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# Functional group analysis by H NMR/chemical derivatization for the characterization of organic aerosol from the SMOCC field campaign

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**Abstract.** Water soluble organic compounds (WSOC) in aerosol samples collected in the Amazon Basin in a period encompassing the middle/late dry season and the beginning of the wet season, were investigated by H NMR spectroscopy. HiVol filter samples (PM<sub>2.5</sub> and PM<sub>>2.5</sub>) and size-segregated samples from multistage impactor were subjected to H NMR characterization. The H NMR methodology, recently developed for the analysis of organic aerosol samples, has been improved by exploiting chemical methylation of carboxylic groups with diazomethane, which allows the direct determination of the carboxylic acid content of WSOC. The content of carboxylic carbons for the different periods and sizes ranged from 12% to 20% of total measured carbon depending on the season and aerosol size, with higher contents for the fine particles in the transition and wet periods with respect to the dry period. A comprehensive picture is presented of WSOC functional groups in aerosol samples representative of the biomass burning period, as well as of transition and semi-clean atmospheric conditions. A difference in composition between fine (PM<sub>2.5</sub>) and coarse (PM<sub>>2.5</sub>) size fractions emerged from the NMR data, the former showing higher alkylic content, the latter being largely dominated by R-O-H (or R-O-R’) functional groups. Very small particles (<0.14 μm), however, present higher alkyl-chain content and less oxygenated carbons than larger fine particles (0.42–1.2 μm). More limited variations were found between the average compositions in the different periods of the campaign.

## 1 Introduction

The LBA-SMOCC (Large-Scale Biosphere/Atmosphere Experiment in Amazonia – Smoke Aerosols, Clouds, Rainfall and Climate) experiment (Andreae et al., 2004) was set up to estimate the effects of smoke particles produced by biomass burning activity in the Amazon Basin on the development of precipitating clouds, and to evaluate the resulting perturbations on the climate system. The project is part of the Large-Scale Atmosphere-Biosphere Experiment in Amazonia (LBA). The SMOCC field campaign was held at a pasture site in a rural area in Rondônia, Brazil in the period September–November 2002, during the transition from the dry to the wet season. During the experiment, extensive measurements were made of the physical, hygroscopic and chemical aerosol properties, and samples were collected by means of filter units and impactor-based techniques for subsequent laboratory analyses (Fuzzi et al., 2006). As part of this experiment attention was focused on the characterization of water-soluble organic compounds (WSOC) extracted from filters and impactor samples and analyzed by proton nuclear magnetic resonance (H NMR) spectroscopy.

The lack of knowledge on the composition of ambient aerosol is a serious drawback in the prediction of its properties and of its role in regional and global climate change. While a good level of information on the inorganic composition of aerosol has been achieved, knowledge of the organic fraction of the aerosol is still poor, and this part is often treated in models as a black box (the “organics”), although important information on the presence of specific compounds and classes of compounds, like some carboxylic acids, carbohydrates, polyols, etc. has become available in recent years. The reasons for this gap in knowledge are

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linked to the very high complexity of the organic aerosol fraction, both in terms of structural diversity and the huge number of different compounds present.

The present authors have recently introduced a conceptually new approach to the problem of characterizing atmospheric aerosol: the investigation of the structural features, i.e., the presence and amount of organic functional groups. Functional group analysis provides information on the average composition of aerosol organic carbon (OC), such as the mean state of oxidation (Matta et al., 2003; Decesari et al., 2005), the surface-active character (Decesari et al., 2005) and the general structures which can be linked to primary and secondary sources of aerosol (Maria et al., 2003). In the case of biomass burning aerosol, the functional group composition was shown to change markedly during the various stages of combustion, with an enrichment of aromatic and alkylic moieties in the char residue, while most of the complex oxygen-rich molecules like cellulose decompose to volatile organic compounds (Knicker et al., 1996). At the same time, biomass burning particles contain many oxygenated functional groups, like hydroxyls, carbonyls and carboxyls (Graham et al., 2002), indicating that volatile organic compounds produced during the combustion recondense onto particles during the cooling of the plume (Gao et al., 2003; Reid et al., 2004). Further changes in the functional group composition of the water-soluble fraction of aerosol OC may also occur following oxidation in the aerosol phase promoted by sunlight (Hoffer et al., 2005).

In this study, functional group analysis was performed by H NMR spectroscopy (Decesari et al., 2000). Our group has already applied this methodology, often coupled to liquid chromatography, to aerosol samples collected in urban (Matta et al., 2003) and remote sites (Cavalli et al., 2005), as well as in rural areas in the Amazon Basin impacted by biomass burning activities (Graham et al., 2002). Other authors have recently followed a similar methodology (Suzuki et al., 2001) for the study of organic aerosol.

Some important drawbacks were encountered, however, in the use of H NMR for the speciation of the aerosol. The main one is intrinsic to the nature of H NMR, i.e. it is a spectroscopy of hydrogens. Furthermore, since D<sub>2</sub>O is the solvent, acidic hydrogens (like those of OH and CO<sub>2</sub>H groups) undergo chemical exchange with D<sub>2</sub>O and elude detection.

A solution is now presented to overcome the above mentioned drawback, i.e., the chemical transformation of some organic functional groups, previously not detected by direct H NMR, into other groups that can be revealed by H NMR. A special interest was taken in the determination of carboxylic acid groups, since they represent the most abundant functional groups in the aerosol which affect the CCN ability of organic particles. To address this problem, a derivatization procedure has been developed that converts carboxylic acids (RCO<sub>2</sub>H) into the corresponding methyl esters (RCO<sub>2</sub>CH<sub>3</sub>) which exhibit a well-defined band in the H NMR spectrum. The overall protocol presented here provides WSOC func-

tional group composition expressed as concentrations of OC divided in aromatic, alkylic, hydroxyl/alkoxyl and carboxyl moieties. Average aerosol compositions were derived for the different periods of the campaign and for the different size intervals. WSOC chemical classes isolated on ion-exchange stationary phases were also subjected to H NMR analysis and methylation for the determination of the CO<sub>2</sub>H groups. The overall set of data was used for the elaboration of a chemical model as a synthetic representation of the aerosol OC composition during the SMOCC experiment (Decesari et al., 2005).

## 2 Experimental

### 2.1 Sampling

The aerosol samples used for this study were collected at the Fazenda Nossa Senhora (FNS) in Rondônia, Brazil, during the SMOCC field campaign from 9 September 2002 to 14 November 2002 using a High Volume Dichotomous Sampler (HVDS) equipped with pre-baked quartz-fiber filters. Size-segregated samples were collected with a 5-stage Berner impactor with lower cut-offs at 0.05, 0.14, 0.42, 1.2 and 3.5 μm. Sampling details are given elsewhere (Decesari et al., 2006). The sampling campaign was divided into three periods according to the meteorological conditions: 1) a first period corresponding to the middle-late dry season lasting until 7 October, 2) a transition phase from 8 to 31 October, and 3) the on-set of the wet season during the first two weeks of November. Aerosol concentrations followed the intensity of the biomass burning activities, which peaked during the dry period and decreased afterwards. Only sparse fires were observed during the wet period, and the aerosol loadings approached the natural background of the Amazon Basin (Fuzzi et al., 2006). Throughout the campaign the aerosol concentrations were different during day and night conditions, due to the diurnal evolution of the boundary layer and to possible differences in the sources and transformation processes of the aerosol particles (Artaxo et al., 2002; Rissler et al., 2005). For this reason, sampling was conducted differentiating between daytime and nighttime.

For the purpose of the present paper, samples are labeled as follows: for HVDS samples: HVDS-day\_of\_samplingD/N(day/night)F/C(fine/coarse). Thus HVDS43NF means the fine fraction collected with the HiVol sampler present on the field during the night of the 43rd day of sampling starting from 9 September 2002; if the D/N indication is missing the sampling refers to the whole day.

Berner impactor samples were labeled BIdate\_of\_samplingD/N(day/night)n(=1 to 5 for the size stages, from the fine to the coarse ones). Thus BI07SeptD1 means the first stage of the Berner impactor sample collected on 7 September in daytime. Size intervals resolved by

the 5-stage Berner impactor are: 0.05–0.14, 0.14–0.42, 0.42–1.2, 1.2–3.5, 3.5–10  $\mu\text{m}$ .

The HVDS filters and Berner impactor samples were stored in a freezer or refrigerator until the analysis.

## 2.2 Sample preparation

A known fraction of the filter was extracted with 30 ml of ultrapure (milliQ) water for 60 min with stirring. The aqueous solution was filtered on 0.45  $\mu\text{m}$  mixed-cellulose-esters membrane (MCE) (Millipore Millex<sup>®</sup> HA) and diluted with deionized water before Total Organic Carbon (TOC) analysis. A second set of samples underwent filtration on hydrophobic 0.45  $\mu\text{m}$  PTFE-membrane (Sartorius Minisart SRP 15) filters instead of the MCE filters allowing the attainment of better blank levels.

An aliquot of the filtered solution was evaporated to dryness under vacuum, collected with 0.7 mL of D<sub>2</sub>O containing sodium 3-trimethylsilyl-2,2,3,3-*d*<sub>4</sub>-propanoate (TSP, 0.24 mM), and used for H NMR analysis (NMR-A). Tedlar foils used to collect aerosol samples with the Berner impactor were extracted in 6 ml deionized water in an ultrasonic bath for 30 min. Aliquots were employed for TOC analysis, ion chromatography and HPLC. The residual volume of extract was dried under vacuum and redissolved in D<sub>2</sub>O for H NMR analysis.

## 2.3 Methylation procedure

Diazomethane solution in ether (about 0.5 M) was prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (de Boer et al., 1963) and stored for short times over KOH pellets in a refrigerator.

