

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7208010>

Absence of Mobile Carbohydrate Domains in Dry Humic Substances Proven by NMR, and Implications for Organic–Contaminant Sorption Models

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · MARCH 2006

Impact Factor: 5.33 · DOI: 10.1021/es0511467 · Source: PubMed

CITATIONS

36

READS

18

2 AUTHORS:



Jingdong Mao

Old Dominion University

126 PUBLICATIONS 2,558 CITATIONS

SEE PROFILE



Klaus Schmidt-Rohr

Brandeis University

255 PUBLICATIONS 8,997 CITATIONS

SEE PROFILE

Absence of Mobile Carbohydrate Domains in Dry Humic Substances Proven by NMR, and Implications for Organic-Contaminant Sorption Models

J. - D. MAO[†] AND K. SCHMIDT-ROHR*

Department of Chemistry, Gilman Hall, Iowa State University, Iowa 50011

The mobility and domain structure of various standard humic substances have been investigated by ¹H and ¹H-¹³C solid-state nuclear magnetic resonance (NMR) experiments. In four dry humic acids, a fulvic acid, a natural organic matter sample, and a whole peat sample, segments that undergo fast, large-amplitude motions account for <9% of the sample. This disproves a previous suggestion, based on ¹H NMR data, that flexible domains, presumably carbohydrates, make up >40% of various humic acids; these putative mobile domains were also linked to dual-mode sorption. In particular, neither the polar alkyl (carbohydrate) nor the aromatic components show any fast, large-amplitude mobility. A small fraction of mobile nonpolar alkyl segments identified by us before is the only component undergoing large-amplitude motions, apart from absorbed water that we observe in humic acids exposed to ambient air. ¹H-¹³C wide-line separation NMR shows that, contrary to previous suggestions, the dipolar couplings in the aromatic regions are smaller than in the polar alkyl segments, most likely due to differences in local ¹H densities. Series of ¹H-¹³C heteronuclear correlation experiments with ¹H spin diffusion reveal close proximity of aromatic and polar alkyl segments in several humic acids, precluding carbohydrate domains on a scale of >1-nm diameter. In the standard peat humic acid, nonpolar aromatic segments also do not form sorption domains of significant size, while nonpolar aliphatic domains, which we had previously shown to correlate with sorption capacity, have been confirmed.

Introduction

Sorption of nonpolar organic contaminants in soil is a topic of significant academic and practical interest (1–20). It has been shown that a large fraction of such contaminants is sorbed by the soil organic matter. However, which structures within the organic components are responsible for sorption is still a contentious question (6–8, 11, 14–17, 19). While much previous work with aromatic model contaminants such as pyrene, anthracene, and phenanthrene has been guided

by the hypothesis that aromatic contaminants should partition into putative aromatic domains, Chefetz et al. (6) and we (20) have shown a correlation between the sorption capacity and the amount of nonpolar aliphatic domains, which were proven by solid-state nuclear magnetic resonance (NMR) (20, 21). Chefetz, Hatcher, and co-workers (6, 16, 17) have confirmed the large capacity of nonpolar aliphatic plant material for sorption of hydrophobic organic contaminants. No correlation of sorption capacity with aromaticity, or even the fraction of aromatic carbons not bonded to oxygen, was found in ref 20.

The commonly observed nonlinearity of sorption curves of soil organic matter has been explained in terms of dual mode sorption. While the term “dual mode” has been taken from polymer science, the description of this model in soil science does not match the original polymer dual-mode sorption model, see Figure 1. The polymer model applies to completely glassy polymers (i.e., below the glass–rubber transition temperature *T_g*, and thus essentially rigid) which can undergo two types of sorption as indicated schematically in Figure 1a: nonlinear Langmuir-type sorption into pre-existing holes and linear partitioning (Freundlich sorption following Henry’s law) into the bulk (which is structurally a supercooled liquid) (22–24). In contrast, applications to soil organic matter (25) describe the dual-mode sorption model in terms of two types of domains, one glassy, the other rubbery (above *T_g*, and softened) that are simultaneously present in the sample. The characteristic properties of any rubbery material are a consequence of relatively fast (*τ_c* < 10 μs), large-amplitude segmental motions. Solid-state NMR is uniquely suited for detecting such motions in terms of the motional narrowing of ¹H spectra, which are broad in rigid solids due to ¹H-¹H dipolar couplings; equivalently, fast motions with large amplitudes will result in an increase of the ¹H *T₂* relaxation time. Conversely, ¹H NMR can prove the absence of such dynamics if the spectra do not exhibit a significant narrowed component. In a previous ¹H NMR study, Gunasekara et al. (19) detected a significant (>40%) mobile component in their samples and, through correlation with structural and sorption-curve features, suggested that it was due to putative flexible carbohydrate domains.

