

Water-soluble organic nitrogen in Amazon Basin aerosols during the dry (biomass burning) and wet seasons

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[1] As part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA), PM₁₀ aerosol was collected during both the wet and dry (biomass burning) seasons of 1999 and analyzed for total water-soluble organic nitrogen (WSON), urea, and 17 amino acids. In addition to total WSON the inorganic N species nitrate (NO₃⁻), nitrite (NO₂⁻), and ammonium (NH₄⁺) were also analyzed. WSON was found to represent ~45% (mean concentration ~3.5 nmol N/m³) and ~43% (mean concentration ~61 nmol N/m³) of the total N in wet and dry season aerosol samples, respectively. Urea and amino N made up ~19% of the total organic N in dry season aerosols and ~2.5% of the total organic N in wet season aerosols; the majority of WSON, ~80% in the dry season and ~97% in the wet season, remained uncharacterized. The results suggest that biomass burning is a source of WSON, yet poorly understood (since this data set represents the first study of WSON in the context of biomass burning). Future studies aimed at determining the magnitude of WSON released from biomass burning globally, its species composition, and its biogeochemical significance are needed. *INDEX TERMS*: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1615 Global Change: Biogeochemical processes (4805); *KEYWORDS*: nitrogen cycling, biomass burning, organic nitrogen

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1. Introduction

[2] The Amazon basin contains the world's largest tropical rain forest, spanning ~4 million km² [Artaxo and Hansson, 1995, and references therein]. Tropical forests contain the largest amount of carbon in vegetation for all biome types worldwide (~40% of total biomass [Houghton and Skole, 1990]). When burned, these forests release large quantities of particles and gases to the atmosphere that absorb and reflect solar radiation and that contribute to the greenhouse effect [Andreae, 1991; Crutzen and Andreae, 1990]. Due to strong convection within the tropical region, entrained particles and gases released through biomass burning may be transported great distances from their origin [Andreae et al., 2001] causing changes in

air quality, climate (through strong aerosol radiative forcing and changes in cloud properties), and the redistribution of nutrients [Graham et al., 2002; Artaxo et al., 2001].

[3] In the Amazon Basin there are two main seasons: a wet season, typically lasting from November to June; and a dry season, lasting from July through October [Artaxo et al., 1998; Andreae et al., 2002]. During the wet season, the atmosphere is characterized by very low concentrations of aerosol particles and gases. CCN (cloud condensation nuclei) and CN (condensation nuclei) concentrations are ~300 cm⁻³ (at 1% supersaturation) and ~400 cm⁻³, respectively [Roberts et al., 2001]. These number concentrations are typical of a background marine atmosphere, and reflect an atmosphere dominated by natural biogenic aerosol and precipitation rates that effectively remove aerosol particles [Roberts et al., 2001; Artaxo, 2001]. Also, the cloud structure and precipitation regime during the wet season resembles marine conditions, instead of continental ones [Roberts et al., 2001, 2002]. In the dry season, biomass burning emissions dominate, leading to an atmosphere characterized by very high concentrations of aerosols and gases that significantly change the cloud structure and the composition of the atmosphere.

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[4] Due to the quantity of aerosols and gases released from biomass burning and the quantity of organic matter produced [Simoneit, 2002; Graham *et al.*, 2002; Mayol-Bracero *et al.*, 2002], a number of studies have investigated possible organic compounds released from biomass burning. A suite of organic compounds often represent a large component of the total aerosol mass in biomass burning plumes within tropical regions [Kubátová *et al.*, 2000; Yamasoe *et al.*, 2000; Andreae and Merlet, 2001]. Solvent extractable organic compounds have been discovered in biomass burning aerosols and include many *n*-alkanes, *n*-alkenes, *n*-alkanoic acids, *n*-alkanols, triacylglycerides, and polycyclic aromatic hydrocarbons (PAH's) [Simoneit, 2002, and references therein; Fang *et al.*, 1999]. While organic extractable compounds have received the most attention, water-soluble organic compounds released during biomass burning have received less attention. However, Graham *et al.* [2002] and Mayol-Bracero *et al.* [2002] have recently reported the presence of a large number of water-soluble organics produced during biomass burning in Amazonia, including sugars (e.g., mannitol, arabinol, erythritol, glucose, fructose, mannose, sucrose - produced by hemicellulose breakdown), di-/tricarboxylic acids (e.g., malonic acid, maleic acid, succinic acid), oxo-/hydroxyacids (e.g., pyruvic acid, lactic acid), and aromatics (e.g., vanillin, phthalic acid).

[5] To date, water-soluble organic nitrogenous compounds have not been investigated from biomass burning emissions. As previously documented, the WSON component may represent a considerable proportion of the total water-soluble nitrogen in precipitation and in atmospheric aerosols [Cornell *et al.*, 1995, 2001; Mace *et al.*, 2003]. Due to the ability of biomass burning aerosols to be transported in the atmosphere long distances from their source [Andreae *et al.*, 2001; Dibb *et al.*, 1996; Simoneit and Elias, 2000; Singh *et al.*, 2000; Simoneit, 2002], and the nitrogen limitation of many ecosystems worldwide [Vitousek and Howarth, 1991; Vitousek, 1994; Schlesinger, 1997, and references therein; Paerl *et al.*, 2000; Vitousek *et al.*, 2002], the atmospheric deposition of nitrogenous compounds released from biomass burning plumes may have implications for ecosystems not directly affected by the act of biomass burning and/or slash and burn agriculture. Crutzen and Andreae [1990] estimate the release of 15–46 Tg N yr⁻¹ from all types of biomass fires - shifting agriculture, deforestation, savanna fires, firewood, and agricultural wastes - in the tropics. However, WSON has not been included in these estimates, and presently there is little information regarding any water-soluble organic N compounds released from biomass burning.

