

TRANSPORT AND FRACTIONATION OF DISSOLVED ORGANIC MATTER IN SOIL COLUMNS

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Dissolved organic matter (DOM) is a heterogeneous mixture of organic compounds that plays an important role in the movement of DOM-associated pollutants. In this study, transport and fractionation of DOM in soils was investigated in flow-through soil columns. Dissolved organic matter derived from spent mushroom substrate weathering was pumped through packed columns (2.5 cm × 10 cm) comprising a coarse-loamy subsoil (mixed, semiactive, mesic Typic Hapludult), and effluents were monitored for changes in the composition of DOM. Effluent DOM was characterized for UV absorbance, molecular weight, acidity, and hydrophilicity. Transport through the columns resulted in preferential retention of specific DOM constituents as indicated by comparison with a Br⁻ tracer. During the transport process, effluent DOM exhibited decreasing values of E₂/E₃ (from 10.3 to 6.2), acidity (from 20.8 to 13.1 mmol_c g⁻¹ C), and hydrophilicity (39.0 to 28.4%), and increasing values of molar absorptivity (from 164 to 310 L mol⁻¹ C cm⁻¹) and number and weight-averaged molecular weight (from 1770 to 3150 and 2450 to 4180 Da, respectively). These results indicate that DOM fractions with higher molecular weight, higher molar absorptivity, lower E₂/E₃ ratio, lower acidity, and lower hydrophilicity were adsorbed preferentially by soil minerals, whereas the inverse fractions were transported preferentially. The adsorbed DOM could not be completely desorbed by DOM-free background solution, indicating a strongly bound fraction. Sorptive fractionation of DOM during transport likely affects the transport behavior of DOM-complexed constituents. (Soil Science 2003;168:108-118)

Key words: Dissolved organic matter (DOM), soil column, transport, fractionation, hydrophilicity, acidity, molar absorptivity, molecular weight.

DISSOLVED organic matter (DOM), comprising soluble biomolecules and humic substances, is a common constituent of aquatic systems and plays an important role in environmental quality. Transport of pollutants in natural environments may be enhanced by their complexation with DOM (Sposito, 1986; Graber et al., 1995; Camobreco et al., 1996; Nelson et al.,

1998). Heavy metals may form complexes with polar functional groups of hydrophilic DOM, and nonpolar organic contaminants may sorb to hydrophobic DOM domains (Sheppard et al., 1980; Berggren et al., 1990; Maxin and Kogel-Knabner, 1995). Therefore, the extent to which these various DOM fractions are mobile in porous media affects the mobility of associated contaminants.

To predict the movement of DOM-associated pollutants, transport and fractionation of DOM in soils must be better understood. Previous studies show that a portion of DOM may be adsorbed by soil solids during transport through the porous media (McDowell and Likens, 1988; McCarthy et al., 1993; Zech et al., 1994; Dosskey and Bertsch, 1997), and sorption to soil minerals

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Received June 17, 2002; accepted Sept. 25, 2002.

DOI: 10.1097/01.ss.0000055306.23789.55

is a primary mechanism of OM retention in soils (McDowell and Wood, 1984; Moore et al., 1992; David et al., 1995).

Natural DOM is a heterogeneous mixture, and different DOM fractions have different affinities for soil materials (Jardine et al., 1989; Dunnivant et al., 1992; Kaiser and Zech, 1997). Fractionation of DOM occurs during the sorption and transport process (Evans, 1986; Gu et al., 1996; Kaiser and Zech, 1999; Meier et al., 1999), and affinities of DOM constituents for soil minerals are controlled by their respective chemical properties (McKnight et al., 1992; Wershaw et al., 1996; Kaiser et al., 1997; Zhou et al., 2001). Investigators using batch isotherm techniques have found that DOM components having low molecular weight (MW), organic N, acidic functional groups, and aromatic structures remain dissolved, whereas high MW components rich in N, acidic groups, and aromatic moieties are sorbed preferentially by Al/Fe oxides (McKnight et al., 1992; Gu et al., 1995; Meier et al., 1999; Chorover and Amistadi, 2001). Increasing the acidity of humic acids decreased their complexation with 2:1 layer-type clay minerals (Nayak et al., 1990), whereas DOM fractions of lower MW were preferentially retained on montmorillonite and no preference for aromatic moieties was observed (Chorover and Amistadi, 2001). Hydrophobic DOM fractions have a stronger affinity for soils than do hydrophilic fractions and are preferentially adsorbed (Jardine et al., 1989; Dunnivant et al., 1992; Gu et al., 1995). Under conditions of limited available binding sites in natural soils, in-

fluent hydrophobic DOM may displace indigenously adsorbed hydrophilic organic substances (Kaiser and Zech, 1997).

