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## DIVISION S-9—SOIL MINERALOGY

### Organic Matter–Surface Area Relationships in Acid Soils

Lawrence M. Mayer\* and Baoshan Xing

#### ABSTRACT

Soil organic matter (OM) and mineral surfaces are intimately related, affecting the dynamics of each and their reactivity with many environmentally important substances. We examined the coverage of mineral surfaces by OM in acid soils of Massachusetts. Specific surface areas are controlled by a combination of clay and sesquioxide contents. Subsurface horizons, especially C horizons with pH 4.6 to 4.8, contained a phase with significant microporosity (pores <2 nm) that could be eliminated by 350°C muffling. Organic C (OC) concentrations in surficial (A, O) horizons have surface area-normalized loadings usually above the monolayer-equivalent (ME) level ( $\approx 1 \text{ mg OC m}^{-2}$ ), while B and C horizons usually have loadings at this level. Surface area-normalized loadings are inversely related to pH for each horizon type. Samples with high loadings show occlusion of the bulk of mineral surface area by OM, as evidenced by release of significant surface area after OM removal. However, a new method of assessing OM coverage of exposed surfaces, using the energetics of gas adsorption, indicate that the bulk of surface area exposed in most untreated samples consists of mineral rather than organic material. The data are consistent with a model in which the occluding OM is present in a low-surface area configuration, such as organoclay aggregates, rather than as dispersed coatings on mineral grains.

ORGANIC MATTER concentrations and fine-grained mineral contents often covary with one another in soils (e.g., Nichols, 1984). This correlation has suggested sorptive control of OM contents that is limited by surface area (Sollins et al., 1996), though protection of OM within clay-OM aggregates provides an alternative hypothesis. Organic matter concentrations, fine-grained

mineral contents, and surface area can be important correlates for other important soil properties or processes, such as contaminant accumulation, nutrient dynamics, or physical characteristics. Distinguishing causal relationships among the latter processes and these three properties requires a deeper understanding of the relationships among the three properties.

Several studies have shown that OC concentrations in continental shelf marine sediments, normalized to sediment specific surface area, are  $\approx 1 \text{ mg OC m}^{-2}$  (Mayer, 1994a, 1994b; Keil et al., 1994). This loading has been previously termed the *monolayer-equivalent* (ME) level, because its value is equivalent to that to be expected for a monolayer of moderately sized organic molecules coating all surfaces. Organic matter loadings relative to surface area have received only minor attention for terrestrial soils. We reported previously that about one-half of soil samples from geographically diverse areas showed OM loading in A horizons, normalized to mineral surface area, similar to the ME level (Mayer, 1994b). However, these loadings have not been examined for other soil horizons.

This ME loading of OM may or may not represent a dispersed coating over all mineral surfaces. Such a question is difficult to answer by most spectroscopic methods for the types of surfaces found in soils. However, to address this question we have developed a method based on the energetics of N gas adsorption (Mayer, 1999). Nitrogen shows higher enthalpy of adsorption onto mineral than onto organic surfaces, so that the difference in enthalpy between an untreated sample and one with its OM removed can be used to determine the extent to which the untreated surfaces

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are organic or mineral in nature. For marine sediments, we found that OM coats only a small fraction of sedimentary minerals, making the ME phrase somewhat misleading.

Little attention has been given to the degree of coating of soil mineral grains by OM, though there has been active consideration of the relative contributions of minerals and OM to total surface area (e.g., Chiou et al., 1990; Pennell et al., 1995). Does OM form continuous coatings on soil mineral surfaces, or does it coat only a minor fraction of mineral surfaces as found for sediments? This question is relevant to a variety of environmental processes such as mineral formation and dissolution or contaminant sorption. Here we address OM/surface area ratios and the question of mineral coverage by OM for a series of acidic soils from the northeastern USA.

## MATERIALS AND METHODS

### Soil Sampling

We sampled various soil series in Massachusetts (Table 1). The soil types examined here are mostly sandy, well-drained, and acidic. Soil pits (1 m<sup>2</sup>) were dug to a depth of at least 1 m or to the bedrock surface. Standard soil profile descriptions were made at each site (Bartos, 1994). Soil samples were collected from identifiable soil horizons. Soil samples were transported back to the laboratory, air-dried, sieved (<2 mm), ground mechanically with a Model 8510 Spex Pulverizer (Spex Industries, Edison, NJ) for 5 min, and stored for subsequent analyses.

### Characterization of Surfaces

Soils were analyzed for surface area and coverage by OM by gas adsorption analysis. Samples were analyzed in both untreated and oxidized conditions, the latter to remove natural OM and assess the surface area and sorption energetics of the underlying mineral surfaces. Organic matter oxidation was performed by 350°C muffling overnight under a normal atmosphere (Keil et al., 1997). Before gas sorption analysis, all samples were outgassed, to remove adsorbed water, in a vacuum oven overnight at 150°C. Gas sorption at 77 K was conducted with a Quantachrome A-1 Autosorb (Quantachrome Corp., Syosset, NY), which doses the surfaces with varying gas pressures in a series of batch adsorption experiments. Surface area values were determined from the Brunauer–Emmett–Teller (BET) equation (Brunauer et al., 1938).