[6] In order to better understand the amount and speciation of water-soluble organic N compounds released from tropical biomass burning, dry and wet season aerosols were collected in a pasture site located in the state of Rondônia, Brazil, during September–October (dry season) and March–May (wet season) 1999. Aerosol collections for the WSON study were done in parallel with measurements for carbon species and other atmospheric measurements obtained as part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA) research effort. For the organic N study presented, inorganic nitrogen (N) species, nitrate (NO₃⁻), nitrite (NO₂⁻), and ammonium (NH₄⁺), were analyzed as well as total WSON. The organic N proportion

is defined in this manuscript as total N from NO₃⁻, NO₂⁻, and NH₄⁺ following a UV digestion procedure minus the same inorganic N ions determined prior to the UV digestion procedure. Several water-soluble organic N compounds potentially contributing to the WSON fraction were also analyzed including urea, aspartic acid, glutamic acid, serine, threonine, glycine, alanine, arginine, proline, valine, methionine, isoleucine, leucine, phenylalanine, cystine, lysine, histidine, and tyrosine. In this manuscript the N contained in the total WSON fraction is often referred to as “organic N,” the N contained in urea is referred to as “urea N,” and the nitrogen contained in the amino acids analyzed is referred to as “amino N.”

2. Sample Collection and Analysis

2.1. Sample Collection

[7] Aerosol samples were collected in the state of Rondônia, near the city of Ji-Parana (county of “Ouro Preto do Oeste”), in a pasture environment known as “Fazenda Nossa Senhora Aparecida” (10°45'44"S, 62°21'27"W) (Figure 1). Rondônia, Brazil, is a region of the Amazon where extensive deforestation has occurred in recent years. Wet season samples, representing natural biogenic emissions, were collected from March to May 1999. Dry season samples, heavily impacted by biomass burning emissions, were collected from September to October 1999. Samples were collected on precombusted (~6 hours at 450°C in a muffle furnace) 47 mm quartz filters using a PM₁₀ inlet sampler, sampling at a rate of ~50 m³ of air per hour during the wet season and ~5 m³ of air per hour during the dry season. Slower flow rates were utilized during the dry (biomass burning) season due to high PM₁₀ concentrations. Quartz fiber filters were utilized during field collections because (1) they have less organic binding material than glass fiber filters, (2) they can be precleaned to remove organics, and (3) because they are easier to use than special denuders in the middle of the Amazonian rain forest. Special care was taken to guarantee minimal contamination of filter blanks. Precombusted filters were treated identically to actual samples, with the exception of turning on the vacuum pumps. Blanks were stored on precleaned filter packs at the same place and for the same amount of time as “real” aerosol samples.

2.2. Sample Analysis

[8] Inorganic ions were measured using a Dionex (Sunnyvale, CA, USA) DX 300 ion chromatograph equipped with a Rheodyne (Cotati, California, USA) 9126 rear-loading valve and Dionex AI450 chromatography software. Cations were analyzed with a Dionex CS12A cation exchange column guarded with a CG12A guard column. A solution of methanesulfonic acid (MSA) served as the eluent. Anions were analyzed with a Dionex AS12A anion exchange column guarded with an AG12A guard column. A solution of sodium bicarbonate and sodium carbonate served as the eluent. Both cation and anion analyses were performed according to column specifications in eluent recycle mode with an appropriate self-regenerating suppressor. The error for all the ion analyses was <6%, as indicated by 2 sets of standards cross referenced to the National Institute of Standards and Technology (NIST), USA.



Figure 1. Map of the sampling region. Samples were collected in the Amazon Basin, in the state of Rondônia, within the region indicated in the circle on the map.

[9] For the total N analysis, aerosol extracts were diluted to an appropriate concentration for inorganic N ions and exposed to UV light in a Metrohm Inc. (Switzerland) 705 UV digester, for 2 hours at a temperature of 85°C [Mace and Duce, 2002a]. Following UV exposure, samples were again analyzed for the inorganic N ions – NO_3^- , NO_2^- , and NH_4^+ . As mentioned previously, organic N is defined as total N minus inorganic N. UV blanks for aerosols ranged from 0 to 9 μM N, representing $\sim 7\%$ of the total N for aerosols collected during the dry season, and $\sim 20\%$ of the total N for aerosols collected during the wet season. All data presented have been corrected for these blanks. Sometimes organic N concentrations were found to be negative after blanks were subtracted from organic N totals. When negative organic N concentrations occur in the data set, organic N has been designated as “below detection” and included in mean calculations as zero.

[10] Urea was analyzed using a new ion chromatography method developed in the laboratory at Texas A&M University [Mace and Duce, 2002b]. The method utilizes a Dionex CS12 cation exchange column, a CG12 guard column, an eluent consisting of 20 mM of methanesulfonic acid (MSA), and UV detection at 190 nm. A UV/Vis spectrophotometer

(a part of the DX 300 ion chromatograph) provided the means for quantitative determination. For the analysis, filtered aerosol extracts were injected onto the column without further preparation. A liquid urea standard purchased from Sigma (St. Louis, Missouri, USA, product 535-30) was utilized for the quantitative determination of urea within samples.

[11] Amino acids were analyzed using a modified 4-dimethylaminoazobenzene-4'-sulfonyl chloride (DABS-Cl) method [Stocchi *et al.*, 1992]. Prior to analysis 10 ml of filtered sample were dried in a Savant speed-vac concentrator (Thermo Savant, Holbrook, New York, USA) and derivitized with DABS-Cl. A LC-DABS 15 cm \times 4.6 mm, 3 μm particle column, guarded with a LC-18-T guard column (Supelco, Bellefonte, Pennsylvania, USA), and a gradient of chromatography grade acetonitrile:methanol and a pH-neutral 25 mM potassium phosphate dibasic solution provided the means for amino acid separation. The DX 300 ion chromatograph, fitted with a Teflon switching valve and set to record absorbance at 436 nm using the UV/Vis detector, was a suitable system for this analysis. A liquid amino acid standard purchased from Sigma (product AA-S-18), containing the 17 amino acids

listed in the introduction, was utilized for quantitative determinations of amino acids within samples.

