Sequestration of Hydrophobic Organic Contaminants by Geosorbents

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The chemical interactions of hydrophobic organic contaminants (HOCs) with soils and sediments (geosorbents) may result in strong binding and slow subsequent release rates that significantly affect remediation rates and endpoints. The underlying physical and chemical phenomena potentially responsible for this apparent sequestration of HOCs by geosorbents are not well understood. This challenges our concepts for assessing exposure and toxicity and for setting environmental quality criteria. Currently there are no direct observational data revealing the molecular-scale locations in which nonpolar organic compounds accumulate when associated with natural soils or sediments. Hence macroscopic observations are used to make inferences about sorption mechanisms and the chemical factors affecting the sequestration of HOCs by geosorbents. Recent observations suggest that HOC interactions with geosorbents comprise different inorganic and organic surfaces and matrices, and distinctions may be drawn along these lines, particularly with regard to the roles of inorganic micropores, natural sorbent organic matter components, combustion

residue particulate carbon, and spilled organic liquids. Certain manipulations of sorbates or sorbent media may help reveal sorption mechanisms, but mixed sorption phenomena complicate the interpretation of macroscopic data regarding diffusion of HOCs into and out of different matrices and the hysteretic sorption and aging effects commonly observed for geosorbents. Analytical characterizations at the microscale, and mechanistic models derived therefrom, are needed to advance scientific knowledge of HOC sequestration, release, and environmental risk.

Introduction

The question of environmentally acceptable concentrations, e.g., "How clean is clean?", is a central issue in the management of soil or sediment contaminated by hydrophobic organic contaminants (HOCs). HOCs comprise broad classes of chemicals that appear as persistent contaminants in soils and sediments (*1*). This includes aromatic compounds in petroleum and fuel residues, tars, and creosotes; chlorinated compounds in commercial solvents; and chemicals no longer produced in the United States such as DDT and polychlorinated biphenyls. The adherence and slow release of such compounds from soil or sediment is proving to be an obstacle in remediation (*1*) and is challenging our concepts about cleanup standards and risks (*2*). Typically, the data that are available for a given site are contaminant concentrations on solids and the toxicity of the pure HOC compounds. What often is not known is the fraction of HOCs held within solids available via a particular exposure route. This paper presents the findings of an evaluation of the fundamental mechanisms that may account for the binding or sequestration of HOCs in soils or sediments. This evolved through a workshop and followup deliberations in an attempt to converge opinions regarding current experimental and modeling work, assess areas of uncertainty, and provide a platform for conducting future research in this area.

Slow Release and Bioavailability

HOCs typically exhibit very slow release rates from soil, sediment, or aquifer solids (e.g., refs 3−5). This raises questions about phenomena affecting the availability of HOCs to the environment and how this relates to soil and sediment quality criteria for HOCs and remediation cleanup goals. As a consequence of binding with soils or sediments and slow subsequent release, residual HOCs may be significantly less leachable by water and less toxic as measured by simple tests (*1,6*). Whether residual hydrocarbons remaining after remediation represent an acceptable treatment endpoint requires understanding of release rates and the mechanisms that bind contaminant HOCs within soils or sediments in combination with the knowledge of factors controlling intrinsic biological and/or chemical degradation and attenuation. This is important for addressing the concept of *biostabilization*, which refers to the biodegradation of the more labile HOC fraction leaving a residual that is much less available and mobile.

Observations from various studies show that hydrophobic aromatic compounds may be biodegraded by microorganisms to a residual concentration that no longer decreases with time or which decreases only very slowly over years with continued treatment (*6−8*). It is believed that further reductions are limited by the availability of hydrocarbons to microorganisms, and all the more so for aged contaminants as compared to freshly added material (*9, 10*). Earthworm uptake and bacterial mineralization show that

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aging reduces HOC availability to both species, but simple chemical extraction tests appear not able to mimic bioavailability (*11*).

Geosorbents

As depicted schematically in Figure 1, soils, sediments, and aquifer solids are heterogeneous at various sample, aggregate, and particle scales. To focus on mechanistic processes, distinctions are not drawn here between various types of soils and sediments, rather such materials are referred to generically as *geosorbents* or simply sorbents. Adherent or entrapped nonaqueous-phase liquids (NAPLs; e.g., solvents, oils, and tars) and combustion residue particulate carbon (e.g., chars, soot, and ashes) can also function as sorbents and are therefore included for discussion. Structurally and/or chemically different constituents of a soil or sediment interact differently with HOCs in terms of binding energies and rates of associated sorption and desorption. Complex assemblages of these constituents can cause complex mass transfer phenomena, and the term *sequestration* refers to some combination of diffusion limitation, adsorption, and partitioning.