To an aliquot of the aerosol extract, 2 mL of 0.1 M HCl were added and the resulting clear solution was evaporated to dryness. The residue was suspended in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) in a 25 mL flask, cooled at 0°C with an ice bath; 2 mL of ethereal CH<sub>2</sub>N<sub>2</sub> solution were added and the suspension was sonicated in an ultrasonic bath at 0°C for 30 min. After filtration on 0.2  $\mu\text{m}$  PTFE filter, and washing with CH<sub>2</sub>Cl<sub>2</sub> (15 mL), the resulting clear CH<sub>2</sub>Cl<sub>2</sub> solution was evaporated under vacuum; the residue was collected with 0.7 ml of CDCl<sub>3</sub> containing 0.02% of tetrakis(trimethylsilyl)silane (TKS), and was used for H NMR analysis (NMR-B). The PTFE filter was then rinsed with 10 mL of pure water and the solution was transferred back to the 25 mL flask. After evaporation the flask was stored in a desiccator overnight. The residue was finally collected with TSP-containing D<sub>2</sub>O and subjected to HNMR analysis (NMR-C).

## 2.4 TOC measurement

TOC in aqueous solution was measured with a Shimadzu 5000A TOC-analyser. The aliquots of aerosol extracts had to be diluted to 4 ml for the TOC analysis. Blank levels were

1 ppmC and 0.25 ppmC, when filtering the extracts of the HVDS filters with hydrophilic cellulose filters and PTFE hydrophobic filters, respectively. Blank levels for the extracts of the Berner impactor tedlar foils were around 0.2 ppmC (Decesari et al., 2005).

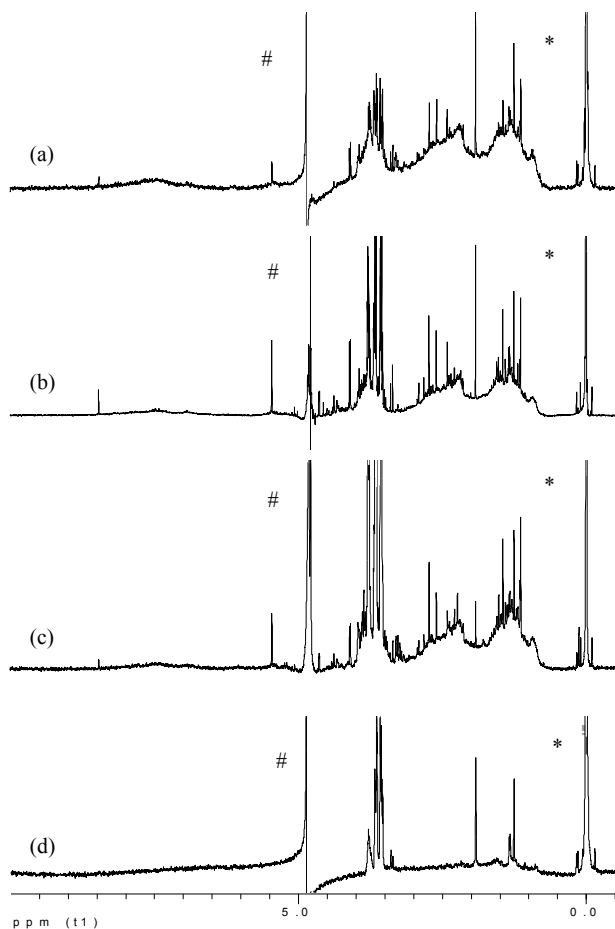
## 2.5 H NMR analysis

H NMR spectra were obtained with Varian Inova 600 or Mercury 400 instruments at 600 MHz or 400 MHz, respectively. For spectra in D<sub>2</sub>O solution (NMR-A and NMR-C), the residue HOD peak was suppressed by presaturation using a PRESAT pulse sequence. From 200 to 1000 scans were acquired depending on the concentration. A 0.5 Hz line broadening (LB) weighting function and baseline correction were generally applied.

Area integration of the spectra was cut in the following regions, which have been attributed to specific functional groups: -0.05–0.30 ppm (Standard); 0.60–1.80 (aliphatic hydrogens, R-*H*); 1.80–3.20 (hydrogens in  $\alpha$ -position to unsaturated carbons, =C-C-*H*); 3.20–4.40 (hydrogens bound to alcoholic, ethereal or estereal carbons, O-C-*H*); 5.00–5.50 (acetalic and vinylic hydrogens, O-CH-O and =C-*H*); 6.50–8.20 (arylic hydrogens, Ar-*H*). The actual sensitivity of the H NMR analysis depends on many factors, the most important being the magnet field strength, the number of scans accumulated in the spectrum (therefore the overall time of scanning) and the quantity of sample available. In particular, signal to noise ratio increases proportionally to the square root of the number of scans and approximately to the third power of the magnetic field strength. To give a rough estimation of the sensitivity we have calculated that the sensitivity achieved in the NMR spectrum of sample HVDS45NF, a rather unfavourable case, would be sufficient to detect levoglucosan at a concentration in the air of 0.04  $\mu\text{g}/\text{m}^3$ . For this sample we used  $\frac{1}{4}$  of the collected filter and we acquired 800 scans corresponding to about 55 min with a 600 MHz instrument.

## 2.6 Ion-exchange chromatography (IC)

Ion-exchange chromatography on a diethylaminoethyl (DEAE) stationary phase was used to fractionate WSOC into neutral compounds (NC), mono-/di-acids (MDA) and polyacids (PA) (Decesari et al., 2000). Chromatographic fractions were isolated on preparative glass columns of DEAE-cellulose gel by eluting with ammonium bicarbonate solutions. In order to improve the resolution while keeping low the volume of mobile phase necessary to elute the strongly retained compounds, two columns, A and B (lengths: 3 cm+11.5 cm), were initially used in series to separate NC from the acidic compounds. MDA were subsequently eluted with 0.08 M ammonium bicarbonate, while in a second step PA were eluted with 0.4 M buffer directly from column A, by-passing column B. The above procedure



**Fig. 1.**  $^1\text{H}$  NMR spectra of the typical samples of fine aerosols WSOC; HVDS15DF from the dry (a), HVDS45NF from the transition (b) and HVDS51NF from the wet (c) periods. Spectrum of blank HVDS7F (d). Spectra are in  $\text{D}_2\text{O}$  solution containing TSP as internal standard. The HOD signal is presaturated. \* = Internal TSP standard. # = residual HOD peak. Vertical scale is adjusted according to the intensity of each spectrum.

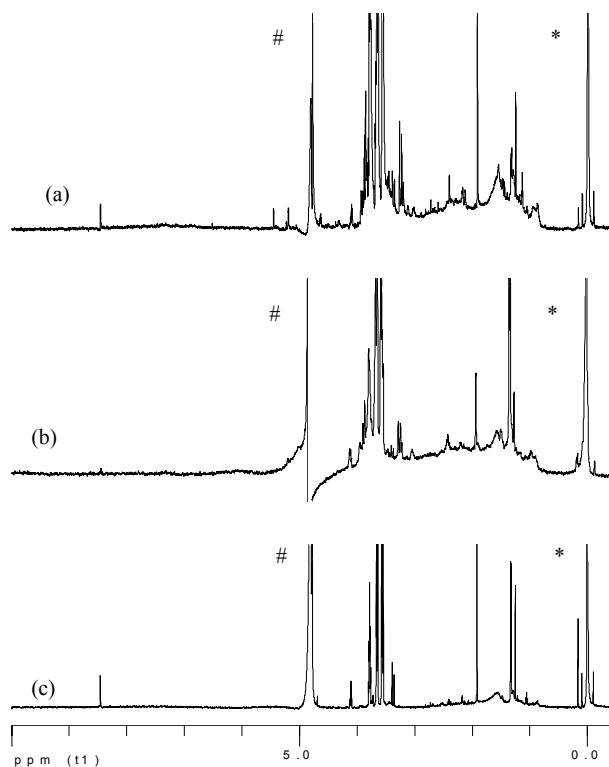
employs longer columns compared to those used for the calibration of the HPLC technique (Decesari et al., 2005), and it allows the fractionation of sample amounts of up to  $1000\ \mu\text{gC}$  of WSOC.

Blank filters were submitted to the same procedures described above for the real samples. Their NMR spectra (NMR-A, NMR-B, NMR-C) were integrated in the usual way and divided into the same regions as real samples.

