Matrix - Hydrophobic Compound Interactions

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Hauke Harms, Lukas Y. Wick, and Kilian E. C. Smith

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Abstract

The fate and transport of hydrophobic organic compounds (HOCs) such as oil hydrocarbons are strongly influenced by their interactions with environmental matrices including soils and sediments. These interactions can be grouped into those of nonaqueous phase liquids (NAPLs), e.g., the spreading of oil on solid surfaces and its movement in porous media, and those of water-dissolved HOC molecules which sorb onto solid surfaces or partition into organic matter or NAPL phases. Generally, these different types of sequestration phenomena lead to reduced contact between organisms and the bioavailable HOC molecules dissolved in the surrounding water phase, and thus to lower uptake and biodeg-

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H. Harms · L. Y. Wick (✉)
Department of Environmental Microbiology, Helmholtz Centre for Environmental Research – UFZ, Leipzig, Germany
e-mail: hauke.harms@ufz.de; lukas.wick@ufz.de

K. E. C. Smith
Institute for Environmental Research (Biology 5), RWTH Aachen University, Aachen, Germany
e-mail: kilian.smith@bio5.rwth-aachen.de

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radation. However, in certain situations, sorption of the HOCs to small and highly mobile HOC-sorbing phases such as dissolved organic carbon or surfactants may mobilize the HOCs and increase their bioavailability and/or toxicological risk.

1 Introduction

Interactions of NAPLs with solids are of importance wherever oil is present in porous media, for instance as is the case in oil reservoirs. Here the interest in extracting the oil has motivated much research into the possibility of pumping the oil out or, if pumping fails, to push residual oil out of the porous matrix by injecting gases or aqueous solutions (e.g., brine). The latter often occurs in combination with selective blocking of alternate flow paths, thermal treatment (e.g., steam injection), or physicochemical enhancement of oil movement using detergents (Banat 1995). A second field of environmental concern is the behavior of spilled fuels, coal tar, or other oily masses in soil, aquifer sediment, fractured rock, on beaches, or in the sediments of rivers, lakes, and oceans. A detailed description of the physics of the residence behavior and movement of oil in these phases goes beyond the purpose of this chapter, but some factors of influence shall be mentioned here. Oil masses of lower viscosity move more readily in porous media than more viscous oil. This viscosity depends on the chemical composition of the oil and is reduced by an increase in temperature. The injection of gases during enhanced oil recovery also reduces the viscosity of oil as some of the gas dissolves in the oil, a phenomenon called oil swelling (McInerney et al. 2007). Emulsifiers are surface-active substances capable of stabilizing emulsions by accumulating at water-oil interfaces. Emulsification of oils with water can influence the viscosity in both ways depending on the oil-water ratio, i.e., if the oil is the continuous phase or the dispersed phase in the emulsion, but also depending on other factors such as the size of the droplets of the dispersed phase. In the environment, quasisolid emulsions of hydrocarbons and water have been observed as viscous interfacial films around aged tar globules (Nelson et al. 1996). Finally, the chemical composition of the solid material and the pore diameter of the solid matrix influence the oil movement via capillary forces. If the oil has a tendency to spread on the solid or, in other words, to form a contact angle (defined as the angle between the oil droplet surface and the underlying solid, and which provides a measure of the surface wettability) with the solid surface below 90°, it will be retained better in pores of smaller diameters. The opposite will be the case if the oil forms a contact angle above 90° with the solid surface. In this case capillary forces will retain the oil better in larger pores. This behavior is described by the Young-Laplace equation (Mozes et al. 1991). Capillary forces can be influenced by surfactants of chemical or biological origin, leading to improved movement of the oil in the porous medium.

