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Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin

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Abstract

A consistent observation of river waters in the Amazon Basin and elsewhere is that suspended fine particulate organic matter (FPOM) is compositionally distinct from coexisting dissolved organic matter (DOM). The present article presents experimental results that show that at least some of these compositional patterns are the outcome of selective partitioning of nitrogen-rich DOM components onto mineral surfaces. Nine laboratory experiments were conducted in which natural DOM from two rivers, one wetland, and two leachates from the Peruvian Amazon were mixed with natural suspended riverine minerals or organic-free kaolinite. Concentrations of organic carbon, organic nitrogen, and hydrolyzable amino acids were measured in both dissolved and particulate phases before and after mixing. In each of these trials, nitrogen was preferentially taken into the particulate fraction relative to the ''parent'' DOM, as were total hydrolyzable amino acids with respect to total organic carbon and nitrogen. Amino acid compositional patterns also indicated preferential sorption of basic amino acids, with positively charged nitrogen side chains, to the negatively charged aluminosilicate clay minerals. In short, sorption of natural DOM to minerals reproduced all contrasting organic nitrogen compositional patterns observed in the Amazon Basin. Although previously conjectured from FPOM-DOM compositional trends from river samples, this is the first direct evidence for preferential uptake of naturally occurring nitrogenous DOM by suspended riverine minerals. Last, nonprotein amino acids, which are commonly used as diagenetic indicators in sediments, preferentially remained dissolved, which suggests that sorptive fractionation may significantly complicate comparisons of FPOM and DOM diagenesis on the basis of interpretation of organic composition.

Riverine transport of organic matter (OM) from land to sea represents a major link in the global cycles of bioactive elements, which modulates the biosphere over geological time (Meybeck 1982). These terrestrial OM losses support significant heterotrophic activity within rivers, estuaries, and marine systems alike (Kaplan and Newbold 1993; Mayer et al. 1998). Where and when this river-borne OM is finally respired is of consequence to global carbon models (Stallard 1998). Thus, understanding the processes that control the pathways from initial source to final mineralization of riverine organic matter is important on both regional and global scales.

Three dominant and competing processes of OM cycling are advective transport, degradation, and sorption. Of these, the importance of sorption has only recently been appreciated. Most mineral surfaces in the biosphere maintain strong physicochemical associations with organic molecules, gels, and microaggregates (Oades 1989; Mayer 1994; Christensen 1996) at relatively consistent organic carbon (OC) to surface area (SA) ratios of 0.5–1.1 mg OC m^{-2} SA (Mayer 1994; Hedges and Keil 1995; Keil et al. 1997). Sorption—defined for the present article as all processes by which organomineral associations are formed—is found to be fast with respect to biodegradation (McKnight et al. 1992; Qualls and Haines 1992; Day et al. 1994) and sparingly reversible (Zhou et al. 1994; Gu et al. 1995). Most important, the intimate association of OM with mineral surfaces significantly decreases its bioavailability (Keil et al. 1994; Nelson et al. 1994; Baldock and Skjemstad 2000). Whether an organic molecule sorbs or remains dissolved determines in large part its transport potential and susceptibility to degradation.

In the Amazon and other major rivers of the world, ~90% of transported organic matter is either sorbed to fine minerals or has remained dissolved (Meybeck 1982; Keil et al. 1997). Worldwide, the compositions of these two fractions are quite distinct, whereas differences within a fraction from one river to another are generally subtle. Relative to coexisting dissolved organic matter (DOM), fine particulate organic matter

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Table 1. Sources for dissolved and particulate samples used in mixing experiments.

Sample	Location	Elevation (m)	Latitude	Longitude	Description
River 1	Rio Ucayali	110	04°28.29′S	73°25.96′W	Amazon River mainstem in lowlands near Iquitos
River 2	Rio Urubamba	290	10°41.95′S	73°44.73′W	Mesoscale tributary (57,000 km^2) in depositional zone
Wetland	Altiplano wetland	3930	14°21.79′S	71°19.11′W	Wetland typical of high-altitude Andean plains
Leachate 1	Gramalote grass	110	04°28.29′S	73°25.96′W	Leached from the dominant lowland riverbank grass
Leachate 2	Altiplano grasses	3930	14°21.79′S	71°19.11′W	Leached from a mixture of typical altiplano grasses

(FPOM, 0.45–63 μm) is generally enriched in ^{13}C and ^{15}N (Quay et al. 1992; Hedges et al. 2000) and depleted in ^{14}C (Hedges et al. 1986; Raymond and Bauer 2001), which suggests different sources and pathways. Biochemically, FPOM consistently has lower carbon : nitrogen ratios (Williams 1968; Meybeck 1982; Lewis et al. 1995; and many others), higher hydrolyzable amino acid and carbohydrate concentrations (Ittekkot et al. 1986; McKnight et al. 1992; Hedges et al. 1994; Mannino and Harvey 2000), fewer nonprotein amino acids (Hedges et al. 1994; Mannino and Harvey 2000), higher ratios of glucose relative to fucose and rhamnose (Hedges et al. 1994, 2000), and lower acid : aldehyde ratios in lignin phenols (Ertel et al. 1986; Hedges et al. 2000; Lobbes et al. 2000). Previous interpretation of these biochemical differences, which were largely based relative to compositions of aquatic primary producers, suggests that riverine FPOM is substantially less degraded than DOM. On the other hand, the biochemical signature of riverine FPOM closely resembles OM in tropical mineral soils.

One biochemical signature, that basic amino acids are enriched in riverine FPOM relative to DOM, has its most plausible explanation in preferential sorption of these amino acids over others (Hedges et al. 1994, 2000). At natural pH, the nitrogenous amine side chain of basic amino acids provides a net positive charge that is attracted to the net negative charge of that aluminosilicate clay minerals comprising the bulk of fine riverine sediments (Gibbs 1967). This type of preferential sorption has been observed for mixtures of dissolved free amino acids (Dashman and Stotzky 1982; Hedges and Hare 1987; Henrichs and Sugai 1993; Wang and Lee 1993) and for melanoidin polymers synthesized from the condensation of glucose with acidic, neutral, and basic amino acids (Hedges 1978). These arguments could be extended to observations of total nitrogen and amino acid enrichment on FPOM as well—two compositional patterns that are commonly interpreted as signs that FPOM is less degraded.

The idea that organic matter biochemically fractionates during sorption is far from new. Evidence for preferential sorption of higher molecular weight, more aromatic and carboxyl rich, and more hydrophobic fractions of natural OM (Davis and Gloor 1981; Jardine et al. 1989; McKnight et al. 1992; Day et al. 1994) has long suggested such fractionation. More recent evidence confirms that sorptive fractionation of natural OM occurs as a result of competition for mineral binding sites (Gu et al. 1995, 1996; Kaiser and Zech 1997). However, no study has specifically tested whether the same biochemical signatures that are used to infer differences in sources or degradation history might also be affected by sorptive fractionation. This study takes a first step in that direction.

The goal of this study is to examine which, if any, of the nitrogen and amino acid compositional signatures of riverine DOM and FPOM directly result from sorptive fractionation. To test this hypothesis, changes in DOM and POM compositions during sorption were directly observed in a set of nine laboratory experiments in which natural suspended river sediments and organic-free kaolinite were mixed with various natural DOM samples from the Peruvian Amazon. Incubation conditions were consciously chosen to best mimic those found in rivers, including inoculation with native microbial consortia. The Amazon Basin in Peru is an ideal site to test these hypotheses. This region contains both tropical lowland and montane river types, which happen to be well characterized with respect to their dissolved and particulate amino acid patterns (Hedges et al. 1994, 2000).

Materials and Methods

Sample collection—All samples were collected during the October 1996 CAMREX (Carbon in the Amazon River Experiment) expedition to Amazon River source basins in Peru (Table 1). Samples spanned most major environments found in the Amazon watershed—from Andean ''Altiplano'' grasslands at 4000+ m elevation, to cobbled ''mesoscale'' rivers in the 200–500 m foothills, and finally to the typical lowland Amazon mainstem at ~100 m elevation near Iquitos.

Natural DOM and suspended sediments were collected from rivers by gentle pumping (ShurFlo DC submersible diaphragm pump), to avoid excessive shear stresses on particles. The pump was submerged to 6/10 the total river depth (4/10 from bottom) in the thalweg (main flow), in order to sample suspended sediment size distributions where water velocities are most representative of depth-integrated fluxes. Wetland waters were collected by submerging bottles 50 cm below the surface. Coarse, sand-sized suspended material was removed in the field from river and wetland waters with a 63-μm sieve. All samples were processed for sorption experiments within several hours of collection.