3. Results and Discussion

[12] Organic N was found to represent $\sim 45\%$ (mean concentration $\sim 3.5 \text{ nmol N m}^{-3}$) and $\sim 43\%$ (mean concentration $\sim 61 \text{ nmol N m}^{-3}$) of the total N in wet and dry season aerosol samples, respectively (Table 1). Urea N was found to represent $\sim 1\%$ (mean concentration $\sim 0.03 \text{ nmol N m}^{-3}$) of the organic N in wet season aerosols, but was found to contribute $\sim 18\%$ (mean concentration $\sim 6 \text{ nmol N m}^{-3}$) of the organic N during the dry season (Table 1). Amino N was found to contribute $\sim 1\%$ of the organic N during the dry season, and $\sim 2\%$ of the organic N during the wet season (Table 1).

[13] Measurements for other parameters were also made for samples collected simultaneously during the wet and dry seasons - including NO_2 concentrations (ppbv), condensation nuclei (CN/cc) concentrations, and black (also known as elemental carbon) carbon, organic carbon, and total carbon concentrations. In Figure 2 the concentrations for N species as well as concentrations for aerosol black and organic carbon that were collected during the same interval as organic N aerosol samples (samples were collected for 24 to 48 hours) during the wet season are presented. As can be seen in Figure 2, total aerosol N concentrations (the sum of NO_2^- , NO_3^- , NH_4^+ , and organic N) were typically below 15 nmol N m^{-3} during the wet season sampling interval. As previously stated, CN concentrations are extremely low during the wet season. Artaxo *et al.* [2002] reported an average concentration of $\sim 250 \text{ ng}$ of black carbon m^{-3} , for the 1999 wet season in Rondônia (the season of aerosol collection for our samples). These low concentrations of black carbon reflect a clean atmosphere, with little influence from pollution sources. In Rondonia, wood burning is used for home cooking all year round, and within a few tens of kilometers from the sampling site, some small-scale wood processing activities takes place. However, the concentrations obtained for organic N during the wet season are similar to those obtained for the clean marine atmosphere [Mace *et al.*, 2003].

[14] In Figure 3, concentrations of N species as well as the concentrations of black carbon and organic carbon determined simultaneously during the dry season are presented. As seen in Figure 3, black carbon concentrations were extremely high during the dry season sampling interval as a result of biomass burning in Amazonia. The mean concentration of black carbon was $\sim 7.6 \mu\text{g m}^{-3}$ during the interval of organic N aerosol collections. Black carbon and total aerosol N concentrations were ~ 30 and ~ 16 times higher, respectively, during the dry season compared to the wet season.

[15] In Figure 4, linear (and nonlinear) comparisons for the organic N, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ and black carbon con-

centrations shown in Figures 2 and 3 are presented. While $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations exhibited statistically significant ($P < 0.05$ at a level of $\alpha = 0.05$) relationships to black carbon during the dry season, organic N concentrations did not. However, organic N concentrations did exhibit a statistically significant inverse relationship to black carbon during the wet season. Since mean organic N concentrations were ~ 20 times higher during the dry season as compared to the wet season, it is evident that biomass burning is a source for organic N in aerosols. However, the lack of a statistically significant correlation between organic N and black carbon suggests that the organic N compounds produced as a result of biomass burning undergo complex cycling in the atmosphere (e.g., gas-to-particle conversions). As indicated in the introduction, a large number of organic compounds are emitted during biomass burning. These compounds may be found in the gas phase [Simoneit, 2002; Andreae and Merlet, 2001] and/or in aerosol [Fang *et al.*, 1999; Kubátová *et al.*, 2000; Zdehal *et al.*, 2001; Graham *et al.*, 2002; Simoneit, 2002]. Since there was no statistically significant relationship for organic N under biomass burning conditions, the water-soluble organic N compounds composing the organic N fraction may be (1) directly emitted as gases from biomass burning, (2) formed in the atmosphere through reactions of volatile organic compounds (VOCs) and NO_x [Atkinson, 2000; Roberts, 1990], and/or (3) undergo gas-to-particle conversion in the atmosphere. Several of these possibilities likely exist for organic N. Additional study, such as a size-separated aerosol study conducted during periods of biomass burning, would add insight regarding the nature of WSON. Chemical analyses of carbon and nitrogen within size-separated aerosols would help us to better understand whether the majority of organic carbon and organic nitrogen is associated with coarse or fine mode aerosols. Such a study may point to gas phase reactions (fine mode) for most of the organic carbon and nitrogen, or to unburned biomass (coarse mode particles). If such a study were combined with stable isotopic analyses, further information regarding carbon and nitrogen sources may also be gleaned.

[16] The inverse correlation between black carbon (elemental carbon) and organic N concentrations during the wet season likely indicates that under natural (background) conditions the forest releases organic N compounds, since black carbon during the wet season would reflect small scale biomass burning emissions and air masses not totally dominated by the surrounding forest. Vegetation naturally releases a number of biogenic gases and aerosols. A size-separated aerosol study would also aid the interpretation for organic N concentrations under wet season (natural background) conditions. With size-separated aerosol data it would be possible to determine whether gas-to-particle conversion of naturally produced water-soluble organics represents a large or a small proportion of the total water-soluble N measured during the wet season.