To assess the coverage of mineral surfaces by OM, we measured gas adsorption energetics using the approach of Mayer (1999). Briefly, we measured N<sub>2</sub> adsorption across the partial pressure range 0 to 0.3, and the C constant of the BET transform (Brunauer et al., 1938) was obtained from the most linear portion of the isotherm. This C constant was converted to its enthalpy equivalent by the expression

$$C = M \exp[(\Delta H_{\text{ads}} - \Delta H_{\text{cond}})/RT] = M \exp(\Delta H_{\text{xs}}/RT) \quad [1]$$

where  $M$  is a preexponential term assumed to equal 1,  $\Delta H_{\text{ads}}$  is the adsorption enthalpy of the gas directly on the surface;  $\Delta H_{\text{cond}}$  is the enthalpy of gas condensation, normally considered equivalent to adsorption of the second and higher layers of gas (Steele, 1974);  $\Delta H_{\text{xs}}$  (excess enthalpy) is their difference;  $R$  is the universal gas constant; and  $T$  is degrees Kelvin. This  $\Delta H_{\text{xs}}$  term was determined on samples before and after 350°C

muffling. To assess the fraction of exposed surface that consists of OM, these two values are processed by an algorithm developed from model systems of various organic molecules adsorbed onto various mineral adsorbants (Mayer, 1999).

### Other Measurements

Organic C and N were analyzed by Perkin-Elmer 2400 CHN analyzer (Perkin-Elmer, Norwalk, CT), according to Mayer (1994a). Particle-size analysis (clay, silt, and sand) was determined by the pipette procedure after pretreatment with H<sub>2</sub>O<sub>2</sub> to remove OM. The pH of each soil was measured in both distilled water and CaCl<sub>2</sub> solutions (Thomas, 1996). Citrate-dithionite-extractable Fe and Al were measured according to Holmgren (1967).

## RESULTS

The surface area values of these soils ranged from <1 to 49 m<sup>2</sup> g<sup>-1</sup> (Table 1). There were significant increases in surface area for many samples upon 350°C muffling, indicating occlusion of mineral surface area by OM. These increases were strongest and most consistent for horizons rich in OM (O, A; Fig. 1) and are similar to increases found in other soil studies (Burford et al., 1964; Feller et al., 1992; Pennell et al., 1995) but significantly greater than are typically found for marine sediments (Mayer, 1994a). For the organic-poor C horizon samples, surface area values showed small differences between the two treatments, indicating little impact of muffling on surface area values of the minerals themselves.

Mineral surface area—that is, after removal of the OM by muffling—showed strong positive correlation ( $P = 0.0004$ ) with the clay content (Fig. 2). The slope of this regression was 0.9 (m<sup>2</sup> g<sup>-1</sup>) (percentage clay)<sup>-1</sup>, similar to those found before for soils and sediments (Farrar and Coleman, 1967; Mayer and Rossi, 1982). This fortuitous numerical relationship is due to the fact that clay (<2 μm) fractions typically have specific surface areas on the order of 50 to 100 m<sup>2</sup> g<sup>-1</sup>, while silt- and sand-sized minerals have much lower specific surface areas of <10 m<sup>2</sup> g<sup>-1</sup> (Keil et al., 1994; Feller et al., 1992; Bock and Mayer, 2000).

We performed no mineralogical work, but the clay size fraction mineralogy of Massachusetts soils has been described by Bodine (1986) as consisting of mica, chlorite, chloritized vermiculite, sesquioxides, quartz, and some kaolinite. The abundance of phyllosilicates in the clay size fraction can explain the high surface area values, as can the colloidal sizes of primary particles of sesquioxides.

The numerical relationship

$$\text{Surface area (m}^2 \text{ g}^{-1}\text{)} = 0.9(\text{percentage clay}) \quad [2]$$

nicely delineates the minimum surface area values found for any given clay content (Fig. 2), but most samples clearly had higher surface area values than are predicted by this line. The y-axis residuals from this clay–surface area relationship correlated positively and strongly ( $P < 0.001$ ) with both the Fe and Al extracted by dithionite-citrate solution, implying that sesquioxides also contributed significantly to the surface area values in samples.

**Table 1.** Soil description, horizon, depth of sampling, surface area of unmuffled samples ( $SFA_u$ ), surface area of muffled samples ( $SFA_m$ ), excess enthalpy of  $N_2$  adsorption on unmuffled samples ( $\Delta H_{xsu}$ ), excess enthalpy of  $N_2$ -adsorption on muffled samples ( $\Delta H_{xsm}$ ), organic C concentration (OC), total N concentration (TN), percentage clay, dithionite-extractable Fe and Al (Dith-Fe and Dith-Al), and pH of samples in  $H_2O$ .†