Sorptive partitioning experiment—Individual partitioning experiments (Fig. 1) were conducted in field labs by mixing 1–2 liters of natural prefiltered DOM (with use of precombusted Whatman GF/F filters, nominal pore size of 0.7 μm) with suspended minerals at concentrations representative of rivers sampled during the field expedition (~300 mg sedi-

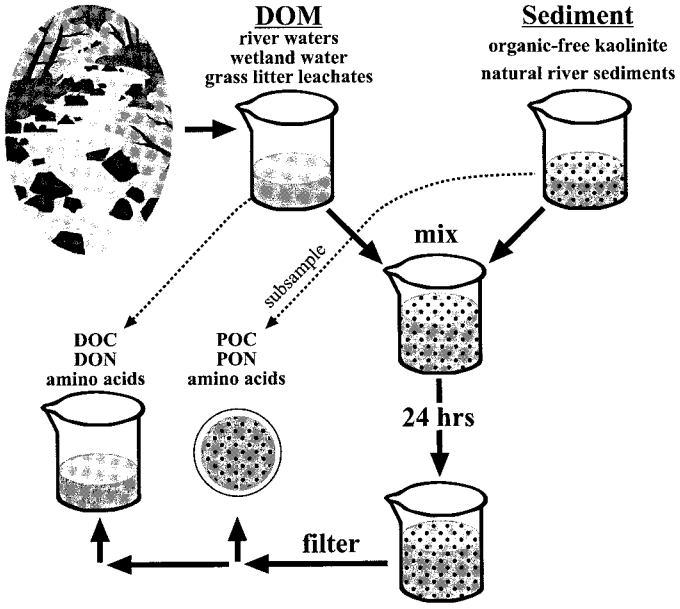

Fig. 1. Schematic of experimental method for batch sorption type incubations. DOM was isolated from five natural sources (see Table 1) and mixed with slurries of either natural river suspended sediments or commercially obtained kaolinite. Analyses were performed on both dissolved and particulate fractions before and after mixing.

ment L^{-1}). DOM samples were collected from two rivers and one wetland (Table 1). In addition, two leaf-litter leachates were created by immersing litter from dominant grass communities in distilled water for 24 h. These five DOM samples were mixed individually with either naturally suspended fine particles from two rivers (added as whole-water suspensions) or with an organic-free kaolinite (Ward's kaolinite API#5 from Bath, South Carolina) as a control sorbent. Organic carbon had been removed from the kaolinite earlier by pretreatment with 30% hydrogen peroxide for 2.5 h at 50°C–60°C—a process that reduced organic carbon concentrations from 0.38% to 0.040% (final molar C : N = 15.5). These dissolved and particulate sample sets each represent a continuum of increasing freshness: the DOM suite follows a history of decreasing exposure to mineral surfaces and to bacterial degradation (Table 2), and the suspended sediments represent end members of equilibration with ambient natural organic substances.

In all, nine different combinations of DOM and sediments were mixed in batch sorption type experiments (Table 2). In order to mimic conditions within rivers, mixtures were incubated for 24 h under live conditions (i.e., with native microbial communities) at ambient temperatures of 20°C–32°C (Fig. 1). During each 24-h experiment, gentle agitation by flipping sample bottles every 1–5 h maintained sediments in suspension as best as possible while not disturbing particle aggregates. Sorption experiments were terminated by filtration, taking care to homogeneously subsample suspended sediments by use of a churn sample splitter (Bel-Art). Fine suspended sediment (FSS) concentrations were determined gravimetrically by filtration of a known water volume onto preweighed membrane filters (Millipore HAWP, 0.45 μm pore size), with FSS replicates confirming the ability to con-

Table 2. Sorption carbon mass balance.

Experiment number	DOM source	Particle source	Initial						Final				Change			Partition
			DOC (mg L^{-1})	DOC	DON	FPOC	FPON	SA (m^2 g^{-1})	DOC	FPOC	FPON	OC/SA	Δ DOC	ΔFPOC	ΔFPON	K_d
				(mg OC 100 mg^{-1} sediment)					(mg OC 100 mg^{-1} sediment)			(mg OC m^{-2})	(mg OC 100 mg^{-1} sediment)			(L g^{-1})
1	River 1	Kaolinite	3.87	1.26	0.14	0.040	0.0030	12.5	1.24	0.135	0.036	0.11	−0.02	0.095	0.033	0.36
2	River 2	Kaolinite	7.72	2.47	0.09	0.040	0.0030	12.5	2.35	0.133	0.028	0.11	−0.12	0.093	0.024	0.18
3	Wetland	Kaolinite	11.0	3.68	0.42	0.040	0.0030	12.5	3.44	0.23	0.038	0.18	−0.24	0.19	0.035	0.22
4	Wetland	River 2	9.60	7.33	0.65	1.55	0.190	15.5	7.38	1.72	0.221	1.11	0.05	0.17	0.031	1.8
5	Leachate 1	Kaolinite	381	64.6	3.98	0.040	0.0030	12.5	59.6	2.53	0.566	2.03	−4.9	2.5	0.563	0.07
6	Leachate 1	River 1	79.4	29.4	1.86	0.85	0.117	22.7	25.9	3.82	0.861	1.68	−3.5	3.0	0.744	0.55
7	Diluted leach. 1	Kaolinite	8.09	2.87	0.17	0.040	0.0030	12.5	1.77	0.75	0.165	0.60	−1.1	0.71	0.162	1.5
8	Diluted leach. 2	Kaolinite	24.2	8.34	0.45	0.040	0.0030	12.5	5.45	1.29	0.308	1.03	−2.9	1.2	0.305	0.82
9	Leachate 2	Kaolinite	268	72.5	3.95	0.040	0.0030	12.5	70.5	2.88	0.635	2.31	−2.0	2.8	0.632	0.11

Except for the first DOC column, all organic carbon concentrations are normalized to 100 mg sediment mineral particles for ease of comparison.

sistently and homogeneously subsample a suspension. Samples for organic analysis were filtered through two stacked glass-fiber filters (Whatman GF/F, 0.7 μm pore size, precombusted at 500°C for 4 h), with the lower of each filter pair serving as a DOM filter blank for all POM analyses. The quantity of water passed through each filter was chosen to maximize filter sediment loading; excessive particle clogging stopped filtration at 25–150 ml for 25-mm filters and 60–250 ml for 47-mm filters. Immediately after filtration, the resulting DOM sample was preserved with $HgCl_2$ to a final concentration of 100 μM, and filtered POM subsamples were air dried in a dehydrating oven (50°C–70°C). Subsamples of both the DOM and the POM, before and after mixing, were analyzed for total organic carbon and nitrogen and hydrolyzable amino acids. After analysis, sorbed components were calculated as the difference between the initial and final concentrations.

Mineral surface characterization—Surface areas were measured by one-point Brauner-Emmett-Teller isotherms of N_2 adsorption by use of a Quantachrome Monosorb SA analyzer and normalized to a certified standard (Mayer 1994). Uncertainties for this method are <5% of measured values. SA was quantified for the two natural riverine suspended mineral samples from material isolated by tangential flow microfiltration with an Amicon H5MP01-43 hollow-fiber filter (0.1 μm pore size). Prior to SA analyses, OC was removed from these natural particle assemblages by combustion at 300°C for 12 h. Preliminary diffuse reflectance infrared Fourier-transform spectra (Janik et al. 1995) of these natural suspended sediment samples suggested appreciable quantities of smectites in addition to kaolinite, which is characteristic of the sampled basins of Peru (Gibbs 1967).

Organic analyses—Particulate carbon and nitrogen were analyzed directly on whole 25-mm Whatman GF/F filters (0.7 μm pore size) with a Leeman Labs CE440 elemental analyzer. For each sample, individual blanks (obtained by analysis of the lower of each filter pair) were subtracted from the total C and N measured. This individual filter blank approach was necessary because, during filtration, nontrivial and highly variable quantities of DOC and DON (2–70 μg C filter^{-1}) sorbed onto the filter versus procedural blanks in which ultra–low DOC Milli-Q water was passed through identical precombusted GF/F filters. Consistent with the findings of Moran et al. (1999), the amount of DOM sorbed into our blank filters was found through multiple linear regression analysis (MLR) to be positively correlated to DOC concentrations, total POC or PON on sample filter, and the total volume filtered (multiple $R^2 = 0.78$ for C and 0.64 for N, $n = 65$). However, because a lower filter blank was analyzed for every sample in our experiments, these MLR results were not used for blank estimation in our study. All POC analyses were run in duplicate on identically filtered subsamples. The combined analytical and experimental uncertainty (including errors propagated through subtraction of lower filter blanks) averaged ±5%, with a maximum of ±14%.

Dissolved organic carbon (DOC) concentrations were measured after acidification and sparging with a modified high temperature combustion MQ Scientific 1001 DOC analyzer (M. L. Peterson et al. pers. comm.). The standard error of three injections per sample vial was generally 2%–5%; however, analytical reproducibility from day to day was closer to ±10%. Dissolved organic nitrogen was measured as the difference in nitrate concentrations before and after high-intensity ultraviolet oxidation, as per the method of Abell et al. (2000). In seawater, this method exhibits essentially 100% oxidation efficiency and ±2% variability for replicates (Abell et al. 2000); however, the $HgCl_2$ preservative in our samples necessitated use of a less precise nitrate analyzer and complicated calibration due to reduction column poisoning. SDs of replicate analyses thus ranged from 3% to 10%, with propagated uncertainties of 6%–17%.