Notes To Table 1

^aConcentrations are displayed as nmol N m^{-3} for all species. Percentages of total N and organic N are shown in parentheses. Dashes represent no analysis for samples or comparisons that are not relevant. Here b.d. indicates samples that are below detection for NO_2^- , NH_4^+ , and urea N. For organic N samples, b.d. indicates samples that were negative after the consideration of blanks. Below detection values have been included in the calculation of the average, by the designation "0." Due to the uncertainty surrounding organic N values below $1 \mu\text{M}$ in solutions, concentrations of urea and amino N are sometimes found in samples when organic N is not. When this occurs, percent values for urea N and amino N of organic N have been excluded from mean and standard deviation calculations.

Table 1. Concentrations of N Species Determined During the Aerosol Sampling at Rondônia^a

Sample	Collection Date	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	Organic N	% Total N	Urea N	% Organic N	Amino N	% Organic N
<i>Dry Season Aerosols</i>										
1	9/13/99	b.d.	21	2.8	3.6	(13)	—	—	0.048	(2.3)
2	9/15–16/99	b.d.	19	1.1	5.4	(20)	—	—	0.015	(0.28)
3	9/21–22/99	b.d.	13	b.d.	b.d.	(0)	—	—	0.25	—
4	9/22–23/99	1.0	35	2.6	53	(58)	15	(28)	—	—
5	9/23–24/99	b.d.	2.0	15	100	(81)	—	—	0.11	(0.11)
6	9/25–26/99	b.d.	11	0.56	2.5	(18)	—	—	0.033	(1.3)
7	9/26–27/99	b.d.	7.7	0.07	b.d.	(0)	—	—	0.040	—
8	9/28–29/99	0.15	12	b.d.	64	(84)	1.7	(2.7)	—	—
9	9/30–10/01/99	0.66	28	3.7	56	(64)	3.4	(6.1)	—	—
10	10/1–2/99	0.67	17	1.7	b.d.	(0)	1.8	—	—	—
11	10/2–3/99	3.9	20	0.65	2.1	(8.0)	—	—	0.33	(16)
12	10/3–4/99	0.14	26	2.1	21	(42)	—	—	0.041	(0.20)
13	10/4–5/99	0.21	49	1.6	69	(57)	—	—	0.015	(0.02)
14	10/5–6/99	b.d.	96	59	30	(17)	15	(50)	—	—
15	10/6–7/99	24	33	28	13	(13)	—	—	0.033	(0.25)
16	10/7–8/99	b.d.	122	52	61	(26)	18	(30)	0.87	(1.4)
17	10/8–9/99	b.d.	61	19	24	(23)	—	—	0.017	(0.07)
18	10/9–10/99	1.2	110	36	79	(35)	—	—	—	—
19	10/10–11/99	2.0	94	3.2	280	(74)	—	—	—	—
20	10/13–14/99	9.4	27	0.63	93	(71)	—	—	—	—
21	10/14/99	1.8	52	3.9	54	(49)	7.6	(14)	—	—
22	10/14–15/99	2.1	31	0.96	120	(77)	2.0	(1.7)	—	—
23	10/15/99	0.28	50	1.3	96	(66)	11	(12)	1.7	(1.8)
24	10/15–16/99	1.8	26	0.49	160	(87)	1.6	(1)	—	—
25	10/16/99	b.d.	31	0.11	3.4	(9.8)	—	—	0.0078	(2.3)
26	10/16–17/99	2.8	27	1.6	69	(69)	4.3	(6.2)	—	—
27	10/17/99	0.49	41	2.9	72	(62)	8.0	(11)	0.019	(0.026)
28	10/17–18/99	2.5	18	1.3	5.0	(18)	3.8	(76)	—	—
29	10/19/99	1.3	44	4.5	110	(69)	49	(4.5)	0.20	(0.18)
30	10/19–20/99	2.0	31	3.6	202	(85)	b.d. ^a	(0)	—	—
31	10/20/99	0.71	58	b.d.	220	(81)	—	—	—	—
32	10/20–21/99	1.5	32	b.d.	b.d.	(0)	—	—	0.11	—
33	10/21–22/99	b.d.	18	1.1	2.9	(13)	—	—	—	—
34	10/22/99	0.81	45	0.33	82	(64)	6.6	(8.0)	—	—
35	10/23–24/99	0.34	21	1.1	31	(58)	1.0	(3.2)	—	—
36	10/24–25/99	b.d.	17	1.3	60	(76)	—	—	0.017	(0.028)
37	10/25–26/99	6.5	9.5	1.3	b.d.	(0)	—	—	0.045	—
Mean		1.8	37	6.9	61	(43)	6.2	(18)	0.21	(0.83)
Standard Deviation		4.2	28	14	67	(31)	5.5	(26)	0.41	(1.4)
<i>Wet Season Aerosols</i>										
1	3/7–8/99	b.d.	3.6	b.d.	5.5	(59)	b.d.	(0)	0.083	(1.5)
2	3/8–9/99	0.15	0.35	b.d.	5.3	(94)	b.d.	(0)	—	—
3	3/9–10/99	b.d.	0.53	1.7	b.d.	(0)	b.d.	(0)	0.34	—
4	3/10–11/99	b.d.	0.49	2.0	4.4	(63)	b.d.	(0)	—	—
5	3/11–12/99	b.d.	1.0	0.64	6.0	(79)	b.d.	(0)	—	—
6	3/20–21/99	b.d.	0.74	0.27	4.6	(82)	—	—	0.042	(0.91)
7	3/21–22/99	b.d.	0.20	b.d.	16	(99)	—	—	—	—
8	3/22–23/99	0.57	b.d.	0.19	1.2	(62)	—	—	0.019	(1.6)
9	3/23–24/99	4.5	0.35	b.d.	8.3	(63)	—	—	0.02	(0.24)
10	3/24–25/99	b.d.	1.1	b.d.	1.5	(59)	—	—	—	—
11	3/25–26/99	b.d.	1.1	b.d.	1.7	(61)	—	—	0.061	(3.6)
12	3/26–27/99	b.d.	0.010	b.d.	1.3	(99)	b.d.	(0)	—	—
13	3/27–28/99	b.d.	3.5	1.3	b.d.	(0)	b.d.	(0)	—	—
14	3/28–29/99	b.d.	1.8	0.044	0.22	(11)	b.d.	(0)	—	—
15	3/29–30/99	b.d.	18	0.03	b.d.	(0)	b.d.	(0)	0.12	—
16	3/30–4/2/99	b.d.	5.5	0.16	b.d.	(0)	b.d.	(0)	0.43	—
17	4/2–5/99	0.086	3.6	b.d.	2.8	(43)	b.d.	(0)	0.15	(5.4)
18	4/5–8/99	0.12	3.7	0.53	7.3	(63)	b.d.	(0)	0.083	(0.074)
19	4/8–11/99	0.20	3.2	b.d.	b.d.	(0)	—	—	0.020	—
20	4/14–17/99	0.13	2.0	b.d.	2.1	(57)	b.d.	(0)	—	—
21	4/17–20/99	b.d.	3.0	0.32	2.0	(37)	0.27	(14)	—	—
22	4/20–23/99	0.35	3.6	0.59	0.24	(5.1)	0.29	(100)	—	—
23	4/23–26/99	b.d.	3.0	b.d.	3.4	(53)	b.d.	(0)	0.007	(0.21)
24	4/26–30/99	b.d.	2.0	b.d.	b.d.	(0)	b.d.	(0)	0.092	—
25	5/6–9/99	0.53	2.2	0.85	3.3	(48)	b.d.	(0)	—	—
26	5/12–15/99	0.14	2.8	0.56	18	(84)	b.d.	(0)	—	—
27	5/15–18/99	0.33	3.4	0.80	b.d.	(0)	b.d.	(0)	—	—
Mean		0.26	2.6	0.37	3.5	(45)	0.028	(0.71)	0.11	(1.8)
Standard Deviation		0.86	3.4	0.55	4.6	(35)	0.086	(1.8)	(1.8)	(1.8)

