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Solid-State ^{19}F NMR Investigation of Hexafluorobenzene Sorption to Soil Organic Matter

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Solid-state ^{19}F NMR observation of the sorptive uptake of hexafluorobenzene (HFB) by two peat samples gives direct spectroscopic evidence for the existence of dual-mode sorption to soil organic matter. The sorption process is shown to be rapid, with all applied HFB sorbed within a few hours. Extractable lipids compete for high energy sorption sites in the organic matter, and their removal increases the amount of rigidly sorbed, immobile species formed. Soil lipids enhance the sorption capacity of the solid-state dissolution domain of the organic matter. This dissolution domain is responsible for partitioning in the dual-mode phenomenon. Removal of the lipids decreases the partitioning capacity of the soil organic matter.

Introduction

Soil organic matter (SOM) is a critical control on the fate and transport of nonpolar organic compounds (NOC) such as polynuclear aromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs) in the environment (*1*−*16*). After initial sorption, many anthropogenic compounds have been shown to interact strongly with humic materials, with a significant fraction becoming irreversibly bound during even brief periods of contact (*16*−*22*). These irreversibly bound compounds or "bound residues" are defined as "... chemical species in soil, plant or animal tissue ... that are unextracted by a standard method, such as Soxhlet solvent extraction ..." (*23*). Though the phenomenon of bound residue formation has been extensively studied, the processes and mechanisms controlling this phenomenon are poorly understood.

Kohl and Rice (*16*) have shown that the majority of a PCB or PAH bound to SOM is associated with the humin fraction. They also demonstrated that a relatively small fraction of the total organic carbon in humin (referred to as "bound" or nonextractable lipids) has an extremely high affinity for the PAH or PCB being bound. Subsequent studies with whole soils have shown that lipids compete with NOCs for initial sorption sites. Removal of the lipids resulted in significant increase in the sorption of PAHs (*24*). Thus, it is apparent that the role of lipids in NOC binding to SOM needs to be examined further.

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Models of NOC Sorption to SOM. The sorption of nonpolar organic compounds to SOM has been viewed as a hydrophobic solid-phase partitioning (*1, 5*−*7, 25*−*29*). This partitioning model has been extensively studies by Chiou and co-workers (*2, 5, 7, 26, 27, 30*−*36*), and in the authors' opinion many of the more recent models are modifications or additions to this basic partitioning model. In the partitioning model, SOM behaves like a nonpolar liquid phase which dissolves and uniformly distributes the NOC inside the SOM matrix. Dissolution in this domain is driven primarily by the hydrophobic effect (*5, 35, 37*). Conceptually, sorption occurring by this mechanism can be compared to the sorption of NOCs to rubbery polymers (*38*). The partitioning mechanism allows for no specific interactions between the sorbate and the sorbent, but rather uptake is driven by the favorable change in entropy of the NOC leaving the aqueous phase.

The partitioning model states that the extent to which a sorbate molecule will distribute itself in the SOM matrix is determined almost exclusively by its water solubility, rather than its solubility in the SOM (*5, 35*). Individual phase partitioning reactions involving wide ranges of sorbate concentrations are characterized by linear sorption isotherms due to constant activity coefficients of the sorbate molecules (*35*). Partition constants, or activities, for multiple sorbates at low relative concentrations are found to be independent of each other resulting in noncompetitive interactions between multiple sorbates. Investigations into the sorption of NOCs by soils with significant organic contents have demonstrated linear sorption isotherms and have attributed the sorption to phase partitioning (*1, 26, 30*).

Despite the large number of studies supporting linear sorption of NOCs to SOM, many recent studies have reported nonlinear isotherms (*9, 11, 12, 24, 39*−*42*), solute−solute competition (*8, 9, 43*), and desorption hysteresis (*44*−*48*). These observations cannot be explained by the partitioning model and have been explained by attributing dual-mode sorption properties to SOM. At least four different conceptual models have been proposed to describe nonideal sorption/desorption behavior of nonpolar compounds on SOM.

Weber and co-workers (*49* and references therein) have developed a distributed reactivity model for subsurface soil materials which describes SOM as having rubbery and glassy regions in which they attribute nonlinear sorption to the presence of a small amount of "hard", diagenetically altered, high-surface-area carbonaceous material. This condensed organic matter has a disproportionately high capacity per unit weight to sorb NOCs in relation to the "soft", geologically immature SOM. The carbonaceous material adsorbs NOCs to surface sites of varying energy levels with much higher binding energies than the NOC interactions with the more abundant amorphous SOM. The mechanism of uptake is similar to that found with the sorption of NOCs to activated charcoal. Carbonaceous material has a nominal presence in most soils and the amorphous SOM continues to sorb additional NOC molecules via a partitioning mechanism after the carbonaceous materials are saturated (*50*−*53*). The different sorption energies of these two organic matter pools results in the observed nonlinear isotherms.

Pignatello and co-workers (*8, 11*−*13, 15, 43, 54*) describe SOM as possessing adsorption and partitioning domains analogous to those found in glassy polymers. Conceptually, the SOM matrix is a bulk partitioning medium containing a finite number of rigid, internal voids or holes. Molecules which enter the holes have the potential for adsorption reactions with the internal surfaces. In this model, these holes are thought to be nonuniform in size and energy and as a

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result discriminate on the basis of molecular structure. Studies using CO_2 as a probe correlate (*13*) the nanoporosity of the sorbent with the degree of nonlinearity found in single-solute sorption experiments as well as with the competitive effects observed between solute−solute sorption studies (*13*).