Previous studies concerning DOM-soil interaction were carried out using batch equilibrium techniques, and it is not clear if the results are directly applicable to the dynamic flow regimes that predominate in open soil systems. Hence, transport and fractionation of DOM in flow-through reactors such as soil columns warrants systematic research. The information gained will set the foundation for predicting the environmental fate of associated pollutants and in understanding DOM-soil interaction mechanisms. The objective of this study was to investigate the transport and fractionation behavior of a compost-derived DOM in saturated soil columns by measuring the compositional changes of effluent DOM during reactive transport.

MATERIALS AND METHODS

Column Experiments

Soil material was collected at 40 to 50-cm depths (Bt1 horizon) under grassland (Coarse-loamy, mixed, semiactive, mesic Typic Hapludult) in West Grove, Pennsylvania. The B horizon was chosen because we wanted to minimize the effects of native organic matter on the fractionation process. The soil was formed in residuum weathered from micaceous schist, and the major mineralogical components are mica, kaolinite, smectite, quartz, and hematite. Selected properties of the soil are listed in Table 1.

TABLE 1

Selected physico-chemical properties of the soil material. All numbers are averages of triplicate measurements (standard deviations are in parentheses)

Parameter	Value
Taxonomic name	Coarse-loamy, mixed, semiactive, mesic Typic Hapludult
Mineralogy	Muscovite, smectite, kaolinite, hematite and quartz
Texture [‡] (g kg ⁻¹)	Clay 87 (1); Silt 329 (3); Sand 584 (1)
pH (soil: H ₂ O = 1:1)	7.33 (0.03)
TOC (g kg ⁻¹)	2.13 (0.06)
CEC (mmol _c kg ⁻¹ soil)	69.10 (0.36)
Organic bound iron [§] (g kg ⁻¹)	0.01 (0.005)
Poorly crystalline iron [†] (g kg ⁻¹)	0.97 (0.07)
Free iron oxides [‡] (g kg ⁻¹)	35.72 (1.23)

TOC: total organic carbon.

CEC: cation exchange capacity.

[‡]Measured by hydrometer method.

[§]Extracted with 30% H₂O₂ at 65°C for 12 h.

[†]Extracted with 0.175 M NH₄-oxalate + 0.1 M oxalic acid (pH 3.0).

[‡]Extracted with CBD reagent (0.3M sodium citrate + 0.1M sodium bicarbonate + sodium dithionite).

Leachate collected from laboratory-simulated spent mushroom substrate (SMS) weathering was used as the input DOM solution. Spent mushroom substrate is composed primarily of composted plant debris (dominantly hay and straw), and the DOM solution was obtained during a field and laboratory study in regard to the environmental impact of SMS weathering (Guo et al., 2001a and b). Briefly, 23.6 kg of fresh SMS were packed into a 150 cm high \times 20 cm i.d. acrylic column and leached with deionized water at 2.5 mL min⁻¹ for 28 consecutive hours every 10 days. Leachate collected in the first 90 days of the weathering process was mixed and stored at 4 °C prior to use. The DOM solution was transformed to K⁺ form by passing it over K⁺-saturated cation exchange resin to remove polyvalent cations that may influence the nominal MW of DOM and its interaction with soil minerals (Römken et al., 1996; Kaiser, 1998). Potassium is also the dominant cation in SMS leachate (Guo et al., 2001a). The K⁺-form DOM solution was then filtered through an Amicon YM10 ultrafiltration membrane (MW cutoff 10,000 Da, Millipore Corp., Bedford, MA) to remove microbial cells, enzymes and other colloidal material. Sodium azide (20 mg L⁻¹) was added to the filtered DOM solution to prevent microbial growth, and 5 mM Br⁻ (as KBr) was added as a tracer. No attempt was made to displace inorganic anions from the DOM solution since our objective was to monitor the SMS DOM migration in a relatively natural state. Selected chemical properties of the DOM solution are listed in Table 2.

Soil columns were prepared in duplicate by packing air-dried soil (sieved to <2 mm) into 10 cm \times 2.5-cm-i.d. glass columns (Sigma-Aldrich Chemical Company, St. Louis, MO). A total of 63 g of soil (oven dry mass) were packed in each column to 10 cm depth. Five grams of <1 mm acid-washed quartz grains were placed above the bottom bed support (pore size 20 μ m, polyethylene) to form a 0.8-cm-thick sand layer that prevented fine soil particles from clogging the bed support. Another sand layer was placed on the top of each column, followed by a piece of column bed support to maintain soil column shape. The packed soil columns had a bulk density of 1.24 g cm⁻³, a pore volume of 27.4 cm³, and hydraulic conductivity of 0.48 cm h⁻¹ at 15 cm of constant head.

The soil columns were saturated with KCl by pumping 0.5 M KCl at 0.05 mL min⁻¹ through the column until no Ca²⁺ was detectable in the effluents (by reaction with 0.1 M Na-oxalate).

