

Fractionation of aquatic natural organic matter upon sorption to goethite and kaolinite

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Abstract

Natural organic matter (NOM) consists of a complex mixture of organic molecules; previous studies have suggested that preferential sorption of higher molecular weight, more hydrophobic, and more aromatic components may lead to fractionation of the NOM pool upon passage through porous media. Our work expands upon previous studies by quantifying the change in solution-phase weight average molecular weight (M_w) upon sorption of bulk (rather than isolated) surface water NOM from the Suwannee River (SR) and the Great Dismal Swamp (GDS) to goethite and kaolinite at different sorption densities and at pH 4, 22°C. High pressure size exclusion chromatography (HPSEC) was used to quantify changes in M_w upon sorption, and molar absorptivities at $\lambda = 280$ nm were used to approximate changes in solution NOM aromaticity. Two SR water samples were used, with $M_w = 2320$ and 2200 Da; a single GDS sample was used, with $M_w = 1890$ Da. The SR NOM was slightly more hydrophobic and aromatic. These differences were reflected in greater sorption of SR NOM than GDS NOM. Both surface water NOMs showed a much greater affinity for goethite than for kaolinite. HPSEC analysis of the NOM remaining in solution after 24 h reaction time with goethite revealed that the largest changes in solution phase M_w s (decreases by 900–1700 Da) occurred at relatively low equilibrium sorbate concentrations (approximately 5–20 mg C l⁻¹); the decrease in solution M_w suggested that reactive surface sites were occupied disproportionately by large and intermediate size NOM moieties. At higher equilibrium NOM concentrations (> 20 mg C l⁻¹), as percent adsorption decreased, M_w in solution was similar to original samples. A smaller decrease in solution NOM M_w (300–500 Da at 10–20 mg C l⁻¹ ~ 100 Da at > 20 mg) also occurred upon sorption to kaolinite. Overall, our results showed that factors (as related to NOM composition, clay mineral surface properties, and position along the sorption isotherm) which promote a higher percent sorption lead to the most pronounced decreases in solution M_w . © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Natural organic matter (NOM) is a ubiquitous component of aquatic environments and it helps to

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control mineral growth and dissolution, trace-metal cycling, and mobility of both inorganic and organic pollutants. A variety of studies (e.g., Davis and Gloor, 1981; Tipping, 1981; Davis, 1982; Ertel et al., 1986; Hedges et al., 1986; Tomaic and Zutic, 1988; Murphy et al., 1990; McKnight et al., 1992; Hedges et al., 1992, 1994; Ochs et al., 1994; Schlautman and Morgan, 1994; Gu et al., 1994, 1995, 1996; Kaiser and Zech, 1997) have suggested that the more hydrophobic, higher molecular weight, and more aromatic fractions of the NOM pool sorb preferentially, leading to fractionation of the NOM pool. A quantitative understanding of the manner in which NOM fractionates upon sorption is central to determining its ability to participate in a wide range of environmental reactions.

In this study, we took advantage of recent advances in high pressure size-exclusion chromatography (HPSEC) to quantify the changes in weight-average molecular weight (M_w) and polydispersity of *unaltered* NOM (i.e., organic matter that has not been subjected to potentially property-altering isolation techniques) upon sorption to the minerals goethite (α -FeOOH) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$). Unlike many past studies which utilized more or less altered NOM isolates (i.e., humic and fulvic acids), these experiments examined the sorption of the entire NOM pool from two surface waters containing relatively large quantities (3–4 mM carbon) of dissolved organic carbon (DOC). M_w and spectroscopic data were combined with sorption isotherms, dissolution data, inorganic constituent analyses and analyses of the hydrophobic/hydrophilic properties of the sorbates to help better understand the mechanisms that control fractionation. Finally, by using a hydrous Fe(III) oxide and an aluminosilicate clay, we investigated the role of the differing sorbent properties on the nature and extent of NOM fractionation.

2. Materials and methods

2.1. NOM water samples

We chose to sample surface waters at the Suwannee River (GA) and the Great Dismal Swamp (VA) because these two sites are organic rich, allowing sorption/fractionation behavior to be measured over a range of sorption densities. While both sites have relatively high NOM concentrations, they have different hydro-bio-geochemical properties which lead to different NOM characteristics, as described below. The Suwannee River is the source of the IHSS standard Suwannee River fulvic acid; previous detailed investigations (e.g., Averett et al., 1989) provide excellent background for our research.