In this paper, we show NMR data that prove that, in dry humic acids, neither is there a significant amount of mobile carbohydrate segments, nor are there domains of polar carbohydrate segments. By various ¹H-¹³C NMR experiments, including heteronuclear correlation with ¹H spin diffusion, we also show that in some humic acids, no significant amounts of nonpolar aromatics and no large aromatic domains are detectable. Our data on humic acids exposed to ambient moisture indicate that a likely origin of the mobile component in the ¹H *T₂* data of ref 19 is relatively strongly bound (but still sufficiently mobile) water, or probehead background. Some implications of our structural findings for models of nonpolar contaminant sorption, which was measured for several of the same samples in our previous work (20), will be discussed.

Material and Methods

Samples. All the samples used in this study were standard samples from IHSS (International Humic Substances Society), kindly provided by Dr. Paul R. Bloom, University of Minnesota, St. Paul. These samples are (a) IHSS Suwannee River natural organic matter (NOM), RO isolation (Cat. #1R101N); (b) IHSS Suwannee River humic acid (HA), Standard II

* Corresponding author phone: 515-294-6105; fax: 515-294-0105; e-mail: srohr@iastate.edu.

[†] Current address: Rocky Mountain College, 1511 Poly Drive, Billings, MT 59102.

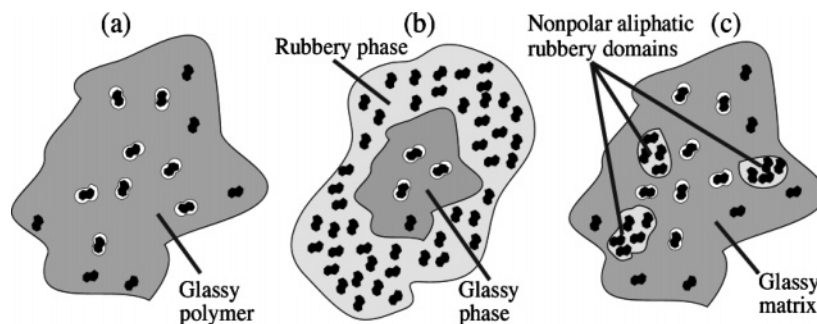


FIGURE 1. Dual-mode models of sorption. Sorbate molecules are shown in black, "hole" sorption sites in white. (a) Original polymer-science model, with two ("dual") sorption modes of (i) hole filling (Langmuir sorption) and (ii) dissolution following Henry's law. (b) Dual mode sorption as commonly represented in soil science (25), with glassy (rigid) and rubbery (soft) domains. The sorption capacity of the expandable rubbery phase is much larger than that of the glassy phase. (c) Structural model derived in ref 20 from solid-state NMR experiments.

(#2S101H); (c) IHSS Suwannee River fulvic acid (FA) Standard II (#2S101F); (d) IHSS (Pahokee, Florida) peat (#2BS103P), (e) IHSS Florida peat HA standard (#1S103H); (f) IHSS (Elliot) soil HA standard (#1S102H); and (g) IHSS Leonardite HA standard (#1S104H). The details of the standard samples can be found on the IHSS homepage <http://www.ihss.gatech.edu/>.

A synthetic random copolymer, poly(styrene - *n*-butyl methacrylate) (PS-*n*BMA), used as a reference compound in ^1H spin diffusion experiments, was purchased from Scientific Polymer Products, Inc., Ontario, New York.

Water Content Measurement. A standard AOAC (Association of Official Analytical Chemistry) method for moisture content analysis (26) was applied to samples exposed to ambient humidity, which exhibit a narrow ^1H NMR resonance attributable to H_2O . A sample was weighed into a preweighed dried bottle and then dried at 105°C in an oven overnight. The bottle with the sample was then cooled in a desiccator for half an hour before being weighed again. The water lost (in g) was converted to the percent moisture content. The following moisture contents were found: IHSS peat, 14.1%; IHSS peat HA, 12.3%; IHSS soil HA, 9.5%; and IHSS Suwannee River natural organic matter, 10.4%.

NMR Experiments. Solid-state NMR experiments were performed on an Avance-400 spectrometer (Bruker Biospin, Billerica MA) at 400-MHz ^1H and 100-MHz ^{13}C frequencies. ^1H data were obtained using a commercial ^1H CRAMPS (combined rotation and multiple-pulse spectroscopy) probehead (Bruker Biospin) with a 4-mm diameter coil and low electric quality factor Q that permits acquisition of ^1H wide-line spectra with little distortion by probehead deadtime. ^1H dipolar transverse (T_2) relaxation was measured with a 90° -pulse- τ - 180° -pulse- τ -detection sequence. The 180° pulse was phase-cycled according to the EXORCYCLE scheme (27).