The Freundlich isotherm is commonly used to relate geosorbent and aqueous-phase HOC concentrations (*12*):

$$q_e = K_f C_e^{\,n} \tag{1}$$

where q_e and C_e are the equilibrium sorbent-phase and aqueous-phase solute concentrations and K_f and n are parameters relating to the amount sorbed and the linearity of the sorption process, respectively. Linear isotherm models (i.e., $n = 1$) have been used to describe sorption over limited concentration ranges (e.g., refs 13−17). For solutes that are significantly hydrophobic and where molecular propensity toward mineral sorption is low, the overall sorption and desorption reactions of geosorbents are dominated by sorbent organic matter (SOM), for which the use of linear models commonly assumes that HOC sorption is dominated by partitioning into a relatively homogeneous and highly amorphous lipophilic, gel-like humic matrix. However, some studies have shown that geosorbents often exhibit nonlinear sorption behavior (e.g., refs 18−21). The observed trends of increasing apparent hysteresis and decreasing desorption rates and extractabilities of HOCs as a function of the sorbate residence time on geosorbents are incompatible with a simple phase partitioning process. However, such observations also may reflect nonequilibrium conditions and heterogeneity effects, such as nonequilibrium prior to the start of a desorption experiment.

Geosorbents have been characterized by some researchers as comprising several domains or components that may exhibit distinctly different sorption reactivities (e.g., refs 22 and 23). Moreover, the intrinsic heterogeneity of natural geosorbents may be augmented by the presence of anthropogenic organic matter, e.g., oils (*24*), soot (*25*), or surfactants (*26*). Overall SOM sorption by such geosorbents may therefore be given by sum of the contributions of several active organic components, i.e.

$$(q_e)_{\text{total SOM}} = (q_e)_{\text{natural SOM linear}} + (q_e)_{\text{natural SOM nonlinear}} + (q_e)_{\text{anthropogenic SOM linear}} + (q_e)_{\text{anthropogenic SOM nonlinear}} \tag{2}$$

where the respective contributions exhibited by natural and anthropogenic SOM carbon matrices are grouped into linear (partitioning) and nonlinear (adsorption) behaviors.

Sorption and desorption rates for HOCs in geosorbents suggest that these processes occur on a range of time scales, fast time scales occurring on the order of minutes to days and slow time scales occurring on the order of weeks or even years (e.g., refs 4, 19, 20, and 27−29). Recent work has attributed these rates to intra-aggregate diffusion and releases
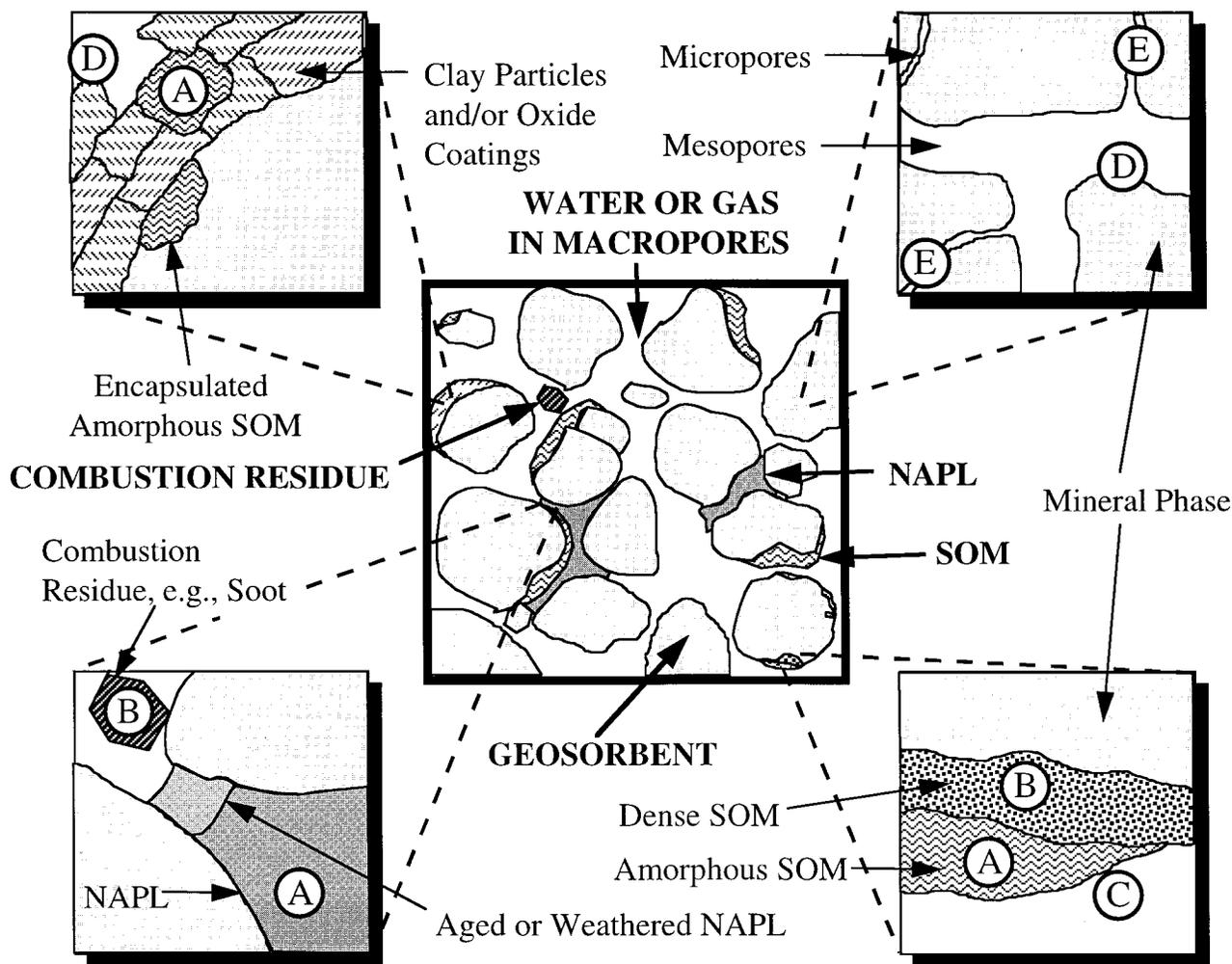
FIGURE 1. Conceptual model of geosorbent domains. The circled letters refer to representations of the sorption mechanisms described in Table 1. The geosorbent domains include different forms of sorbent organic matter (SOM), combustion residue particulate carbon such as soot, and anthropogenic carbon including nonaqueous-phase liquids (NAPLs).