TABLE 2

Chemical properties of the dissolved organic matter input solution. All values are averages of triplicate measurements (standard deviations are in parentheses)

Parameter	Value
<i>Chemical background</i>	
pH	8.80 (0.01)
EC (dS m ⁻¹)	11.60 (0.07)
K ⁺ (mmol L ⁻¹)	92.7 (0.15)
Na ⁺ (mmol L ⁻¹)	0.77 (0.005)
Ca ²⁺ (mmol L ⁻¹)	0.61 (0.009)
Mg ²⁺ (mmol L ⁻¹)	0.20 (0.006)
Cl ⁻ (mmol L ⁻¹)	15.54 (0.02)
SO ₄ ²⁻ (mmol L ⁻¹)	20.2 (0.10)
NO ₃ ⁻ (mmol L ⁻¹)	5.18 (0.04)
Br ⁻ (mmol L ⁻¹)	5.02 (0.02)
<i>Dissolved organic matter</i>	
DOC (mg L ⁻¹)	1430 (3.9)
E2/E3	6.08 (0.014)
Molar absorptivity (L mol ⁻¹ C cm ⁻¹)	312 (3.42)
Hydrophilicity (% of total C)	28.4 (0.54)
Carboxylic acidity (mmol _c g ⁻¹ C)	9.9 (0.22)
Phenolic acidity (mmol _c g ⁻¹ C)	3.02 (0.03)
M _w	4190 (248)
M _n	3190 (27)

EC: electrical conductivity.

DOC: dissolved organic carbon.

M_w: weight-averaged molecular weight.

M_n: number-averaged molecular weight.

The pore water ionic strength was then reduced by flushing the column with three pore volumes of 0.1 M KCl. Finally, a background solution (0.093 M KCl with 20 mg L⁻¹ NaN₃, pH 8.8) was passed through the columns until effluents had the same EC and pH values as the input solution. This background electrolyte concentration was selected because it is consistent with that of SMS leachate chemistry as observed in the field (Guo et al., 2001a).

The DOM solution was loaded to the soil columns with a peristaltic pump at a rate of 0.05 mL min⁻¹ (0.59 cm hr⁻¹). Effluents were collected with an automatic fraction collector (ISCO, Inc., Lincoln, NE) at 5-mL increments for the first 10 samples, followed by 10-mL increments for the remaining samples, to a total of 10 pore volumes. Following DOM adsorption, the DOC-free (0.093 M) background solution was applied to the columns, and effluents were collected until effluent DOC concentration achieved steady state. At the end of the experiment, the soil columns were air dried and analyzed for total organic carbon (TOC) contents.

Analytical Methods

Bromide concentrations in the effluents were measured by ion chromatography (IC) (Dionex DX 500 with an AS40 automated sampler, an IonPac AS14 ion exchange column, and an ED40 electrochemical detector, Dionex Corp., Sunnyvale, CA). The flow rate was 1 mL min^{-1} , and run time was 16 min per sample. An isocratic mobile phase comprising water and $27 \text{ mM Na}_2\text{CO}_3/10 \text{ mM NaHCO}_3$, was employed. Dissolved organic carbon (DOC) content was determined using a Shimadzu TOC-5000A total organic carbon analyzer (Shimadzu Scientific Instruments, Columbia, MD) with an ASI-5000A auto sampler.

Dissolved organic matter effluent was analyzed for molar absorptivity, E2/E3 ratio, molecular weight distribution, acidity and hydrophilicity. Molar absorptivity was determined using UV spectroscopy (Shimadzu 3101PC UV-Vis-NIR, Columbia, MD) as absorbance at 280 nm, normalized by DOC concentration, and E2/E3 ratio was the quotient of the absorbance at 250 nm to that at 365 nm.

Molecular weight distributions of DOM were assessed by high performance size exclusion chromatography (HPSEC) using the method of Zhou et al. (2001). The HPSEC data were collected on a HPLC system (Waters Inc., Milford, MA) equipped with a HEMA Bio 40, $8 \times 300\text{-mm}$ column (PSS Polymer Standards Service-USA, Silver Spring, MD) and Millennium³² software (Waters Inc., Milford, MA). Weight-average molecular weight (M_w) and number-average molecular weight (M_n) of DOM were calculated in the Millennium³² software:

$$M_w = \frac{\sum_{i=1}^N h_i(M_i)}{\sum_{i=1}^N h_i} \quad (1)$$

$$M_n = \frac{\sum_{i=1}^N h_i}{\sum_{i=1}^N (h_i/M_i)} \quad (2)$$

where h_i is the height of the sample HPSEC curve eluted at volume i , and M_i is the molecular weight of the sample HPSEC curve eluted at volume i , as calibrated using polystyrene sulfonate standards.