2 Phenomena of Molecular Sorption to Solid Matrices

The total amount of HOC in an environmental compartment can be conceptually divided into three pools: the irreversibly bound, the reversibly bound, and the freely dissolved pool (Fig. 1) (Ortega-Calvo et al. 2015). The mechanistic interpretation of

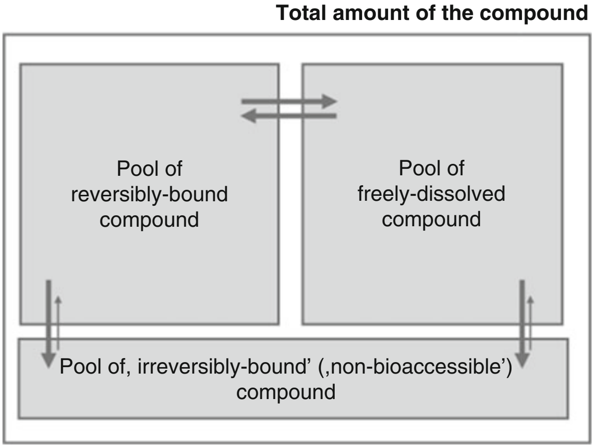

Fig. 1 The schematic shows how the total amount of a compound in an environmental system can be conceptually divided into the freely dissolved, the reversibly and the irreversibly bound pools. From the perspective of microbial degradation, the kinetics of the release of hydrophobic organic compounds (HOCs) into the water phase, i.e., into the freely dissolved pool, is of primary importance. Soft organic matter and NAPL-absorbed HOC as well as surface-adsorbed HOC appear to be more readily bioaccessible than quasi irreversibly bound HOC "stuck" in hard organic matter and micropores

the macroscopically observed sorption behavior of HOCs in soils and sediments has been an issue of much debate in the last decades. It is therefore highly appreciable that in 1997 leading experts in the field, among them proponents of contrasting views, jointly published an article categorizing the various mechanisms of HOC sorption to geosorbents (Luthy et al. 1997). These authors distinguish five microscopic sorption mechanisms of HOC in geosorbents: (A) **ab**sorption **into** amorphous or "soft" natural organic matter or NAPL; (B) **ab**sorption **into** condensed or "hard" organic polymeric matter or combustion residues such as soot; (C) **ad**sorption **onto** water-wet organic surfaces such as soot; (D) **ad**sorption **onto** exposed water-wet mineral surfaces; and (E) **ad**sorption **into** microvoids or microporous minerals. An important conclusion was that none of these sorption mechanisms is likely to occur exclusively in natural geomaterials, and that the complex sorption and desorption equilibria and kinetics that are often observed can be explained as overall effects of varying contributions of these different mechanisms. These mechanisms were then examined for their impact on the behavior of HOCs in terms of linearity of the sorption isotherms, competition between sorbates for sorption sites, sorption kinetics, and, in the case of desorption hysteresis (i.e., when the sorption and desorption curves cannot be superimposed), selectivity for steric features of the sorbents as well as the ease at which the HOCs can be extracted.

Absorption into soft organic matter and NAPLs (A in the above list), as well as both types of adsorption onto exposed surfaces (C, D), were identified to be fast and readily reverted by solvent extraction. In contrast, absorption into hard organic matter (B) and adsorption in microvoids (E) were characterized as being slower, difficult to revert by solvent extraction and often showing desorption hysteresis

(Greenberg et al. 2005). From the perspective of microbial degradation, the release kinetics of sorbed HOCs into the water phase is of primary importance since uptake of dissolved compound is generally required for biodegradation (Volkering et al. 1992). Soft organic matter and NAPL-absorbed HOCs, as well as surface-adsorbed HOCs, appear to be more readily bioaccessible than HOCs "stuck" in hard organic matter and micropores (Cornelissen et al. 1997). The case of pore-obstructed HOC illustrates that there is also a geometric aspect to bioaccessibility (in this case the exclusion of microbes from micropores that spatially separates the HOC source from its biological sink), further to the influence of chemical interactions. This is due to the dynamic nature of microbial degradation and the fact that rates of mass transfer depend largely on the distances that need to be bridged (Bosma et al. 1997, Harms and Wick 2004).

