

## Water-soluble organic compounds in biomass burning aerosols over Amazonia

### 2. Apportionment of the chemical composition and importance of the polyacidic fraction

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[1] Chemical characterization was performed on carbonaceous aerosols from Rondônia in the Brazilian Amazon region as part of the European contribution to the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA-EUSTACH). The sampling period (October 1999) included the peak of the burning season as well as the dry-to-wet season transition. Characterization of the carbonaceous material was performed by using a thermal combustion method. This enabled determination of aerosol total carbon (TC), black carbon (BC), and organic carbon (OC). A significant fraction of the BC material (on average about 50%) seemed to be highly refractory organic material soluble in water. A more detailed analysis of the water-soluble organic carbon (WSOC) fraction of the TC was undertaken, involving measurements of WSOC content, high-performance liquid chromatography (HPLC) separation (with UV detection) of the water-soluble components, and characterization of individual components by gas chromatography/mass spectrometry (GC/MS). The WSOC fraction accounted for 45–75% of the OC. This high WSOC fraction suggests an aerosol derived mainly from smoldering combustion. Using GC/MS, many different compounds, containing hydroxy, carboxylate, and carbonyl groups, were detected. The fraction of the WSOC identified by GC/MS was about 10%. Three classes of compounds were separated by HPLC/UV: neutral compounds (N), monocarboxylic and dicarboxylic acids (MDA), and polycarboxylic acids (PA). The sum of these three groups accounted for about 70% of the WSOC, with MDA and PA being most abundant (about 50%). Good correlations ( $r^2$  between 0.84 and 0.99) of  $BC_{\text{water}}$  (BC after water extraction) and levoglucosan (both indicators of biomass combustion) with the water-soluble species (i.e., WSOC, N, MDA, and PA), and their increase in concentrations during the burning period provided strong evidence that biomass burning is a major source of the WSOC. Particularly interesting is that PA and therefore, probably, humic-like substances (due to their polyacidic nature) are generated in significant amounts during biomass burning. These substances, due to their water solubility and surface tension-lowering effects, may play an important role in determining the overall cloud condensation nuclei activity of biomass burning aerosols and, consequently, could be important in cloud processes and climate forcing.

*INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere

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## 1. Introduction

[2] Biomass burning is one of the major sources of fine carbonaceous aerosols (black carbon (BC) and organic carbon (OC)) to the atmosphere [Penner *et al.*, 1991; Andreae, 1993]. Because OC scatters and BC principally absorbs solar radiation, these species, together with the inorganic aerosol material, influence aerosol climate direct forcing [Penner *et al.*, 1998, and references therein]. Biomass smoke particles are also efficient cloud condensation nuclei (CCN) [Holben *et al.*, 1991; Hudson *et al.*, 1991; Kaufman *et al.*, 1992; Novakov and Corrigan, 1996, and references therein] in spite of the fact that they consist predominantly of organic material (>90% of the aerosol mass) [Andreae and Crutzen, 1997]. However, it is still not known if it is their organic component that is inherently CCN active or if they are made active through association with water-soluble inorganic species [Roberts *et al.*, 2001, 2002]. In laboratory experiments, Novakov and Corrigan [1996] provided strong evidence that water-soluble organic species in smoke particles from smoldering combustion could be responsible for their CCN activity; however, no field measurements have confirmed this to date.

[3] The question, therefore, remains as to the chemical identity of the species that make smoke particles CCN. To answer this, information is needed about the chemical composition of the water-soluble organic carbon (WSOC) fraction of these particles. Several studies have reported that a significant portion of smoke particles (from 11% to as high as 99%) is water-soluble organic material [Novakov and Corrigan, 1996; Narukawa *et al.*, 1999; Ruellan *et al.*, 1999]. However, to our knowledge, up to now there has been no detailed field study on the chemical composition of the WSOC fraction of particles generated by biomass burning, apart from the characterization of water-soluble dicarboxylic acids in the 1997 Indonesian forest fires by Narukawa *et al.* [1999]. Detailed knowledge on the chemical identity of the WSOC fraction is essential in order to understand the interaction of smoke aerosol with atmospheric water and hence hygroscopic growth, cloud formation, and aqueous phase chemistry.

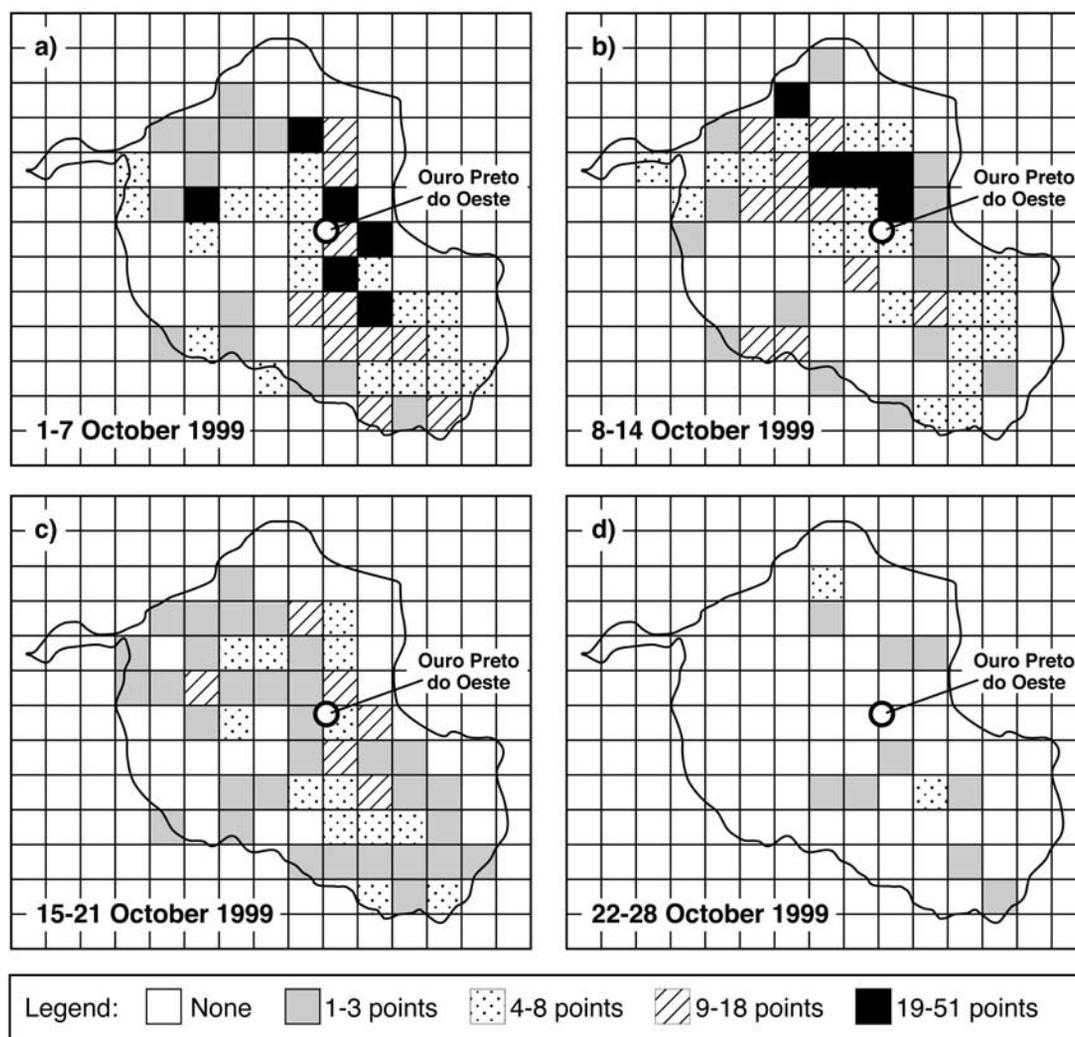
[4] Understanding the composition of WSOC in smoke aerosols is particularly important for tropical regions. Each year, extensive forest clearing is carried out in the tropics by slash-and-burn techniques, resulting in massive inputs of various gaseous and aerosol species into the atmosphere [Crutzen and Andreae, 1990]. Of these regions, one of the most important from a global perspective is the Brazilian Amazon, since this area incorporates the world's largest rainforest (about 4, 000, 000 km<sup>2</sup>) and continues to experience one of the highest deforestation rates in the world ( $1.5\text{--}2.0 \times 10^6$  ha yr<sup>-1</sup>) [Skole *et al.*, 1994]. The

great extent and expansion of biomass burning occurring in the Amazon Basin, together with the intense convective activity associated with its equatorial location, mean that the aerosols generated in this region may have impacts on the global climate.

[5] There have already been some intensive measurement campaigns (e.g., Atmospheric Boundary Layer Experiment 2 (ABLE 2) and Smoke, Clouds, and Radiation-Brazil (SCAR-B)) carried out in the Amazon Basin, which have begun to improve our understanding of the aerosol composition over this region during the dry season [Harriss *et al.*, 1985; Kaufman *et al.*, 1998]. The SCAR-B experiment, in particular, focussed on the analysis of the composition and atmospheric effects of biomass burning aerosols. In-depth studies of the inorganic components, morphology, and optical properties of smoke aerosols were carried out in this study. However, there still remains a large gap in our knowledge regarding the organic component of these aerosols.

