

Water-soluble organic compounds in biomass burning aerosols over Amazonia

1. Characterization by NMR and GC-MS

Bim Graham,¹ Olga L. Mayol-Bracero,² Pascal Guyon,³ Gregory C. Roberts,⁴ Stefano Decesari,⁵ M. Cristina Facchini,⁵ Paulo Artaxo,⁶ Willy Maenhaut,⁷ Peter Köll,⁸ and Meinrat O. Andreae³

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[1] As part of the European contribution to the Large-Scale Atmosphere-Biosphere Experiment in Amazonia (LBA-EUSTACH), aerosols were sampled at representative pasture and primary rainforest sites in Rondônia, Brazil, during the 1999 “burning season” and dry-to-wet season transition (September–October). Water-soluble organic compounds (WSOCs) within the samples were characterized using a combination of ¹H Nuclear Magnetic Resonance (NMR) spectroscopy for chemical functional group analysis, and Gas Chromatography–Mass Spectrometry (GC-MS) for identification and quantification of individual low-molecular-weight compounds. The ¹H NMR analysis indicates that WSOCs are predominantly aliphatic or oxygenated aliphatic compounds (alcohols, carboxylic acids, etc.), with a minor content of aromatic rings carrying carboxylic and phenolic groups. Levoglucosan (1,6-anhydro-β-D-glucose), a well-known cellulose combustion product, was the most abundant individual compound identified by GC-MS (0.04–6.90 μg m⁻³), accounting for 1–6% of the total carbon (TC) and 2–8% of the water-soluble organic carbon (WSOC). Other anhydrosugars, produced by hemicellulose breakdown, were detected in much smaller amounts, in addition to series of acids, hydroxyacids, oxoacids, and polyalcohols (altogether 2–5% of TC, 3–6% of WSOC). Most correlated well with organic carbon, black carbon, and potassium, indicating biomass burning to be the major source. A series of sugar alcohols (mannitol, arabitol, erythritol) and sugars (glucose, fructose, mannose, galactose, sucrose, trehalose) were identified as part of the natural background aerosol and are probably derived from airborne microbes and other biogenic material. The bulk of the WSOCs (86–91% WSOC) eluded analysis by GC-MS and may be predominantly high-molecular weight in nature.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution--urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere--composition and chemistry *KEYWORDS:* organic aerosols, biomass burning, GC-MS, NMR, levoglucosan, Amazon.

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1. Introduction

[2] Biomass burning is increasingly being recognized as a globally important source of radiatively and chemically active

trace gases and aerosols [e.g., *Crutzen and Andreae, 1990; Crutzen and Goldammer, 1993*]. The majority of biomass burning is carried out in tropical regions like the Amazon Basin, where slash-and-burn techniques are widely utilized for both primary deforestation and seasonal burning of secondary forests and pastures [*Fearnside, 1990*]. The intense convective activity associated with the tropics means that the products of these burning activities may be rapidly uplifted to high altitudes [*Greco et al., 1990; Andreae et al., 2001*], where they can be transported over long distances and have effects on global air quality, climate, and the biogeochemical distribution of nutrients. This potential for far-reaching impacts has been part of the motivation for intensive measurement campaigns, such as the Smoke, Cloud, Aerosol, and Radiation–Brazil (SCAR-B) experiment [*Kaufman et al., 1998*] and the dry season Amazon Boundary Layer Ex-

¹CSIRO Atmospheric Research, Melbourne, Australia.

²Institute for Tropical Ecosystem Studies, University of Puerto Rico, Rio Piedras, Puerto Rico, USA.

³Department of Biogeochemistry, Max Planck Institute for Chemistry, Mainz, Germany.

⁴Scripps Institute for Oceanography, La Jolla, California, USA.

⁵Institute for Atmospheric and Oceanic Sciences, CNR, Bologna, Italy.

⁶Institute for Physics, University of São Paulo, São Paulo, Brazil.

⁷Institute for Nuclear Sciences, Ghent University, Ghent, Belgium.

⁸Department of Chemistry, University of Oldenburg, Oldenburg, Germany.

periment (ABLE-2A) [Harriss *et al.*, 1988], which have sought specifically to gain a better understanding of the environmental effects of biomass burning.

[3] Aerosol particles emitted during biomass burning are predominantly in the form of submicrometer, accumulation mode particles (smoke) [Reid and Hobbs, 1998; Kleeman *et al.*, 1999]. These can affect Earth's albedo, as well as decrease local and regional visibility, because of their light-scattering properties [Crutzen and Andreae, 1990; Andreae, 1995]. In addition, smoke particles can act as efficient cloud condensation nuclei (CCN), which modify the cloud droplet size distribution and hence the reflectivity of clouds [Rogers *et al.*, 1991; Roberts *et al.*, 2002]. On a global scale, these combined direct and indirect radiative effects are estimated to be responsible for a net radiative forcing that is comparable to that from sulfate aerosol [Penner *et al.*, 2001]. The alteration of cloud microphysical processes by smoke aerosols may also lead to changes in precipitation patterns, as confirmed by recent satellite data from the Tropical-Rainfall-Measuring Mission (TRMM) which show that rain processes in convective tropical clouds may be effectively suppressed upon contact with smoke aerosols [Rosenfeld, 1999].

[4] Vegetation is the major fuel consumed in biomass burning and is composed predominantly of cellulose, hemicellulose and lignin [Pettersen, 1984]. Together, these three polymeric materials account for over 90% of the dry weight of most vascular plants, with the remaining mass being composed of various lipids, proteins, and other metabolites, as well as minerals and water. The combustion of the organic components of biomass involves a complex series of physical transformations and chemical reactions, including pyrolysis, depolymerization, water elimination, fragmentation, oxidation, char formation, and volatilization [Shafizadeh, 1984]. During the earlier stages of combustion, known as flaming combustion, hydrocarbons volatilized from the decomposing biomass are rapidly oxidized in a flame upon mixing with air. Once the flux of these combustible volatile compounds falls below a critical level, however, flaming expires and smoldering or glowing combustion commences. This lower-temperature process involves a gradual gas-solid phase reaction between oxygen and the remaining reactive char and emits large amounts of incompletely oxidized pyrolysis products. Many of these compounds have sufficiently low vapor pressures to be found in the particulate phase when released into the ambient atmosphere. For this reason, organic matter is most often found to constitute the major fraction of smoke aerosols, sometimes accounting for over 90% of the total aerosol mass [Yamasoe *et al.*, 2000; Andreae and Merlet, 2001].

[5] The organic material within smoke aerosols is composed of a highly complex mixture of compounds covering a wide range of molecular structures, physical properties, and reactivities [Jacobson *et al.*, 2000]. This complexity renders complete characterization at the molecular level difficult. Nevertheless, compositional data for this fraction is essential for improving our understanding of the contribution of smoke aerosols to atmospheric chemistry and climate. Numerous studies, predominantly laboratory-based, have contributed toward our current knowledge of the organic products of biomass combustion. Many of these have involved controlled pyrolysis of individual components of plant matter [e.g., Shafizadeh, 1984; Köll *et al.*, 1990, 1991], or the burning of actual vegetation samples [e.g., Abas *et al.*, 1995; Simoneit *et al.*, 1999]. There have also been some characterization studies of

smoke aerosols collected during field campaigns [Fang *et al.*, 1999; Narukawa *et al.*, 1999]. As a result of this extensive body of work, sugar derivatives have been identified as major products of cellulose and hemicellulose pyrolysis [e.g., Shafizadeh, 1984; Simoneit *et al.*, 1999] and substituted methoxyphenols as primary products of lignin breakdown [e.g., Hawthorne *et al.*, 1988; Simoneit *et al.*, 1993; Kjallstrand *et al.*, 1998]. A great many other solvent-extractable compounds have also been identified, including series of relatively high molecular weight hydrocarbons (waxes, terpenes), ketones, acids, alcohols, sterols, phenols, olefins, and polycyclic aromatic hydrocarbons (PAHs) [e.g., Abas *et al.*, 1995; Fang *et al.*, 1999]. A number of these compounds serve as useful tracers for biomass burning [Simoneit *et al.*, 1993, 1999, 2000; Simoneit and Elias, 2000].

[6] Aside from a few rare field studies that have shown that water-soluble organic acids are significantly enriched in smoke aerosols [e.g., Andreae *et al.*, 1988; Narukawa *et al.*, 1999; Yamasoe *et al.*, 2000], very little work has gone into the sampling of ambient fires to determine the quantity and molecular forms of oxygenated, water-soluble organics produced in biomass burning. The need for the analysis of this fraction, however, has gained increased pertinence in light of a report by Novakov and Corrigan [1996] that the burning of cellulose produces smoke particles that are nearly 100% water-soluble, coupled with mounting evidence that water-soluble organic compounds (WSOCs) may contribute toward the CCN activity of aerosols [Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Facchini *et al.*, 1999a, 2000]. Moreover, the high concentrations of WSOCs within smoke aerosols suggest that they may play a significant role in the aqueous-phase chemistry occurring within cloud droplets nucleated by smoke.

[7] Candidates for WSOCs within aerosols include dicarboxylic acids, ketoacids, dicarbonyls, polyalcohols, hydroxyamines, amino acids, and other multifunctional compounds [Saxena and Hildemann, 1996]. There is also increasing evidence that a significant portion could be composed of high-molecular-weight compounds with properties similar to humic substances [Mukai and Ambe, 1986; Havers *et al.*, 1998; Zappoli *et al.*, 1999; Facchini *et al.*, 1999b; Decesari *et al.*, 2000]. To date, however, attempts to characterize WSOCs in aerosols have focused almost exclusively on low-molecular-weight acidic compounds [e.g., Kawamura, 1993; Kawamura and Ikushima, 1993; Kawamura *et al.*, 1996; Narukawa *et al.*, 1999; Limbeck and Puxbaum, 1999; Neusüss *et al.*, 2000]. In most cases these species can account for at most 15% of the water-soluble organic carbon (WSOC). Thus there is a clear need to develop and apply additional methods for the analysis of other classes of WSOCs.

[8] This paper describes our efforts to further speciate the WSOCs within biomass burning aerosols. The samples analyzed in this work were collected in the Brazilian State of Rondônia, located on the southwestern periphery of the Amazon Basin, as part of the European contribution to the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA-EUSTACH). While the vast Amazonian rain forest provides a year-round release of biogenic particles, formed either by direct emission (primary) or by gas-to-particle conversion of biogenic gases (secondary) [Artaxo *et al.*, 1988, 1990; Artaxo and Hansson, 1995], a massive injection of smoke particles occurs each dry season which overwhelms this natural background material. The sampling period was specifically chosen to encompass part of this "burning season" as well as the dry-to-wet season transition (September-October 1999). We

used a combination of ^1H NMR spectroscopy [Decesari *et al.*, 2000] and GC-MS in an attempt to characterize the WSOCs fraction of the aerosols in terms of the abundance of major chemical functional groups, as well as to identify individual compounds. These analyses confirm that the WSOCs fraction is composed of a complex mixture of highly oxygenated compounds, both aromatic and aliphatic in nature. Numerous combustion products were positively identified, including a number of compounds previously unobserved in atmospheric aerosols. The inclusion of the dry-to-wet season transition period within the sampling regime allowed us to more accurately assess the importance of biomass burning as a source for the various compounds.