^1H - ^{13}C experiments were performed in a Bruker double-resonance magic-angle-spinning probehead with 7-mm diameter coil, at a spinning frequency of 6.5 kHz. TOSS (total suppression of sidebands) by four 180° pulses was applied before ^{13}C detection. ^1H - ^{13}C wide-line separation (WISE) experiments (28) were performed with ^{13}C decoupling during evolution (29) and with 200 μs of Lee-Goldburg cross polarization (LGCP), which minimizes spin diffusion. The t_1 -dimension was incremented in 28 steps of 5 μs . ^1H - ^{13}C heteronuclear correlation (HETCOR) experiments were run with frequency-switched Lee-Goldburg homonuclear ^1H decoupling (30) in the t_1 dimension and 80 μs of LGCP to prevent any long-range transfers during CP. Spinning speed: 6.5 kHz; recycle delay: 0.5 s; LGCP duration: 80 μs ; 160 t_1 slices; scans per t_1 slice: 208 for regular HETCOR, 128 with chemical-shift filter added. Spectral intensities used in the spin diffusion analysis have been corrected for ^1H T_1

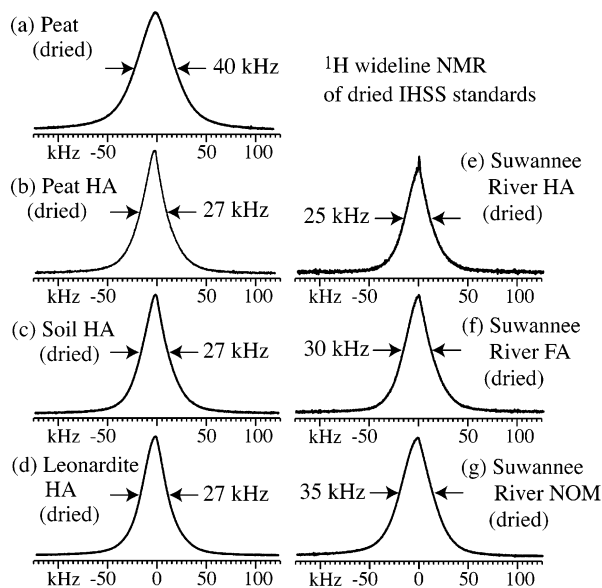


FIGURE 2. Mobility assessment in dry IHSS standard humic substances by ^1H wide-line spectra with probehead background suppression (31), without sample rotation. (a) IHSS peat; (b) IHSS peat HA; (c) IHSS soil HA; (d) IHSS Leonardite HA; (e) IHSS Suwannee River HA; (f) IHSS Suwannee River FA; (g) IHSS Suwannee River NOM. The full width at half-maximum is indicated for each spectrum. For probehead background-suppression, two experiments were run: one with a ^1H 90° pulse length of 3 μs and another with 6 μs . The second spectrum was scaled by one half and subtracted from the first to yield the background-free spectrum. Recycle delay: 1 s; number of scans: 64 for all, except IHSS peat HA for which 128 scans were used.

(spin-lattice) relaxation during the spin-diffusion time, based on separate ^1H T_1 -relaxation measurements.

^1H Probehead Background Suppression. The CRAMPS probehead is designed to have a low background signal from ^1H in the material surrounding the NMR coil. A residual probehead background signal was suppressed by the simple and reliable scheme of ref 31. In short, two one-pulse spectra, with pulse flip angles of β and 2β (e.g., 90° and 180°), are acquired. The essentially background-free spectrum is obtained by subtracting the second spectrum, scaled by 0.5, from the first.

Results and Discussion

Immobility and Absorbed water. Figure 2 shows ^1H wide-line NMR spectra of seven IHSS standard humic substances that had been freeze-dried and prevented from exposure to ambient moisture. These static ^1H spectra reflect dipolar

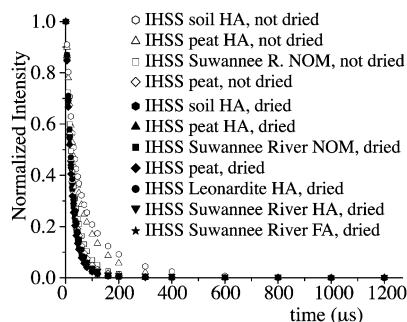


FIGURE 3. Mobility assessment by ^1H T_2 measurements without sample rotation, similar to Fig. 3 of ref 19. Data from samples rigorously dried shortly before the NMR experiments are shown with filled symbols, while those from samples initially freeze-dried but then exposed to ambient moisture for several months ("not dried") are represented by open symbols. Triangles: IHSS peat HA; hexagons: IHSS soil HA; squares: IHSS Suwannee River NOM; diamonds: IHSS peat; Circles: IHSS Leonardite HA; reversed triangles: IHSS Suwannee River HA; stars: IHSS Suwannee River FA. Only samples exposed to moisture from the air (open symbols) show a slow-decaying, mobile component as observed in ref 19. 24 experiments with different τ values were run for each sample. For each experiment, the recycle delay was 1 s; the ^1H 90° pulse length, 3 μs ; the number of scans, 128.

couplings between protons. These depend somewhat on the local proton density, but it is safe to say that line widths >25 kHz prove that the segments probed are not undergoing fast large-amplitude motions, while liquidlike or rubbery components would exhibit significant motional narrowing. Examples of such a narrowed peak, due to absorbed water, can be seen in Figures 4b and d below. The broad spectra in Figure 2, whose peak areas are quantitative, are consistent only with small amounts of narrow bands from rubbery components. We had previously shown that in many humic substances, 2–9 wt % of the organic fraction are mobile nonpolar aliphatic domains, including $(-\text{CH}_2-)_n$ segments (20). The spectra of Figure 2 clearly preclude the presence of $>40\%$ of mobile domains that were claimed in ref 19. Note that the peat HA used in ref 19 and the IHSS peat HA studied here are virtually identical materials.