[6] To date, characterization of the organic component of smoke aerosols in general has involved primarily molecular speciation of solvent extracts by gas chromatography/mass spectrometry (GC/MS) analysis [Abas *et al.*, 1995; Elias *et al.*, 1999; Oros and Simoneit, 1999; Simoneit *et al.*, 1999, 2000; Simoneit and Elias, 2000; Fang *et al.*, 1999]. There have been some studies of water-soluble species, all focusing exclusively on the analysis of carboxylic acids [Andreae *et al.*, 1988; Narukawa *et al.*, 1999; Yamasoe *et al.*, 2000]. In most cases, the aerosol mass accounted for by these species is fairly minimal. Thus there is a clear need to develop additional methods for the analysis of WSOC in smoke aerosols. Furthermore, there is increasing evidence that a significant fraction of the water-soluble organic material in aerosols may be of high molecular weight [Mukai and Ambe, 1986; Zappoli *et al.*, 1999; Facchini *et al.*, 1999a; Gelencsér *et al.*, 2000a] and composed of multifunctional polycarboxylic acids [Decesari *et al.*, 2000]. These species in particular will require the application of alternative techniques to those traditionally used for the analysis of low molecular weight compounds. Some such techniques have recently begun to be used by Decesari *et al.* [2000, 2001] in the characterization of atmospheric aerosols. They developed a new approach toward the analysis of the WSOC analysis based on a combination of chromatographic separation, functional group investigation by proton nuclear magnetic resonance (<sup>1</sup>H NMR) and total organic carbon (TOC) determination. However, to date, there has been no study that has described the detailed analysis of biomass burning aerosols with these techniques.

[7] Here we present results on the chemical composition of fine carbonaceous aerosols (aerodynamic particle diameter,  $D_p < \sim 2.6$  μm) collected in Fazenda Nossa



**Figure 1.** Maps of the weekly number of fire points detected by the NOAA 12 satellite during nighttime (Rondônia, October 1999). The location of Ouro Preto do Oeste (dot), where the FNS site was located, is also shown. The total number of fire points for the different weeks was (a) 491, (b) 457, (c) 78, and (d) 25. Data were obtained from <http://www.queimadas.cnpm.embrapa.br/index.html>.

Senhora Aparecida (FNS), a pasture site in Rondônia, during the peak of the burning season and the dry-to-wet season transition as part of the European contribution to the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA-EUSTACH) [Andreae *et al.*, 2002]. First, we discuss the results on the characterization of the carbonaceous aerosol (total carbon (TC), BC, and OC) and present a mass and chemical balance of the carbon fraction, emphasizing the apportionment of the water-soluble fraction using TOC, high-performance liquid chromatography (HPLC) with ultraviolet detection, and GC/MS analyses. Second, we discuss biomass burning as a significant source of WSOC species. Finally, we connect the polyacidic fraction to the humic-like substances (HULIS), cited several times in literature [Mukai and Ambe, 1986; Havers *et al.*, 1998; Facchini *et al.*, 1999a; Zappoli *et al.*, 1999; Gelencsér *et al.*, 2000a; Krivácsy *et al.*, 2000], and discuss their potential origin

from biomass burning on the basis of their chemical composition and thermal properties.

## 2. Methods

### 2.1. Sampling

#### 2.1.1. Sampling Site

[8] Aerosol sampling was conducted during October 1999 at Fazenda Nossa Senhora Aparecida ( $10^{\circ}45'44''\text{S}$ ,  $62^{\circ}21'27''\text{W}$ , 315 m above sea level), a ground station in a pasture site located approximately 8 km southwest of the town Ouro Preto do Oeste in the state of Rondônia, Brazil. This place was deforested by fire about 20 years ago. A detailed description of the site is provided by Andreae *et al.* [2002] and Kirkman *et al.* [2002]. During the campaign, the site was stocked with cattle, and a strong influence of burning, mainly from wood, pasture, charcoal, and refuse, was experienced in the proximity

of the site, especially at the beginning of the project. This can be observed from the orbital monitoring of burned areas performed by the Brazilian Agency for Agricultural Research (EMBRAPA) and ECOFORÇA (Figure 1) (<http://www.queimadas.cnpm.embrapa.br/index.html>). At the end of the campaign, the intensity of the fires decreased (also evident in Figure 1), and the rainfall increased with the beginning of the wet season.

[9] A summary of the meteorological data, and the trace gas ( $O_3$ , NO,  $NO_2$ , and volatile organic compounds) and aerosol measurements performed at FNS is presented by *Andreae et al.* [2002] and references therein.

### 2.1.2. Collection of Samples

[10] Aerosol samples were collected on quartz filters (Pallflex Tissuquartz 2500 QAT-UP) using a high-volume dichotomous sampler (HVDS) [*Solomon et al.*, 1983], mounted on FNS tower A at about 5 m from the ground. The HVDS sampler allows the collection of particles in fine ( $D_p < \sim 2.5 \mu\text{m}$ ) and coarse ( $D_p > \sim 2.5 \mu\text{m}$ ) modes. The face velocity was around  $86 \text{ cm s}^{-1}$  for a total average flow of about  $330 \text{ L min}^{-1}$ . The sampling periods were 12 hours daytime, 12 hours nighttime, 24 hours, and 48 hours. The results presented here correspond only to the fine fraction. The mass concentrations obtained were corrected according to *Dzubay et al.* [1978]. This correction is necessary, since about one tenth of the fine particles entering the inlet are collected on the coarse particle filter.

[11] Before use, the quartz filters were prebaked at  $600^\circ\text{C}$  for about 15 hours to remove residual organic impurities. In the sampler, two quartz filters were placed directly on top of each other (tandem arrangement) in each filter holder (fine and coarse). The tandem arrangement is used to correct for the adsorption of gaseous organic compounds by the filter material (i.e., positive artifact). If not accounted for, this artifact results in an overestimation of organic aerosol mass concentrations.

[12] A small closed hut at the pasture site was dedicated to the loading and unloading of the filter units. After the unloading process, filter samples were stored in a freezer at  $-18^\circ\text{C}$  in precleaned glass vials (prebaked for about 15 hours at  $600^\circ\text{C}$ ) until analysis. Handling of filters and jars was according to the procedures recommended by *Salmon et al.* [1998].

[13] Blank filters were collected by using filter units loaded in the sample preparation area. These units were connected to the aerosol inlet in the same way as that for the collection of real samples, with flow being applied only for about 15 s.

## 2.2. Analysis

### 2.2.1. Total Carbon, Black Carbon, and Organic Carbon

[14] Characterization of the carbonaceous aerosol was performed by using a linear temperature thermal combustion method known as evolved gas analysis (EGA) [*Novakov et al.*, 1997a, 1997b, 2000]. This method enabled the determination of the mass loadings of the aerosol total carbon (TC) as well as of BC and OC.

[15] Briefly, in the EGA analysis an aliquot of the sample (here one or two punches of  $0.5 \text{ cm}^2$  taken from the  $63.6\text{-cm}^2$  exposed area of the 100-mm quartz filters) is progressively heated at a linear rate (here  $20^\circ\text{C min}^{-1}$ ) in an oxygen atmosphere from  $50^\circ\text{C}$  to a suitable endpoint

temperature,  $650^\circ\text{C}$  in this application. The carbon-containing gases evolving from the sample are converted to  $CO_2$  over a  $MnO_2$  catalyst maintained at  $800^\circ\text{C}$  and measured with a nondispersive infrared analyzer (Beckman model 870). A plot of the rate of evolution of  $CO_2$  (or C) as a function of temperature is called a thermogram, and the area under the thermogram is proportional to the total carbon content of the analyzed sample. Thermograms show a structure, often in the form of well-defined peaks, that is indicative of volatilization, decomposition, and combustion of the carbonaceous material (TC, BC, and OC) contained in the sample. The EGA method is quantitative for total carbon within  $\sim 10\%$ , shows a reproducibility of 3–5%, and has a carbon detection limit of  $\sim 0.2 \mu\text{g}$  per sample [*Dod et al.*, 1979; *Gundel et al.*, 1984].

[16] Sample punches were analyzed as collected (non-extracted) and after removal of their water-soluble content (water extracted) (Figure 2a). For the removal of the water-soluble material, samples were soaked in Milli-Q water for  $\sim 30$  min. After extraction, samples were dried at room temperature on a prebaked surface of aluminum foil and analyzed. Blank samples were also subject to the same treatment to monitor if the preparation process resulted in any contamination. These analyses were carried out at the Lawrence Berkeley National Laboratory (LBNL).