Acidity of the DOM was measured using the acid-base titration method of Inbar et al. (1990) with slight modifications. The DOM solutions were acidified with HCl to below pH 2.5, degassed with N_2 for 10 min, and then titrated with freshly prepared and calibrated 0.1 M NaOH to pH 8.00 under an N_2 atmosphere. After equilibration at pH 8.00 for 10 min, the solutions were

titrated continuously to pH 10.00. Carboxyl group content was calculated from the amount of base required to titrate the solution between pH 3.00 and 8.00. Phenolic group content was calculated by assuming that 50% of the phenolic sites are dissociated at pH 10.00 and that the base consumption between pH 8.00 and 10.00 represented half of the phenolic content (Bowles et al., 1989). Total acidity was calculated from the sum of carboxylic and phenolic acidity. Equal volumes of the background solution (0.093 M KCl) were titrated as blanks.

Hydrophilicity of DOM was measured using the method of Leenheer (1981). The DOM solutions were first diluted with MilliQ-water to $<50 \text{ mg L}^{-1}$ DOC, acidified to pH 2.0 with HCl, and then passed through an XAD-8 resin column ($10 \text{ cm} \times 2.5 \text{ cm i.d.}$, SupeliteTM DAX-8, Sigma-Aldrich, St. Louis, MO) at 2.4 mL min^{-1} . The column was rinsed with 2 pore volumes of 0.01 M HCl before and after each DOM solution application, and DOM eluted during the post application rinse was combined with the effluent. The DOM passing through the column is defined operationally as *hydrophilic*, whereas the adsorbed mass is defined as *hydrophobic*. The operational nature of these terms must be emphasized inasmuch as all of the DOM is sufficiently hydrophilic to enter the solution initially. The DAX-8 sorption technique is simply intended to remove from solution the less hydrophilic constituents. Hydrophilicity was quantified as the percentage of bulk DOC that passes through the DAX-8 column. The adsorbed DOM was back-eluted out of the column with 6 pore volumes of 0.1 M NaOH at 2.0 mL min^{-1} .

To gain insight into the functional group chemistry of hydrophilic and hydrophobic fractions, influent DOM solution was fractionated on XAD-8 resin (using the method outlined above) and then analyzed by transmission Fourier transform infrared spectroscopy (FTIR). The hydrophobic fraction was desorbed from the XAD-8 resin by back eluting with 0.1 M KOH . Both fractions were concentrated by rotating evaporation at 50°C , then adjusted to pH 8.8 with 0.1 M KOH or HCl, and analyzed for DOC concentration. A 0.5-mL aliquot of solution was pipetted onto an infrared transparent ZnSe window and vacuum dried at room temperature (20°C). The drying process was repeated until $50 \text{ }\mu\text{g}$ of carbon formed a thin film on the window, which was then placed in the IR beam for collection of IR absorbance spectra with a Nicolet Magna 560 FTIR spectrometer (Thermo Nicolet, Madison, WI).

RESULTS AND DISCUSSION

Transport of DOM in Soil Columns

Duplicated transport experiments are reported for input solutions comprising 5 mM Br⁻ and 1433 mg L⁻¹ DOC. Concentration ratios (C/C_0) were calculated from effluent (C) and influent (C_0) concentrations for both Br⁻ and DOC, and breakthrough curves (BTCs) are presented in Fig. 1. These BTCs are typical of homogenous soil media (Jury et al., 1991; Dunnivant et al., 1992; Camobreco et al., 1996), suggesting no preferential flow occurred in the repacked soil columns. The BTCs of Br⁻ were characterized by an abrupt concentration increase to $C/C_0 = 1$ at 1.1 pore volumes, and the BTCs of DOC were distinguished by a rapid concentration increase at 0.9 pore volumes followed by extended tailing to 5.5 pore volumes before reaching the influent concentration (Fig. 1). The DOC BTCs initially overlapped those for Br⁻, but they shifted to the right at 0.9 pore volumes, with the remainder of the DOC eluting significantly later than the nonreactive tracer. Some DOC eluted out of the soil columns ($C/C_0 = 0.25$) simultaneously with Br⁻ at 1.1 pore volumes, suggesting that approximately one-fourth of the DOM constituents are transported conservatively in the soil columns, and the delayed breakthrough of DOC relative to Br⁻ results from selective and competitive adsorption of DOM components by soil solids. Delayed breakthrough of DOC relative to Cl⁻ or Br⁻ in soil column studies has been reported previously

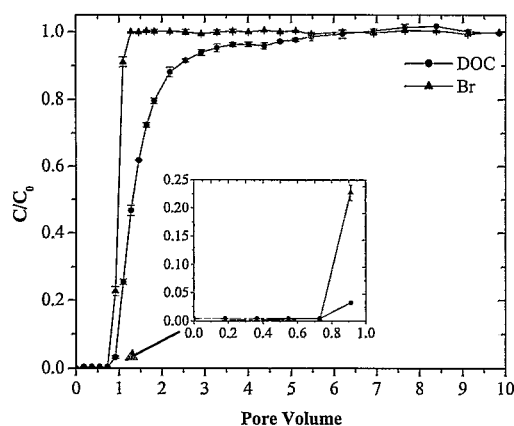


Fig. 1. Breakthrough curves for Bromide (Br⁻) and dissolved organic carbon (DOC) transported through soil columns. Error bars represent standard deviations of duplicated measurements.