### 3 Results

#### 3.1 $^1\text{H}$ NMR analysis of HVDS filter sample

$^1\text{H}$  NMR spectra of three samples representative for the fine fraction of the dry (a), transition (b) and wet (c) periods and of blank (d) are presented in Fig. 1. As normally found



**Fig. 2.**  $^1\text{H}$  NMR spectra of the typical samples of coarse aerosols WSOC; HVDS45NC from the transition (a) and HVDS51NC from the wet (b) periods. (c) Spectrum of blank HVDSB2F. Spectra are in  $\text{D}_2\text{O}$  solution containing TSP as internal standard. The HOD signal is presaturated. \* = Internal TSP standard. # = residual HOD peak. Vertical scale is adjusted according to the intensity of each spectrum.

in this type of NMR spectra, the general shape is given by large bands deriving from the convolution of signals from a huge amount of different compounds, while it is superimposed by a relatively small number of sharp peaks, coming from few major substances. Among these substances, the most clearly identifiable are acetate, formate, the H-1 proton of levoglucosan at 5.46 ppm and the methyl protons of 2-methylerythritol at 1.13 ppm. The latter two compounds are, respectively, the major substance formed from the pyrolysis of cellulose and the major aerosol derivative of the photo-oxidation of isoprene (Claeys et al., 2004)

The spectrum of blank, Fig. 1d, shows strong signals in the 3.5–3.8 ppm range due to dissolved cellulose derivatives derived from the filter used in the sample work-up. The interference arising from such impurities is more important in the spectra of the less concentrated samples, i.e., those from the wet period (Fig. 1c). Apart from the different contribution of the blank signals, the spectra of the three samples show a similar pattern with respect to the main identified bands. Intense, broad, and partly-overlapping bands are found in the aliphatic part of the spectra, and can be attributed

**Table 1.** H NMR and TOC data for fine aerosol samples from the HVDS sampler.

| Sample                                 | R-H         | Non-exchangeable H content<br>( $\mu\text{mol}/\text{m}^3$ ) <sup>a</sup> |             |                    |             | Arylic                   | WSOC <sup>b</sup><br>( $\mu\text{mol}/\text{C}/\text{m}^3$ ) | H/C molar<br>ratio |
|--|-------------|---|-------------|--------------------|-------------|--------------------------|--|--------------------|
|  |             | =C-C-H  | O-C-H       | O-CH-O<br>and =C-H |             |                          |  |                    |
| <i>Fine aerosol, dry period</i>        |             |   |             |                    |             |                          |  |                    |
| HVDS08NF                               | 0.57±0.02   | 0.71±0.02   | 0.38±0.02   | 0.013±0.003        | 0.10±0.04   | 2.23±0.11                | 0.80   |                    |
| HVDS09DF                               | 0.26±0.01   | 0.40±0.02   | 0.27±0.01   | 0.016±0.005        | 0.08±0.03   | 1.62±0.08                | 0.63   |                    |
| HVDS12DF                               | 0.20±0.01   | 0.30±0.01   | 0.17±0.01   | 0.010±0.005        | 0.06±0.03   | 1.20±0.06                | 0.61   |                    |
| HVDS15DF                               | 0.78±0.03   | 1.01±0.03   | 0.59±0.03   | ≤ 0.015            | 0.14±0.09   | 2.53±0.13                | 1.00   |                    |
| HVDS15NF                               | 0.65±0.04   | 0.78±0.05   | 0.44±0.05   | ≤ 0.015            | 0.13±0.09   | 1.80±0.09                | 1.11   |                    |
| HVDS17DF                               | 0.90±0.03   | 1.14±0.04   | 0.63±0.04   | 0.002±0.001        | 0.24±0.07   | 3.24±0.16                | 0.90   |                    |
| HVDS17NF                               | 0.97±0.02   | 1.20±0.03   | 0.66±0.03   | 0.018±0.008        | 0.26±0.05   | 3.75±0.19                | 0.83   |                    |
| HVDS26DF                               | 0.49±0.03   | 0.50±0.04   | 0.30±0.04   | 0.005±0.003        | ≤ 0.06      | 1.22±0.06                | 1.13   |                    |
| Averaged                               | 0.60±0.03   | 0.76±0.03   | 0.43±0.03   | 0.011±0.006        | 0.14±0.05   | 2.20±0.11                | 0.88   |                    |
| <i>Fine aerosol, transition period</i> |             |   |             |                    |             |                          |  |                    |
| HVDS37F                                | 0.13±0.01   | 0.15±0.01   | 0.10±0.01   | 0.004±0.001        | 0.032±0.021 | 0.51±0.03                | 0.81   |                    |
| HVDS40F                                | 0.154±0.002 | 0.130±0.003   | 0.068±0.003 | 0.005±0.001        | 0.035±0.005 | 0.61±0.03                | 0.64   |                    |
| HVDS43NF                               | 0.063±0.006 | 0.076±0.007   | 0.056±0.007 | 0.003±0.001        | ≤ 0.013     | 0.32±0.02                | 0.64   |                    |
| HVDS45NF                               | 0.054±0.002 | 0.065±0.002   | 0.038±0.002 | 0.002±0.001        | 0.012±0.004 | 0.36±0.02                | 0.47   |                    |
| Averaged                               | 0.101±0.005 | 0.105±0.006   | 0.065±0.006 | 0.003±0.001        | 0.023±0.01  | 0.45±0.07                | 0.64   |                    |
| <i>Fine aerosol, wet period</i>        |             |   |             |                    |             |                          |  |                    |
| HVDS51NF                               | 0.003±0.001 | 0.010±0.001   | 0.007±0.001 | ≤ 0.001            | ≤ 0.001     | 0.003±2×10 <sup>-4</sup> | 0.40   |                    |
| HVDS53NF                               | 0.031±0.003 | 0.043±0.004   | 0.019±0.004 | ≤ 0.001            | ≤ 0.005     | 0.031±0.002              | 0.83   |                    |
| HVDS54F                                | 0.008±0.001 | 0.019±0.001   | 0.016±0.001 | ≤ 0.001            | 0.002±0.001 | 0.008±4×10 <sup>-4</sup> | 0.79   |                    |
| HVDS55F                                | 0.004±0.001 | 0.005±0.001   | 0.002±0.001 | ≤ 0.001            | ≤ 0.002     | 0.004±2×10 <sup>-4</sup> | 0.85   |                    |
| Averaged                               | 0.01±0.001  | 0.02±0.001  | 0.011±0.001 | ≤ 0.001            | 0.002±0.001 | 0.059±0.002              | 0.72   |                    |

<sup>a</sup> Uncertainty is estimated from the variability of noise in the NMR spectra. Other error sources are believed to be of minor importance. When concentrations fall below the detection limit (D. L.), the value of the D. L. is reported.

<sup>b</sup> Uncertainty on TOC is ≤ 5%

to purely alkylic hydrogens, hydrogens in  $\alpha$ -position to unsaturated carbons, and hydrogens bound to alcoholic, etheral or estereal carbons. The band of alkylic R-H ( $\delta_H$ : 0.60–1.80 ppm) shows maxima at 0.9 ppm from terminal methyl hydrogens H<sub>3</sub>C-C and 1.3 ppm from polymethylene chains (CH<sub>2</sub>)<sub>n</sub>. The peaks are, however, poorly pronounced, indicating that long aliphatic chains, such as those of fatty acids, are not particularly abundant in these samples. This finding contrasts with the NMR analysis of samples from polluted environments at middle-latitudes (Decesari et al., 2000, 2006). Aromatic hydrogen atoms are responsible for the very broad band, with chemical shifts extending from 6 to 8.2 ppm, that shows two distinct maxima at 7.0 and 7.6 ppm. The first can be attributed to aromatic rings with electron-donor substituents (e.g., phenolic groups), while the second is characteristic of aromatic rings carrying both electron-donor and electron-acceptor (e.g., carbonyls and carboxyls) groups. The overall spectral features observed for the PM<sub>2.5</sub> HVDS samples collected during the SMOCC campaign substantially match those found for analogous samples collected during the dry and transition periods in 1999, during the EUSTACH-2 experiment (Graham et al., 2002).

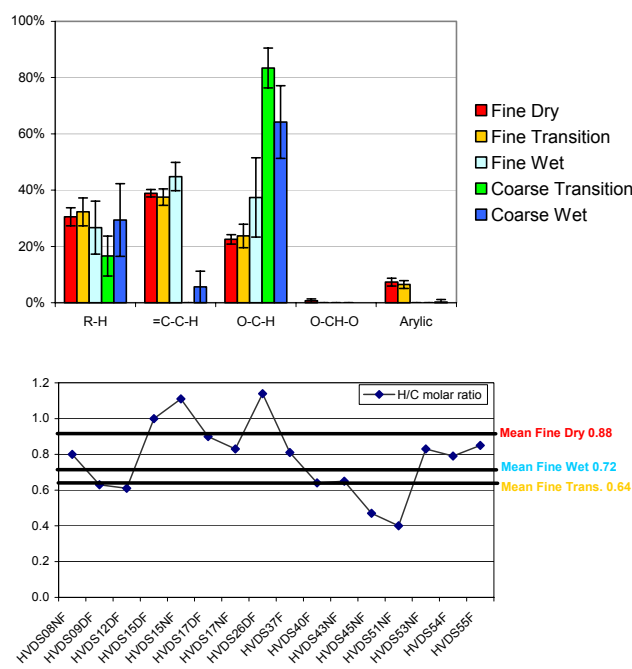
Figure 2 shows spectra for the coarse aerosol fraction of samples representative for the transition (a) and wet (b) periods. The NMR investigation of the coarse filters from the dry period, when the concentrations of fine particles overwhelmed those of coarse ones, could not be carried out because of the contribution from fine aerosols in the coarse fraction, which is inherent in dichotomous samplers (Dzubay et al., 1977; Graham et al., 2002). Although the spectra are not very different from those in Fig. 1, the band characteristic of hydrogens in  $\alpha$ -position to unsaturated carbon atoms (H-C-C=) is relatively less intense in the coarse samples compared to the fine samples. The same can be noticed in the case of the aromatic hydrogen atoms. Furthermore, there are several differences in the fine structure of the spectra between the coarse and the fine filter samples: a) intense peaks at 3.2 ppm due to unidentified substances in the coarse aerosol samples, b) a complex system of peaks at 3.8–4.0 ppm – strongly resembling the peaks of mannitol (Suzuki et al., 2001) – which are not seen in the PM<sub>2.5</sub> samples from the dry and transition period; c) the anomeric hydrogen of levoglucosan, which is absent or occurs in small concentrations in the coarse samples. It should be noted that the imperfect

