

LeBoeuf's Comment on "Evaluation of the Glassy/Rubbery Model for Soil Organic Matter"

SIR: In a recent article Graber and Borisover (1) presented their evaluation of the rubbery/glassy model for characterizing soil organic matter (SOM). In that article, the authors reviewed a select group of literature in ways that allowed them to present a claim that characteristics of SOM other than those identified in the rubbery/glassy model are operative in influencing the sorption and desorption behavior of organic chemicals. Given the complex nature of SOM (and the contaminants sorbing therein), it is in fact likely that a number of structural features of SOM act concurrently to influence overall sorption behavior as suggested in numerous prior studies. While their article provides a few valid points, I believe it is worthwhile to examine portions of the authors' critical and often flawed evaluation of the rubber/glassy model referenced in our work and that of others cited in their discussion. Space limitations restrict me from providing more comprehensive remarks.

(1) Structural Features of Soil Organic Matter. Graber and Borisover note that structural features such as crystallinity, cross-linking, and chemical composition (e.g., aromaticity) are distinct features that are not interchangeable with the term glassy to describe more rigid regions of SOM. The rubbery/glassy model noted in our work does not presuppose that other structural features are unimportant to observed sorption behavior. On the contrary, development of this model is based on a thorough understanding of structural features that can affect macromolecular mobility, which, in turn may largely affect sorption behavior. For example, increased cross-linking restricts chain mobility of larger macromolecule segments, while cross-links of shorter covalent bonds tend to replace van der Waals bonds between adjacent macromolecule chains, resulting in a decrease in the total volume occupied by the macromolecule (2). The reductions in chain mobility and free volume give rise to increased glass transition temperatures (T_g 's). Increased attractive forces between molecules, as measured by a larger solubility parameter, σ_p , requires more thermal energy to produce molecular motion. This results in an increase in the T_g with increasing σ_p . Thus, more polar macromolecules that possess greater cohesive energy densities generally lead to higher glass transition temperatures.

Macromolecule chains with aromatic backbones or parallel bonds in their backbone have extremely stiff bonds, with resulting reduction in molecular mobility and increased glass transition temperature (3) (e.g., coals with T_g 's generally ranging from 307 to 355 °C (4)). Similar behavior was reported in a recent 2D NMR study (5) of humic acid derived from an alluvial soil in Wisconsin. This study revealed a marked segregation in macromolecular mobility between the aliphatic and the more rigid aromatic structures regardless of pH. Previous work with Aldrich humic acid in our laboratories revealed that pH has little influence on the detected glass transition temperature using differential scanning calorimetry. At pH 2.7, water-wet Aldrich humic acid displays a T_g at 45 °C, while decreasing to only 43 and 40 °C at pH 7.0 and 10.0, respectively. Given the evidence provided by ref 5, it is possible that the Aldrich humic acid glass transitions reported in ref 6 account only for the mobility of the more rigid (aromatic) portions of the macromolecule; other T_g 's may exist for the more fluid aliphatic regions of this natural organic manner. Furthermore, no portion of our work suggests that crystallinity, which refers to the *nonamorphous* regions of

macromolecules, is synonymous to glassy states, which are attributed to the *amorphous* regions of SOM.

(2) Glass Transitions in Aldrich and Leonardite Humic Acids. First we would like to thank Graber (7) for confirming the observance of glass transition behavior of Aldrich humic acid through their own independent DSC analysis of samples provided by our group as well as samples obtained directly from Aldrich Chemical Company. Second, Graber and Borisover suggested that observance of glass transition behavior in Aldrich and Leonardite humic substances may not be applicable to soil organic matter due to their more diagenetically altered origin. It is apparent from reviews of the literature that geologic organic matter such as kerogens and coals can be important components of soils and sediments, and their presence may even largely control sorption of hydrophobic organic compounds (e.g., ref 8).

Third, Graber and Borisover imply that the glass transition behavior of Aldrich and Leonardite humic acids are similar. Although we concur with the Malcolm and MacCarthy study (9) that suggests that Aldrich humic acid displays somewhat similar chemical characteristics to diagenetically altered Wyoming Dopplerite and Leonardite humic acids, the reported glass transition temperatures of 60 (± 3) °C (6) and 72 (± 2) °C (10) for "dry" Aldrich and Leonardite humic acids, respectively, are different from one another. Furthermore, we wish to emphasize that the T_g values for whole coals are likely different from the T_g for humic acid derived from those coals. While glass transitions for parent Leonardite coal have not been reported to our knowledge, one may use the Lucht et al. (4) relationship of T_g as a function of carbon content to provide an estimate. For a low-rank coal such as Leonardite, the glass transition would likely appear between 307 °C and 320 °C (although report of secondary relaxation processes observed in Illinois no. 6 and other coals may suggest that T_g 's may occur at temperatures as low as 110 °C (11)). This is obviously different than the T_g for humic acid derived from Leonardite coal. This additional evidence further points to the need to identify different components of SOM (even within the same parent material) that can display a variety of macromolecular mobilities, thus leading to a distribution of T_g 's and a corresponding distribution of environmental reactivity.

