such as SPMD or nd-SPME, or for measuring the freely dissolved plus contaminant sorbed to the “fast” sites, SPE (e.g. Tenax, XAD) or SFE (weak extraction conditions). It is generally agreed to employ a procedure that will not influence contaminant distribution or alter the geosorbent matrix properties so that it could as closely as possible represent the intact natural sorbent conditions, therefore, the use of chemical extractants may not be the first choice as a method to mimic availability.

Assessing the likelihood of uptake and accumulation by, and toxicity to, biota is another reason for determining availability. It is suggested that physical–chemical assays which measure the freely dissolved concentration and rapidly desorbing fraction simulate availability to microbes (Alexander, 2000; Reid et al., 2000a), however, the uptake mechanisms of higher organisms are more complex and could be more difficult to evaluate with a physical–chemical test (Reid et al., 2000a; White et al., 1997).

The sequestered concentration might not be of significant importance here since these pollutants may not be accessible

Table 2
Summary of principal biomimetic studies

Reference/contaminant(s)	Physical–chemical biomimetic method	Bioassay correlation	Geosorbent	Fraction/type of availability
Kelsey et al. (1997)/atrazine, phenanthrene	Methanol/water (9:1/1:1), <i>n</i> -butanol ^d	<i>E. foetida</i> uptake, biodegradation	Spiked, laboratory aging	Freely dissolved, rapidly desorbing/degradation, accumulation, leaching, toxicity ^a
Chung and Alexander (1998)/atrazine, phenanthrene	Ethanol: 95%, 71% v/v ^a	Biodegradation	Spiked, laboratory aging	^a
Tang and Alexander (1999)/anthracene, fluoranthene, pyrene (single compounds)	<i>n</i> -butanol, propanol, ethyl acetate ^a	Biodegradation, <i>E. foetida</i> uptake, retention by plants (wheat, barley)	Spiked, laboratory aging	^a
Tang et al. (1999)/DDT, DDE, DDD	THF (25% v/v) ^a , C ₁₈ membrane ^b	<i>E. foetida</i> uptake	Historically contaminated, laboratory aging	^a Freely dissolved/degradation, accumulation, leaching, toxicity ^b
Tang et al. (2002)/PAH (mixture)	THF (25% v/v), ethanol (95% v/v) ^a , C ₁₈ membrane ^b	<i>E. foetida</i> uptake	Spiked, laboratory aging	^a ^b
Krauss and Wilcke (2001)/PAH, PCB	C ₁₈ membrane ^b	<i>L. terrestris</i> uptake	Historically contaminated	^b
Leppänen and Kukkonen (2000)/pyrene, benzo[<i>a</i>]pyrene	Polyethylene tubing ^b	<i>L. variegatus</i> uptake	Spiked and laboratory aging	^b
Macrae and Hall (1998)/PAH (mixtures)	Polyethylene tubing ^b , PTD ^b , Tenax TA ^c	ND ^g	Spiked historically contaminated sediment	^b Exposure potential (PTD). Freely dissolved, rapidly desorbing/degradation, accumulation, leaching, toxicity ^c
Cornelissen et al. (1997a,b, 1998a, 2001), Van Noort et al. (2003)/PCB, PAH, chlorobenzenes	Tenax TA ^c	Bioremediation	Spiked, laboratory-aging & historically contaminated	^c
Ten Hulscher et al. (2003)/PCB, PAH, DDE, DDD, chlorobenzenes	Tenax TA ^c	<i>Limnodrilus</i> sp., <i>L. rubellus</i> uptake	Spiked, laboratory-aging	^c
Huesemann et al. (2003)/petroleum hydrocarbons (mixture)	XAD-2 ^c	ND ^g	Spiked, laboratory and field aging	^c
Morrison et al. (2000)/DDT, DDE, DDD, dieldrin	Tenax TA ^c	<i>E. foetida</i> uptake	Historically contaminated, spiked laboratory-aging	^c
Van der Wal et al. (2004)/PCB, HCB, dieldrin, telodrin	Poly(dimethylsiloxane)-coated fiber ^d	<i>E. andrei</i> , <i>A. caliginosa</i> uptake	Historically contaminated	Freely dissolved/degradation, accumulation, leaching, toxicity ^d
Parkerton et al. (2000)/petroleum hydrocarbon mixture	Poly(dimethylsiloxane)-coated fiber ^d	Rainbow trout toxicity	In solution	^d
Leslie et al. (2002a,b)/chlorinated hydrocarbons	Poly(dimethylsiloxane)-coated fiber ^d	<i>C. riparius</i> uptake	In solution	^d
Nilsson et al. (2002, 2003)/PCB	Supercritical CO ₂ ^e	<i>C. pallidivittatis</i> uptake	Historically contaminated	Rapidly desorbing (mild conditions) → slow desorbing (strong conditions)/degradation, accumulation, leaching, toxicity → potentially not available ^e
Hawthorne and Grabanski (2000), Hawthorne et al. (2002)/PAH	Supercritical CO ₂ ^e , XAD-2 ^c	Bioremediation (land treatment)	Historically contaminated	^e ^c
Loibner et al. (1997, 2000), Szolar et al. (2004)/PAH	Supercritical CO ₂ ^e	Biodegradation, <i>Vibrio fischeri</i> toxicity	Spiked, laboratory and historically contaminated	^e

Cuypers et al. (2002b)/PAH	Tenax TA ^c , hydroxypropyl- β -cyclodextrin, Triton X-100 ^f	Biodegradation	Historically contaminated	Freely dissolved, rapidly desorbing/ degradation, accumulation, leaching, toxicity ^f
Reid et al. (1999, 2000b, 2004)/PAH Cuypers et al. (2000)/PAH	Hydroxypropyl- β -cyclodextrin ^f Persulphate oxidation, Tenax TA ^c	Biodegradation Biodegradation	Spiked, laboratory aging Historically contaminated	

^a Chemical extractants.