To make this point more clearly, Figure 3 plots ^1H T_2 data of the IHSS materials in a graph directly comparable to the plot of the untreated HA in Fig. 3 of ref 19. For the dry samples (filled symbols), no significant slow-decaying component ($<0.5\%$) is detected at $t > 200 \mu\text{s}$, while ref. 19 shows such a component at a level $>10\%$. Their mobile component may be due to background signals from rubbery materials in the NMR probehead. Another possible origin of this mobile component is revealed by the T_2 data of samples that had not been kept sealed from the air. These data, shown by open symbols, indeed display a long T_2 component, which must be attributed to water in the sample. The mobile fraction in the T_2 data and the peak area fraction of the narrow component in the ^1H wide-line spectra of Figure 4 is consistent with the water content of 9–14% measured by gravimetry.

The narrow signal has a chemical shift of 5.3 ppm relative to tetramethylsilane, which is inconsistent with aromatic H, aliphatic H, or OCH protons in carbohydrates. It is only 0.4 ppm downfield from liquid water. In fact, dissolved water can have widely varying chemical shifts. The slight downfield shift relative to pure water indicates somewhat stronger H-bonding to acid groups in the HAs than to other H_2O molecules in liquid water. The residual line broadening observed is homogeneous, indicating an intermediate motional rate ($\sim 10^6/\text{s}$). The rate can be estimated from the fast decay of spin-locked ^1H magnetization, on the order of 0.2

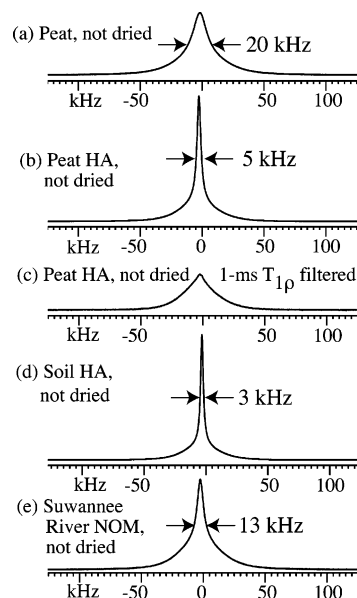


FIGURE 4. ^1H wide-line spectra of IHSS standard humic substances that had been freeze-dried but not prevented from re-absorbing moisture from the air for several months before the NMR measurements. (a) IHSS peat, (b) IHSS peat HA, (c) IHSS peat HA after a 1-ms $T_{1\rho}$ filter, which suppresses the signal of the mobile component, (d) IHSS soil HA, and (e) IHSS Suwannee River NOM. Except for experiment (c), the probehead background suppression described in the caption of Figure 2 was applied. Recycle delay: 1 s; scans: 64. The spectrum in (c) was run with a 1-s recycle delay after a 1-ms spin lock for $T_{1\rho}$ filtering.

ms. Figure 4c demonstrates the suppression of the H_2O peak after a 1-ms spin lock. This means that this mobile component is near the $T_{1\rho}$ minimum, which occurs at motional rates of around $k = \gamma B_1 = 2\pi 60 \text{ kHz} = 380 \text{ kHz}$, where γ is the ^1H gyromagnetic ratio and B_1 is the radio frequency field strength. We have observed very similar behavior for "bound" water in certain synthetic polymers (unpublished).

Site-Resolved ^1H Dipolar Couplings. In ref 19, it was suggested that the ^1H - ^1H dipolar couplings of the carbohydrate protons are reduced due to segmental mobility in expanded domains, while the aromatic protons are in condensed domains and, therefore, have larger line widths. This hypothesis can be tested by measuring the ^1H line shapes of the carbohydrate and aromatic protons separately, using wide-line (WISE) NMR (28), which provides the ^1H wide-line spectrum in the first dimension for each protonated-carbon signal detected in the second (^{13}C) dimension. The effect of the absorbed water on segmental mobility of the various chemical groups in the humic substances can also be assessed in this way. Figure 5 compares the ^1H wide-line patterns extracted from WISE spectra of dry and moist IHSS peat humic acid at various ^{13}C peak positions. Similar line width data were obtained for IHSS soil (mollisol) humic acid (spectra not shown due to space limitations). The data show that the line widths of the OCH protons are consistently larger than those of the aromatic protons, which precludes fast, large-amplitude, motions of carbohydrates. The reduced line width of the aromatic protons is most likely a result of the smaller local proton density at the aromatic rings; many of these are substituted by multiple oxygens or carbons, which reduces the average number of protons bonded to a ring to three or fewer.

