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Evaluation of the Glassy/Rubbery Model for Soil Organic Matter

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The glassy/rubbery model for soil organic matter (SOM) has been proposed to explain nonlinear sorption uptake isotherms, site-specific bisolute competition, increased isotherm nonlinearity with increasing uptake time, and desorption hysteresis observed for nonspecifically interacting solutes. The glassy SOM phase has been considered the locus of this nonlinear sorption behavior and of greater sorption (increased Freundlich constant K_f or Langmuir capacity term) as contrasted with the rubbery phase. The report of a glass transition in Aldrich humic acid has been considered the linchpin of this model. In the current analysis, a number of points are made, including (i) a glassy polymer phase does not necessarily result in nonlinear sorption behavior; (ii) Aldrich humic acid, kerogen, and coal are poor models for soil organic matter; and (iii) a number of different mechanisms may result in nonpartitioning-like sorption behavior, such as complex formation with an organic matter macromolecule, interactions at the surface of organic matter, or cross-linking of organic matter macromolecules resulting in a finite sorption domain.

Introduction

Linear sorption uptake isotherms for many compounds, sorption enthalpies more positive than corresponding condensation enthalpies, and a strong correlation between sorption distribution coefficients and solute aqueous solubilities (or supercooled liquid aqueous solubilities) were initially interpreted as evidence for partitioning of organic solutes into soil organic matter (SOM) (1). The theory that SOM provides a partitioning medium for organic solutes has been supported by many subsequent observations of linear uptake isotherms, nonhysteretic desorption behavior, and noncompetitive sorption for nonpolar solutes, despite certain caveats concerning its general applicability (2).

Recently, several studies have reported nonlinear uptake isotherms (Freundlich exponent < 1) on SOM for nonpolar solutes such as phenanthrene and 1,3-dichlorobenzene (3–7). Likewise there have been reports of bisolute competition (8, 9), increased isotherm nonlinearity with increasing uptake time (4, 10), and desorption hysteresis (11–13). To explain these observations (of what may be termed nonpartitioning-like sorption behavior), it has been proposed that SOM consists of glassy and rubbery regions in analogy to glassy and rubbery polymers. The glassy phase of SOM has been considered to provide a site-specific sorption domain and thus to be the locus of nonpartitioning-like sorption behavior (3, 5–7). It has been also considered to provide greater sorption capacity (increased Freundlich constant K_f or

Langmuir capacity term) as contrasted with the rubbery phase (3, 5–7, 13).

Glassy and rubbery polymer phases are distinguished by degree of macromolecular fragment mobility where the rubbery phase has greater mobility and flexibility than does the more rigid glassy phase (14). A glassy phase of a polymer is a nonequilibrium phase consisting of a supercooled amorphous liquid and is distinct from equilibrium phases, which may be rubbery, crystalline, or microcrystalline (15). A cross-linked polymer may be either rubbery or glassy, but cross-linking substantially reduces the possibility for crystallization (16). A transition from glassy to rubbery phase is characterized by a narrow temperature region (T_g) in which a sharp increase in macromolecular fragment mobility occurs (16).

One basis for the argument that soil organic matter may have glassy regions is the observed differential scanning calorimetric (DSC) transition measured for Aldrich humic acid (6). Two main points will be considered here: (a) Does a glassy phase necessarily result in nonpartitioning-like sorption behavior for nonspecifically interacting solutes and (b) What is the nature of the nonlinear sorption domain in SOM?

Glassy Phase and Nonspecifically Interacting Sorbate Behavior

Sorption Energetics and Temperature-Dependent Sorption Capacity. To develop and support the glassy/rubbery model of SOM, sorption of phenanthrene at different temperatures on natural organic materials and isosteric heats of phenanthrene sorption on several polymers in glassy and rubbery phases were reported (e.g., refs 3, 6, 17, and 18). Isosteric heat, determined using the Clausius–Clapeyron equation, represents the enthalpy change for solute transfer from some standard state (such as infinite dilution or supercooled liquid) to the sorbed state at some uptake. The approach for measuring isosteric heats of sorption referred to the supercooled liquid state as summarized in ref 18 needs clarification. It was therein claimed that only sorption enthalpies referred to the pure supercooled liquid state can be considered accurate and to have the correct sign. This argument is erroneous in that enthalpy may be compared with *any* standard state including infinite dilution; any reported sorption enthalpy has meaning (assuming it is measured correctly and that variability is small) when referenced to a well-defined standard state. The difference between the infinite dilution and supercooled liquid standard states is represented by the transfer enthalpy of the compound from the supercooled liquid state to aqueous solution (solution enthalpy of a liquid compound). The importance of considering solution enthalpies in water has been recognized for years in the environmental chemistry literature (e.g., refs 1 and 19–21). For example, in ref 21, measured sorption enthalpies were explicitly corrected for solution enthalpies in water (ref 21, p 1085); this important point was ignored in ref 18 (p 3242).