Suwannee River (SR) water samples were collected near Fargo, GA (USA) on March 16, 1996 (96) and on January 28, 1997 (97). Sample pHs were determined to be 3.85 and 3.93, respectively. The chemical composition of the samples was similar (Table 1). The Great Dismal Swamp (GDS) water sample was obtained on January 28, 1997 from a location 3 miles north of the North Carolina–Virginia border on Route 17. The pH of samples collected at this site was 3.85; inorganic analyses are shown in Table 1. All water samples were filtered using pre-cleaned Gelman Type A/E glass fiber filters ($\sim 1.2 \mu\text{m}$ nominal pore size) followed by pre-rinsed $0.4 \mu\text{m}$ Nuclepore polycarbonate membranes, and stored in glass bottles in the dark at 4°C (Use of trade names in this paper is for identification purposes only and does not represent endorsement by the US Geological Survey, Kent State University, or Ohio State University). Splits were taken from each sample for inorganic component analysis by ICP-MS at the Ohio Agricultural Research and Development Center in Wooster, OH.

Table 1

Selected chemical constituents present in the Great Dismal Swamp and Suwannee River water samples (concentrations in mg l^{-1})

NOM	Al	Ca	Fe	K	Mg	Mn	Na	Cl	SO ₄	DOC
SR'96	0.24	0.76	0.30	< 0.17	0.60	0.01	3.67	2.83	< 0.10	37.4
SR'97	0.51	0.69	0.32	0.37	0.57	0.01	3.53	6.30	3.51	37.0
GDS	1.09	11.9	0.71	1.41	2.72	0.05	6.78	12.3	58.66	41.5

The Suwannee River is a type locality for NOM which originates in the Okefenokee Swamp, a blackwater wetland in southeastern Georgia containing extensive peat deposits and swamp vegetation. The small concentration of inorganic constituents in the surface water indicates minimal contact with underlying calcareous deposits (Table 1) (Averett et al., 1989). The Great Dismal Swamp is another blackwater swamp and is known for its mixed deciduous peat content (Orem and Hatcher, 1987). Water from this swamp contains higher concentrations of inorganic species (Table 1). An analysis of the so-called ‘hydrophobicity’ of the two NOM waters performed using XAD-8 chromatography (Leenheer and Huffman, 1979) at Huffman Labs, Boulder, CO, revealed that the SR DOC was 8% more hydrophobic than the GDS DOC, due primarily to differences in the hydrophobic/hydrophilic acid concentrations (Table 2). Because the principle driving force in NOM sorption to XAD-8 resin appears to be the ‘hydrophobic effect,’ (e.g., Aiken, 1985), the material retained on the column resin is generally referred to as the hydrophobic fraction. The lesser hydrophobicity and lower M_w of the GDS sample may be due in part to the higher divalent cation concentrations in the GDS waters, which could potentially cause adsorption or precipitation of more hydrophobic and higher M_w components within the watershed (e.g., Dempsey and O’Melia, 1983; Swift, 1989).

Table 2
Hydrophilic and hydrophobic components present in the Suwannee River and Great Dismal Swamp samples, as measured by XAD-8 chromatography

	Suwannee River NOM		Great Dismal Swamp NOM	
	mg l ⁻¹	%	mg l ⁻¹	%
DOC	37.0		41.5	
<i>Hydrophobics</i>				
Total	14.5	39	13.5	31
Bases		nd		nd
Acids		39		30
Neutral		nd		nd
<i>Hydrophilics</i>				
Total	22.5	61	28.5	68
Bases		3		5
Acids		56		62
Neutrals		3		1

2.2. Mineral oxide synthesis

Goethite was synthesized according to the method described by Wang (1997). X-ray diffraction (XRD) (Philips XRD 300 Generator using Cu K(α) radiation) analysis showed primarily goethite (α -FeOOH) with a trace of hematite (α -Fe₂O₃). BET specific surface area measured by N₂ adsorption = 58.0 ± 0.8 m² g⁻¹. The goethite was suspended in purified water at a concentration of 534 m² l⁻¹ (9.21 g l⁻¹) and stored in a plastic bottle in the dark at room temperature.