Taxonomy	Horizon	Depth cm	$SFA$		$\Delta H$		OC	TN	Clay	Dith		pH- $H_2O$
			$SFA_u$	$SFA_m$	$\Delta H_{xsu}$	$\Delta H_{xsm}$				Fe	Al	
			$m^2 g^{-1}$		$kJ mol^{-1}$		$mg g^{-1}$	%				
Aquic Udifluent (Winooski series)	Ap	0-25	6.9	14.2	10.7	10.8	14.5	1.30	9			6
	C3	86-119	6.7	8.8	10.8	11.3	4.25	0.41	4.5			6
	C4	119-152	2.8	3.9	9.8	11.0	2.55	0.27	1.5			5.6
Aeric Endoaquept (Walpole)	Apl	0-10	1.6	3.3	8.1	10.6	36.9	2.77				4.8
	2C2	38-53	10.9	14.3	11.6	11.1	2.35	0.21	5.2	3.08	0.12	5.65
	3Cg3	53-79	3.5	3.5	10.3	11.1	1.65	0.11	1.7	0.13	0.01	5.9
Oxyaquic Dystrudept (Paxton)	Ap	0-13	6.2	21.4	12.4	11.1	42.8	2.66	15.4	1.6	0.4	4.45
	Bw2	30-58	16.4	17.9	13.2	11.8	6.85	0.37	16	1.81	0.32	4.45
	Cd1	79-114	15.3	11.4	13.7	11.8	4.89	0.21	13.5	1.61	0.21	4.65
Oxyaquic Dystrudept (Scituate)	Ap	0-20	1.6	22.0	9.0	10.9	58.9	4.67	3	0.9	0.7	4.6
	Bw2	30-48	6.2	11.9	13.0	11.4	6.48	0.40	0.4	0.54	0.35	5.3
	Cd2	102-127	7.4	7.2	12.9	11.5	2.79	0.13	6.1	0.37	0.14	6.2
Dystric Eutrochrept (Stockbridge)	Ap	0-18	6.5	49.0	10.2	11.0	20.2	1.68	17.8	1.7	0.3	5.3
	Bw1	18-43	10.6	15.6	10.0	11.4	5.51	0.32	16.3	1.85	0.27	5.65
	C	53-137	11.8	15.3	10.0	11.2	2.73	0.32	19.7	1.74	0.21	7.15
Oxyaquic Haplorthod (Marlow)	A	0-8	1.1	9.0	7.5	11.1	60.0	3.73	10.7	0.7	0.1	3.4
	Bs2	13-18	3.4	24.0	9.9	10.2	46.6	2.51	8	3.4	0.5	4
	Bs3	18-28	5.9	22.3	12.4	10.4	31.2	1.67	6.9	2.5	0.7	4.3
	Cd	56-102	6.3	9.5	14.5	12.2	2.67	0.19	6.2	1.18	0.23	4.65
Typic Endoaquept (Scitico)	Ap	0-18	6.3	13.4	10.2	11.1	28.9	2.43	16.3	1.5	0.3	5.2
	Bg1	28-48	18.9	22.1	11.4	11.7	4.26	0.28	22.2	1.76	0.21	6.3
	Bg3	48-74	18.0	21.5	10.6	12.0	3.63	0.20	29	1.50	0.14	7.5
Oxyaquic Dystrudept (Broadbrook)	A	0-3	1.4	17.5	10.2	11.3	81.3	4.42	12.9			4.1
	Bw2	25-38	7.1	12.0	12.2	12.0	8.08	0.36	3.4	0.99	0.33	4.45
	Cd2	84-105	9.8	10.5	14.4	11.8	1.79	0.12	9.4	0.95	0.11	4.8
Typic Udorthent (Hinckley)	A	0-3	1.5	16.4	6.5	13.0	96.2	3.68	10			3.9
	Bw2	15-38	10.1	17.7	12.5	12.9	10.7	0.51	2.8	0.57	0.27	4.4
	2C1	38-64	6.1	10.4	13.9	13.1	9.71	0.46	1.2	0.25	0.16	4.8
Typic Dystrudept (Canton)	A	4-13	1.6	8.7	8.2	10.4	31.6	1.23	4.4	0.7	0.2	4.35
	Bw2	29-42	6.6	10.1	11.4	11.9	6.14	0.44	5	0.48	0.31	4.7
	C3	84-98	3.9	3.4	13.5	12.5	0.91	0.02	3.5	0.18	0.15	4.61
Oxyaquic Dystrudept (Bernardston)	Bw2	11-20	14.1	21.5	11.1	11.5	15.0	0.75	10.3	1.83	0.65	4.58
	Bw3	20-38	14.2	18.6	11.2	11.7	7.39	0.45	10.5	1.57	0.42	4.45
	Cd	58-102	7.7	8.6	11.7	11.9	3.46	0.12	9.9	0.75	0.17	4.62
	E	6-12	2.4	6.4	9.0	10.6	29.5	0.76	8.3	0.8	0.1	3.72
Oxyaquic Dystrudept (Lanesboro series)	Bw1	12-22	21.5	31.7	12.0	10.8	30.3	1.23	12.5	4.73	0.88	4.2
	Cd1	56-83	4.9	5.7	12.4	11.1	1.88	0.18	5	0.67	0.19	4.68
Typic Dystrudept (Brookfield)	Bw2	22-41	30.8	40.9			10.8	0.97	13	6.4	1.04	4.45
	C1	53-86	38.5	45.4			3.98	0.25	13.9	5.2	0.46	4.71
Oxyaquic Haplorthod (Marlow)	E	10-15	0.5	1.7			15.7	0.60	3.5	0.1	0.0	3.7
	Bhs	15-18	2.0	19.5			72.6	3.51	8.1	2.35	0.49	3.71
	Cd	66-140	5.2	4.8	14.0		2.15	0.07	4.2	0.46	0.15	4.72
Oxyaquic Dystrudept (Paxton)	A	5-10	1.8	19.4			72.7	5.03	10.6	0.9	0.6	4.35
	Bw2	23-37	8.6	16.5	11.6	11.7	14.4	1.02	11.2	0.78	0.76	4.63
	Bw4	56-66	7.0	8.9	12.1	12.3	3.71	0.26	8.3	0.49	0.30	4.8
Terric Haplosaprist (Swansea)	Oa1	0-10	2.8	16.4			256	15.02				
	Oa2	15-25	1.5	27.3			417	21.73				
	Oa3	50-60	2.4	9.6	7.2	11.3	264	8.15				

† Blank cells indicate not determined.

The slopes of these correlations were consistent with surface area values of several hundred square meters per gram for the sesquioxide phases, in agreement with previous measurements (e.g., Borggaard, 1982; Crosby et al., 1983). This finding is compatible with a previous report of the importance of Fe oxides in contributing to the surface area of soils (Borggaard, 1982). Because the clay content and dithionite-extractable Fe and Al all correlated with one another, it is impossible from our data to specify their relative influence on the surface area. Stepwise regression showed that each variable could explain surface area variance left over from regression on another variable, so it is likely that each of these phases plays a role in the overall surface area

values. Further, analytical artifacts such as 350°C muffling or 150°C outgassing prior to surface area analysis may reduce or enhance the surface areas of sesquioxides (e.g., Aldcroft et al., 1968), making it more difficult to determine the relative contributions of these three variables.