Kan and co-workers (*44, 55, 56*) attribute adsorption/desorption hysteresis of organic pollutants with SOM to possible physical alteration of the soil matrix upon adsorption of the contaminant. These alterations could include "configuration changes to the organic matter as a consequence of changes in ionic strength, pH, or relative humidity, or coagulation of either mineral or organic soil particles" (*44*). Kan and co-workers have also shown that the possibility for matrix rearrangement upon the introduction of the contaminant to the SOM could also lead to the well documented irreversible binding phenomenon as the molecule desorbing from the SOM is in a different matrix from which it originally adsorbed onto/into.

Chiou and Kile (*42, 57*) have also recently investigated deviations from sorption linearity on soils by nonpolar organic compounds. These investigators have attributed the nonlinear isotherms observed to a small amount of high-surface-area carbonaceous material (HSACM). This theory defines HSACM as a contaminant or extraneous material found in SOM and does not treat HSACM as an integral part of SOM. This HSACM exhibits greater nonlinear adsorption at low relative concentrations than the linear portion to SOM and is only important at very low relative loadings of the contaminant to the SOM.

Supporting evidence for either the partitioning or the dual-mode sorption model thus far has been the result of macroscopic observations through batch sorption isotherms (*5, 8, 9, 12, 36, 39*), vapor phase deposition (*34*), or similar bulk property experiments. It has been noted that the interpretation of macroscopic data is complicated by the presence of mixed sorption phenomenon (*58*). These investigations do not provide definitive information about the interactions which are occurring at the microscopic or molecular levels. Information about these molecular level interactions are of vital importance if the sorption process is to be understood well enough to make accurate analysis of environmental hazards and appropriate remediation decisions. In addition, the dual-mode sorption model makes specific claims about the presence of microscopic SOM domains whose existence cannot be proven through macroscopic sorption experiments. There is question over the actual existence of different organic matter phases (*42, 59*) or local chemical moieties which are cited as being responsible for the nonlinear isotherms, competitive sorption, desorption hysteresis, and other evidence that seems to contradict solid-phase partitioning.

The heterogeneity of SOM makes direct observation of these domains difficult. A recent review of the chemical interactions of hydrophobic organic contaminants with soils and sediments recognized the need for "direct observational data revealing the molecular-scale locations in which nonpolar organic compounds accumulate when associated with natural soils or sediments" (*58*). The characterization of a contaminant "probe" molecule sorbed into these domains would be an ideal way to "see" the environment that the contaminant experiences. The use of ^{19}F-labeled probes has three distinct advantages in this respect. First, fluorinated analogues of many NOCs are commercially available. Second, it is an element normally present at very low levels in most soils. Third, the natural abundance of ^{19}F is 100%, and it has an NMR sensitivity almost equal to that of ^{1}H.

This study, for the first time, provides direct observational data of the local chemical environments of sorption domains and provides critical data with which the different models can be evaluated. Using solid-state NMR's ability to describe the local chemical environment of an NMR-active nuclei, such as ^{19}F, we will demonstrate the existence of at least two sorption domains in SOM.

Materials and Methods

The Guanella Pass peat (GP) sample was collected from a boggy soil on Guanella Pass, Clear County, CO (T55, R74W, S20). It contains 40.05% C, 38.70% ash (*60*), and 2.79 mL H_2O/g paste saturation capacity. The International Humic Substances Society reference peat, referred to as the Pahokee peat, contains 45.7% C, 15% ash (*61*), and 1.26 mL H_2O/g paste saturation capacity. Hexafluorobenzene (99%) was obtained from Aldrich and has a reported estimated water solubility of 342 mg/L and a log K_{ow} of 2.55 (*62*). All other solvents and chemicals used were reagent grade or better and were used as received.

Lipid-extracted peats were prepared by the following procedure. The air-dried peat was wetted by placing the peat in a cellulose thimble and immersing the thimble for 24 h in type 1 reagent H_2O (conductivity >18 megohms at 25 °C). Following wetting, the peat was extracted with benzene:methanol (3:1, v:v) for 72 h in a Soxhlet apparatus. After 24 h the solvent was exchanged with fresh benzene:methanol due to the large quantity of water removed during the extraction. Extractable-lipid organic content was determined by weight upon evaporation of the extraction solvent and found to be 8.54 and 1.61% of the total organic carbon (TOC) for GP and Pahokee peats, respectively.

Short-Term Kinetics Experiments. Liquid HFB was placed directly onto air-dried peat samples at room temperature at levels corresponding to 9800, 8900, 7400, and 10 900 mg/kg for the whole GP, extracted GP, whole Pahokee, and extracted Pahokee peats, respectively. Immediately after the application of HFB, water was added, via Pasteur pipet, to the peat to achieve a moisture level of 65% of its paste saturation capacity. The sample was then vigorously stirred by hand for 60 s with a micro spatula to homogenize the sample. The sample was immediately placed in a 5 mm o.d. boron nitride NMR rotor equipped with Aurum or vespel endcaps and examined by magic angle spinning (MAS) NMR experiments.