3 Transfer of Hydrocarbons Between the NAPL and Aqueous Phases

NAPLs are varied with respect to both the environmental compartment in which they are found (e.g., the open sea, sediment, or soil), but also their physical and chemical characteristics. Typical examples of environmentally relevant NAPLs include crude oil, its various refinement products, and anthropogenic wastes such as the aromatic rich coal-tars contaminating groundwater at industrial sites. Natural oil seeps in marine and terrestrial environments mean that the interplay between microorganisms and certain types of NAPLs is not a recent phenomenon, and there has been sufficient time for microbial populations to evolve strategies for an increased exploitation of this rich hydrocarbon resource (Head et al. 2006). Furthermore, NAPLs are typically composed of many classes of hydrocarbons in combination with other nonhydrocarbon compounds that are often unresolved, e.g., crude oil (Marshall and Rodgers 2004). It is therefore not usually the case that a single microorganism has the metabolic ability to degrade the full range of components present in oil, and a range of microorganisms are involved in the biodegradation process of NAPL hydrocarbons (Head et al. 2006). Therefore, biodegradation in the field becomes a complex interplay between HOC bioavailability, toxicity, and microbial ecology.

NAPL hydrocarbons represent a potential source of carbon and energy in a form that is difficult to exploit (Volkering et al. 1992). Lighter oil hydrocarbons rapidly dissipate via volatilization or dissolution, and the following focusses on hydrophobic NAPL compounds and groups them under the general term HOCs. Thermodynamic considerations indicate that even at equilibrium (i.e., the maximum dissolved aqueous concentrations that can be attained when partitioning is involved), HOCs preferentially remain in the NAPL with only low concentrations being reached in the aqueous phase (Efroymonson and Alexander 1995). Furthermore, in non-equilibrium situations their hydrophobicity means that the mass transfer between the NAPL and the aqueous phase is usually slow (Schluep et al. 2002). Therefore, it is normally the case that despite the high levels of HOCs in the NAPL phase, these have a low bioavailability and biodegradation is mass transfer limited (e.g., Ramaswami et al. 1997). Although this low bioavailability is not ideal for degrading microorganisms, it does mean exposure to potentially toxic NAPL phase HOCs is reduced for nondegraders and other organisms.

Adjacent NAPL and aqueous compartments, each with homogenous bulk HOC concentrations, are separated by the NAPL:water interface. On each side of this interface, thin unstirred boundary layers (BLs) exist as depicted in Fig. 2. Within these BLs, transport of the HOCs occurs by the relatively slow process of molecular diffusion, and transfer across the BLs has the determining role in the overall mass flux from the NAPL into the bioavailable dissolved phase. Therefore, the mass transfer pathway between a NAPL and the aqueous phase can be considered as being composed of two barriers to mass transfer aligned in series (Schwarzenbach et al. 2017). For HOCs, it is particularly the BL on the aqueous side that limits the overall mass flux (Ghoshal and Luthy 1996). Special cases where the main resistance to mass transfer of HOCS occurs in the NAPL phase are discussed at the end of this section.

The mass flux can be defined as the HOC mass from the NAPL phase entering the aqueous phase (where the degrading microorganisms are present) over a given period of time. This can be described in general terms as follows

$$\text{Mass flux} = \text{Area} \times \text{Transfer velocity} \times \text{Driving force} \tag{1}$$

The role of the interface area is obvious, the larger this is the bigger the surface for mass exchange. The transfer velocity can be further rationalized as being composed of the ratio between the aqueous diffusivity of the HOC molecules and the thickness of the BL (Schwarzenbach et al. 2017). This is also intuitively obvious, a higher aqueous diffusivity of a molecule is indicative of more rapid motion and a thinner BL will be more quickly traversed. The driving force is determined by the gradient in chemical activity of the HOC between the bulk NAPL and aqueous compartments. Molecular diffusion occurs from regions of high to low chemical activity (Reichenberg and Mayer 2006), and the greater this difference the greater the mass flux. Chemical activity is a function of the HOC concentration, its physicochemical properties as well as those of the environmental matrix in which it is found (Schwarzenbach et al. 2017). This means a compound can have the same chemical activity in two phases (i.e., be at equibrium) but at very different concentrations. A well-known illustration of this is the equilibrium octanol:water partition coefficient, where a HOC has the same chemical activity in the water and octanol phases but very different concentrations. The usual practice is to measure mass concentrations in the NAPL and aqueous phases; the driving force is then computed from these mass concentrations in conjunction with experimentally determined partition coefficients (e.g., Schluep et al. 2002). Note that equilibrium sampling techniques such as passive sampling allow direct determination of chemical activity gradients between adjacent phases (Mayer et al. 2003).

