Variations in the composition and adsorption behavior of dissolved organic matter at a small, forested watershed

MONIQUE MEIER[1], YU-PING CHIN[1,*] and PATRICIA MAURICE[2]
*[1]Dept of Geological Sciences, The Ohio State University, Columbus, OH 43210, USA; [2]Dept. of Civil Engineering and Geological Sciences, The University of Notre Dame, Notre Dame, IN 46556, USA; *Author for correspondence (e-mail: yo@geology.ohio-state.edu; phone: 614-292-6953)*

Abstract. This study investigated the properties and sorption by goethite of bulk (unfractionated) dissolved organic matter (DOM) from surface and shallow groundwaters at McDonalds Branch, a small freshwater fen in the New Jersey Pine Barrens (USA). Water samples were collected in the spring and fall seasons from two surface-water sampling sites, an upstream potential recharge area and a downstream discharge area, as well as from a set of in-stream nested wells in the upstream potential recharge area. Changes in DOM concentration, molecular weight distribution, and molar absorptivity at 280 nm were measured. Surface and shallow (1.6 m below land surface) groundwater samples collected in spring 1997 in the potential recharge zone (actual recharge impeded by an extensive clay lens) were found to be very similar in terms of DOM concentrations and physicochemical properties and is believe to originate from a common source. Samples taken in fall 1997 yielded no surface water because of drought conditions, and the shallow groundwater DOM collected from the recharge well contained significantly less and chemically altered DOM. This change in chemical properties is believed to be caused in part by fractionation resulting from sorption to mineral phases. Batch isotherm experiments show that sorption by goethite of the DOM from both spring surface and shallow groundwaters in the potential recharge area were similar, whereas the fall groundwater possessed a much lower affinity for the sorbent. This study demonstrated that shallow groundwaters collected under different climatic and hydrologic conditions (spring, high flow versus fall, drought conditions) resulted in different physicochemical properties and adsorption affinities.

Introduction

The sorption of dissolved organic matter (DOM) onto metal oxides affects a variety of geochemical and environmental processes including the growth and dissolution of mineral phases, the cycling of trace metals, and the fate and transport of contaminants in the aquatic environment (Parfitt et al. 1977; Davis and Leckie 1979; Davis and Gloor 1981; Tipping 1981a; Chiou et al. 1983; Jardine et al. 1989; McKnight and Bencala 1990; Dunnivant et al. 1992a, 1992b; Schlautman and Morgan 1993a, 1993b; Gu et al. 1994; Murphy et al. 1994). The DOM pool (which is comprised of compounds of variable size, structure, and functional group content) has been shown to fractionate upon sorption between the sorbed and dissolved

phases (Davis and Gloor 1981; Tipping 1981a, 1981b; Zutic and Tomaic 1988; Murphy et al. 1990; McKnight et al. 1992; Ochs et al. 1994; Schlautman and Morgan 1994; Gu et al. 1994, 1995, 1996; Wang et al. 1997a; Kaiser and Zech 1997). The sorbed DOM properties may affect chemical interactions that occur at the mineral/water interface such as immobilization of metals by surface-complexation processes or of hydrophobic organic pollutants by partitioning. Conversely, the DOM fraction remaining in solution may act as a competitive phase by altering the speciation of ″particle-reactive″ contaminants such as metals or hydrophobic organic compounds.

Temporal changes in the sorptive and physicochemical properties of DOM from a single watershed have not been well documented. Recent studies of DOM and sorption processes within small watersheds demonstrated annual peak concentrations of DOM in natural waters following the spring snowmelt and flood events (Lewis and Grant 1979; Foster and Grieve 1982; Cronan and Aiken 1985; McDowell and Likens 1988; Baron et al. 1991; McKnight et al. 1993; Hornberger et al. 1994). This ″pulse″ is followed by an exponential decrease in DOM levels over time, and a simple flushing mechanism has been widely proposed to explain this phenomenon (Lewis and Grant 1979; Foster and Grieve 1982; Baron et al. 1991; McKnight et al. 1993; Hornberger et al. 1994). While, these investigators only measured changes in DOM concentration, we hypothesized that both concentrations and the reactivity of DOM will vary temporally and spatially in small watersheds. Thus, we sampled surface waters and shallow ground waters during a spring high-flow period, followed by sampling of only shallow ground waters during a fall low-flow period (there was no fall surface water because of a severe drought). This allowed us to determine effects of drought conditions on the shallow ground water DOM characteristics.

The goals of this investigation were: 1) to compare the inorganic composition, DOM concentrations, and DOM molecular weights and light absorbance properties in natural water samples collected from a shallow (~ 1.6 m deep) ground water and surface water sites at a small, well-characterized watershed (McDonalds Branch in the New Jersey Pine Barrens, USA). Although the sampling sites were not along a single hydrologic flow path, they are representative of waters in the basin's recharge zone; 2) to compare differences in the shallow ground water samples in the spring high flow conditions versus the fall drought conditions; and 3) to observe and compare differences in the DOM sorptive reactivity using goethite (α-FeOOH) as the mineral phase.

Materials and methods

Site description

McDonalds Branch basin in the New Jersey Pine Barrens (USA) was selected for this study because it is a small freshwater fen with significant concentrations of

natural organic matter in both surface and shallow ground waters. The surficial geology is dominated by the Miocene Age Cohansey formation, which consists primarily of pure quartz sand with localized clay lenses (fine-grained quartz, kaolinite, and illite) and Fe(III)(hydr)oxide cemented units (Rhodehamel 1979; Lord et al. 1990). The low concentrations of weatherable minerals, coupled with the wetland conditions, result in low-ionic-strength, acidic, organic-rich surface and shallow ground waters (Johnsson and Barringer 1993). McDonalds Branch has been a United States Geological Survey (USGS) hydrologic bench-mark station since the 1953, and the basin was the subject of extensive hydrologic and geochemical investigations conducted by one of us (Maurice/Johnsson) and USGS colleagues in the 1960s–1980s (Lord et al. 1990; Johnsson and Barringer 1993).

McDonalds Branch basin is located in Lebanon State Forest in southern New Jersey, approximately 20 miles from the Atlantic Ocean, immediately west of the main surface-water and shallow groundwater drainage divide in the Pine Barrens (Figure 1). The basin is 2.35 square miles in area. Physiographic relief is low, with elevations ranging from about 200 ft above sea level (a.s.l.) in the southeastern corner to about 120 ft a.s.l. in the northwestern corner (Lord et al. 1990).