Amino acid analysis was performed with reverse-phase high-performance liquid chromatography (HPLC) of hydrolysates versus charged-matched recovery standards based on the method of Cowie and Hedges (1992*a*). Sample quantities corresponding to 10–30 μg N were measured into 4-ml reaction vials via evaporation of whole water for DOM and via portions of 47-mm filters (punched out with cork bores to reproducibly cut out exact filter areas) for POM. The vial was then spiked with a mixture of acidic, basic, and neutral nonprotein amino acids (α-aminoadipic acid, γ-methylleucine, and δ-hydroxylysine, respectively) as recovery standards for the corresponding charge classes of protein amino acids. All samples were hydrolyzed with 6 N HCl under N_2 in a sealed vial for 60–65 min at 150°C. Reaction mixtures were immediately neutralized by repeated evaporation (Jouan RC1022 centrifugal vacuum evaporator) and borate buffer addition until reaching a pH of 8.5–9.5, pipetted into a clean vial (discarding the mineral matrix), and dried for frozen storage. Just prior to HPLC analysis, samples were redissolved in 1.0 ml Milli-Q water, filtered (Gelman A/E glass fiber filter), and spiked with *o*-methylthreonine as an analytical recovery standard. Amino acids in standards and samples were derivatized online immediately prior to injection (Gilson Model 231 sample injector) with *o*-phthaldialdehyde (OPA) and resolved on a 15 cm × 4.6 mm (inner diameter) C_{18} analytical column (Beckman ODS ultrasphere, 5 μm pore size) by use of a binary solvent gradient of methanol versus aqueous sodium acetate (adjusted to pH 6.4). Fluorescent OPA derivatives were detected with a Waters Model 420 fluorescent detector (set to 328 nm excitation and monitoring >450 nm emissions) and quantified by use of EZ-Chrom Data System v. 6.5 (Scientific Software). Of the 20 amino acids found in protein, 16 can be quantified by this OPA method, along with 4 natural nonprotein amino acids. However, because of poor reproducibility of ornithine due to hydrolytic degradation (Cowie and Hedges 1992*a*), only 19 amino acids are presented here. The detection limits of this method with the Waters 420 fluorometer vary from amino acid to amino acid, ranging from 100 to 300 pmol injection^{-1}. Duplicate analyses were run on most samples, with variation <5% for all amino acids from POM samples and generally <15% for DOM samples (excepting a few cases of larger relative uncertainty for trace amino acids in a few samples).

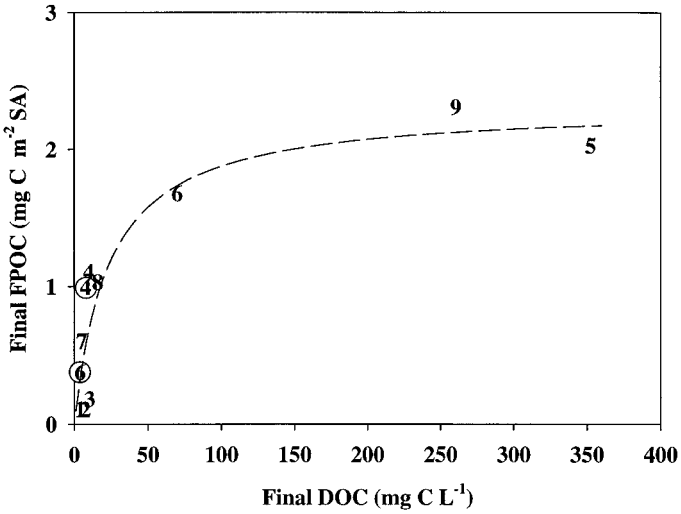

Fig. 2. Sorption isotherms of the nine respective mixing experiments given in Table 2, plotted as SA-normalized FPOC as a function of DOC. Experiments 1–4 and 6 are strictly one-point isotherms, and pairs 5, 7 and 8, 9 are two-point isotherms. However, these points, including the original riverine FPOC from experiments 4 and 6 relative to riverine DOC (circled values), give a reasonable fit to a Langmuir isotherm model (dashed line, $r^2 = 0.84$, $n = 11$, $q_{max} = 2.3 \pm 1.1$ mg OC m^{-2} SA, $K = 0.043 \pm 0.015$ L mg^{-1} C).

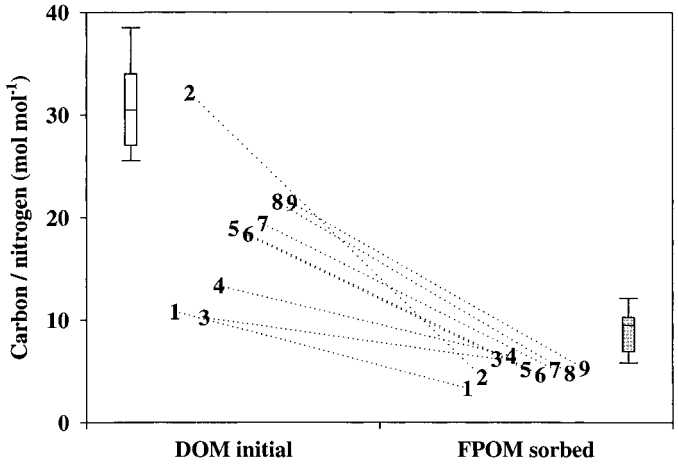

Fig. 3. Molar carbon : nitrogen ratios of sorbed FPOM (calculated from the difference between initial and final FPOC and FPON) relative to the ''parent'' DOM for the nine respective mixing experiments given in Table 2. As a reference, box plots present the distribution of values measured in 15 natural river samples from the Amazon Basin (Hedges et al. 1994, 2000). The median value is framed by boxes showing the 25th and 75th percentile of values and by ''whiskers'' showing the 10th and 90th percentile.

Results

Carbon and nitrogen sorption—Appreciable sorption of DOM to sediments occurred in all nine mixing sets (Table 2), with newly sorbed organic matter ranging from 0.1 to 3.0 weight percent particulate organic carbon (POC, mg OC 100 mg^{-1} sediment). By analyzing both initial and final DOC and fine POC (FPOC), mass balances could be calculated for each sorption experiment. Because mineral concentrations remained constant during each experiment, the mass balance of organic carbon can be assessed from sediment mass normalized values (as in Table 2) or from volume or surface area normalized values (which can be calculated from Table 2). In general, carbon lost from the DOM pool was gained by the FPOM pool, with additional DOM losses likely due to respiration during the experiment. Small changes relative to total concentration for the dissolved fractions make calculations of lost DOC much less sensitive than those for gained FPOC. Thus, for experiment numbers 1, 4, and 9, much less DOC disappeared than is reasonable (Table 2). Excluding these samples, respiration losses (estimated from OC loss) ranged from 22% to 25% of sorbed carbon for the natural river and wetland waters (or ~1% of initial DOC) and from 15% to 60% of sorbed carbon for the leachates (or 2%–20% of initial DOC).

SA loadings of all nine sorption experiments fell within the full range of values commonly observed in the natural environment (Table 2) (Hedges and Keil 1995). River and wetland DOM sorbed within the range of 0.1–0.2 mg OC m^{-2} SA, diluted leachates sorbed at 0.7–1.2 mg OC m^{-2} SA, and undiluted leachates sorbed at the highest levels of 2.4–2.7 mg OC m^{-2} SA. The extent of sorption generally increased with increasing DOM freshness.

Results of batch sorption experiments such as these are commonly expressed in terms of a partitioning coefficient (K_d), calculated as the ratio of final POC (mg OC g^{-1} particle) to final DOC (mg OC L^{-1} water). Values determined for these nine experiments ranged from 0.07 to 1.8 L g^{-1} (Table 2). Plots of final sorbed versus dissolved concentrations, or adsorption isotherms, illustrate systematic changes in sorptive partitioning with changes in OC concentrations within a system (Fig. 2). Such a treatment of all of our data collectively is not conventional, because of the diverse sources of DOM and sediments used. Experiment numbers 1, 2, 3, 4, and 6 are strictly one-point isotherms, and pairs 5, 7 and 8, 9 are two-point isotherms. Despite this caveat, it appears that a composite isotherm of SA-normalized particulate concentrations for all nine experiments (Fig. 2) follows the classic hyperbolic form of the site-limited Langmuir isotherm ($r^2 = 0.84$), as is commonly observed for natural DOM sorption (Day et al. 1994; Gu et al. 1995). Natural suspended sediments from two different rivers both fall on the Langmuir isotherm line after equilibration with new DOM (experiments 4 and 6), despite containing appreciable quantities of smectite clays. Even the original river particles from these two experiments fall on the model line when compared with DOC concentrations in their respective rivers at the time of collection (Fig. 2). The asymptotic surface loading of the Langmuir model fit (2.3 ± 1.1 mg OC m^{-2} SA) approached maximal surface loadings found in the environment (Hedges and Keil 1995).

Relative to carbon, dissolved organic nitrogen was preferentially partitioned onto mineral particles in all nine experiments (Table 2). Atomic carbon to nitrogen ratios of initial ''parent'' DOM and final FPOM ranged from 10 to 32 and from 4.3 to 9.1, respectively. Sorbed FPOM had atomic C : N ratios (calculated as the ratio of final minus initial carbon over final minus initial nitrogen) of 3.3–6.5 (Fig. 3).

Regressions of OC as a function of N for the initial DOM show a highly linear fit ($r^2 = 0.997$) with a slope of 19.6 ± 0.6 (mol C mol^{-1} N) and an intercept of −1.1 ± 4.5 mg C L^{-1}. A similar regression for the final FPOM associated with the kaolinite gave $r^2 = 0.999$, slope = 5.2 ± 0.09 mol C mol^{-1} N, and y-intercept = 0.00 ± 0.02 mg C L^{-1}. The zero intercepts, especially for the FPOM fractions, are strong evidence that inorganic nitrogen, such as sorbed NH_4^+, did not contribute appreciably to C : N ratios.