(Abdul et al., 1990; Dunnivant et al., 1992). The extensive tailing of the DOC BTCs may be explained by the competitive adsorption of strongly binding DOM components and displacement of those weakly bound constituents along the flow path (Gu et al., 1996). The initial low DOC concentrations in the effluents (ca. 6 mg L⁻¹) were most likely caused by dissolution of indigenous soil organic matter (TOC 2.13 g kg⁻¹, Table 1). No input DOC eluted before the conservative tracer, indicating that size exclusion processes, if any, were insignificant during DOM transport in soil columns (Dunnivant et al., 1992).

E2/E3 Ratio

The quotient of absorbance at 250 nm to that at 365 nm, referred to as E2/E3 ratio, is a bulk spectroscopic property that has been related to the molecular size of DOM (Peuravuori and Pihlaja, 1997). Generally, a low E2/E3 ratio reflects a high average molecular weight. The E2/E3 ratios of the effluent DOM ranged from 6.2 to 10.3 (Fig. 2, solid symbols and lines), values that are higher than those reported previously for bulk natural DOM (Peuravuori and Pihlaja, 1997), possibly because of removal of the MW > 10K Da fractions (Table 2). Dissolved organic matter in the first several effluent samples was the result of dissolution of the indigenous soil organic carbon and had E2/E3 ratios of approximately 6.0 (Fig. 2, solid symbols, and lines). As DOM breakthrough occurred at pore volume 0.9 (Fig. 1), the E2/E3 ra-

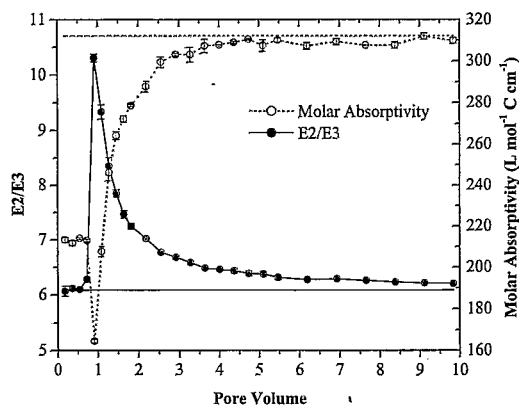


Fig. 2. E2/E3 ratios (solid symbols and line) and molar absorptivities (hollow symbols and dotted line) of dissolved organic matter in the soil column effluents. Error bars represent standard deviations of duplicate measurements. The solid and dotted straight lines denote E2/E3 and molar absorptivity of the influent DOM solution, respectively.

tio of the effluent DOM increased abruptly to 10.3 and then decreased gradually (Fig. 2, solid symbols and lines). The early breakthrough DOM had the highest E2/E3 ratio, suggesting that DOM fractions with low molecular weight eluted out of the soil columns and those with high molecular weight were adsorbed. The high molecular weight DOM fractions eluted later, as less soil adsorption sites were available, and, as a result, the E2/E3 ratio of the effluent DOM decreased (Fig. 2, solid symbols and lines). Even after 10 pore volumes in our experiments, the effluent DOM had a slightly higher E2/E3 of 6.2 (Fig. 2, solid symbols and lines) than the influent DOM (E2/E3 = 6.1, Table 2), implying adsorption equilibrium had not yet been achieved.

Molar Absorptivity

Molar absorptivity (ϵ) at 280 nm is commonly used to index DOM aromaticity. Chin et al., (1994) and Peuravuori and Pihlaja (1997) observed a strong positive correlation between ϵ and aromaticity, as measured by ^{13}C -NMR, of DOM in natural waters. Assuming this correlation is applicable in the present study, significant preferential adsorption of aromatic moieties was observed in our transport experiments (Fig. 2, hollow symbols and dotted lines). The DOM from indigenous soil organic matter dissolution had molar absorptivities of ca. $212 \text{ L mol}^{-1} \text{ C cm}^{-1}$. As the input DOM broke through the column at 0.9 pore volumes, molar absorptivity of the effluents decreased abruptly to $164 \text{ L mol}^{-1} \text{ C cm}^{-1}$ and then increased gradually over the next several pore volumes to $310 \text{ L mol}^{-1} \text{ C cm}^{-1}$ (Fig. 2, hollow symbols and dotted lines), which is close to the input solution value of $312 \text{ L mol}^{-1} \text{ C cm}^{-1}$ (Table 2). The initial low molar absorptivity of DOM in the effluents suggests organic molecules with lower aromaticity eluted without retention, whereas components with higher aromaticity were preferentially adsorbed by soil minerals. Preferential adsorption of DOM fractions with high aromaticity onto hydroxylated soil minerals (e.g., goethite, hematite) has been reported previously (McKnight et al., 1992; Gu et al., 1995; Meier et al., 1999; Chorover and Amistadi, 2001).