McDonalds Branch flows westward from its headwaters in the central uplands region of the Pine Barrens toward Rancocas Creek, which discharges into the Delaware River (Figure 1). In much of the shallow aquifer system, groundwater follows short local flowpaths and discharges into small streams (Rhodehamel 1979). Studies by Lord et al. (1990) and Johnsson and Barringer (1993) showed that the basin hydrology is complex, with shallow groundwater flow often occurring laterally to the stream. The upstream, hardwood swamp portion of McDonalds Branch is a potential groundwater recharge area, receiving interflow from organic-rich soils. Actual recharge is impeded by the presence of a clay lens ~ 2–2.5 meters below the stream bed. The stream then flows through an intermittently ponded "open channel" area, which can be either recharge or discharge, depending upon mostly seasonal hydrologic conditions. The downstream portion of the basin is an Atlantic white cedar swamp. which generally receives groundwater discharge, although it may become a recharge zone when surface-water levels are high and groundwater heads become depressed (Johnsson and Barringer (1993) and Maurice, unpublished data).

Precipitation in upland areas of the McDonalds Branch basin percolates through the sandy soil (spodosols) and either discharges locally or recharges the deep regional groundwater flow system. Groundwater discharge provides approximately 89% of the baseflow for streams in the Pinelands region (Rhodehamel 1979).

Collection of natural water samples

Water samples were collected in early May 1997 from within the McDonalds Branch basin at an upstream site in the hardwood swamp recharge area and from a shallow well located within the streambed. In this portion of the basin, the stream is underlain by an organic muck unit, beneath which is a sandy zone underlain by a mostly kaolinitic clay lens (Lord et al. 1990; Johnsson and Barringer 1993). The shallow well is screened above the clay lens from 0.76 to 1.68 m below land sur-
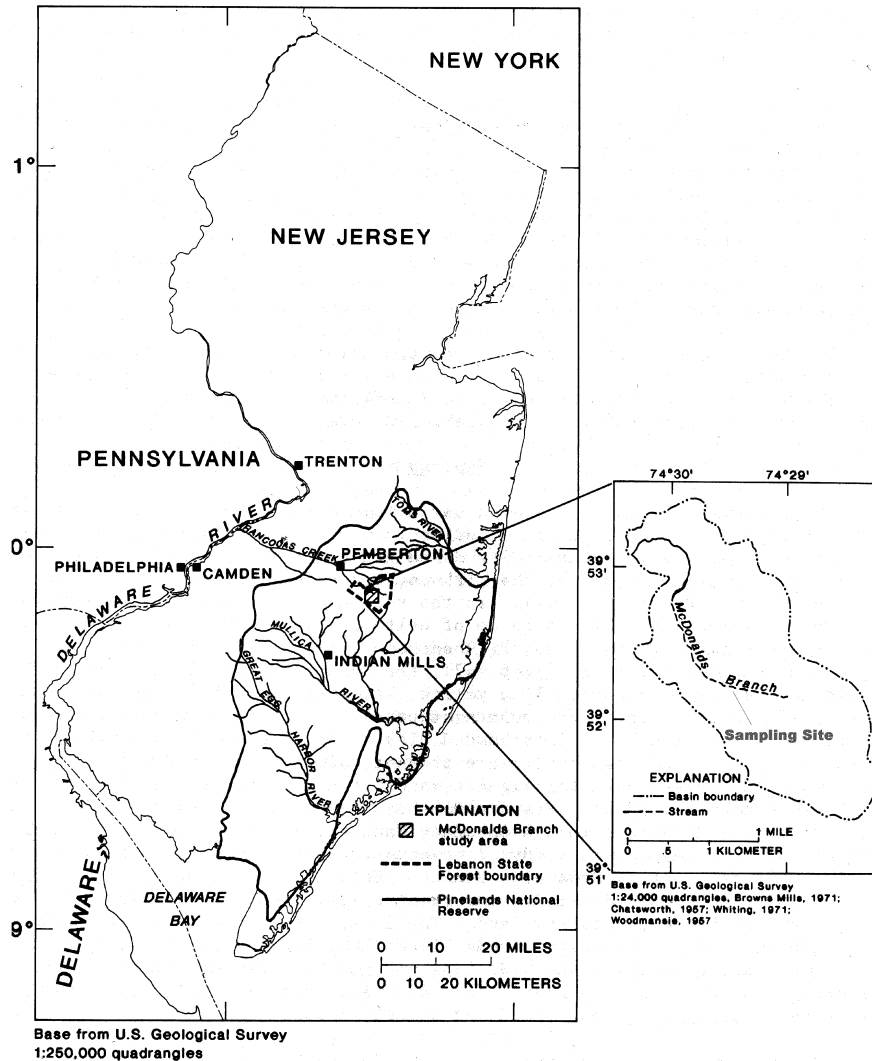
Figure 1. Map showing the location of the McDonalds Branch watershed

face (bls). The surface water grab sample was collected from the stream bank using a polyethylene bottle attached to a pole, filtered on-site using an in-line cartridge membrane filter (0.45 μm) and stored in 4-L amber glass bottles. The groundwater samples were obtained using low-flow peristaltic pumps (200 mL/min) and Tygon® tubing and stored in 20-L polyethylene carboys. A surface water sample was also obtained from the downstream cedar swamp site and filtered as described previously.

In October 1997, a surface water sample from the upstream hardwood swamp site was not collected because the streambed was dry, the result of an exceptionally

dry summer and fall. A shallow groundwater sample was collected from the upstream site using a peristaltic pump and a surface water grab sample taken from the downstream site as described previously. Both samples were filtered and all water samples were stored in glass containers in the dark and refrigerated at 4 °C. Splits were set aside for iron analysis by graphite furnace atomic absorption spectroscopy. Additional samples were taken and stored in acid-washed polyethylene bottles for the analysis of major cation and anions by ICP-MS. Subsets of samples were analyzed for their hydrophobic/hydrophilic properties by relative retention by a hydrophobic resin (XAD-8) packed in a glass column. These analyses were conducted by Huffman Labs of Golden, Colorado, USA

Iron oxide synthesis

Goethite (α-FeOOH) was used as the mineral phase in the subsequent laboratory experiments. The procedure for goethite synthesis and details concerning its preparation for use are described elsewhere (Wang et al. 1997a; Meier et al. 1999). The goethite possessed a N_2 BET specific surface area of 63.8 ± 1.30 m^2/g and its X-ray diffraction pattern showed that the majority of the material was goethite (α-FeOOH) with a trace amount of hematite (α-Fe$_2$O$_3$). The goethite was suspended in Milli-Q water at a concentration of 534 m^2/L (8.37 g/L). The dry weights of goethite suspension aliquots were measured for each experiment to account for density changes due to varying mixing rates.

