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The Surface Area of Soil Organic Matter

Cary T. Chiou*

U.S. Geological Survey, Box 25046, MS 408, Denver Federal Center, Denver, Colorado 80225

Jlunn-Fwu Lee[†] and Stephen A. Boyd

Department of Crop and Soil Sciences, Michigan State University, East Lansing, Michigan 48824

■ The previously reported surface area for soil organic matter (SOM) of 560-800 m²/g as determined by the ethylene glycol (EG) retention method was reexamined by the standard BET method based on nitrogen adsorption at liquid nitrogen temperature. Test samples consisted of two high organic content soils, a freeze-dried soil humic acid, and an oven-dried soil humic acid. The measured BET areas for these samples were less than 1 m²/g, except for the freeze-dried humic acid. The results suggest that surface adsorption of nonionic organic compounds by SOM is practically insignificant in comparison to uptake by partition. The discrepancy between the surface areas of SOM obtained by BET and EG methods was explained in terms of the "free surface area" and the "apparent surface area" associated with these measurements.

Introduction

In spite of the general acceptance that sorption of organic pollutants and pesticides from water by soils (or sediments) is controlled primarily by the organic matter content of the soil (1-7), the mechanistic function of the soil organic matter (SOM) in uptake of the organic compound has been a subject of active discussion (3-15). Before 1979, most studies regarded the SOM as a high-surface-area adsorbent in analogy with other traditional solid adsorbents (1, 16-18). This assumption appeared to result partially from the suggested apparent surface area for the SOM (of the order of 560-800 m²/g), as first reported by Bower and Gschwend (19) and propagated subsequently by others (16-20). The reported surface area of SOM was derived from the retention of ethylene glycol (EG) by this material at room temperature, the assumption of monolayer surface adsorption, and the area-mass conversion factor obtained from the EG uptake by reference clay minerals of known BET (Brunauer-Emmett-Teller) surface areas. In more recent studies, however, Chiou and co-workers (3, 6-10) took close account of the aqueous-sorption and vapor-sorption behavior of soils and soil humic acids and suggested that SOM functioned primarily as a partition medium rather than as an adsorbent in the uptake of (nonionic) organic compounds. Evidence supporting the partition model consists of linear sorption isotherms of organic solutes (or organic vapors) to high relative concentrations, low heats of sorption, no compe-

titive effects in uptake of binary solutes, and the general compliance of the sorption data with the Flory-Huggins theory (21, 22) for solute solubility behavior in (amorphous) polymers and macromolecular substances.

Although the partition model has successfully explained a wide variety of observations (3, 6-10, 13, 15, 23), the surface adsorption concept is still being advocated by some researchers as the mechanistic basis for organic compound uptake by SOM (11, 12, 14, 20, 24, 25). Since the magnitude of the SOM surface area would serve as a primary indicator of the adsorption power of SOM, reexamination of the previously reported surface area for SOM by a generally accepted method is necessary, because the basic assumptions for the surface-area determination of SOM by EG retention have not been rigorously confirmed, despite the conventional use of EG retention in characterizing clay minerals. In other words, if the observed EG retention by SOM were due primarily to monolayer adsorption rather than other contributions, one would expect similar monolayer adsorption of nitrogen at liquid nitrogen temperature. In this study, we used the standard BET method (26) to measure the surface areas of high organic content soils and extracted soil humic acids and discussed the mechanistic uptake of organic compounds by SOM in terms of the surface areas as determined by the BET and EG methods.

Experimental Section

The BET surface areas were determined by nitrogen adsorption at liquid nitrogen temperature for the following organic soils and purified soil humic acids: a Florida peat soil from Everglades, FL, which contains 86.4% organic matter (OM) on a dry weight basis; a Houghton muck soil from the Michigan State University Muck Research Farm, Laingsburg, MI (91.9% OM content); a purified soil humic acid in freeze-dried form (98.8% OM) isolated from Sanhedron soil in the Mattole River Valley of northern California (9); and the oven-dried soil humic acid obtained from the alkaline solution of the above freeze-dried humic acid, followed by dialysis of the sample to bring the pH to 6.5, and then drying at 65-70 °C. A Quantasorb Jr. surface area analyzer (Quanta Chrome Corp.) was used to measure the monolayer capacity of nitrogen gas at liquid nitrogen temperature. All samples were outgassed under vacuum at 105 °C for 6 h before N₂ adsorption. Helium was used as the carrier and dilution gas to fix the relative pressure of N₂ in the range of 0.05-0.25, the region where the data conformed to a linear BET plot (8). The molecular surface area of 16.2 × 10⁻²⁰ m² for nitrogen was used

* Present address: Department of Environmental Engineering and Water Resources, Tamkang University, Taipei, Taiwan 10620, Republic of China.