The kaolinite sample was standard KGa-1b from The Clay Minerals Society. This well crystallized kaolinite from Warren County, GA was cleaned to remove metal oxyhydroxides by rinsing 100 g of kaolinite approximately 4 times in 1 l of 1 M NaCl at pH 3, after which the sample was washed repeatedly in Milli-Q UV water. The kaolinite was then freeze-dried, and its BET surface area determined to be 12.6 m² g⁻¹. The pH_{pznpc} was found to be 5.3 (Sutheimer et al., 1999), which is in good agreement with reported values for KGa-1, a similar well crystallized standard (Schroth and Sposito, 1997). Atomic force microscopy (AFM) revealed hexagonal platelets with a mean ratio of edge-to-basal plane surface areas of 0.2 (Sutheimer et al., 1999).

2.3. NOM adsorption experiments

All adsorption experiments were conducted in a manner similar to that described by Gu et al. (1994). For each set of samples, surface water was added to six Erlenmeyer flasks in varying amounts and diluted with Milli-Q UV (ultraviolet treated) water to a range of concentrations. A set of blanks also was prepared using Milli-Q UV water rather than surface water. 1 M NaCl was added to each flask to attain a constant background electrolyte concentration of 0.01 M and the pH of the solutions was adjusted to 4.00 ± 0.05 using 0.01 M HCl and NaOH. Solutions from each flask (representing different NOM concentrations; see Table 3) were then split into four 40 ml polypropylene centrifuge tubes. Mineral suspensions were added to 3 of these centrifuge tubes; the fourth tube representing a sorption control. Goethite and kaolinite suspensions were stirred for about 1 h prior

Table 3
Summary of samples used in sorption/fractionation experiments:
DOC concentrations are in mg C l⁻¹

DOC in control samples				
SR'96		SR'97	GDS	
Kaolinite	Goethite	Kaolinite	Kaolinite	Goethite
0	0	0	0	0
8.457	8.585	9.7	9.224	3.33
13.12	13.29	14.3	13.74	13.39
18.37	17.38	20.08	18.25	17.933
22.27	21.48	24.8	28.16	22.833
26.92	25.61	30.2	34.71	32.583
36.28	33.38	37.8	40.46	41.823

Samples were reacted with kaolinite and goethite in triplicate. 0 values are MilliQ-UV water blanks with measured DOC less than 0.5 mg C l⁻¹.

to addition of aliquots to each sample to obtain a constant total surface area to solution ratio of 41.1 m² l⁻¹ for kaolinite and 48.0 m² l⁻¹ for goethite. An equal volume of Milli-Q water was added to the controls. The tubes were then placed on a shaker table at 22°C and allowed to equilibrate in the dark for 24 h. A time-course study showed that the sorption reaction equilibrated within 10 h or less, in terms of amount of adsorbed DOC.

Goethite samples and controls were centrifuged for 30 min at 2000 rcf (Beckman GS-6R Centrifuge) and the resulting supernatants were microfuged for 15 min at 30,000 rcf (Beckman Microfuge E). Kaolinite samples were centrifuged for 20 min at 11,220 rcf at 4°C (Sorvall RC-5B Refrigerated Superspeed Centrifuge). The pH values of the supernatants were measured (for both kaolinite and goethite reacted samples pH change was < 0.2 units) and samples were immediately analyzed by UV/VIS spectroscopy (scanned 200–600 nm, 400 nm min⁻¹, Cary 1, Varian Instruments or double beam Hitachi U2000) and DOC (samples acidified to pH 2–3, purged, and analyzed using a TOC5000, Shimadzu Instruments, MD). Additional samples of the supernatants were stored in plastic bottles and assayed for Fe (goethite-reacted samples) or Al (kaolinite-reacted samples), or stored in glass bottles, and analyzed for average molecular weight using HPSEC within 1 week.

In making up samples at different dilutions, no attempt was made to maintain constant inorganic

concentrations, although pH and ionic strength were standardized. We anticipated minimal effect because both surface waters have relatively low concentrations of inorganic constituents. Although Ca²⁺, in particular, has been shown to influence NOM sorption, this effect is minimized at low pH (as in our experiments) and for low to moderate sorption densities (Tipping, 1981), as were observed in our experiments and described below.