NOM adsorption experiments

All adsorption experiments were conducted in a manner similar to that described by Gu et al. (1994) and Meier et al. (1999). The water samples were added to several Erlenmeyer flasks in varying amounts and diluted to a range of dissolved organic carbon (DOC) concentrations and a set of blanks containing no DOM. NaCl (0.01 m) was added to each flask as a swamping electrolyte and the pH of the solutions was adjusted to 4.00 ± 0.05 using 0.01 m HCl and 0.01 NaOH solutions. This pH was chosen to represent that of the watershed from which the samples were collected. Each solution was then split into four 40-mL polypropylene centrifuge tubes comprised of three samples and one control (no solids added) for each discrete concentration. The mineral oxide suspensions were stirred for about 1 hour prior to the addition of aliquots to each sample to obtain a constant total surface area to solution ratio of approximately 41.1 m^2/L. Again, dry weights were measured for aliquots for each experiment to account for variable mixing rates. An equal volume of Milli-Q water was added to the controls. The tubes were then placed on a shaker table and allowed to equilibrate in the dark for 24 hours. A time-course study showed that the sorption reaction equilibrated within 10 hours or less (data not shown here).

   The goethite samples and controls were centrifuged for 30 minutes at 2000 rcf (Beckman GS-6R Centrifuge) and the resulting supernatants were microfuged for 15 minutes at 30,000 rcf (Beckman Microfuge E). The pH values of the super-

natants were measured and samples were immediately analyzed by UV/VIS spectroscopy (scanned 200–600 nm, 400 nm/min, Cary 1, Varian Instruments). Although full spectra were collected, we report here the molar absorptivities (ϵ), which were calculated based only on data at $\lambda = 280$ nm. Past studies (Traina 1990; Chin et al. 1994) have shown that molar absorptivity collected at this wavelength correlated well with the total aromaticity of humic materials as determined by quantitative ^{13}C-NMR. All samples for organic carbon analysis were acidified to pH = 2–3 using 2 N HCl and purged for 2 minutes prior to analysis (TOC 5000, Shimadzu Instruments, MD). Additional unacidified samples of the supernatants were assayed for Fe, stored in plastic bottles, and analyzed for average molecular weight using HPSEC.

Size exclusion chromatography

Molecular weight distributions before and after sorption were measured by high pressure size exclusion chromatography (HPSEC) as described by Chin et al. (1994). Briefly, the system consisted of a Waters 510 solvent pump, a Waters 486 variable wavelength absorbance detector, a Rheodyne rotary injector valve equipped with a 20-μL sample loop, and a Waters Protein-Pak 125 modified silica column (Waters Associates, Milford, MA). The column had a general molecular weight cutoff of less than 100–1000 and the column packing material was chosen for its low residual hydrophobicity and minimal ion-exchange capacity.

The mobile phase consists of 0.1 m NaCl, 0.002 m KH_2PO_4 and 0.002 m Na_2HPO_4 solutions buffered to an approximate pH of 6.8. The SEC system was calibrated using random coil sodium polystyrene sulfonates (Polysciences, Inc.) (18 K, 8 K, 5.4 K, 1.8 K) and acetone (MW = 58). These standards were reported to represent the configuration and size of DOM molecules more accurately than other macromolecules such as proteins (Chin et al. 1994). All standards and samples were detected at 230 nm except acetone, which was determined at 280 nm. Details regarding column calibration and standard selection are presented in detail elsewhere (Chin et al. 1994).

Results and discussion

Chemical characteristics of the water samples

Analyses of the unprocessed waters revealed that all the samples contain low levels of multivalent cations (Table 1). The one exception is the shallow groundwater sample collected in May, which has a natural iron concentration that is ten times higher than the waters from the other sites (Table 1). Conversely, DOM levels were highest for the upstream surface water and shallow groundwater, while the spring downstream sites and deep groundwater contain significantly less DOM. As discussed by Johnsson and Barringer (1993) and Maurice et al. (2001), groundwater

Table 1. Concentrations of inorganic constituents of surface and groundwater samples (given in mg/L) collected in the McDonalds Branch basin. nd = not detected

Recharge	Al_T	Ca_T	Fe_T	K_T	Mg_T	Mn_T	Na_T	S_T	F_T	Cl_T	SO_{4T}
Spr. Surface	0.68	0.31	0.76	0.53	0.13	0.01	1.87	1.32	0.00	3.88	7.61
Spr. Shallow	1.01	0.45	2.45	0.63	0.21	0.01	1.99	2.00	0.00	4.04	9.04
Fall Shallow	1.45	1.24	1.53	3.83	0.62	0.03	3.56	7.50	0.30	5.72	23.05
Discharge											
Spr. Surface	0.18	0.63	0.18	0.31	0.40	0.01	2.11	1.69	0.00	4.03	8.67
Fall Surface	0.11	0.43	0.09	2.43	0.46	0.01	1.93	1.40	nd	nd	nd

discharge into the stream in the downstream, cedar swamp region tends to dilute the DOM concentration, although other factors such as photocatalyzed degradation reactions (Maurice et al., unpublished data) may also play a role. The chemical constituents present in the fall shallow groundwater were considerably different from the spring sample composition, and contain about half the iron concentration and considerably less DOM (Table 1).

DOM can participate in a number of geochemical reactions that can alter its abundance and properties. For example, when DOM-rich water flows through porous media with a high clay content, significant sorption occurs thereby depleting the water with respect to dissolved organic carbon. Typically, preferential removal of the hydrophobic acids and neutrals occurs by sorption, leaving the water enriched with the hydrophilic acid fraction. It was previously believed that this apparent relative increase in hydrophilic constituents might be related to the breakdown of the hydrophobic acids into hydrophilic acids (Cronan and Aiken 1985; Guggenberger et al. 1994). Recent work has yielded new hypotheses to explain this phenomenon, including the possibility that hydrophobic components displace indigenous hydrophilic substances in the soil horizons, thereby enriching the solution phase with respect to hydrophilic compounds (Kaiser and Zech 1997). At McDonalds Branch, low permeability clay lenses, some > 1-m thick) occur throughout the unsaturated zone in the upstream hardwood swamp area near the stream source (Johnsson and Barringer 1993). These lenses may result in a discontinuity between the shallow groundwater and deep groundwater flow systems.