2. Sampling and Analytical Methods

2.1. Aerosol Sampling

[9] Sampling of aerosols was carried out at a representative pasture site (Fazenda Nossa Senhora Aparecida (FNS), $10^\circ 45' 44''$ S, $62^\circ 21' 27''$ W, 315 m above sea level (asl) from 1–29 Oct 1999, and a primary rainforest site (Reserva Biológica Jarú (RBJ), $10^\circ 04' 55''$ S, $61^\circ 55' 48''$ W, 110 m asl) from 1 September to 25 October 1999, as part of the LBA-EUSTACH-2 campaigns. Both sites are located within Rondônia, Brazil, a region where extensive deforestation has occurred in recent years (for further details on the campaigns and sites, see *Andrae et al.* [2002]). At both locations, high volume (HiVol) dichotomous virtual impactors [Solomon *et al.*, 1983] were used to separate and collect aerosol particles in “coarse” (aerodynamic diameter, $D_p > \sim 2.5 \mu\text{m}$) and “fine” fractions. During the operation of this sampler, coarse particles are impacted onto a filter behind an orifice directly in line with the inlet at a flow of $\sim 30 \text{ L min}^{-1}$. Fine particles are diverted by a much stronger flow ($\sim 300 \text{ L min}^{-1}$) perpendicular to the inlet flow and impact on a second filter. The forest site sampler was mounted on the RBJ tower A at a height of ~ 50 m above the forest floor (~ 20 m above the top of the forest canopy), while the pasture site sampler was placed on the FNS tower A ~ 5 m above ground level. Both samplers were attached to retractable booms that extended ~ 2 m away from the side of the towers during sampling. Samples were collected on Pallflex quartz fiber filters (prebaked for at least 15 hours at 600°C) for between 12 and 72 hours, depending on aerosol loadings. Loaded filters were placed immediately in clean glass jars (prebaked for at least 15 hours at 600°C) and stored in the dark at -18°C until the time of analysis. Filter blanks were obtained using the same loading and unloading procedure as for normal filters but with a sampling time of only 15 s.

[10] Because of the operational design of the HiVol sampler, one tenth of the fine fraction particles entering the inlet is deposited on the coarse fraction filter. In the case of smoke samples, which are composed predominantly of submicrometer particles [Reid and Hobbs, 1998; Kleeman *et al.*, 1999], this means that the majority of material depositing on the coarse fraction filter will actually be fine particles. For this reason the analyses described herein were only performed on the fine fraction filters.

2.2. Thermal Analysis

[11] The total carbon (TC), organic carbon (OC), and black carbon (BC) contents of the samples were measured by the thermal-optical transmission technique of Birch and Cary [1996], using the procedure described for laboratory 11 by

Schmid *et al.* [2001]. The WSOC content of aqueous aerosol extracts (prepared by soaking filter punches in 3 mL of Milli-Q water overnight and filtering through a $0.22 \mu\text{m}$ pore-size PTFE filter) was determined using a Shimadzu TOC-5000A liquid analyzer according to the method described by Decesari *et al.* [2000] and Mayol-Bracero *et al.* [2002]. The inorganic carbon content of the extracts was found to be below the detection limit of $0.008 \mu\text{g C mm}^{-2}$ of filter.

2.3. Proton Nuclear Magnetic Resonance (^1H NMR) Spectroscopy

[12] Extracts of five aerosol samples from the pasture site were analyzed by ^1H NMR spectroscopy according to the method of Decesari *et al.* [2000]. Extraction of the samples was performed with D_2O , containing 0.05% (by weight) sodium 3-(trimethylsilyl)-2,2,3,3- d_4 -propionate (TSP d_4) as an internal standard. The spectra were recorded on a Varian GEMINI 300 spectrometer at 300 MHz in a 5 mm probe. Further details are given by Decesari *et al.* [2000].

2.4. Gas Chromatography-Mass Spectrometry (GC-MS)

[13] For each sample, up to eight filter punches (1.5 cm diameter) were placed in a capped glass vial, together with 4 mL of Milli-Q water containing phenyl- β -D-glucoside (20.5 μg), 3,3-dimethylglutaric acid (3.2 μg), and 4-hydroxybutyric acid (2.8 μg) as internal standards. The mixture was shaken for 20 s every 5 min with a vortex agitator over a period of 30 min. A 2 mL aliquot was then filtered through a $0.45 \mu\text{m}$ pore-size PTFE syringe filter that had been thoroughly pre-rinsed with Milli-Q water, and evaporated at room temperature in a 3 mL borosilicate glass vial with a gentle stream of pure nitrogen. Two 1 mL aliquots of dichloromethane were added and evaporated with the nitrogen stream to azeotrope off any residual water. The dried residue was then derivatized in a two-step procedure. First, 70 μL of 2% methoxyamine hydrochloride/pyridine (Pierce) was added, the vial closed with a Teflon-lined cap, and the mixture heated to 70°C for 45 min. After cooling to room temperature and centrifuging to settle the solution to the bottom of the vial, 70 μL of bis(trimethylsilyl)trifluoroacetamide (BSTFA), containing 1% trimethylchlorosilane (TMCS) as a catalyst (Supelco), was then added, and the mixture heated to 70°C for an additional 30 min. After cooling to room temperature, samples were analyzed within 2 hours by GC-MS.

[14] A Hewlett-Packard (HP) 6890 GC-MSD was used for the analysis, with ionization achieved by electron impact at 70 eV. The capillary column used was a J&W Scientific DB-1 (methylsiloxane, $60 \text{ m} \times 0.32 \text{ mm ID}$, $0.25 \mu\text{m}$ thick film) fitted with a Supelco guard column (deactivated methylsiloxane, $1 \text{ m} \times 0.32 \text{ mm ID}$). The operating conditions were injection port temperature, 280°C ; interface temperature, 280°C ; column oven temperature, 75°C for 3 min, ramped at 5°C min^{-1} to 150°C , followed by $2.5^\circ\text{C min}^{-1}$ to 210°C , and then $10^\circ\text{C min}^{-1}$ to 290°C with a 10 min hold; helium carrier gas (flow rate of 2.3 mL min^{-1} at 75°C); 0.5–1 μL injection volume. The split/splitless injector was operated in the splitless mode for 1 min after injection of the sample. Regular replacement of the injection port liner and guard column was found to be necessary for this procedure because of the presence of large amounts of involatile, possibly high-molecular weight, compounds in the analyzed samples.

[15] For identification purposes, the mass spectrum of each peak was recorded in the total ion current mode of the mass

spectrometer, within a m/z range of 50 to 500. Identification of compounds was achieved using the 6th edition of the Wiley mass spectral database and then by comparing the mass spectra and retention times of the chromatographic peaks with those of authentic samples. For quantification, the mass spectrometer was scanned in the selective ion-monitoring mode with the monitoring of selected ions present in the mass spectra of the identified compounds. Calibration curves were constructed by analyzing aliquots of a stock solution of authentic standards that had been made up to 2 mL with water and evaporated and derivatized in the fashion described above. Duplicate analyses showed that the precision of the determination is typically 20%. Samples of the commercially unavailable compounds, arabinosan (1,5-anhydro- α -D-arabinofuranose), xylosan (1,5-anhydro- β -D-xylofuranose), 1,6-anhydro- β -D-glucofuranose, and *N*-acetyl-2-aminoglucosan (1,6-anhydro-2-acetamido-2-deoxyglucose) were synthesized according to published procedures [Köll *et al.*, 1973, 1982, 1990, 1991]. Authentic standards of all the other compounds were obtained from Sigma Chemical Company.

[16] Procedural blanks were also analyzed. Small amounts of glycerol, glyoxylic acid, pyruvic acid, and lactic acid were the only contaminants encountered. The concentrations reported here are corrected for the procedural blanks.

2.5. Ion Chromatography (IC)

[17] Aqueous aerosol extracts for IC analysis were prepared by agitating single filter punches (1.1 cm diameter) with 2 mL of Milli-Q water in capped plastic vials as described in section 2.4 and then centrifuging to settle the quartz fibers. Oxalate concentrations were determined using a Dionex AS4A-SC analytical column, ASRS-Ultra suppressor in chemical suppression mode (20 mM sulfuric acid), 2 mM Na_2CO_3 eluent, and conductivity detection. Potassium concentrations were measured using a Dionex CS14 analytical column, CSRS-Ultra suppressor in chemical suppression mode (20 mM tetrabutylammonium hydroxide), 10 mM methanesulfonic acid/10% methanol eluent, and conductivity detection.

3. Results and Discussion

[18] During much of the sampling period, both measurement sites were heavily influenced by biomass burning activities. Burning of pasture, secondary forest, charcoal, and refuse were carried out in very close proximity to the FNS pasture site, while slash-and-burn clearing of primary rainforest occurred near the boundaries of the RBJ. Thus it was expected that combustion products from biomass would dominate the sampled aerosols.

[19] Concentration ranges for TC in the samples discussed herein were 3.0–82.2 $\mu\text{g m}^{-3}$ and 1.6–38.3 $\mu\text{g m}^{-3}$ for the pasture and forest site samples, respectively, while WSOC ranged between 2.2 and 39.6 $\mu\text{g m}^{-3}$ (measured for pasture site samples only). The higher concentrations of TC observed at the pasture are consistent with the fact that burning activities were carried out in closer proximity to this site. TC and WSOC concentrations were highest during extreme haze periods associated with burning, and lowest following periodic rainfall events, especially toward the end of the campaign (dry-to-wet transition) when rainfall frequency increased and burning activity began to cease. This suggests that biomass burning was the primary source for TC and WSOC in the aerosols. Moreover, both TC and WSOC showed temporal variations

similar to BC, an indicator for combustion [Andreae, 1983; Penner *et al.*, 1993; Lioussé *et al.*, 1996; Maenhaut *et al.* 1996a]. Further in-depth discussions of the temporal variations of TC, BC and other combustion indicators, which highlight the overwhelming contribution of biomass burning to aerosol loadings during the sampling period, are provided by Mayol-Bracero *et al.* [2002] and Artaxo *et al.* [2002].

[20] WSOC was found to account for 41–74% of TC at the pasture site. Novakov and Corrigan [1996] have reported WSOC/TC ratios of more than 40% for smoldering combustion and less than 5% for flaming combustion. This suggests that the aerosols sampled in the current study were derived predominantly from smoldering combustion of biomass. The WSOC/TC ratios are higher than those reported by Narukawa *et al.* [1999] for smoke samples collected during the 1997 Indonesian forest fires (average of 29% for smoke haze periods). This may be due to differences in the composition of the biomass from the two regions (e.g., water content). In addition, sampling in the current study was carried out in closer proximity to actual fires, and at ground level, which tends to bias toward smoldering emissions (and hence water-soluble species), since these are emitted during the less vigorous phases of a fire [Andreae *et al.*, 1996]. The high WSOC/TC ratios observed further highlight the potential for WSOC to be important in shaping microphysical processes within clouds influenced by smoke aerosols.

