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# Correspondence. Reply to comment on "The surface area of soil organic matter"

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groups, are linked together by weak interactions, such as hydrogen bonding, hydrophobic interactions, and  $\pi$  bonding (14). Thus, the multipolymer phase possesses an internal porosity, which may expand and contract depending on solvent properties and can account for the large cation-exchange capacities characteristic of SOM via polar (ionic) functional groups. When the multipolymer phase is air-dried, polar functional groups orient toward the interior of the structure, while the external surface becomes primarily hydrophobic in nature (13). Thus, under anhydrous conditions nonpolar organic vapors condense on the external surface of SOM, whereas polar molecules explore the internal surfaces and solvate exchangeable cations in a manner analogous to that observed for expandable clay minerals. Under saturated conditions, the multipolymer phase functions as a conventional partition medium for nonionic organic compounds.

The interpretation of surface area measurements is a formidable task and should be considered in the context of both the probe molecule, or adsorbate, and the adsorbent. The data presented herein indicate that the adsorption of nonpolar molecules occurs primarily on external surfaces of SOM, whereas polar adsorbates explore both the external and internal surfaces of SOM. On the basis of the  $N_2$ /BET surface areas measured by Chiou et al. (1), it is reasonable to conclude that the external surface area of SOM is quite small. However, the  $N_2$ /BET surface area of freeze-dried soil humic acid ( $18 \text{ m}^2/\text{g}$ ) is considerably greater than that of oven-dried soil humic acid ( $\sim 0.7 \text{ m}^2/\text{g}$ ) (1). In general, air-drying results in the collapse and shrinkage of soil humic acids, whereas freeze-dried soil humic acid maintains an intricate structural network (15, 16). Thus, under natural conditions the external surface area of SOM is likely to be greater than  $1 \text{ m}^2/\text{g}$ . We also contend that (a) SOM does in fact possess an internal surface area, albeit ill-defined, which plays an important role in many soil processes and (b) a simple polymer phase cannot be used to describe vapor-phase sorption on anhydrous SOM. However, surface area measurements of clay minerals, based on the retention of EG or EGME and the adsorption of water, have been shown to be dependent upon the exchangeable cation species (17, 18). Given the potential for specific interactions between polar molecules and SOM, it is likely that experimental error will be associated with measurements of the total surface area of SOM. Nevertheless, the retention of polar adsorbates by SOM yields a measure of surface area that may be quite useful to environmental scientists, provided the operational nature of surface area measurements is recognized.

#### Literature Cited

- (1) Chiou, C. T.; Lee, J.-F.; Boyd, S. A. *Environ. Sci. Technol.* 1990, 24, 1164.
- (2) Bower, C. A.; Gschwend, F. B. *Soil Sci. Soc. Proc.* 1952, 16, 342.
- (3) Sposito, G. *The Chemistry of Soils*; Oxford University Press: New York, 1984.
- (4) Call, F. J. *Sci. Food Agric.* 1957, 8, 630.
- (5) Pennell, K. D. Ph.D. Dissertation, University of Florida, 1990.
- (6) Rhue, R. D.; Rao, P. S. C.; Smith, R. E. *Chemosphere* 1988, 17, 727.
- (7) Jurinak, J. J.; Volman, D. H. *Soil Sci.* 1957, 33, 487.
- (8) Lee, J.-F.; Mortland, M. M.; Boyd, S. A.; Chiou, C. T. *Chem. Soc., Faraday Trans. 1* 1989, 85, 2953.
- (9) Chiou, C. T.; Kile, D. E.; Malcolm, R. L. *Environ. Sci. Technol.* 1988, 22, 298.
- (10) Kiselev, A. V. *Q. Rev. Chem. Soc.* 1961, 15, 99.
- (11) Whalen, J. W. *J. Colloid Interface Sci.* 1968, 28, 443.

- (12) Greg, S. J.; Sing, K. S. W. *Adsorption Surface Area and Porosity*, 2nd Ed.; Academic Press: New York, 1982.
- (13) Hayes, M. B. H.; MacCarthy, P.; Malcolm, R. L.; Swift, R. S. In *Humic Substances II: In Search of Structure*; Hayes, M. B. H., MacCarthy, P., Malcolm, R. L., Swift, R. S., Eds.; John Wiley & Sons: New York, 1989; Chapter 24, pp 689-733.
- (14) Wershaw, R. L. *J. Contam. Hydrol.* 1986, 1, 29.
- (15) Chen, Y.; Schnitzer, M. In *Humic Substances II: In Search of Structure*; Hayes, M. B. H., MacCarthy, P., Malcolm, R. L., Swift, R. S., Eds.; John Wiley & Sons: New York, 1989; Chapter 22, pp 622-638.
- (16) Tan, K. H. *Soil Sci. Soc. Am. J.* 1985, 49, 1185.
- (17) McNeal, B. L. *Soil Sci.* 1964, 97, 96.
- (18) Quirk, J. P. *Soil Sci.* 1955, 80, 423.