**Table 2.** H NMR and TOC data for coarse aerosol samples from the HVDS sampler.

| Sample                                   | Non-exchangeable H content ( $\mu\text{mol}/\text{m}^3$ ) <sup>a</sup> |                    |                    |               | Arylic        | WSOC <sup>b</sup> ( $\mu\text{molC}/\text{m}^3$ ) | H/C molar ratio |
|--|--|--------------------|--------------------|---------------|---------------|---|-----------------|
|  | R-H  | =C-C-H             | O-C-H<br>and=C-H   | O-CH-O        |               |   |                 |
| <i>Coarse aerosol, transition period</i> |  |                    |                    |               |               |   |                 |
| HVDS43NC                                 | $\leq 0.005$   | $\leq 0.006$       | $0.03 \pm 0.005$   | $\leq 0.0003$ | $\leq 0.003$  | $0.041 \pm 0.002$                                 | 0.90            |
| HVDS45NC                                 | $0.010 \pm 0.003$  | $\leq 0.003$       | $0.017 \pm 0.002$  | $\leq 0.001$  | $\leq 0.005$  | $0.056 \pm 0.003$                                 | 0.58            |
| Averaged                                 | $0.005 \pm 0.002$  | $\leq 0.005$       | $0.025 \pm 0.004$  | $\leq 0.0007$ | $\leq 0.004$  | $0.049 \pm 0.002$                                 | 0.74            |
| <i>Coarse aerosol, wet period</i>        |  |                    |                    |               |               |   |                 |
| HVDS51NC                                 | $0.018 \pm 0.007$  | $\leq 0.009$       | $0.015 \pm 0.007$  | $\leq 0.002$  | $\leq 0.16$   | $0.027 \pm 0.001$                                 | 1.62            |
| HVDS54C                                  | $0.006 \pm 0.0001$   | $0.002 \pm 0.0002$ | $0.025 \pm 0.0001$ | $\leq 0.0001$ | $\leq 0.0002$ | $0.038 \pm 0.002$                                 | 0.93            |
| HVDS55C                                  | $\leq 0.002$   | $0.005 \pm 0.002$  | $0.016 \pm 0.002$  | $\leq 0.0001$ | $\leq 0.0003$ | $0.025 \pm 0.001$                                 | 0.92            |
| Averaged                                 | $\leq 0.003$   | $0.005 \pm 0.003$  | $0.019 \pm 0.003$  | $\leq 0.0009$ | $\leq 0.005$  | $0.030 \pm 0.002$                                 | 1.16            |

<sup>a</sup> Uncertainty is estimated from the variability of noise in the NMR spectra. Other error sources are believed to be of minor importance. When concentrations fall below the detection limit (D. L.), the value of the D. L. is reported.

<sup>b</sup> Uncertainty on TOC is  $\leq 5\%$ .



**Fig. 3.** (a) Average relative functional group percentage composition of fine WSOC samples in terms of moles of H. (b) H/C molar ratios of specific WSOC aerosol samples and mean values.

separation in the dichotomous sampler (Dzubay et al., 1977; Graham et al., 2002) is likely to explain partly the observed similarity between the spectra of the coarse and fine filters. To take into account the limited efficiency of the HVDS in separating the  $\text{PM}>2.5$  fraction from the fine aerosol, the

$\mu\text{mol}$  of H of each functional groups of coarse WSOC was corrected for the contribution of the fine particles, estimated on the basis of the relative volumes of air passed through the fine and coarse filters (Dzubay et al., 1977). The concentrations of the functional groups in  $\text{PM}>2.5$ , reported in the following tables are already corrected according to this procedure.

The amounts of organic non-exchangeable hydrogens and their uncertainty for the fine fraction of WSOC in the different spectral regions reported in Table 1, in terms of  $\mu\text{mol}$  of H per  $\text{m}^3$  of air sampled. All data are already corrected for the blank contribution. The same table reports the WSOC content in terms of  $\mu\text{mol}$  of  $\text{C}/\text{m}^3$  (from TOC measurements). The last column of Table 1 gives the measured molar H/C ratio, as a rough estimation of the degree of unsaturation of the organic matter in the samples. Table 2 gives the same data for the coarse size fraction, the coarse fraction data are also corrected for the fine fraction contribution. Average relative amounts of hydrogens in the different functional groups for the fine and the coarse fraction are also shown in Fig. 3a.

Among the spectral regions, the 5.0–5.5 ppm region attributed to acetalic and vinylic hydrogens is generally dominated by the levoglucosan anomeric hydrogen. The amount of levoglucosan calculated from our NMR data is in fair agreement with that found by GC/MS analysis (Claeys et al., 2005<sup>1</sup>) and ion-exclusion chromatography (Schkolnik et al., 2005) on the same samples. The comparison with the data

<sup>1</sup>Claeys, M., Kourtchev, I., Pashynska, V., Vas, G., Vermeylen, R., Cafmeyer, J., Chi, X., Artaxo, P., and Maenhaut, W.: Polar organic marker compounds in boundary layer aerosols during the LBA-SMOCC 2002 biomass burning experiment in Rondonia, Brazil: time trends, diurnal variations and size distribution, in preparation, 2005.

**Table 3.** Averaged H content percentage of WSOC aerosols.

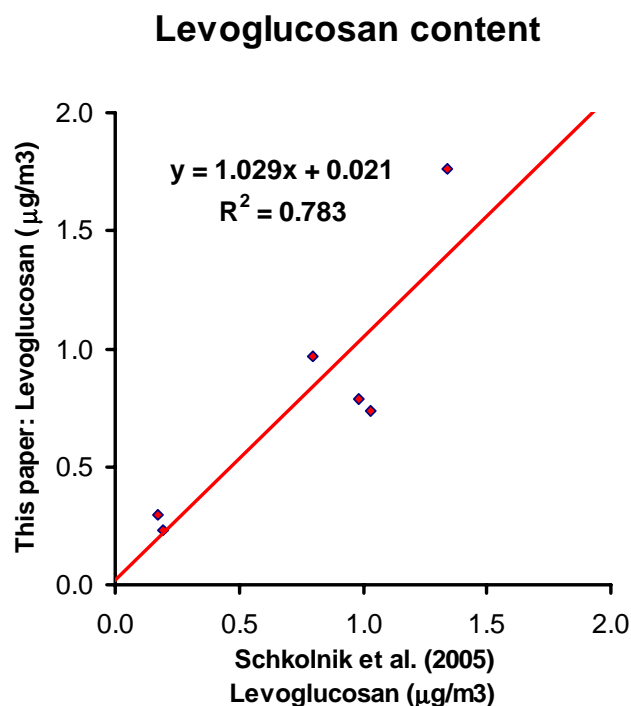
|                           | R-H       | =C-C-H         | O-C-H<br>and =C-H | O-CH-O         | Arylic         |
|---------------------------|-----------|----------------|-------------------|----------------|----------------|
| Fine, dry period          | 31.1±0.6  | 39.0±0.8       | 22.2±0.6          | 0.6±0.2        | 7.2±1.4        |
| Fine, transition period   | 33.9±0.8  | 35.3±0.9       | 21.9±0.8          | 1.1±0.1        | 7.7±1.8        |
| Fine, wet period          | 25.5±0.7  | 43.7±1.3       | 25.5±0.6          | 0.9±0.1        | 4.4±2.2        |
| Coarse, transition period | 16.6±7.1  | — <sup>a</sup> | 83.4±7.1          | — <sup>a</sup> | — <sup>a</sup> |
| Coarse, wet period        | 29.4±12.9 | ≤5.6           | 64.2±12.9         | — <sup>a</sup> | — <sup>a</sup> |

<sup>a</sup> In these cases no significant data from the single samples could be achieved.

from Schkolnik et al. (2005) is shown in Fig. 4; there is a fairly good correlation ( $R^2=0.78$ ); only 3% overestimation is observed in the H NMR analysis. Two clear trends immediately emerge from the inspection of Tables 1 and 2: a) samples collected in the dry period have 4–10 times higher concentrations than the samples from the transition period, which are, in turn, have 5–100 times higher concentrations than the samples from the wet period; b) within each period, only minor differences are observed among the samples, and, for the dry period, no clear variation between samples collected during day and night is visible. It is not possible to establish a similar trend for the other two periods since no day/night differentiated samples were available or analyzed. A less clear conclusion can be drawn with regard to the H/C molar ratio (Fig. 3b), since the data vary from 0.4 to 1.6. Nonetheless it can be roughly stated that the H/C ratio is higher in the dry period than in the transition and wet periods, although this statement is made cautiously, since some signals fall below the detection limit in the weaker spectra of the transition and wet period samples. This was due to the low aerosol loading, which was sometimes below detection limit, leading to an underestimation of the overall H content, an aspect that will be discussed in detail below.

Considering the relative uniformity of the samples, it was decided to compare the average relative distribution of hydrogens among the functional groups for the fine and coarse aerosol in the three periods in Table 3. It can be seen that the samples from the dry and transition periods have very similar functional group composition, with about 30% purely aliphatic hydrogens, a little more hydrogens in  $\alpha$  position to unsaturated carbon atoms, 20% hydrogens on oxygenated carbons, 1% acetalic and about 7% aryllic. The WSOC from the wet period has less aliphatic moieties, more unsaturated and oxygenated positions and less aryllic hydrogens, and is thus, in synthesis, more “oxidized” than the aerosol of the two previous periods.

Our results are generally consistent with those obtained in a previous sampling campaign in 1999 in the same region for the dry and transition periods (Graham et al., 2002); however, the present samples revealed a larger fraction of unsaturated compounds.



**Fig. 4.** Comparison between the levoglucosan data of Schkolnik et al. (2005) and the data obtained by our method for the same samples. Samples are: HVDS09DF, HVDS15DF, HVDS15NF, HVDS26DF, HVDS43NF, HVDS45NF.