2.4. Size exclusion chromatography

Molecular weight distributions before and after sorption were measured by HPSEC in the method described in detail by Chin et al. (1994). The SEC system was calibrated using random coil sodium polystyrene sulfonates (Polysciences) (18 K, 8 K, 5.4 K, 1.8 K) which were reported to represent the configuration and size of NOM molecules more accurately than other macromolecules such as proteins (Chin et al., 1994). Acetone was also used. All standards and samples were detected at 230 nm except for acetone which was determined at 280 nm. Details regarding column calibration and standard selection are presented in detail by Chin et al. (1994). Typical standard deviations for M_w s determined by our group using HPSEC are ± 50 Da.

2.5. Dissolved iron and aluminum analysis

Al was measured using a flow-injection analysis (FIA) system as described by Sutheimer and Cabaniss (1995). The method has no interference from organic complexing agents or from other metals, but it is not capable of detecting polymeric Al species. Thus, the Al measured is either the dissolved organic and/or inorganic monomeric forms. Fe was measured using a Perkin Elmer graphite-furnace AA with an automatic sampler.

3. Results and discussion

3.1. Adsorption of NOM onto mineral surfaces

Amount of NOM sorbed was calculated as control–equilibrium DOC concentrations. Resulting data,

normalized to surface area, are presented in Fig. 1. Because we were constrained by the original surface-water DOCs, only a partial sorption isotherm at relatively low equilibrium NOM concentrations was obtained for the SR NOM/goethite combination (Fig. 1). Nevertheless, this partial isotherm does provide important information regarding the *relative* sorption affinities of SR and GDS NOM for the sorbents.

Both SR and GDS NOMs sorbed to a greater extent onto goethite than onto kaolinite (Figs. 1 and 2). The maximum amount sorbed was approximately 0.30 mg C m^{-2} for SR goethite versus 0.10 mg C m^{-2} for SR kaolinite and 0.25 mg C m^{-2} for GDS goethite versus 0.08 mg C m^{-2} for GDS kaolinite. Gu et al. (1996) studied sorption of Suwannee River reverse osmosis isolate onto Fe oxide at $\text{pH} \sim 4$; they reported a sorption maximum of slightly less than 0.4 mg C m^{-2} . Schlautman and Morgan (1994) studied sorption of Suwannee River fulvic acid standard onto alumina at $\text{pH} 4$; they reported a sorption maximum of $\sim 0.3 \text{ mg C m}^{-2}$ (recalculated from graphical data). Hence, our data are in overall good agreement with previous results, although it should be noted that we did not obtain a true sorption maximum for the SR NOM-goethite combination.

Several factors may contribute to the greater amount of sorption onto goethite than onto kaolinite,

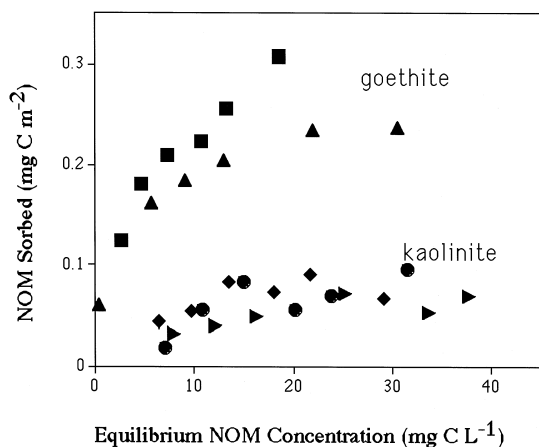


Fig. 1. Sorption of SR and GDS NOM by goethite and kaolinite. In this and future figures, data points are averages of 3 separate experimental runs. With the exception of the kaolinite sorption data, error bars are within the size of the printed data points. Legend is same as in Fig. 2.