Isosteric heats of sorption referred to the pure supercooled liquid were recently reported for phenanthrene on poly(butyl methacrylate) (PBMA), an amorphous polymer with a reported glass transition temperature (T_g) of 20 °C (17). Sorption was measured at temperatures spanning the T_g (between 5 and 45 °C) and, accordingly, in both glassy and rubbery polymer phases (Figure 1A). The data were reported as natural log activity in the solution phase versus inverse temperature at five different uptakes (Figure 1A). Since

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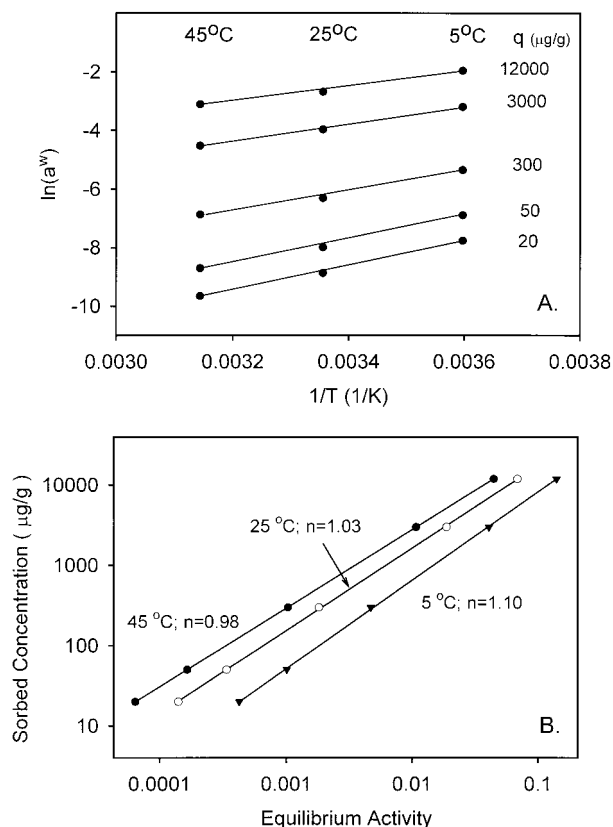


FIGURE 1. (A) Natural log activities ($\ln a^w$) of phenanthrene in the equilibrium aqueous phase plotted versus inverse temperature ($1/T$) at five different sorption uptake levels (q) on PBMA. Data from ref 14. (B) Sorption of phenanthrene on PBMA at 5, 25, and 45 °C plotted against equilibrium solution activity. The values for n represent the Freundlich exponent.

systems were in apparent sorption equilibrium, compound activity in the solid phase was the same as its activity in the aqueous phase.

From the data reported, it is possible to reconstruct the sorption isotherms as sorbed phase concentration versus compound activity in solution (Figure 1B). It is clear that the three isotherms are linear or have a Freundlich exponent slightly greater than unity in both glassy (5 °C) and rubbery PBMA phases (25 and 45 °C) (Figure 1B). As such, even a highly structured, repeating polymer with a well-known transition point will not necessarily demonstrate nonlinear (Freundlich exponent < 1) sorption in the glassy state.

Additionally, at any given loading, the natural log of compound activity in both glassy and rubbery phases form a single trend spanning the studied temperatures (Figure 1A). This indicates that sorption enthalpy is the same for both rubbery and glassy PBMA. This observation corresponds well to the fact that simple gases exhibit approximately the same linear dependencies of solution enthalpy and solubility on gas Lennard–Jones temperature in both rubbery and glassy polymer phases, with some reduction of solubility in the glassy state (ref 22, p 541).

Since compound activities in both glassy and rubbery phases form a single trend at a given uptake and display no discontinuities (Figure 1A), it is possible to predict compound activity in the rubbery phase on the basis of compound activity in the glassy phase and vice versa. Thus the glassy phase of PBMA has no additional specific sites, or 'microvoids', for phenanthrene as compared with the rubbery phase under the experimental protocol.

The results for sorption of phenanthrene on PBMA may be compared with results for sorption of phenanthrene on

poly(isobutyl methacrylate) (PIMA), with a reported glass transition (T_g) at 50.4 °C (6). Sorption uptake on PIMA after 4 weeks at 5 °C was nonlinear, and the isotherm was interpreted using a dual-mode model with contributions from both a partitioning (linear) domain and a Langmuir (nonlinear) domain (6). Sorption after 4 weeks at 45 °C (below PIMA T_g) was linear (6). There are two possible explanations for this behavior. First, if adsorption is an exothermic process, an increase in temperature will result in decreased affinity, thus eliminating isotherm nonlinearity. Alternatively, despite the fact that PIMA at 45 °C is glassy, molecular motions may have been sufficiently free in the 4-week uptake interval for Langmuir sites to be eliminated, resulting in a linear isotherm. Because of the nonequilibrium nature of the glassy phase, the degree of isotherm linearity will be controlled by the interplay between glass relaxation time and time allotted for sorption. A system with a glass relaxation time \gg sorption time can achieve some apparent sorption equilibrium involving a nonlinear isotherm, whereas a system in which the glass relaxation time is comparable to the sorption time may demonstrate a linear sorption uptake isotherm. The relationship between characteristic time for solute diffusion and polymer molecular motions will determine if temporal and temperature-dependent sorption trends will be observed.