from micropores or different forms of geosorbent organic matter. But our knowledge of these physicochemical mass transfer processes is primarily empirical, relying on macroscopic observations.

Macroscopic Observations Indicative of Sorption Phenomena

Figure 1 shows a conceptualization of geosorbent domains. Presently there are no direct observational data revealing the molecular-scale location or locations in which HOCs accumulate when they associate with natural geosorbents. As a result, researchers must rely on experimental inferences of sorption for various sorbate/sorbent/solution cases of interest to develop an understanding of the physicochemical distribution of organic molecules in these solids. Table 1 lists the kinds of macroscopic experimental observations that capture overall behavior and provide empirical evidence for deducing sorption processes and constructing mechanistic models for the cases illustrated in Figure 1. Fortunately, a variety of distinguishing features can be used to separate the various possibilities. For example, absorption into amorphous organic carbon or NAPLs (case A) should probably always show linear isotherms, while that for condensed carbon (case B) may exhibit some combination of linear and nonlinear behavior. Adsorption cases may yield either linear or nonlinear isotherms depending on surface properties. Although adsorption to nonpolar, heterogeneous organic surfaces should exhibit nonlinear isotherms (case C), the same

may not be true for adsorption onto hydrophilic mineral surfaces because coverage is low and energy differences among sites is small (case D). Nonlinear isotherms have been observed for adsorption of HOCs into an adsorbed organic phase, e.g., Murphy et al. (30) for humic acids adsorbed to clay minerals and Edwards et al. (31) with respect to the amount of adsorbed surfactant for low dose regions of surfactant adsorbed onto aquifer sediments, indicating that hydrophobic adsorption rather than phase partitioning may be the dominant HOC interaction.

The kinetics of exchange are revealing only in a general sense for HOC sorption mechanisms since these associations arise chiefly from nonspecific physiosorption interactions rather than chemisorption. Surface exchanges and absorption into exposed natural amorphous organic matter (cases A, C, and D) seem to occur on fast time scales that push our laboratory abilities to monitor such. However, absorption into condensed organic matter (case B) or diffusion into hydrophobic microporous regions of minerals (case E) may require protracted times.

Certain sorbate properties may assist in distinguishing sorption mechanisms. For all cases described in Table 1, increasing the hydrophobicity of sorbates will promote sorption. However, only certain sorption cases should be sensitive to isomeric or steric arrangements of the sorbates. This sensitivity could arise from the need to optimize surface contact with a sorbent (e.g., cases C and D), or it could influence greatly the rate of exchange (cases B and E).

TABLE 1. Qualitative Comparison of Hypothesized Mechanisms and Macroscopic Observations That May Be Useful To Assess Sorption Mechanisms of Nonpolar Organic Compounds with Geosorbents

Case A: Absorption into Amorphous or "Soft" Natural Organic Matter or NAPL

kinetics	fast (<minutes) if particles disaggregated
isotherm	linear
activation energy	low
heat of sorption	low
competitive	no
sorbate	steric effects not important
solvent extractability	high

Case B: Absorption into Condensed or "Hard" Organic Polymeric Matter or Combustion Residue (e.g., Soot)

kinetics	slow (>days); sorption−desorption hysteresis
isotherm	possibly linear isotherm after very long equilibration; nonlinear if variable size matrix spaces
activation energy	high
heat of sorption	moderate to high increasing with density of organic matter
competitive	yes
sorbate	steric differences important for diffusion through matrix
solvent extractability	low

Case C: Adsorption onto Water−Wet Organic Surfaces (e.g., Soot)

kinetics	fast (<minutes)
isotherm	nonlinear
activation energy	low
heat of sorption	low to high depending on sorbate hydrophobicity
competitive	yes
sorbate	steric factors important insofar as they allow planar interaction region between sorbate and sorbent
solvent extractability	high

Case D: Adsorption to Exposed Water−Wet Mineral Surfaces (e.g., Quartz)

kinetics	fast (<minutes)
isotherm	linear because of competition with water
activation energy	low
heat of sorption	low
competitive	no because coverage is small (plenty of weakly attractive sites)
sorbate	steric factors important insofar as they allow planar interaction region between sorbate and sorbent
solvent extractability	high