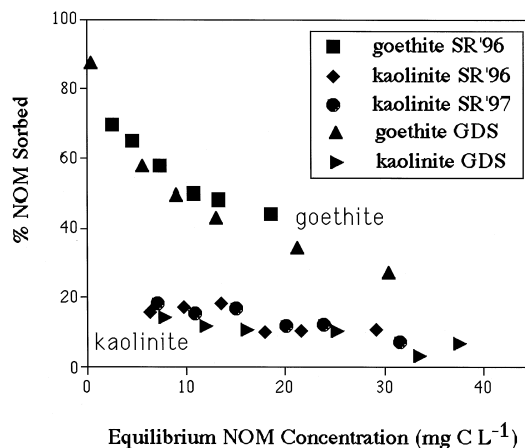


Fig. 2. Percent of GDS and SR NOM sorbed by goethite and kaolinite as a function of the sorbate equilibrium concentration.

as observed in our experiments (Fig. 1). First, if at least some sorption is electrostatically driven, then the greater pH_{pznpc} (pH of point of zero net proton condition) of goethite may play an important role. Goethite has a relatively high pH_{pznpc} (7.7; Sposito, 1984), while kaolinite's pH_{pznpc} is significantly lower (5.3, Sutherland et al., 1999, measured on KGa-1b). Perdue (1985) extrapolated nominal NOM pK_a values using a Gaussian distribution approach, and reported average values of 4.5 for carboxyl functional groups and 10 for phenolic moieties. Hence, at the pH of our experiments (4), most of the NOM would possess a net negative charge, while the goethite surface should have a relatively high positive surface charge based upon its pH_{pznpc} value. Although at $\text{pH} = 4$, the overall charge on the kaolinite particles should be closer to neutral, the edge surfaces should be positively charged. Perhaps more importantly, NOM sorption to clay mineral surfaces has been shown to occur largely through ligand exchange at surface hydroxyl sites (Parfitt et al., 1977; Davis, 1982; Sposito, 1984; Murphy et al., 1990; Gu et al., 1994). Goethite has a greater density of reactive hydroxyl sites, which are spread over the entire mineral surface (Parfitt et al., 1977; Davis, 1982), while reactive hydroxyl sites (aluminol groups) on the surface of kaolinite are located exclusively at the edges of its crystal structure (e.g., Sposito, 1984). Finally, there may be a lesser affinity for Al- versus Fe-centered sorption sites; sorption is probably minimal on Si-centered sites on kaolinite.

As shown in Fig. 1, the low affinity and resulting scatter in the kaolinite data make it difficult to determine which NOM (SR or GDS) shows greater affinity for kaolinite; SR NOM appears to adsorb slightly more than GDS. However, for goethite-reacted samples, SR NOM demonstrates a greater sorption affinity than GDS NOM, as a function of equilibrium NOM concentration. Several factors may be responsible for the greater sorption affinity of the SR sample. First, as shown in Table 2, above, the SR sample contains a slightly higher percentage of so-called hydrophobic (and a lower percentage of hydrophilic) organic components than does the GDS sample. Second, the M_w of the SR NOM (2300 Da) control was greater than the M_w of the GDS NOM (1890 Da) control. Several studies using humic materials have shown that hydrophobicity can be correlated to molecular size; larger humic acids tend to be more hydrophobic than smaller fulvic acids from similar sources (Chin et al., 1994; Hess and Chin, 1996; Wang, 1997). Evidence for this relationship can also be indirectly extrapolated from the interactions of hydrophobic organic pollutants and NOM. Larger NOM constituents are better able to interact with hydrophobic compounds than are more polar, smaller fractions (Gauthier et al., 1987; Chiou et al., 1987; Chin et al., 1997). Third, the SR sample appears to be more aromatic than the GDS sample. The average molar absorptivity (measured at 280 nm and normalized by DOC) of the SR NOM control samples ($380 \text{ l mol C}^{-1} \text{ cm}^{-1}$) is slightly higher than that of the GDS NOM ($320 \text{ l mol C}^{-1} \text{ cm}^{-1}$), which suggests that the SR NOM may be slightly enriched in its aromatic group content.

3.2. Changes in solution phase M_w upon sorption

The M_w of the experimental controls (water samples both diluted and undiluted in the absence of any sorbent) were found to be 2320 for one SR sample (control for goethite reaction), 2200 for another SR sample (control for kaolinite reaction), and 1890 Daltons for the GDS sample (Fig. 3a,b). As shown below (Fig. 4a), the molar absorptivities for the two SR controls also varied, suggesting that there is some degree of inhomogeneity in the surface water NOM properties, even for samples collected from the same location, and at approximately the same time. The