Aqueous Phase Sorption Experiments. Five hundred milliliters of a saturated hexafluorobenzene solution (actual concentration obtained was 333.7 ± 8.5 mg/L) in a simulated soil solution background electrolyte of 0.01 M $CaCl_2$ was allowed to stand with 1.000 g whole GP, extracted GP, whole Pahokee, and extracted Pahokee peats, respectively, for 24 h with periodic shaking every 4 h. The supernatants were quantitatively analyzed before and after sorption using a Varian Saturn Star 3400 C_X gas chromatograph coupled to a Varian Saturn 2000 GC/MS/MS mass spectrometer. This analysis showed that no statistically significant change in HFB solution concentrations before and after sorption occurred. This indicates that the sorption solutions can be considered infinite baths.

Following the sorption incubation, the peat was removed from the solution via gravity filtration and placed in a 5 mm o.d. boron nitride rotor equipped with Aurum or vespel endcaps and observed via MAS and static NMR experiments. MAS experiments revealed the existence of a very broad resonance which might be lost, at least in part, in the background. To more carefully observe this resonance, judge its actual width, and get a more complete picture as to the actual mobility of the different sites, static experiments were also performed on the samples.

NMR Parameters. Initial ^{19}F NMR experiments were performed in the single-pulse mode to optimize the acquisition rate while avoiding saturation of the nuclei due to inappropriately short recycle or delay times. Subsequent static and MAS ^{19}F NMR experiments were performed in the single-

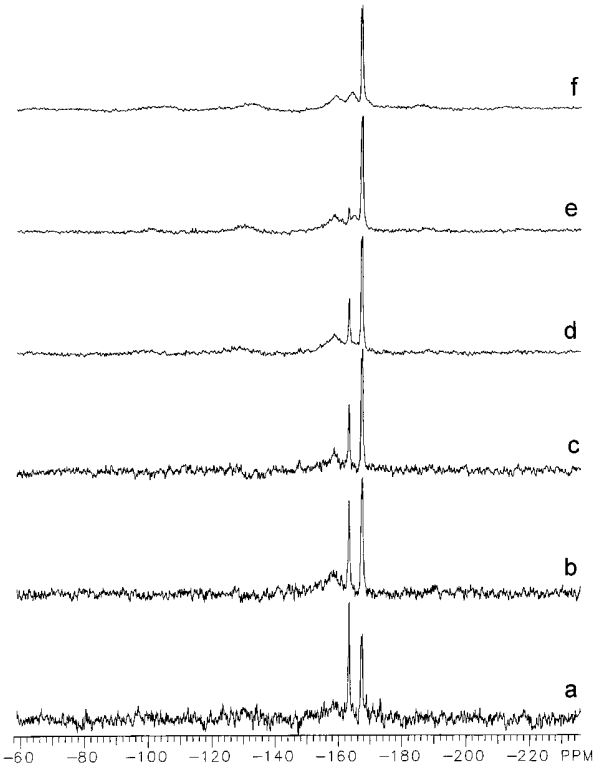

FIGURE 1. ^{19}F solid-state MAS NMR spectra of HFB sorbed to whole GP peat wetted to 65% of the maximum H_2O capacity. Spectra acquired at (a) 17 min (463 scans), (b) 25 min (891 scans), (c) 37 min (1171 scans), (d) 1 h (5300 scans), (e) 4 h (5300 scans), and (f) 24 h (21200 scans) after application of HFB. Spectra acquired at 8.0 kHz MAS spinning rate.

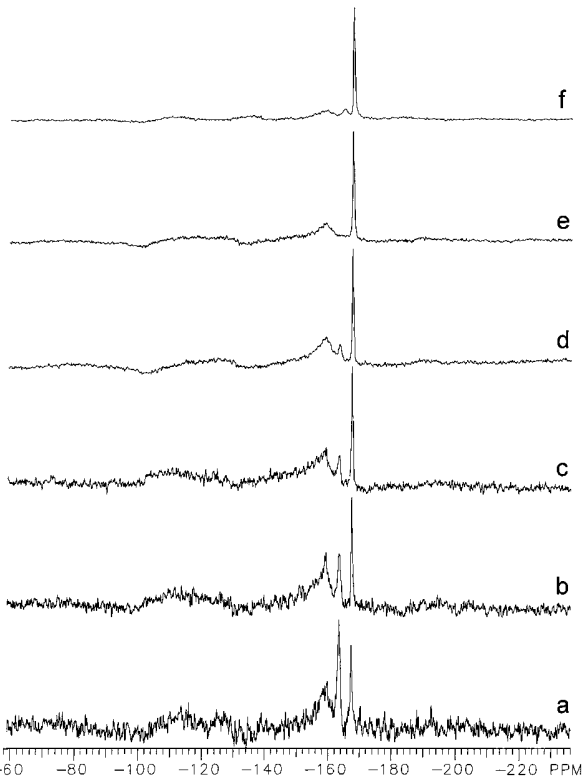

FIGURE 2. ^{19}F solid-state MAS NMR spectra of HFB sorbed to lipid extracted GP peat wetted to 65% of the maximum H_2O capacity. Spectra acquired at (a) 13 min (410 scans), (b) 25 min (945 scans), (c) 37 min (1300 scans), (d) 1 h (5300 scans), (e) 3 h (5300 scans), and (f) 24 h (21200 scans) after application of HFB. Spectra acquired at 7.0 kHz MAS spinning rate.

pulse mode (10 μs pulse, 50 kHz window, 0.15 s acquisition, 0.50 s delay between pulses) on a Varian XL-300 spectrometer equipped with a Doty ^{19}F MAS NMR probe at a frequency of 282.205 MHz and externally referenced with respect to $CFCl_3$ (neat HFB taken as −163.0 ppm) (*63*). Rotor spin rates were held constant for each spectra acquired but were varied between 5 and 9 kHz for identification of spinning sidebands. A line broadening of 50 Hz was applied to all spectra except the fine detail inserts shown in Figure 3 which have no line broadening applied. Spectral times noted in the figures are given as the average times for which each spectrum was acquired at after the application of HFB.