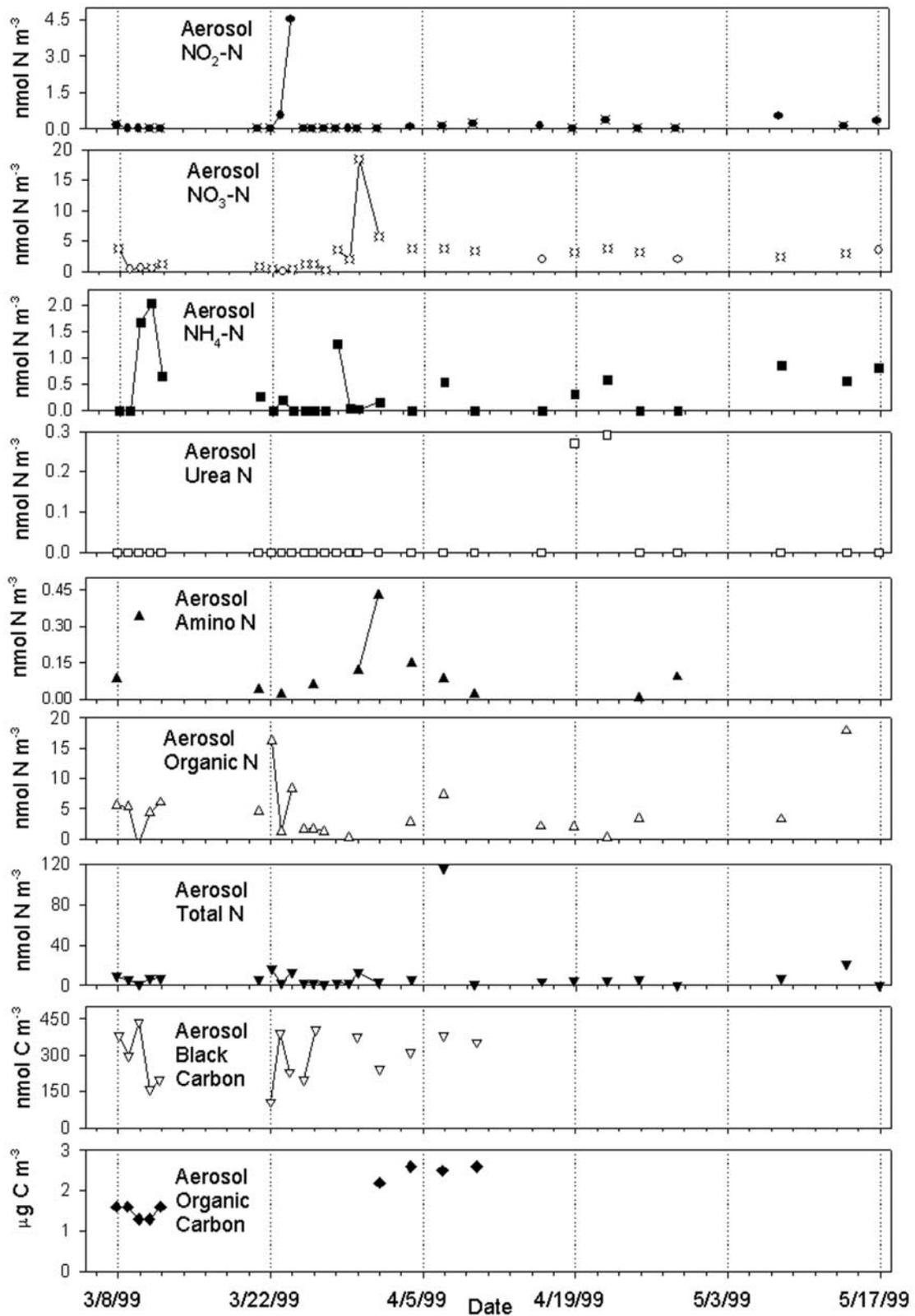


Figure 2. Concentrations of the water-soluble N species analyzed and carbon species data obtained during the wet season sampling interval. Water-soluble N species are presented in units of nmol N m^{-3} . Carbon species are presented as ng C m^{-3} . Individual data points represent samples collected for 24–48 hours.