Only small reductions of line width are observed in Figure 5 going from the dry to the moist sample. The predominantly broad ^1H pattern of the OCH segments in the moist samples proves that most of the polar segments are still not moving with large amplitudes. In other words, they have not been

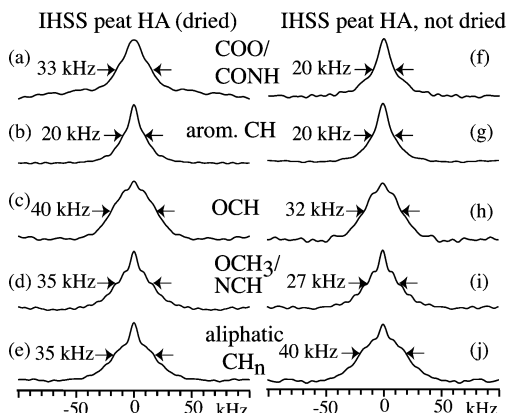


FIGURE 5. ^1H cross sections from ^1H - ^{13}C wide-line separation (WISE) spectra of IHSS peat HA (a–e) dried and (f–j) not dried. (a and f): At the COO/CONH peak; (b and g): protonated aromatics; (c and h): O-alkyl; (d and i): OCH_3/NCH ; and (e and j): nonpolar aliphatics. The LGCP contact time was $200\ \mu\text{s}$; $40\ t_1$ increments of $5\ \mu\text{s}$ were used; the recycle delay was $0.5\ \text{s}$, the spinning speed, $6.5\ \text{kHz}$. The number of scans per t_1 increment was 3584 for the dried sample and 2048 for the sample that was not dried.

plasticized (made rubbery) by the absorbed water. Thus, even with some water present, flexible carbohydrate domains do not exist.

Degree of Mixing of Humic Components. Most interpretations of nonpolar-contaminant sorption in humics explicitly or implicitly postulate the presence of domains of nonpolar aromatic (7, 8, 14), carbohydrate/polar alkyl (19), or nonpolar alkyl (6, 20) segments, into which contaminants could partition. Only nonpolar aliphatic domains have been proven experimentally (20, 21). Here, we disprove the presence of carbohydrate domains, suggested in ref 19 based on sorption and bleaching studies, using ^1H - ^{13}C heteronuclear-correlation (HETCOR) NMR with ^1H spin diffusion, which can probe domains on a 0.5 – $30\ \text{nm}$ scale (32). Spin diffusion is the diffusion of ^1H z-magnetization; it equilibrates magnetization faster in small heterogeneities, and more slowly in larger domains. This process can be observed in terms of changes in the NMR peak intensities with spin-diffusion time. For instance, in the ^1H - ^{13}C HETCOR spectrum, ^1H diffusion from aromatic protons to polar alkyl domains can be detected in terms of a specific cross-peak at $7.5\ \text{ppm}$ in the ^1H and $70\ \text{ppm}$ in the ^{13}C dimension.

Figure 6 shows HETCOR NMR spectra, for three characteristic values of the spin-diffusion time (mixing time t_m) out of a series with 12 t_m values. At $t_m = 5\ \mu\text{s}$, only one-bond ^1H - ^{13}C correlations are observed, e.g., between aromatic protons and carbons. Within $200\ \mu\text{s}$, the spectral intensity pattern has dramatically changed, with additional intensity indicating correlations between all types of protons and carbons. After $2\ \text{ms}$, equilibration has been achieved, as indicated by equal patterns in cross sections at all ^1H or all ^{13}C frequencies, for all components except some nonpolar aliphatics (band near $30\ \text{ppm}$). The cross-peaks from aromatic H to alkyl C are confirmed clearly in the chemical-shift-filtered HETCOR spectra of Figure 6d–f, where the strong OCH proton band has been suppressed by a ^1H chemical-shift filter (32) before the ^1H evolution. Cross sections at the aromatic-proton frequency show the aromatic to alkyl spin diffusion even more clearly, and make it easier to present the full series of mixing times, see Figure 7; strong O-alkyl peaks (65 – $80\ \text{ppm}$) appear after $50\ \mu\text{s}$.

For a quantitative analysis, the integral intensities of the 65 – $80\ \text{ppm}$ OCH peak in the aromatic-proton cross sections of Figs. 7a and b have been plotted in Figure 8 as a function of $t_m^{1/2}$. Within a very short time, $t_m < 100\ \mu\text{s}$, half equilibration has been achieved. The corresponding data for the soil HA