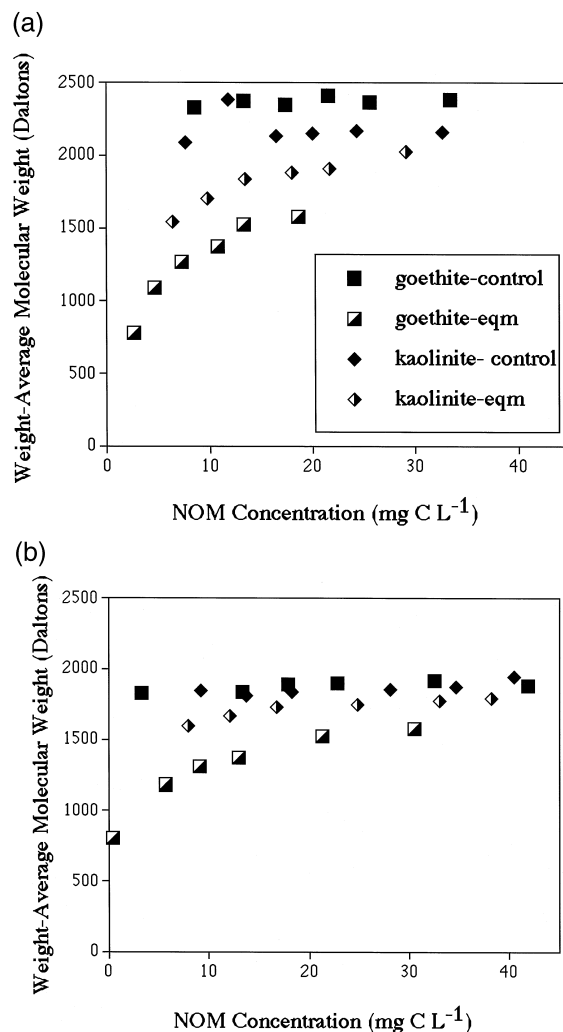


Fig. 3. (a and b) Change in weight-average molecular weight (M_w) of SR (a) and GDS (b) NOM after adsorption by goethite and kaolinite. 'eqm' refers to equilibrium concentration following 24 h reaction. Legend is same for both figures.

SR NOM polydispersity (the ratio of the weight-to-number average molecular weights, M_w/M_n) was found to be greater than GDS NOM polydispersity, with respective values of 1.54 and 1.37.

For both the SR and GDS samples, decrease in solution-phase M_w upon sorption was considerably greater for sorption to goethite than kaolinite (Fig. 3a,b). The change in M_w was greatest at low initial NOM concentrations, where the percentage of sorption was greatest, and decreased as the percentage of

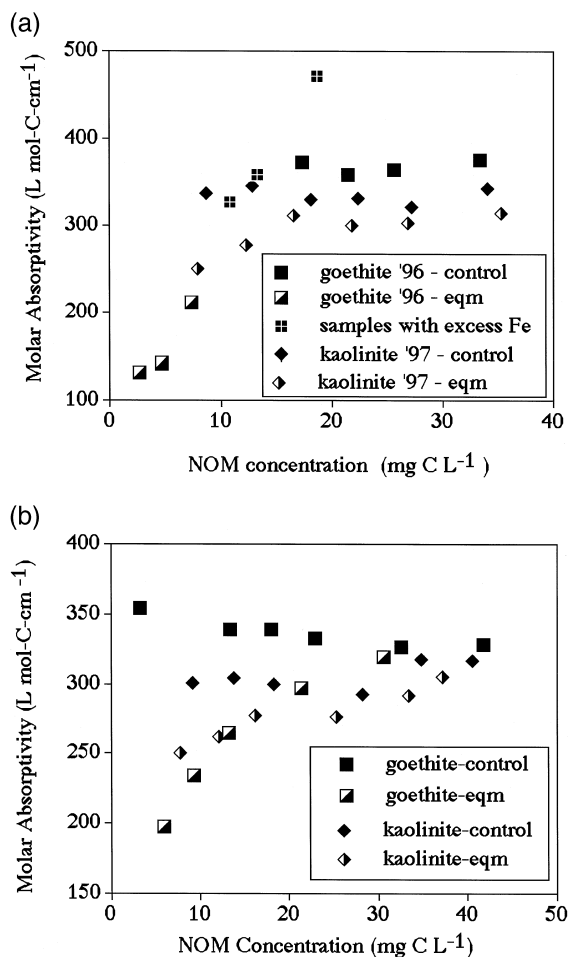


Fig. 4. (a and b) Change in the molar absorptivity (ϵ) of the SR (a) and GDS (b) sorbates after adsorption by goethite and kaolinite.