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SIR: Pennell and Rao (1) considered the surface area of a bulk solid to be an "operationally defined" quantity. By this assumption, they postulated the existence of a "semistructured multipolymer phase" in soil organic matter (SOM) to account for the large discrepancy of the measured surface areas of SOM by the standard BET/ $N_2$  method and by the ethylene glycol (EG) retention method. In their opinion SOM possesses an internal porosity which can either expand or contract depending on the solvent (adsorbate) properties and thus results in different measured surface areas of SOM. To support their contention, Pennell and Rao (1) drew an analogy to the behavior of smectites in uptake of  $N_2$  and polar liquids (such as EG and water) and cited results from other sorption studies of organic vapors with soils and organoclays.

It is rather unfortunate that Pennell and Rao take a view of surface area that is at odds with accepted terminology in allied fields; this leads to an unnecessarily pessimistic view of the complexity of the sorption of organic compounds by SOM. The argument of Pennell and Rao is essentially a redefinition of the surface area to fit the experimental data produced by different methods. The concept of the "surface areas" for divided solids is quite straightforward. They are the values customarily measured by determining the adsorption of gases or vapors that can reach the solid's surfaces (i.e., they are not excluded by molecular sieving) but do not penetrate into the bulk solid. These surfaces represent the vacuum-solid interfaces that exist before the measurement is taken and are external to the bulk material. Some porous solids may have "internal surfaces" in the sense that they are internal to the (outer) granule boundary (as in activated carbon) but are nevertheless external to the bulk solid. These "internal surfaces" make sense only if they are accessible to gases of low molecular weights.

When different appropriate adsorbate gases are used in separate experiments to determine the surface area of a solid, the results are generally quite consistent, provided of course that they are known not to dissolve in or react with the solid material. By contrast, if the adsorbate gases or vapors can penetrate into the bulk substance, they are clearly of no use to determine the surface area (as is commonly understood in such fields as solid-state adsorption, catalysis, and polymer chemistry). If one attempts to measure the surface area of a solid by an adsorbate that penetrates into the solid (e.g., water vapor on NaOH or benzene on rubber), then one would overestimate the surface area, as the term is commonly understood, by orders of magnitude. It is simply not economical of hypothesis to assume that every sorption measurement must lead to some kind of surface area depending on the type of "adsorbate" used.

Whereas we used the term "partition" or "solubility" to account for the sorption of a much larger quantity of polar liquids (e.g., EG and water) by SOM than can be accounted for by the external surface surfaces of SOM by the BET/N<sub>2</sub> method, our critics preferred to state that these liquids "explore the inner surfaces" of the SOM (i.e., the surfaces that are impervious to low molecular weight gases). We think not only that this is a distinction without difference, but also that the "inner surface areas" that one calculates by using this concept are not meaningful. We would ask them to suggest experiments that could make the supposed distinction. As a "reductio ad absurdum", one could calculate the "surface area of water" by sucrose dissolved in water and attribute this to "internal surfaces of water explored by the sucrose". We maintain that this kind of argument obscures rather than clarifies our understanding of the phenomenon.

As we pointed out in our article (2), it is best to restrict the term "surface areas" to areas that exist before the measurement and do not change during the course of measurement. In the case of the well-known high uptake of polar liquids such as water and EG (or EGME) by smectite, although one may argue that these liquids measure some kind of "internal surface" of smectites, it should be clear that these surfaces do not exist before the measurement is made and therefore are not "seen" by low molecular weight gases. One may talk about and calculate the area of "water-smectite interface" only if one knows the thickness of each water layer in the interlayer lattice of smectite. The presumed solvation of cations in smectite by water and polar liquids does not provide a theoretical basis for calculating the water-smectite interfacial area. The large discrepancy of the surface area data for soils and clays measured by sorption of water and EG (or EGME) relative to those by BET/N<sub>2</sub> in Tables I and II of Pennell and Rao (1) can thus be attributed to solubility of water and EG (or EGME) in SOM and/or to structural changes of the samples by their reaction with clay minerals.