Organic C concentrations ranged from 0.9 to 417  $mg g^{-1}$ —that is, from essentially organic-free C horizons to essentially pure organic litter in an O horizon (Table 1). Total N content ranged from 0.02 to 21.7  $mg g^{-1}$ , with the consequent C/N ratios ranging from 8.7 to 45.5. Lower C/N values are typical of OM stabilized in organoclay aggregates (Stevenson, 1994), and here we found that higher clay contents generally led to lower

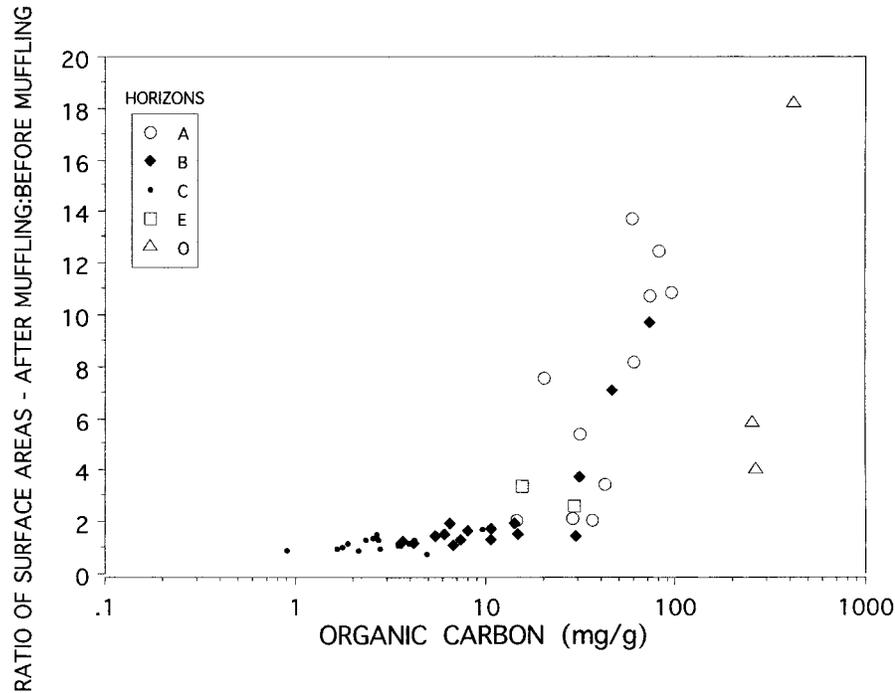


Fig. 1. Ratio of specific surface area values for soils subjected to only degassing to those subjected to 350°C muffle to remove organic matter, plotted against the organic C content of the unmuffled samples. Samples with ratio of  $\approx 1$  (i.e., most C horizons) thus had little change in surface area upon muffle. Abscissa expanded to log scale only to show data more clearly.

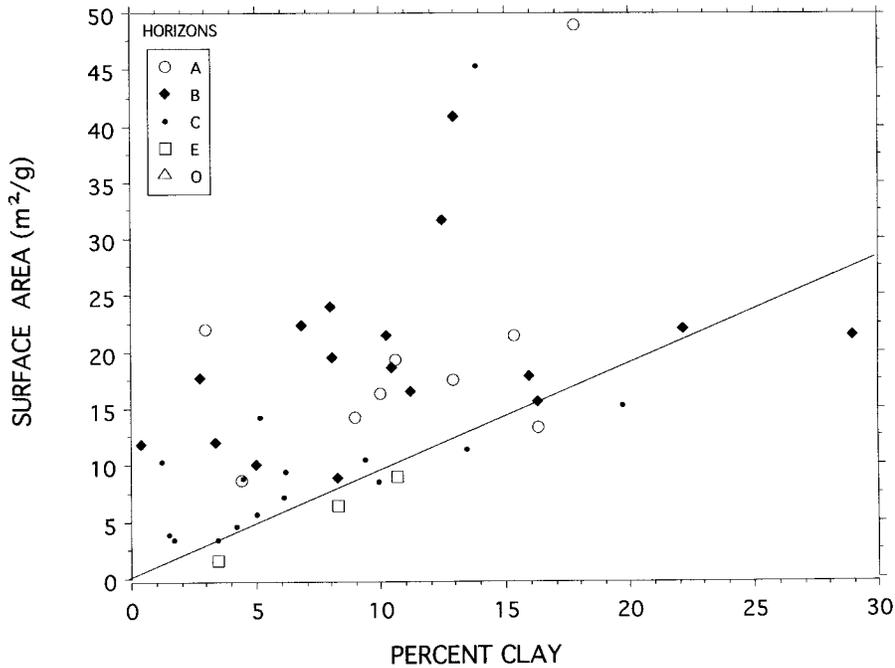


Fig. 2. Specific surface area (m<sup>2</sup> g<sup>-1</sup>) of 350°C-treated samples vs. the percentage clay, which are positively correlated ( $P = 0.0004$ ). Diagonal line represents the relationship: Surface Area (m<sup>2</sup> g<sup>-1</sup>) = 0.9(Percentage Clay), and roughly bounds the lower limit of the data.

C/N ratios, although low C/N values were also found in some samples with low clay content.