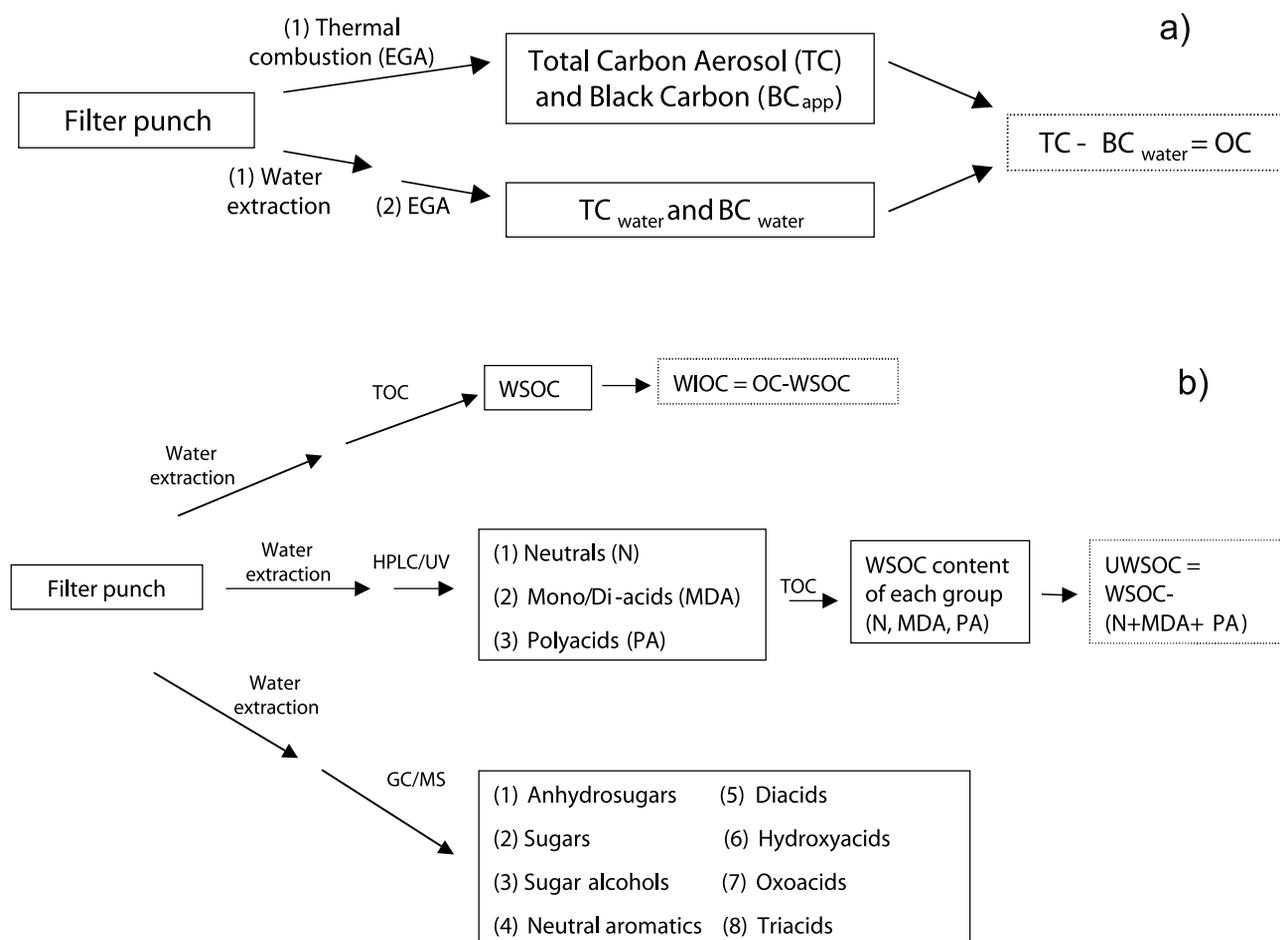
### 2.2.2. Water-Soluble Organic Fraction

[17] A more detailed analysis of the water-soluble organic fraction was undertaken by means of the methods described by *Decesari et al.* [2000, 2001] and *Graham et al.* [2002]. This included the analysis of water extracts by (1) TOC analysis for the determination of the WSOC, (2) high-performance liquid chromatography (HPLC/UV) to fractionate the water extracts based on charge, and (3) GC/MS for molecular speciation. Figure 2b presents the analyses performed and the chemical information obtained from them.

[18] Extraction of the filter samples was performed by soaking the  $0.5 \text{ cm}^2$  punches in 3 mL of Milli-Q water for 24 hours. The extracts were then filtered on PTFE filters in order to remove any particles suspended in the solutions. Extracts prepared in this way were used for the TOC and HPLC/UV analyses.

1. In TOC analysis, an aliquot of the filter water extract was used to determine the WSOC content of the samples, using a Shimadzu TOC-5000A liquid analyzer. The detector response was calibrated with standard solutions of potassium hydrogen phthalate provided by Shimadzu. The accuracy of the measurements ranges from 7% for 1 ppm C solution to 3% for concentrations higher than 2 ppm C, and the detection limit is 0.1 ppm C. In addition to the direct determination of the dissolved carbon content, the water extracts were also analyzed after removal of the inorganic carbon (acidification with HCl to pH 2 followed by 5-minutes sparging). The water-insoluble organic carbon (WIOC) was estimated from the difference between OC (from EGA) and WSOC.

2. For HPLC/UV, in order to fractionate the WSOC, aliquots of the water extracts were analyzed at a constant flow of  $0.7 \text{ mL min}^{-1}$  on a Hitachi L-7100 high-pressure liquid chromatograph equipped with a  $100\text{-}\mu\text{L}$  loop, an ion exchange column (DEAE-TSK gel column,  $7.5 \text{ mm i.d.} \times 7.5 \text{ cm}$  length), and a Varian 2550 UV detector. While pH was held constant at 8.0, the ionic strength of the mobile phase composition increased during the analysis, following two



**Figure 2.** Diagram of the analytical procedure for the assessment of the different carbon species. (a) Carbonaceous aerosol (TC, BC<sub>app</sub>, TC<sub>water</sub>, and BC<sub>water</sub>); TC<sub>water</sub> and BC<sub>water</sub> are TC and BC<sub>app</sub> after water extraction.  $TC - BC_{water} = OC$ . (b) Water-soluble organic fraction.

gradients (from deionized water (0 M) to 0.02 M NaClO<sub>4</sub>, up to a final concentration of 0.4 M). The absorbance wavelength monitored by the detector was 254 nm. Under these conditions, anionic species (both organic and inorganic) with increasing number of charges per molecule were sequentially eluted. As reported by *Decesari et al.* [2000], at 254 nm the only detectable inorganic anion that absorbs is nitrate, and the remaining detected peaks are due to UV-absorbing organic species. The detected species were classified in three different classes: (1) neutrals (N), not retained by the column; (2) monocarboxylic and dicarboxylic acids (MDA), containing compounds bearing one or two carboxylic groups per molecule; and (3) polycarboxylic acids (PA), polycharged compounds with at least three carboxylic groups per molecule. Calibration was performed by isolating the three classes of compounds on a DEAE-cellulose-gel preparative column and by analyzing the separated fractions for total organic carbon by TOC (samples FNS1 and FNS2 were selected for this purpose). More details about this method are presented by *Decesari et al.* [2000].

3. A GC/MS method was employed to characterize low molecular weight, water-soluble compounds within the aerosol samples. This method included a sample pretreatment procedure that involved aqueous extraction of the filters, evaporation of the extract with nitrogen, and then a

two-step derivatization designed to convert hydroxyl groups to trimethylsilyl (TMS) ethers, carboxyl groups to TMS esters, and carbonyl groups to methoxime derivatives. With this method, it was possible to identify and quantify a number of highly oxygenated compounds in the aerosols: polyalcohols (including sugars, sugar alcohols, and anhydrosugars), diacids, hydroxyacids, and oxoacids. The precision of this method is typically 20%. Application of the extraction/derivatization procedure to blank filters spiked with an aliquot of standards indicated that the aqueous extraction is sufficient to quantitatively recover the analyzed compounds (within experimental error). Calibration curves were constructed by diluting aliquots of standards to the same volume as the sample extracts and subjecting them to the same evaporation/derivatization procedure, in order to compensate for possible losses. Further details are given by *Graham et al.* [2002].

### 3. Results and Discussion

[19] The analysis of the carbonaceous aerosol began with the use of thermal analysis to determine TC, BC, and OC and focussed on the characterization of the water-soluble organic fraction by means of TOC analysis, HPLC/UV, and

**Table 1.** Summary of Results for the Chemical Composition of Fine Carbonaceous Aerosol Collected at FNS During LBA-EUSTACH-2<sup>a</sup>

Sample	1999 Start Date	1999 End Date	Volume, m <sup>3</sup>	EGA		WSOC	WIOC	N	HPLC			UWSOC	GC/MS		
				TC	BC <sub>app</sub>				BC <sub>water</sub>	MDA	PA		HPLC <sub>total</sub>	GC/MS <sub>total</sub>	GC/MS <sub>carbon</sub>
FNS1	2 Oct.	3 Oct.	381	26.5	9.0	4.4 <sup>b</sup>	11.1	4.0	3.4	2.8	10.2	1.0	3.67	1.52	0.91
FNS2	5 Oct.	6 Oct.	384	83.0	31.5	12.3 <sup>b</sup>	39.1	9.2	12.6	12.2	34.1	5.0	11.65	4.91	3.07
FNS3	6 Oct.	7 Oct.	197	67.2	24.4	9.5	38.2	7.0	9.0	9.3	25.3	12.9	ND	ND	ND
FNS4	10 Oct.	10 Oct.	197	68.4	21.4	9.1	45.7	6.0	9.3	14.7	30.0	15.7	ND	ND	ND
FNS5	12 Oct.	12 Oct.	197	38.5	11.9	5.8	23.1	3.7	5.5	5.6	14.7	8.4	5.52	2.24	1.26
FNS6	16 Oct.	17 Oct.	204	24.4	8.7	3.8	17.1	2.5	3.7	2.9	9.1	8.0	4.46	1.87	1.30
FNS7	17 Oct.	18 Oct.	197	20.6	7.6	4.0	11.1	2.4	2.4	1.7	6.5	4.6	ND	ND	ND
FNS8	21 Oct.	21 Oct.	197	21.5	8.3	4.1	12.7	2.0	3.5	3.8	9.3	3.4	2.82	1.11	0.52
FNS9	21 Oct.	22 Oct.	195	21.7	8.3	4.1 <sup>b</sup>	11.3	3.0	3.4	2.8	9.2	2.1	3.03	1.23	0.65
FNS10 <sup>c</sup>	25 Oct.	27 Oct.	755	5.1	2.3	2.0 <sup>b</sup>	3.1	0.4	0.7	0.8	1.9	1.2	0.71	0.27	0.11
Mean (burning period)				41	15	6	23	4	6	6	16	7	5.2	2.1	1.3
Standard deviation				25	9	3	14	2	4	5	10	5	3.3	1.4	0.9

<sup>a</sup>All concentrations of species are given in mass carbon per volume air except GC/MS<sub>total</sub>, which is in mass aerosol per volume air ( $\mu\text{g m}^{-3}$ ). ND, not determined. WIOC = OC - WSOC, where OC = TC - BC<sub>water</sub>.