Molecular Weight

Trends in the number- (M_n) and weight- (M_w) average molecular weight of the effluent DOM, determined by HPSEC, are shown in Fig. 3. Both the M_n and M_w of the effluent DOM increased over time and showed trends similar to

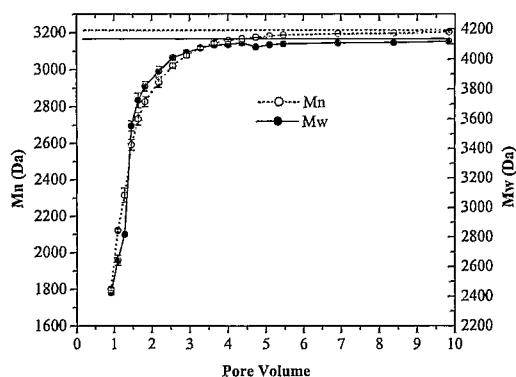


Fig. 3. Number- (M_n) and weight- (M_w) average molecular weight of dissolved organic matter in the soil column effluents. Error bars represent standard deviations of duplicate measurements.

molar absorptivity (Fig. 2, hollow symbols and dotted lines). Initially the effluent DOM had a M_n of 1770 Da and M_w of 2450 Da, demonstrating that the unreactive DOM pool (Fig. 1) was biased to low MW molecules. At 10 pore volumes, the M_n and M_w of the effluent DOM reached 3150 Da and 4180 Da, respectively, but they were still slightly lower than the values of input solution, indicating that the flow-through system was approaching, but had not yet reached, equilibrium. These data agree with the E2/E3, confirming that larger-sized DOM molecules had greater affinity for soil solids during transport than did smaller-sized molecules, and the former were preferentially adsorbed in the soil columns. The slow adsorption equilibrium (Fig. 1) and continuous change in effluent DOM properties such as E2/E3, molar absorptivity (Fig. 2), and molecular weight (Fig. 3) are suggestive of competitive adsorption of DOM components and progressive displacement of DOM constituents with lower affinity during transport. The fractionation of DOM on the basis of E2/E3 ratio, molar absorptivity, and molecular weight agree with previous batch studies that indicated higher MW fractions have a lower E2/E3 ratio and greater molar absorptivity (Chin et al., 1994; Peuravuori and Pihlaja, 1997; Meier et al., 1999; Guo, 2001).

Acidity

Phenolic and carboxylic acidity of the effluent DOM were analyzed by titration, and the data are shown in Fig. 4. As a result of the low DOC concentrations and inadequate volume of initial

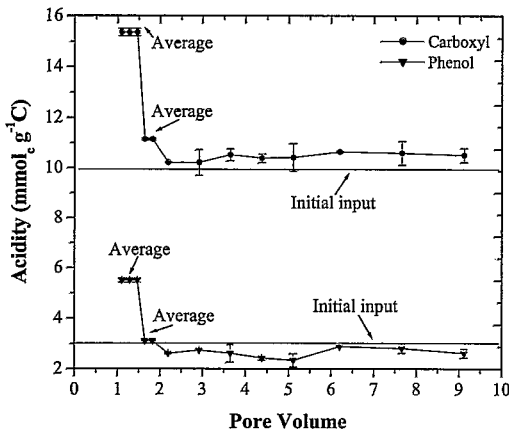


Fig. 4. Titrateable acidity of dissolved organic matter in the soil column effluents. Error bars represent standard deviations of duplicate measurements.

effluents, samples collected at 0.91, 1.09, and 1.28 pore volume were combined for analysis, as were effluent samples collected at 1.46 and 1.64 pore volumes. Acidity data presented in Fig. 4 are, therefore, weighted averages of these samples. The input DOM had phenolic and carboxylic acidities of 3.02 and 9.94 $\text{mmol}_c \text{g}^{-1} \text{C}$, respectively (Table 2). Initial effluents had much higher acidities than the influent solution, suggesting DOM fractions with higher charge had lower affinity for soil solids and were more mobile than the fractions with lower acidity. Earlier reports indicate that DOM fractions of lower molecular weight have higher acidity (Gu et al., 1995; Guo, 2001), and the decrease in acidity is consistent with the concurrent increase in molecular size of the effluent DOM. Acidic functional groups (dominantly phenolic and carboxylic) play an important role in DOM-soil interaction. Several studies have indicated that DOM is adsorbed onto Fe/Al oxides by ligand exchange of these acidic groups for surface hydroxyls, resulting in a decrease in solution phase organic acidity per mole of C (Murphy et al., 1992; Gu et al., 1995; Wang et al., 1997; Chorover and Amistadi, 2001). It has also been proposed that carboxyl groups participate in anion exchange or cation bridging reactions (Jardine et al., 1989; Avena and Koopal, 1998). In contrast, our results show a relative enrichment of solution phase acidity (per unit mass of DOC) at early times, when larger molecules are preferentially adsorbed. Entropic effects drive DOM adsorption to 2:1 clay minerals; increasing acidity on sorptive solutes may decrease or in-

crease adsorption, depending on the relative importance of electrostatic repulsion, cation bridging, and hydrophobic interactions (Nayak et al., 1990).