Plotted against specific surface area, the OC concentrations of most of the samples from B and C horizons studied here fell into the ME zone as defined by the marine sediments studied previously (Fig. 3). All O, all E, and most A horizon samples had OC loadings higher than the ME level. However, OC concentrations did

not show overall significant correlations with either clay content or surface area, although the C horizons alone did show significant correlations. The loadings, parameterized as a ratio of OC to surface area, instead showed a strong inverse relationship ( $P = 0.001$ ) with soil pH (Fig. 4), whether measured in H<sub>2</sub>O or CaCl<sub>2</sub>. This inverse relationship was driven by trends seen with the A and B horizons, with the A horizons having generally higher

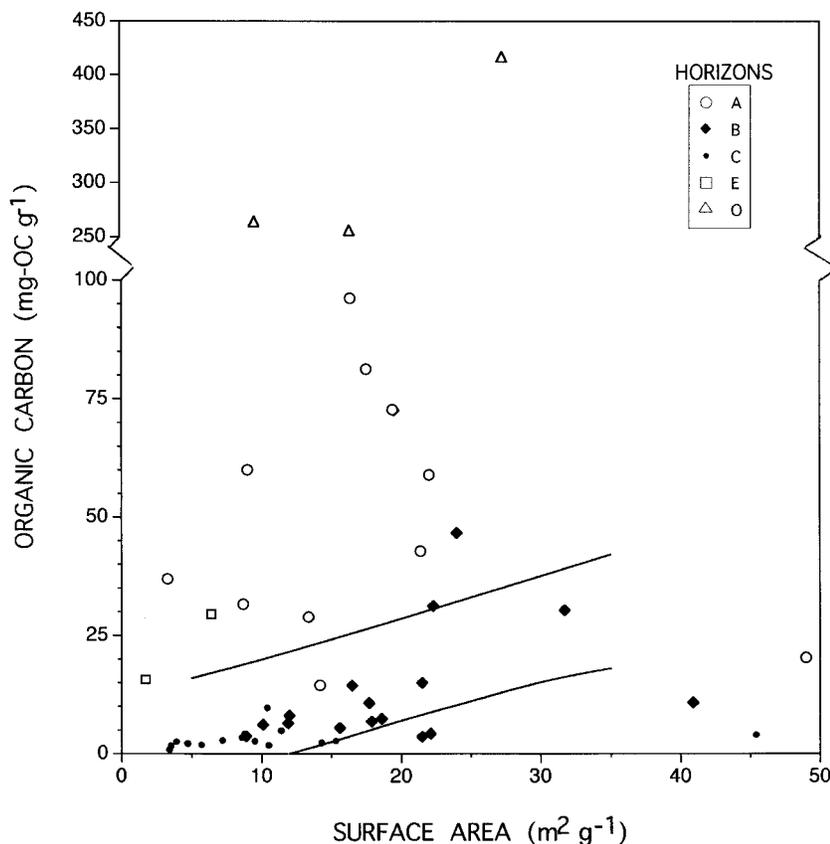


Fig. 3. Organic C concentrations vs. specific surface area. The diagonal lines bound the 95% confidence interval of the monolayer-equivalent zone from Mayer (1994a).

ratios at any given pH. Considered alone, the C horizon loadings showed no dependence on pH.

The  $\Delta H_{xs}$  values found for untreated samples (Fig. 5) ranged from 6.5 to 14.5 kJ mol<sup>-1</sup>, broader than the range previously found (Mayer, 1999) for mineral endmembers ( $\approx 10$ –12 kJ mol<sup>-1</sup>), OM endmembers (8–10 kJ mol<sup>-1</sup>), and minerals and sediments that were artificially or naturally coated with OM (7.5–12 kJ mol<sup>-1</sup>). Especially unusual were the high values ( $>12.5$  kJ mol<sup>-1</sup>) found in a number of C and B horizon samples. Our findings are consistent with the C constant data reported by Pennell et al. (1995).

High  $\Delta H_{xs}$  values can result from the presence of micropores with diameters of  $<2$  nm, so we examined microporosity using the *t*-plot method (deBoer et al., 1966). This method compares gas adsorption volume with a standard presumed to be a nonmicroporous representative of the material in question. Our previous use of this approach (Mayer, 1999) led us to believe that the standard employed by the instrumental software was appropriate (LeCloux and Pirard, 1979) for the bulk minerals in these samples. In this study, we found a strong correlation between  $\Delta H_{xs}$  values and the percentage of surface area in micropores (Fig. 5a), a relationship that implies that the unusually high values in the C and B horizon samples were due to microporosity. The relationship was either hidden or not present in some samples for which the *t*-plot approach found no indication of microporosity. This latter result may have de-

rived from the use of an inappropriate standard reference curve for samples with largely organic surfaces. While the exact values for percentage microporosity may not be accurate (they depend on a combination of correct standard curve and assumptions of micropore size distribution), the functional relationship does imply that significant microporosity (though accounting for no more than 10–30% of the total surface area) was present in some of these samples and can strongly influence  $\Delta H_{xs}$  values.

The highest  $\Delta H_{xs}$  values were found in soil horizons with pH (H<sub>2</sub>O) values of  $\approx 4.6$  to 4.8 (Fig. 5b). C horizons with low OC/surface area ratio exhibited these anomalous  $\Delta H_{xs}$  values most strongly. Loss of these  $\Delta H_{xs}$  values upon muffling (see below) implies a loss of microporosity. A possible reason for this loss is that the microporosity in the untreated samples originates from a phase such as Fe or Al oxyhydroxides, which can exhibit significant microporosity (Torrent et al., 1992) and might recrystallize upon muffling to new phases with loss of surface area and microporosity. However, there was no correlation of these high  $\Delta H_{xs}$  values with high levels of dithionite-citrate-extractable Fe or Al. This lack of correlation does not necessarily exclude Fe or Al oxyhydroxides as the source of the microporosity, but the responsible phases remain unidentified. The high  $\Delta H_{xs}$  values are consistent with the common presence of sesquioxides in the lower horizons of podsoles (e.g., Gustafsson et al., 1999). The maximal  $\Delta H_{xs}$  values in the C rather than