Volatilization of HFB. To investigate the rate of volatilization of HFB from the sample rotors, a pinhole was made in one of the rotor caps during one short-term kinetic experiment. Initially there was very good signal-to-noise, and the HFB was observed to behave in a fashion similar to that observed in the early hours of experiments performed with undamaged caps. However, the signal began to degrade due to loss of HFB by volatilization after 6 h, and at 14 h there was no detectable ^{19}F signal. Also, normally prepared rotors containing HFB samples showed negligible loss in signal after 40 days in the rotors. These two experiments show that HFB does not volatize out of properly prepared rotors but volatizes rapidly through a rotor leak. Since all kinetic experiments reported below were carried out for only 24 h, change in signal intensity due to loss of HFB by volatilization out of the rotor was judged to be negligible.

Results

Results obtained from both the Pahokee and GP peats were similar, and in the interest of brevity, displayed spectra and subsequent discussion will be limited to experiments from the GP samples. The complete set of spectra from both peats has been published by Kohl (*64*).

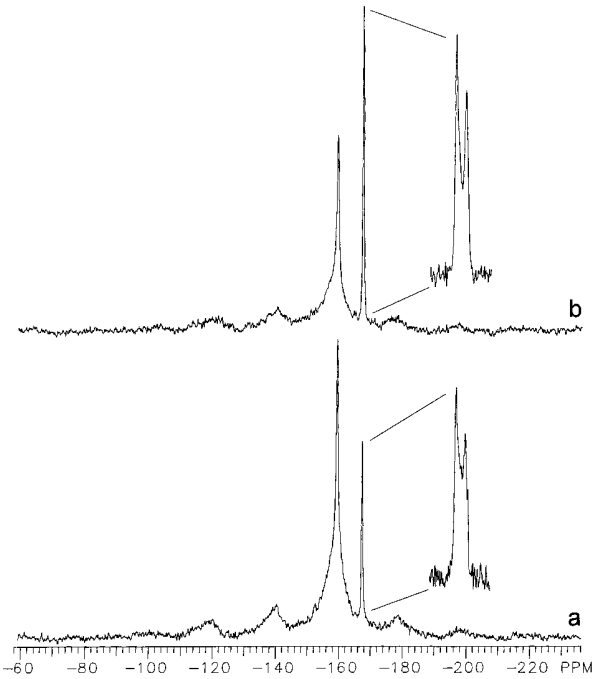

FIGURE 3. ^{19}F solid-state MAS NMR spectra of HFB sorbed to (a) extracted (5700 scans) and (b) whole GP peat (5460 scans) from saturated aqueous solution after 24 h incubation. Spectra acquired at 6.0 kHz MAS spinning rate.

TABLE 1. Relative Proportions of ^{19}F Signal Intensity as Observed by MAS and Static Solid-State NMR Experiments

experiment	sample	spectral time	% free	% mobile	% immobile
kinetic	whole GP	17 min	28	32	40
kinetic	whole GP	25 min	20	28	52
kinetic	whole GP	37 min	13	36	51
kinetic	whole GP	60 min	11	38	51
kinetic	whole GP	4 h	4	30	67
kinetic	whole GP	24 h	0	30	70
kinetic	extracted GP	13 min	19	18	63
kinetic	extracted GP	25 min	12	22	66
kinetic	extracted GP	37 min	6	26	68
kinetic	extracted GP	60 min	3	26	71
kinetic	extracted GP	3 h	0	37	63
kinetic	extracted GP	24 h	0	37	63
aqueous sorption	whole GP	24 h	0	38	62
aqueous sorption	extracted GP	24 h	0	13	87
aqueous sorption[a]	whole GP	24 h	0	20	80

[a] Denotes integration from acquisition of spectrum in static mode.

Sorption to Whole Peat. Sorption of hexafluorobenzene to whole GP peat over 24 h time is shown in Figure 1. After 17 min of incubation there are sharp peaks at −163.2, −167.0, and −167.4 ppm. The prominent −163.2 ppm peak at 17 min decreases with time until after 4 h it is almost gone. This rapid decrease is attributed to free, liquid HFB which has not been sorbed into the SOM (the chemical shift of neat HFB was observed to be −163.0 ppm). The peaks at −167.0 and −167.4 ppm increase rapidly between 17 and 25 min and continue to slowly increase up to 4 h, after which they only increase slightly with increasing incubation times. These peaks persist throughout the incubation experiment. Due to their narrowness, both in the MAS and static spectra, they are attributed to loosely bound, mobile HFB. A fourth, much broader peak centered roughly at −158.7 ppm begins to appear after 25 min and persists throughout the rest of the incubation. This peak appears to continue to grow even past 4 h, but because of its very broad nature the actual point at which it stops growing is difficult to determine. Due to the broadness of this fourth peak under both static and MAS conditions, it is attributed to immobile HFB. After 4 h an additional peak at −164.5 ppm begins to form which is quite apparent after 24 h. This peak is not as sharp or as tall as the peaks at −167.0 and −167.4 ppm attributed to mobile HFB, but it appears sharper than the peak at −158.7 ppm. It is attributed to binding in sites in which the HFB has intermediate mobility.