Case E: Adsorption into Microvoids or Microporous Minerals (e.g., Zeolites) with Porous Surfaces at Water Saturation <100%

kinetics	slow (>days); sorption−desorption hysteresis
isotherm	nonlinear if pore size is variable
activation energy	high
heat of sorption	moderate to high, increasing with decreasing micropore size
competitive	yes due to limited number of high energy sites
sorbate	steric factors important insofar as they influence sorbate ability to diffuse through constricted pores in the sorbent
solvent extractability	low

Manipulations of the sorbent media may likewise help reveal sorption mechanisms. The sensitivity of the kinetics to temperature could indicate difficult diffusion phenomena (cases B and E) (29). Extractability with organic solvents or supercritical carbon dioxide should also be useful for indicating the accessibility of the sorbate to the exterior (e.g., ref 32); hence, cases A, C, and D should exhibit ready extraction.

All of these observations are confounded by the aggregated nature of natural geosorbents, which prevents immediate exposure of solutes to all the relevant sorption domains, hence the debate between intra-aggregate and pore-retarded diffusion models reflecting transport over tens to hundreds of micrometers (4, 19, 27, 33) and intra-organic matter diffusion models reflecting transport over tens to hundreds of nanometers (34−36). Note that cases B and E may exhibit similar characteristic macroscopic behavior, thus also contributing to debate over conceptual mechanisms. There is no reason to presume that only one sorption mechanism dominates in any particular case, and in real systems more than one process likely contributes to rate-limited sorption behavior, which complicates the interpretation of macroscopic data.

Not discussed here are *transformation* processes. These may lead to sequestration through oxidative coupling via enzyme-mediated (e.g., ref 37) or mineral-surface catalyzed (e.g., ref 38) reactions that can produce covalent attachment to humics (ref 39). Other transformation processes include partial biodegradation of an HOC followed by the sorption of accumulated metabolites. Extracellular accumulation of polycyclic aromatic hydrocarbon compound metabolites have been observed (40, 41), which potentially could lead to chemisorption-reactive daughter products.

Geosorbent Components

Inorganic. Inorganic surfaces associated with geosorbent mineral components include: (i) external surfaces; (ii) swelling clay interlayer surfaces; (iii) and internal surfaces that can be classified based on sorbate behavior (42): macropores larger than 500 Å that only fill with sorbate if submerged in it, internal mesopores (pore diameters 20−500) that due to capillary condensation fill with sorbate at relative vapor pressures approaching saturation, and micropores (pore diameters <20 Å) that influence sorbate sorption by the proximity of two solid surfaces. The respective roles of these different types of surfaces on the sorption affinity of HOCs have not been investigated systematically, and conclusions and hypotheses drawn from indirect experimental evidence are sometimes contradictory. Tortuosity should be independent of sorbate properties, while effects related to steric factors and competition for water molecules for sorption should be important

as pore geometry approaches the same order of magnitude as sorbate molecular size (43).

In mineral phases, it is quite likely that the slow release kinetics of HOCs is due to diffusion in and out of micropores (29). Molecular diffusion in hydrophobic microporous materials, such as zeolites, glasses, and carbon molecular sieves, occurs by a series of activated jumps and is governed primarily by steric energy barriers (44). The diffusion activation energy depends strongly on diffusant and pore sizes (45), and diffusivities typically fall below 10^{-12} cm^2/s. The influence of geosorbent pore structure on desorption isotherm and kinetic profiles has been shown for trichloroethylene (TCE) at 100% humidity (20, 43). At low TCE gas phase concentration, sorbed aqueous equilibrium values drop sharply with decreasing C_e, causing isotherms measured at 60 °C to deviate from log−log linear behavior and from 15 and 30 °C isotherms. This behavior, a large estimated heat of sorption (34 kJ/mol) for the silt and clay fraction, and desorption kinetic profiles suggest to these researchers that adsorption is occurring in micropores (29). However, the mass of TCE sorbed at equilibrium in micropores was less than 10% of the slow desorbing TCE mass, suggesting that micropore constrictions connect larger cavities of mesopore size.

Organic. There is growing awareness that the affinity of SOM for nonpolar organic compounds depends on its origin and geologic history. During sedimentation and diagenesis, biopolymers are degraded and cross-linked, forming residues (e.g., humic material) that may be further altered to form kerogen, coal, and graphite under metamorphic conditions. Thus different sorptive properties for HOCs can be expected due to the diversity in composition and structure of SOM (e.g., refs 22 and 23). Grathwohl (22) showed that organic matter in unweathered shales and high-grade coals enhanced sorption capacities more than an order of magnitude larger than organic matter in recent soils or geologically immature material or highly weathered SOM. Similar inferences were made by Weber et al. (23) with respect to shale fraction of soils.