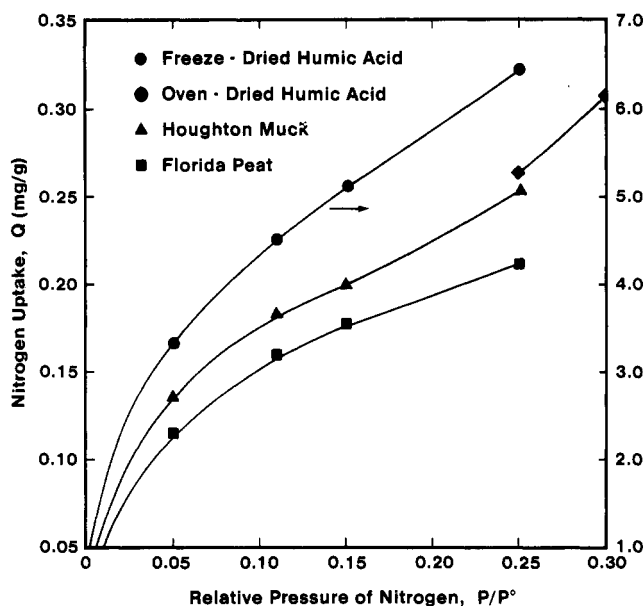


Figure 1. Adsorption isotherms of nitrogen vapor at liquid nitrogen temperature on selected organic soils and soil humic acids.

in the surface area determination of the test samples.

Results and Discussion

The adsorption data of nitrogen on four test samples at liquid nitrogen temperature are given in Figure 1. To obtain the surface area, the data in Figure 1 were expressed in a linear BET form as

$$\frac{1}{Q(P^\circ/P - 1)} = \frac{C - 1}{CQ_m} \frac{P}{P^\circ} + \frac{1}{CQ_m} \quad (1)$$

in which P/P° is the relative pressure of nitrogen, Q is the amount of nitrogen adsorbed at given P/P° , Q_m is the monolayer adsorption capacity, and C is a constant related to the net heat of monolayer adsorption. The Q_m value for each sample was determined from the slope, $(C - 1)/CQ_m$, and the intercept, $1/CQ_m$, of the plot of $1/Q(P^\circ/P - 1)$ against P/P° ; the BET surface area was then calculated from the Q_m value and the molecular surface area of nitrogen. Plots of $1/Q(P^\circ/P - 1)$ vs P/P° for the freeze-dried humic acid, Houghton muck, and Florida peat are shown in Figure 2, in which the data exhibit a good fit to the BET equation. Because of the very small sample size of the oven-dried humic acid used in this study (~ 0.05 g), the adsorption data with this sample at low P/P° could not be accurately measured. The surface area of this sample was estimated from the data points at $P/P^\circ = 0.25$ and 0.30 by the one-point approximation method (27):

$$Q_m = Q(1 - P/P^\circ) \quad (2)$$

which generally gives a good estimate of Q_m for systems with $C > 10$ and $P/P^\circ = 0.05 - 0.3$; the present data for the other three samples ($C > 20$) fit eq 2 reasonably well over the stated P/P° range.

The determined BET surface areas for the above samples were as follows: $0.61 \text{ m}^2/\text{g}$ for the Florida peat, $0.73 \text{ m}^2/\text{g}$ for the Houghton muck, $18 \text{ m}^2/\text{g}$ for the freeze-dried soil humic acid, and $\sim 0.70 \text{ m}^2/\text{g}$ for the oven-dried soil humic acid. These values are extremely small in comparison with the surface area previously reported for SOM. In this study, the much larger area for the freeze-dried humic acid sample relative to the oven-dried sample may be attributed to the freeze-drying process, which frequently increases surface areas of low-surface substances. That the surface areas for the two organic-rich soils are comparable to that of the oven-dried soil humic acid suggests

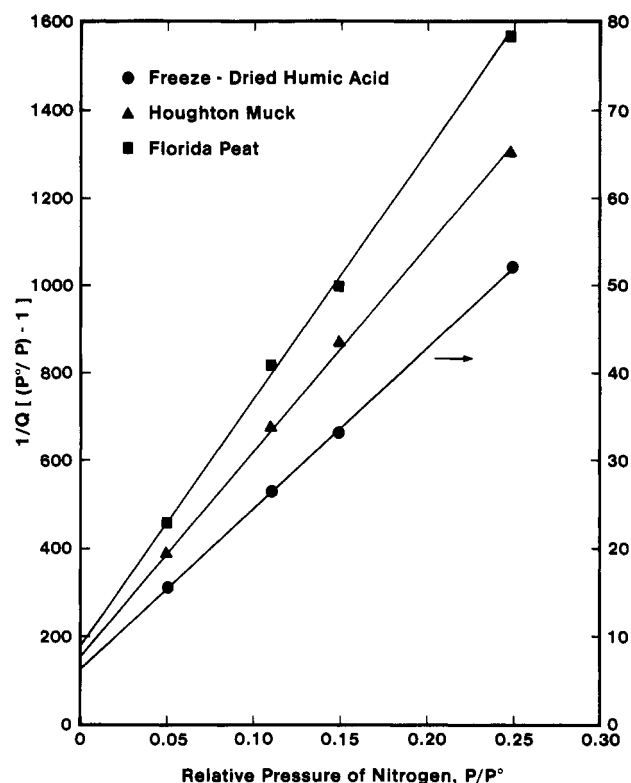


Figure 2. Plots of nitrogen adsorption data in a linear BET equation.

that the minor mineral fractions in these soils are not readily accessible to vapor adsorption, presumably because they are deeply enclosed by the organic matter. In light of the notably low surface areas for these samples, surface adsorption of nonionic organic compounds by SOM should be extremely small.