Amino acid composition—The percentage of total organic carbon measurable as amino acids ($\%T_{AA}C$) in natural river and wetland DOM (experiments 1–4) ranged from 0.6% to 3.5% (Table 3). Before sorption, amino acids made up 4.4%–5.2% of DOC in leachates and 8.0%–9.5% of FPOC on the two natural river sediments. Amino acids accounted for 5.9%–46% of FPOC for all sediments after sorption. In all nine cases, the organic material that sorbed was clearly enriched in amino acids relative to its parent DOM (Fig. 4A). Although sorption of natural waters produced FPOM with $\%T_{AA}C$ values characteristic of natural river sediments, the $\%T_{AA}C$ of FPOM sorbed from leachates greatly exceeded values of previously measured river sediments (Ittekkot et al. 1986; Hedges et al. 1994). As was seen for OM surface loading, the degree of amino acid enrichment during sorption seemed to increase with increasing DOM freshness (Fig. 4A).

The preferential sorption of amino acids over other compounds was even apparent when normalized to total organic nitrogen ($\%T_{AA}N$) (Fig. 4B). Generally about twice the fraction of the sorbed nitrogen pool could be identified as occurring in amino acids when compared with the corresponding DON pool. In these experiments, $\%T_{AA}N$ values of both dissolved and particulate fractions were roughly comparable to those found for natural samples (Hedges et al. 1994, 2000). Similar to $\%T_{AA}C$ trends, preferential enrichment of amino acids relative to bulk nitrogen appeared to increase with increasing DOM freshness.

Analysis of the relative abundance of individual amino acids in each sample revealed distinct compositional trends between DOM and sorbed FPOM (Table 3). As is commonly done, amino acid compositions are presented and discussed here on a mole percent (mol%) basis, in which molar concentrations of each amino acid for a sample were normalized to the total concentration of all amino acids such that their sum equals 100%. Amino acid compositions of DOM and FPOM were comparable to previously published data obtained that used similar analytical methods (Keil et al. 2000). Glycine and alanine dominate, followed by glutamic acid/glutamine, valine, and threonine. Mole percentages of methionine, tyrosine, and histidine are all generally <1.

Changes in amino acid compositions during sorption can be visualized in two ways (Fig. 5). First, direct changes in the contribution of an amino acid to the total pool can be calculated by subtracting mol% values of each initial DOM sample from the respective sorbed FPOM values. The resulting ''difference'' spectra (Fig. 5A) have units of Δmol%, such that positive values indicate enrichment in FPOM relative to DOM. The sum of these mol% differences for each sample equals 0. Visualizing enrichment in this way, the pattern of amino acid fractionation was remarkably consistent from one sample to another. These patterns could be generally grouped by the side-chain functionality of individual amino acids. Basic amino acids, with positively charged nitrogenous side chains, were strongly enriched in the sorbed FPOM relative to the initial DOM. The summed contribution of basic amino acids as a group increased by 3–11 mol%. Amino acids with more hydrophobic side chains—with the exception of valine—were also enriched in the FPOM, generally by 2%–4% each. Concentrations of nonprotein amino acids (NPAA) as a group approached the detection limit in FPOM, whereas NPAAs comprised 8–12 mol% in dissolved samples. Glycine and alanine showed large, negative Δmol% values for a few of the experiments. However, as dominant amino acids, these depletions in the FPOM were relatively minor compared with their overall concentrations. In fact, much of this depletion may simply result from mathematical artifacts introduced by presenting compositions on a mol% basis. Because the sum of mol% values of all amino acids in a sample must equal 100%, a change in the absolute concentration of only one amino acid will change the mol% values of all other amino acids. Furthermore, this change is not uniformly distributed. For each amino acid, the change is directly proportional to the new mol% value of that amino acid. Therefore, the depiction of compositional differences in Fig. 5A may misrepresent sorptive fractionation for certain of the more abundant amino acids.

An alternate way to visualize fractionation patterns that does not present these biases is through an enrichment factor (Fig. 5B), in which proportional changes in the contribution of each amino acid in the initial fraction are compared relative to the final fraction. The enrichment factor is calculated as the mol% value found in FPOM divided by the mol% in DOM, yielding values >1 for amino acids enriched in FPOM. To ease graphical comparison with amino acids depleted in FPOM, the negative inverse, $-\text{mol}\%_{DOM}/\text{mol}\%_{FPOM}$, was used to calculate DOM enrichment factors in lieu of values between 0 and 1. This visualization highlights the large fractionation of basic and nonprotein amino acids. Basic amino acids were enriched in FPOM by a factor of 2–10 over their original contributions in DOM. NPAA, on the other hand, were highly depleted in the FPOM by factors generally ranging from 3 to 60. Hydrophobic amino acids (excepting valine) were enriched in FPOM by factors of 1.5–2.2. Alanine and glycine, because of their high relative abundance in DOM, were relatively depleted by generally less than a factor of 1.5. Methionine is perhaps the one amino acid misrepresented by this presentation. As a result of its trace levels in DOM, methionine showed large relative enrichment factors for six sorption experiments.

Following previous convention (Cowie and Hedges 1994; Hedges et al. 1994; Keil et al. 1998), the most striking of these dissolved versus particulate amino acid patterns can be summarized by two parameters, a sorption proxy B/(B + A) and a degradation proxy %(βAla + γAba). B/(B + A) represents the ratio of basic amino acids, arginine and lysine, to the sum of these basic plus the two acidic amino acids, aspartic and glutamic acid. Values for sorbed FPOM in these experiments are 0.15–0.20 larger than those for DOM (Fig. 6A); %(βAla + γAba) is the total mol% of β-alanine and

Table 3. Amino acid compositions of DOM and POM before and after mixing.

Experiment number	Fraction	THAA (mg 100 mg^{-1} OC)	% $T_{AA}C$	% $T_{AA}N$	ASP (mol %)	GLU (mol %)	SER (mol %)	GLY (mol %)	THR (mol %)	ALA (mol %)	TYR (mol %)	MET (mol %)	VAL (mol %)	PHE (mol %)	ILE (mol %)	LEU (mol %)	HIS (mol %)	ARG (mol %)	LYS (mol %)	βALA (mol %)	γABA (mol %)	αABA (mol %)
1	$DOM_{initial}$	3.2	1.4	3.9	6.4	11.4	5.5	19.6	7.9	13.9	0.9	0.0	7.8	3.3	4.0	4.6	0.0	0.6	2.5	8.2	2.1	1.3
2	$DOM_{initial}$	1.3	0.6	4.7	6.7	13.6	8.5	17.9	8.2	13.6	0.0	0.5	7.6	4.5	3.8	5.1	0.0	0.0	2.4	4.2	1.3	2.2
3	$DOM_{initial}$	8.4	3.5	10.0	6.0	8.9	13.3	18.7	8.1	14.0	0.9	0.0	9.2	2.5	2.8	3.9	0.7	0.8	1.8	6.0	0.8	1.6
4	$DOM_{initial}$	6.0	2.5	9.3	6.0	9.2	13.0	18.7	8.1	14.0	0.8	0.04	9.1	2.6	2.9	4.0	0.6	0.8	1.9	5.9	0.8	1.7
5	$DOM_{initial}$	10.4	4.6	22.4	5.5	10.5	6.7	12.8	6.5	22.7	1.0	0.03	10.6	2.2	4.1	4.4	0.7	0.5	0.5	1.8	7.6	1.8
6	$DOM_{initial}$	10.2	4.4	21.2	5.5	10.5	6.7	12.9	6.6	22.6	1.0	0.03	10.6	2.2	4.1	4.4	0.7	0.5	0.6	1.9	7.5	1.8
7	$DOM_{initial}$	10.3	4.5	22.7	5.5	10.5	6.7	12.8	6.5	22.7	1.0	0.03	10.6	2.2	4.1	4.4	0.7	0.5	0.5	1.8	7.6	1.8
8	$DOM_{initial}$	11.9	5.2	29.4	3.3	10.5	5.6	12.6	5.1	29.1	1.2	0.4	8.2	2.1	4.2	4.5	0.4	0.5	1.4	2.3	8.4	0.4
9	$DOM_{initial}$	10.6	4.6	26.1	3.3	10.5	5.6	12.6	5.1	29.1	1.2	0.4	8.2	2.1	4.2	4.5	0.4	0.5	1.4	2.3	8.4	0.4
4	$FPOM_{initial}$	18.1	8.0	21.5	6.4	9.2	8.9	16.3	8.0	15.0	1.6	0.2	7.9	4.3	5.1	6.1	1.7	3.8	4.7	0.4	0.5	0.1
6	$FPOM_{initial}$	21.5	9.5	23.0	6.6	9.6	11.1	14.6	7.8	14.1	1.6	0.0	7.9	4.0	4.4	5.7	2.2	3.7	3.8	1.3	1.4	0.2
1	DOM_{final}	3.0	1.3	3.6	6.5	12.6	7.0	19.2	7.6	11.5	1.0	0.0	7.0	3.5	3.9	6.3	0.0	0.6	2.7	5.8	3.1	1.7
2	DOM_{final}	1.2	0.5	3.6	6.5	10.5	7.6	17.2	10.3	13.6	0.7	0.7	6.5	2.9	3.8	4.0	0.0	0.9	5.4	5.8	2.5	1.3
3	DOM_{final}	7.4	3.2	8.0	5.9	8.9	11.8	17.5	8.4	14.0	1.0	0.0	10.4	2.3	2.8	3.5	0.0	0.0	3.4	7.5	0.5	2.1
4	DOM_{final}	3.8	1.6	6.8	6.7	10.1	7.1	16.6	9.0	16.8	1.0	0.2	7.8	2.8	3.8	5.4	0.0	0.2	1.4	9.1	1.3	0.7
5	DOM_{final}	10.6	4.6	24.4	6.2	9.4	8.0	14.2	8.0	20.5	1.2	0.0	11.6	2.1	4.0	4.8	1.1	0.6	0.5	2.6	3.4	1.8
6	DOM_{final}	7.9	3.4	34.9	7.3	11.0	10.1	14.5	10.7	15.3	0.7	0.0	9.1	2.8	3.9	4.8	1.3	0.6	1.0	4.3	0.9	1.7
7	DOM_{final}	Not determined (sample lost)																				
8	DOM_{final}	7.7	3.4	25.6	6.7	12.1	5.0	16.0	5.9	16.6	1.1	0.0	9.3	2.9	4.5	5.5	0.0	0.0	1.9	8.7	2.2	1.6
9	DOM_{final}	7.9	3.5	26.7	3.8	9.3	5.1	13.5	5.4	26.5	1.2	0.1	10.0	2.2	4.1	5.2	0.5	0.5	1.0	2.9	8.0	0.7
1	$FPOM_{final}$	13.3	5.9	7.6	7.3	10.3	9.9	11.4	7.1	16.5	3.1	0.0	8.2	4.0	4.5	6.5	1.9	4.0	4.2	0.5	0.4	0.4
2	$FPOM_{final}$	20.3	9.1	14.4	6.2	10.2	7.5	15.0	7.7	15.9	2.4	0.0	9.1	4.4	5.5	6.7	1.1	3.7	3.8	0.0	0.2	0.4
3	$FPOM_{final}$	19.2	8.5	15.6	7.2	12.0	9.5	14.5	9.1	12.7	2.0	0.0	8.0	4.3	5.0	8.2	0.7	2.6	3.0	0.9	0.1	0.2
4	$FPOM_{final}$	21.2	9.4	23.7	6.4	10.1	9.4	14.4	8.4	14.3	1.7	0.4	7.9	4.4	5.1	6.6	1.5	3.9	4.5	0.4	0.4	0.1
5	$FPOM_{final}$	46.8	21.1	30.1	6.4	12.5	7.1	11.1	7.1	16.2	2.4	0.8	7.7	4.4	5.3	7.6	1.7	4.6	4.6	0.0	0.4	0.1
6	$FPOM_{final}$	75.0	33.8	48.8	5.9	11.1	6.7	11.8	6.5	16.8	2.4	1.1	7.8	4.4	5.5	7.2	1.5	4.9	5.7	0.2	0.4	0.1
7	$FPOM_{final}$	81.3	36.6	53.2	6.3	10.6	6.7	11.4	7.3	17.7	2.4	0.3	7.6	4.5	5.3	7.2	1.6	3.8	4.9	2.2	0.0	0.1
8	$FPOM_{final}$	83.2	37.2	51.8	5.3	11.8	5.5	16.2	6.0	15.6	2.0	0.9	7.5	3.9	5.4	7.1	1.6	4.8	5.9	0.2	0.1	0.1
9	$FPOM_{final}$	103.3	46.6	70.9	6.2	11.2	5.8	13.5	6.7	14.5	2.3	1.7	8.0	4.3	6.0	7.4	1.8	4.6	6.0	0.1	0.1	0.0