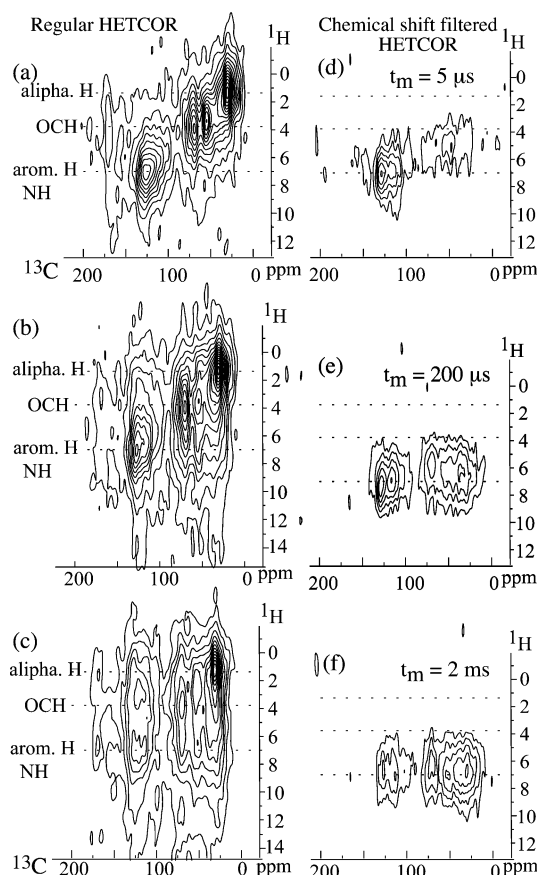


FIGURE 6. Measurements of component mixing by ^1H - ^{13}C HETCOR experiments with ^1H spin diffusion during t_m , applied to IHSS peat HA. (a–c): regular HETCOR and (d–f): HETCOR after ^1H chemical shift filter centered at the aromatic-proton resonance; this removes overlap from strong peaks at other ^1H resonance positions. (a and d): $t_m = 5\ \mu\text{s}$, showing signals only of directly bonded proton-carbon pairs. (b and e): $t_m = 200\ \mu\text{s}$, already showing major spin diffusion between different functional groups. (c and f): $t_m = 2000\ \mu\text{s}$, showing equilibration of magnetization (equal ^1H cross sections at all ^{13}C chemical-shift positions), except the nonpolar aliphatic segments which show a peak in the upper right corner of (c). Spinning speed: $6.5\ \text{kHz}$; LGCP duration: $80\ \mu\text{s}$; $160\ t_1$ slices.

are also plotted and display a similar behavior. For reference, we have performed the corresponding series of HETCOR experiments on a synthetic random copolymer, where mixing on the length scale of a few bonds is imposed by covalent bonding between the two types of monomer units (see structures in Figure 8b). The equilibration in the HAs occurs on the same time scale as in the copolymer, proving the extremely close proximity of aromatic and polar alkyl components in the HAs. As a reference for spin diffusion between real domains, we have also included data from ref 32, obtained for a 50:50 block copolymer (PS-*b*-PMMA, $18\ \text{kg/mol}$); the domain size in this system is $5 \pm 1\ \text{nm}$ and the long period is $10 \pm 3\ \text{nm}$ (32). It is clearly seen that equilibration of ^1H magnetization between domains on this 5-nm size scale is much slower than the spin exchange in the HAs.

By all standards, the equilibration between aromatic and polar alkyl segments observed in the humic acids is extremely fast. It indicates close proximity of aromatic rings and most, if not all, O-alkyl segments on a 1-nm scale and thus excludes carbohydrate domains. It also precludes the presence of significant nonpolar aromatic domains in the peat HA.

It is interesting to note that at $t_m = 2\ \text{ms}$ (see Figure 6c), the nonpolar aliphatic components, near 1.5 and $30\ \text{ppm}$ in the ^1H and ^{13}C dimensions, respectively, exhibit a pronounced

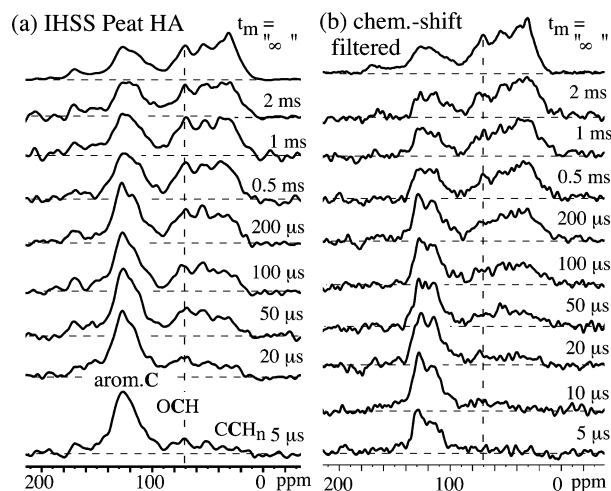


FIGURE 7. (a) Cross sections from 2D HETCOR spectra as shown in Figure 6a-c, taken at the aromatic-proton resonance position, for different mixing times. Spin diffusion from the aromatic protons to O-alkyl segments goes to completion within 1 ms. Sample: IHSS peat HA (dried). (b) Similar to (a), but from HETCOR spectra preceded by the ^1H chemical-shift filter as in Figure 6d-f.