Equation 1 indicates that the magnitude of the mass flux is influenced by the NAPL:aqueous interface area, the speed of transfer across the BLs, and the driving force between the NAPL and aqueous compartments. Therefore, a change in any of the above parameters can result in an increase or decrease in the mass flux of HOCs into the aqueous phase, and thus have a knock-on effect on HOC bioavailability and biodegradation. This is shown schematically in Fig. 2, where different scenarios have been depicted in terms of the above three factors. Figures 2a–d illustrate that a range of abiotic processes can potentially impact the mass transfer of HOCs into the bioavailable aqueous phase. These processes can occur simultaneously and may vary with respect to one another over time and have been summarized in Table 1. Some of these changes can have other beneficial effects with respect to microbial growth, in addition to any enhancement in the HOC mass transfer. For example, increased mixing might also lead to improved aeration and prevent the formation of nutrient-depleted patches or changes in temperature might lead to an increase (or decrease) in growth depending on the degrader.

In specific situations, the resistance to diffusive mass transfer on the NAPL side can become significant (Fig. 2e). Such scenarios include the mass transfer of more water-soluble hydrocarbons (Schluep et al. 2002), highly viscous NAPLs (Ortiz et al. 1999), or situations where there is a weathering of the surface layers of multicomponent NAPL mixtures leading to the formation of more impermeable surface skins. The latter is believed to be the result of viscous NAPL:water emulsions forming at the surface rather than because of changes in the composition due to preferential dissolution of the more soluble components (Nelson et al. 1996). In terms of microbial degradation of NAPL hydrocarbons such cases are significant for

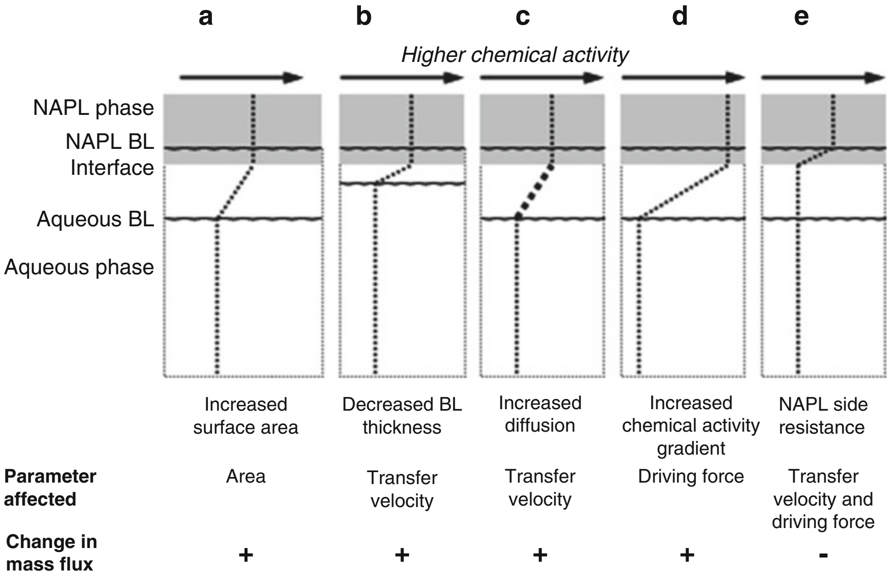

Fig. 2 Chemical activity profile (·····) of a hypothetical hydrophobic organic compound (HOC) across the NAPL:aqueous interface under various environmental conditions. The resultant effect on the HOC mass flux is shown at the bottom by a positive or negative symbol