<sup>b</sup>Estimated from regression analysis of BC<sub>water</sub> as a function of BC<sub>app</sub> (equation used was BC<sub>water</sub> = 0.354BC<sub>app</sub> + 1.187).

<sup>c</sup>Considered to belong to the wet season.

GC/MS. Here we present detailed results on the thermal, TOC, and HPLC/UV analyses. GC/MS is only briefly discussed; the detailed results are presented by *Graham et al.* [2002]. This study concentrates on the samples collected during the burning period (FNS1 to FNS9); the sample collected on 25 October (FNS10, Table 1) is considered more representative of the wet season, since it was collected at the end of the campaign, when the amount of fires had decreased and the rain events were increasing.

### 3.1. Total Carbon, Black Carbon, and Organic Carbon

[20] The results presented here for the TC, BC, and OC mass concentrations were obtained from the EGA (Table 1). A complete discussion on the interpretation of thermograms (from the EGA) and the uncertainties associated with this type of measurement (e.g., charring effects, presence of highly refractory organic material and calcium carbonate) is presented elsewhere [*Novakov et al.*, 2000; *Mayol-Bracero et al.*, 2002]. All thermograms obtained for samples collected at FNS showed profiles similar to the one presented in Figure 3a.

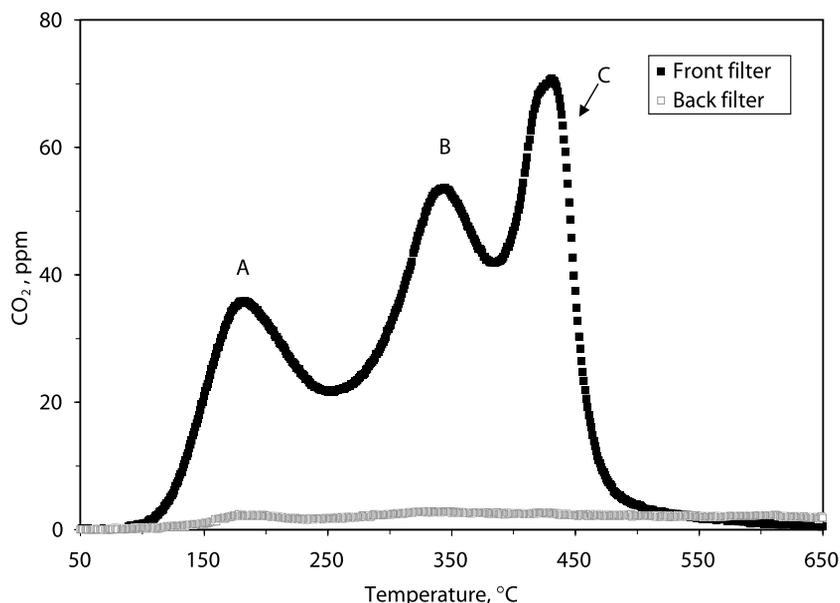
#### 3.1.1. Total Carbon

[21] In general, thermograms of the front filter samples (solid squares in Figure 3a) consisted of three different peaks (A, B, and C) with carbon evolution extending to 600°C. As explained in section 2.1.2, comparison of front and back filters allows correction for the positive artifact through subtraction of the TC concentration on the backup filter from that on the front filter (for a complete discussion, see *Kirchstetter et al.* [2001]). Figure 3a shows that, in our case, the concentrations of carbon detectable on the back filter were insignificant in relation to the front filter (TC on the back filter was about 4% of the TC on the front filter). This suggests that the bulk of the aerosol-phase TC was present as low-volatility material, rather than as semivolatile organic compounds, which have been shown to be partially lost from the front filter during sampling [*Limbeck et al.*, 2001]. Since no corrections for the positive artifact were required, TC was determined from the total area of the carbon evolving from the front filter.

[22] During the burning period (abundant haze events), the carbon concentrations in the form of TC were in the range of 20 to 83  $\mu\text{g m}^{-3}$  with an average of  $41 \pm 25 \mu\text{g m}^{-3}$  (standard deviation given). These values compare well with the values (30 to 80  $\mu\text{g m}^{-3}$ ) observed by *Narukawa et al.* [1999] during intensive haze events associated with the extreme fires in Indonesia during 1997. Our TC values were 4 to 15 times higher during the burning period than at the end of the campaign (beginning of the wet season).

#### 3.1.2. Black Carbon and Organic Carbon

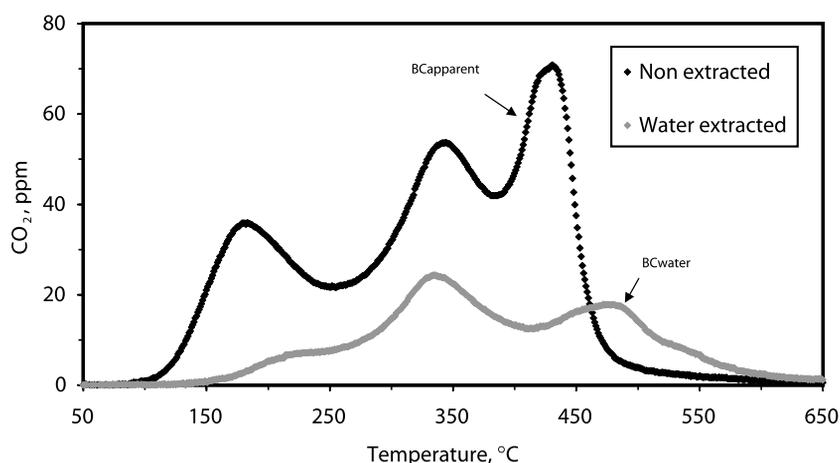
[23] The term BC<sub>soot</sub> is used to describe the most polymerized and refractory fraction of combustion-produced atmospheric carbonaceous aerosols, having chemical properties similar to graphitic carbon (disordered graphite lattice, mostly with carbon, but also with some oxygen and hydrogen atoms, and highly resistant to thermal degradation and oxidation) [*Lioussse et al.*, 1993; *Charlson and Heintzenberg*, 1995; *Cachier*, 1998]. This species is insoluble either in water or organic solvents. Usually, in EGA analysis, it is represented by the peak C evolving above  $\sim 400^\circ\text{C}$  in the thermograms (Figure 3a). However, our results show that between 45 and 60% (on average,  $\sim 53\%$ ) of the material



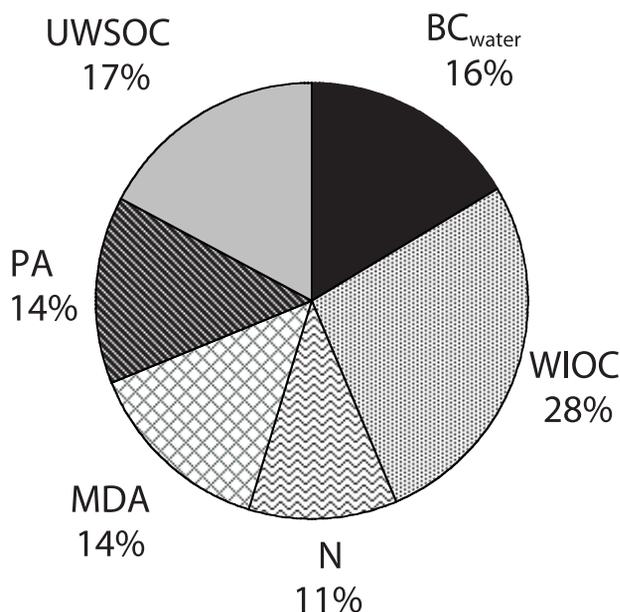
**Figure 3a.** Thermograms of front (solid squares) and back (open squares) quartz filters. Assignments of peaks A, B, and C are discussed in section 3.1. This sample (FNS5) was collected on 12 October 1999.

corresponding to peak C was removed by extraction with water (Figure 3b, Table 1). In the most loaded samples ( $TC > 65 \mu\text{g m}^{-3}$ ) the removal of material belonging to peak C could have been due not only to water solubilization, but also mechanical dislodging. Our  $BC_{\text{soot}}$  values for the high-loaded samples may, therefore, be an underestimation of the true values. Nevertheless, the results presented here suggest that (1) peak C is not solely due to  $BC_{\text{soot}}$ , (2) the species responsible for this peak contain a large number of polar (hydrophilic) functional groups and, therefore, (3) a better determination of  $BC_{\text{soot}}$  for these samples could be obtained after the solvent-extraction process. *Novakov and Corrigan* [1995] have called peak C (Figure 3a) “apparent black carbon” ( $BC_{\text{app}}$ ) after finding similar results in laboratory biomass burning experiments, and we are adopting their term here.