[21] Two different techniques were employed in this work to characterize the WSOCs within the aerosol samples. First, to broadly characterize this fraction in terms of the chemical functional groups present, ^1H NMR spectra were recorded of the aqueous extracts of selected samples [Decesari *et al.*, 2000]. This technique has only rarely been utilized in the characterization of atmospheric aerosol extracts [Havers *et al.*, 1998; Decesari *et al.*, 2000]. Second, for identification and quantification of specific low-molecular-weight compounds, a newly developed analytical GC-MS procedure was employed.

3.1. NMR Spectroscopy

[22] ^1H NMR spectroscopy can provide useful information regarding the major organic functional groups of the aerosol water-soluble fraction. Five samples collected at the pasture site were analyzed by this method. Figure 1 shows the ^1H NMR spectra of samples collected on 5 and 25 October 1999, corresponding to the beginning and the end of the sampling period, respectively. A few sharp signals are attributable to individual compounds present at relatively high concentration. The major portions of the spectra, however, appear as continuous distributions of unresolved signals, suggesting a complex mixture of substances, each occurring in low concentration. The bulk of the total organic hydrogen atom (“proton”) distribution can be divided into four main categories: (1) Ar-H, aromatic protons (6.5–8.4 ppm); (2) H-C-O, protons attached to carbon atoms singly bonded to oxygen (3.5–4.1 ppm); (3) H-C-C=, aliphatic protons attached to carbon atoms adjacent to a carbonyl or aromatic group (2.0–3.4 ppm); and (4) H-C, aliphatic protons in extended alkyl chains (0.8–2.0 ppm).

[23] Other functional groups that could have been detected in regions of the spectra but for which low intensity (or no) signal were actually observed include aliphatic amines and sulfonates (2.9–3.2 ppm), aliphatic organic nitrates (4.1–5.0 ppm), hemiacetals and acetals (4.1–5.5 ppm) (except one peak of levoglucosan, see below), olefins (5–7 ppm), and nonhydrated aldehydes (9–10 ppm).

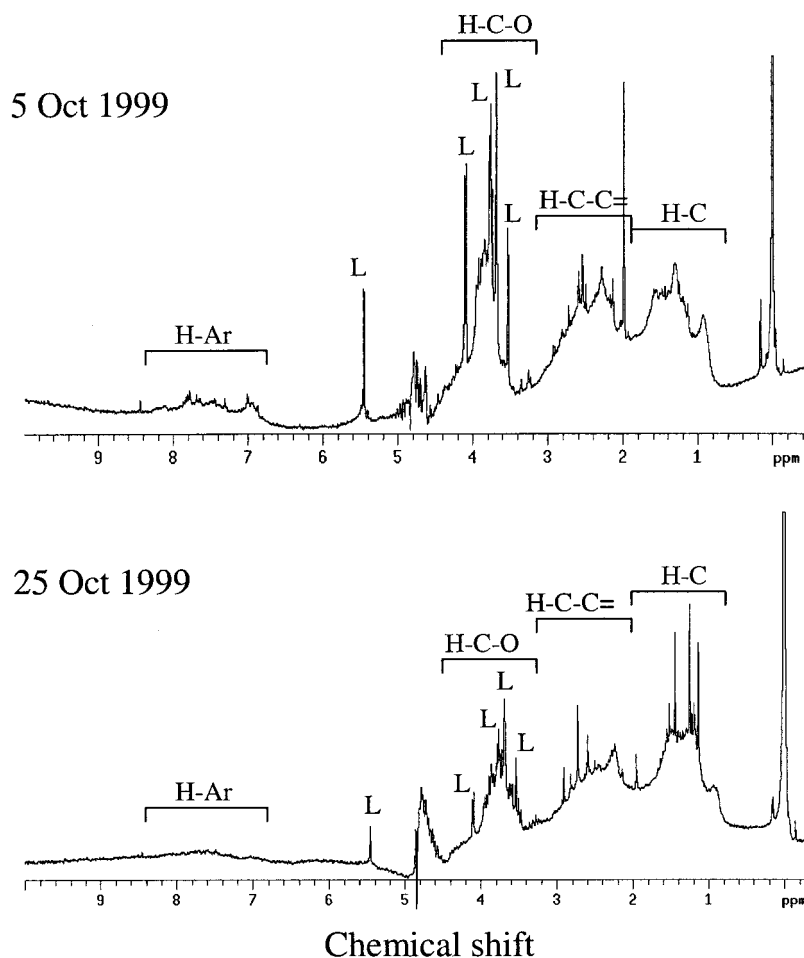


Figure 1. ^1H NMR spectra of the deuterated water extracts of aerosol samples collected at FNS (pasture site), Rondônia, Brazil, 1999, during heavy biomass burning (5 Oct 1999), and at the end of the dry season (25 Oct 1999). The reported chemical shifts are relative to the internal standard, TSPd_4 . Experimental details are given by *Decesari et al.* [2000]. The signals between 4.5–5 ppm are instrumental noise due to water suppression. Peaks marked “L” correspond to levoglucosan.

[24] The wide range of chemical shifts of the signals attributed to aromatic protons suggests the occurrence of substituted aromatic rings: phenols and alkylbenzenes (around 6.6–7.0 ppm); benzoic acids or esters and, perhaps, nitroaromatics

(>7.7 ppm). Other fine features of the spectral bands reveal some differences in the internal composition of the aliphatic moieties, which are more abundant in methyl groups (0.8–1.1 ppm) in the case of the sample from 5 October 1999, as compared to that from 25 October 1999. On the contrary, long chains and/or alicyclic moieties dominate the aliphatic structures in the latter sample.

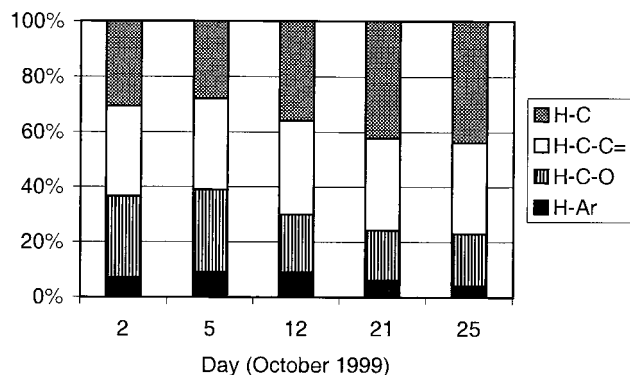


Figure 2. Normalized abundance of nonexchangeable protons in aqueous extracts of aerosol samples from FNS (pasture site), Rondônia, Brazil, 1999. The four categories are described in the text.

[25] The abundance of the four main categories of structural units listed above can be estimated from the area of the ^1H NMR bands (Figure 2). These distributions are characterized by a very high hydroxyl content, in particular in samples collected on 2 and 5 October 1999, corresponding to the burning season. In contrast, closer to the wet season the aliphatic moieties and H-C-C= groups dominate the average chemical structure of WSOCs. Intermediate compositions are observed during the transition period. The intensity of the band attributed to aromatics is more intense during the burning and the transition periods, whereas the sample from 25 October 1999 exhibits the lowest aromatic content.

[26] We conclude that WSOCs are composed of a very complex mixture of oxygenated organic compounds, both aliphatic and aromatic. It should be noted that ^1H NMR is inherently a low sensitivity technique for detection of highly

Table 1. Concentrations of Levoglucosan in Aqueous Extracts of Aerosol Samples From FNS (Pasture Site), Rondônia, Brazil, 1999, As Determined by ^1H NMR Spectroscopy^a

Sample	Levoglucosan Concentration		
	$\mu\text{g m}^{-3}$	%WSOC	%H-C-O
2 Oct.	1.7 (2.1)	7	21
5 Oct.	5.8 (6.9)	7	25
12 Oct.	1.2 (2.8)	3	13
21 Oct.	0.52 (1.2)	2	11
25 Oct.	0.15 (0.26)	2	11

^aConcentrations determined by GC-MS are also shown in parentheses for comparison. Column 3 shows the contribution of levoglucosan carbon to the total WSOC. Column 4 reports the contribution of levoglucosan to total hydroxyl H-C-O groups, determined by the integrated ^1H NMR spectral bands.

unsaturated functional groups, such as condensed aromatic rings, aromatic carboxylic acids, etc. The molar ratio between total nonexchangeable H atoms and total C atoms determined by ^1H NMR and WSOC analyses, respectively, is $\sim 0.7\text{--}0.9$ for the five considered samples. These values are characteristic of fairly oxidized species, suggesting that the above unsaturated chemical structures may also play a role in samples from the pasture site, but these classes of compounds cannot be accurately investigated by this method.

[27] The most abundant individual compound identified in the samples by GC-MS analysis (see below) was levoglucosan (1,6-anhydro- β -D-glucopyranose), a product of cellulose combustion [Shafizadeh and Fu, 1973; Shafizadeh et al., 1979, 1984]. On the basis of this observation the ^1H NMR spectrum of levoglucosan was recorded for comparison with that of the samples. The dominant sharp peaks marked "L" in Figure 1 correspond to this compound. The concentration of levoglucosan in the samples was estimated by comparing the integral of the peak at 5.4 ppm with that of the internal standard. According to this procedure, levoglucosan concentrations were determined for five samples, as shown in Table 1. There is reasonable agreement between the obtained values and the levoglucosan concentrations determined by the GC-MS procedure (also shown in Table 1). The relative concentrations with respect to the total WSOC (i.e., the fraction of WSOC accounted for by the carbon present in levoglucosan) vary from 3 to 7%, decreasing toward the end of the dry season. Also, the contribution of levoglucosan to the total of compounds carrying hydroxyl groups, estimated on the basis of intensities of the ^1H NMR bands, decreases from $\sim 25\%$ down to 11%.

3.2. GC-MS

[28] To date, GC-MS has been the method of choice for characterizing individual organic compounds within aerosol samples, primarily because of its high sensitivity and resolving power [Jacobson et al., 2000]. The analysis of the water-soluble organic fraction of aerosols, however, poses special challenges because it most likely contains significant amounts of polar, oxygenated compounds incorporating two or more COOH, C=O, CHO, COH, COC, CONO₂, CNH, and/or CONH₂ groups per molecule [Saxena and Hildemann, 1996]. Characterization of such compounds by GC-MS requires that they first be derivatized, i.e., converted to less polar compounds, so that they will elute through a GC column. Previous studies of

WSOCs in aerosols by GC methods have focused almost exclusively on the characterization of organic acids as their ester derivatives [e.g., Kawamura, 1993; Kawamura and Ikushima, 1993; Kawamura et al., 1996; Narukawa et al., 1999; Limbeck and Puxbaum, 1999].