Given the heterogeneity of DOM and mineral constituents, all of these chemical and physical mechanisms likely play a role in soils, with principal determinants being mineral composition and surface chemistry of soil particles, as well as chemical properties of particular DOM molecules. Although the soil employed in this study has a high iron oxide content (Table 1), our data suggest that physical sorption of larger, less polar, and more aromatic molecules is more important to sorption in the present case than are chemical reactions mediated by acidic functional groups (ligand exchange, anion exchange, cation bridging reactions).

Hydrophilicity

Effluent DOM was separated into hydrophobic and hydrophilic fractions by passing solutions over XAD-8 resin. Because of the low DOC concentrations and the inadequate volume of initial effluents, samples collected at 0.91, 1.09, and 1.28 pore volume were combined for analysis, as were effluent samples collected at 1.46 and 1.64 pore volumes. Initially, the effluent DOM was much more hydrophilic than input, indicating that hydrophobic molecules had stronger affinities for soil solids than hydrophilic molecules and were preferentially adsorbed (Fig. 5). With a reduction in available sorption sites, less hydrophobic C was desorbed. Consequently, the hy-

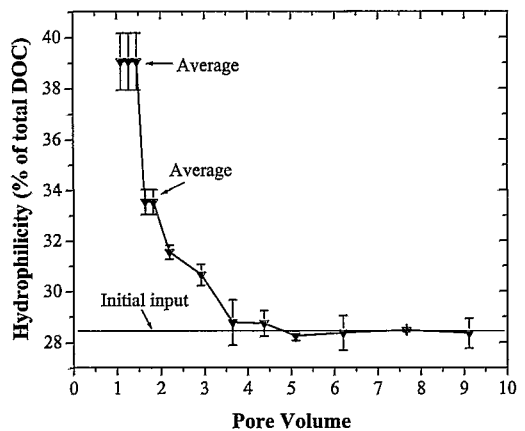


Fig. 5. Hydrophilicity of dissolved organic matter in the soil column effluents. Error bars represent standard deviations of duplicate measurements.

drophilicity of the effluent DOM increased gradually and reached a level similar to input DOM after 4 pore volumes (Fig. 5). Preferential adsorption of hydrophobic DOM fractions on soil minerals has been reported by a number of investigators using batch methods (Jardine et al., 1989; Dunnivant et al., 1992; Gu et al., 1995; Kaiser and Zech, 1997). The present results corroborate earlier studies that reported hydrophilic DOM fractions having lower molecular weight, lower molar absorptivity, higher E2/E3 ratio, and higher acidity than hydrophobic fractions (Aiken et al., 1992; Dai et al., 1996; Nambu and Yonebayashi, 1999; Guo, 2001). For SMS leachate, low molecular weight (<1000 Da) molecules with high acidity predominate in the hydrophilic DOM fractions (Guo, 2001).

Because SO_4^{2-} was present in our DOM solutions, it may have competed with DOM in anion exchange reactions at hydroxylated sites (Inoue and Wada, 1968), but the portion of DOM adsorbed via anion exchange is small relative to the total adsorbed amount, even on soils with high AEC (Jardine et al., 1989). Generally, SO_4^{2-} has been shown to induce little reduction in DOM sorption to forest soils (Kaiser and Zech, 1997), whereas DOM reduces SO_4^{2-} adsorption (Kaiser et al., 1996; Vance and David, 1992) significantly. Kaiser and Zech (1997) reported the following affinity sequence for adsorption to oxide-rich forest soils: $\text{H}_2\text{PO}_4^- >$ hydrophobic DOM $>$ hydrophilic DOM $>$ SO_4^{2-} . As in our study, hydrophilic DOM seems to be the most mobile organic component in soil solutions.