Table 1 Overview of the physical, environmental, and chemical factors influencing the mass transfer of a hydrocarbon from the NAPL into the aqueous phase. The letters in brackets correspond to the scenarios depicted in Fig. 2

Category	Description	Parameter affected
Physical	NAPL architecture and amount, e.g., film, droplets, micropores	Surface area **[A]**
Environmental	Hydrodynamic mixing	Break-up of NAPL **[A]** Boundary layer thickness **[B]**
	Temperature	Molecular diffusion **[C]** Chemical activity gradient **[D]**
	Sorption in the aqueous phase	Chemical activity gradient **[D]**
Chemical	Hydrocarbon concentration	Chemical activity gradient **[D]**
	Hydrocarbon properties	Diffusivity **[C]** Chemical activity gradient **[D]**
	NAPL properties	Diffusivity **[C]** Chemical activity gradient **[D]** Wetting properties **[A]**
	Weathering of multicomponent NAPLs	Formation of impermeable skins **[E]**
	NAPL side resistance	Diffusivity and chemical activity gradient **[E]**

two reasons. Firstly, there is a reduction in HOC mass transfer into the aqueous phase (Luthy et al. 1993). Secondly, those environmental processes listed in Table 1 that affect the mass transfer through the aqueous BL no longer play the same role. For example, hydrodynamic mixing will not increase or decrease the mass transfer via altering the aqueous BL thickness as this no longer controls the mass flux.

From the point of view of the degrading microorganism, there is little that can be done to influence such abiotic processes and thus they can only react passively to any resulting changes in the mass flux and bioavailability. An interesting example is that of sorption, which had the consequence of lowering the dissolved phase activity and thus maintaining a high diffusive gradient between the NAPL and aqueous phases as illustrated in Fig. 2d. This figure shows that there is potentially a feedback between biotic growth of the microorganism due to HOC degradation and abiotic sorption. A bacterial population actively degrading a certain NAPL component(s) will increase in biomass, which in turn leads to an increase in the sorption capacity of the aqueous phase, thus potentially enhancing the mass transfer of other NAPL HOCs.

4 Sorption of HOCs to Mobile-Sorbing Phases

Various types of hydrocarbon interactions with the geosorbents present in soils and sediments have been considered above. These sorbents can in the main be considered as relatively immobile, with only small fractions being slowly displaced by processes such as bioturbation or erosion by wind and water. Therefore, for microorganisms to colonize such sorbents, they need to initially be brought into contact with and subsequently attach to the surface.

Some sorbing phases, though, are smaller and much more mobile and even move with the aqueous phase. This is a diverse category, encompassing everything from suspended inorganic minerals, particulate and dissolved organic matter, living bacteria- and phytoplankton to biosurfactants. Of course, there is no defined cut-off between what constitutes a mobile- and immobile-sorbing phase, and furthermore, the significance these have in terms of the total HOC sorption depends on the environment in which they are found. For example, in soils and sediment, most of the HOCs are primarily associated with larger sized and stationary particulate material (e.g., Hawthorne et al. 2005). However, in the fresh and marine water column, mobile sorbents such as plankton and particulate organic carbon can comprise the dominant-sorbing phase (e.g., Schulz-Bull et al. 1998). Some of these small and mobile sorbing phases have been shown to play an important role with respect to HOC bioavailability and biodegradation.

HOCs associate with these matrices via the same set of sorption mechanisms discussed above (Luthy et al. 1997). Therefore, their role in terms of reducing the bioavailability of HOCs can be understood using the same terms of reference. However, their small size, and thus high surface area to volume ratio, imply that the exchange kinetics are rapid (Poerschmann et al. 1997). Therefore, processes such as retarded diffusion play less of a bioavailability-limiting role. Their small size also enables them to readily move with, for example, the advective flow of water. This, together with their propensity to associate with cellular membranes, confers on them a particular role in the bioavailability and biodegradation of HOCs.