The discrepancy of the determined surface areas for the SOM by the BET and EG methods may be put into perspective in terms of the "free surface area" and "apparent surface area" associated with these measurements. The free surface area corresponds to the solid-vacuum interfacial area of a solid, which exists before adsorption and is unequivocally measured by an adsorbate that does not change the structure of the solid. Determination of free surface areas by the BET method is based on the assumptions that (i) only physical adsorption is involved, (ii) surface area is not changed by the adsorption process, and (iii) no solution is formed by the adsorbate in the solid. The apparent surface area of a solid is the one measured by the uptake of an "adsorbate" that either changes the structure of the solid, dissolves in it, or both. For example, the very large so-called "total surface area" of a smectite determined by the uptake of polar liquids (such as water and EG) (28) results from creation of interlamellar surfaces by lattice swelling; it does not exist before the liquid uptake. Similarly, amorphous organic polymers or macromolecular substances also give rise to large apparent surface areas when they are calculated from the uptake of solvents of similar polarities that form solutions in the solid amorphous material. Solutions of the vapors of benzene in natural rubber (29-32) and poly(isobutylene) (33), cyclohexane in poly(isobutylene) (34), and *n*-pentane in poly(isobutylene) (35) are just a few well-known systems in which the polymers have negligible BET surface areas (except those polymers specially made to produce porosity) but take up large amounts of solvents by partition (solubility). In general, the apparent surface area is not well-defined and can be ambiguous, because it does not refer to the surface area of the solid before the measurement

is taken; in many cases, it is difficult to make a distinction between true surface adsorption and such phenomena as expansion of the solid lattice by the adsorbate, accessibility of the adsorbate to a presumed "internal surface", and solubility of the "adsorbate" in the solid. In a rigorous manner, one should limit the concept of "surface area" to those cases in which the surface area of the solid remains invariant to the adsorption measurement.

The enormously large surface area reported by Bower and Gschwend (19) for SOM is presumably an artifact of their calculation method, which assumed only surface adsorption of EG on SOM and the absence of significant bulk solubility of the compound. In the study of Bower and Gschwend (19), the assumed monolayer capacity of EG on SOM (corresponding to 17–25% by weight) was empirically obtained from a single retention data point rather than determined from isotherms; these data give no evidence for exclusive monolayer adsorption of EG by SOM. There are good reasons to believe that the relatively high EG retention by SOM at room temperature is due essentially to partition, when one considers the polar nature of both EG and amorphous SOM. For example, ethanol, a polar liquid similar in composition to EG, has been shown to partition effectively in soil humic acid and to give rise to a practically linear isotherm, with the limiting partition capacity approaching 35% by weight (9) (also note that there is no theoretical basis for deriving a surface area from a practically linear isotherm). Water uptake by soil humic acid exhibits similar results (9). The difference in magnitude between surface adsorption and solubility is further illustrated for a nonpolar solid sorbent-vapor system by the uptake of benzene vapor on a specially made poly(styrene-co-divinylbenzene), as Chromosorb 101 from Supelco, Inc., with 30–35 m²/g BET surface area (technical data from Manville Corp., Lompoc, CA). Here one finds a relatively linear isotherm with a limiting capacity of ~30% by weight (9), while the monolayer surface adsorption of benzene would correspond to less than 1.5% by weight. Thus, the benzene uptake in this case is still predominantly by bulk solubility in the polymer.

In conclusion, our findings on SOM are consistent with the well-known behavior of polymers and are best accounted for by solution of organic vapors or solvents in (solid) amorphous, macromolecular substances (21, 22, 29–35). To insist on the primacy of surface adsorption of EG on SOM, one would be forced to postulate some sort of poorly defined "inner surface" with SOM that is accessible to EG and ethanol but that somehow excludes smaller molecules like N₂; this hypothesis would however seem rather excessive, especially when one is faced with linear isotherms and other noted effects that are characteristic of solubility. The partition model reconciles the large uptake of polar liquids (such as ethanol and EG) by SOM with the relatively low BET surface area for the SOM. The low BET areas for the samples tested in this study and the various other sorption characteristics of organic compounds on SOM (3, 4, 6–10, 13, 15, 23) suggest that it is no longer tenable to ascribe the sorption of organic pollutants and pesticides by soil organic matter to a high-surface area that it in fact does not possess.

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