[29] In this work, a two-step derivatization scheme was developed, which is adapted from a method described by Bartolozzi et al. [1997] for the analysis of organic acids and sugars in fruits. It involves successive derivatizations with methoxyamine (CH_3ONH_2) and the silylating reagent, BSTFA. Using this procedure, labile protons of hydroxy, carboxyl, and phenolic functional groups are all replaced by trimethylsilyl (TMS) groups, while carbonyl groups are converted to methoxime functionalities. For sugars (which were identified in all the samples), the use of such a two-step derivatization procedure has the advantage of reducing the number of chromatographic peaks arising from different isomers. Reducing sugars, such as fructose and glucose, may potentially yield up to six peaks upon direct silylation due to the existence of cyclic α , β -pyranose/furanose, and acyclic hydrate/carbonyl forms of the sugars [Ratsimba et al., 1999]. After sequential oximation and silylation, however, each reducing sugar gives rise to only two peaks, corresponding to the synoximes and antioximes.

[30] Fifty-three different compounds were identified in the samples using the new derivatization procedure (Table 2). All of these were able to be successfully quantified by the GC-MS method, with the exception of oxalic acid, whose TMS derivative was found to be unstable and was measured instead by IC. As anticipated from their water solubility, the identified compounds were all found to be highly polar, oxygenated compounds containing two or more COOH, C=O and/or OH functional groups. A summary of the concentration data for these compounds at both measurement sites is presented in Table 2, with the compounds grouped into five major categories: anhydrosugars, sugars/sugar alcohols, aliphatic di/tricarboxylic acids, aliphatic oxo-/hydroxyacids, and aromatic compounds. To highlight the significant contribution of biomass burning to the WSOCs concentrations, compositional data are also given for selected samples collected in early October, when burning was most intense, and at the end of October, when rainfall frequency increased and burning activity began to cease.

[31] The sum of the concentrations of the identified compounds showed a temporal variation similar to OC, BC, and potassium (K) at both measurement sites, as well as CO measured at the pasture site (data for the pasture site are shown in Figure 3). The latter three are good indicators for combustion [Andreae, 1983] and point to biomass burning as the major source for much of the identified material. In addition, the majority of individual compounds themselves showed similar temporal variations to these indicators, with a decrease in concentration occurring during the transition toward the wet season. Little difference was observed between the samples from the pasture and forest sites in terms of the compounds identified and their relative proportions. We did, however, observe higher absolute concentrations of most compounds at FNS, which serves as further evidence for biomass burning as the principal source of the identified WSOCs, since fire activity was more pronounced in the vicinity of this site.

[32] While many of the identified compounds are indeed known pyrolysis products from the thermal breakdown of plant polysaccharides and lignin, we performed linear regression analysis of the compound concentrations against BC, OC, and

Table 2. Selected Data for Aerosol Samples and Compounds Identified by GC-MS and IC in Aqueous Extracts of Aerosol Samples From FNS (Pasture Site) and RBJ (Forest Site), Rondônia, Brazil, 1999^a

Component	Pasture Site (<i>n</i> = 9)					Forest Site (<i>n</i> = 12)				
	Range	Mean	Median	5 Oct.	27 Oct.	Range	Mean	Median	9 Oct.	29 Oct.
BC ($\mu\text{g m}^{-3}$)	0.1–4.4	1.4	0.9	4.4	0.1	0.1–1.5	0.7	0.6	1.5	0.1
OC ($\mu\text{g m}^{-3}$)	2.8–77.8	29.2	21.6	77.8	2.8	1.6–36.8	14.5	12.1	36.8	1.6
WSOC ($\mu\text{g m}^{-3}$)	2.2–39.6	17.3	12.3	37.8	2.2	--	--	--	--	--
K ($\mu\text{g m}^{-3}$)	0.1–2.3	0.8	0.5	2.3	0.1	0.0–0.9	0.4	0.3	0.9	0.0
<i>Anhydrosugars (ng m⁻³)</i>										
Levoglucosan	1182–6900	2460	2050	6900	118	39.9–2660	1180	1040	2660	39.9
1,6-Anhydroglucofuranose	5.0–248	82.2	68.2	248	5.0	1.9–115	50.3	46.8	115	1.9
Galactosan	2.3–148	55.4	42.5	148	2.3	1.6–44.6	22.7	23.7	44.6	1.6
Mannosan	6.0–371	126	103	371	6.0	1.7–127	49.5	40.9	127	1.7
Arabinosan	0.1–23.5	7.4	5.4	16.9	0.1	0.0–5.4	1.8	1.2	5.4	0.0
Xylosan	2.5–155	55.0	37.9	129	2.5	0.4–27.5	10.2	7.7	27.5	0.4
<i>N</i> -acetyl-2-aminoglucosan	0.4–38.7	12.4	10.6	38.7	0.4	0.2–15.0	5.8	4.3	15.0	0.2
<i>Sugars/Sugar Alcohols (ng m⁻³)</i>										
Xylose	1.3–33.2	12.7	10.0	33.2	1.3	0.5–19.8	7.3	6.7	19.8	0.5
Fructose	2.8–19.9	8.9	7.5	19.9	4.4	2.3–22.8	10.1	9.3	12.2	2.4
Mannose	0.6–4.1	2.1	1.8	4.1	1.4	0.5–3.1	1.6	1.4	3.1	0.5
Galactose	0.2–2.4	0.9	0.8	2.4	0.2	0.1–1.3	0.6	0.5	1.3	0.1
Glucose	13.9–62.1	36.7	35.5	57.3	31.7	4.6–40.9	20.1	18.8	28.6	4.6
Sucrose	0.8–25.7	7.2	4.2	25.7	0.8	1.4–39.4	14.6	11.1	20.3	1.4
Trehalose	5.1–17.8	8.9	8.7	6.1	9.5	2.3–20.1	8.7	7.0	5.1	8.0
Glycerol	0.5–21.0	8.2	5.8	21.0	1.8	1.1–10.3	5.0	4.0	10.3	1.1
Threitol	0.2–6.2	2.3	1.9	6.2	0.2	0.1–4.5	1.7	1.4	4.5	0.1
Erythritol	2.3–39.1	15.9	15.2	39.1	2.3	2.5–27.7	13.6	13.5	17.3	2.5
Arabitol	9.2–32.2	19.5	17.7	24.2	16.0	6.3–38.6	19.0	18.6	23.6	8.0
Mannitol	9.9–50.1	26.3	23.9	22.9	31.6	4.7–55.9	22.3	17.2	18.6	10.4
Sorbitol	0.0–1.7	0.8	0.7	0.6	1.5	0.3–2.6	1.2	0.8	1.4	0.6
Inositol	0.5–9.3	2.9	2.1	9.3	0.5	0.2–3.5	1.8	1.8	3.3	0.2
<i>Aliphatic Di-/Tricarboxylic Acids (ng m⁻³)</i>										
Oxalic acid	140–1330	619	456	1160	140	50.9–691	329	287	691	50.9
Malonic acid	20.6–256	115	94.7	256	20.6	7.4–149	55.7	45.3	149	7.4
Methylmalonic acid	0.4–9.6	3.0	2.6	4.8	0.4	0.3–3.2	1.2	1.0	3.2	0.3
Succinic acid	7.8–261	95.4	68.0	208	7.8	3.5–76.1	30.6	24.0	76.1	3.5
Methylsuccinic acid	0.8–32.1	11.6	8.7	24.1	0.8	0.5–11.8	5.1	4.5	11.8	0.5
Glutaric acid	1.8–47.1	18.8	14.2	42.2	1.8	0.6–17.7	7.3	6.5	17.7	0.6
Adipic acid	0.7–16.1	6.5	4.4	15.2	0.7	0.3–7.2	3.0	2.5	7.2	0.3
Azelaic acid	1.3–30.2	11.3	7.6	30.2	1.3	0.8–12.9	5.9	5.3	12.9	0.8
Maleic acid	0.9–36.0	15.6	16.4	36.0	0.9	0.6–12.9	6.3	6.2	12.9	0.6
Fumaric acid	0.8–26.7	11.0	10.3	26.7	0.8	0.4–9.0	4.1	4.0	9.0	0.4
Tricarballic acid	6.7–83.4	25.1	18.3	23.3	7.9	4.5–40.9	17.5	14.5	40.9	4.5
<i>Aliphatic Oxo-/Hydroxyacids (ng m⁻³)</i>										
Glyoxylic acid	6.8–172	59.5	48.5	172	6.8	1.6–65.5	24.8	15.9	65.5	1.6
Pyruvic acid	2.0–54.0	20.0	17.8	54.0	2.0	1.2–28.0	10.7	7.5	28.0	1.2
2-Ketoglutaric acid	1.2–57.4	24.3	16.8	52.6	1.2	0.8–32.5	12.2	9.8	32.5	0.8
4-Ketopimelic acid	2.4–26.6	11.2	9.0	19.6	2.4	1.2–17.7	8.2	8.3	17.7	1.2
Lactic acid	0.6–56.5	22.1	16.9	56.5	0.6	0.5–26.1	9.2	6.4	21.3	0.5
Glycolic acid	14.6–397	144	101	296	14.6	7.7–237	71.1	53.8	237	7.7
Glyceric acid	7.0–125	45.8	31.3	90.6	7.0	2.1–62.5	22.5	19.7	62.5	2.1
Threonic acid	1.3–18.6	7.0	5.3	13.1	1.3	0.4–11.1	4.1	3.9	11.1	0.4
Hydroxymalonic acid	1.0–39.3	13.7	10.8	21.3	1.0	0.8–20.9	8.2	7.4	20.9	0.8
Malic acid	29.3–277	115	99.7	190	29.3	12.1–146	67.3	64.7	146	12.1
2-Hydroxyglutaric acid	7.5–130	58.0	48.4	130	7.5	2.3–57.0	27.8	25.5	57.0	2.3
Tartaric acid	8.0–51.9	19.5	17.9	19.5	8.0	1.8–23.0	12.2	12.6	23.0	1.8
<i>Aromatic Compounds (ng m⁻³)</i>										
Phthalic acid	3.7–56.9	23.9	18.5	45.4	3.7	1.3–30.8	13.6	12.9	30.8	1.3
3-Hydroxybenzoic acid	0.1–24.8	6.0	3.1	24.8	0.1	0.1–6.0	2.0	1.3	6.0	0.1
4-Hydroxybenzoic acid	0.6–145	32.0	19.6	145	0.6	0.2–29.5	8.7	5.3	29.5	0.2
3,4-Dihydroxybenzoic acid	0.8–82.1	28.3	26.0	82.1	0.8	0.3–30.8	12.2	9.3	30.8	0.3
Vanillic acid	0.3–67.4	22.1	13.2	67.4	0.3	0.2–24.8	7.4	4.1	24.8	0.2
Syringic acid	0.5–121	38.7	23.8	121	0.5	0.2–52.3	17.1	14.6	52.3	0.2
Vanillin	0.0–9.2	3.2	2.6	9.2	0.0	0.0–2.8	1.2	0.9	2.8	0.1
Syringaldehyde	0.1–85.6	25.2	14.8	55.3	0.1	0.1–8.9	3.1	2.5	8.9	0.1
Vanilethanediol	0.1–42.2	13.3	9.2	42.2	0.1	0.1–9.0	4.0	4.2	9.0	0.1

^aConcentrations of the individual compounds are given in units of ng compound m⁻³.