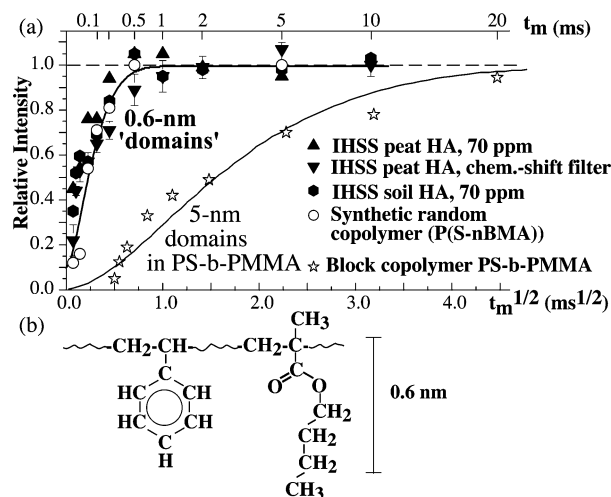


FIGURE 8. (a) Plot of OCH (O-alkyl) peak intensities in the aromatic-proton cross sections shown in Figure 7 as a function of the square-root of the spin-diffusion time t_m . This shows spin diffusion from aromatic protons to O-alkyl segments. Filled triangles: Signal intensities at 70 ppm (OCH) for the IHSS peat humic acid. Filled inverted triangles: Signal intensities at 70 ppm (OCH) for the IHSS peat humic acid with chemical shift filter. Filled hexagons: Signal intensities at 70 ppm (OCH) for IHSS soil humic acid (spectra not shown). Open circles: Signal intensity at 63.6 ppm for a synthetic random copolymer poly(styrene-*n*BMA); the monomer structures are shown in (b). Open stars: data from ref 32 included here for reference, obtained for a 50:50 block copolymer (PS-*b*-PMMA); the domain size in this system is 5 nm, the long period 10 nm. The fast spin diffusion in the humic acids, which is similar to that in the synthetic random copolymer, indicates monomer-length-scale (<1 nm) mixing of aromatic and carbohydrate components in the humic acids. (b) Schematic representation of the monomer units in the poly(styrene-*n*BMA) random copolymer, with an approximate length scale indicated.

self-correlation peak which shows that they have not fully equilibrated with the other protons in the system. This confirms the presence of a small amount of nonpolar aliphatic domains, as detected and quantified in our previous work on phenanthrene sorption (20).

Implications for Contaminant Sorption. The dual-mode model of sorption, as interpreted in soil science, assumes

the presence of rubbery (mobile) domains into which contaminants can partition. While glassy and rubbery domains do not coexist in a homogeneous polymer (which is either above or below its glass-rubber transition temperature), rubbery and glassy components of different compositions can coexist in humic substances. If the rubbery components are nonpolar and sufficiently abundant, nonpolar contaminants will partition into them. We had shown previously (20) that, indeed, rubbery nonpolar aliphatic domains account for 2 to 9% of various humic substances, and that their amount correlates with the phenanthrene sorption capacity. A schematic representation of these domains is shown in Figure 1c. Chefetz, Hatcher, and co-workers (6, 16, 17) have confirmed that plant-derived nonpolar aliphatic polymers with mobile components readily absorb nonpolar aromatic contaminants such as pyrene or phenanthrene, with sorption coefficients almost as high as those of activated black carbon. Significant amounts of, supposedly highly mobile, carbohydrate domains in humic substances, as postulated in ref 19, are excluded by the mobility and spin-diffusion data shown in the present work.

Acknowledgments

This work was supported by the National Science Foundation (grant CHE-0138117). The authors thank Drs. Paul Bloom and Ed Clapp for making several of the IHSS standard samples available.

Literature Cited

- Weber, W. J., Jr.; Huang, W., A distributed reactivity model for sorption by soils and sediments. 4. Intraparticle heterogeneity and phase-distribution relationships under nonequilibrium conditions. *Environ. Sci. Technol.* **1996**, *30*, 881.
- Weber, W. J., Jr.; Huang, W.; Yu, H., Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments. 2. Effects of soil organic matter heterogeneity. *J. Contam. Hydrol.* **1998**, *31*, 149.
- Schwarzenbach, R. P.; Westall, J., Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.* **1981**, *15*, 1360.
- Mingelgrin, U.; Gerstl, Z., Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. *J. Environ. Qual.* **1983**, *12*, 1.
- Carmo, A. M.; Hundal, L. S.; Thompson, M. L., Sorption of hydrophobic organic compounds by soil materials: Application of unit equivalent Freundlich coefficients. *Environ. Sci. Technol.* **2000**, *34*, 4363.
- Chefetz, B.; Deshmukh, A. P.; Hatcher, P. G.; Guthrie, E. A., Pyrene sorption by natural organic matter. *Environ. Sci. Technol.* **2000**, *34*, 2925.
- Chin, Y.-P.; Aiken, G. R.; Danielsen, K. M., Binding of pyrene to aquatic and commercial humic substances: the role of molecular weight and aromaticity. *Environ. Sci. Technol.* **1997**, *31*, 1630.
- Chiou, C. T.; McGroddy, S. E.; Kile, D. E., Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. *Environ. Sci. Technol.* **1998**, *32*, 264.
- Karickhoff, S. W.; Brown, D. S.; Scott, T. A., Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **1979**, *13*, 241.
- Kile, D. E.; Chiou, C. T.; Zhou, H.; Li, H.; Xu, O., Partition of nonpolar organic pollutants from water to soil and sediment organic matter. *Environ. Sci. Technol.* **1995**, *29*, 1401.
- Kile, D. E.; Wershaw, R. L.; Chiou, C. T., Correlation of soil and sediment organic matter polarity to aqueous sorption of nonionic compounds. *Environ. Sci. Technol.* **1999**, *33*, 2053.
- Kohl, S. D.; Toscano, P. J.; Hou, W.; Rice, J. A., Solid-state ^{19}F NMR investigation of hexafluorobenzene sorption to soil organic matter. *Environ. Sci. Technol.* **2000**, *24*, 204.
- Luthy, R. G., et al., Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* **1997**, *31*, 3341.
- Perminova, I. V.; Nataliya Yu, G.; Petrosyan, V. S., Relationships between structure and binding affinity of humic substances for polycyclic aromatic hydrocarbons: relevance of molecular descriptors. *Environ. Sci. Technol.* **1999**, *33*, 3781.