[24] The distinction of OC from  $BC_{\text{soot}}$  using thermal combustion methods is particularly difficult when dealing with biomass burning samples, since they have a large organic component (>90% of the TC) and a significant fraction of this component seems to be high molecular weight organic material with thermal and oxidative properties similar to  $BC_{\text{soot}}$  (our  $BC_{\text{app}}$ ) (Figure 3). Similar observations were made by *Gelencsér et al.* [2000a] in thermal analyses of samples collected at a rural site in Hungary. They suggested that the species showing up as the  $BC_{\text{app}}$  (less volatile/oxidizable material) might include polymer-type secondary organic species and natural polymers such as lignin, cellulose, and humic substances. Nevertheless, there is still not enough information on this topic, and therefore the specific chemical identity of this material remains unknown.



**Figure 3b.** Thermograms of sample FNS5. Black and gray diamonds correspond to the nonextracted and water-extracted samples, respectively. Carbon concentrations for  $BC_{\text{app}}$  ( $BC$  of nonextracted sample) and  $BC_{\text{water}}$  ( $BC$  after water extraction) are  $11.9 \mu\text{g m}^{-3}$  and  $5.8 \mu\text{g m}^{-3}$ , respectively.



**Figure 4.** Carbonaceous aerosol composition during the burning period of LBA-EUSTACH-2 at FNS. Carbon concentrations of TC and OC were  $41 \pm 25 \mu\text{g m}^{-3}$  and  $35 \pm 22 \mu\text{g m}^{-3}$ , respectively. UWSOC stands for unrecoverable WSOC and WIOC stands for water-insoluble organic component.

[25] Another situation that complicates the distinction between  $\text{BC}_{\text{soot}}$  and OC by thermal analysis is the presence of high concentrations of ions such as  $\text{Na}^+$  and  $\text{K}^+$  in biomass samples, which catalyze the combustion of BC material at lower temperatures [Novakov and Corrigan, 1995]. These ions are removed during the water extraction, leading to evolution of peak C (called  $\text{BC}_{\text{water}}$  after the extraction) at higher temperatures (Figure 3b).

[26] Charring during the thermal analysis can be excluded as a possible explanation for the large amounts of  $\text{BC}_{\text{app}}$  observed (carbon concentrations as high as  $31 \mu\text{g m}^{-3}$ ) (Table 1). The contribution of charring to  $\text{BC}_{\text{app}}$  was assessed by comparing the light absorption (using an optical transmission analysis described by Novakov *et al.* [2000]) of the filter sample before the EGA analysis (nonheated sample) with the one of the filter analyzed by EGA only until  $345^\circ\text{C}$ . If charring were occurring, the absorption measurements of the samples analyzed up to  $345^\circ\text{C}$  should be higher than those for the nonheated samples, meaning that some OC has been pyrolyzed. However, for our samples we estimated that BC generation from charring was less than 4%.

[27]  $\text{BC}_{\text{app}}$  concentrations during the burning period ranged between 8 and  $31 \mu\text{g m}^{-3}$ , but after water extraction the  $\text{BC}_{\text{water}}$  concentrations were only 4– $12 \mu\text{g m}^{-3}$ . OC carbon concentrations, determined from  $\text{TC} - \text{BC}_{\text{water}}$ , were 17 to  $71 \mu\text{g m}^{-3}$ . The mean  $\text{BC}_{\text{water}}/\text{TC}$  ratio was 0.16, indicating that about 16% of the total carbon could have been present as  $\text{BC}_{\text{soot}}$ . The lower limit for  $\text{BC}_{\text{soot}}$  would be zero, since EGA is not specific for soot, and all  $\text{BC}_{\text{water}}$  could in principle have been refractory organic matter. Organic carbon therefore accounts on average for 84–100% of the carbonaceous aerosol in our samples.

Overall, these results serve to highlight the fact that the use of thermograms is likely to produce an overestimate of  $\text{BC}_{\text{soot}}$  and an underestimate of OC, especially for biomass burning aerosols. A combination of thermal, optical, and solvent extraction methods must be used to accurately estimate these species [Gundel *et al.*, 1984].

### 3.2. Water-Soluble Organic Fraction

#### 3.2.1. WSOC

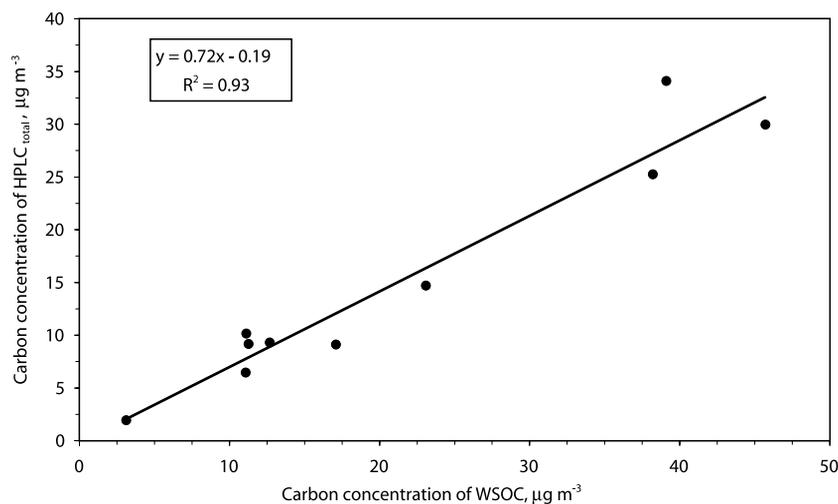
[28] As was seen from the TC,  $\text{BC}_{\text{water}}$ , and OC results, the dominant fraction of the carbonaceous aerosol derived from biomass burning (smoldering) is organic, and a significant fraction of it is water soluble (Figure 3b) and can, therefore, contribute to the CCN activity of biomass smoke particles. For this reason, we concentrated our further analytical efforts on the characterization of the water-soluble OC (WSOC) material.

[29] The WSOC concentrations reported here (as well as the TC values described in section 3.1.1) refer to uncorrected values determined for the front filters. The WSOC content of the back filters was found to be about 5% of that of the front filters, i.e., within the instrumental error of the TOC analysis of the front filter samples.

[30] WSOC concentrations ranged from 11 to  $46 \mu\text{g m}^{-3}$ , with an average of  $23 \pm 14 \mu\text{g m}^{-3}$  (Table 1). This fraction represents between 42 and 70% of the TC (56% on average) (Figure 4). The high water-soluble fraction suggests an aerosol produced mainly by smoldering processes [Andreae *et al.*, 1996; Novakov and Corrigan, 1996]. Other studies of biomass burning activities have also shown a high fraction of TC to consist of WSOC (up to 99%) [Novakov and Corrigan, 1996; Narukawa *et al.*, 1999; Ruellan *et al.*, 1999]. Carbonaceous aerosols derived from sources other than biomass burning have shown values ranging from 7 to 68% [Zappoli *et al.*, 1999; Ruellan and Cachier, 2001]. Ruellan and Cachier [2001] present the lowest values (7 to 19%), probably because particles emitted from vehicles contain low concentrations of oxygenated organics (low WSOC).

[31] The water-insoluble organic fraction of the samples ( $\text{WIOC} = \text{OC} - \text{WSOC}$ ) represents between 14 and 41% of the TC (average of  $\sim 28\%$ , Figure 4), with carbon concentrations ranging between 5 and  $32 \mu\text{g m}^{-3}$ . This fraction probably includes significant amounts of incompletely combusted biogenic detritus. Previous studies of biomass burning aerosols involving GC analysis of organic solvent extracts [Fang *et al.*, 1999; Simoneit *et al.*, 2000; Simoneit and Elias, 2000 and references therein] indicate that there is also likely to be a mixture of incomplete combustion products and biogenic detritus such as wax esters, aliphatic hydrocarbons, triglycerides, long-chain ketones, alkanols, and polycyclic aromatic hydrocarbons included in the WIOC. As will be discussed later, it is also possible that some of this fraction is made up of water-insoluble humic-like substances [Mukai and Ambe, 1986; Havers *et al.*, 1998].

[32] Water-soluble inorganic carbon (IC) can be estimated from the TOC measurements ( $\text{IC} = \text{TC}$  of the water extract minus the TC of the extract after acidification). However, this value was below the detection limit ( $0.008 \mu\text{g mm}^{-2}$  of filter, equivalent to carbon concentrations of  $0.07\text{--}0.26 \mu\text{g m}^{-3}$ ) for all the samples analyzed.