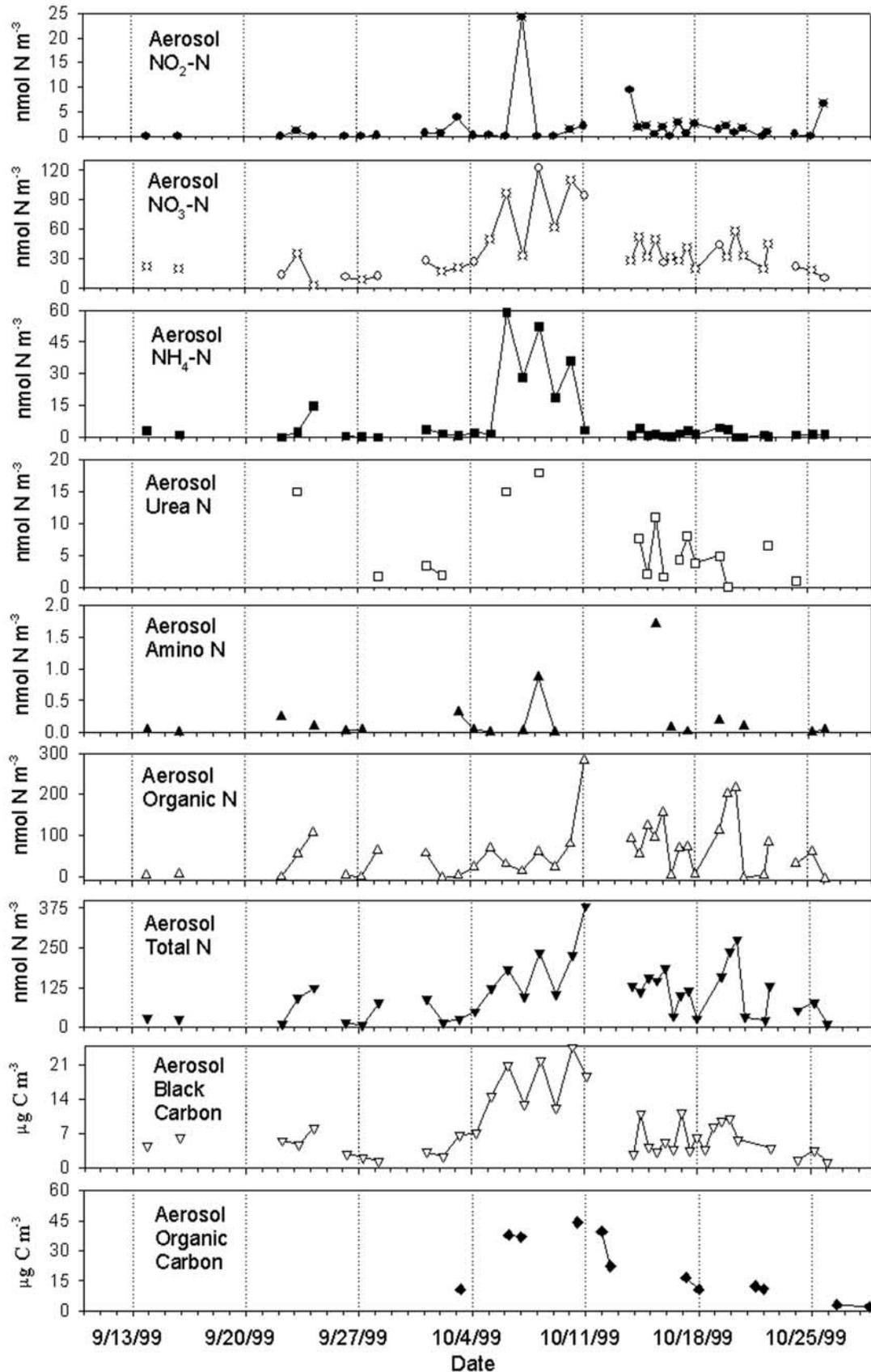


Figure 3. Concentrations of the water-soluble N species analyzed, and black carbon and organic carbon obtained during the dry season sampling interval. Water-soluble N species are presented in units of nmol N m^{-3} . Carbon species are presented as $\mu\text{g C m}^{-3}$. Individual data points represent samples collected for 12–24 hours.