Sorption to Extracted Peat. Sorption of HFB to lipid-extracted GP peat (Figure 2) reveals a different interaction between the contaminant and peat. Again there are initially two sharp peaks at −163.2 and −167.5 ppm attributed to free, liquid HFB and loosely bound, mobile HFB, respectively. However, in the first spectrum, acquired after only 13 min, there is a distinct, broad resonance at −159.1 ppm which is again attributed to immobile HFB. The progression of the sorption phenomenon in the extracted peat is similar to that in the whole peat, except that the sorption process proceeds faster, with all free, liquid HFB being sorbed after 3 h in the extracted peat. The same level of sorption was not achieved in the whole peat until after 10 h (spectrum not shown). After 24 h of contact, both the whole and lipid extracted peat samples display similar spectra with the whole peat showing more distinct peaks at −158.7 and −164.5 ppm.

Aqueous Sorption to Peat under MAS Conditions. Sorption of HFB from a saturated aqueous solution to the whole- and lipid-extracted-GP peat is shown in Figure 3. Due to the much higher concentrations of HFB on the peats, these spectra provide interesting insights into the nature of the different sorption domains. First, both spectra again show highly mobile HFB (∼ −167 ppm). This resonance is again split into two sharp resonances centered at −167.2 and −167.5 ppm. The reason for this splitting is unclear but may represent two similar, but distinct, mobile sites, possibly involving ring stacking of the HFB aromatic ring to the different but abundant functionalized aromatic moieties present in peat organic matter. This resonance in whole peat is approximately 1.8 times as large as in the extracted peat. Also, the immobile HFB resonance (−158.9 ppm) is much smaller and slightly narrower in the whole peat than the extracted peat. This difference shows that extracting the lipids increases the capacity for the peat to strongly sorb the HFB. The peak at −164.5 ppm present in the low loading kinetic experiments shown in Figures 1 and 2 is absent in Figure 3. This absence is presumably due to the higher concentration of HFB in these experiments filling more sorption sites and merging the two resonances at −164.5 and −158.7 into one broad resonance.

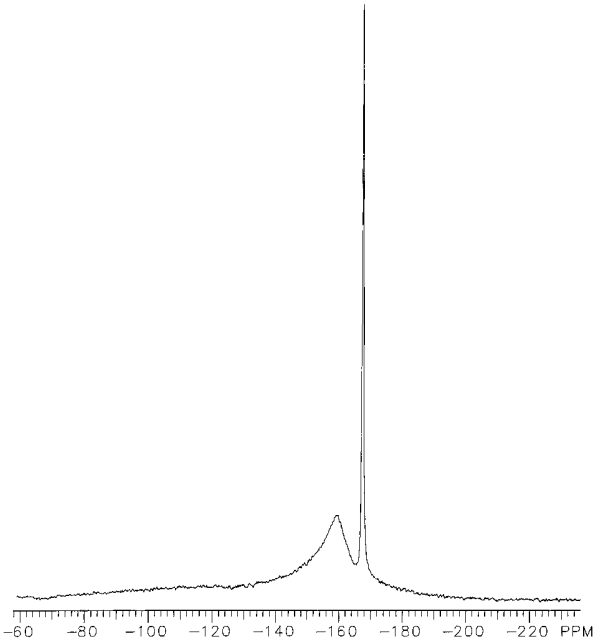

FIGURE 4. ^{19}F solid-state static NMR spectrum (75 000 scans) of HFB sorbed to whole GP peat from saturated aqueous solution after 24 h incubation.

Aqueous Sorption to Peat under Static Conditions. Figure 4 shows the same sample as Figure 3b but acquired under static conditions. This spectrum shows only the mobile resonance at −167.4 ppm and a very broad resonance centered at −159.1 ppm. As would be expected in a solid-state static spectrum, the fine detail in the mobile HFB resonance is lost; however, the resonance is still remarkably sharp indicating that this site has very mobile ^{19}F nuclei. The broad resonance at −159.1 ppm, which in MAS spectra dropped down to baseline noise rapidly, could actually extend from as far as −80 to −190 ppm.

Discussion

The narrow resonance (−167.4 ppm) in Figure 4 is clearly due to HFB molecules which have a high degree of mobility. This peak cannot be due to free, liquid HFB which resonates at −163.0 ppm or HFB dissolved in the small amount of soil solution present which resonates at −159.4 ppm. The spectrum shown was taken after 24 h incubation. The sorption experiments were conducted in amber bottles, and it is unlikely that significant photodegradation or biological degradation occurred in this time frame. Further evidence that this resonance is due to HFB and not a degradation

product is the presence of this resonance in the earliest spectra (13 and 17 min) shown in Figures 1 and 2. This narrow resonance must then be due to HFB molecules sorbed to the organic matter which are motionally unrestricted or mobile.