The presence of clay lenses in the hardwood swamp recharge area likely is responsible for high DOM concentrations in the shallow groundwater underlying the streambed. Portions of the aquifer above these extensive clay lenses receive a considerable amount of DOM from interflow through the soil zone and from surface water sources. The May 97 McDonalds Branch shallow groundwater sample contains a significant amount of DOC and is even slightly higher in DOM concentration than the surface water (Table 2). Our observations appear at first to be somewhat surprising in that groundwaters typically are depleted in DOM relative to surface waters (Cronan and Aiken 1985). Our observation suggests that the surface and groundwater at this site share a common DOM source; namely, interflow from surrounding organic-rich spodosol soils. Indeed, following major rain storms, or-

Table 2. Dissolved organic carbon, molar absorptivity, and molecular weight of hydrophobic and hydrophilic components (as analyzed by XAD-8 chromatography) of surface and groundwater samples collected in McDonalds Branch basin. Due to the low DOC concentrations in the fall surface discharge samples, the error in the analysis was too large, and is reported as not detected (nd)

Recharge	Depth (ft)	DOC (mg/L)	Mol. Abs. (L/mol-cm)	Hydrophobics (%)	Hydrophilics (%)	Wt.avg. MW (Da)
Spr. Surface	0	25.2	433	44	57.0	2430
Spr. Shallow	5.5	31.0	436	60	40.0	2300
Fall Shallow	5.5	18.7	303	47	42.0	1460
Discharge						
Spr. Surface	0	8.67	343	43	58.0	1950
Fall Surface	0	3.48	249	nd	nd	1950

ganic-rich interflow water can sometimes be seen pouring out of the stream banks and into the stream. Moreover because this shallow aquifer is isolated from the deep groundwater flow system by the clay lens, we believe that it is hydrologically linked to the stream water resulting in a DOM phase with common chemical properties.

A comparison of the DOM of the spring and fall shallow groundwater samples reveals seasonal differences, including drought effects. Fall DOCs in the surface water discharge area were less than half of those measured in spring. Similarly, the DOM properties also changed, with molecular weights and molar absorptivities that were significantly smaller (Table 2). For the reasons stated previously we were unable to compare spring and fall surface water properties from the recharge area. Thus, the DOM in the MacDonald's Branch watershed in the shallow groundwaters underwent changes in the type and amounts of organic carbon present. We believe that these changes are partially attributable to the reactive nature of the DOM pool, which maybe biologically transformed or undergo sorption to the indigenous sediments/soils. In both cases we would anticipate a pool of DOM that will be smaller in molecular weight. Several investigators (Amon and Benner 1996; Burdige and Gardner 1997) demonstrated that the largest fractions of the DOM pool are most susceptible to microbial degradation (size–reactivity continuum model). Indeed the most recalcitrant DOM is relatively small (less than a thousand daltons or Da). These investigators proposed that microorganisms continually breakdown the larger DOM molecules to the point where they "no longer resemble bio-molecules" thereby escaping further degradation. Thus, DOM introduced to the shallow groundwater in spring could be over time degraded to the lower molecular weight material measured by us in the fall.
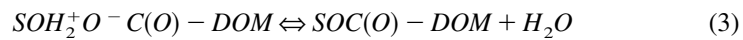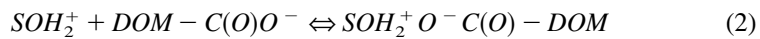
The other significant diagenetic pathway for DOM at this site is through sorption to solid phases. Evidence from the literature (Gu et al. 1994, 1996; Wang et al. 1997a; Meier et al. 1999) have demonstrated that DOM sorption to mineral oxides preferentially removes the larger moieties from solution. The material that remains behind is not only smaller, but possesses a lower molar absorptivity at 280 nm, which is what we observed for the field samples (Table 2). The magnitude of this

fractionation-upon-sorption phenomenon is highly dependent upon the type of sorbent present and the solution conditions. In MacDonald's Branch many of the unconsolidated materials are comprised of minerals grains held together by iron oxide cements. Moreover, there exists a significant amount of kaolinite present. Based upon our past work (Meier et al. 1999) DOM sorption to both iron oxides (goethite) and kaolinite was significant at pH values of 5 or less. Given that the natural pH of both the streamwater and groundwater from this site is 4 or less, we would expect sorption to be a significant process in fractionating the shallow groundwater.

Adsorption of DOM onto goethite

Sorption isotherm experiments were conducted using those samples that contained dissolved organic carbon concentrations in excess of 15 mg/L. These samples include the surface and shallow groundwater samples collected in the upstream recharge area in May 1997, and the shallow groundwater sample collected in the same location in October 1997. Because the highest initial sorbate concentration was equivalent to the amount of DOC present in our *undiluted* natural water samples, we were unable to measure a sorption maximum (Q_{max}) for some of the isotherms.

These isotherms provide important information regarding the relative sorption affinities of the DOM samples for the iron oxide surface. All samples exhibited "Langmuir-like" behavior where sorption is greatest at low initial sorbate concentrations and approaches Q_{max} at higher initial DOM concentrations (Figure 2). A ligand-exchange reaction involving the hydroxyl groups on the goethite surface and the carboxyl groups of the DOM appears to provide the best explanation for this type of behavior. The ligand exchange reaction is believed to follow the following sequence (Parfitt et al. 1977; Davis 1982; Sposito 1984, 1989; Murphy et al. 1990; Gu et al. 1994):

$$SOH + H^+ \Leftrightarrow SOH_2^+ \tag{1}$$

$$SOH_2^+ + DOM - C(O)O^- \Leftrightarrow SOH_2^+ O^- C(O) - DOM \tag{2}$$

$$SOH_2^+ O^- C(O) - DOM \Leftrightarrow SOC(O) - DOM + H_2O \tag{3}$$

Here, SOH represents the surface hydroxyl group on the sorbent and DOM -COO⁻ represents a carboxyl group on the DOM. In addition to ligand-exchange, we also believe that the larger fractions and presumably more hydrophobic DOM fractions will also contribute to the sorption process (Gu et al. 1996; Wang et al. 1997a; Meier et al. 1999).