Sorption enthalpies referred to the pure supercooled liquid between 5 and 45 °C were reported for phenanthrene on rubbery cellulose ($T_g = -45$ °C) and on two glassy substrates: poly(phenyl methacrylate) ($T_g = 110$ °C) and Illinois no. 6 coal ($T_g = 355$ °C) (17). For rubbery cellulose and glassy coal, reported isosteric heats are indistinguishable within the reported error range (rubbery cellulose average heats and standard error vary from 9 ± 20 to 7 ± 18 kJ/mol; glassy coal average heats and standard error vary from 12 ± 22 to 13 ± 2 kJ/mol). Therefore, no effect of solute loading on sorption enthalpy was observed. The isosteric heats of phenanthrene sorption on PBMA, where a single value was determined for both rubbery and glassy phases, are comparable to or more exothermic than those determined for glassy poly(phenyl methacrylate) (PBMA average heats and standard error vary from 35 ± 2 to 22 ± 3 kJ/mol; poly(phenyl methacrylate) average heats and standard error vary from 47 ± 22 to 73 ± 2 kJ/mol) (17). In other words, phenanthrene sorption enthalpies on these different matrixes give no insight into the glassy or rubbery nature of the matrix or into sorption mechanisms. The point that sorption enthalpies are not useful for distinguishing sorption mechanisms in SOM has been discussed previously (2, 23).

Sorption uptake in humic substances has been shown to decrease as temperature increases (5, 6). Indeed, for sorption of phenanthrene from water by Aldrich humic acid, capacity was greater below the reported T_g (presumed glassy phase) than above the reported T_g (presumed rubbery phase) (6). In contrast to this sorption behavior in organic matter, sorption uptake of phenanthrene on rubbery PBMA was found to be greater than sorption uptake on glassy PBMA (17) (Figure 1B). Sorption uptake of 1,3-dichlorobenzene on rubbery poly(vinyl chloride) (PVC) ($T_g = 85$ °C) was similarly found to be greater than sorption uptake by glassy PVC (5). Sorption uptake of phenanthrene by PIMA near its T_g was reported to be greater than sorption uptake at lower temperatures (6). As such, there is no reason that a glassy phase should be considered the locus of greater sorption capacity in humic materials as suggested in the literature (3, 5–7). Indeed, by analogy to the polymers studied by these groups, a rubbery humic phase should provide greater sorption capacity than a glassy humic phase. Thus these glassy/rubbery polymers do not successfully model temperature-dependent sorption behavior in SOM.

Increasing Isotherm Nonlinearity with Increasing Uptake Time. Isotherms for 1,3-dichlorobenzene, 2,4-dichlo-

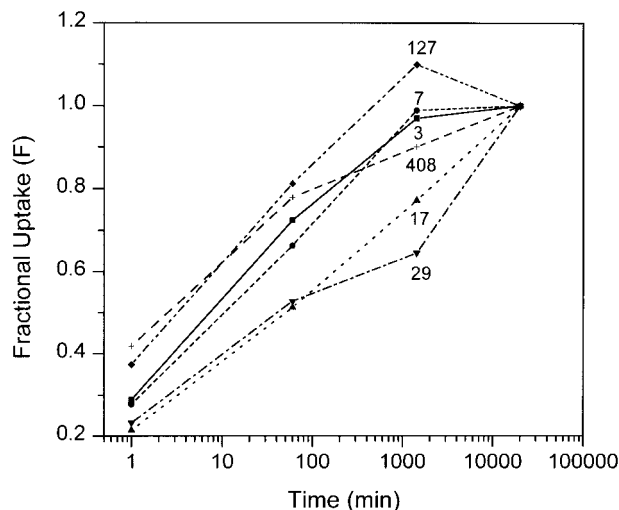


FIGURE 2. Fractional uptake (F) of phenanthrene on EPA-23 sediment plotted versus sorption uptake time at six different initial solution phase concentrations. The values indicated on the graph represent solution concentrations at 1 day (1440 min). Data scanned from isotherms in Figure 1, ref 10.

rophenol, and metolachlor in peat and soil (4) and phenanthrene in three sediments and a soil (10) were said to become increasingly nonlinear with increasing uptake time until equilibrium was attained. Nonequilibrium and equilibrium isotherms were described using the Freundlich model $S = K_f C^n$ (C is the solution concentration, K_f is the Freundlich constant, and n is the Freundlich exponent); the measure of isotherm nonlinearity was taken to be the Freundlich exponent n . Trends of decreasing n with increasing uptake time were interpreted to be a function of a nonhomogeneous sorption site distribution (glassy phase coated by rubbery phase) (5) or to result from faster rate of attainment of sorbed phase equilibrium in higher concentration solutions due to swelling of the macromolecular matrix (10). This method of using the Freundlich model for evaluating the rate of attainment of sorbed phase equilibrium is predicated on the assumption that the Freundlich model adequately describes all the data, including equilibrium and nonequilibrium isotherms. If the model provides a good description, then conclusions concerning rate of attainment of sorbed phase equilibrium based on the Freundlich model should be comparable to conclusions obtained from the standard method for evaluating rate of attaining equilibrium, or *fractional uptake*, as discussed in ref 24.

Fractional uptake (F) is defined (24) as the ratio of sorbed concentration at a given uptake time (S_t) to equilibrium sorbed concentration (S_e) [$F = S_t/S_e$] for different initial concentrations. Use of fractional uptake as a measure of rate of attainment of equilibrium is based on the assumption that the external solution phase is well stirred and that all rate-limiting processes occur only inside the solid phase. This approach can be used for external solutions of any volume and for systems exhibiting nonlinear sorption uptake isotherms (24).