The very broad resonance centered at −159.1 ppm in Figure 4 is again unlikely to be due to degradation products as it is also present after only 13 min in the extracted GP peat kinetics study (Figure 2) and is more likely due to molecules which are experiencing restricted mobility. The extreme broadness of this resonance indicates that there may be a large continuum of different local chemical environments into which the HFB may strongly sorb. The peat in all experiments presented here is wet; water has been shown to essentially prevent all sorption of NOCs to mineral surfaces (*2*, *5*, *30*). Thus, sorption must be occurring to organic sorption sites which provide different chemical environments for the HFB molecules. Considering the extremely heterogeneous nature of SOM, a large range of sorption sites with different local chemical environments would be expected. The existence of mobile and immobile sorbed HFB pools gives strong evidence that the sorption of HFB to SOM, and presumably other nonpolar hydrophobic compounds as well, proceeds by a dual-mode or possibly even more complex mechanism.

A phase partitioning system acts as a solvating medium. Sorbate molecules taken up by such a mechanism should experience only one chemical environment and display one resonance frequency. The existence of several distinct resonances gives strong evidence for at least two distinct modes of uptake and also provides strong evidence that the sorption mechanism is more complicated that a simple partitioning phenomenon.

The distributed reactivity, hole-filling, matrix rearrangement, and HSACM models all allow for specific interactions of nonpolar compounds with organic matter found in soils. The very broad resonance (−159 ppm) observed in these experiments is due to HFB molecules being located in many different local chemical environments over the NMR time scale. This could be the result of many different rigid sorption sites of varying energy distribution or local chemical environment. Such distributions would be found in a system corresponding to the distributed reactivity, hole-filling, and HSACM models. The matrix rearrangement model could also give rise to a large distribution of NMR signals as the sorbate molecules would likely be in many different chemical environments depending on the specific rearrangement of organic molecules occurring for each individual or small group of sorbate molecule(s).

Experimentally, the distributed reactivity and HSACM models could potentially be differentiated from the hole-filling model by the rate at which rigid binding occurs. The hole-filling mechanism logically requires the sorbing molecules to move through at least some portion of the bulk organic matter, which acts as a partitioning medium, before entering the hole or void. This movement would require a finite amount of time and would result in the observation of a mobile resonance before the rigid resonance became significantly intense. The distributed reactivity and HSACM models do not require this lag time, and the two resonances could appear simultaneously or the rigid domain could even appear before the mobile domain. Figures 1 and 2 provide qualitative kinetic sorption data for this system. Although Figure 1 shows the mobile resonance appearing before the rigid one, the extreme broadness of the rigid resonance (as shown in Figure 4) and weak signal in Figure 1 indicates that no conclusion can be drawn as to whether the rigid environment was present initially because, even if present, it would likely be lost in the background. Closer observation of the sorption phenomenon through carefully controlled experiments is necessary before one of these models can be selected as more likely than the other.

The extraction of lipids from the peat increases the quantity of immobile species formed (Figure 3). This can be explained if the lipids compete for sorption sites which lead to rigidly sorbed species in the organic matter. The removal of these competing molecules from the organic matter frees up additional sorption sites for the HFB resulting in a larger fraction of the NOC reaching the immobile domain. In addition to increasing the amount found in the immobile fraction, removal of lipids also results in a decrease in the amount of mobile species. As the concentration of the original HFB solution did not measureably change during the incubations, the amount of HFB partitioned into a fluid domain should be independent of the amount sorbed to a rigid domain. However, removal of the lipids affects both domains, leading to the conclusion that either the fluid domain interacts with the rigid domain or else the extraction procedure somehow alters the fluid domain.

The matrix rearrangement model describes a rearrangement in the orientation or confirmation of matrix molecules due to the presence of sorbate molecules which have entered into the organic matter. This phenomenon could give rise to different chemical shifts which would be observed in NMR experiments due to different local chemical environments which the sorbate molecules would experience in the organic matrix. Though different local environments are observed in these experiments, it is significant that extracting the lipids does not change the location of the chemical shifts observed in the peat, merely the strength of the signal observed (though the line shape of the aqueous and kinetic experiments are different and discussed below). If matrix rearrangements are occurring and are the cause of the dual-mode sorption observed, it would be expected that removing the lipids would alter the organic matrix significantly enough to change the local chemical environments experienced by the sorbing HFB molecules. Though not necessary, it is likely that such an alteration would change the chemical shift observed between the whole and lipid extracted samples. No movement in the chemical shift is observed in these experiments. Though the matrix rearrangement model does provide an interesting and somewhat intuitively satisfying view of the interactions of nonpolar sorbates with SOM, the data obtained in this work does not directly support such a view.