Variability in the nature of SOM, especially with respect to changes in polarity and aromatic carbon content, appears to be significant in controlling reactivity with HOCs (46). Diagenesis and weathering of organic matter results in changes in the relative amount of oxygen-containing functional groups, and the H/O or O/C atomic ratios and inferences regarding the degree of condensation have been proposed as a first approximation to describe the affinity of SOM for sorption of HOCs (21, 22). Attention needs to be given to the source of the SOM (i.e., algae, lignin, crude oil, etc.) and how chemical origins and differences influence sorption. That there are differences in the sorption of organic compounds on different fractions of organic matter (e.g., fulvic and humic acids and humins) is known (47, 48).

Intraorganic Matter Diffusion. While it is generally accepted that diffusion is at least partially responsible for rate-limited sorption/desorption, the specific nature remains unclear. An emerging view for some researchers is that intraorganic matter diffusion plays a dominant role (35, 36, 49, 50), and investigators have employed different techniques to characterize the rate-limiting character of SOM. Carroll et al. (51), Young and Weber (32), Weber et al. (23), Pignatello and Xing (28), and Xing et al. (52, 65) have invoked a "soft or rubbery" versus "hard or glassy" carbon concept to distinguish two broad categories of expanded and condensed SOM having different diagenetic histories and different sorption properties. Oxidation resistance, as measured by low-temperature persulfate wet oxidation and high-temperature combustion, has been employed as an operational differentiation between soft carbon and more resistant hard carbon, for which the latter accounted for the majority of the overall sorption properties of the parent soils, particularly with respect to deviations from isotherm linearity and competition among sorbing HOCs (23, 52, 53, 65). Other researchers believe that more direct evidence is required for confirmation of these arguments. Additionally, there is need to assess SOM heterogeneous distribution, such as that in lower meso-range pores that may be responsible for extremely slow kinetics. Also there are concerns whether oxidation resistance measurements are sufficiently discriminating, e.g., cellulose is not oxidized well by the persulfate method (54).

In rubbery polymers, the diffusion coefficients of HOCs up to 10 Å minimum diameter range from 10^{-10} to 10^{-7} cm^2/s (55), which are too large to account for the observed slow desorption rates in soils but which some believe may account for the initial rapid phase of desorption. Results of Pignatello et al. (56), Steinberg et al. (3), and Carroll et al. (51) suggest for the resistant fraction that the diffusion length scale is <1 μm and that the effective diffusivity may be <10^{-17} cm^2/s. Work is needed to determine diffusivities in SOM. With the exception of special material like soot (25), some researchers believe that the arguments for intraorganic matter diffusion are inconclusive (57). If the expanded organic matter is playing a role, it must be micrometers thick, and this is not seen with microscopic observations. Further, if the organic matter is glassy and only nanometers thick, then various members of HOC compound classes should show extremely different time scales since diffusion in glassy polymers is so sorbate size dependent, but data do not show this dependency with aquifer sands.

Adherent or Entrapped NAPLs. In assessing the transport of solutes from contaminant organic liquids, referred to as nonaqueous-phase liquids (NAPLs), it is common to treat such liquids as homogeneous with no organic phase or interfacial resistance to mass transfer. Thus, mass transfer rates are described in terms of water velocity, the contact area between NAPL and water, and the physical properties of the porous medium (58, 59). The applicability of such mass transfer models has not been tested for aged, multicomponent organic liquids. Petroleum residues, creosotes, and coal tars have reactive surface constituents, and time-dependent changes in interfacial chemistry may be especially important for organic solute partitioning, interphase mass transfer, and wettability phenomena.

Investigations with liquid coal tar globules have discovered interfacial films that develop on aging of coal tar in aqueous systems and that may affect organic solute mass transfer (60). Inferences from GC/MS, ^{13}C- and proton-nuclear magnetic resonance, and Fourier transform infrared spectrometry analyses of coal tar interfacial film material suggest water hydrogen-bonding with aromatic π-electrons in polycyclic aromatic hydrocarbons to form films and emulsions (61). The occurrence of viscous interfacial films comprising crude oil asphaltenes has been described in the petroleum literature (62). In the context of the previous discussion, such interfacial films may undergo transition to a structured or condensed material, thus likely changing interfacial mass transfer rates.

Conceptual Geosorbent Framework

The schematic in Figure 1 indicates conceptual HOC−geosorbent interactions. The types of reactivity are distributed among three principal domains. The first of these is the mineral domain with surface reactivity attributable to: (i) exposed external mineral surfaces at the particle scale and surfaces within macropores; (ii) interlayer surfaces of swelling clays at the nanometer scale; and (iii) the surfaces within mesopores and micropores of inorganic mineral matrices. The soft and hard carbon SOM components constitute a second principal domain at the nanometer scale of the composite geosorbent. Adherent or entrapped NAPLs comprise a third domain and may function in this regard as soft carbon organic matter except possibly for highly weathered material or interfacial films. Combustion residue, e.g., soot,

is another type of organic matter; it might act the same as hard carbon. Also shown is natural organic matter that may not be accessible to HOCs because of encapsulation. Due to the lack of direct measurement techniques, conflicting views may be expressed on the principal mechanisms affecting sorption, e.g., the role of soot versus hard carbon organic matter or the release of HOCs from adherent or entrapped NAPLs versus SOM.