THAA, total hydrolyzable amino acids; $\%T_{AA}C$ and $\%T_{AA}N$, percentage of total organic carbon (or nitrogen) measurable as amino acids; ASP, aspartic acid (includes asparagine, which converts to aspartic acid during hydrolysis); GLU, glutamic acid (includes glutamine, which converts to glutamic acid during hydrolysis); SER, serine; GLY, glycine; THR, threonine; ALA, alanine; TYR, tyrosine; MET, methionine; VAL, valine; PHE, phenylalanine; ILE, isoleucine; LEU, leucine; HIS, histidine; ARG, arginine; LYS, lysine; βALA, β-alanine; γABA, γ-amino butyric acid; αABA, α-amino butyric acid.

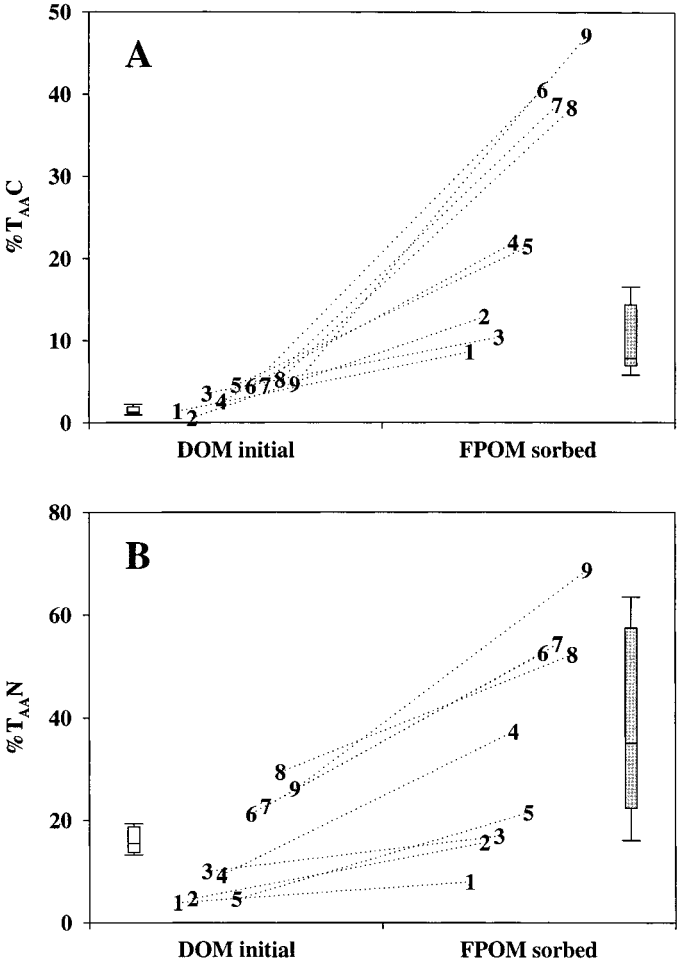

Fig. 4. Total amino acid content, normalized to (A) carbon and (B) nitrogen, of sorbed FPOM relative to the ''parent'' DOM. Amazon compositions illustrated as in Fig. 3.

γ-aminobutyric acid, the two most abundant NPAA. Values of this parameter ranged from 5.4% to 10.7% for initial DOM in these nine experiments, whereas sorbed FPOM never exceeded 2.2% (Fig. 6B). With the exception of river 1, dissolved %(βAla + γAba) increased with increasing DOM freshness.

Discussion

Patterns of sorptive fractionation—The elemental and amino acid compositions of dissolved and particulate organic matter in these nine experiments—including those directly resulting from sorption—closely mimic compositional patterns of coexisting DOM and FPOM in the Amazon (Fig. 7) and other rivers of the world. Experimental carbon : nitrogen ratios are substantially lower in all FPOM samples relative to the corresponding DOM (Fig. 3). Such nitrogen enrichment on particles is a dominant characteristic of organic matter in the Amazon River (Williams 1968; Hedges et al. 1994, 2000) and other rivers around the world (Meybeck 1982; Lewis et al. 1995; Lobbes et al. 2000). The amino acid content of all DOM samples and of FPOM sorbed from natural river and wetland waters matched the range of $\%T_{AA}C$ and $\%T_{AA}N$ values observed previously at 15 sites within the Amazon (Fig. 4) (Hedges et al. 1994, 2000), reproducing the typically strong pattern seen in rivers of amino acid enrichment on particles versus the dissolved phase (Ittekkot et al. 1986; McKnight et al. 1992; Mannino and Harvey 2000). Differences in mol% contributions of individual amino acids between DOM and FPOM in the experiments (Table 3, Fig. 5) also closely mirrored patterns observed between naturally co-occurring DOM and FPOM fractions collected in the Amazon (Hedges et al. 1994, 2000). Plots similar to those in Fig. 5 for these natural samples (not shown) reveal few exceptions to the trends shown here. Last, FPOM compositions in these experiments are all directly the result of sorbing DOM to particles with surface loadings within the typical range (0.1–2.0 mg OC m^{-2} SA) found for most riverine suspended sediments (Keil et al. 1997; Mayer et al. 1998).

The present study thus has presented substantial evidence that sorptive processes play a significant role in determining the organic nitrogen compositions of particulate material in river systems. Although the contrasting compositions of coexisting DOM and FPOM in rivers have long been noticed, substantial differences between the two phases with respect to likely sources, ages, and diagenetic histories have obscured the role of sorption. By using well-characterized DOM sources in sorption experiments conducted under natural conditions, we have clearly demonstrated that the contrasting nitrogen and amino acid patterns of DOM and aluminosilicate bound FPOM are primarily determined by preferential sorption of nitrogenous OM components.