Time-dependent isotherms for phenanthrene uptake on EPA-23 sediment (10) can be evaluated using the fractional uptake approach by scanning the reported data. Fractional uptake versus uptake time for six different initial concentrations is plotted in Figure 2. From the figure it is clear that there is no trend of fractional uptake with concentration, and thus no effect of concentration on rate of attainment of sorbed phase equilibrium. As such, these data may not be used to support an interpretation of faster approach to equilibrium in higher concentration solutions. Furthermore, the fact that there is no concentration effect on rate of

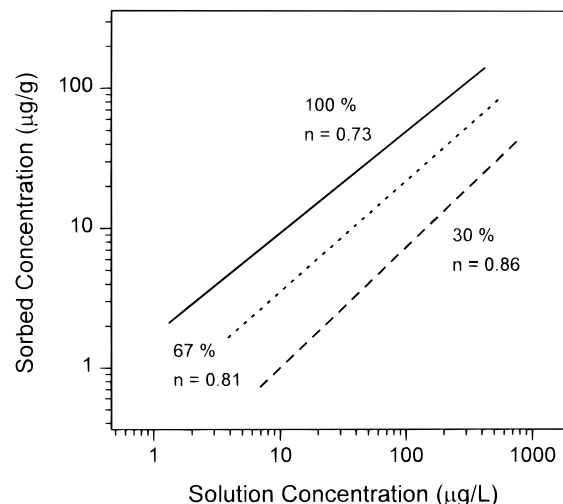


FIGURE 3. Generated isotherms based on reported 14-day Freundlich parameters for phenanthrene sorption on EPA-23 sediment (ref 10). Isotherms for 30% and 67% fractional uptake (representative of 1 min and 1 h uptake data, respectively) are generated using a concentration-independent approach, such that $S_x = X S_e$ and $C_x = (1 - X) k S_e + C_e$, where X is the fractional uptake, k is the solid-to-liquid ratio, S is the sorbed concentration, C is the solution concentration, and e is equilibrium.

attainment of sorbed phase equilibrium demonstrates that the Freundlich model does not provide an adequate description of the time-dependent isotherms. It can be proved that when fractional uptake is not concentration dependent and the Freundlich model describes equilibrium data, the Freundlich model does not describe nonequilibrium data (Appendix). As these temporal sorption data sets do not demonstrate any effect of solution concentration on the rate of attainment of sorbed phase concentration, there is no basis for the conclusion that the effective diffusion coefficient is concentration dependent.

When there is no effect of concentration on fractional uptake and the Freundlich model is mistakenly applied to nonequilibrium data, a trend of decreasing apparent n with increasing uptake time will be the natural outcome of the trivial fact that the approach to equilibrium involves a nonproportional shift in solution concentration range. This can be demonstrated graphically using, for example, reported equilibrium Freundlich parameters for 14-day sorption of phenanthrene on EPA-23 sediment ($\log K_f = 0.235$, $n = 0.727$; Table 2 from ref 10) and the scanned solution concentration range (1.5–390 $\mu\text{g/g}$). Solution and sorbed concentrations can be calculated for fractional uptakes of 30% and 67% (approximately representing 1 min and 1 h uptake data, respectively; ref 10), such that $S_x = X S_e$ and $C_x = (1 - X) k S_e + C_e$, where X is fractional uptake, k is solid-to-liquid ratio (1 g:300 mL), S is sorbed concentration, C is solution concentration, and e is equilibrium. It is clearly seen in Figure 3 that such generated isotherms have increasingly smaller n values with increasing approach to equilibrium and that generated n values are very similar to reported n values for approximately equivalent uptakes (for 67% uptake generated $n = 0.81$ and reported $n = 0.80$; for 30% uptake generated $n = 0.86$ and reported $n = 0.93$; reported n values from ref 10).

It is also possible to employ the fractional uptake measure to evaluate the rate of attainment of sorbed phase equilibrium for 2,4-dichlorophenol in peat and soil and for 1,3-dichlorobenzene in peat (data from ref 4) (Figure 4). In this figure, it can be seen that none of the data sets demonstrate a general trend of increasing fractional uptake with increasing solution phase concentration, over 5–6 orders of magnitude in

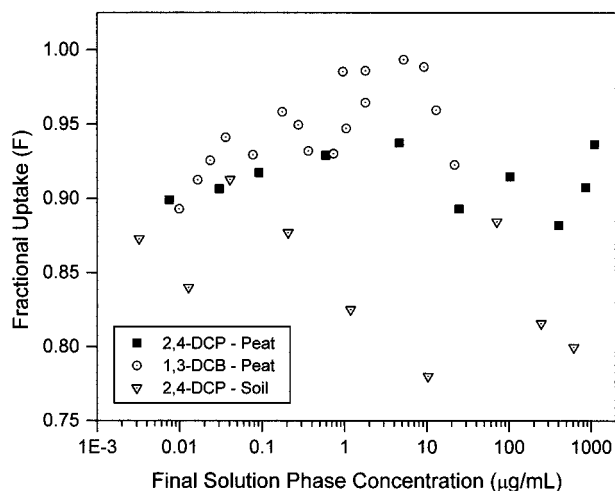


FIGURE 4. Fractional uptake (F) of 2,4-dichlorophenol (2,4-DCP) on peat, 1,3-dichlorobenzene (1,3-DCB) on peat, and 2,4-DCP on soil plotted versus final solution phase concentration. Isotherm data for 2,4-DCP and 1,3-DCB on peat were provided by the authors of ref 4; data for 2,4-DCP on soil was scanned directly from ref 4.

concentration range. As such, it is clear that the Freundlich model cannot provide an adequate description for these data sets and that trends in n cannot be considered mechanistically.