**Figure 5a.** Regression analysis of the total species determined by HPLC/UV ( $\text{HPLC}_{\text{total}} = \text{N} + \text{MDA} + \text{PA}$ ) ( $r^2 = 0.93$ ). Concentrations are given in mass carbon per volume air.

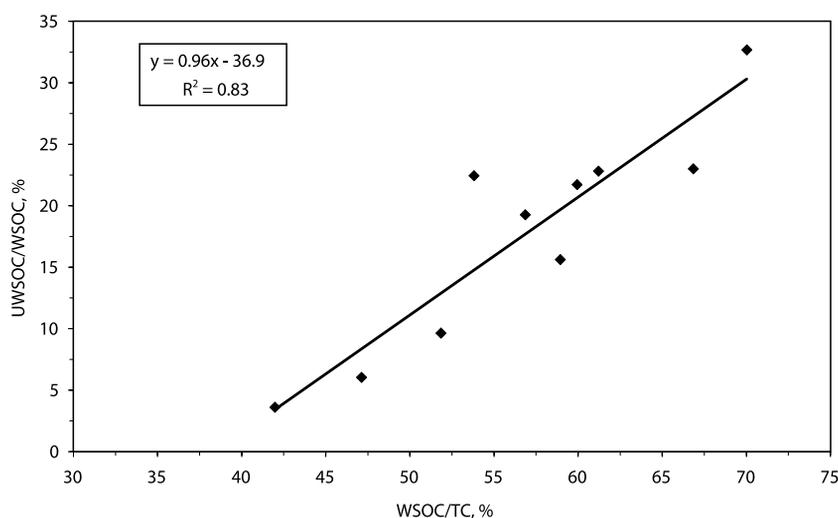
[33] In order to further characterize the water-soluble organic fraction, we used a combination of HPLC/UV and GC/MS.

### 3.2.2. Neutral Compounds, Monocarboxylic and Dicarboxylic Acids, and Polycarboxylic Acids

[34] The anion exchange HPLC/UV technique [Decesari *et al.*, 2000] allowed the fractionation of the water extract into three different UV-active ( $\lambda = 254$  nm) classes as explained in section 2.2.2 (i.e., N, MDA, and PA). The amount of material in each of these classes was quantified by measuring the carbon content of the eluted fractions. According to this procedure, the carbon content (in mass carbon per volume air) of the water-soluble N, MDA, and PA fractions ranged between 2 and 9 (average  $4 \pm 2$ ), 2 and 13 (average  $6 \pm 4$ ), and 2 and 15 (average  $6 \pm 5$ )  $\mu\text{g m}^{-3}$ , respectively (Table 1). The average percentage contribution of these groups of compounds to TC is presented in Figure 4. The acids (MDA and PA) accounted for about

51% of the WSOC, and the N accounted for about 21%. These classes of compounds have been observed in similar ratios in fog and aerosol samples collected in northern Italy [Decesari *et al.*, 2000].

[35] The correlation between the sum of the three fractions ( $\text{HPLC}_{\text{total}} = \text{N} + \text{MDA} + \text{PA}$ ) determined by HPLC/UV and WSOC is very good ( $r^2 = 0.93$ ) (Figure 5a), with  $\text{HPLC}_{\text{total}}$  constituting between 53 and 91% of WSOC. On average,  $\text{HPLC}_{\text{total}}$  represented  $71 \pm 13\%$  of the WSOC ( $39 \pm 4\%$  of the TC). The carbon concentration of WSOC that was not recovered by HPLC/UV (i.e.,  $\text{UWSOC} = \text{WSOC} - \text{HPLC}_{\text{total}}$ ) was about  $7 \pm 5$   $\mu\text{g m}^{-3}$  ( $29 \pm 13\%$  of the WSOC and  $17 \pm 9\%$  of the TC, Figure 4). UWSOC is likely to include semi volatile compounds that are lost during the analytical procedure, as well as compounds that bind too strongly to the anion exchange column to be removed under the elution conditions used. The latter may include highly negatively charged species or compounds that interact with



**Figure 5b.** Regression analysis of the percent of unidentified WSOC (UWSOC) as a function of the total WSOC ( $r^2 = 0.83$ ).

**Table 2.** Mean Carbon Concentrations and Standard Deviations of the Groups of Compounds Identified by GC/MS and the Fraction That They Represent From the GC/MS<sub>total</sub>, the HPLC<sub>total</sub>, and the TC for the Samples Collected at FNS During the Burning-Dominated Period of LBA-EUSTACH-2

GC/MS Class	Carbon Concentration, $\mu\text{g m}^{-3}$
<i>Neutrals</i>	
Anhydrosugars	1.46 ± 1.06
Sugars	0.033 ± 0.015
Sugar alcohols	0.031 ± 0.012
Neutral aromatics	0.025 ± 0.020
Total	1.55 ± 1.06
GC/MS <sub>total</sub> , %	65
HPLC <sub>total</sub> , %	9
TC, %	4
<i>Monocarboxylic and Dicarboxylic Acids</i>	
Diacids	0.32 ± 0.16
Hydroxyacids	0.23 ± 0.15
Oxoacids	0.046 ± 0.028
Total	0.60 ± 0.18
GC/MS <sub>total</sub> , %	35
HPLC <sub>total</sub> , %	4
TC, %	2
<i>Polycarboxylic Acids</i>	
Triacids	0.009 ± 0.004
GC/MS <sub>total</sub> , %	0.5
HPLC <sub>total</sub> , %	0.05
TC, %	0.03

the column material through forces that are not disrupted by increasing ionic strength (e.g., hydrophobic compounds).

[36] The correlation between UWSOC/WSOC and WSOC/TC (Figure 5b) was found to be very good ( $r^2 = 0.83$ ); i.e., samples with a higher water-soluble fraction (WSOC/TC) yielded lower recoveries (higher fraction of species not detected by HPLC/UV). This suggests that the WSOC unaccounted for has an important role with respect to the soluble fraction.

### 3.2.3. Molecular Speciation

[37] Molecular speciation was performed on the water extracts using GC/MS. A discussion on the method, the identified compounds, and their probable sources is presented by *Graham et al.* [2002]. The concentrations of the compounds identified by GC/MS are expressed in mass carbon per volume air (micrograms per cubic meter) in this paper in order to allow direct comparison with the rest of the measurements and to determine how much of the various fractions (TC, OC, WSOC, etc.) could be accounted for by this technique.

[38] The identified compounds were classified into eight different groups (Table 2). An average total mass concentration of  $\sim 5 \mu\text{g m}^{-3}$ , corresponding to a carbon mass concentration of  $\sim 2.0 \mu\text{g m}^{-3}$ , was estimated. This accounts for, on average,  $6 \pm 1\%$  of TC,  $11 \pm 2\%$  of WSOC, and about  $15 \pm 3\%$  of the material recovered by HPLC. The neutral compounds (sugars, anhydrosugars, sugar alcohols, and neutral aromatics) made up, on average, 65% of the carbonaceous material identified by GC/MS. By far, the most abundant were the anhydrosugars, representing about 61% of the determined mass. From this group, levoglucosan (a major product of cellulose pyrolysis and a tracer for biomass burning [*Shafizadeh*, 1984; *Simoneit et al.*, 1999]) accounted for between 87 and 91% [*Graham et al.*, 2002].

This compound accounted for only about 4% of TC, however, although it is about 54% of the material identified by GC/MS.

[39] To see how much of the fraction identified by HPLC/UV could be accounted for by GC/MS, we further classified the eight groups of GC/MS identified compounds into N, MDA, and PA (Table 2). On average, about 9, 4, and 0.05% of the three HPLC fractions, N, MDA, and PA, respectively, could be accounted for by the GC/MS technique, leaving about 87% unaccounted. Some caution is needed in interpreting these results because of the possible losses of material during the HPLC/UV analyses (as discussed in the previous section) and during the GC/MS analyses [*Graham et al.*, 2002] and because neutral compounds identified by GC/MS absorb inefficiently at the wavelength of detection for the HPLC/UV technique (at 254 nm). The identified compounds represent a relatively small fraction of the WSOC, suggesting that a large amount of the WSOC may be composed of high molecular weight and polar compounds with multifunctional groups, very difficult to derivatize and to separate by GC/MS.

[40] Compiling all of the information we obtained from the various analyses, a chemical and mass balance of the carbonaceous aerosol found during the burning period was carried out (Figure 6). Here the BC concentrations used were the ones from the thermal analyses after water extraction ( $\text{BC}_{\text{water}}$ , Table 1), which are the most representative considering the emphasis in the characterization of the water-soluble fraction.