The sorption isotherms for the spring surface and shallow groundwater samples from the recharge site show remarkably similar sorption behavior and affinity for the goethite surface (Figure 2). The Q_{max} for the shallow groundwater appears to be slightly higher, and this small difference may reflect its higher hydrophobicity (Table 2), which would render it more particle-reactive.
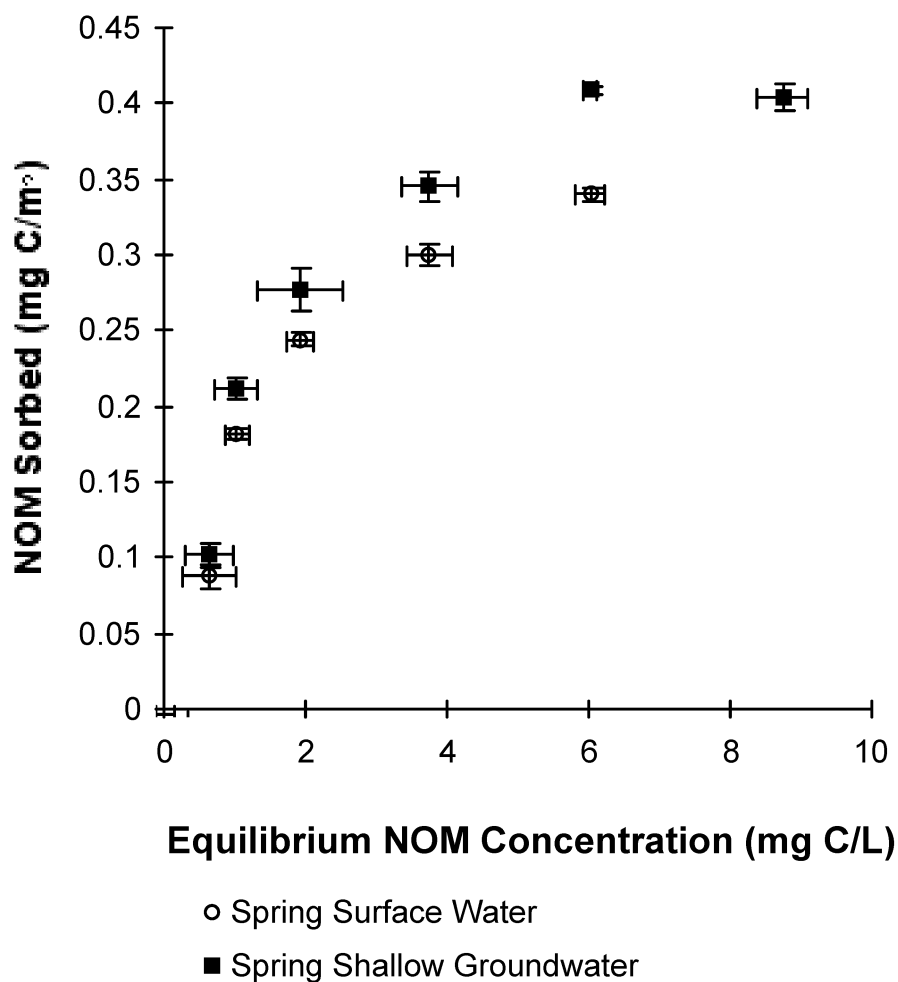
Figure 2. Sorption of dissolved organic matter for the spring surface and shallow groundwater samples by goethite

DOM in the spring and fall shallow recharge groundwater samples possessed remarkably different sorption behavior, which reflects the seasonal variability in their chemical composition (Figure 3). The organic carbon content of the fall shallow groundwater sample is approximately two-thirds that of the spring sample and the DOM is less hydrophobic (Table 2). The Q_{max} of the fall groundwater sample is significantly smaller than the spring groundwater sample. Interestingly, the maximum *solution-phase equilibrium DOC* in the samples following sorption is similar (see Figure 3 dashed line). This suggests that the components remaining behind in solution after sorption for both the fall and spring shallow groundwater sample may possess similar properties.
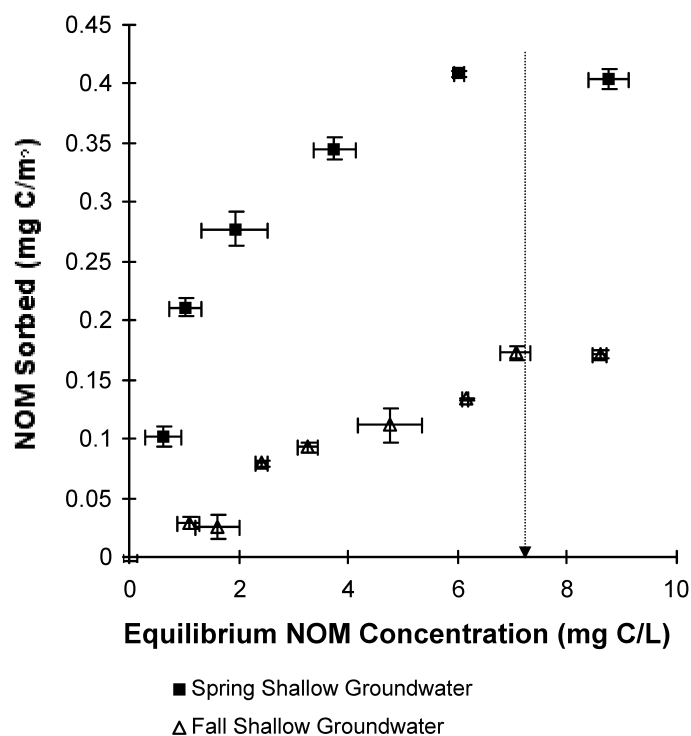
Figure 3. Sorption of dissolved organic matter for the spring and fall shallow groundwater samples by goethite. Dashed line shows similar equilibrium solution phase DOM concentration for both waters at Q_{max}.

We believe that the significantly higher DOM concentration present in the spring shallow groundwater probably represents the release of fresh soil organic matter to the watershed after large precipitation events and is similar to the surface water material. Based upon our characterization and sorption studies this DOM contains more labile and particle-reactive components. The lack of precipitation over the summer, which carried over into fall prevented significant amounts of new organic matter from entering the system. Thus, over time sorption, biological, and chemical transformation processes altered the original spring DOM, and removed the more "particle-reactive" constituents. Thus, for this hydrologic system it appears that the DOM pool is dynamically variable over space and time and its ultimate composition is closely linked to the hydrology of the watershed.