If a trend of increasing fractional uptake with increasing solution phase concentration would be demonstrated, then it would be possible to conclude that the effective diffusion coefficient was concentration-dependent, such as shown for CO_2 diffusion in polycarbonate (25). Then at any given time before reaching equilibrium, sorption from higher concentration solutions would be relatively closer to equilibrium (S_t/S_e) as compared with sorption from lower concentration solutions. With increasing uptake time, the relative approach to equilibrium in low concentration solutions would be less than in high concentration solutions, resulting in greater isotherm curvature and nonlinearity with increased uptake time. This behavior could be anticipated, following the dual-mode model development for diffusion coefficients (ref 22, Table 18.9), by the very virtue of the fact that sorption has a nonlinear Langmuir component. As such, the proffered explanation for concentration-dependent uptake, as swelling of the macromolecular matrix in high concentration solutions (10), is not necessary for understanding this phenomenon. If the approach to equilibrium is concentration-dependent because sorption has a nonlinear Langmuir component and the experimental protocol does not account for this effect, desorption hysteresis will be observed. This may be one of the many different factors resulting in apparent desorption hysteresis (see, for example, ref 26).

The Freundlich model has been commonly used to describe sorption uptake isotherms. The popular habit of presenting sorption data on a log-log plot and subsequent incomplete attention to the quality of description results in misapplication of the Freundlich model, including this inappropriate method for demonstrating time dependence of isotherm nonlinearity. There are many instances in the literature of poor Freundlich model fits to data, where poor model fits are obscured by the condensed scale and non-proportionally sized data points (e.g., 2,4-dichlorophenol uptake on peat after 1 day, Figure 2a from ref 4; 2,4-dichlorophenol uptake on soil after 180 days, Figure 3a from ref 4; 1,3-dichlorobenzene uptake on PVC after 15 days, Figure 4 from ref 4; phenanthrene uptake on muck, Figure 2 from ref 7; phenanthrene uptake on EPA-6, Figure 5 from ref 7; phenanthrene uptake on EPA-14, Figure 6 from ref 7;

phenanthrene uptake on EPA-23 at 14 days, Figure 1 from ref 10; phenanthrene uptake on PBMA after 5 h and 7 days, Figure 1 from ref 17; phenanthrene uptake on coal after 3 days, 42 days, and 3 months, Figure 2 from ref 17). The use of log-log plots is particularly misleading because very large deviations between model fit and data can be easily masked. Misapplication of a sorption model is considered problematic for at least two reasons. First, it is inappropriate to draw mechanistic conclusions on the basis of poor model fits. Second, mechanistically important information may be disregarded by applying the incorrect model. For example, sigmoidal sorption behavior may really indicate an uptake-related increase in sorption sites, where the use Langmuir or Freundlich models should be avoided completely.

What Is the Nature of the Nonlinear Sorption Domain in SOM?

Dissolved Organic Matter. Nonlinear sorption behavior for phenanthrene has been reported in different organic matter bearing solids (7, 13), but phenanthrene binding to dissolved organic matter has been reported to be linear (27–30). Thus, nonlinear sorption behavior for phenanthrene is presumably related to the solid phase as opposed to specific sites associated with individual macromolecules or micelles. Most reports of binding between nonspecifically interacting compounds and dissolved organic matter report linear isotherms (e.g., refs 27–33). However, a tendency toward nonlinear sorption isotherms for two polynuclear aromatic hydrocarbons, benzo[e]pyrene and benzo[k]fluoranthene, on water-soluble Aldrich humic acid and for benzo[k]fluoranthene on an additional sample of water-soluble natural humic materials is observable in data reported in ref 30. The range of dissolved organic carbon concentrations used in these experiments was between 10 and 30 mg C/L and thus far below any potential critical micelle concentration for humic substances (34, 35). Therefore, nonlinear sorption behavior for non-hydrogen bonding compounds may be exhibited without a solid state.

Surface Sorption. Not all nonlinear sorption behavior of nonspecifically interacting solutes in SOM can be considered necessarily to be a function of sorption inside the bulk phase. For example, the nonlinear portion of phenanthrene sorption by an organic matter-rich muck (7) may be explained by surface adsorption (36). Some calculations are instructive: The maximal external fractal surface capacity of the muck for phenanthrene was estimated to be 336 mg/kg on the basis of N_2 BET surface area (36). A Langmuir capacity term of 364 mg/kg (95% confidence interval = 155 mg/kg) obtained from a dual-mode model fitting for phenanthrene sorption from water (7) is comparable to the maximal external fractal surface capacity (36). This demonstrates that the muck external surface was sufficiently large to account for nonlinear sorption of phenanthrene, with no necessity of resorting to an interior glassy phase to explain nonlinear uptake. A similar observation can be made for data from ref 6 for phenanthrene sorption by Aldrich humic acid fit to the dual-mode model. The Aldrich humic acid Langmuir capacity reported for phenanthrene is approximately 3 times the muck Langmuir capacity for phenanthrene, while the humic acid N_2 BET surface area is greater by a factor of 4 than that of the muck (6). As such, the maximal external surface capacity of Aldrich humic acid was certainly capacious enough to account for nonlinear sorption of phenanthrene. In other words, nonlinear sorption behavior of phenanthrene in these materials does not exclude a surface adsorption mechanism and cannot be taken necessarily as evidence for a glassy domain, or indeed, for an internal site-specific domain. It was recently shown that, for large molecules such as atrazine and phenanthrene, maximal external surface capacity is the same or greater than capacities obtained for the Langmuir sorption