Exactly what role do such mobile HOC-sorbing phases play with respect to bioavailability? They can alter both the kinetics of abiotic mass transfer and the equilibrium distribution of HOCs between the (stationary) sorbed and aqueous compartments. In many environments, bioavailability and thus biodegradation is limited by the slow HOC mass transfer from the sorbed state and into the aqueous phase (Harms and Bosma 1997). Here, the stationary sorbing material can be anything from a geosorbent such as particulate matter to a nonaqueous phase liquid (NAPL). The presence of an additional sorbing phase in the surrounding aqueous medium can enhance the rate of dissolution. For example, both natural and synthetic surfactants increase the dissolution rate of HOCs such as PAHs from their pure solid state (Grimberg et al. 1995) or when present in NAPLs (Garcia-Junco et al. 2001). Dissolved organic carbon (DOC) (Smith et al. 2011) or DOC associated with mineral surfaces (Garcia-Junco et al. 2003) enhance the mass transfer of HOCs from NAPLs into the water phase. Finally, particularly relevant in terms of the microbial blooms developing after an oil spill is the observation that small motile organisms such as protozoa increase the mass transfer of HOCs from the sorbed to the dissolved state (Gilbert et al. 2014). In part, the increased mass transfer observed in the above studies can be explained by HOC sorption to the surfactant micelles, DOC, or organisms in the aqueous phase reducing the dissolved phase concentrations and maintaining the high chemical activity gradients driving the dissolution process.

However, it also appears that in parallel these small and mobile sorbing phases function as carriers, enhancing the transport of the HOCs across the aqueous BL and into the bulk solution (Grimberg et al. 1995).

An enhancement in the dissolution rates has two implications for bioavailability. Firstly, the rate of mass transfer out of the nonaccessible phase is increased which can be particularly important for those HOCs where dissolution is very low to start with. Secondly, the total amount of HOCs in the aqueous phase can be increased above solubility, albeit partly sorbed. Should a fraction of this sorbed aqueous amount be accessible by the degrading microorganisms then this could have a positive overall effect on bioavailability.

When considering natural environments, the distribution of HOCs is generally heterogeneous. In soils and sediments, such microscale inhomogeneities are particularly important in lowering the overall bioavailability. Since microbial colonies are spatially distributed and mainly exist attached to various surfaces rather than suspended in the interstitial solution, they “see” a relatively small volume of the environment (Postma and Vanveen 1990). Should this volume become depleted of HOCs via consumption, then it is rapidly the case that the distance to a replenishing source becomes too large for a sufficient resupply via solely aqueous diffusion (Bosma et al. 1997). Therefore, HOC association with an advectively transported sorbing phase such as surfactants or DOC could also have implications for redistribution, functioning at the microscale as “carriers” from a site of contamination to that of biodegradation. When considering the aquatic ecosystem, the more thorough mixing of the water column by turbulence probably means that such microscale inhomogeneities are less of an issue. Nevertheless, in some cases heterogeneity in compound distribution might also play a role but over a larger scale. An oil spill at the water surface is an example. Oil hydrocarbon sorption to suspended mineral and organic matter in the water column initially might enhance the dissolution process, and then be transported away via the water currents to more distant locations, forming a plume of bioavailable HOC. Although the relevance of such roles remains to be demonstrated in the field, these are the general principles behind bioremediation of soils using surfactant washing solutions.

5 Contaminant Aging and Release Kinetics

Contaminants in geomaterials may undergo changes that have been summarized as processes of contaminant aging or weathering. It has been observed that the efficiency of chemical extraction and biodegradation of contaminants is lower when the contact time between contaminant and the geomaterials before these interventions was longer (Cornellissen et al. 1997). In many cases, recent contaminations may thus be treated with higher efficiency than historical ones (Hatzinger and Alexander 1995). For instance, it has been frequently seen that when the biodegradation of a historical contamination in soil has come to an end despite a still relatively high residual concentration, a contaminant of the same kind that is freshly spiked to the same soil is rapidly degraded (Valo and Salkinoja-Salonen 1986). From this experiment and similar real-world observations, it can be inferred that the different portions of the contaminant show different degrees of bioaccessibility (Ortega-Calvo et al. 2015). This differential behavior of contaminant fractions is not only a problem for the remediation process but also limits the value of spiking soil with radioactively labelled contaminant as an indicator of the biodegradation potential.