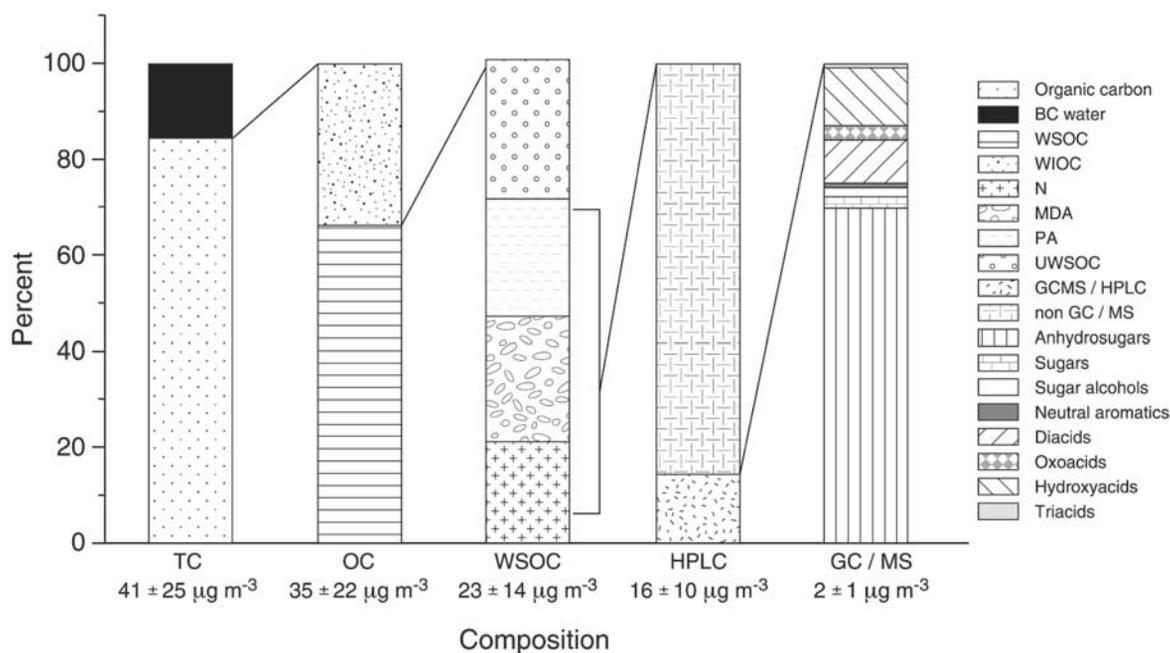
### 3.3. Biomass Burning as a Source of the Water-Soluble Organic Components

[41] Figures 7a and 7b show that the concentrations of all of the different species were highest when burning was most pronounced and decreased at the end of the campaign (corresponding to the beginning of the wet season). This indicates that biomass burning was the major source of most of the identified species.

[42] The use of two major species that serve as specific indicators of combustion ( $\text{BC}_{\text{water}}$  and levoglucosan) additionally confirmed that biomass burning is an important source of the WSOC. Good correlations ( $r^2$  between 0.84 and 0.99) were found between the water-soluble species (i.e., WSOC, N, MDA, and PA) and  $\text{BC}_{\text{water}}$  and levoglucosan (Table 3). Since  $\text{BC}_{\text{soot}}$  and, in this case,  $\text{BC}_{\text{water}}$  can originate either from biomass combustion, or fossil fuel combustion, it is worth to noting here the very good correlation between  $\text{BC}_{\text{water}}$  and levoglucosan ( $r^2 = 0.92$ ), suggesting that most of the  $\text{BC}_{\text{water}}$  originated from biomass burning. Additional evidence supporting that the main source of the BC species and the carbonaceous aerosol, in general, during the dry season is the burning of biomass is presented by *Artaxo et al.* [2002]. That study clearly shows how drastic was the increase in the concentration of carbonaceous aerosols from the wet to the dry season (up to 35 and 53 times higher in terms of the TC and the elemental carbon, respectively).

### 3.4. Polyacidic Fraction and Humic-Like Matter

[43] Several studies have shown that high molecular weight compounds may constitute a significant fraction of the organic component of atmospheric aerosols [*Gelencsér et al.*, 2000b; *Krivácsy et al.*, 2000, and references therein].



**Figure 6.** Apportionment of the carbonaceous aerosol chemical composition.  $TC = BC_{\text{water}} + OC$ ,  $OC = WIOC + WSOC$ ,  $WSOC = UWSOC + HPLC_{\text{total}}$  or  $WSOC = UWSOC + (N + MDA + PA)$ ,  $HPLC_{\text{total}} = \text{nonGC/MS} + \text{GC/MS}$ , and  $GC/MS = \text{anhydrosugars} + \text{sugars} + \text{sugar alcohols} + \text{neutral aromatics} + \text{diacids} + \text{hydroxyacids} + \text{oxoacids} + \text{triacids}$ .

These studies have demonstrated experimentally to some extent that these compounds have physical and chemical properties similar to humic acids. As a result, the term “humic-like substances” has been adopted by most researchers to denote this macromolecular material present in atmospheric aerosols, although a few have employed the more general term “macromolecular compounds” (MMC).

[44] There is not much detailed information in terms of the chemical identity of HULIS. However, *Decesari et al.* [2000] suggested that the structure of the water-soluble polyacidic compounds observed by  $^1\text{H}$  NMR is strictly analogous to that of other naturally occurring polyacids: the humic substances. In addition, they found that a commercially available standard of water-soluble HULIS exhibited a chromatographic behavior similar to the PA. Furthermore, *Krivácsy et al.* [2000], with the use of size-exclusion chromatography/mass spectrometry and capillary electrophoresis, also have suggested that HULIS may be polyacidic in nature. These results suggest a strong connection between the class of polycarboxylic acids and the humic-like substances, at least for the fraction of HULIS soluble in water.

#### 3.4.1. Biomass Burning as a Source of Humic-Like Matter

[45] It is important to stress, however, that unlike for true humic acids, soils may not necessarily be the origin for these fine aerosol phase compounds. Indeed, some authors have postulated that HULIS may be derived primarily from biomass combustion [*Mukai and Ambe*, 1986; *Facchini et al.*, 1999a; *Zappoli et al.*, 1999]. Conclusive evidence for this hypothesis, however, has been lacking to date.

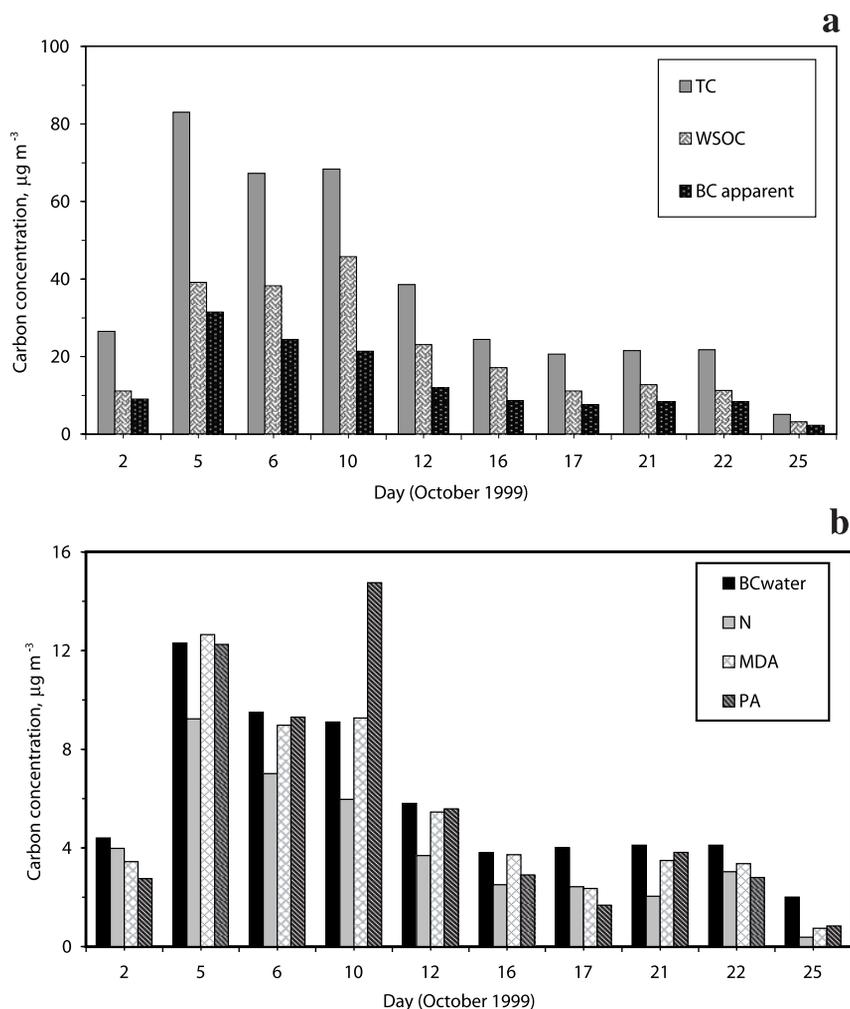
[46] The current study provided us with a very good opportunity to determine if biomass burning really repre-

sents a significant source for atmospheric PA and therefore, probably, HULIS, because the sampling was carried out in very close proximity to biomass burning activity and also extended over a period of time during which the intensity of the burning changed. As detailed below, we believe that the results of this study provide conclusive evidence that biomass burning may indeed be a major source of HULIS in atmospheric aerosols.

[47] Given that HULIS has been suggested to be polyacidic in nature [*Decesari et al.*, 2000; *Krivácsy et al.*, 2000], it is to be expected that any water-soluble HULIS would be found in the PA fraction separated by the HPLC/UV procedure, provided they can be eluted from the column. Our results for the samples collected at FNS show that PA constitute, on average, 14% of TC in the sampled aerosols. Moreover, a clear increase in concentration of the PA fraction with biomass burning (as indicated by  $BC_{\text{water}}$  and levoglucosan concentrations) was observed, with regression analysis of PA with  $BC_{\text{water}}$  and levoglucosan yielding  $r^2$  values of 0.84 and 0.89, respectively (Table 3 and Figure 7). This is strong evidence that PA and therefore HULIS are generated in significant amounts during biomass burning. It is important to observe that, in analogy to naturally occurring HULIS, similar structures with higher molecular weight could be water insoluble and hence could be found in the water-insoluble fraction. This hypothesis needs further investigation.