^b SPMD.

^c SPE.

^d nd-SPME.

^e SFE.

^f Solubilising agents and surfactants.

^g ND = not determined.

or available to microbes or other biota, however, future situations have to be borne in mind. Changes in environmental conditions, natural degradation of SOM and aging might affect the availability of the pollutant. Implementing a testing programme to simulate the long-term effects in the laboratory is one method to assess how changing sorbent conditions influence contaminant availability over time monitored by spectroscopic and biomimetic methods. Moreover, employing a technique such as sequential SFE where extraction conditions could be altered to remove the slower desorbing fractions, future availability expectations, albeit conjectural, can be determined.

The correlation between detailed characteristics of SOM, such as structural and molecular properties, and immobilisation—mobilisation behaviour of HOC should ultimately advance the understanding of how these two factors are interlinked and could be applied in bioavailability and risk assessments. Luthy et al. (1997) and Huang et al. (2003) acceded that laboratory study and observation are necessary for microscopic evaluation to understand and identify dominant matrix properties, and consequently the mechanisms, that govern sorption activity. The information could be incorporated into models for the quantification and prediction of availability, leaching and, ultimately, contaminant fate in the environment. The extrapolation of laboratory-generated results to the field is unrealistic because studies for bridging this gap are currently insufficient mostly due to the complexity and heterogeneous nature of environmental systems and cost restrictions to document chemical and physical properties at field scale.

The advent of molecular spectroscopic techniques has made it possible to characterise SOM and determine molecular interactions involved in compound binding. In particular, the application of NMR spectroscopy has proven to be a powerful investigative tool with molecular descriptors derived from NMR data the most useful. Characterisation studies (SOM structure) in conjunction with isotherms (adsorption/desorption activity) can be used to evaluate the immobilisation and release of contaminants. This is analogue to the quantitative structure—activity relationship (QSAR) approach that is employed in ecotoxicology. Quantitative relationships particularly between organic carbon-normalised adsorption coefficients and NMR-generated molecular descriptors (i.e. K_{oc} vs. $\sum C_{AR}/\sum C_{ALK}$, Perminova et al., 1999) or molar elemental ratios (i.e. polarity index, K_{oc} vs. $[N + O]/C$, Cuypers et al., 2002a; Kile et al., 1999; Rutherford et al., 1992) may allow for the prediction of the impact of structural variations and structure-related sorption properties of a sorbent matrix on contaminant uptake; and by carrying out long-term testing programmes one may be able to accommodate dynamic processes such as aging. Consequently, a biomimetic study could be implemented to evaluate the potential for release, leaching or uptake of the sorbed contaminant. Therefore, it could be possible to establish a structure—activity—prediction relationship (SAPR) by which one can relate the characteristics of a sorbent to the sorption activity of the sorbate taking into account a specific molecular descriptor(s) linked with a biomimetic method to predict availability.

The selection of physical–chemical and biological assays should ultimately depend on the choice of application for the SAPR, which would be affected by the target of the procedure: remediation, leaching, toxicity or accumulation potential. In order to compensate for the variable molecular characteristics that exist in the soil and sediment environment, a series of geosorbents will have to be selected for spectroscopic and/or elemental analysis to represent a wide range in SOM content. The objective of such a procedure would be that if good correlation between a range of soils' molecular descriptor factor and experimentally-derived K_{oc} values exists, it would be possible by determining the descriptor factor of a soil (by spectroscopic/elemental analysis) contaminated with an identical or matching ('like') contaminant to obtain K_{oc} for the soil and predict availability as expressed by the biomimetic method. This, however, relies on the molecular characterisation of a series of soils to represent a reasonable SOM range and good correlation between K_{oc} values and the descriptor factor.

Most risk assessment procedures consider the total pollutant concentration in soil as bioavailable resulting in an overestimation of risk. By using measures to quantify the bioavailable fraction of a certain pollutant and including this information in risk assessment, one would be able to obtain a more representative picture of the actual risk posed to humans and the environment. Though the SAPR approach represents a simplification of a complex set of mechanisms and interactive processes it could be used as a viable method to predict availability. By considering factors such as spatial and temporal differences laboratory-generated data could be extrapolated to field conditions. Recognising the uncertainties associated with any individual methodology (physical–chemical biomimetic assays, sorbent descriptor factors or bioassays), it is suggested to base site management decisions on an approach, such as the SAPR, that includes multiple categories of tests to evaluate pollutant availability.

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