Changes in solution phase molecular weight upon sorption

The weight-average molecular weight (MW) of the experimental controls (water samples both diluted and undiluted in the absence of any sorbent) were found to be nearly identical (2430 Da for the spring surface water sample and 2300 Da for the spring shallow groundwater sample). The similarity in average MW for these sam-
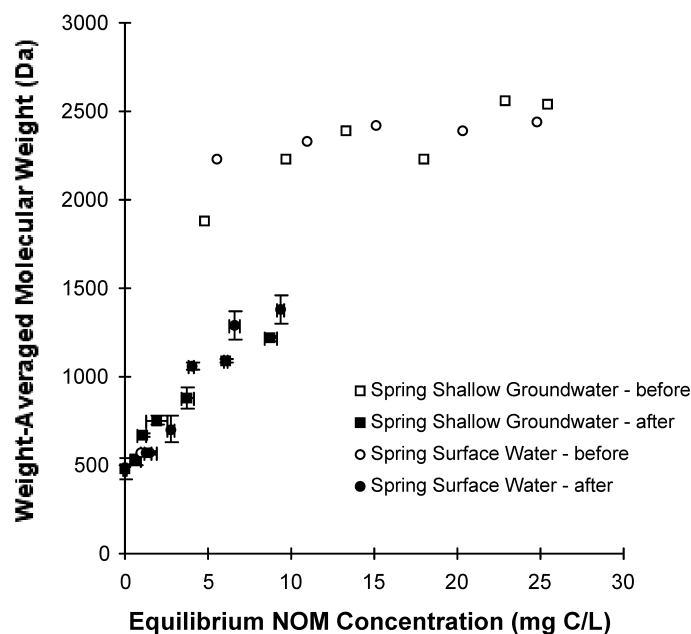
Figure 4. The weight-average molecular weight of the spring surface water and shallow groundwater dissolved organic matter before and after sorption by goethite

ples again suggests similar composition and origin. Conversely, the fall shallow groundwater sample has a much lower average MW (1460 Da), which suggests that either the DOM originates from a different source or that the original spring DOM had undergone some type of biogeochemical transformation as speculated above.

Sorption of the two analytes by goethite resulted in significant decreases in solution phase average MWs. The lower equilibrium DOM concentrations of the spring surface and spring shallow groundwater samples show a decrease in average MW of over 1500 Da, whereas the higher equilibrium DOM concentrations samples drop approximately 1000 Da. (Figure 4). This trend again demonstrates that the selective sorption of larger MW moieties occurs for this system. At higher initial sorbate concentration the reactive sites on the goethite surface become occupied by only the largest and most reactive DOM components. As a result the DOM solution is less fractionated relative to low initial sorbate concentrations where reactive sites are more plentiful. We observed similar albeit less significant decreases in solution phase average MW values for the fall shallow groundwater samples. The average MW of these samples decreases by 200–500 Da. (Figure 5).

The theory that these three water samples represent a similar primary DOM source may be further corroborated by the similarity in the sorbate molecular weights following sorption by the goethite surface. At low equilibrium sorbate concentration all the samples appear to possess molecular weights of approximately 500 Da, while at the highest equilibrium values the MW ranged from 1050–1250 Da (Figures 4 and 5). The spring shallow groundwater shows a slightly lower av-
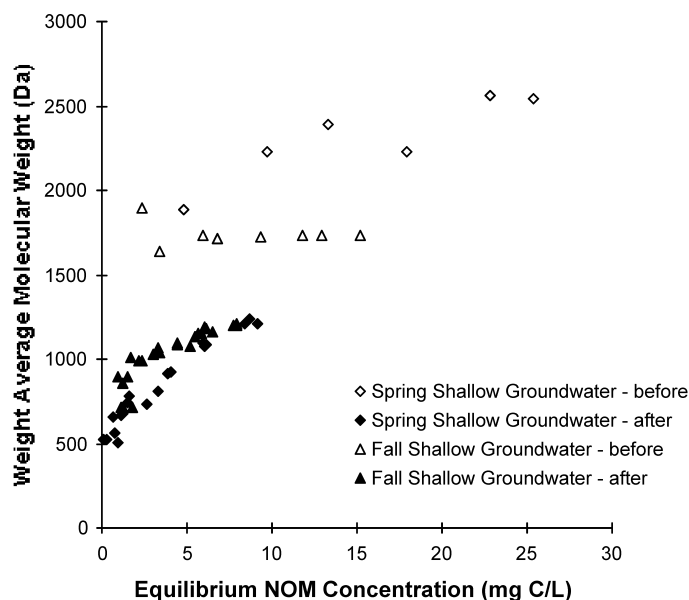
Figure 5. The weight-average molecular weight of the spring and fall shallow groundwater dissolved organic matter before and after sorption by goethite

erage MW at the high equilibrium DOM concentrations, suggesting a greater sorbent affinity, which is corroborated by our observed Q_{max} values. The smaller change in average MW of the pre and post-sorbed fall shallow groundwater samples again imply a different or an *in situ* altered DOM material that is less reactive.

Effects of sorption on sorbate molar absorptivity

Decreases in the molar absorptivity (ϵ) at 280 nm were observed for all sorbates in the solution phase after sorption by goethite (Figures 6 and 7). Molar absorptivity has been shown to correlate with the weight average MWs of purified aquatic humic materials (Chin et al. 1994). This relationship is based on the assumption that larger humic and fulvic acids are enriched in aromatic components (Traina 1990; Gu et al. 1996). Chin et al. (1994) reported that all plots of weight-average MW versus ϵ for *purified* (i.e., metal-free) aquatic humic and fulvic acids, regardless of origin, obey the same correlation (represented by the lines in Figures 6 and 7).