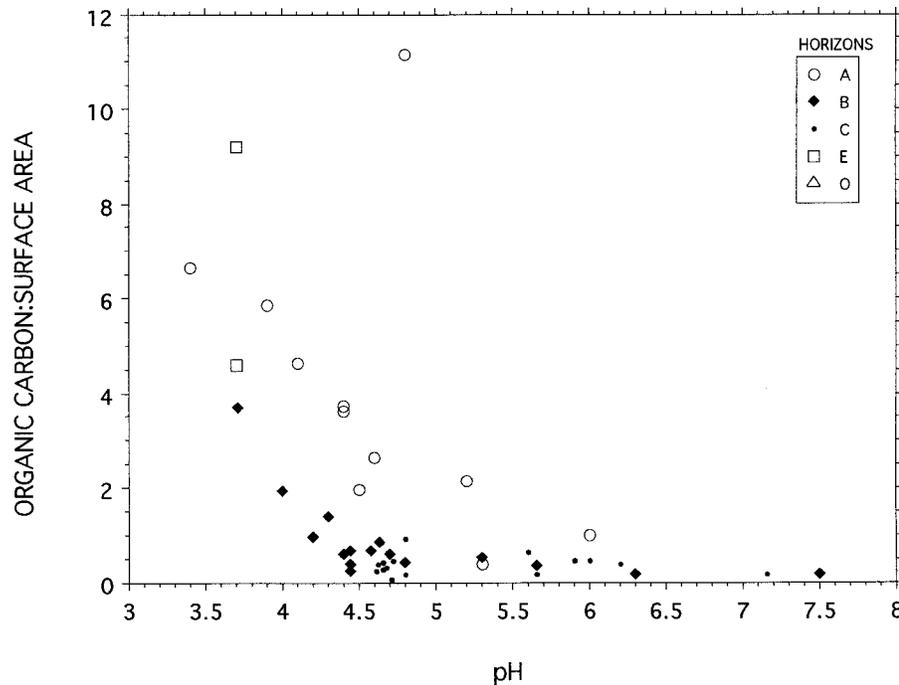


Fig. 4. Surface area-normalized organic C (OC) concentrations ( $\text{mg OC m}^{-2}$ ) vs. soil pH (measured in  $\text{H}_2\text{O}$ ). Inverse correlation significant at  $P = 0.001$ .

the B horizons, in which sesquioxide concentrations generally peak, may be due to occlusion of micropores by adsorption of OM in B horizon sesquioxides (Farmer, 1982). An alternative explanation for this microporosity is the possibility that OM causes clay platelets to orient in a fashion that creates interparticle micropores, which are lost upon destruction of the OM via muffling. Microporosity is known to arise from clay mineral interparticle contacts (Murray and Quirk, 1990), but this explanation seems less likely than one involving sesquioxides.

The  $\Delta H_{\text{xs}}$  values of the untreated samples (i.e., those with their OM still present) were inversely correlated with the ratio of OC to the surface area of the mineral fraction (i.e., the surface area of the muffled samples)

(Fig. 5c). Most C and B horizon samples had  $\Delta H_{\text{xs}}$  values similar to those of mineral surfaces, while A horizons showed a gradation from mineral to organic surface values and O horizons showed values characteristic of largely organic surfaces.

Upon muffling of the samples, the range of  $\Delta H_{\text{xs}}$  values narrowed to 10.2 to 13  $\text{kJ mol}^{-1}$ , so that samples with previously low values yielded higher  $\Delta H_{\text{xs}}$  values and the converse for samples with previously high values (Table 1). This narrower range is consistent with bulk aluminosilicate mineral surfaces (Mayer, 1999). Although the unusually high  $\Delta H_{\text{xs}}$  values disappeared upon muffling, there were no accompanying decreases in surface area values, consistent with the relatively minor

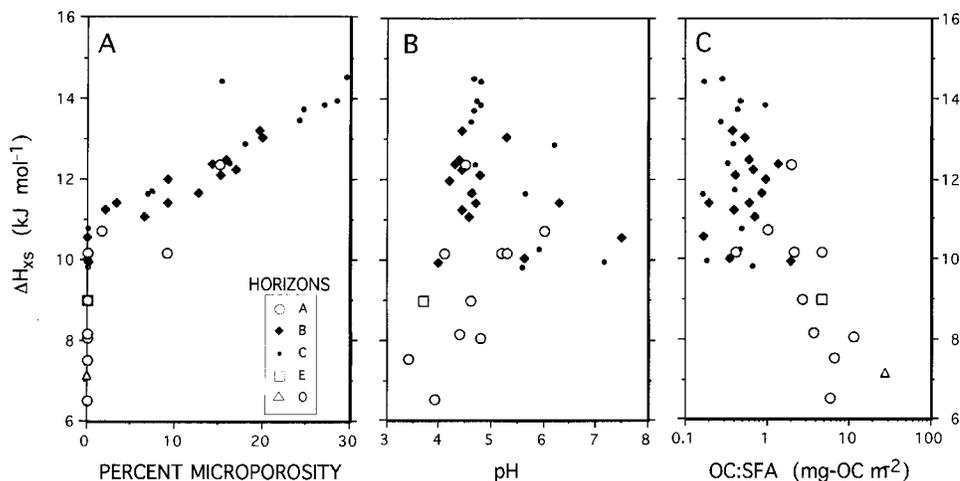


Fig. 5. Excess enthalpy ( $\Delta H_{\text{xs}}$ ) of  $\text{N}_2$  gas adsorption onto untreated soil samples, vs. (A) the percentage of Brunauer–Emmett–Teller surface area contained in micropores of  $<2$  nm; (B) pH of the soil, measured in  $\text{H}_2\text{O}$ ; (C) the ratio of organic C (OC) concentration to the mineral surface area (SFA) (i.e., of muffled samples) ( $\text{OC/SFA: mg OC m}^{-2}$ ).