sorption increased. For goethite-reacted samples at relatively low equilibrium NOM concentrations (2–10 mg C l⁻¹), M_w dropped by more than half (900–1700 Da). The decreases in M_w of the solution-phase NOM presumably reflect preferential sorption of the larger NOM components. At higher equilibrium NOM concentrations (10–20 mg C l⁻¹), a much smaller change in solution M_w was observed; at these concentrations, there was also a smaller percentage of sorption. Hence, although the surface might have contained a different NOM distribution than is present in solution, any effects would tend to be overwhelmed by relatively high equilib-

rium NOM concentrations in solution. Experiments using kaolinite resulted in similar, but less pronounced trends in M_w change upon sorption, consistent with overall lower percentage of sorption. At lower equilibrium NOM concentrations (7–12 mg C l⁻¹), the M_w is 300–500 Da lower than that of the unreacted samples (Fig. 3a,b); at higher concentrations, the solution M_w approaches that of unreacted samples.

3.3. Effects of sorption on sorbate molar absorptivity

Previous studies (Traina, 1990; Chin et al., 1994) have shown that molar absorptivity (ϵ) at $\lambda = 280$ nm correlates well with the total aromaticity of humic materials as determined by quantitative ¹³C-NMR. We observed decreases in ϵ for both GDS and SR samples in the solution phase after sorption by kaolinite and goethite (Fig. 4a,b). Our data corroborate similar observations by several other investigators (Gu et al., 1996; Wang, 1997). The data suggest that the more aromatic components of the NOM pool are preferentially sorbed. This phenomenon provides indirect evidence that hydrophobic interactions play an important role in the sorption of NOM.

The fractionation after sorption that occurs for both NOM samples (Fig. 5a,b) appears to result in broadly similar molecular weight–molar absorptivity relationships to the relationship observed by Chin et al. (1994) for purified humic substances (lines on Fig. 5a,b are regression lines from Chin et al.'s data). This phenomenon was observed for both kaolinite- and goethite-reacted sorbates. A few of the goethite-reacted NOM samples (all at the highest concentrations) did not follow this trend (Fig. 5a,b). We suspect that this is in part caused by the dissolution of goethite by the NOM at relatively high NOM concentrations. The resultant formation of quasi-stable Fe–NOM complexes, inorganic iron colloids, and/or colloidal phases could cause 'red-shifts' in the light absorbance spectra or excessive light scattering in the presence of colloids. This would result in higher than anticipated absorbance measurements, which would in turn influence the magnitude of ϵ . Nonetheless, these data provide strong supporting evidence that the higher molecular weight and more aromatic NOM components are preferentially sorbed to mineral oxide surfaces.

Although we did not collect Fe data for all samples, results for reaction of SR water onto goethite at control concentrations of 37 mg C l^{-1} showed substantial increase in Fe concentration upon reaction with goethite. The control dissolved Fe concentration was determined to be $272 \text{ } \mu\text{g Fe l}^{-1}$, while reacted samples had a mean Fe concentration of $577 \text{ } \mu\text{g Fe l}^{-1}$. As stated previously, the presence of dissolved or colloidal iron may affect the light absorption