The importance of sorptive fractionation to FPOM, and possibly DOM, compositions is likely not limited to riverine environments. Clear interpretation of published marine and soil data is hampered by the fact that few studies provide elemental and biochemical compositions of both DOM and coexisting mineral-associated FPOM. Many studies also use classic humic extraction methods (i.e., XAD resins) that preferentially exclude nitrogen and proteinaceous OM. Nevertheless, the pattern of enrichment of nitrogen and hydrolyzable amino acids in FPOM versus DOM does seem to extend to marine and soil environments. Molar carbon : nitrogen ratios of fine-grained marine sediments generally exhibit C : N ratios of 6–12 (Carter and Mitterer 1978; Cowie and Hedges 1992*b;* Keil et al. 1998; and many others), yet the few dissolved organic C : N ratios measured in pore waters range from 8 to 25 (Burdige and Zheng 1998; Lomstein et al. 1998), and coastal and oceanic DOM exhibits C : N values from 9 to 23 (McCarthy et al. 1996; Benner in press). Likewise, amino acids comprise 7%–25% of organic carbon in coastal sediments (Carter and Mitterer 1978; Keil et al. 1998, 2000), yet $\%T_{AA}C$ values are ~9% for pore water DOM (Lomstein et al. 1998) and 2%–6% for coastal and oceanic DOM (McCarthy et al. 1996; Benner in press). Even compositional patterns for basic, acidic, and nonprotein amino acids in marine environments show trends similar to those in rivers (McCarthy et al. 1996; Keil et al. 1998; Lomstein et al. 1998). In soils, mineral-associated FPOM exhibits C : N ratios of 7–14 (Oades 1989; Amelung et al. 1998), whereas water-extracted soil DOM has C : N ratios of 26–55 (Qualls and Haines 1992; Gu et al. 1995; Kaiser and Zech

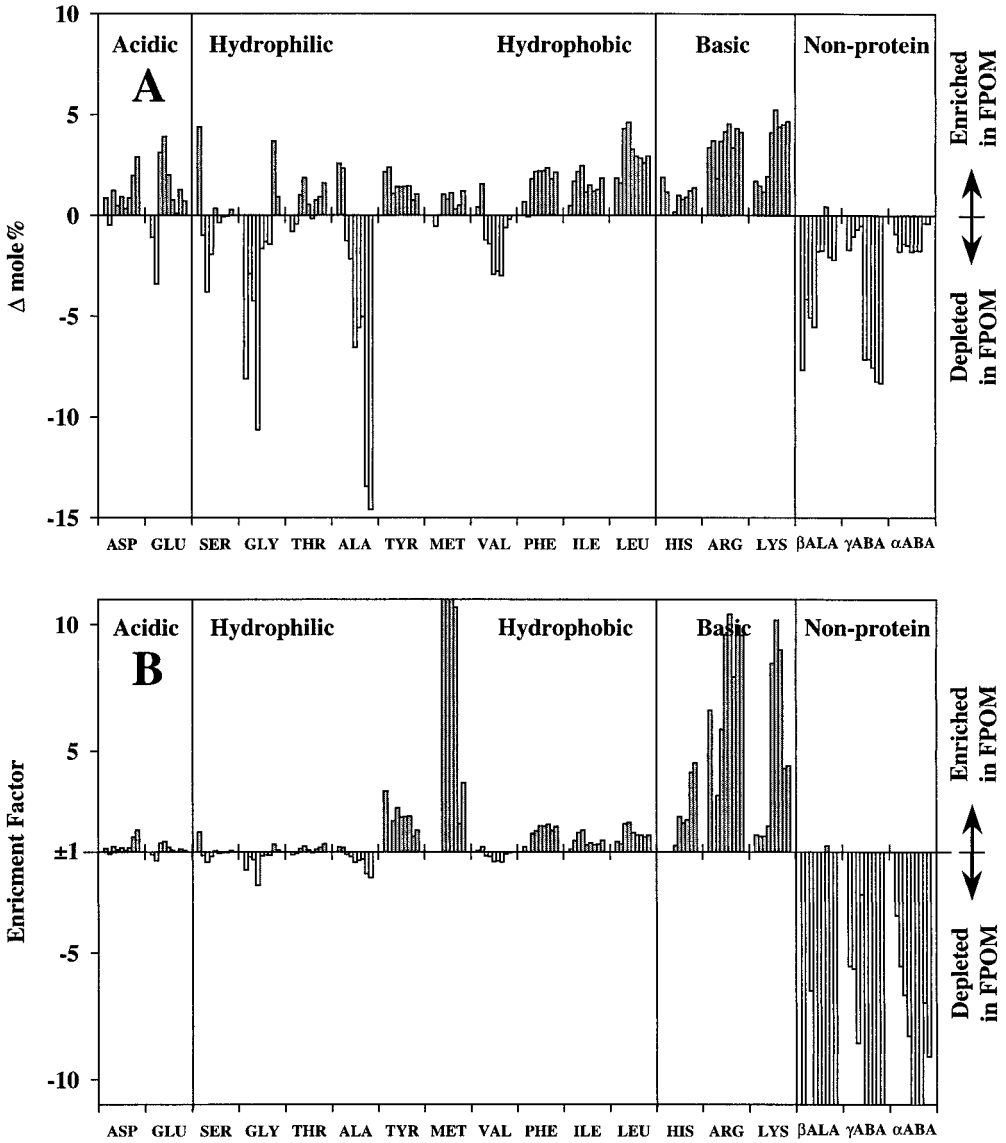

Fig. 5. Patterns of amino acid enrichment on sorbed FPOM relative to initial DOM, plotted (A) as the difference between the mol% amino acid composition of FPOM and DOM and (B) as the factor by which an amino acid is enriched or depleted in FPOM relative to its mol% in DOM. Positive values in both A and B correspond to enrichment of that amino acid in the FPOM relative to its parent DOM. Off-scale values in B are less than +40 and more than −60. For each individual amino acid, the bars are presented in order from left to right for experiments 1–9, respectively. Amino acids are presented within each functional grouping in chromatographic elution order. Although neutral amino acids are given in this relative order of hydrophobicity, only serine, threonine, and tyrosine actually have polar side chains.

1997). Although these compositional patterns in marine and soil environments are consistent with the results of these experiments, the mechanisms that cause the observed differences between phases could be quite diverse and include microbial-mediated processes.

Mechanisms for fractionation—Investigations of DOM association with sediments have identified a wide variety of mechanisms that contribute to total sorption. These are surface complexation or ligand exchange by carboxyl groups (Gu et al. 1995; Kaiser and Zech 1997; Arnarson and Keil 2000), electrostatic anion exchange (Jardine et al. 1989), hydrophobic and other entropy-driven physical interactions (Jardine et al. 1989; Gu et al. 1996; Kaiser et al. 1997), and cation bridging (Day et al. 1994; Arnarson and Keil 2000). In addition, recent applications of theory from polymer gel physics have been quite successful in unifying these various mechanisms to describe natural OM sorption behavior over wide ranges of conditions (van de Weerd et al. 1999; Filius et al. 2000). Essentially, all of these mechanisms and conceptualizations exhibit the potential to drive the selective sorption of certain functional groups (and thus molecules)

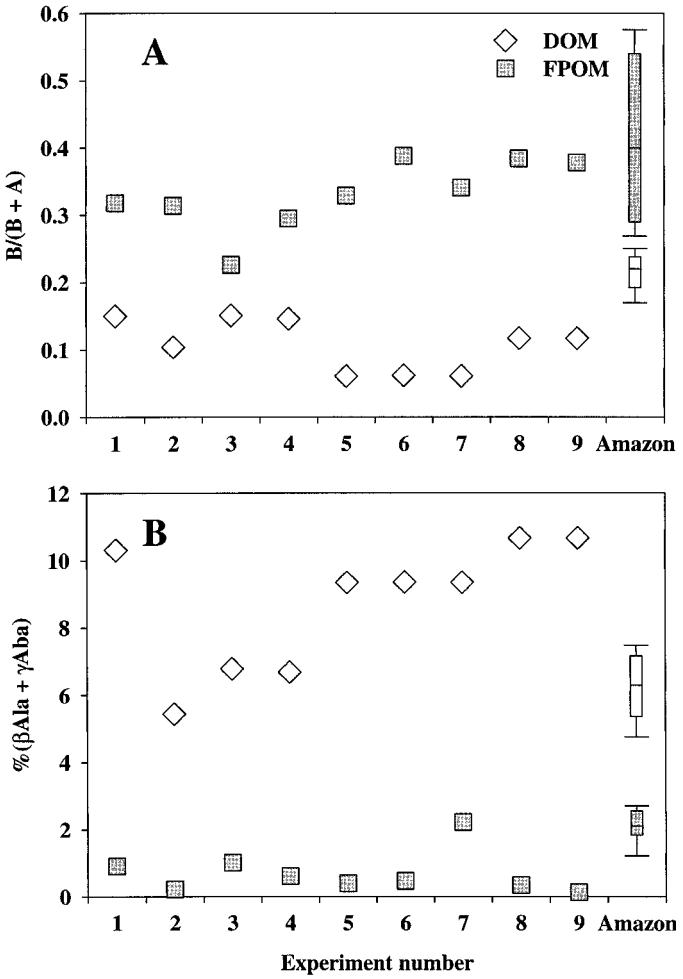

Fig. 6. Amino acid parameters of initial DOM and sorbed FPOM for each mixing experiment. Subplots compare (A) B/(B + A) as an indicator for sorption and (B) %(βAla + γAba) as an indicator for microbial degradation. Amazon compositions illustrated as in Fig. 3.

over others—this competitive sorption has been observed in numerous studies (e.g., Gu et al. 1996; Kaiser and Zech 1997).