capacity term (36, 37). Small molecules, on the other hand, such as 1,3-dichlorobenzene, phenol, and pyridine, had Langmuir capacities that were significantly greater than maximal external surface capacities (36). These observations suggest that small molecules may be more suitable probes for interior site specificity than large molecules.

Discovery of a T_g in Aldrich Humic Acid. A DSC transition for purified Aldrich humic acid was interpreted to indicate that Aldrich humic acid has glassy regions (6). It is necessary to consider how well Aldrich humic acid represents SOM. Seven samples of commercial humic acids, including purified and original Aldrich humic acid sodium salt and Aldrich humic acid, were characterized using cross-polarization and magic-angle spinning ^{13}C NMR spectroscopy and elemental analysis (38). Numerous samples of humic and fulvic acids isolated from streams, soils, peat, leonardite (from coal), and dopplerite (a low rank coal) were also characterized for comparison. Cross-polarization and magic-angle spinning ^{13}C NMR spectroscopy showed clear pronounced differences between the commercial materials and noncommercial soil-derived humic materials, and as such, the use of commercial preparations, where provenance is unknown, in soil and water investigations was specifically discouraged (38). It was concluded that commercial humic acids such as Aldrich humic acid are similar to humic acids extracted from coals (leonardite and dopplerite). Coals are well-known to undergo glass transitions (39).

The idea that coal-derived humic acid can display a DSC transition is supported by the recent report of a DSC transition in leonardite humic acid obtained from the International Humic Substances Society (IHSS) (40). According to provenance information supplied by the IHSS, the leonardite sample was obtained from an oxidized coal seam (41). In contrast, no glass transitions for soil and peat-derived humic acids have been observed (6, 9). It should be recalled that the occurrence of a glassy phase does not specify that it will have any effect on sorption, as discussed above.

'Hard' versus 'Soft' Organic Matter. The glassy/rubbery conception for SOM as derived from the 'distributed reactivity theory' (3, 8, 9, 42) represents a continuation of the view that soil organic matter consists of soft carbon providing a partitioning domain and hard carbon providing a site-limited domain. The soft carbon domain was originally considered to be comprised of relatively young, oxidized humic materials while the hard carbon domain was thought to consist of aged, diagenetically altered organic material (geologic material) (42). Hard carbon was suggested to consist of more aromatic moieties with lower functionality than humic materials. The distributed reactivity series discusses the nature of hard carbon variably in terms of condensed, microcrystalline, aromatic, reduced, cross-linked, and glassy. However, these are not interchangeable terms. They represent important structural features of a solid that may have variable effects on organic compound sorption, depending on the compound and nature of the structural feature.

It was claimed that phenanthrene $\log K_{oc}$ values (K_d normalized to soil OC content) on kerogen and on peat and soil-derived humic materials demonstrated a linear trend with O/C atomic ratio in OM (13). This was taken to indicate a trend of increasing K_{oc} with increasing organic matter age. K_{oc} values were calculated from tabulated Freundlich isotherm parameters and OC contents (13). However, for two of the three isotherm data sets (adsorption and desorption) that were presented graphically (Figures 4–6, ref 13), the tabulated Freundlich model parameters (Table 2) do not correspond with the graphed data (Norwood shale and Norwood kerogen, Figures 5 and 6 respectively, ref 13). Sorbed concentrations calculated from given model parameters vary as much as 55% from sorbed concentrations depicted in the figures. For example, for Norwood shale at the highest

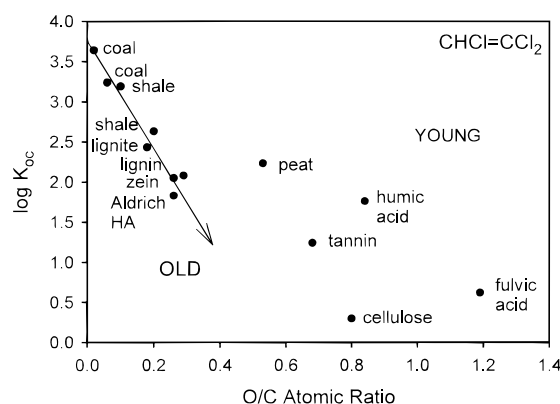


FIGURE 5. Trichloroethene $\log K_{oc}$ values plotted against O/C atomic ratio in organic matter. From data compiled in ref 43. Denoted line is empirical.