Quantitative data from the coarse fraction must be taken with great care since the relative uncertainty is high. Nevertheless, a dramatically different pattern can be observed for these samples with respect to the fine aerosol samples. In fact, the composition of coarse particles in the transition and wet periods, also reported in Table 3, is dominated by oxygenated carbons, the hydrogens bond to them being 64–83% of the total, with a minor contribution from saturated and unsaturated alkyl chains. The  $\mu$ mols of aromatic rings and, for the transition period samples, of unsaturated alkyl chains are negligible. On the other hand, polyoxygenated alkylic chains are very abundant moieties in the coarse aerosol samples.



**Table 4.** H NMR and TOC data for size-segregated samples from the Berner impactor.

| Sample     | Non-exchangeable H percent <sup>a</sup> |                |                   |               |               | WSOC <sup>b</sup> ( $\mu\text{molC}/\text{m}^3$ ) | H/C molar ratio |
|------------|---|----------------|-------------------|---------------|---------------|---|-----------------|
|            | R-H                                     | =C-C-H         | O-C-H<br>and =C-H | O-CH-O        | Alkylic       |   |                 |
| BI23SeptD  |   |                |                   |               |               |   |                 |
| BI23SeptD1 | 37.4 $\pm$ 4.0                          | 42.9 $\pm$ 4.6 | 14.1 $\pm$ 3.9    | $\leq$ 2.6    | $\leq$ 16.3   | 0.15 $\pm$ 0.007                                  | 0.84            |
| BI23SeptD2 | 35.3 $\pm$ 1.9                          | 38.3 $\pm$ 2.2 | 18.7 $\pm$ 1.9    | $\leq$ 1.3    | $\leq$ 7.8    | 0.48 $\pm$ 0.02                                   | 0.83            |
| BI23SeptD3 | 37.0 $\pm$ 1.1                          | 35.9 $\pm$ 1.3 | 19.2 $\pm$ 1.1    | 1.0 $\pm$ 0.4 | 7.0 $\pm$ 2.7 | 0.83 $\pm$ 0.04                                   | 0.97            |
| BI25SeptN  |   |                |                   |               |               |   |                 |
| BI25SeptN1 | 52.3 $\pm$ 1.7                          | 31.3 $\pm$ 1.4 | 12.9 $\pm$ 1.2    | $\leq$ 0.8    | $\leq$ 4.7    | 0.11 $\pm$ 0.006                                  | 1.63            |
| BI25SeptN2 | 42.5 $\pm$ 0.9                          | 33.5 $\pm$ 1.0 | 18.1 $\pm$ 0.9    | 0.9 $\pm$ 0.3 | 5.0 $\pm$ 1.8 | 0.75 $\pm$ 0.004                                  | 0.97            |
| BI25SeptN3 | 34.7 $\pm$ 1.1                          | 34.9 $\pm$ 1.3 | 22.3 $\pm$ 1.1    | $\leq$ 0.7    | 7.3 $\pm$ 2.3 | 2.55 $\pm$ 0.13                                   | 0.81            |
| BI25SeptN4 | 50.1 $\pm$ 6.7                          | 31.7 $\pm$ 7.9 | 15.7 $\pm$ 6.8    | $\leq$ 4.5    | $\leq$ 28.1   | 0.07 $\pm$ 0.003                                  | 2.65            |
| BI25SeptN5 | 56.6 $\pm$ 1.9                          | 32.0 $\pm$ 2.2 | 10.9 $\pm$ 1.9    | $\leq$ 1.2    | $\leq$ 7.7    | 0.02 $\pm$ 0.001                                  | 3.91            |

<sup>a</sup> Uncertainty is estimated from the variability of noise in the NMR spectra. Other error sources are believed to be of minor importance. When concentrations fall below the detection limit (D. L.), the value of the D. L. is reported.

<sup>b</sup> Uncertainty on TOC is  $\leq$ 5%.

### 3.2 Size segregated samples

Two size segregated Berner impactor sample sets collected in the dry period during the day of 23 September and the night of 25 September 2005 were also used for HNMR investigation of WSOC. The spectra in D<sub>2</sub>O solution of the five fractions of the sample collected on 25 September and one spectrum of the blank are shown in Fig. 5. Percentage distributions of hydrogens in the different spectral regions, TOC values and H/C ratios are reported in Table 4. The functional group composition of the nocturnal sample BI25SeptN shows marked variations among the size intervals. While the composition of the third impactor stage (0.42–1.2  $\mu\text{m}$ ) is similar to the mean composition of the fine samples collected with the HVDS in the same period, all the other size fractions show a higher content of alkylic groups and a lower content of oxygenated and aromatic functional groups. In particular, the smallest size range, 0.05–0.14  $\mu\text{m}$ , shows a high proportion (45%) of alkylic hydrogens and a low content of H-C-O groups. The results obtained for the Berner impactor samples do not contradict those from the HVDS fine filters, since the mass of submicrometer particles is almost completely accounted for by particles with diameter of 0.14–1.2  $\mu\text{m}$  (Fig. 6).

Although the risk of contamination is high for very diluted samples and data obtained from such samples must be treated with care, it must be emphasized that the H NMR spectrum of the water-extract of the 0.05–0.14  $\mu\text{m}$  particles does not resemble any other published spectrum of ambient aerosol that has been collected so far (e.g., Decesari et al., 2000, 2005; Suzuki et al., 2001; Graham et al., 2002). Instead, similar spectra were obtained from the analysis of smoke particles produced by the combustion of sugar cane in the Max

Planck combustion facility, during the SMOCC intercomparison experiment (unpublished results). Apparently, the peculiar functional group composition of the finest size range of sample BI25SeptN is characteristic of freshly-emitted smoke particles. This hypothesis is consistent with the results of the analysis of inorganic ions and WSOC chromatographic classes carried out on 32 size-segregated samples collected during the dry period (Fuzzi et al., 2006). Such results indicate an enrichment of fresh smoke particles in the smallest size intervals, and a higher proportion of such particles in the nocturnal aerosol samples. Conversely, aerosol samples collected during daytime show a more aged character and a more homogeneous composition in the submicrometer size range. This finding is in agreement with the NMR functional group composition of the size-segregated sample BI23SeptD, which shows only limited variation from the size intervals in the fine size range (Table 4).

Due to the small number of impactor samples analyzed, the present data do not allow the derivation of average size-segregated NMR compositions for the different periods of the campaign. On the other hand, these findings support potentially strong variations of the functional group composition between the different size intervals, which cannot be seen by fractionating the aerosol with a cut-off of 2.5  $\mu\text{m}$  (or even 1.0 or 2.0  $\mu\text{m}$ ). Thus there is definitely a call for further investigation by means of sampling techniques based on multistage-impactors.

### 3.3 Fractions from preparative ion chromatography

One filter sample from the dry season, HVDS17NF, was subjected to chromatographic preparative separation on a DEAE column (Decesari et al., 2000, 2006). This procedure allows

**Table 5.** H NMR data for IC fractions for sample HVDS17NF.

|          | Non-exchangeable H content ( $\mu\text{mol}/\text{m}^3$ ) <sup>a</sup> |           |           |                    | Arylic | Total C <sup>b</sup> ( $\mu\text{mol}/\text{m}^3$ ) | H/C molar ratio |
|----------|--|-----------|-----------|--------------------|--------|---|-----------------|
|          | R-H  | =C-C-H    | O-C-H     | O-CH-O<br>and =C-H |        |   |                 |
| HVDS17NF |  |           |           |                    |        |   |                 |
| NC       | 0.16±0.01  | 0.18±0.01 | 0.22±0.01 | 0.019±0.003        | ≤0.10  | 0.77±0.04   | 0.83            |
| MDA      | 0.34±0.01  | 0.30±0.01 | 0.20±0.01 | ≤0.007             | ≤0.10  | 0.95±0.05   | 0.96            |
| PA       | 0.21±0.01  | 0.26±0.01 | 0.11±0.01 | ≤0.006             | ≤0.10  | 1.08±0.05   | 0.61            |

<sup>a</sup> Uncertainty is estimated from the variability of noise in the NMR spectra. Other error sources are believed to be of minor importance. When concentrations fall below the detection limit (D. L.), the value of the D. L. is reported.

<sup>b</sup> Total C is measured by TOC for the separated fractions after complete removal of  $\text{NH}_4\text{HCO}_3$ . Uncertainty on Total C is ≤5%.

the separation of the three main fractions, operationally identified on the basis of their chromatographic behavior as neutral compounds (NC), mono- and dicarboxylic acids (MDA) and polycarboxylic acids (PA). The H-NMR spectra of the three fractions of sample HVDS17NF are shown in Fig. 7, while the corresponding hydrogen content is reported in Table 5 and plotted in Fig. 8.

Considering the overall amount of non-exchangeable hydrogens, the NC, MDA and PA fractions represent 27, 38 and 35%, respectively. When compared to the TOC data, the following H/C ratios are obtained: 0.83, 0.96, and 0.61, therefore the PA fraction is significantly more rich in double bonds and rings than the other two. Looking at the relative composition, the three fractions are very different: the NC fraction is dominated by hydrogens bound to oxygenated carbons, this can be due to the conspicuous presence of polyols or sugar-like compounds; the relatively high concentration of acetalic hydrogens, mostly derived from H-1 of levoglucosan, accounts for the presence of anhydrosugars; moreover, consistent aromatic and aliphatic chain moieties are present in this fraction, testifying to its complex composition; the MDA fraction contains a more unbiased distribution of hydrogens in the different spectral regions and can be interpreted as a complex mixture of hydroxylated or alkoxyated aliphatic and aromatic carboxylic acids; the PA fraction exhibits a large aromatic content and a reduced amount of hydroxylated and alkoxyated carbons with respect to the previous one. The spectral features and other characteristics of the PA fraction were previously attributed to humic-like substances (HULIS); indeed the presence of HULIS in samples collected during the SMOCC campaign has been suggested (Hoffer et al., 2005). The functional groups of the PA in sample HVDS17NF indicate that the overall composition of HULIS produced by biomass burning marginally matches that of humic and fulvic acids derived from the early diagenesis of lignin and cellulose. Indeed, careful examination of the aromatic hydrogens region (6.5–8 ppm) of Fig. 7c shows that the maximum of the band is located at 7.6 ppm, (not indica-

tive of phenols and anisols); on the contrary, aromatic compounds characteristic of lignin are characterized by a massive presence of hydroxy and alkoxy substituents.