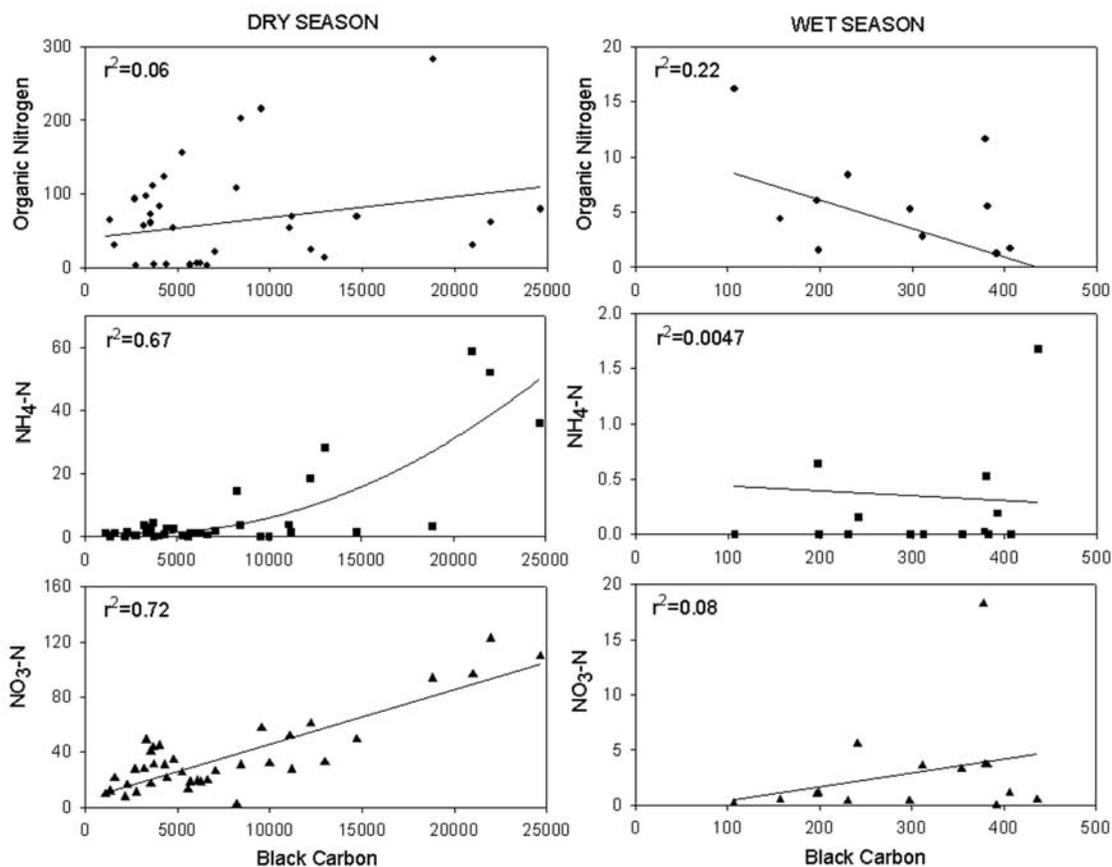


Figure 4. Regression analysis for black carbon concentrations obtained during the wet and dry seasons and organic N, NH₄⁺-N, and NO₃⁻-N concentrations.

[17] Total carbon: total nitrogen and organic carbon: organic nitrogen ratios were calculated for wet season aerosol samples for which both measurements were available, using data reported in Figure 2. The mean total C/N ratio for calculated samples was ~ 50 (± 70). The mean organic C/N ratio for calculated samples was ~ 30 (± 20). These C/N values are indicative of biological turnover of organic matter. Tropical forests typically have a C/N ratio of ~ 150 [Vitousek *et al.*, 1988]. As microbial degradation of biomass continues the C/N ratio of the forest biomass decreases because microbes have lower C/N ratios and are nutrient rich compared to forest biomass [Schlesinger, 1997]. The C/N ratios calculated for wet season aerosols suggest that under natural background conditions the organic N present in aerosols is the result of natural processes rather than anthropogenic ones. These natural processes could include the recycling of organic matter by biological species such as bacteria or the breakdown of complex organic matter.

[18] As mentioned above, urea N comprised $\sim 18\%$ of the organic N within dry season aerosol samples, but $<1\%$ of the organic N within wet season aerosol samples. Concentrations of urea N in dry season aerosol samples were ~ 200 times those in wet season samples suggesting that biomass burning is a source of urea N. As seen in Figure 3, the highest concentrations of urea occurred during periods of high black carbon concentrations (the period from 10/4/99 to 10/11/99 in Figure 3). Linear regression analysis between these two parameters yielded a positive statistically signif-

icant relationship ($r^2 = 0.28$, $P < 0.05$) suggesting that biomass burning is a likely direct source for aerosol urea. Ureides (i.e., allantoin and allantoic acid) are present in the leaf tissues and the xylum of higher plants [Thomas and Schrader, 1981]. These compounds are decomposed to urea by bacteria and by metabolic pathways [Salway, 1999]. Although no information exists regarding the transformation of ureides during biomass burning, it is possible that they may be transformed to urea during the smoldering and flaming stages of biomass burning. As indicated by Graham *et al.* [2002], cellulose decomposition products (e.g., levoglucosan and other sugars) are components of the water-soluble organic fraction of aerosols. The presence of urea in such a high concentration within dry season aerosols as compared to wet season aerosols suggests that ureides are released from plant tissues during biomass burning. Although urea was generally below detection in wet season aerosol samples, two of the aerosol samples analyzed contained urea. This urea is likely naturally produced by vegetation, insect, and/or animal species; and/or by the degradation of vegetation and waste products by primitive organisms or thermal and photochemical processes.

[19] Concentrations of dissolved free amino acids within wet and dry season aerosols were similar (Table 1). Amino acids containing more than 1 N atom generally dominated amino N percent totals, presented in Table 2. Arginine (4 N atoms), histidine (3 N atoms), and lysine (2 N atoms) comprised $\sim 50\%$ of the amino N in both wet and dry season