Pennell and Rao (1) claim that nonpolar organic vapors adsorb on (rather than partition in) anhydrous SOM in much the same manner as N<sub>2</sub> while in aqueous systems organic solutes partition into the hydrated SOM. They present results in their Tables I and II to show that dry soils exhibit comparable surface areas determined by BET/N<sub>2</sub> and BET/ethylene dibromide (EDB). We think that these data are less than rigorous for the reason that in dry soils with organic matter content being a minor component the overall soil uptake of organic vapors is undoubtedly controlled by adsorption on minerals (3). As to the accuracy of surface area determinations, one would not find a large discrepancy in the surface areas by BET/N<sub>2</sub> and by adsorption of nonpolar vapors for low

organic content soils because the solubility of low-polarity vapors in SOM is low (4). To make this point evident, let us consider the surface area data of Whittlesey Black Fen [Table I (1)], which has the highest organic content among all soils and gives surface areas of 12.7 m<sup>2</sup>/g by BET/N<sub>2</sub> and 17.5 m<sup>2</sup>/g by BET/EDB. For this high organic content soil, the assumption of EDB adsorption on (rather than partition in) SOM would lead to an overestimate of the "surface area" by BET/EDB over that by standard BET/N<sub>2</sub>. The reported data showing about 5 m<sup>2</sup>/g higher surface area by BET/EDB than by BET/N<sub>2</sub> are in agreement with this expectation. For relatively pure SOM (peat and muck), the observed uptake of nonpolar vapors greatly exceeds that which can be accounted for by the BET/N<sub>2</sub> area of the sample (5).

The sorption data from Lee et al. (6) of organic vapors with tetramethylammonium (TMA)-smectite, cited by Pennell and Rao to support their view that dry SOM behaves as an adsorbent, have no relevance to the subject issue. There is no equivalence between the small organic moiety of TMA ion and the relatively high molecular weight natural SOM. In addition, Lee et al. (6) have clearly pointed out that the uptake of benzene and other vapors by dry TMA-smectite consists of adsorption on both mineral surfaces and the "organic-coated" TMA surfaces. These surfaces should be equally "seen" by N<sub>2</sub>. Therefore, it is not surprising that when the benzene adsorption isotherms with smectites having different amounts of exchanged TMA ions are normalized to the BET/N<sub>2</sub> surface areas, they show nearly a single adsorption isotherm.

The claim by Pennell and Rao that the isotherms of Chiou et al. (4) for some vapors with soil humic acid are type III is incorrect. These isotherms do not exhibit the upward concavity at low coverage that is characteristic of type III isotherms. The organic vapor sorption isotherms of Chiou et al. (4) are all relatively linear over the range of  $P/P^\circ = 0-0.7$ , except for a few that exhibit a slight curvature at low loading (which can be attributed to some adsorption of vapors on the freeze-dried humic acid in addition to the partition effect). Likewise, they do not resemble typical type II isotherms.

Pennell and Rao attribute type III isotherms only to adsorption that results from weak adsorbate-adsorbent interactions. However, type III isotherm is not a unique indicator of this special kind of surface adsorption. There is an extensive literature on the sorption of vapors by polymer which gives type III isotherms in which the primary mechanism is known as partition (solubility), rather than surface adsorption or "exploration of inner surfaces". For example, typical type III vapor isotherms are found for benzene, toluene, xylene, and CCl<sub>4</sub> on polystyrene (7, 8) and for benzene on rubber and polyisobutylene (9, 10); these data have been used by Flory and others (7-10) to characterize the solubility behavior of liquid-polymer mixtures. In these systems, where the solubility of liquids in polymer is large, the solvency of the polymer for corresponding vapors increases with the solute content in the polymer. By comparison, when liquids exhibit limited solubility in polymer, as for low-polarity organic liquids in SOM, the resulting vapor sorption isotherms are essentially linear, since small amounts of solutes in polymer do not significantly affect the solvency of the polymer. The idea that organic compounds dissolve in polymer is common knowledge to polymer chemists. Our description of organic compound partition in SOM should be straightforward rather than controversial. The notion that polar liquids such as water and EG (or EGME) "explore the inner surfaces" of SOM merely introduces confusion into terminology that is quite standard in related fields.

### Literature Cited

- (1) Pennell, K. D.; Rao, P. S. C. *Environ. Sci. Technol.*, preceding comment in this issue.
- (2) Chiou, C. T.; Lee, J.-F.; Boyd, S. A. *Environ. Sci. Technol.* **1990**, *24*, 1164.
- (3) Chiou, C. T.; Shoup, T. D. *Environ. Sci. Technol.* **1985**, *19*, 1196.
- (4) Chiou, C. T.; Kile, D. E.; Malcolm, R. L. *Environ. Sci. Technol.* **1988**, *22*, 298.
- (5) Rutherford, D. W.; Chiou, C. T. submitted for publication to *Environ. Sci. Technol.*
- (6) Lee, J.-F.; Mortland, M. M.; Boyd, S. A.; Chiou, C. T. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2953.
- (7) Baughan, E. G. *Trans. Faraday Soc.* **1948**, *44*, 495.
- (8) Bawn, C. E. H.; Freeman, R. F. J.; Kamaliddin, A. K. *Trans. Faraday Soc.* **1950**, *46*, 677.
- (9) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2035.
- (10) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2053.

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