The McDonalds Branch DOM samples deviate from this line, especially at higher equilibrium DOM concentrations, due to the presence of dissolved iron. Dissolved Fe(III) can absorb light at 280 nm at micromolar concentrations, and both Fe(III) and Fe(II) can complex DOM and alter its light absorption properties. The McDonalds Branch data appear to deviate in a manner similar to that observed for the Suwannee River and Great Dismal Swamp DOM as reported in an earlier paper (Meier et al. 1999). The unreacted samples fall slightly above the observed correlation and the goethite-reacted samples consistently fall below the line with much
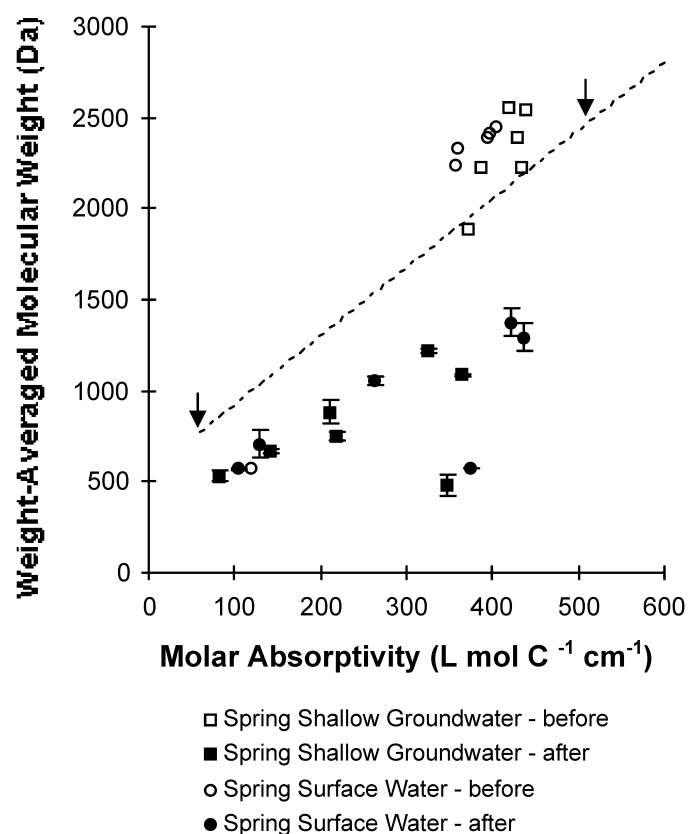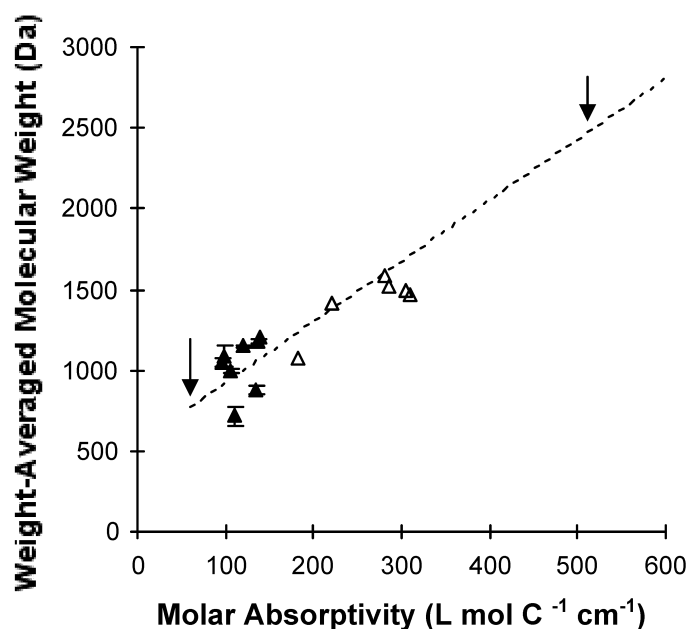
Figure 6. Changes in the molar absorptivity at 280 nm of the spring surface water and shallow groundwater dissolved organic matter before and after sorption by goethite. Dashed line is the regression for data taken from Chin et al. (1994).

larger standard deviations than were seen by previous investigators (Gu et al. 1996; Wang et al. 1997a). The *total* dissolved Fe concentrations of the unreacted samples ranged from 5.37 to 48.4 μM and those of the goethite-reacted samples contained up to 16.1 μM. Because, we were unable to determine the speciation of the Fe in our system it is plausible that Fe(II) and Fe(II)-DOM complexes could have been lost by sorption to the iron oxide at our system pH (Klausen et al. 1995). Conversely, Fe(III) could have been released to the solution phase through ligand enhanced dissolution. Thus, while *total* iron in the aqueous phase may have decreased, the presence of μM Fe(III) from dissolution of the sorbent could explain our results.

This deviation from the typical behavior of isolated, pre-purified DOM components appears to be one result of using unaltered natural water samples containing a complex mixture of chemical constituents that may either be capable of absorbing light and/or altering the light absorption properties of DOM. These natural

Figure 7. Changes in the molar absorptivity at 280 nm of the fall shallow groundwater dissolved organic matter before and after sorption by goethite. Dashed line is the regression for data taken from Chin et al. (1994).

"matrix effects" could introduce significant error to the interpretation of data generated using unaltered DOM. Dissolved metals could be removed from the samples prior to conducting sorption experiments using a cation exchange resin. This procedure would eliminate some of the artifacts associated with the measurement of ϵ values before and after sorption. At present, however, we have insufficient evidence to prove (or disprove) the observed deviation.

Conclusions

Water samples from the surface and the shallow groundwater at MacDonald's branch revealed significant differences in the bulk DOM properties. Spring surface water and shallow groundwater samples collected in the potential recharge area of the basin were very similar in terms of DOC levels and the molecular weight of the DOM phase. Conversely, shallow groundwater collected in the fall from the same well had DOM constituents that differed significantly in properties from the spring

samples. These differences may be attributable to biogeochemical changes in the DOM pool over the summer and fall seasons under drought conditions.

Sorption of DOM constituents by goethite from three of the samples revealed differences in the degree of sorption that occurred. HPSEC data and UV/VIS spectroscopy again indicate that the DOM pool in both surface and groundwater samples fractionates upon sorption onto goethite, resulting in the preferential removal of larger molecular weight, more aromatic, and more hydrophobic components from the solution phase. Our studies suggest that the properties and "particle-reactivity" of DOM is spatially and temporally variable even when confined to a small hydrologically well-defined watershed.

Acknowledgements

References

Amon R.M.W. and Benner R. 1996. Bacterial utilization of different size classes of dissolved organic matter. Limnol. Ocean 41: 41–51.

Baron J., McKnight D. and Denning A.S. 1991. Sources of dissolved and particulate organic material in Loch Vale Watershed, Rocky Mountain National Park, Colorado, USA. Biogeochemistry 15: 89–110.

Burdige D.J. and Gardner K.G. 1997. Molecular weight distribution of dissolved organic carbon in marine porewater. Mar. Chem. 62: 45–64.

Chin Y.P., Aiken G.R. and O'Loughlin E. 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environmental Science & Technology 28: 1853–1858.

Chiou C.T., Porter P.E. and Schmedding D.W. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. Environmental Science & Technology 17: 227–231.

Cronan C.S. and Aiken G.R. 1985. Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. Geochimica et Cosmochimica Acta 49: 1697–1705.

Davis J.A. and Leckie J.O. 1979. Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. Environmental Science and Technology 12: 1309–1315.

Davis J.A. and Gloor R. 1981. Adsorption of dissolved organics in lake water by aluminum oxide. Effect of molecular weight. Environmental Science & Technology 15: 1223–1229.

Davis J.A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. Geochimica et Cosmochimica Acta 46: 2381–2393.

Dunnivant F.M., Jardine P.M., Taylor D.L. and McCarthy J.F. 1992a. Transport of naturally occurring dissolved organic carbon in laboratory columns containing aquifer material. Soil Science Society of America Journal 56: 437–444.

Dunnivant F.M., Jardine P.M., Taylor D.L. and McCarthy J.F. 1992b. Cotransport of cadmium and hexachlorobiphenyl by dissolved organic carbon through columns containing aquifer material. Environmental Science & Technology 26: 360–368.