Previous work (*1*, *5*−*7*, *25*−*29*) strongly indicates the presence of a fluid, partitioning domain which is likely the mobile domain observed in this work. That being the case, the profound change in sorptive capacity of the partitioning domain when the lipids are extracted (Figure 3), is somewhat difficult to explain. As the absolute quantity of organic matter removed during extraction is rather small (8.54% and 1.61% of the TOC for GP and Pahokee peat, respectively), it could be argued that the partitioning domain is due to a small fraction of the total SOM. Alternatively, the lipids may somehow alter the character of the partitioning domain through interactions with the humic matrix allowing for much greater uptake. The interaction of a minor quantity of material significantly altering the properties of a much larger mass of material is not unreasonable; indeed the interactions of minor components of plastics, i.e., plasticizers, greatly affect the properties of the polymers by making them flexible (*65*). It may be that the lipids somehow soften the other humic materials in an analogous fashion to plasticizers. These data give evidence that lipids play an important role in SOM sorption characteristics; however, the exact role they have in the partitioning character of SOM is unknown and an area we are actively exploring.

Comparing the spectra from the kinetic experiments to the spectra from the aqueous experiments after 24 h sorption time (Figures 1f to 3b and 2f to 3a) there appears to be significant differences in the nature of the rigid domain. There is only one rigid resonance apparent in the aqueous

experiments, while two distinct resonances are observable in the kinetic experiments. In addition, the line shape observed for the aqueous experiments is much sharper in relation to the mobile resonance than in the kinetic experiments. These differences could be due to the higher concentration of HFB in the aqueous experiments versus the kinetic experiments. This higher concentration could swamp out the two distinct resonances observed in the kinetic experiments and merge them into the one resonance observed in the aqueous experiments. The difference in the line shape could also be attributed to this higher loading; however, it is more likely that the organic matter in the aqueous experiments is swollen and expanded, due to the penetration of water into the organic matter, to a larger degree than in the kinetic experiments. This expanded organic matter could sorb additional HFB as well as "soften" the rigid domains giving rise to a more mobile resonance.

Sorption proceeds rapidly, as seen in Figures 1 and 2, with the bulk of the sorption occurring within the first few hours (much has happened within the first few minutes). It is clear that removing the lipids increases the rate of the sorption phenomenon for the "fast" component of sorption. This is particularly evident in the rate at which the rigidly sorbed resonance develops. It clearly demonstrates that the lipids compete for higher energy, rigid sorption sites in the SOM matrix.

Conclusions

Dual-mode sorption domains in SOM have been observed by solid-state ^{19}F NMR examination of the sorption of HFB to peat. The sorption process is rapid with the majority of the sorption occurring within the first few hours. Sorption is essentially complete after 24 h. Extractable lipids compete for high energy sorption sites found in the peat organic matter. Extractable lipids also significantly enhance the partitioning character of the organic matter. Removal of the lipids speeds the sorption process; in the GP peat system the rate of sorption was approximately doubled.