### 3.4 H NMR analysis of derivatized WSOC samples

The carboxylic acid functional group has a special role in the chemistry of water soluble aerosol: it is the most diffused group that can be ionised, allowing organic compounds to assume a negative charge. In its undissociated form, it is a strong hydrogen-bond donor and acceptor. Both these features can influence the activity and surface tension of water, two crucial parameters in determining the CCN ability of aerosol particles. Due to these outstanding properties, many carboxylic acids have been investigated and detected in the aerosol, including short chain aliphatic acids, saturated and unsaturated fatty acids, di- and tricarboxylic acids, mono- and polycarboxylic hydroxyacids, benzoic acids etc. Almost all of them have been found in biomass burning aerosol and specifically during the SMOCC campaign (Decesari et al., 2006). However, a measurement of the overall amount of  $\text{CO}_2\text{H}$  groups within aerosol samples is still missing, to our best knowledge.

It was decided to apply the functional group approach to the analysis of biomass burning WSOC aerosol from Rondônia also to the carboxylic acid group. Since the direct information was missing in the H NMR spectrum in  $\text{D}_2\text{O}$  because of the chemical exchange of the  $\text{CO}_2\text{H}$  hydrogen with the solvent, a method was developed to convert the NMR invisible  $\text{CO}_2\text{H}$  groups in the NMR detectable  $\text{CO}_2\text{CH}_3$  group. A similar transformation for NMR analysis has previously been applied to the investigation of humic acids (Noyes and Leenheer, 1989), but never to atmospheric aerosols.

The reagent chosen to perform methylation is diazomethane  $\text{CH}_2\text{N}_2$ , a gas that can be prepared as ethereal solution from the decomposition of N-methyl-N-nitroso-*p*-toluensulfonamide. The choice was due to the fast and clean reaction of  $\text{CH}_2\text{N}_2$  under very mild conditions, also in the heterogeneous phase. The reaction mechanism is described

**Table 6.** H NMR data from methylation procedure.

| Sample                      | CO <sub>2</sub> H ( $\mu\text{molC}/\text{m}^3$ ) <sup>a</sup> | WSOC ( $\mu\text{molC}/\text{m}^3$ ) <sup>b</sup> | CO <sub>2</sub> H percentage (C mole%) |
|-----------------------------|--|---|--|
| Fine aerosols               |  |   |  |
| HVDS8NF                     | 0.25±0.01  | 2.23±0.11   | 11.2±0.9                               |
| HVDS09DF                    | 0.14±0.01  | 1.62±0.08   | 8.9±0.8                                |
| HVDS12DF                    | 0.21±0.01  | 1.20±0.06   | 17.1±1.2                               |
| HVDS15NF                    | 0.21±0.02  | 1.80±0.09   | 11.7±1.4                               |
| HVDS37F                     | 0.08±0.003   | 0.51±0.03   | 16.0±1.4                               |
| HVDS40F                     | 0.151±0.001  | 0.61±0.03   | 24.7±1.4                               |
| HVDS43NF                    | 0.055±0.002  | 0.32±0.02   | 17.0±1.5                               |
| HVDS45NF                    | 0.039±0.001  | 0.36±0.02   | 10.7±0.7                               |
| Mean Fine Transition Period |  |   | 17.1±1.3                               |
| HVDS53NF                    | 0.020±0.001  | 0.031±0.002                                       | 17.0±1.8                               |
| Mean Fine Wet Period        |  |   | 17.0±1.8                               |
| Coarse aerosols             |  |   |  |
| HVDS43NC                    | ≤0.01  | 0.041±0.002                                       | ≤33.9                                  |
| HVDS51NC                    | ≤0.08  | 0.027±0.001                                       | ≤29.4                                  |
| IC Fractions                |  |   |  |
| HVDS17NF-NC                 | ≤0.04  | 0.77±0.04   | ≤4.8                                   |
| HVDS17NF-MDA                | 0.11±0.04  | 0.95±0.05   | 11.8±5.2                               |
| HVDS17NF-PA                 | 0.14±0.03  | 1.08±0.05   | 13.2±3.9                               |

<sup>a</sup> Uncertainty is estimated from the variability of noise in the NMR spectra. Other error sources are believed to be of minor importance. When concentrations fall below the detection limit (D. L.), the value of the D. L. is reported.

<sup>b</sup> Uncertainty on TOC is ≤5%.

in Fig. 9. Since only carboxylic acids and not carboxylates ( $\text{RCO}_2^-$ ) react with  $\text{CH}_2\text{N}_2$ , acidification with excess HCl is carried out prior to reaction, in order to convert carboxylates into carboxylic acids.  $\text{CH}_2\text{N}_2$  is a dangerous and toxic substance (R: 45; S: 53–45), but the very small amounts required allow safe operation by well trained personnel.

Methylation is performed on dried, acidified WSOC extract in  $\text{CH}_2\text{Cl}_2$  suspension by adding a strong molar excess of  $\text{CH}_2\text{N}_2$  solution in diethyl ether at 0° C. The reagent in excess is then removed by evaporation. Conversion of acids into methyl esters strongly reduces the polarity of such compounds, making them soluble in organic solvents. The parts of WSOC that do not contain acids, mainly sugars and polyols, are unaffected and remain soluble only in water. Therefore our procedure ends up with two products for NMR analysis: one in  $\text{CDCl}_3$  solution, containing the methyl ester of carboxylic acids, and one in  $\text{D}_2\text{O}$  solution, containing the species other than carboxylic acids. The H NMR spectra of these two fractions (NMR-B in  $\text{CDCl}_3$  and in NMR-C  $\text{D}_2\text{O}$ ) are compared in Fig. 10 with that of the original sample HVDS8NF in  $\text{D}_2\text{O}$  (NMR-A) and of a blank sample in  $\text{CDCl}_3$ . The signals present in this last spectrum come from impurities of the reagent and provide some small interference contribution in the methylesters region (3.20–4.40 ppm) region. Looking at NMR-C, one immediately observes a similarity with the spectrum of fraction NC in Fig. 7. The integrated data are also similar. It suggests that this non-

methylable residue is the same as the neutral compounds isolated by liquid chromatography. The NMR-B spectrum, besides some impurities in the aliphatic region caused by the reagents used, shows a strong signal in the 3.20–4.40 region that is attributable to the methyl ester groups, but also contains the  $\text{CH-O}$  hydrogens already present in the original sample. To account for this part, the moles of H present in the NMR-A in the same spectral region are subtracted from the moles found in the same interval in NMR-C (that are no longer present in the  $\text{CDCl}_3$  spectrum). The result represents the contribution of the original  $\text{CH-O}$  hydrogens to spectrum NMR-B. Subtraction of this amount from the moles of H present in NMR-B leaves the moles of hydrogens due to methyl esters formed from the diazomethane reaction, once the contribution from the blank is also subtracted. The resulting concentrations, divided by 3 to account for the stoichiometry of the methyl group, directly represents the moles of  $\text{CO}_2\text{H}$  groups present in the original WSOC sample. It is worth noting that when the same subtraction is applied to the  $\text{CH-C=}$  spectral region, which is not affected by methylation and is free from peaks of contaminants, it gives values very close to 0, testifying how a complete recovery of material is achieved in the procedure. The contribution from the blank represents a limit to the detection of  $\text{CO}_2\text{H}$  groups that has been calculated and generally corresponds to less than 20% of the signal of methyl esters. The mole concentration of  $\text{CO}_2\text{H}$  is reported in Table 6 for selected samples

**Table 7.** Average carbon percentages in aerosol WSOC.

|                                   | C content (moles%) <sup>a</sup> |                |           |                    |                | CO <sub>2</sub> H <sup>b</sup> | Unaccounted Carbon <sup>c</sup> |
|-----------------------------------|---------------------------------|----------------|-----------|--------------------|----------------|--------------------------------|---------------------------------|
|                                   | R-H                             | =C-C-H         | O-C-H     | O-CH-O<br>and =C-H | Arylic         |                                |                                 |
| Guessed H/C ratio                 | 1.8                             | 1.8            | 1.2       | 1.0                | 0.4            |                                |                                 |
| Fine aerosol, dry period          | 15.2±0.3                        | 19.1±0.4       | 16.3±0.4  | 0.5±0.2            | 15.8±2.4       | 12.1±1.5                       | 28.1±1.2                        |
| Fine aerosol, Transition period   | 11.7±0.3                        | 13.0±0.3       | 11.3±0.4  | 0.9±0.1            | 12.0±2.8       | 17.9±1.3                       | 33.2±1.3                        |
| Fine aerosol, wet period          | 9.9±0.3                         | 18.5±0.6       | 16.1±0.3  | 0.7±0.1            | 8.1±4.0        | 17.0±1.8                       | 24.6±1.8                        |
| Coarse aerosol, transition period | 9.7±4.2                         | – <sup>d</sup> | 90.3±7.7  | – <sup>d</sup>     | – <sup>d</sup> | – <sup>d</sup>                 | –                               |
| Coarse aerosol, wet period        | 19.5±8.4                        | ≤10.0          | 70.6±14.2 | – <sup>d</sup>     | – <sup>d</sup> | – <sup>d</sup>                 | –                               |

<sup>a</sup> Percentage C content calculated from H NMR data of Tables 1 and 2, dividing each value by the H/C ratios reported here and averaging over the samples of each period.