solution concentration, the Freundlich model calculated sorbed concentration was 11 100 $\mu\text{g/g}$ while the actual sorbed concentration (from Figure 5, ref 13) was approximately 8400 $\mu\text{g/g}$. For desorption from Norwood shale at a solution concentration of approximately 100 $\mu\text{g/L}$, the Freundlich model sorbed concentration can be calculated to be more than 7100 $\mu\text{g/g}$ while the sorbed concentration in the figure is approximately 4600 $\mu\text{g/g}$. Similar large deviations between model calculated sorbed concentrations and data presented in graphic form are evident for the Norwood kerogen. When K_{oc} values are recalculated as indicated in the text (using tabulated Freundlich model parameters and OC content; ref 13), the recalculated values do not correspond to the reported K_{oc} values (Table 2, ref 13). For example, tabulated K_{oc} at $C_e = 1000 \mu\text{g/L}$ is given as 136 L/g (Table 2, ref 13), while recalculation using the methodology indicated in the paper gives a K_{oc} value of 45 L/g. From the data given, it is not possible to determine if the tabulated parameters are in error or the figures are in error. However, as the tabulated parameters are clearly inconsistent with the data presented in the figures, and as there are discrepancies between K_{oc} values reported in Table 2 (and Figure 7, ref 13) and recalculated values based on reported parameters, it is impossible to make any conclusions about trends in K_{oc} values with O/C atomic ratio or with age. Similarly, the reported correlation between Freundlich n values and O/C atomic ratio is questionable. Finally, it can be determined that reported hysteresis index values (Table 2, ref 13) were calculated from the tabulated Freundlich model parameters. As these parameters are inconsistent with the data presented in the figures, the correlation presented between hysteresis index and O/C atomic ratio is also questionable.

In an attempt to determine the relationship (if any) between K_{oc} and organic matter age, data compiled in ref 43 for trichloroethylene (TCE) sorption in soils and organic materials of different ages and organic matter O/C atomic ratios were examined (Figure 5). In a plot of TCE $\log K_{oc}$ versus O/C atomic ratio (Figure 5), a distinct difference between TCE sorption behavior in geologic materials as compared with younger materials is observable. For geologic materials, O/C atomic ratio has a strong inverse linear relationship to $\log K_{oc}$ of TCE. In young organic matter, the relationship between K_{oc} and O/C atomic ratio is far more tenuous. In fact, $\log K_{oc}$ in young material appears to be much greater than expected on the basis of the trend delineated by geologic material. Thus, there does not appear to be any overall trend of K_{oc} with age or with O/C atomic ratio.

It is debatable whether geologic organic matter is an appropriate model for glassy/rubbery behavior in soil humic materials. Kerogen (representative of old or geologic organic

matter) consists of a carbon skeleton containing aromatic units joined by short aliphatic chains and containing principally oxygen and hydrogen heteroatoms (44, 45). X-ray studies have revealed regions of order (termed crystallites or microcrystallites) in coal and kerogen, interpreted in terms of planar aromatic units. Sorption in activated coal and carbon, for example, is considered to occur in the pore spaces between such microcrystallites (46). It seems therefore that microcrystallinity and resultant nonlinear sorption and high sorption capacity in kerogen should not be considered the same system as a glassy phase in young soil humic materials.

Molecular changes in soil organic matter as a function of soil age were characterized using elemental analysis, off-line pyrolysis, and pyrolysis-field ionization mass spectrometry (47). It was reported that soil organic matter in Pleistocene soils ranging in age from 9000 to greater than 20 000 years became increasingly enriched in aliphatic compounds with increasing soil age. This is in strict contrast to the increasingly aromatic character of coal with increasing diagenetic rank (44).

The function of condensed aromatic sheets in increased sorption is not at all clear from reported data. For example, in ref 12, a negative correlation based on four data points (two estimated variables) was reported between phenanthrene Freundlich constant and soil organic carbon content, using data from desorption isotherms in supercritical CO₂. In contrast, in a companion paper by the same authors (48), a positive correlation based on five data points (three estimated variables) between phenanthrene K_d (linear distribution coefficient) and soil organic carbon content was reported using data from desorption isotherms in supercritical CO₂ amended with methanol.

In geologic organic matter, high-sorption capacity and sorption nonlinearity may be explained by mechanisms other than an internal glassy state or condensed aromatic sheets. For example, strong, comparable nonlinear sorption isotherms on a molar basis were obtained for compounds from different classes (nonpolar *m*-xylene, polar ametryn, and ionized 2,4,6-tribromophenol) on relatively organic carbon rich-chalk (1.3% OC) (49). The organic matter was found to be largely composed of chain aliphatics (H/C equivalent of 6–7 methylene groups for every benzene ring) with low oxygen functionality (50). The comparable nonlinear sorption of ionized and neutral compounds to such hydrophobic organic matter was interpreted to indicate that sorption occurred at the surface interface, such that nonpolar moieties of sorbate molecules interacted at the hydrophobic surface and polar or ionized moieties (in the case of ametryn and 2,4,6-tribromophenol, respectively) interacted in the interface water phase. The observed adsorption of these compounds on such hydrophobic organic matter, rather than distribution inside the bulk, was suggestive that the organic matter was arranged as a monolayer on carbonate mineral surfaces (49). In other fine grained porous materials, organic matter also may be in part distributed as a thin layer on mineral surfaces resulting in non linear sorption behavior.