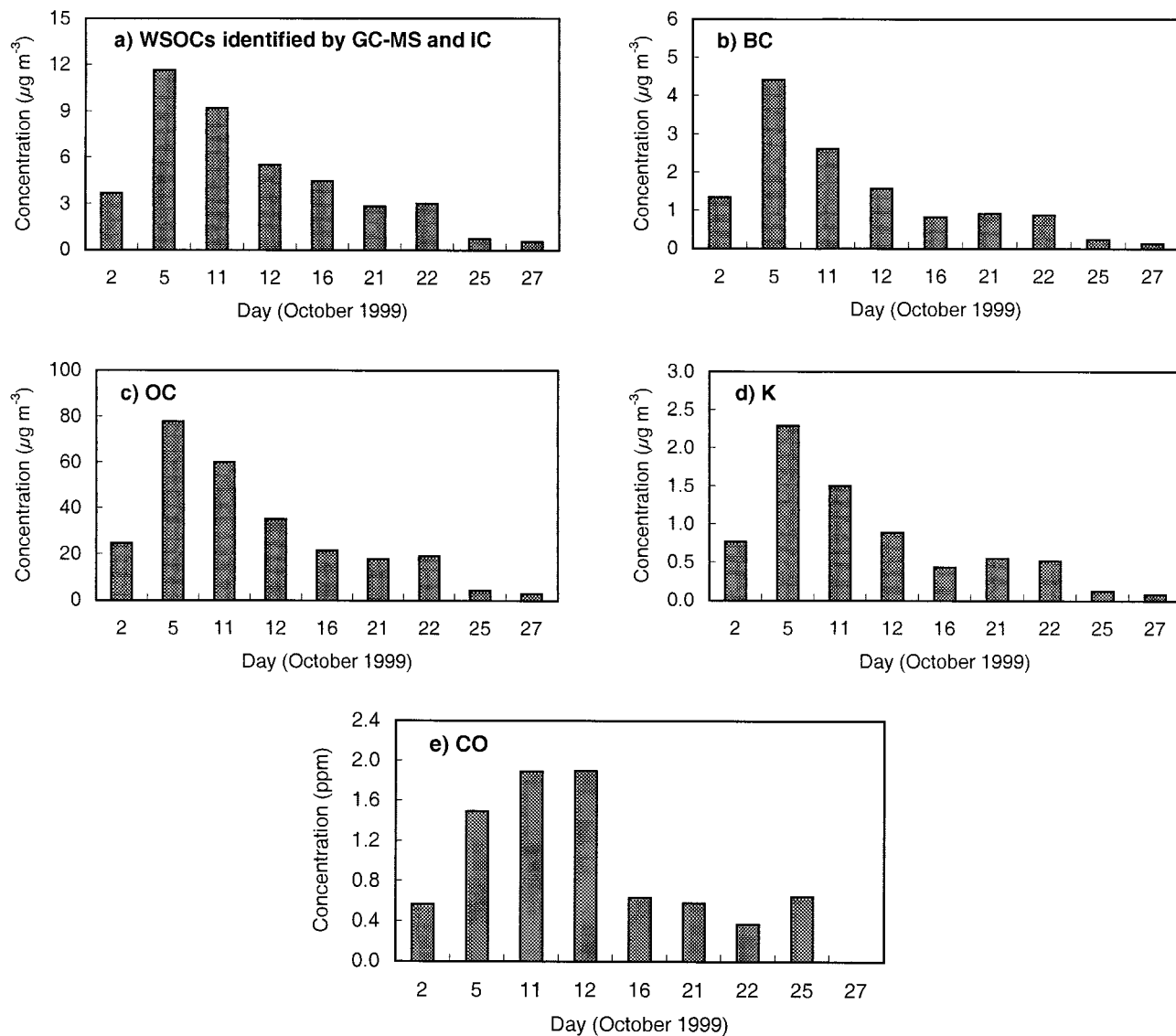


Figure 3. Temporal variations of (a) total WSOCs identified by GC-MS and IC (sum of the concentrations of the individual compounds in units of $\mu\text{g compound m}^{-3}$), (b) BC, (c) OC, (d) K, and (e) CO observed at FNS (pasture site), Rondônia, Brazil, 1999.

K values, as well as CO data for the pasture site, in order to more accurately assess whether biomass burning was the primary source for the compounds. The results are summarized in Table 3. A discussion of the different classes of identified compounds and their probable source(s) follows.

3.2.1. Anhydrosugars

[33] The most abundant class of compounds identified in the samples was the series of anhydrosugars shown in Figure 4. These are known to be derived solely from the breakdown of polysaccharide materials and therefore serve as excellent indicators for the contribution of biomass burning to the overall aerosol mass [Shafizadeh and Fu, 1973; Shafizadeh et al., 1979, 1984; Simoneit et al., 1999]. Accordingly, the correlations of the compounds with BC and OC were found to be very good (Figure 5, Table 3). Correlations with K were somewhat poorer, which is most likely due to the existence of additional sources of atmospheric K over Amazonia, namely, soil dust

[Maenhaut et al., 1996b] and primary biogenic aerosols [Artaxo and Hansson, 1995; Andreae and Crutzen, 1997].

[34] The anhydrosugars, as well as other combustion-derived compounds, did not correlate strongly with CO (Figure 5, Table 3), probably due to differences in the aerosol/CO emission ratios between different fires and the different atmospheric residence times of the gaseous and aerosol species. Figure 3 suggests an increased persistence of elevated CO levels in the atmosphere after heightened biomass burning activity compared with the aerosol components.

[35] By far, the most abundant of the anhydrosugars was levoglucosan, a 1,6-anhydro derivative of glucose, whose carbon component accounted for 1–6% of TC (2–8% of WSOC) within the samples. Numerous laboratory studies have established that levoglucosan is a major product of cellulose pyrolysis [Shafizadeh and Fu, 1973; Shafizadeh et al., 1979, 1984]. Cellulose itself accounts for between 40 and 50% of the dry weight of wood and is built solely from glucose units linked in

Table 3. Regression Coefficients (R^2) and Slopes (in Parentheses) for Concentrations of Compounds Identified by GC-MS (nanograms Compound per cubic meter) Determined Against BC, OC, K ($\mu\text{g m}^{-3}$), and CO (ppm) for FNS (Pasture Site) and RBJ (Forest Site), Rondônia, Brazil, 1999