- (15) Rutherford, D. W.; Chiou, C. T.; Kile, D. E., Influence of soil organic matter composition on the partition of organic compounds. *Environ. Sci. Technol.* **1992**, 26, 336.
- (16) Chefetz, B., Sorption of phenanthrene and atrazine by plant cuticular fractions. *Environ. Toxicol. Chem.* **2003**, 22, 2492.
- (17) Salloum, M. J.; Chefetz, B.; Hatcher, P. G., Phenanthrene sorption by aliphatic-rich natural organic matter. *Environ. Sci. Technol.* **2002**, 36, 1953. Sachleben, J. R.; Chefetz, B.; Deshmukh, A.; Hatcher, P. G., Solid-state NMR characterization of pyrene-cuticular matter interactions. *Environ. Sci. Technol.* **2004**, 38, 4369.
- (18) Xiong, J.; Lock, H.; Chung, I.-S.; Keeler, C.; Maciel, G. E., Local Motions of organic pollutants in soil components, as studied by ^2H NMR. *Environ. Sci. Technol.* **1999**, 33, 2224.
- (19) Gunasekara, A. S.; Simpson, M. J.; Xing, B., Identification and characterization of sorption domains in soil organic matter using structurally modified humic acids. *Environ. Sci. Technol.* **2003**, 37, 852.
- (20) Mao, J.-D.; Hundal, L. S.; Thompson, M. L.; Schmidt-Rohr, K., Correlation of poly(methylene)-rich aliphatic domains in humic substances with sorption of a nonpolar organic contaminant, phenanthrene. *Environ. Sci. Technol.* **2002**, 36, 929.
- (21) Hu, W.-G.; Mao, J.-D.; Xing, B.; Schmidt-Rohr, K., Poly(methylene) crystallites in humic substances detected by nuclear magnetic resonance. *Environ. Sci. Technol.* **2000**, 34, 530.
- (22) *The Physics of Glassy Polymers*; Haward, R. N., Ed.; John Wiley & Sons: New York, 1973.
- (23) Horas, J. A.; Nieto, F., A Generalization of Dual Mode Transport Theory for Glassy Polymers. *J. Polym. Sci. B* **1994**, 32, 1889.
- (24) Vieth, W. R.; Howell, J. M.; Hsieh, J. H., Dual Sorption Theory. *J. Membr. Sci.* **1976**, 1, 177.
- (25) Xing, B.; Pignatello, J. J., Dual-mode sorption of low-polarity compounds in glassy Poly(Vinyl chloride) and soil organic matter. *Environ. Sci. Technol.* **1997**, 31, 792.
- (26) AOAC Method: Ash and Moisture Content. In. *Official Methods of Analysis*. 15th ed.; Association of Official Analytical Chemists: Arlington, Virginia, USA, 1990; p. 777.
- (27) Mao, J. D.; Schmidt-Rohr, K., Accurate quantification of aromaticity and nonprotonated aromatic carbon fraction in natural organic matter by C-13 solid-state nuclear magnetic resonance. *Environ. Sci. Technol.* **2004**, 38, 2680.
- (28) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W., Correlation of structure, mobility, and morphological information in heterogeneous polymer materials by two-dimensional wide-line-separation NMR spectroscopy. *Macromolecules* **1992**, 25, 3273.
- (29) Tekely, P.; Palmas, P.; Mutzenhardt, P., Elimination of heteronuclear dipolar interactions from carbon-13-detected proton spectra in wide-line-separation nuclear magnetic resonance spectroscopy. *Macromolecules* **1993**, 26, 7363.
- (30) Bielecki, A.; Kolbert, A. C.; Levitt, M. H., Frequency-switched pulse sequences: Homonuclear decoupling and dilute spin NMR in solids. *Chem. Phys. Lett.* **1989**, 155, 341.
- (31) Chen, Q.; Hou, S. S.; Schmidt-Rohr, K., A simple scheme for probehead background suppression in one-pulse ^1H NMR. *Solid State Nucl. Magn. Reson.* **2004**, 26, 11.
- (32) Clauss, J.; Schmidt-Rohr, K.; Spiess, H. W., Determination of domain size in heterogeneous polymers by solid-state NMR. *Acta Polym.* **1993**, 44, 1.

Received for review June 16, 2005. Revised manuscript received October 28, 2005. Accepted January 16, 2006.

ES0511467