<sup>b</sup> CO<sub>2</sub>H content is averaged over those samples for which its amount was determined (see Table 6).

<sup>c</sup> Percentage difference between the amount of C calculated from NMR and the WSOC amount obtained by TOC reported in Tables 1 and 2.

<sup>d</sup> In these cases no significant data from the single samples could be achieved.

**Table 8.** Carbon percentages in size-segregated samples.

| Sample     | C content (moles%) <sup>a</sup> |          |          |                    |          | Unaccounted (moles%) <sup>b</sup> |
|------------|---------------------------------|----------|----------|--------------------|----------|-----------------------------------|
|            | R-H                             | =C-C-H   | O-C-H    | O-CH-O<br>and =C-H | Arylic   |                                   |
| BI23SeptD  |                                 |          |          |                    |          |                                   |
| BI23SeptD1 | 17.4±1.9                        | 20.0±2.1 | 9.8±2.7  | ≤ 1.6              | ≤ 9.8    | 40.9±4.8                          |
| BI23SeptD2 | 16.4±0.9                        | 17.8±2.1 | 13.0±1.3 | ≤ 0.8              | ≤ 4.8    | 37.5±2.5                          |
| BI23SeptD3 | 19.9±0.6                        | 19.3±0.7 | 15.5±0.9 | 1.0±0.4            | 16.9±6.5 | 27.3±3.0                          |
| BI25SeptN  |                                 |          |          |                    |          |                                   |
| BI25SeptN1 | 47.5±1.5                        | 28.4±1.3 | 17.6±1.6 | ≤0.8               | ≤4.7     | –5.5±4.8                          |
| BI25SeptN2 | 22.8±0.5                        | 18.0±0.5 | 14.6±0.7 | 0.8±0.3            | 12.2±4.4 | 31.5±2.0                          |
| BI25SeptN3 | 15.6±0.5                        | 15.7±0.6 | 15.1±0.7 | ≤0.4               | 14.9±4.6 | 38.2±2.1                          |
| BI25SeptN4 | 44.2±5.2                        | 28.0±7.0 | 20.8±9.0 | ≤4.5               | ≤28.1    | – <sup>c</sup>                    |
| BI25SeptN5 | 52.9±1.9                        | 29.9±1.1 | 15.3±2.7 | ≤1.2               | ≤7.7     | – <sup>c</sup>                    |

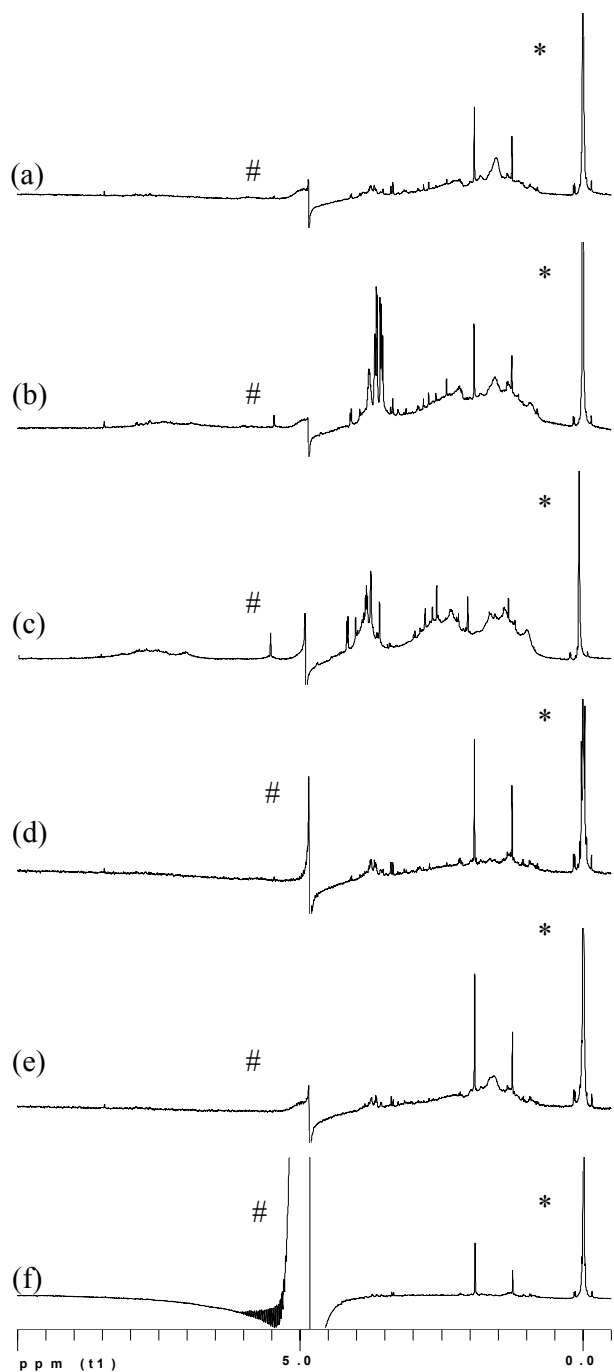
<sup>a</sup> Uncertainty is estimated from the variability of noise in the NMR spectra. Other error sources are believed to be of minor importance. When concentrations fall below the detection limit (D. L.), the value of the D. L. is reported.

<sup>b</sup> Percentage difference between the amount of C calculated from H NMR and the WSOC amount obtained by TOC measurements reported in Table 4.

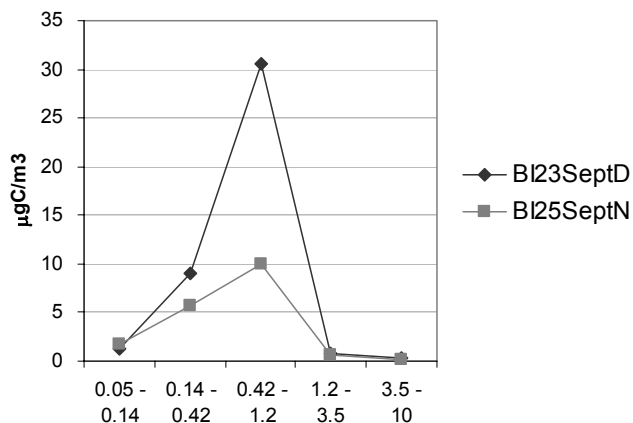
<sup>c</sup> Carbon content calculated from NMR was significantly higher than WSOC. For these samples C percentages are relative to the accounted carbon.

of fine and coarse aerosols and for the IC fractions of sample HVDS17NF, together with the overall moles of C in WSOC from TOC measurements. The last column of Table 6 gives the percentage of carboxylic carbons with respect to the total moles of water-soluble carbon. This last figure is about 11% for nighttime samples of fine aerosol during the dry period, but both higher and lower values are observed for integral daily samples, reaching 17% in samples from the transition and wet periods. In summary, 1 carbon in 9 up to 1 carbon

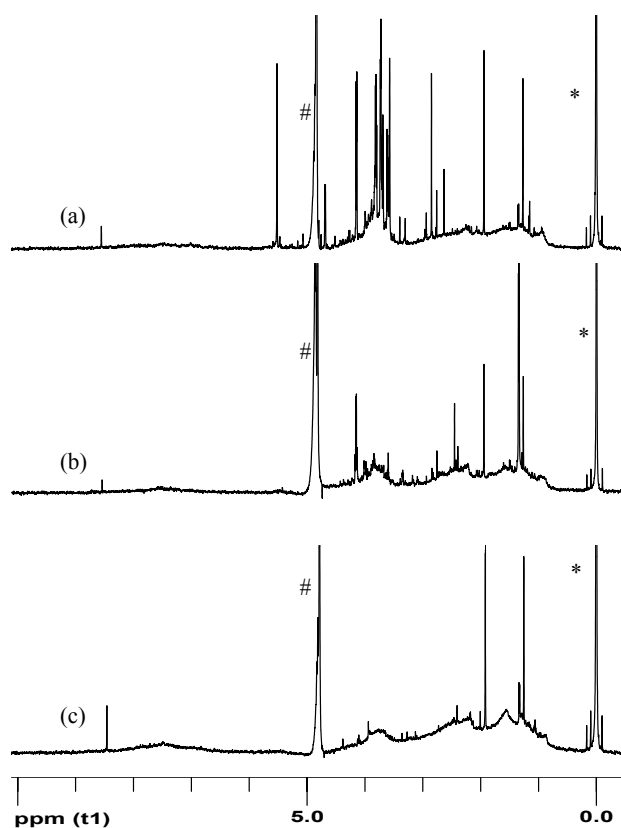
in 6 is a carboxylic group in the fine aerosol WSOC fraction. Undoubtedly, the background aerosol collected during the wet period contains significantly more carboxylic acids than the biomass burning aerosol of the dry period. Concerning the PM<sub>>2.5</sub> samples, we could not provide CO<sub>2</sub>H concentrations significant respect to blanks and to the expected contribution from fine particles. Turning to the IC fractions of sample HVDS17NF, surprisingly, some carboxylic acids were also found in fraction. NC fraction, although it is



**Fig. 5.**  $^1\text{H}$  NMR spectra of a size-segregated sample BI25SeptN. Spectra (a) to (e), are from the different stages of the impactor (a: 0.05–0.14, b: 0.14–0.42, c: 0.42–1.2, d: 1.2–3.5, e: 3.5–10  $\mu\text{m}$ ); (f) blank. Spectra are in  $\text{D}_2\text{O}$  solution containing TSP as internal standard. The HOD signal is presaturated. \* = Internal TSP standard. # = residual HOD peak. Vertical scale is adjusted according to the intensity of each spectrum. Impurities from MCE are visible in the second spectrum (b), corresponding to the only one sample that has been subjected to filtration because of its high turbidity.