Compound	BC		OC		K		CO
	Pasture	Forest	Pasture	Forest	Pasture	Forest	Pasture Only
<i>Anhydrosugars</i>							
Levoglucosan	0.930 (1550)	0.734 (1610)	0.948 (83.9)	0.895 (78.4)	0.922 (2930)	0.638 (2520)	0.433 (2160)
1,6-Anhydroglucofuranose	0.978 (55.9)	0.759 (68.0)	0.970 (3.00)	0.889 (3.25)	0.969 (106)	0.642 (105)	0.430 (76.9)
Galactosan	0.949 (35.4)	0.671 (27.8)	0.997 (1.95)	0.782 (1.33)	0.964 (68.0)	0.316 (32.1)	0.550 (55.3)
Mannosan	0.956 (85.3)	0.805 (72.7)	0.970 (4.62)	0.952 (3.50)	0.951 (162)	0.570 (103)	0.468 (124)
Arabinosan	0.699 (4.99)	0.734 (3.32)	0.818 (0.290)	0.771 (0.150)	0.749 (9.82)	0.281 (3.45)	0.650 (10.1)
Xylosan	0.784 (35.6)	0.858 (16.6)	0.892 (2.04)	0.878 (0.742)	0.828 (69.6)	0.411 (19.3)	0.671 (68.8)
N-acetyl-2-aminoglucosan	0.955 (8.55)	0.874 (9.76)	0.926 (0.453)	0.826 (0.419)	0.941 (16.2)	0.332 (10.1)	0.298 (9.91)
<i>Sugars/Sugar Alcohols</i>							
Xylose	0.924 (7.68)	0.822 (10.3)	0.975 (0.424)	0.934 (0.483)	0.932 (14.7)	0.573 (14.4)	0.489 (11.5)
Fructose	0.851 (3.83)	0.079 (3.95)	0.809 (0.201)	0.024 (0.097)	0.848 (7.28)	0.019 (3.26)	0.240 (4.35)
Mannose	0.862 (0.769)	0.589 (1.31)	0.916 (0.043)	0.445 (0.050)	0.875 (1.47)	0.297 (1.56)	0.425 (1.18)
Galactose	0.949 (0.519)	0.775 (0.678)	0.944 (0.028)	0.645 (0.027)	0.942 (0.983)	0.432 (0.850)	0.415 (0.723)
Glucose	0.627 (9.20)	0.263 (12.3)	0.704 (0.524)	0.122 (0.370)	0.641 (17.7)	0.032 (7.15)	0.461 (17.6)
Sucrose	0.980 (5.85)	0.330 (15.9)	0.917 (0.304)	0.158 (0.487)	0.967 (11.1)	0.113 (15.7)	0.360 (7.58)
Trehalose	0.007 (-0.222)	0.004 (0.863)	0.005 (-0.011)	0.043 (-0.118)	0.004 (-0.319)	0.114 (-7.31)	0.025 (-0.979)
Glycerol	0.874 (5.26)	0.814 (5.88)	0.942 (0.294)	0.796 (0.257)	0.903 (10.2)	0.435 (7.22)	0.525 (8.68)
Threitol	0.960 (1.44)	0.916 (2.96)	0.985 (0.079)	0.926 (0.131)	0.970 (2.76)	0.544 (3.83)	0.451 (2.03)
Erythritol	0.956 (8.34)	0.432 (11.6)	0.946 (0.446)	0.219 (0.366)	0.968 (16.0)	0.272 (15.5)	0.351 (10.1)
Arabitol	0.384 (3.63)	0.152 (9.07)	0.459 (0.213)	0.021 (0.150)	0.417 (7.20)	0.003 (2.14)	0.254 (6.55)
Mannitol	0.031 (1.64)	0.034 (6.67)	0.047 (0.108)	0.005 (-0.112)	0.038 (3.48)	0.042 (-12.4)	0.064 (5.25)
Sorbitol	0.002 (0.018)	0.029 (0.330)	0.009 (0.002)	0.002 (-0.004)	0.003 (0.045)	0.017 (-0.424)	0.159 (0.337)
Inositol	0.921 (1.94)	0.888 (2.23)	0.820 (0.099)	0.674 (0.086)	0.896 (3.65)	0.469 (2.72)	0.189 (1.87)
<i>Aliphatic Di-/Tricarboxylic Acids</i>							
Oxalic acid	0.747 (271)	0.813 (396)	0.870 (15.7)	0.876 (18.2)	0.791 (530)	0.805 (663)	0.763 (556)
Malonic acid	0.875 (57.4)	0.781 (78.7)	0.939 (3.20)	0.848 (3.62)	0.906 (111)	0.507 (106)	0.591 (95.6)
Methylmalonic acid	0.811 (3.43)	0.650 (1.41)	0.856 (0.154)	0.800 (0.069)	0.825 (6.05)	0.486 (2.05)	0.586 (3.61)
Succinic acid	0.746 (56.8)	0.844 (43.9)	0.864 (3.29)	0.914 (2.02)	0.793 (111)	0.528 (58.3)	0.695 (114)
Methylsuccinic acid	0.702 (6.69)	0.716 (6.35)	0.834 (0.392)	0.856 (0.307)	0.751 (13.2)	0.412 (8.10)	0.718 (14.1)
Glutaric acid	0.781 (10.8)	0.822 (10.0)	0.884 (0.619)	0.949 (0.475)	0.823 (21.1)	0.582 (14.2)	0.656 (20.5)
Adipic acid	0.827 (3.84)	0.813 (4.06)	0.921 (0.218)	0.920 (0.191)	0.863 (7.47)	0.721 (6.43)	0.618 (6.88)
Azelaic acid	0.931 (7.31)	0.872 (7.46)	0.988 (0.405)	0.936 (0.341)	0.947 (14.0)	0.710 (11.3)	0.636 (12.6)
Maleic acid	0.848 (8.25)	0.893 (8.26)	0.889 (0.454)	0.779 (0.341)	0.874 (15.9)	0.422 (9.54)	0.366 (10.8)
Fumaric acid	0.916 (6.19)	0.949 (5.44)	0.953 (0.339)	0.887 (0.232)	0.939 (11.9)	0.624 (7.40)	0.506 (9.26)
Tricarballic acid	0.769 (28.4)	0.565 (14.9)	0.843 (1.30)	0.731 (0.751)	0.772 (49.7)	0.643 (26.8)	0.717 (34.4)
<i>Aliphatic Oxo-/Hydroxyacids</i>							
Glyoxylic acid	0.944 (35.4)	0.829 (40.1)	0.863 (1.82)	0.840 (1.78)	0.929 (66.8)	0.803 (66.3)	0.202 (33.6)
Pyruvic acid	0.966 (11.3)	0.894 (16.8)	0.910 (0.588)	0.925 (0.757)	0.961 (21.4)	0.748 (25.9)	0.311 (12.9)
2-Ketoglutaric acid	0.827 (13.5)	0.903 (20.8)	0.932 (0.772)	0.869 (0.902)	0.866 (26.4)	0.469 (25.2)	0.689 (25.0)
4-Ketopimelic acid	0.837 (8.95)	0.786 (8.61)	0.895 (0.403)	0.855 (0.397)	0.845 (15.7)	0.732 (14.0)	0.635 (9.32)
Lactic acid	0.908 (14.1)	0.793 (15.7)	0.965 (0.780)	0.806 (0.701)	0.938 (27.2)	0.776 (26.2)	0.532 (22.1)
Glycolic acid	0.713 (79.6)	0.742 (123)	0.846 (4.66)	0.890 (5.93)	0.761 (156)	0.721 (203)	0.626 (155)
Glyceric acid	0.892 (45.1)	0.750 (31.1)	0.936 (2.02)	0.873 (1.48)	0.897 (79.1)	0.725 (51.4)	0.678 (48.1)
Threonic acid	0.883 (6.49)	0.799 (5.61)	0.941 (0.292)	0.880 (0.260)	0.884 (11.3)	0.723 (8.97)	0.635 (6.69)
Hydroxymalonic acid	0.886 (13.6)	0.838 (11.8)	0.918 (0.605)	0.876 (0.531)	0.889 (23.8)	0.790 (19.2)	0.500 (12.2)
Malic acid	0.879 (91.8)	0.819 (70.3)	0.936 (4.13)	0.858 (3.18)	0.882 (161)	0.788 (116)	0.625 (92.7)
2-Hydroxyglutaric acid	0.896 (30.4)	0.980 (38.8)	0.976 (1.71)	0.884 (1.63)	0.925 (58.8)	0.573 (49.8)	0.582 (49.4)
Tartaric acid	0.768 (15.6)	0.421 (8.86)	0.853 (0.715)	0.415 (0.389)	0.769 (27.2)	0.734 (19.7)	0.574 (16.6)
<i>Aromatic Compounds</i>							
Phthalic acid	0.715 (11.3)	0.820 (16.2)	0.852 (0.663)	0.874 (0.737)	0.761 (22.2)	0.607 (23.4)	0.764 (23.8)
3-Hydroxybenzoic acid	0.974 (4.44)	0.745 (3.65)	0.987 (0.195)	0.912 (0.179)	0.972 (7.75)	0.503 (5.05)	0.671 (4.41)
4-Hydroxybenzoic acid	0.945 (19.2)	0.744 (17.8)	0.975 (0.852)	0.886 (0.859)	0.940 (33.5)	0.496 (24.5)	0.510 (16.5)
3,4-Dihydroxybenzoic acid	0.970 (18.1)	0.948 (22.7)	0.939 (0.958)	0.904 (0.978)	0.961 (34.3)	0.479 (27.1)	0.347 (22.1)
Vanillic acid	0.901 (17.6)	0.730 (15.4)	0.956 (0.977)	0.879 (0.747)	0.924 (34.0)	0.475 (20.9)	0.573 (29.9)
Syringic acid	0.951 (30.0)	0.678 (28.5)	0.989 (1.65)	0.911 (1.46)	0.957 (57.3)	0.621 (45.9)	0.564 (48.7)
Vanillin	0.933 (2.23)	0.845 (2.12)	0.946 (0.121)	0.846 (0.094)	0.954 (4.29)	0.333 (2.24)	0.369 (2.91)
Syringaldehyde	0.606 (16.9)	0.750 (5.51)	0.740 (1.00)	0.901 (0.267)	0.655 (33.3)	0.459 (7.24)	0.593 (35.4)
Vanilthanediol	0.993 (9.91)	0.845 (6.69)	0.978 (0.529)	0.870 (0.300)	0.990 (18.8)	0.502 (8.67)	0.439 (13.7)

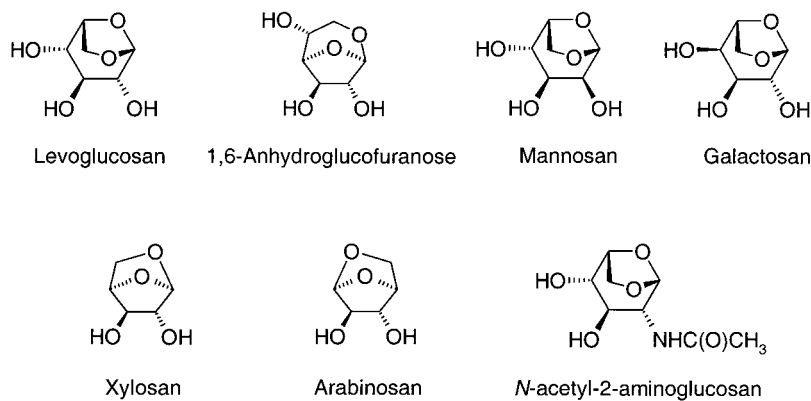


Figure 4. Chemical structures of anhydrosugars identified by GC-MS in aqueous extracts of aerosol samples from FNS (pasture site) and RBJ (forest site), Rondônia, Brazil, 1999.

linear chains of up to 15,000 residues in length [Pettersson, 1984]. Thus the presence of levoglucosan in high concentrations is not unexpected.

[36] Levoglucosan has previously been identified as a major component of organic particulate matter in urban areas impacted by wood smoke [Hornig *et al.*, 1985; Simoneit *et al.*, 1999; Simoneit and Elias, 2000]. Simoneit *et al.* [1999] and Simoneit and Elias [2000] have highlighted its usefulness as a source-specific tracer for biomass burning due to a high resistance to degradation in the atmosphere and the fact that it cannot be generated by noncombustive processes, e.g., hydrolysis or microbial degradation of carbohydrates.

[37] In addition to levoglucosan we identified 1,6-anhydro-

β -D-glucofuranose, the furanose isomer of levoglucosan, within all of the analyzed samples. This compound is also a well-characterized product of cellulose pyrolysis [Shafizadeh and Fu, 1973; Shafizadeh *et al.*, 1979, 1984]; however, its presence in aerosol samples has not been confirmed previously with an authentic standard. Little work has been done to characterize the thermal decomposition products of hemicellulose; however, combustion of this material would be anticipated to yield anhydroderivatives of the constituent sugars in an analogous fashion to cellulose pyrolysis. Hemicellulose, which contributes 20–30% to the dry weight of wood, is a mixture of heteropolysaccharides built almost entirely from glucose, mannose, galactose, xylose, arabinose, 4-O-methylglucuronic acid,

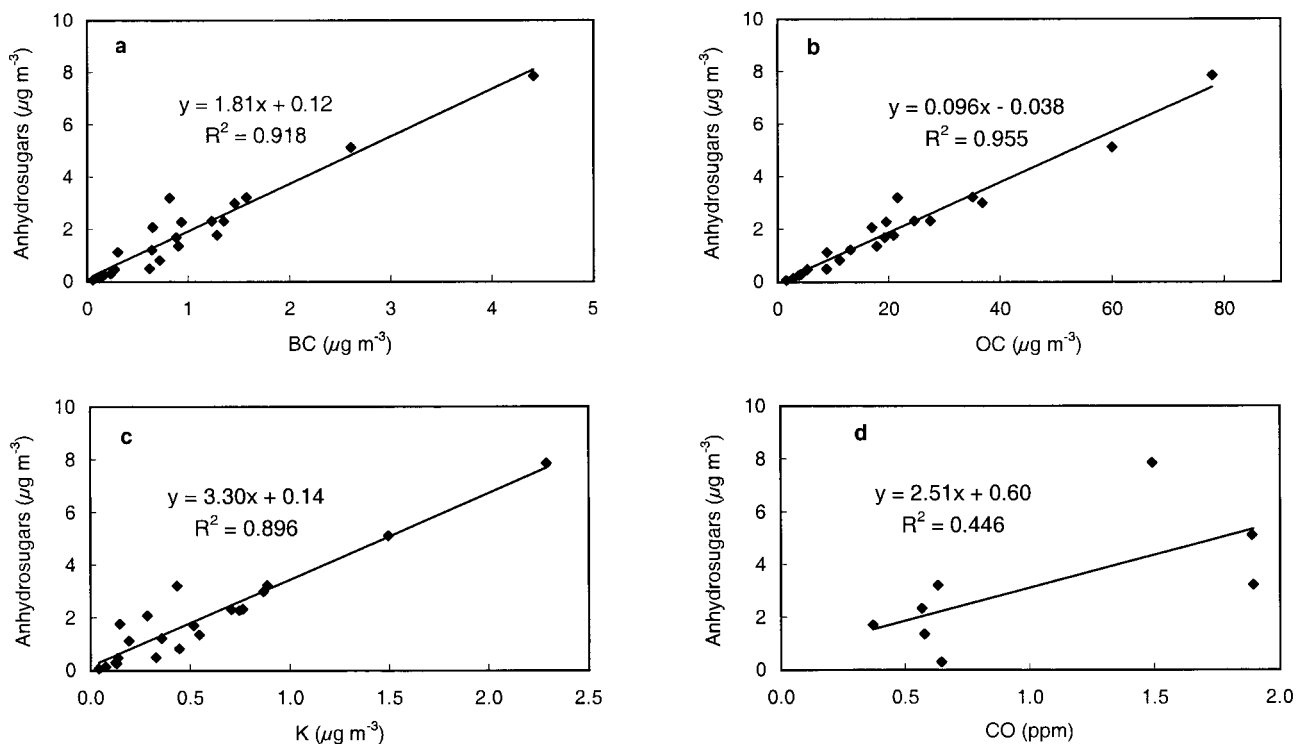


Figure 5. Correlations of total anhydrosugar concentration (sum of the concentrations of the individual anhydrosugars in units of $\mu\text{g compound m}^{-3}$) with (a) BC, (b) OC, (c) K, and (d) CO for FNS (pasture site) and RBJ (forest site), Rondônia, Brazil, 1999.