Table 2. Percentage of Amino N for the Individual Amino Acids Analyzed

Sample	ASP	GLU	SER	THR	GLY	ALA	ARG	PRO	VAL	MET	ILE	LEU	PHE	CYS	LYS	HIS	TYR
<i>Wet Seasons Samples</i>																	
1	0	0	0	0	21	8.2	31	16	8.3	0	2.1	1.4	1.6	0	0	10	0
3	0	0	0	0	14	5.5	55	11	5.3	0	1.0	1.7	1.2	0	0	5.3	0
6	0	24	0	0	0	0	0	0	0	0	0	0	0	0	4.7	47	24
8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	68	6.7	26
9	0	0	0	0	0	4.9	0	8.4	1.2	0	0	0	0	0	51	35	0
11	0	16	0	0	0	0	23	3.0	0.44	0	0	0	0	0	7.8	31	19
15	0	0	8.4	9.8	17	12	20	6.4	11	0	3.7	4.0	0.13	0	0	7.8	0
16	4.7	33	4.3	3.3	22	14	0	3.0	6.6	0	2.0	2.8	1.1	0	0.51	1.4	1.3
18	3.9	25	4.9	2.1	22	12	1.7	2.1	7.2	0	2.6	4.2	0.98	0	2.4	0	8.8
18	7.5	35	0	0	11	15	0	6.3	13	0	3.2	4.7	2.3	0	1.7	0	0
19	0	0	0	0	0	4.2	58	0	9	0	0	0	0	0	0	24	14
23	0	0	0	0	0	3.8	0	13	4.2	0	0	0	0	0	57	22	0
24	5.7	17	13	13	5.9	7.5	0	13	9.3	0	1.9	7.3	6.0	0	2.2	2.4	3.7
Average	1.7	12	1.9	2.2	8.7	6.7	15	6.3	5.1	0	1.3	2.0	1.0	0	15	15	7.4
Deviation	2.7	14	3.0	4.3	9.4	5.3	21	5.5	4.5	0	1.4	2.4	1.7	0	25	15	9.9
<i>Dry Season Samples</i>																	
1	0	0	0	0	2.4	4.7	9.6	5.2	8.9	0	0	0	0	0	0	36	33
2	0	8.8	0	0	0	5.6	20	5.0	0	0	0	0	0	0	4.5	22	34
3	0	0	0	0	0.44	0	92	4.7	2.8	0	0	0	0	0	0	0	0
5	3.9	0	0	0	4.7	6.2	9.2	4.0	10	0.92	1.1	0	0	0	0	10	50
6	0	16	0	0	0	0	0	3.4	0.36	0	0	0	0	0	5.7	51	24
7	0	15	0	6.6	4.2	2.7	0	6.9	3.7	0	2.1	3.9	3.9	0	8.2	27	16
11	0	0	0	0	1.3	1.3	91	3.5	2.1	0	0	0.3	0.36	0	0	0	0
12	14	29	0	0	0	2.5	1.6	4.7	2.2	4.7	0.98	1.2	0.87	0	0	11	27
13	0	0	0	0	0	4.3	0	11	2.5	0	0	0	0	0	0	29	53
15	0	21	0	0	0	3.2	0	8.3	3.8	0	0	0	0	0	6.4	16	41
16	2.0	0	0	0	1.5	1.1	44	9.9	6.9	0	0	5.5	4.0	0	7.4	1.4	17
17	0	0	0	0	0	16	60	20	4.3	0	0	0	0	0	0	0	0
23	2.1	0	1.3	0.55	38	4.2	27	12	9.6	0.79	0.73	0.71	0.45	0	1.7	0	0
25	0	0	7.0	6.7	7.5	0	60	6.1	2.1	0	0	0	0	0	0	0	11
27	0	0	0	0	0	0	0	7.3	0	0	0	0	0	0	67	13	13
29	0	0	0	0	5.0	4.7	39	7.1	26	5.7	2.4	0	1.5	0	1.4	7.1	0
32	12	0	18	0	8.7	6.9	5.4	12	37	0	0	0	0	0	0	0	0
36	0	0	0	0	0	5.7	0	2.4	0	0	0	0	0	0	78	0	14
37	0	19	0	0	0	4.3	0	0.79	0	0	0	0	0	0	9.8	46	20
Average	1.8	5.7	1.4	0.73	3.9	3.9	24	7.1	6.4	0.64	0.38	0.61	0.58	0	15	14	13
Deviation	4.1	9.4	4.3	2.1	8.7	3.7	31	4.5	9.6	1.6	0.75	1.5	1.2	0	24	17	14

samples. There were no statistically significant relationships between amino N concentrations and the concentrations of the other species presented in Figures 2 and 3. A surprising finding was the presence of methionine in dry season aerosol samples. This amino acid is generally not detected in environmental samples [Gorzelska *et al.*, 1992], and was not detected in any of the wet season samples (Table 2). Its presence may reflect that a proportion of the amino N fraction was formed from protein decomposition during burning, or through a gas phase reaction. Unhydrolyzed amino acids may exist in the background atmosphere (wet season) and in biomass burning plumes (dry season). However, they were not analyzed in this study. To accurately estimate the proportion of amino N released naturally and during biomass burning events, all forms of amino N need to be analyzed in the atmosphere of the Amazon Basin. Although it appears from our data that biomass burning is not a source of amino acid N, it is too early to draw any conclusions regarding the presence or absence of amino acids.

4. Conclusion

[20] PM₁₀ aerosol samples from the dry season contained organic N at concentrations ~30 times higher than the concentrations measured for wet season aerosols. The presented data suggest that biomass burning is a source of

WSON. However, organic N within dry season aerosols did not exhibit statistically significant relationships to black carbon, indicating that organic N undergoes complex atmospheric cycling. Given the magnitude of the WSON fraction in the dry season aerosol samples analyzed, biomass burning derived WSON may be an important global source of N released to the atmosphere. Since urea and water-soluble amino acids only comprised ~20% of the total water-soluble organic N during the biomass burning season, the majority of organic N species remain uncharacterized. Future study is needed to determine the magnitude of the WSON fraction released to the atmosphere from biomass burning. Additionally, future study aimed at examining the species composition of the WSON fraction may lead to insights regarding its biogeochemical availability, or to insights regarding water-soluble organics and their ability to act as cloud condensation nuclei.

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