HOC sorption on external mineral surfaces and on macropore surfaces within mineral matrices is typically a linear and reversible process with equilibrium being attained essentially instantaneously under completely mixed conditions (63). The contribution of such surfaces to overall sorption capacity as well as retarded rates is likely unimportant for hydrophobic compounds and most geosorbents. Contrary reports exist on whether nonpolar organic solutes are inaccessible or variably accessible to interlayer surfaces of swelling clay minerals (20, 63, 64).

By analogy to the glassy state of a polymer, the hard carbon or condensed organic domain would exhibit some combination of sorption behaviors involving both linear partitioning and nonlinear intramatrix, micropore-filling retention (28, 32, 51, 65). Because the relaxation speeds of glassy polymeric structures are both slow and dependent on solute concentration, diffusion of solute molecules into and out of condensed organic matter could be extremely slow, and the associated sorption process would likely be nonlinear, hysteric, and subject to solute−solute competition. In contrast, and by analogy to a rubbery polymer, the soft carbon or amorphous organic matter domain may exhibit partitioning behavior associated with linear local isotherms, rapid diffusion, no competition for sorption, and sorption reversibility (e.g., refs 23, 51, and 52). Like a polymer, SOM may exhibit transition from a condensed state to a loosely-knit rubbery state as temperature is increased (65, 66).

At the aggregate and particle scales, SOM and high surface area clay particles may be encapsulated by inorganic precipitates and weathering products. Under such conditions, some SOM may be inaccessible to HOC molecules. Holmén and Gschwend (57) demonstrated for quartz sands ranging in age from 10^4 to 10^7 years that solute uptake falls short of predictions, and it is hypothesized that the discrepancies are caused by mineral-phase encapsulation of some of the organic matter. This and diagenetic changes in SOM suggest that sorbent media are dynamic and constantly undergoing transformation. Sorption rates are likely to be limited by extremely slow coupled pore diffusion (within precipitates and within mineral particles) and intra-SOM matrix diffusion processes. One potential ramification is that long-polluted systems may contain pollutants co-encapsulated with the SOM in which they were originally associated. The encapsulation of such SOMs and clay surfaces when it occurs *after* HOC sorption might trap sorbed molecules within matrices from which they cannot readily escape and contribute significantly in some cases to the "aging" phenomenon commonly observed for field samples.

Characterization Methods

The compositional and structural complexity of the systems of interest is a significant problem in refining our understanding of the various chemical phenomena that drive the interactions of HOCs with geosorbents. This is especially important with regard to: (1) quantifying the distribution of HOCs among geosorbent domains including NAPLs; (2) determining the strength of the HOC interaction and diffusivity with different types of SOM; and (3) assessing independently micropore geometries and connections. Despite some developments, new approaches are needed to better define processes and to validate conceptual geosorbent models.

Nitrogen adsorption at 77 K has traditionally been used to measure surface area and microporosity. However, at such low temperature, gas diffusion in pores <~10 Å and across organic surfaces is activated and slow. Carbon dioxide has been considered as an alternative, as CO_2 undergoes only physical adsorption and is fast to attain sorption equilibrium since higher temperatures can be used to construct isotherms (196−273 K). The few reports available on its application to soils indicate that SOM has appreciable internal microporosity not detected with N_2 (67), and this microporosity has been correlated with the degree of nonlinearity and competitive effects for chlorinated benzene sorption from solution (65).

Methods that have been suggested for determining hardness of SOM, chemical oxidation, and combustion will always draw a sharp line between the two fractions, and moreover, these assume that chemical reactivity is correlated with physical structure *vis a vis* the material's nature as a sorbent. Clearly, alternative methods for characterizing the hard and soft state of SOM and observing its significance are needed. Presently there is no way to quantitatively separate SOM from minerals, which limits X-ray spectroscopic and ^{13}C-NMR techniques that have been used to assess the crystallinity, aromaticity, and functional group character of extracted humics (68).

Time-resolved measurements of fluorescence quenching, along with stop-flow injection of quencher molecules, could be used to measure the diffusion rates of fluorescent HOCs in surrogate SOM matrices. Fluorescence quenching has been used by a number of investigators in aqueous systems to study the associations of HOCs with natural dissolved organic matter; however, this method must be approached with caution as it is subject to significant artifacts (69, 70).

Reconciling Models for Heterogeneous Materials

The information discussed here addresses the problem of developing physicochemical process models for heterogeneous natural materials. A relevant question is the practicality of dividing geosorbents into sorption domains given the lack of microscopic data for most systems. We believe that microscopic understanding is necessary for identification of dominant mechanisms. This in turn will improve prediction of environmental fate, assist assessment of exposure and toxicity, and help justify soil and sediment quality criteria. Model development can be approached mechanistically from the synthesis of knowledge gained from the study of simpler systems or semi-empirically as a mathematical representation of processes too complex to be described from fundamental principles derived from well-characterized systems. Iterative exchange of ideas between these two approaches is potentially an effective direction. This needs to be combined with strong effort to bring new analytical techniques to bear on the problem. The discipline is in need of a more sophisticated understanding of a complex set of mechanisms at the microscale, and some progress is being made toward identifying the more salient issues.