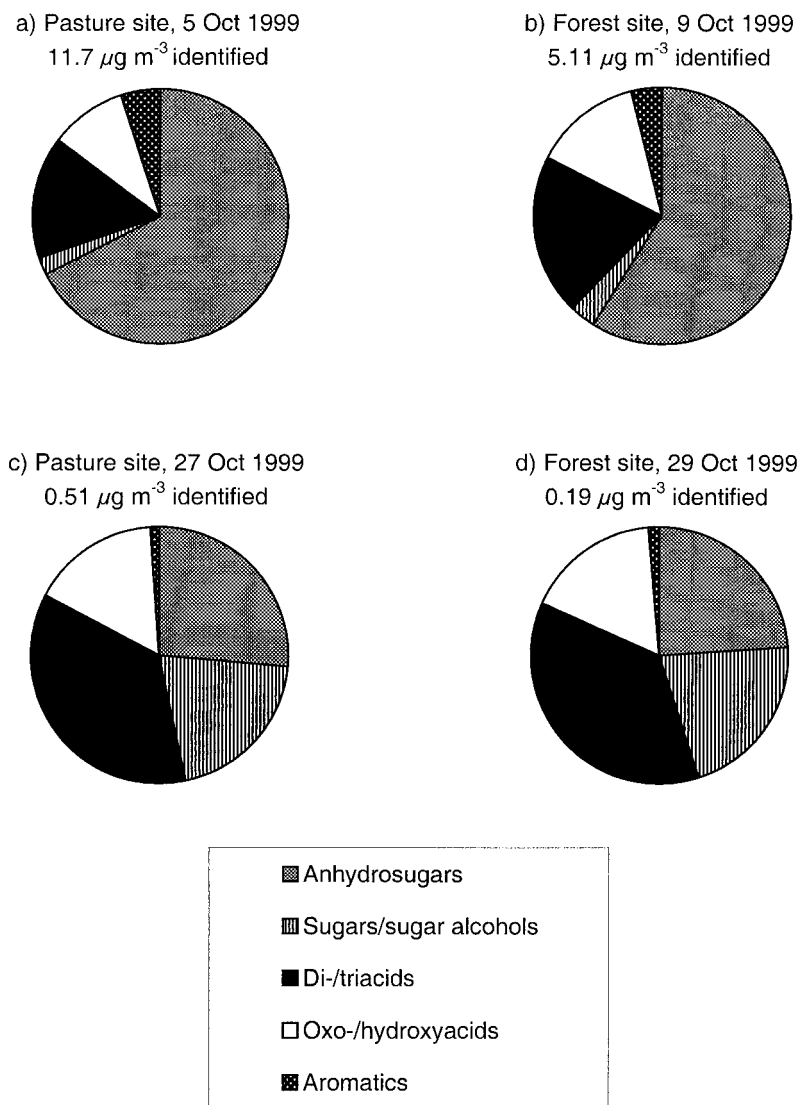


Figure 6. Pie diagrams showing the composition of WSOCs identified by GC-MS and IC for samples collected during (a, b) heavy biomass burning and (c, d) at the end of the dry season at FNS (pasture site) and RBJ (forest site), Rondônia, Brazil, 1999. The identified masses are the sum of the concentrations of the individual compounds in units of $\mu\text{g compound m}^{-3}$.

and galacturonic acid residues [Pettersson, 1984]. In accord with this we consistently observed mannosan, galactosan, xylosan, and arabinosan (the 1,6-anhydro derivatives of mannose and galactose and the 1,5-anhydro derivatives of xylose and arabinose, respectively) in the samples. These compounds were found in much lower amounts than levoglucosan, consistent with the lower concentrations of the corresponding sugar residues in plant matter compared to glucose residues. Mannosan and galactosan have previously been identified in aerosol samples influenced by biomass burning [Simoneit and Elias, 2000].

[38] In addition to the anhydrosugars produced from the breakdown of plant carbohydrates, we also detected the substituted anhydrosugar, poly-*N*-acetyl-2-aminoglucosan, in samples from both forest and pasture sites. This compound is known to be produced via the thermal breakdown of the polysaccharide chitin (poly(*N*-acetyl-2-aminoglucose)) [Köll et al., 1990, 1991] and has also previously been identified in atmospheric aerosols by Simoneit et al. [2000], who proposed it as a

specific indicator for the grilling of crustacean seafood. Chitin is an important constituent of the exoskeletons of arthropods and the cell walls of fungi, and its presence in the current samples is most likely due to thermal breakdown of these materials during biomass burning.

[39] Overall, the anhydrosugars were found to account for 27–74% of the total organic mass identified by GC-MS and IC. This fraction was highest for samples collected during periods of intense burning and decreased with the transition toward the wet season. This is clearly illustrated in Figure 6, which compares the compositions of the selected pasture and forest site samples referred to in Table 2.

3.2.2. Sugars and Sugar Alcohols

[40] Sugars and sugar alcohols were identified in samples from both measurement sites. It is possible that a number of these are primary products of combustion, formed either through direct volatilization from plant matter or as products

of the breakdown of polysaccharides. Glucose, for example, has previously been identified as a minor product of cellulose pyrolysis [Shafizadeh and Fu., 1973; Shafizadeh et al., 1979, 1984]. Some of the sugars may also be produced by hydrolysis of the corresponding anhydrosugars under the acidic atmospheric conditions created by biomass burning.

[41] The sugars and sugar alcohols accounted for 2–24% of the total organic mass identified by GC-MS and IC. The highest percentage contribution of these compounds to the identified mass was observed at the end of the campaign (Figure 6), suggesting an additional source for at least some of the compounds aside from biomass burning. Glycerol, threitol, inositol, and xylose correlated well with BC and OC at both sites, and K at the pasture site (Table 3), suggesting a dominant combustion source for these compounds. The concentrations of fructose, glucose, galactose, mannose, sucrose, and erythritol correlated quite well with BC, OC, and K at the pasture site but not so well at the forest site. Arabitol, mannitol, sorbitol, and trehalose did not correlate with BC, OC, or K at either site.

[42] We believe that a further, in some cases dominant, source for these compounds may be suspended biogenic detritus which forms part of the natural background aerosol material (plant detritus, airborne microbes comprised of bacteria, viruses, spores of lichens and fungi, small algae, and protozoan cysts [Simoneit and Mazurek, 1981]). Indeed, polyalcohols and trehalose are well-known constituents of bacteria, fungi, lower plants, and invertebrates [Bialeski, 1982], serving as reserve carbohydrates and/or cell protectants against stressful conditions [Eleutherio et al., 1993; Chaturvedi et al., 1997]. Prior to the current study, Wauters et al. [1979] identified a number of polyalcohols in the methanol extract of an aerosol sample and speculated that they could originate from microbiological action in the atmosphere. Recently, Sattler et al. [2001] reported concentrations of 1000–10,000 bacteria mL⁻¹ of cloudwater at a mountain site, corresponding to ~1000–10,000 bacteria m⁻³ of air.

[43] If primary biogenic aerosols are a source for these compounds, it is possible that the poorer correlation between the concentrations of the sugars/sugar alcohols and BC/OC/K data for the forest site is due to a more dominant contribution of biogenic material to the total aerosol mass above the rain-forest. This is consistent with the fact that the sugars/sugar alcohols that showed the poorest correlations with BC, OC, and K were generally present in higher concentrations at the forest site (Table 2).

[44] The biogenic sugars and sugar alcohols which are detected by the GC-MS method are most likely from ruptured cells, since the contents of intact cells would not be accessible via the relatively mild water extraction procedure used. Given that the majority of airborne cells are probably intact, the detection of these compounds in the samples is thus an indication that large quantities of the aerosol mass are probably biogenic particles. Indeed, electron microprobe analyses performed on filter samples collected in the Amazon Basin have confirmed that there is an enormous diversity of biogenic particles, including pollen, fungal spores, bacteria, algae, fragments of leaves, excrement and fragments of insects [Artaxo et al., 1990; Artaxo and Hannson, 1995]. Moreover, preliminary analysis of samples collected during the LBA-EUSTACH-1 wet-to-dry season campaign shows that sugars and sugar alcohols are the major species identified by the GC-MS method in

the absence of biomass burning (B. Graham et al., unpublished data, 2001).

3.2.3. Aliphatic Dicarboxylic and Tricarboxylic Acids

[45] Dicarboxylic acids have previously been identified as ubiquitous organic aerosol constituents, which may derive from photochemical oxidation of hydrocarbons, as well as direct emission from fossil fuel or biomass combustion [Grosjean et al., 1978; Kawamura, 1993; Kawamura and Ikushima, 1993; Narukawa et al., 1999; Limbeck and Puxbaum, 1999]. A series of dicarboxylic acids (C₂–C₆ and C₉) were quantified in all the samples we analyzed (13–34% the total organic mass identified). In addition, we consistently observed propane-1,2,3-tricarboxylic acid (tricarballic acid), which has only recently been identified in tropical and urban aerosols [Kubátová et al., 2000].

[46] All of the acids correlated well with BC and OC at both sites, and K at the pasture site (Table 3), indicating combustion as the dominant source during the sampling period. Most are probably formed during the breakdown of cellulose, hemicellulose, and lignin. Azelaic acid is also known to derive from the oxidation of biogenic fatty acids (such as oleic acid) containing a double bond predominantly at the C-9 position, and was likely formed by the oxidation of these unsaturated fatty acids during combustion [Narukawa et al., 1999].