Acknowledgments

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Literature Cited

(1) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241.
(2) Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1981**, *213*, 683.
(3) Karickhoff, S. W. *Chemosphere* **1981**, *10*, 833.
(4) Mingelgrin, U.; Gerstle, J. *J. Environ. Qual.* **1983**, *12*, 1.
(5) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 227.
(6) Shian-chee, W.; Gschwend, P. M. *Environ. Sci. Technol.* **1986**, *20*, 717.
(7) Chiou, C. T. In *Reactions and Movement of Organic Chemicals in Soils*; Sawhney B. L., Brown K., Eds.; Soil Science Society of America, American Society of Agronomy: Madison, WI, 1989; pp 1−29.
(8) Pignatello, J. J. In *Organic Substances and Sediments in Water*; Lewis Publishers: Chelsea, MI, 1991; pp 291−309.
(9) McGinley, P. M.; Katz, L. E.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1993**, *27*, 1524.
(10) Murphy, E. M.; Zachara, J. M. *Geoderma* **1995**, *67*, 103.
(11) Xing, B.; Pignatello, J. J. *Environ. Toxicol. Chem*. **1996**, *15*, 1282.
(12) Xing, B.; Pignatello, J. J. *Environ. Sci. Technol.* **1997**, *31*, 792.
(13) Pignatello, J. J. *Adv. Colloid Interface Sci.* **1998**, *76−77*, 445.
(14) Schlebaum, W.; Badora, A.; Schraa, G.; Van Riemsdijk, W. H. *Environ. Sci. Technol.* **1998**, *32*, 2273.
(15) Xing, B.; Pignatello, J. J. *Environ. Sci. Technol.* **1998**, *32*, 614.
(16) Kohl, S. D.; Rice, J. A. *Chemosphere* **1998**, *26*, 251.
(17) Lichtenstein, E. P.; Katan, J.; Anderegg, B. N. *J. Agric. Food Chem*. **1977**, *25*, 43.
(18) Viswanathan, R.; Scheunert, I.; Kohli, J.; Klein, W.; Korte, F. *J. Environ. Sci. Health* **1978**, *B13(3)*, 243.
(19) Führ, F. In *Pesticide Science and Biotechnology*; Greenhalgh R., Roberts T. R., Eds.; Blackwell Science Publications: UK, 1987; pp 383−389.
(20) Kloskowski, R.; Fuhr, F. *J. Environ. Sci. Health* **1987**, *B22*, 509.
(21) Kloskowski, R.; Fuhr, F. *J. Environ. Sci. Health* **1987**, *B22*, 623.
(22) Xie, H.; Guetzloff, T. F.; Rice, J. A. *Soil Sci.* **1997**, *162*, 421.
(23) Holland, P. T. *Pure Appl. Chem*. **1996**, *68*, 1167.
(24) Kohl, S. D.; Rice, J. A. *Org. Geochem*. **1999**, *30*, 929.
(25) Kyle, B. G. *Science* **1981**, *213*, 683.
(26) Rutherford, D. W.; Chiou, C. T.; Kile, D. E. *Environ. Sci. Technol.* **1992**, *26*, 336.
(27) Rutherford, D. W.; Chiou, C. T. *Environ. Sci. Technol.* **1992**, *26*, 965.
(28) McGroddy, S. E.; Farrington, J. W.; Gschwend, P. M. *Environ. Sci. Technol.* **1996**, *30*, 172.
(29) Maruya, K. A.; Risebrough, R. W.; Horne, A. J. *Environ. Sci. Technol.* **1996**, *30*, 2942.
(30) Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1979**, *206*, 831.
(31) Chiou, C. T. In *Hazard Assessment of Chemicals: Current Developments*; Saxena, F. F., Ed.; Academic Press: New York, 1981; pp 117−153.
(32) Chiou, C. T.; Shoup, T. D.; Porter, P. E. *Org. Geochem*. **1985**, *8*, 9.
(33) Chiou, C. T.; Malcolm, R. L.; Brinton, T. I.; Kile, D. E. *Environ. Sci. Technol.* **1986**, *20*, 502.
(34) Chiou, C. T.; Kile, D. E.; Malcolm, R. L. *Environ. Sci. Technol.* **1988**, *22*, 298.
(35) Chiou, C. T. In *Humic Substances in Soil and Crop Sciences; Selected Readings*; MacCarthy, P., Clapp, C. E., Malcolm, R. L., Bloom, P. R., Eds.; American Society of Agronomy and Soil Science Society of America: Madison, 1990; pp 111−160.
(36) Chiou, C. T.; McGroddy, S. E.; Kile, D. E. *Environ. Sci. Technol.* **1998**, *32*, 264.
(37) Chiou, C. T.; Schmedding, D. W.; Manes, M. *Environ. Sci. Technol.* **1982**, *16*, 4.
(38) Flory, P. J. *J. Chem. Phys.* **1942**, 51.
(39) Young, T. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1995**, *29*, 92.
(40) Leboeuf, E. J.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1697.
(41) Huang, W.; Young, T. M.; Schlautman, M. A.; Yu, H.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1703.
(42) Chiou, C. T.; Kile, D. E. *Environ. Sci. Technol.* **1998**, *32*, 338.
(43) Xing, B.; Pignatello, J. J.; Gigliotti, B. *Environ. Sci. Technol.* **1996**, *30*, 2432.
(44) Kan, A. T.; Fu, G.; Tomson, M. B. *Environ. Sci. Technol.* **1994**, *28*, 859.
(45) Aochi, Y. O.; Farmer, W. J. *Environ. Sci. Technol.* **1997**, *31*, 2520.
(46) Cornelissen, G.; Van Noort, P. C. M.; Govers, H. A. J. *Environ. Sci. Technol.* **1998**, *32*, 3124.
(47) Huang, W.; Yu, H.; Weber, W. J., Jr. *J. Contam. Hydrol.* **1998**, *31*, 129.
(48) Weber, W. J., Jr.; Huang, W.; Yu, H. *J. Contam. Hydrol.* **1998**, *31*, 149.
(49) Huang, W.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1998**, *32*, 3549.
(50) Carter, M. C.; Weber, W. J., Jr.; Olmstead, K. P. *J. Am. Water Works* **1992**, *84*, 81.
(51) Carter, M. C.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1994**, *28*, 614.
(52) Karanfil, T.; Schlautman, M. A.; Kilduff, J. E.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1996**, *30*, 2195.
(53) Karanfil, T.; Kilduff, J. E.; Schlautman, M. A.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1996**, *30*, 2187.
(54) Pignatello, J. J.; Xing, B. *Environ. Sci. Technol.* **1996**, *30*, 1.
(55) Kan, A. T.; Gongmin, F.; Hunter, M. A.; Tomson, M. B. *Environ. Sci. Technol.* **1997**, *31*, 2176.
(56) Kan, A. T.; Fu, G.; Hunter, M.; Chen, W.; Ward, C. H.; Tomson, M. B. *Environ. Sci. Technol.* **1998**, *32*, 892.
(57) Chiou, C. T. *Environ. Sci. Technol.* **1995**, *29*, 1421.
(58) Luthy, R. G.; Aiken, G. R.; Brusseau, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Reinhard, M.; Traina, S. J.; Weber, W. J., Jr.; Westall, J. C. *Environ. Sci. Technol.* **1997**, *31*, 3341.

(59) Graber, E. R.; Borisover, M. D. *Environ. Sci. Technol.* **1998**, *32*, 3286.
(60) Rice, J. A. Ph.D. Dissertation, Colorado School of Mines, 1986.
(61) Senesi, N. Universita di Bari, Italy, personal communication, 1998.
(62) In *Handbook of Physical Properties of Organic Chemicals*; Howard P. H., Meylan W. M., Eds.; Lewis Publishers: New York, 1997; p 322.
(63) Emsley, J. W.; Phillips, L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, *7*, 1.
(64) Kohl, S. D. Ph.D. Dissertation, South Dakota State University, 1999.
(65) Immergut, E. H.; Mark, H. F. In *Plasticization and Plasticizer Processes*; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1964; pp 1−29.

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