Acknowledgments

Literature Cited

(1) NRC. *Alternatives for Groundwater Cleanup*; National Research Council Report; National Academy Press: Washington, D.C. 1994.

(2) Alexander, M. *Environ. Sci. Technol.* **1995**, *29*, 2713−2717.

(3) Steinberg, S. M.; Pignatello, J. J.; Sawhney, B. L. *Environ. Sci. Technol.* **1987**, *21*, 1201−1208.

(4) Ball, W. P.; Roberts, P. V. *Environ. Sci. Technol.* **1991**, *25*, 1237−1249.

(5) Connaughten, D. F.; Stedinger, J. R.; Lion, L. W.; Shuler, M. L. *Environ. Sci. Technol.* **1993**, *27*, 2397−2403.

(6) Linz, D. G., Nakles, D. V., Eds. *Environmentally Acceptable Endpoints in Soil*; American Academy of Environmental Engineers: Annapolis, MD, 1997.

(7) Luthy, R. G.; Dzombak, D. A.; Peters, C. A.; Roy, S. B.; Ramaswami, A.; Nakles, D. V.; Nott, B. R. *Environ. Sci. Technol.* **1994**, *28*, 266A−277A.

(8) Smith, J. R.; Egbe, M. E.; Lyman, W. J. Bioremediation of Polychlorinated Biphenyls (PCBs) and Polynuclear Aromatic Hydrocarbons (PAHs). In *Monograph on Bioremediation of Contaminated Soils*; American Society of Agronomy/Soil Science Society of America: Madison, WI, 1997; in publication.

(9) Erickson, D. C.; Loehr, R. C.; Neuhauser, E. F. *Water Res.* **1993**, *27*, 911−919.

(10) Bosma, R. M. P.; Middeldorp, P. J. M.; Schraa, G.; Zehnder, A. J. B. *Environ. Sci. Technol.* **1997**, *31*, 248−252.

(11) Kelsey, J. W.; Kottler, B. D.; Alexander, M. *Environ. Sci. Technol.* **1997**, *31*, 214−217.

(12) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: New York, 1993.

(13) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241−248.

(14) Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1979**, *206*, 831−832.

(15) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 277−231.

(16) Means, J. C.; Wood, S. G.; Hassett, J. J.; Banwart, W. L. *Environ. Sci. Technol.* **1980**, *14*, 1524−1528.

(17) Schwarzenbach, R. P.; Westall, J. *Environ. Sci. Technol.* **1981**, *15*, 1360−1367.

(18) Mingelgrin, U.; Gerstl, Z. *J. Environ. Qual.* **1982**, *12*, 1−12.

(19) Miller, C. T.; Weber, W. J., Jr. *J. Contam. Hydrol.* **1986**, *1*, 243−261.

(20) Farrell, J.; Reinhard, M. *Environ. Sci. Technol.* **1994**, *28*, 53−62.

(21) Huang, W.; Weber, W. J., Jr. *Environ. Sci. Technol.* Submitted for publication.

(22) Grathwohl, P. *Environ. Sci. Technol.* **1990**, *24*, 1687−1693.

(23) Weber, W. J., Jr.; McGinley, P. M.; Katz, L. E. *Environ. Sci. Technol.* **1992**, *26*, 1955−1962.

(24) Boyd, S. A.; Sun, S. *Environ. Sci. Technol.* **1990**, *24*, 142−144.

(25) Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, *31*, 203−209.

(26) Edwards, D. A.; Liu, Z.; Luthy, R. G. *J. Environ. Eng.* **1994**, *120*, 5−22.

(27) Grathwohl, P.; Reinhard, M. *Environ. Sci. Technol.* **1993**, *27*, 2360−2366.

(28) Pignatello, J. J.; Xing, B. *Environ. Sci. Technol.* **1996**, *30*, 1−11.

(29) Werth, C. J.; Reinhard, M. *Environ. Sci. Technol.* **1997**, *31*, 697−703.

(30) Murphy, E. M.; Zachara, J. M.; Smith, S. C.; Philips, J. C.; Weitsma, T. W. *Environ. Sci. Technol.* **1994**, *28*, 1291−1299.

(31) Edwards, D. A.; Adeel, Z.; Luthy, R. G. *Environ. Sci. Technol.* **1994**, *28*, 1550−1560.

(32) Young, T. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1995**, *29*, 92−97.

(33) Wu, S.; Gschwend, P. M. *Water Resour. Res.* **1988**, *24*, 1373−1383.

(34) Nkedi-Kizza, P.; Brusseau, M. L.; Rao, P. S. C.; Hornsby, A. G. *Environ. Sci. Technol.* **1989**, *23*, 814−820.

(35) Pignatello, J. J. Sorption Dynamics of Organic Compounds in Soils. In *Reactions and Movement of Organic Chemicals in Soils*; Sawhney, B. L., Brown, K., Eds.; Special Publication No. 22; Soil Science Society of America: Special Publication No. 22; Madison, WI, 1989; pp 45−80.