Electrostatic mechanisms are a logical choice to explain the observed nitrogen and amino acid fractionation patterns. Most primary amines and many nitrogenous functional groups, including the side chains of basic amino acids, have a net positive charge at pH $<$ 8 (histidine is an exception, with pK_A = 6.0 for the side chain). Aluminosilicate clay minerals, including kaolinite and smectite, have a net negative surface charge at natural pH. For small molecules ($<$200 Da), electrostatic attractions and repulsions are well known to produce patterns of selective sorption similar to those found here (Dashman and Stotzky 1982; Henrichs and Sugai 1993; Wang and Lee 1993). In nature, however, the fact that most OM is sorbed as macromolecules adds a level of complication in using these electrostatic arguments to explain the enrichment of certain amino acids over others. From a geochemical perspective, bulk amino acid compositions of OM are rather uniform, with only subtle variability from source to source and sample to sample (Cowie and Hedges 1992*b;* Keil et al. 2000). However, individual proteins within organisms are well known to exhibit much larger ranges in the compositions of constituent amino acids (National Center for Biotechnology Information, http://www.ncbi.nlm.nih.gov/). That polypeptides might sort themselves during sorption, based on the cumulative effects of differences in side-chain abundances rather than from relatively minor differences in net macromolecular charge (Henrichs 1995), is not only plausible but is also consistent with results from polymer gel physics (van de Weerd et al. 1999).

If electrostatic interactions do indeed control the fractionation pattern of amino acids, then one might expect very different amino acid distributions in organic matter sorbed to minerals exhibiting a positive net surface charge. Two previous studies show this to be the case. Carter (1978) conducted OM sorption experiments similar to those presented here in which he found substantial enrichment of acidic amino acids on positively charged carbonate minerals—patterns that matched those in natural marine carbonate sands (Carter and Mitterer 1978). On the other hand, he found that sorption of the same DOM to quartz sand resulted in relative depletion of acidic amino acids accompanied by strong enrichment of basic amino acids, similar to our results with aluminosilicates. McKnight et al. (1992) studied sorption in situ at the confluence of a blackwater stream with a stream dominated by hydrous iron and aluminum oxide precipitates. Among other findings, metal oxide minerals below the confluence sorbed OM that was enriched in total organic nitrogen, in total amino acids and notably in acidic amino acids relative to the DOM of the blackwater stream. Thus, electrostatic mechanisms do appear to drive fractionation of polypeptides based on subtle differences in amino acid composition. Furthermore, the range of functional group types (basics, acidics, hydrophobics, etc.) available for peptide binding can explain why nitrogen in general and proteinaceous material in particular appear to be preferentially sorbed to diverse mineral types exhibiting either positive or negative net surface charge.

Another striking observation from these experiments was that the total amount of OM sorbed (Fig. 2), and the fractionation of that OM (Figs. 4, 5, 6A), seemed to be a function of the freshness of the initial DOM. Experiments 1–9 used initial DOM of increasing freshness with respect to previous exposure to mineral surfaces and with respect to bacterial degradation. There are thus two families of possible explanations for the observed trends.

Considering that DOM fractionates during sorption, it is clear that successive interactions with minerals will leave a ''parcel'' of DOM more and more depleted in its surface-active components. For each interaction with minerals, bulk DOM should exhibit decreasing average partition coefficients, K_d. Thus, on average, the DOM that is freshest with respect to previous contact with mineral surfaces should sorb most. Given the results of this study with aluminosilicate minerals, the most surface-active DOM components (highest K_d) are likely those exhibiting lower C : N ratios, higher amino acid contents, and greater proportions of basic and hydrophobic functional groups. Whether sorption in other systems would result in the observed patterns seen here depends

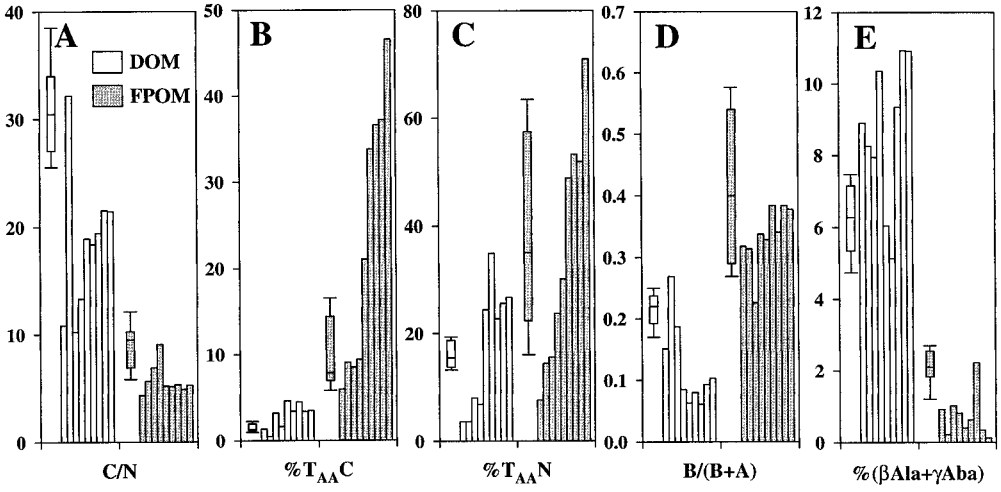

Fig. 7. Final composition of DOM and FPOM for the nine sorption experiments in this study, as shown by (A) molar carbon to nitrogen ratio, (B) %T_{AA}C, (C) percent total nitrogen as amino acids, (D) ratio of basic to basic plus acidic amino acids, and (E) sum of mol%, βAla, and γAba. Initial DOM values are used in lieu of final values for experiment 7. Amazon compositions illustrated as in Fig. 3.

largely on the solid : solution ratio. Systems with excess surface relative to DOM (such as highly erosive streams or soil B horizons) might exhibit the highest fractionation at lower surface loadings. Increased sorption would deplete the pool of available high-K_d compounds, and sorption of DOM components with more average compositions would mask the initial fractionation. The fact that most minerals also show surface-site heterogeneity (Mayer 1999) would enhance these effects as the ''best'' sites fill first. The residual DOM in those systems with excess surface area would tend to show strong patterns of depletion of surface-active components. Conversely, in systems where DOM is in relative excess to available surfaces (such as these experiments, wetlands, or organic-rich soil horizons), the pool of high-K_d compounds might not be measurably depleted, even at the highest surface coverages. Thus, biochemical fractionation in surface-limited systems would be most apparent on minerals, whereas fractionation of residual DOM might be undetectable. Likewise, DOM with little history of mineral contact will yield sorbed FPOM with a strong fractionation signature, whereas DOM with an extensive history of previous mineral interactions will sorb FPOM that has a less distinct fractionation signature.

These ideas have been codified by van de Weerd et al. (1999), who have developed a set of competitive Langmuir-type equations to explicitly address the kinetics and thermodynamics of interacting species within a heterogeneous DOM mixture. Their application of this model to the experimental data of Gu et al. (1994) shows excellent agreement with measured sorption and desorption behavior of bulk OM. The ability of this treatment to simulate all the data without changing model parameters, including desorption hystereses, supports the concept of cumulative sorptive fractionation. Modeled fractionation increases with increasing surface loading, just as was observed in our experiments, and evolves with increased interaction time. Although those authors used polymer gel theory to independently estimate most model parameters, the concept of increasing fractionation with increasing surface loading is valid for any suite of reversible association mechanisms in a surface-limited system.

The second family of mechanistic explanations stems from the observation that the sequence of experiments 1–9 also corresponds to a likely history of decreasing diagenesis and increasing bioavailability of the initial DOM. In general, hydrolyzable amino acids are preferentially used by bacteria and become depleted relative to bulk OM during diagenesis (Cowie and Hedges 1992*b;* Wakeham et al. 1997). Evidence is also accumulating in support of the size-reactivity-continuum model of Amon and Benner (1996), which suggests that the size of remnant DOM will decrease with degradation (Burdige and Gardner 1998). Both of these trends could result in decreasing average surface affinity of DOM with advancing degradation regardless of mineral type (Davis and Gloor 1981; McKnight et al. 1992; van de Weerd et al. 1999), without requiring prior sorption of high K_d components. However, increasing degradation will also tend to increase in OM the relative abundance of carboxyl and hydroxyl groups (Sun et al. 1997), which are known to be important in the complexation of OM onto positively charged minerals (McKnight et al. 1992; Gu et al. 1995; Kaiser et al. 1997). How these opposing diagenetic trends might combine to enhance or reduce sorption for various mineral types is open to speculation. It is worth noting that the surface loadings obtained in these experiments matched closely those observed along the continuum of increasing oxygen exposure time in marine systems (Hedges et al. 1999). Sorption of river and wetland DOM occurred within the 0.1–0.5 mg OC m^{-2} range that is observed in deep sea and deltaic sediments (Hedges and Keil 1995; Keil et al. 1997). Diluted leachates sorbed within the range of 0.5–1.1 mg OC m^{-2} that is typical of coastal margin sediments. Undiluted leachates sorbed at higher levels, within the range of 1.5–3.0 mg OC m^{-2} commonly found in sediments under

anoxic bottom waters (Hedges and Keil 1995). A question that certainly deserves to be tested is whether degradation alone can substantially change the K_d distribution in DOM.