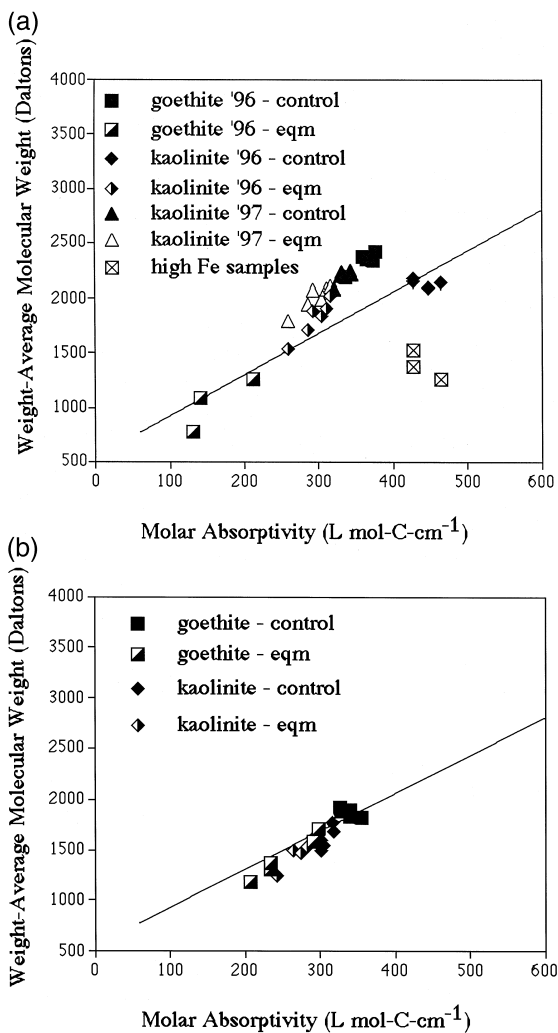


Fig. 5. (a and b) Molar absorptivity–weight–average molecular weight relationships for unfractionated and fractionated SR (a) and GDS (b) NOM. The lines in these figures are regression lines from Chin et al. (1994) showing trends observed for aquatic humic substances.

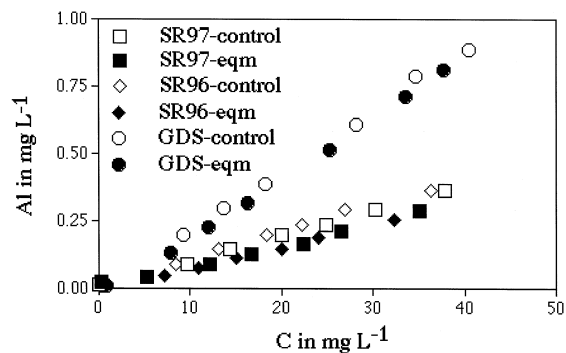


Fig. 6. Change in the solution phase aluminum concentration as a function of the sorbates' equilibrium concentrations.

properties of the sorbate remaining in solution. This indicates that changes in light absorption cannot be used reliably to estimate aromatic/aliphatic characteristics, for goethite-reacted samples at higher NOM concentrations.

Aluminum (Al) concentrations are higher in control than reacted samples (Fig. 6), indicating that Al present in the original samples adsorbs to the mineral surfaces, most probably as Al–NOM complexes. The results show no evidence for kaolinite dissolution, although it should be noted that our methods could not detect potential polymeric Al species. Dissolved Al should not affect light absorption properties; hence, light absorption should be a reliable indicator of aromaticity for kaolinite-reacted samples over the full range of NOM concentrations.

4. Conclusions

HPSEC and molar absorptivity data demonstrate that M_w of solution NOM decreases in the presence of adsorbing clay minerals, suggesting that larger molecular weight and more aromatic moieties are preferentially sorbed to goethite and kaolinite. The NOM constituents remaining in solution are on average smaller and less aromatic, which would presumably alter their chemical reactivity. Moreover, the fractionation that occurs appears to obey the molar absorptivity–molecular weight trend observed for a wide range of aquatic humic materials. Our research is thus consistent with previous results involving

NOM isolates, but expands our knowledge to include bulk-water NOMs which are representative of natural waters.

For both NOM containing waters, and both minerals, the magnitude of the change in solution NOM M_w appears to decrease with decreasing percentage of sorption to the mineral surfaces; i.e., as one moves up the sorption isotherm. Moreover, SR NOM sorbs to a greater extent (greater percentage of sorption) than GDS NOM, and it shows larger magnitude decreases in M_w . Sorption of both GDS and SR NOM is greater onto goethite than onto kaolinite, and changes in M_w are more pronounced for goethite-reacted samples. Hence, we can expect that factors which enhance the percentage of NOM sorption will also enhance the magnitude of the M_w decrease upon passage through porous media, at least where clay mineral surfaces dominate the available sorption sites.

Overall, our results suggest that NOM sorption to clay minerals may influence the distribution, size, and reactivity of NOM components in natural aquatic systems. However, other processes such as microbial degradation and variations in inorganic ion compositions require further investigation on both a laboratory and a watershed scale.

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