(<30%) contributions to surface area from microporosity calculated by the *t*-plot approach (Fig. 5a). Moreover, none of the relationships between  $\Delta H_{xs}$  values and percentage microporosity, pH, or OC/surface area ratio (Fig. 5) persisted after muffling. Thus, phases affected by muffling were implicated for the low and high  $\Delta H_{xs}$  values found with the untreated samples—that is, phases such as OM for samples with low  $\Delta H_{xs}$  values and metal oxyhydroxides for samples with high  $\Delta H_{xs}$  values. As noted above, micropores in inorganic phases may have been present in samples with higher organic loading, but filled with OM. Such samples would exhibit less microporosity in the unmuffled treatments but would lose both microporosity and OM upon muffling.

**DISCUSSION**

**Organic Matter Loadings**

It is clear that OC levels in these soils were often higher than is consistent with ME loadings found in marine sediments and soils from other regions (Mayer, 1994a, 1994b). The A horizons studied here had higher loadings than found for many A horizons, but in keeping with those of acidic soils in other parts of the USA (compare Fig. 3 with Fig. 5 in Mayer, 1994b). It is also clear that the higher loadings occurred in association with lower pH values (Fig. 4). There was also an inverse correlation between C/N ratio and pH (Fig. 6) so that these excess loadings in lower pH soils may represent largely undecomposed vascular plant detritus, which was visible in many of the samples. Samples from soils with higher pH, or from lower soil horizons, had OC/surface area ratios and C/N ratios similar to organomineral aggregates (Mayer et al., 1993; Bock and Mayer, 2000; Stevenson, 1994). This pH trend is in accord with the preferential preservation of lignin biomarkers in acid soils and relative abundance of nitrogenous compounds in higher pH soils found by van Bergen et al. (1998).

**Organic Coating of Mineral Surfaces**

What fraction of the exposed surfaces in these soils consists of OM and what fraction is uncoated mineral?

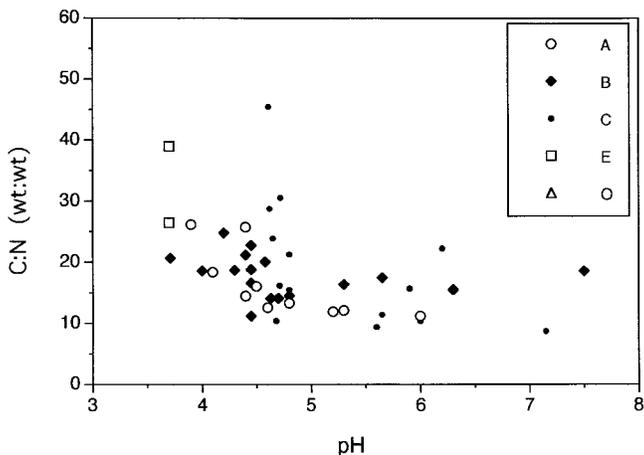


Fig. 6. Carbon/N ratio (w/w) vs. soil pH (measured in H<sub>2</sub>O).

We previously developed a model to calculate the fractional coverage of mineral grains by OM (Mayer, 1999). This model relied on the difference in  $\Delta H_{xs}$  values between an untreated and muffled sample, using a calibration derived by progressively coating various mineral phases with various monomeric organic compounds. That model is applicable to marine sediments because very little of the mineral surface area is occluded, so that the  $\Delta H_{xs}$  values of untreated sediment represent an average of all mineral surfaces, whether coated with OM or not. However, the very high occlusion of mineral surfaces found in this study, as evidenced by the release of surface area upon muffling (Fig. 1), implies that the  $\Delta H_{xs}$  values of the untreated samples do not represent all mineral surface. Thus, use of this approach provides a measure only of the fraction of surface exposed in the untreated sediments (Fig. 7, upper) that is organic. If OM occludes most mineral surface, then this approach will not estimate the fractional coverage of all mineral surface (Fig. 7, lower) that was covered by OM in the untreated soils. We therefore assessed both the fraction of untreated sample surface that was covered by OM (Fig. 7, upper) and the fraction of total mineral surface covered by OM (Fig. 7, lower).

For the first calculation we used the approach described in Mayer (1999), comparing the  $\Delta H_{xs}$  values of the untreated and oxidized samples. With this approach, most of the surface area in most untreated samples is dominated by uncoated mineral surfaces (Fig. 8a). The only samples showing significant fractions of organic surfaces are the E horizons, a few of the A horizons, and the O horizon (which is not plotted due to lack of pH data, but was completely organic). In other words, despite coverage of most mineral surfaces by OM, the remaining surface area is still dominated by uncoated, fine-grained, mineral surfaces. Clearly the OM that oc-

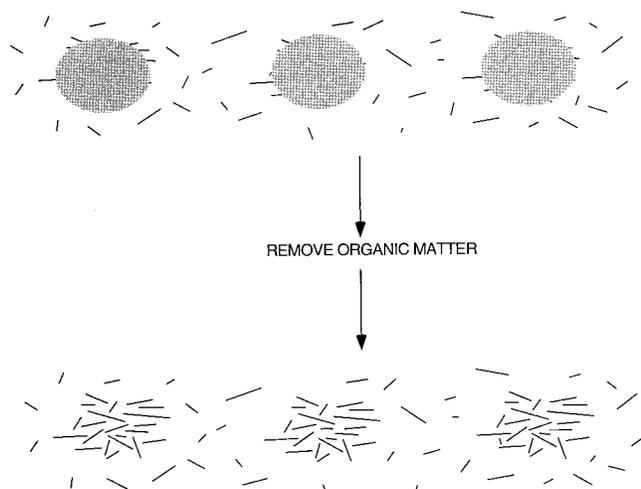


Fig. 7. Schematic diagram of clay minerals in soil, with organic matter binding some fraction of them into aggregates in untreated soil (above, with organic matter represented as solid ovals), such that a major fraction of the exposed surface area is due to uncoated minerals. Upon removal of the organic matter by muffling (below) the clays previously contained within aggregates are exposed, vastly increasing the surface area.

cludes most surfaces is present in a form that has little surface area. Because simple organic coatings on mineral surfaces are capable of exhibiting high surface area (Mayer, 1999), the configuration of the OM is probably of the type pictured in Fig. 7—an organoclay aggregate with a small fraction of the OM exposed as surface. This configuration is consistent with the findings of Pennell et al. (1995), showing soil OM to be capable of taking up ethylene glycol (EG) well in excess of the amount predicted from adsorption on its external surface as measured by N<sub>2</sub> gas adsorption.