Another possible explanation for observed increases in fractionation with increasing freshness is that microorganisms might mediate these sorptive patterns indirectly through growth on the minerals. Given typical bacterial abundances ($<10^7$ ml^{-1}) (Benner et al. 1995) and typical bacterial amino acid compositions (Cowie and Hedges 1992*b*), it is unlikely that microbial biomass alone could account for observed concentrations of C, N, and amino acids in these experiments. However, even where bacterial biomass contributes insignificantly to total OC, the cumulative remains of bacterial cell walls and exopolymers might be quantitatively important (Oades 1989). Our batch sorption incubations lasted 24 h at 20°–32°C, which allowed numerous generations of microbial colonies to leave behind their biofilms and necromass. Given crudely estimated respiration losses of 15%–60% of sorbed carbon and possible growth efficiencies of 10%–50% (Amon and Benner 1996), microbial residues could account for as little as 1.5% or as much as 30% of FPOM analyzed in these experiments. Regardless, the quantity of material produced should be a function of growth rate, growth efficiency, and, thus, the bioavailability of the DOM substrate. That this experiment was conducted with living microbial assemblages distinguishes it from otherwise similar studies (Day et al. 1994; Gu et al. 1995; Filius et al. 2000). It is thus interesting to note that these same studies all find sorptive loadings below 0.4 mg OC m^{-2} SA, despite the use of highly surface-active goethite. Could the much greater surface loadings observed here on kaolinite and natural mineral assemblages be due to microbial remains? One count against this argument is the moderate enrichment of glycine in the DOM of natural waters (experiments 1–4) and alanine in leachates (experiments 5–9) relative to FPOM in those experiments (Fig. 5). Both amino acids are generally highly enriched in peptidoglycan of bacterial cell walls (Keil et al. 2000), which suggests that DOM might contain the larger fraction of bacterial necromass. However, little is known regarding the amino acid composition of bacterial biofilms, and it is conceivable that bacteria could employ peptide adhesives with compositions dominated by surface-active basic and hydrophobic amino acids.

Nonprotein amino acids—In addition to reproducing natural patterns of nitrogen, total amino acid, and basic amino acid enrichment on particles, these sorption experiments also generated the lower mol% NPAA that is typical of riverine FPOM relative to DOM (Figs. 5–7). This result was not entirely expected. Because NPAA are thought to be products of bacterial alteration (Lee and Cronin 1982), the observed pattern in rivers had been interpreted as evidence that DOM was significantly more degraded than FPOM. In studies of sedimentary organic matter, the parameter %(βAla + γAba) is a clear indicator of diagenetic alteration (Cowie and Hedges 1994; Dauwe et al. 1999). In contrast, our partitioning experiments clearly demonstrate that peptides containing NPAA have very low surface affinity and are thus preferentially retained in solution.

A plausible explanation for this result is that NPAA are likely to reside in degraded peptides that are considerably smaller than peptides without NPAA. Because β-alanine and γ-aminobutyric acid are produced by decarboxylation of the peptide-forming carboxyl group of aspartic acid and glutamic acid, respectively, they must exist on the C terminus of peptide cleavage products or as free amino acids (Keil et al. 2000). These ideas are supported by findings in sedimentary pore waters of substantially higher contributions of NPAA to the dissolved free amino acid pool relative to total (free and combined) dissolved amino acids (Burdige and Martens 1990; Lomstein et al. 1998). Our study, in which whole-water DOM was analyzed, evidenced higher NPAA concentrations than studies of similar rivers in which only high-molecular-weight (>1000 Da) DOM was analyzed (Hedges et al. 1994, 2000). If NPAA are indeed predominantly in smaller peptides, they could easily be out-competed for surface sites by larger molecules with greater numbers of surface-active functional groups (Henrichs 1995). Furthermore, the observation that experimentally sorbed FPOM contained fewer NPAA than is typical of riverine and marine sediments (Hedges et al. 1994, 2000; Keil et al. 2000) suggests that the accumulation of sedimentary NPAA may require degradation of peptides that are already associated with minerals. Regardless of mechanism, NPAA can no longer be interpreted solely as a diagenetic parameter when comparing between dissolved and particulate phases.

Implications for interpreting OM compositional patterns—The results of this study, especially those for NPAA, imply that sorption could be responsible for other compositional signatures that might otherwise be attributed to diagenetic processes or varying source. An example of a diagenetic parameter exhibiting sensitivity to sorptive fractionation is the amino acid degradation index of Dauwe et al. (1999). Although being developed from (and for) diagenetic sequences in marine sediments, it might be tempting to apply the index to infer differences in diagenetic history between DOM and FPOM samples. The wide separation of index values between DOM and FPOM samples in these experiments (Fig. 8) clearly demonstrates the complications that sorptive processes introduce to comparisons between dissolved and particulate organic matter. For each sorption experiment, organic matter in the final dissolved and particulate fractions both have essentially the same age and gross diagenetic history, yet DOM fractions consistently give lower index values, which suggests that they are more degraded. Interestingly enough, the index does seem appropriate for distinguishing differences between FPOM samples. Natural river FPOM has lower values indicative of more degraded material, sorbed riverine and wetland DOM have intermediate values, and sorbed leachates give the highest values (Fig. 8)—which suggests increasing freshness, as one would expect. One might thus argue that, for these experiments, the Dauwe index reflects increasing average partition coefficients for a sample.

These observations highlight a number of important questions regarding linkages between the roles of sorption and degradation in determining OM compositions. As was previously discussed, more degraded (smaller, N-poor) molecules should exhibit lower surface affinity relative to fresher

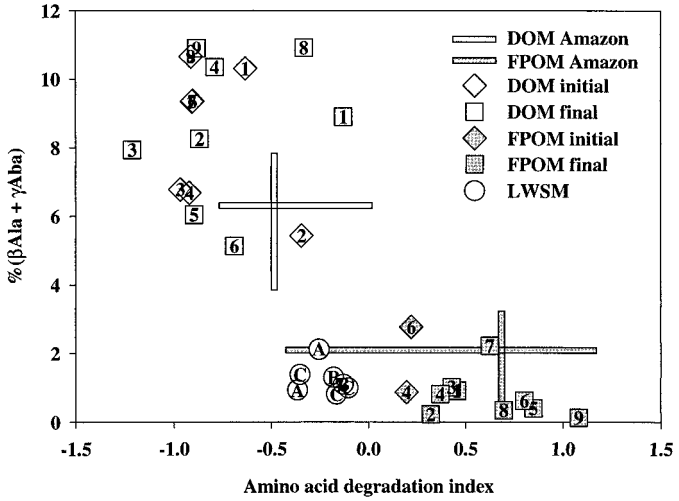

Fig. 8. Dauwe et al. (1999) degradation index for samples used (or produced in) our mixing experiments. Crosses represent the median and range of values from rivers in the Amazon Basin. Replicate analyses of Lake Washington Standard Mud (LWSM) demonstrates potential analytical variability in these indices, with letters distinguishing different analysts. Values inside other symbols represent mixing experiment number.

(larger, N-rich) OM. If this is so, sorptive fractionation cannot be viewed independently from diagenetic OM alteration. Separating the effects of these two processes may prove to be quite difficult. In natural systems, does sorption serve primarily to separate more degraded OM from less degraded OM, or does sorption serve primarily as a means of protecting mineral-associated molecules from degradation? The answer will likely depend on environmental conditions and may change over short temporal and spatial scales. In addition to sorption's role in determining nitrogen and amino acid compositional patterns, the possibility exists that some of the other commonly used OM diagenetic or source parameters might also be affected by sorptive fractionation. For instance, Guggenberger et al. (1994) found distinct lignin and carbohydrate compositions in the hydrophilic acid fraction of soil DOM relative to the much more easily sorbed hydrophobic fractions or soil horizons. Comparisons of clay-bound soil OM versus soil DOM support the possibility that these compound classes may also fractionate during sorption (Kaiser and Guggenberger 2000). Overall, diagenetic processes can no longer be considered alone when interpreting OM compositions between dissolved and particulate phases. It is clearly important to first understand sorptive fractionation patterns within a biochemical class prior to interpreting compositional differences between its dissolved and particulate fractions.

Where in a river basin does sorptive fractionation occur?—The specific goal of this study has been to examine whether sorption can explain the compositional patterns of co-occurring DOM and FPOM within rivers of the Amazon. Although tested in the context of sediments suspended within a river, it is likely that sorptive signatures are imprinted anywhere that ''fresh,'' surface-active DOM contacts mineral surfaces. Therefore, surface soil horizons are likely to be important for initial imprinting, followed by confluences of sediment-rich streams with ''blackwaters.'' However, rivers are active systems with continuous inputs, degradation, and exchange. That >60% of FPOM in the lower Amazon is derived from lowlands (on the basis of stable isotope mass balance) (Hedges et al. 2000), despite ~85% of associated minerals originating in the Andes (Gibbs 1967), is a strong indication that mineral-associated OM actively repartitions on timescales less than its transit time to the sea. Continuous re-equilibration of riverine sediments with surface-active DOM components thus likely occurs over the entire length of the river corridor.

The present study has demonstrated that all the published organic nitrogen compositional patterns of the Amazon Basin can be recreated in a beaker by sorbing natural dissolved organic matter to aluminosilicate mineral surfaces under natural conditions. Furthermore, because nitrogen and amino-acid–rich OM is preferentially sorbed, the availability of mineral surfaces provides ecosystems with a mechanism for retaining fresher, more reactive organic matter. Additional studies are under way to investigate the relative importance of abiotic, physicochemical mechanisms versus microbially mediated processes in determining these compositional patterns. Regardless of mechanism, the process of associating organic molecules with mineral surfaces is clearly of prime importance in determining the compositions of DOM and FPOM in river basins.

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