Notwithstanding the above evidence, if one were to use the Graber and Borisover definition of SOM as being exclusive of geologic organic matter, one should still allow for the inclusion of identifiable biopolymers which generally constitute 10–20% or more of SOM (12). A brief review of ref 6 and other literature (e.g., refs 13 and 14) reveals a large number of biopolymers exhibit glass transition behavior, including glucose, sucrose, cellulose, maize starch, legumin, and lignin. Lignin, and even to some extent cellulose, has been reported to be resistant to degradation (15) and thus is likely to remain in its original form for some time after its original deposition in soil. This evidence, by itself, provides a strong statement to refute the authors' implication that rubbery and glassy regions of SOM do not exist.

(3) Sorption Nonlinearity and the Glassy State. Graber and Borisover allege "that the occurrence of a glassy phase does not specify that it will have any effect on sorption". While a plethora of literature suggests otherwise (e.g., ref 16), the authors chose to support their argument in part by reconstructing isotherms from isosteric heats data for poly(butyl methacrylate) (PBMA) to conclude that PBMA will not necessarily demonstrate nonlinear sorption in the glassy state. As noted in ref 17, PBMA has a manufacturer reported T_g of 20 °C. Graber and Borisover neglect the fact that this

is the "dry" T_g , and thus it does not reflect the influence of water and phenanthrene sorption within the matrix. Subsequent DSC evaluation of cleansed PBMA used in our studies reveals a "dry" T_g near 30 °C and an inability to detect a T_g above 0 °C for PBMA immersed in aqueous solution for 7 days. The presence of phenanthrene will only lower the T_g further; PBMA is therefore likely rubbery throughout the temperature range employed in that study. Further evidence of T_g lowering by phenanthrene is provided by observed linear isotherms and linear nonequilibrium phase distribution relationships (PDRs) of poly(isobutyl methacrylate) (PIMA) at both 25 °C and 45 °C even though PIMA possesses a water-wet T_g of 50 °C (18).

Graber and Borisover also compared the reported (6) sorption of phenanthrene within PIMA at 5 and 45 °C, suggesting that the change from nonlinear sorption behavior at 5 °C to linear sorption behavior at 45 °C may be partially explained by so-called "glass relaxation" times being much greater than sorption times. Their point simply reemphasizes our previous statements (6) regarding the importance of macromolecular mobility in evaluating sorption behavior. Although it is conceivable that plasticization of the PIMA matrix C_{40} result in increased isotherm linearity (e.g., PIMA at 25 °C and 45 °C), review of nonequilibrium PDR sorption of phenanthrene in PIMA at 5 °C reported in ref 18 clearly shows a trend towards *decreased* PDR linearity with increased equilibration times—a trend *opposite* that expected when swelling of the macromolecule over time brings about a reduction in the T_g and consequent increase in isotherm linearity. PIMA thus likely remains in the glassy state at 5 °C; which may account for the observed nonlinear sorption behavior. Although more work needs to be done to confirm the combined water-wet and sorbate-loaded T_g , it is not apparent from Graber and Borisover's discussion that they understand the effects of sorbate inhibition within the sorbent.

(4) Nonlinear Sorption Behavior within Dissolved SOM. Graber and Borisover cited observation of nonlinear sorption of benzo[e]pyrene and benzo[k]fluoranthene within soil-derived and Aldrich humic acids (19) to suggest that nonlinear sorption may be observed for nonpolar compounds within dissolved SOM "without a solid state". Perhaps a "solid state" may be exemplified by regions of reduced macromolecular mobility. Review of ref 19 indicates that sorption experiments were conducted at room temperature in pH 6.5–8.4 solution (7.5 for Aldrich humic acid). As noted previously, dissolved humic acids may retain regions of macromolecular immobility (or "solid states") at room temperature regardless of pH range employed in that study. As noted in ref 6, these regions of immobility can result in site-specific, nonlinear sorption.

In summary, a number of structural features of SOM may be important in influencing the sorption behavior of organic chemicals, but macromolecular mobility, as partially quantified by rubbery/glassy behavior, is likely the single largest contributing factor in the nonlinear sorption of nonpolar

organic compounds from aqueous solution. While efforts such as this by Graber and Borisover can afford the scientific community opportunities to view scientific advances in different lights, a more *balanced critical review* of this topic that is not as narrow in its selection and interpretation of available literature would be a more appropriate and valuable contribution to science.

Acknowledgments

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