For the second calculation—determination of the fraction of total mineral surface that is covered by OM—we used an alternate approach based on the occlusion of surface area that is released by muffling. If we assume that all surface area uncovered during the muffling process represents surfaces that were occluded by OM in the untreated state (in the sense of being inaccessible to N<sub>2</sub> gas during the surface area analysis), then we can calculate the fraction of total mineral surface covered by OM by the relation

$$\text{Fractional cover by OM} = (\text{SFA}_m - \text{SFA}_u) / \text{SFA}_m \quad [3]$$

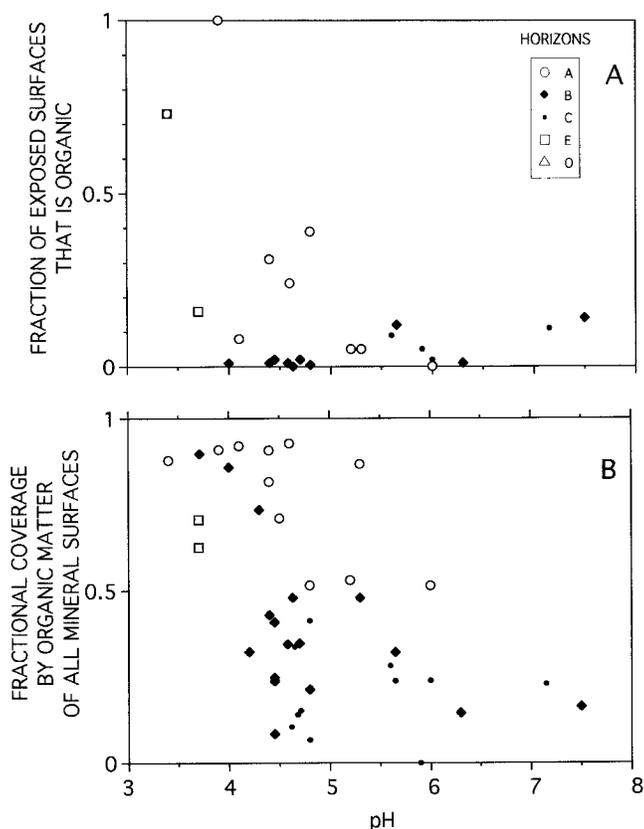


Fig. 8. Fraction of surfaces in soils that is organic, plotted vs. soil pH: (A) fraction of exposed surfaces (in the untreated samples) that is organic, as calculated according to the excess enthalpy method of Mayer (1999); (B) fractional coverage by organic matter of all mineral surface area, and is a minimum estimate based on the extent of occlusion of total mineral surface area that is exposed by organic matter removal. O horizon samples are not plotted because of lack of pH data; their organic coverage values are  $\approx 1$  according to either calculation method.

where  $\text{SFA}_m$  is the surface area of the muffled sample (i.e., total mineral surface area) and  $\text{SFA}_u$  is the surface area of the untreated sample. This estimate is conservative because it assumes that all surface area measured on the untreated sample had no OM coating. This assumption is generally supported by the enthalpy-based calculations (Fig. 8a), which show that exposed surfaces in most samples were largely inorganic mineral in nature. To the small extent that this assumption is incorrect, fractional cover of minerals by OM will be even greater than the estimates derived from Eq. [3]. Nevertheless, using Eq. [3] with this assumption, only samples with higher pH values have exposed surfaces dominated by uncoated minerals (Fig. 8b). Samples with lower pH, especially from upper soil horizons, have most mineral surfaces covered by OM.

The differing fractional coverages in Fig. 8a and 8b are not different answers to the same question, but rather differ in the question they address. Figure 8a shows that most exposed surface area (accessible to N<sub>2</sub> at 77°K) is inorganic mineral, while Fig. 8b implies that most mineral surface is covered by OM. These relationships imply that coverage of soil mineral surfaces occurs via an occlusion rather than a simple adsorption mechanism.

The pH dependence of surface coverage is consistent with simple adsorption of OM as predicted by laboratory experiments (e.g., Gu et al., 1995). However, adsorption by relatively small molecules in a thin coating probably would not reduce surface area of the minerals (Mayer, 1999).

### Implications for Soil Reactivity

The high degree of mineral surface occlusion in these lower pH soil horizons differed considerably from the greater mineral exposure found in marine sediments (Mayer, 1999) and perhaps higher pH soils. One consequence of this occlusion may be greater protection of minerals from equilibration with bulk soil solutions. This protection may lead to either inhibited reactivity (e.g., via simple armoring of the mineral surface) or enhanced reactivity (e.g., via formation of microenvironments enriched in organic acids).

The high occlusion also implies that organomineral aggregates in the lower pH soils have reduced diffusional access for contaminant sorption, relative to their organic content. Organic matter types vary in their abilities to sorb contaminants (Xing et al., 1994; Xing and Pignatello, 1997; Huang and Weber, 1997). It seems likely that the type of OM responsible for ME loadings, with its minimal occlusion of mineral surface area, will have different sorbing characteristics than the OM in low-pH soils that strongly occludes the minerals. Again, it is difficult to predict even the direction of the net effect; for example, the sorption potential of occluded aggregates might be greater because of geometric considerations but lesser because of compositional ones. The different sorbent characteristics may be exhibited as different sorption capacities, kinetics, or degree of adsorption–desorption hysteresis; these implications merit further attention.

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