#### 3.4.2. Possible Mechanism of Formation of Humic-Like Substances During Biomass Combustion Processes

[48] Given that biomass burning appears to be a definite and significant source for HULIS, the question is raised as to how these compounds may be formed by the biomass combustion process. One possibility is that some or all of



**Figure 7.** Temporal variation for the carbon mass concentrations of the species determined at FNS: (a) TC, BC<sub>app</sub>, and WSOC; (b) BC<sub>water</sub>, N, MDA, and PA.

the HULIS is simply humic matter from soil and/or decaying leaf litter lofted during combustion. Another possibility is that it may actually be generated through chemical transformations of the biomass fuel and/or the initial volatile combustion products. Combustion is a highly complex process involving many physical processes and chemical reactions. Some detailed aspects of the overall process have been outlined by *Shafizadeh* [1984] and *Andreae and Merlet* [2001]. In the case of plant biomass, combustion involves primarily the thermal breakdown of polymeric carbohydrate and lignin materials, which may make up over 90% of the dry weight of plant matter. It is possible to envisage that incomplete breakdown of these polymeric structures may result in the generation of relatively high molecular weight species. In the case of cellulose, *Köll et al.* [1990] have already shown that oligosaccharides are primary pyrolysis products. The species that have been identified are all neutral; however, it is not unlikely that a number of the hydroxyl functional groups within such structures could be oxidized to carboxylate groups during combustion, yielding poly-acidic species, which contribute to the HULIS fraction. Important in this regard is the observation of *Shafizadeh* [1984] that the content of carboxylate groups in char

increases during the initial stages of combustion. Lignin breakdown may likewise yield fragments that are relatively high molecular weight in nature and which contribute to the HULIS content of biomass burning aerosols. These fragments may constitute a large fraction of the insoluble organic aerosol material.

[49] A second possible route to HULIS involves the recombination of the volatile, low molecular weight, primary

**Table 3.** Regression Slopes and Correlation Coefficients for Carbon Concentrations of Carbonaceous Species Determined Against Carbon Concentrations of Indicators of Biomass Burning, Levoglucosan, and BC<sub>water</sub><sup>a</sup>

Species	Levoglucosan			BC <sub>water</sub>		
	Slope	Standard Error	$r^2$	Slope	Standard Error	$r^2$
BC <sub>water</sub>	3.32	0.44	0.92	NA	NA	NA
WSOC	11.73	1.31	0.94	4.17	0.58	0.86
N	2.76	0.40	0.91	0.79	0.06	0.96
MDA	3.83	0.41	0.94	1.13	0.05	0.99
PA	3.68	0.57	0.89	1.34	0.20	0.84

<sup>a</sup>Carbon concentrations are in micrograms per cubic meter. NA, not applicable.

products of combustion. The mixture of organic compounds emitted during biomass burning is enormous and includes a large variety of compounds bearing multiple hydroxyl, carboxylate, carbonyl and other functional groups [Shafizadeh, 1984; Pouwels *et al.*, 1989; Edye and Richards, 1991; Galleti and Bocchini, 1995]. A number of them could feasibly undergo condensation reactions with other molecules to build up higher molecular weight structures. Shafizadeh [1984] has already suggested that oligosaccharides and polysaccharides may derive from repolymerization of sugar derivatives produced during the pyrolysis of cellulose and hemicellulose structures in wood.

[50] Significantly, the high molecular weight species (HULIS) formed by the combustion process (by either of the proposed mechanisms) might have thermal and oxidation properties approaching those of black carbon due to their bulky structure and unsaturated character. Such species could, therefore, be potentially responsible for the  $BC_{app}$  peak in the thermograms of the nonextracted smoke aerosol samples (Figures 3a and 3b).

#### 3.4.3. Potential Impacts of Humic-Like Substances on Cloud Properties

[51] Although some HULIS could be insoluble in the aqueous phase, a significant fraction of these compounds (PA) are water soluble. In our study, PA accounted for  $25 \pm 6\%$  of the WSOC fraction. Indeed, the sample with the highest concentration of WSOC (FNS4, 10 October 1999, Figure 6) also showed the highest concentration of PA. It is possible that some or even all of the material not recovered during the HPLC/UV technique is also HULIS, so that up to about 50–60% of WSOC could potentially be composed of this class of compounds. The water solubility and potential surface tension effects of HULIS (or at least a significant fraction of it) raise interesting and important questions about their potential role in cloud processes and climate forcing. Facchini *et al.* [1999b] found a significant decrease in surface tension of cloud/fog water that had been evaporated to concentrations expected in droplets near their critical diameter. A reduction in surface tension enhances cloud condensation nuclei activity and could lead to an increase in droplet population and, hence, in cloud albedo and lifetime. Recently, Facchini *et al.* [2000] compared the effects of the three separated organic fractions (N, MDA, and PA) on surface tension and showed that PA were the most effective surface-active species (3 times more effective than MDA and 1 order of magnitude more than N). The results of the present study, coupled with the conclusions of Facchini *et al.* [1999b, 2000], suggest a potential influence of PA in shaping the CCN activity of biomass burning aerosols. These results support the findings that pure organic smoke from cellulose is able to form CCN without the presence of sulfates or other inorganic compounds [Novakov and Corrigan, 1996]. As a large fraction of the biomass burning aerosol consists of HULIS, the solubility and surface tension effects of PA may play an important role in increasing the CCN activity during the dry season.

[52] CCN measurements in the Amazon Basin during the wet and dry seasons show that biomass burning aerosol does serve as CCN [Roberts *et al.*, 2002]. Results showed that concentrations during the dry season were about an order of magnitude higher than those during the wet season. Since the

CCN activity of aerosols has a direct impact on cloud properties and biomass smoke particles can perturb the radiation balance by modifying cloud microphysics [Kaufman and Fraser, 1997; Rosenfeld, 1999], PA may ultimately have a significant role in modifying the radiation balance and hydrological cycle in regions heavily influenced by biomass burning, such as Amazonia, Indonesia, South Africa, and Central Africa.

## 4. Conclusions

[53] The thermal analyses of fine carbonaceous aerosols collected over the Amazon Basin during the dry-to-wet season transition (September–October 1999) suggest that a significant fraction (30 to 70%) of the apparent BC is high molecular weight organic matter with thermal and oxidative properties similar to  $BC_{soot}$ . About 50% of this apparent BC material is water soluble.

[54] The chemical and mass balance of the carbonaceous aerosol (TC) showed that the black carbon remaining after water extraction ( $BC_{water}$ ) and the water-soluble organic fraction (WSOC) accounted for about 16% and 56%, respectively. The three classes of compounds obtained by the HPLC analyses (neutrals, monocarboxylic and dicarboxylic acids, and polycarboxylic acids) represented about 70% of the WSOC. Molecular speciation using GC/MS could only account for about 11% of the WSOC.

[55] Strong evidence of biomass burning as a major source of the identified water-soluble organic species (i.e., WSOC, N, MDA, and PA) is supported by the increase in the concentrations of these species when burning events were most pronounced and by the good correlations ( $r^2$  between 0.84 and 0.99) of these species with  $BC_{water}$  and levoglucosan.

[56] Owing to the polyacidic nature of HULIS, it is expected that the PA fraction will correspond to or at least include a fraction (the water-soluble fraction) of these humic-like substances. These compounds could be formed during the burning process either via the incomplete breakdown of polymeric structures such as cellulose and lignin or by the recombination of the volatile, low molecular weight, primary products of combustion. PA and probably HULIS, because of its bulky structure and highly unsaturated character, may be responsible for at least part of the apparent BC detected in the thermal combustion analyses. These compounds also represent a significant fraction of the WSOC (~26%). Previous studies have shown that the PA water-soluble fraction is effective at lowering the surface tension of cloud droplets; therefore it is possible that these compounds might play an important role in the CCN activity of biomass burning aerosols and, consequently, in cloud microphysics, radiative processes, and climate forcing.

[57] In our ongoing studies, we will emphasize the characterization of the WSOC fraction and the effects that this fraction could have on CCN activity. We plan to measure the surface tension effects of PA (as well as the other fractions) in the sampled biomass burning aerosols and then incorporate the results into cloud models in order to investigate their potential effects on the radiation budget and precipitation patterns in regions where biomass burning contributes significantly to the total aerosol mass.

[58] **Acknowledgments.** This study is part of the Large-Scale Atmosphere Biosphere Experiment in Amazonia (LBA). We thank our Brazilian partners (Eduardo Fernandes, Alcides Camargo, and Marcos Moura) for their help during the campaign, and we thank T. Novakov and T.W. Kirchstetter for their collaboration with the thermal and optical transmission analyses. The staff of the MPIC mechanical workshop is gratefully acknowledged for help with building the sampling systems. P. Artaxo acknowledges financial support by FAPESP through grant FAPESP 97/11358-9. This research was supported by the German Max Planck Society and the Environmental and Climate Program of the European commission (project EUSTACH-LBA).

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