Polar Compound Sorption Domain. The glassy/rubbery conception as described in the recent soils literature cannot account for sorption behavior of H-bonding solutes in soil organic matter. In a recent study, it was shown that sorption uptake of phenol and pyridine from water was the same as their respective uptake from *n*-hexadecane at low solute activities, while at relatively higher solute activities, sorption uptake in aqueous systems was far greater than in non-aqueous systems (36). This was interpreted to reflect water-aided interruption of inter- and intramolecular contacts in organic matter macromolecules upon phenol and pyridine sorption. As nonpolar molecules do not show this effect (if anything, sorption uptake of nonpolar compounds in aqueous systems is less than in nonaqueous systems; refs 51 and

52), it was inferred that these contacts have a polar nature. Nonlinear sorption behavior of nonpolar solutes was considered to reflect a limited sorption domain imposed on nonpolar solutes by virtue of cross-linking at polar functional groups. It was hypothesized that such a limited domain may cause nonpartitioning-like behavior for nonpolar solutes, such as nonlinear sorption uptake and bisolute competition.

The sorption behavior of polar molecules such as phenol and pyridine can only be reconciled by the glassy/rubbery model through consideration of the polar nature of contacts and recourse to an extension of the dual-mode sorption model that includes the concept of plasticization of the glassy phase caused by sorption uptake. Plasticization occurs at some uptake of sorbate molecules at which secondary bonds along segments of polymer chains are broken, freeing up segments for increased mobility, as observed in ref 53. Such sorbate-induced plasticization obviates interpretations of sorption isotherms based on models such as Langmuir, which assumes a fixed number of sorption sites, or Freundlich, when considered to represent the sum of different Langmuir sites (36).

A number of different structural features of a solid may result in similar sorption behavior of sorbate molecules. So for example, desorption hysteresis may be observed in polymers with a high degree of cross-linking, high degree of crystallinity, stiff and inflexible chains, or very strong cohesive forces between adjacent polymer segments or when microvoids, cavities, or pores are present within a polymer matrix (54). These structural features are not interchangeable, but all manifest some stiffness or inflexibility that will affect sorption behavior. By the judicious use of molecular probes, it may be possible to distinguish one structural feature from another and thus to achieve a better understanding of the physicochemical nature of soil organic matter.

Acknowledgments

This work was conducted under a grant from the United States of America–Israel Binational Agricultural Research and Development (BARD) Fund and grants from the Israel Ministry of Agriculture and Rural Development and the Israel Ministry of Environmental Quality. We appreciate the conversations we had with J. J. Pignatello and B. Xing related to these topics and acknowledge their readiness to provide us with data. E. J. LeBoeuf supplied us with details of the DSC experiments. We are indebted to an anonymous reviewer, who suggested we verify the quality of the Freundlich analysis in ref 13.

Appendix

Let us consider equilibrium sorption uptake S_e obeying the Freundlich equation:

$$S_e = K_e C_e^{n_e} \quad (1)$$

where e indicates equilibrium, C is the solution concentration, K is the Freundlich constant, and n is the Freundlich exponent other than unity. Let us assume that sorption S_t measured at some time t before equilibrium also obeys the Freundlich equation:

$$S_t = K_t C_t^{n_t} \quad (2)$$

We will examine the case of concentration-independent approach to equilibrium. As such, the fractional uptake may be found as $X = S_t/S_e$, where X is identical for any given pair of S_e and S_t values in time t . Hence

$$X = \frac{K_t C_t^{n_t}}{K_e C_e^{n_e}} \quad (3)$$

Solution concentration C_t may be then evaluated for any

time t as

$$C_t = \left(\frac{K_e X}{K_t} \right)^{1/n_t} C_e^{n_e/n_t} \quad (4)$$

C_t corresponding to X approach to equilibrium also may be calculated directly:

$$C_t = C_e + kS_e(1 - X) \quad (5)$$

where k is the solid-to-liquid ratio.

Incorporating eq 1 into eq 5, it is seen that

$$C_t = C_e + kK_e C_e^{n_e} (1 - X) \quad (6)$$

The right-hand side of eqs 4 and 6 must be identical for any C_e value at a given time t (or approach to equilibrium X):

$$\left(\frac{K_e X}{K_t} \right)^{1/n_t} C_e^{n_e/n_t} = C_e^{n_e/n_t} (C_e^{1-(n_e/n_t)} + kK_e C_e^{n_e-(n_e/n_t)} (1 - X)) \quad (7)$$

or

$$\left(\frac{K_e X}{K_t} \right)^{1/n_t} = (C_e^{1-(n_e/n_t)} + kK_e C_e^{n_e-(n_e/n_t)} (1 - X)) \quad (8)$$

It can be seen that the right-hand side of eq 8 will be concentration-independent only when $n_e = n_t = 1$.

However, the condition $n_e = 1$ contradicts the initial assumption that the equilibrium isotherm is nonlinear. In other words, if the approach to equilibrium is concentration-independent and equilibrium uptake can be described by the nonlinear Freundlich model, then sorption measured at time t strictly cannot be represented by the Freundlich equation.

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Received for review February 5, 1998. Revised manuscript received June 25, 1998. Accepted July 8, 1998.

ES9801238