Which kinds of mechanisms can lead to reduced contaminant bioaccessibility and extractability? Mechanisms include chemical changes, changes in the soil or sediment structure, and shifts in the spatial distribution of the chemical due to diffusive transfer in combination with the exclusion of microorganisms (or extractants) from certain parts of the geomaterial. An example for chemical changes would be the successive occupation of high-energy sorption sites by contaminant molecules. The probability that individual contaminant molecules that are initially absorbed in "soft" organic matter or NAPL come into contact with either "hard" organic matter, high-energy sorption sites (e.g., on the surface of soot) or enter the swollen interlayers of clay minerals increases with time. A declining reversibility of sorption would also arise from the metamorphosis of organic matter into forms that retain absorbed molecules more efficiently. Structural changes in the soil matrix could lead to contaminant aging by burying formerly labile contaminant pools under poorly permeable phases. The encapsulation of "soft" organic matter by "hard" organic matter as exemplified by Luthy et al. (1997), or by mineral soil constituents, would be examples. One can easily imagine that bioturbation or processing of soil materials inside the digestive tracts of soil-dwelling organisms could lead to the obstruction of diffusion pathways. The successive formation of poorly permeable interphases around tar globules would also fall into the category of structural changes. Aging can occur even in the absence of chemical or structural changes due to diffusive mass transfer. Soil and sediment contaminants typically enter via the larger pores. From thereon diffusive processes carry part of the contaminant in regions and size classes of pores that are increasingly difficult to access by microbes. Before an equilibrium distribution of the contaminant is achieved, there will be a continuous inward-bound diffusive flux of contaminant into soil aggregates that carries contaminant fractions further away from the biota. Using experimental model polymers that exclude the possibility of chemical or structural changes, the effects of diffusion distances due to the pore-size exclusion of microbes was shown (Harms and Zehnder 1995).

The observable effect of all types of contaminant aging is an apparent desorption hysteresis, i.e., much longer time scales are needed to complete desorption compared to adsorption. Biodegradation curves as well as release curves obtained by continuous mild extraction (e.g., flushing with water) show pronounced tailing that may be interpreted as successive emptying of sorption sites of increasing sorption energy or as growing diffusion distances of the contaminant molecules within a matrix composed of particles that empty from the outside to the center (also referred to as "shrinking core" desorption). Mathematically, the observed desorption progress can be easily fitted by applying the first-order two-compartment models that distinguish a rapidly and a slowly desorbing contaminant fraction with largely different release rate constants (Cornelissen et al. 1998). Further distinction of a third, very slowly desorbing fraction, may give even better fits (e.g., Greenberg et al. 2005). However, given the wealth of possible mechanisms that may bring about the earlier release of one contaminant molecule than another one, the existence of a continuum of sorption strengths and travel distances appears much more likely than the existence of two or three distinct states of sorption. The rapidly desorbing fraction has nevertheless been found to be a relatively good descriptor of the bioaccessible fraction (Cornelissen et al. 1998), whereas the extremely slowly desorbing chemicals have been conceptually defined as "nonbioaccessible" (Semple et al. 2004) or "irreversibly bound" (Reichenberg and Mayer 2006).

6 Research Needs

To date, the influence of small and mobile sorbents and their potential to increase HOC mobility at the microscale has been largely neglected. Therefore, the common opinion that sorption generally reduces both bioavailability and risk is a simplification requiring knowledge-based specification, particularly using systems that more accurately mimic the complexity in the field. Another area requiring further research is the interaction of the components found in complex contaminant mixtures such as oils. For instance, biologically inactive components may well influence the partitioning behavior of bioactive components either directly or via stimulating the growth of specific degraders. Finally, directly applying chemical activity-based measurements to understand the dynamics and fate of HOCs may in some cases be more appropriate than common water-solubility and concentration-based approaches.

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