FTIR spectra of the DOM input solution after fractionation on XAD-8 resin indicate that the hydrophilic fraction is significantly enriched in aliphatic constituents as indicated by intense bands corresponding to C-H bending and C-O or C-C stretching of polysaccharides and other aliphatic constituents at 1380 and 1080 cm^{-1} , respectively (Fig. 6a). Although the 1380 cm^{-1} band also contains contributions from symmetric $-\text{COO}^-$ stretching, the asymmetric carboxylate stretch of this same sample, which resides at 1620 cm^{-1} , is significantly smaller. Thus, in addition to being enriched in carboxyl acidity (as indicated by alkalimetric titration), the mobile hydrophilic fraction is significantly more aliphatic in character than the hydrophobic fraction. The FTIR spectrum of the hydrophobic fraction (Fig. 6b) is similar to published spectra of soil fulvic acids (Baes and Bloom, 1989); peak intensities corresponding to asymmetric and symmetric carboxylic stretching (1590 and 1400 cm^{-1}) are

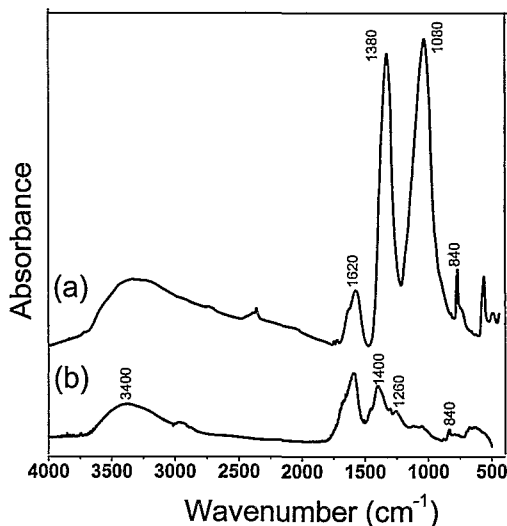


Fig. 6. Fourier transform infrared transmission spectra of influent DOM fractionated into (a) hydrophilic and (b) hydrophobic fractions using standard XAD-8 resin column sorption methods. Large relative absorbance of aliphatic constituents (1380 and 1080 cm^{-1}) is observed in (a).

comparable, and the contribution of aliphatic constituents (i.e., 1050–1120 cm^{-1}) is greatly reduced. Based on these spectra and Fig. 5, it is clear that the "fulvic-like" hydrophobic fraction exhibits a higher affinity for sorption to the soil. The soil column fractionation of DOM on the basis of hydrophilicity strengthens our contention that physical attraction contributes significantly to DOM adsorption to these soils.

It is noteworthy that not all of the adsorbed organic matter could be desorbed from the soil columns. Following DOM adsorption, the 0.093 M KCl background solution was applied continuously to the columns at the same rate, and DOC was measured in the effluent. When application of the background solution reached 0.9 pore volumes, DOC and Br^- concentrations in the effluents began to decrease abruptly (Fig. 7). At 1.1 pore volumes, both DOC and Br^- concentrations decreased to approximately 29% of the initial input values. At 1.6 pore volumes, no Br^- was detected in the effluents, and DOC was 5% of the initial input values, indicating soil entrained DOM was completely displaced and adsorbed OM had begun to enter solution. The desorption of OM was a slow process, such that even after 15 pore volumes of background solution had been applied, the DOC concentrations in the effluents

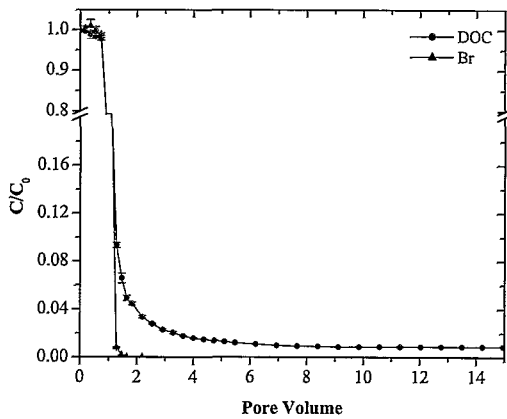


Fig. 7. Flushing and desorption of bromide (Br^-) and dissolved organic carbon (DOC) in the soil columns. Error bars represent standard deviations of duplicate measurements.

remained stable at *ca.* 12 mg L^{-1} ($C/C_0 = 0.9\%$). The measured soil TOC content was $5.07 \pm 0.01 \text{ g kg}^{-1}$ after the desorption runs, more than double the level measured before DOM adsorption ($2.13 \pm 0.06 \text{ g kg}^{-1}$, Table 1). Clearly, a portion of retained DOM forms a strong association with soil solids.

CONCLUSIONS

Reactive transport of DOM in typical Hapludult soil columns involves selective uptake of high molecular weight hydrophobic and aromatic molecules, whereas smaller, more acidic compounds are preferentially eluted. This fractionation behavior suggests that physical processes, including the hydrophobic effect, bear heavily on DOM transport in soils. The effects of this fractionation on transport of DOM-complexing metals and organic pollutants is, therefore, likely to be important in the many cases where DOM-pollutant interactions are governed by the physico-chemical characteristics of solid-phase and dissolved organic matter.

ACKNOWLEDGMENTS

Research reported in this paper was supported by National Science Foundation Grant No. CHE-00-89156.

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