Foster I.D.L. and Grieve I.C. 1982. Short term fluctuations in dissolved organic matter concentrations in streamflow draining a forested watershed and their relation to the catchment budget. Earth Surface Processes and Landforms 7: 417–425.

Gu B., Schmitt J., Chen Z., Liang L. and McCarthy J.F. 1994. Adsorption and desorption of natural organic matter on iron oxide. Environmental Science & Technology 28: 38–46.

Gu B., Schmitt J., Chen Z., Liang L. and McCarthy J.F. 1995. Adsorption and desorption of different organic matter fractions on iron oxide. Geochimica et Cosmochimica Acta 59: 219–229.

Gu B., Mehlhorn T.L., Liang L. and McCarthy J.F. 1996. Competitive adsorption, displacement, and transport of organic matter fractions on iron oxide. Geochimica et Cosmochimica Acta 60: 1943–1950.

Guggenberger G., Zech W. and Schulten H.-R. 1994. Formation and mobilization pathways of dissolved organic matter: evidence from chemical structural studies of organic matter fractions in acid forest floor solutions. Organic Geochemistry 21: 51–66.

Hornberger G.M., Bencala K.E. and McKnight D.M. 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochemistry 25: 147–165.

Jardine P.M., Weber N.L. and McCarthy J.F. 1989. Mechanisms of dissolved organic carbon adsorption on soil. Soil Science Society of America Journal 53: 1378–1385.

Johnsson P.A. and Barringer J.L. 1993. Water quality and hydrogeochemical processes in McDonalds Branch basin, New Jersey Pinelands, 1984–1988. Water-Resources Investigations Report 91-4081. U.S. Geological Survey, West Trenton, NJ, USA.

Kaiser K. and Zech W. 1997. Competitive sorption of dissolved organic matter fractions to soils and related mineral phases. Soil Science Society of America Journal 61: 64–69.

Klausen J., Trober S.P., Haderlein S.B. and Schwarzenbach R.P. 1995. Reduction of substituted nitrobenzenes by Fe(II) in aqueous mineral suspensions. Environ. Sci. Technol. 29: 2396–2404.

Lewis W.M. and Grant M.C. 1979. Relationships between stream discharge and yield of dissolved substances from a Colorado mountain watershed. Soil Science 128: 353–363.

Lord D.G., Barringer J.L., Johnsson P.A., Schuster P.F., Walker R.L., Fairchild J.E. et al. 1990. Hydrogeochemical data from an acidic deposition study at McDonalds Branch basin in the New Jersey Pinelands. Open-File Report 88-500. U.S. Geological Survey, West Trenton, NJ, USA.

Maurice P.A., Cabaniss S.E., Drummond J., Ito E. and Palmer D. 2001. Hydrogeochemical controls on the chemical characteristics of natural organic matter in a small freshwater wetland. Geochim. Cosmochim. Acta.

McDowell W.H. and Likens G.E. 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook valley. Ecological Monographs 58: 17–195.

McKnight D.M. and Bencala K.E. 1990. The chemistry of iron, aluminum, and dissolved organic material in three acidic, metal-enriched mountain streams, as controlled by watershed and in-stream processes. Water Resources Research 26: 3087–3100.

McKnight D.M., Bencala K.E., Zellweger G.W., Aiken G.R., Feder G.L. and Thorn K.A. 1992. Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. Environmental Science & Technology 26: 1388–1396.

McKnight D.M., Smith R.L., Harnish R.A., Miller C.L. and Bencala K.E. 1993. Seasonal relationships between planktonic microorganisms and dissolved organic material in an alpine stream. Biogeochemistry 21: 39–53.

Meier K., Namejesnik-Dejanovic, Chin Y.P., Maurice P. and Aiken G.R. 1999. Fractionation of natural organic matter upon sorption to goethitite and kaolinite. Chemical Geology 157: 275–284.

Murphy E.M., Zachara J.M. and Smith S.C. 1990. Influence of mineral-bound humic substances on the sorption of hydrophobic organic compounds. Environmental Science & Technology 24: 1507–1516.

Murphy E.M., Zachara J.M., Smith S.C., Phillips J.L. and Wietsma T.W. 1994. Interaction of hydrophobic organic compounds with mineral-bound humic substances. Environmental Science & Technology 28: 1291–1299.

Ochs M., Cosovic B. and Stumm W. 1994. Coordinative and hydrophobic interaction of humic substances with hydrophilic Al_2O_3 and hydrophobic mercury surfaces. Geochimica et Cosmochimica Acta 58: 639–650.

Parfitt R.L., Fraser A.R. and Farmer V.C. 1977. Adsorption on hydrous oxides. III. Fulvic acid and humic acid on goethite, gibbsite and imogolite. Journal of Soil Science 28: 289–296.

Rhodehamel E.C. 1979. Geology of the Pine Barrens of New Jersey. In: Forman and Richard T.T. (eds), Pine Barrens: Ecosystem and Landscape. Academic Press, New York, pp. 39–60.

Schlautman M.A. and Morgan J.J. 1993a. Effects of aqueous chemistry on the binding of polycylic aromatic hydrocarbons by dissolved humic materials. Environmental Science & Technology 27: 961–969.

Schlautman M.A. and Morgan J.J. 1993b. Binding of a fluorescent hydrophobic organic probe by dissolved humic substances and organically-coated aluminum oxide surfaces. Environmental Science & Technology 27: 2523–2532.

Schlautman M.A. and Morgan J.J. 1994. Adsorption of aquatic humic substances on colloidal-size aluminum oxide particles: Influence of solution chemistry. Geochimica Cosmochimica Acta 58: 4293–4303.

Sposito G. 1984. The Surface Chemistry of Soils. Oxford Univ. Press.

Sposito G. 1989. The Chemistry of Soils. Oxford Univ. Press.

Tipping E. 1981a. The adsorption of aquatic humic substances by iron oxide. Geochimica et Cosmochimica Acta 45: 191–199.

Tipping E. 1981b. Adsorption by goethite of humic substances from three different lakes. Chemical Geology 33: 81–89.

Traina S.J. 1990. Applications of luminescence spectroscopy to studies of colloid-solution interfaces. Advanced Soil Science 14: 167–189.

Wang L., Chin Y.P. and Traina S.J. 1997a. Adsorption of (poly)maleic acid and an aquatic fulvic acid by goethite. Geochimica et Cosmochimica Acta 61: 5313–5324.

Zutic V. and Tomaic J. 1988. On the formation of organic coatings on marine particles: Interactions of organic matter at hydrous alumina/seawater interfaces. Marine Chemistry 23: 51–67.