(36) Brusseau, M. C.; Jessup, R. E.; Rao, P. S. C. *Environ. Sci. Technol.* **1991**, *25*, 134−142.

(37) Suflita, J. M.; Bollag, J.-M. *Soil Sci. Soc. Am. J.* **1981**, *45*, 297−302.

(38) Stone, A. T. *Environ. Sci. Technol.* **1987**, *21*, 979−988.

(39) Hatcher, P. G.; Bortiatynski, J. M.; Minard, Dec, J.; Bollag, J.-M. *Environ. Sci. Technol.* **1993**, *27*, 2098−2103.

(40) Guerin, W. F.; Jones, G. E. *Appl. Environ. Microbiol.* **1988**, *54*, 929−936.

(41) Heitkamp, M. A.; Cerniglia, C. E. *Appl. Environ. Microbiol.* **1988**, *54*, 1612−1614.

(42) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area, and Porosity*, 2nd ed.; Academic Press: New York, 1982.

(43) Werth, C. J.; Reinhard, M. *Environ. Sci. Technol.* **1997**, *31*, 689−696.

(44) Kärger, J.; Ruthven, D. M. *Diffusion in Zeolites and other Microporous Materials*; John Wiley & Sons: New York, 1992.

(45) Chantong, A.; Massoth, F. E. *AIChE J.* **1983**, *29*, 725−731.

(46) Kile, D. E.; Chiou, C. T.; Zhou, H.; Li, H.; Xu, O. *Environ. Sci. Technol.* **1995**, *29*, 1401−1406.

(47) Garbarini, D. R.; Lion, L. W. *Environ. Sci. Technol.* **1986**, *20*, 1263−1269.

(48) Gauthier, T. H.; Seitz, W. R.; Grant, C. L. *Environ. Sci. Technol.* **1987**, *21*, 243−248.

(49) Hu, Q.; Wang, X.; Brusseau, M. L. *Environ. Toxicol. Chem.* **1995**, *14*, 1133−1140.

(50) Weber, W. J., Jr.; Huang, W. *Environ. Sci. Technol.* **1996**, *30*, 881−888.

(51) Carroll, K. M.; Harkness, M. R.; Bracco, A. A.; Balcarcel, R. R. *Environ. Sci. Technol.* **1994**, *28*, 253−258.

(52) Xing, B.; Pignatello, J. J.; Gigliotti, B. *Environ. Sci. Technol.* **1996**, *30*, 2432−2440.

(53) McGinley, P. M.; Katz, L. E.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1993**, *27*, 1524−1531.

(54) Ball, W. P.; Buehler, Ch.; Harmon, T. C.; Mackay, D. M.; Roberts, P. V. *J. Contam. Hydrol.* **1990**, *5*, 253−295.

(55) Berens, A. R. *Makromol. Chem. Macrol. Symp.* **1989**, *29*, 95−108.

(56) Pignatello, J. J.; Ferrandino, F. J.; Huang, L. Q. *Environ. Sci. Technol.* **1993**, *27*, 1563−1571.

(57) Holmén, B. A.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, *31*, 105−113.

(58) Powers, S. E.; Abriola, L. M.; Weber, W. J., Jr. *Water Resour. Res.* **1994**, *30*, 321.

(59) Ali, M.; Dzombak, D. A.; Roy, S. B. *Water Environment Res.* **1995**, *67*, 16−24.

(60) Luthy, R. G.; Ramaswami, A.; Ghoshal, S.; Merkel, W. *Environ. Sci. Technol.* **1993**, *27*, 2914−2918; **1994**, *28*, 756.

(61) Nelson, E. C.; Ghoshal, S.; Edwards, J. C.; Marsh, G. X.; Luthy, R. G. *Environ. Sci. Technol.* **1996**, *30*, 1014−1022.

(62) Mohammed, R. A.; Bailey, A. I.; Luckham, P. F.; Taylor, S. E. *Colloids Surf. A: Physicochem. Eng. Aspects* **1993**, *80*, 223−242.

(63) Huang, W.; Schlautman, M. A.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1996**, *30*, 2993−3000.

(64) Parfitt, R. L.; Greenland, D. J. *Clay Miner.* **1970**, *8*, 305.

(65) Xing, B.; Pignatello, J. J. *Environ. Sci. Technol.* **1997**, *31*, 792−799.

(66) LeBoeuf, E. J.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1697−1702.

(67) de Jonge, H.; Mittelmeijer-Hazeleger, M. C. *Environ. Sci. Technol.* **1996**, *30*, 408−413.

(68) Wershaw, R. L. Application of Nuclear Magnetic Resonance Spectroscopy for Determining Functionality in Humic Substances. In *Humic Substances in Soil Sediment and Water*; Aiken, G. R., McNight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; John Wiley & Sons, New York, 1985; pp 561−582.

(69) Danielsen, K. M.; Chin, Y.-P.; Buterbaugh, J. S.; Gustafson, T. L.; Traina, S. J. *Environ. Sci. Technol.* **1995**, *29*, 2162−2165.

(70) Traina, S. J.; McAvoy, D. C.; Versteeg, D. J. *Environ. Sci. Technol.* **1996**, *30*, 1300−1309.