[47] For the 1997 Indonesian forest fires, Narukawa et al. [1999] also reported the concentrations of a homologous series of dicarboxylic acids (C₂ – C₁₂). Oxalic acid was found to be the dominant species, followed by succinic and malonic acids, with the carbon component of the dicarboxylic acids accounting for 2–8% of WSOC. In our samples, the simple aliphatic acids constituted a somewhat lower fraction on average (1–2% of WSOC). This may be due to the fact that the sampling in Indonesia was carried out at a greater distance from actual fires, which may have allowed time for a buildup in the concentrations of dicarboxylic acids through photochemical production from other combustion-derived compounds.

[48] Interestingly, Narukawa et al. [1999] observed an increase in the concentrations of all acids during fire-induced haze events except adipic acid, which they suggested was probably derived predominantly from local anthropogenic sources. In the current study, however, adipic acid was found to correlate strongly with BC, OC, and K, indicating that biomass burning was the major, although not necessarily sole, source for this compound in our samples. Adipic acid is observed in urban aerosols at concentrations close to those of malonic and succinic acids but is found in much lower amounts at rural sites [Limbeck and Puxbaum, 1999].

[49] It is worth noting here that Limbeck et al. [2001] recently presented evidence for the semivolatile behavior of dicarboxylic acids. The values reported in Table 2 should therefore be considered as lower limits for the concentrations of these species in the atmosphere.

3.2.4. Aliphatic Oxoacids and Hydroxyacids

[50] In addition to the simple aliphatic acids, a series of aliphatic hydroxyacids and oxoacids were identified, all of which correlated well with BC, OC, and K (Table 3), except for tartaric acid. The compounds together accounted for 7–17% of the total organic mass identified by GC-MS and IC. As with the di-/tricarboxylic acids, their relative contribution to the identified mass was greatest at the end of the campaign, although highest absolute concentrations were encountered during

burning periods (Figure 6). This suggests the existence of an additional source for these compounds apart from direct emission from biomass burning, e.g., secondary formation via oxidation of biogenic gases or volatile combustion products.

[51] Of the four oxoacids identified in the samples (glyoxylic, pyruvic, 2-ketoglutaric, and 4-ketopimelic acids), glyoxylic acid was the most abundant. Glyoxylic and pyruvic acids are ubiquitous aerosol components and have been reported in a number of studies [e.g., Kawamura, 1993; Limbeck and Puxbaum, 1999; Souza *et al.*, 1999]. Pyruvic acid has previously been observed in burning plumes over Amazonia by Andreae *et al.* [1987], and in the gas phase during the wet season [Talbot *et al.*, 1990], where its presence was ascribed to direct emission from plants, photochemical oxidation of isoprene, as well as other as yet unidentified atmospheric processes. The 4-ketopimelic acid (4-ketoheptanedioic acid) has been reported in aerosols from a diverse range of locations [Kawamura *et al.*, 1996; Kubátová *et al.*, 2000]; however, we know of no report of 2-ketoglutaric acid in aerosols up to now.

[52] The hydroxylated dicarboxylic acids we identified have all been observed in aerosols previously [e.g., Kawamura and Ikushima, 1993; Kawamura *et al.*, 1996; Neusüss *et al.*, 2000], and Kawamura and Ikushima [1993] have postulated that some are most likely oxidation products of the corresponding dicarboxylic acids. Of the hydroxylated monocarboxylic acids we found, however, only glycolic acid has been reported in aerosols to date [e.g., Souza *et al.*, 1999]. This compound has been identified in wood pyrolysis oils [Piskorz *et al.*, 1986], confirming biomass burning as a source. Souza *et al.* [1999] have also suggested that glycolic acid may be derived from biogenic emissions.

[53] Glycolic, lactic, glyceric, and threonic acids would be expected to elude analysis by the popular ester derivatization method of Kawamura [1993] since they bear only a single carboxyl group and would yield derivatives too water-soluble to be extracted with an organic solvent (a prerequisite for the method). The analysis of these compounds via the current derivatization method is possible because both the carboxyl and the hydroxyl groups within the molecules are derivatized.

3.2.5. Aromatic Compounds

[54] A number of aromatic species carrying hydroxyl, carbonyl, and carboxyl functional groups were consistently found in the samples: phthalic acid, 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid, vanillic acid, syringic acid, vanillin, syringaldehyde, and vanilethanediol (4-hydroxy-3-methoxyphenylglycol). Their most likely source is the combustion of lignin, although functionalized aromatic compounds are also known to be produced during the pyrolysis of polysaccharides [Richards *et al.*, 1983]. Lignin constitutes 20–35% of the dry weight of wood and is a polyphenolic substance constructed from variously bonded hydroxy- and methoxy-substituted phenylpropanoid units [Pettersson, 1984]. Many different lignin breakdown products, mostly methoxyphenols, have been identified in previous studies and proposed as tracers for wood smoke pollution [Hawthorne *et al.*, 1988; Simoneit *et al.*, 1993; Kjallstrand *et al.*, 1998]. We did not observe the majority of these lignin compounds because of their insolubility in water, and the identified aromatic compounds were found to account for only a minor portion (1–5%) of the total organic mass quantified by GC-MS (Figure 6). Their contribution to the identified mass decreased at the end of the campaign, suggesting that biomass burning was the prevailing,

perhaps sole, source for these compounds in the samples we collected.

[55] The relative distribution of OH/OCH₃ substituents on the aromatic products of lignin combustion has been shown to be a useful indicator for the class of plant that is burnt [Hawthorne *et al.*, 1988; Simoneit *et al.*, 1993; Kjallstrand *et al.*, 1998]. Softwoods give rise to 4-hydroxy-3-methoxyphenyl (vanillyl) compounds, while hardwoods yield predominantly 4-hydroxy-3,5-dimethoxyphenyl (syringyl) compounds and grasses mainly 4-hydroxyphenyl (coumaryl) products. In all of our samples we observed a greater abundance of syringic acid and syringaldehyde compared to vanillic acid and vanillin, consistent with the hardwood nature of tropical forests [Abas *et al.*, 1995]. The 4-hydroxybenzoic acid has been identified in grass smoke previously [Simoneit *et al.*, 1993], and this was the probable source for this compound in the present study.

[56] Overall, only 4–8% of TC (9–14% of the WSOC) could be accounted for by the GC-MS and IC analyses. Although the GC chromatograms contained numerous peaks that could not be identified, it is clear that these cannot make up for the large portion of WSOC unaccounted for. Instead, the remaining material is likely to include significant amounts of semivolatile compounds lost upon evaporation of the water extract prior to derivatization, as well as compounds whose derivatives are too volatile or unstable to be observed. Perhaps more significant, however, is the potential contribution of compounds that are insufficiently volatile to pass through the GC column. Indeed, HPLC analysis of the WSOCs within the samples indicates that polyacids may account for up to 32% of the carbon within this fraction [Mayol-Bracero *et al.*, 2002]. These polyacidic compounds are thought to consist predominantly of high-molecular-weight “air polymers” with properties resembling those of humic substances [Havers *et al.*, 1998; Zappoli *et al.*, 1999; Decesari *et al.*, 2000; Facchini *et al.*, 2000; Krivácsy *et al.*, 2000]. It has also been shown that neutral, high-molecular-weight oligosaccharides are primary thermal degradation products of plant polysaccharides, derived either from the incomplete breakdown of polymeric chains [Köll *et al.*, 1990] or from recondensation of the initial monomeric anhydrosugar products [Shafizadeh and Fu, 1973]. Thus it is likely that a significant fraction of the WSOC fraction is composed of a range of high-molecular-weight species, both acidic and neutral, which would be expected to elude analysis by GC because of their low volatility.

4. Conclusion

[57] The data set presented in this paper indicates that the WSOCs fraction of aerosol samples collected in the Amazon Basin during the 1999 burning season is a complex mixture of oxygenated compounds derived primarily from biomass burning. According to ¹H NMR spectroscopy, both highly substituted aromatic and aliphatic compounds contribute significantly to WSOCs. The individual compounds identified by the GC-MS analysis are mostly known pyrolysis products of cellulose, hemicellulose, and lignin, with levoglucosan being the single most abundant compound identified (up to 7 μg m⁻³). The transition from the dry season toward the wet season was indicated by a decrease in the concentrations of many of these combustion-derived compounds and an increase in the relative contribution of biogenic sugars and sugar alcohols. It is possible that the high WSOCs concentrations observed in smoke aerosols exert some influence on cloud microphysical pro-

cesses and aqueous-phase chemistry occurring within the atmosphere [Roberts *et al.*, 2002]. Given this possibility, coupled with the widespread extent of fire-led deforestation in Amazonia and the intense convective activity associated with the region, we consider it vital that efforts to characterize WSOCs in smoke aerosols continue. Further data on the bulk characteristics of the WSOCs fraction within Amazonian biomass burning aerosols are reported in a companion paper [Mayol-Bracero *et al.*, 2002].

[58] **Note Added in Proof.** During the review process a number of relevant publications relating to the quantification of levoglucosan and related anhydrosugars in aerosol samples influenced by biomass burning have appeared [Fraser and Lakshmanan, 2000; Nolte *et al.*, 2001; Zdráhal *et al.*, 2002].

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- M. O. Andreae and P. Guyon, Department of Biogeochemistry, Max-Planck-Institute for Chemistry, Postfach 3060, D-55020 Mainz, Germany. (moa@mpch-mainz.mpg.de; guyon@mpch-mainz.mpg.de)
- P. Artaxo, Institute for Physics, University of São Paulo, P.O. Box 66318, CEP 05315-970 São Paulo, SP, Brazil. (artaxo@if.usp.br)
- S. Decesari and M. C. Facchini, Instituto di Scienze dell' Atmosfera e dell' Oceano-CNR, Via Gobetti 101, I-40129 Bologna, Italy. (s.decesari@isao.bo.cnr.it; mc.facchini@isao.bo.cnr.it)
- B. Graham, CSIRO Atmospheric Research, PMBI Aspendale VIC 3195, Australia. (bim.graham@dar.csiro.au)
- P. Köll, Universität Oldenburg, Fachbereich Chemie (FB9), Organische Chemie, Carl-von-Ossietzky Strasse 9-11, Postfach 2503, D-26111 Oldenburg, Germany. (koell@uni-oldenburg.de)
- W. Maenhaut, Institute for Nuclear Sciences, University of Ghent, Proeftunstraat 86, B-9000 Ghent, Belgium. (maenhaut@inwchem.rug.ac.be)
- O. L. Mayol-Bracero, Institute for Tropical Ecosystem Studies, University of Puerto Rico, P. O. Box 23341, San Juan, PR 00931-3341, USA (omayol@sunites.upr.clu.edu)
- G. C. Roberts, C4 / Scripps Institute for Oceanography, Nierenburg Hall 326, 9500 Gilman Dr.#0239, La Jolla, CA 92093, USA. (greg@fiji.ucsd.edu)