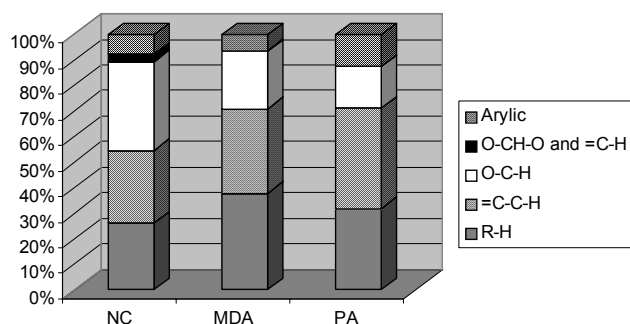


**Fig. 6.** TOC content in the different stages of size-segregated samples.

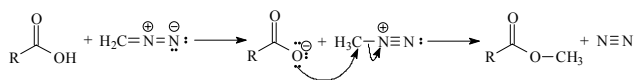


**Fig. 7.** IC fractions from sample HVDS17NF. (a) NC fraction, (b) MDA fraction, (c) PA fraction. Spectra are in  $\text{D}_2\text{O}$  solution containing TSP as internal standard. The HOD signal is presaturated. \* = Internal TSP standard. # = residual HOD peak. Vertical scale is adjusted according to the intensity of each spectrum.

thought that this is due to the imperfect separation of neutral compounds from acids by IC chromatography. In the MDA fraction, the  $\text{CO}_2\text{H}$  content is similar to that of some



**Fig. 8.** Functional groups composition of IC fractions of WSOC of sample HVDS17NF.

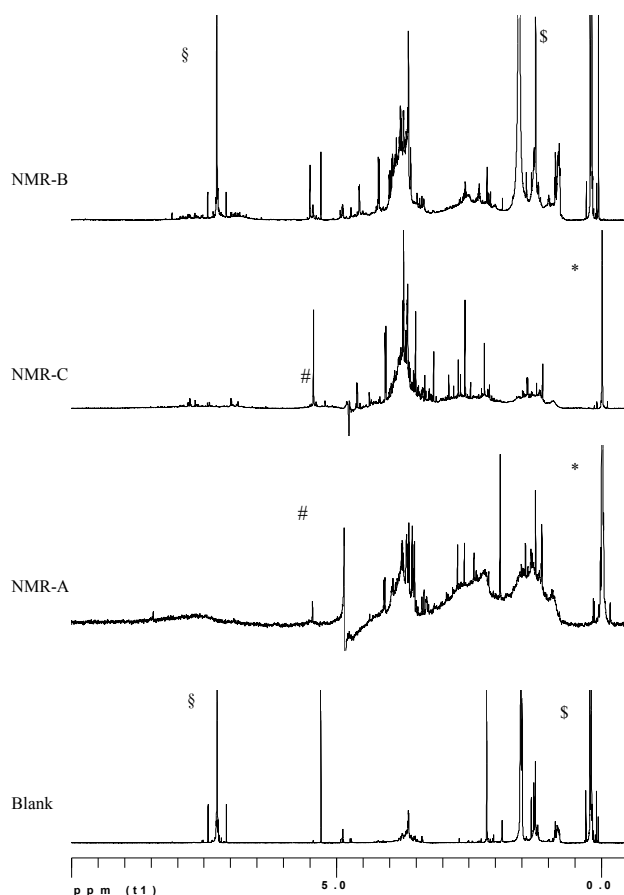


**Fig. 9.** Conversion of carboxylic acids into methyl esters by reaction with diazomethane.

unfractionated samples of the same period, and corresponds to the  $\text{CO}_2\text{H}$  content of dodecanoic acid (i.e., 1 carbon in 12), while in the PA fractions that value significantly increases, but not more than to 1 carbon in 9, is a carboxylic acid.

#### 4 Discussion

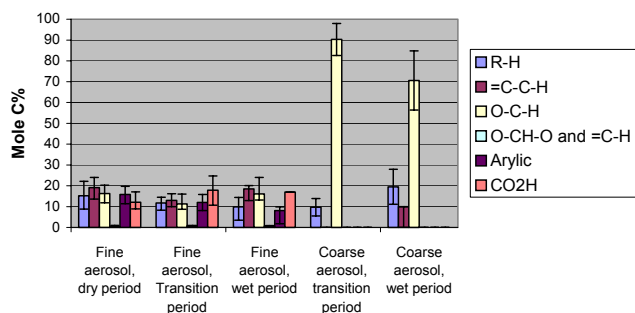
The above section presented H NMR functional group compositions of aerosol samples collected on  $\text{PM}_{2.5}$  and  $\text{PM}_{>2.5}$  quartz filters, as well as by means of a five-stage Berner impactor. However, in order to compare the results obtained with other data from the SMOCC campaign, e.g. those from TOC-analysis or thermal evolution measurements, and to attempt a carbon mass balance, hydrogen amounts from H NMR must be converted into carbon units. To convert H into C amounts it was necessary to guess specific H/C figures for the different functional groups defined in the previous section. This aspect has already been discussed in a previous paper (Fuzzi et al., 2001), and we refer to that paper for details. The H/C values chosen here are almost the same as those of the previous work, but a specific value was also defined for the aryllic carbons, which were set at a value  $\text{H/C}=0.4$ , corresponding to the average H/C ratio for aromatic rings of lignins (Table 7). On this basis, the H content of Tables 1–5 were converted into C content. The averaged molar percentage amounts of C in HVDS samples are reported in Table 7, while the corresponding values for size segregated and chromatographic fraction samples are reported in Tables 8 and 9, respectively. The total carbon content of each sample calculated the above way was compared with the actual WSOC content from TOC measurements. The differences found are also reported, as per-



**Fig. 10.** H NMR spectra of sample HVDS8NF: NMR-A original spectrum in  $\text{D}_2\text{O}$ ; NMR-B spectrum of the methyl ester in  $\text{CDCl}_3$ ; NMR-C spectrum of the  $\text{CDCl}_3$ -insoluble residue, dissolved in  $\text{D}_2\text{O}$ , blank in  $\text{CDCl}_3$ . \* = Internal TSP standard, # = residual HOD peak, § TKS standard, § residual  $\text{CHCl}_3$ . Vertical scale is adjusted according to the intensity of each spectrum.

centage of total WSOC, in Tables 7–9. If outliers are excluded, the “unaccounted” carbon ranges from 20 to 40% of total WSOC, but the mean values reported in Table 7 for the fine aerosol are about 20% for the dry period and about 30% for the transition and wet periods. No clear correlation can be found with total carbon content; however, the higher values of unaccounted C are generally found for lightly-loaded samples. It is very difficult to explain this imbalance in the carbon content. The following, non reciprocally excluding, hypotheses can be formulated:

1. A significant part of the material is colloidal or highly polymerised and is not revealed by NMR because of its unfavourable spectroscopic properties (very long  $T_1$ ); some volatile compounds (like low molecular weight acids) are lost in the manipulations.
2. The proposed H/C ratios are significantly lower than the real ones. The figures are based on a reasonable



**Fig. 11.** Mean and variability composition of WSOC samples from HVDS in terms of moles of C.

assumption concerning the structure of the molecules composing the aerosols, but some values remain questionable, especially the degree of substitution of the aromatic rings and the relative amounts of alcohols, ethers and esters; moreover, there are many hydrogenless functional organic groups that would not be revealed at all in H NMR spectra: ketones, quaternary carbons in alkyl chains, fully substituted alkenes, aryllic rings etc..

The presence of high molecular weight compounds and the presence of non-hydrogenated functional groups are believed to be the most likely causes of the carbon imbalance, but further investigation needs to be performed on these specific aspects.

What is reported for the HVDS samples holds also for the size-segregated samples and IC fractions, if we exclude some very diluted samples from the Berner impactor like BI25SeptN4 and BI25SeptN5. In these cases, a large overestimation of C amount was found, possibly due to some contamination during sample preparation and analysis.

The relative average composition of the fine and coarse aerosol samples in terms of distribution of C among the different functional groups is also shown in Fig. 11 together with their range of variation. This composition does not account for all the measured carbon, as already remarked.

Any consideration about the IC fractions must be made with caution, since only one sample could be subjected to the chromatographic separation. Nevertheless, looking at Table 9 a clear difference appears between the three classes of WSOC. In particular, the PA fraction shows a strong aromatic character and a high CO<sub>2</sub>H content (almost 1 carbon out of 7 of the accounted carbons are carboxylic acids), resembling more closely humic-like substances.

The functional group compositions expressed in terms of carbon budget (Tables 7–9) can be directly compared to those obtained by speciation of individual WSOC by GC/MS, IC and IEC analysis on the same samples. A full treatment of the subject is given in a companion paper by Decesari et al., 2006. It turns out that the WSOC speciated at the molecular level accounts for a small fraction of the functional groups determined by H NMR on bulk samples. On the other hand,

a substantial fraction of the H-C-O groups of the neutral fraction of WSOC could be apportioned into low-molecular weight polyhydroxylated compounds, such as sugar-anhydrides (e.g., levoglucosan) and sugar-alcohols (e.g., mannitol). Furthermore, the carboxylic groups of the MDA fraction of sample HVDS17NF are largely accounted for by short-chain aliphatic acids and hydroxyacids. Conversely, the speciation of PA was insignificant, and alkylic and aromatic groups of all three IC fractions and of bulk samples could not be accounted for by the WSOC identified through high-resolution chromatographic techniques.

The lack of matching between the H NMR compositions and the individually detected compounds complicates the understanding of the processes leading to the observed functional group distributions. Moreover, the results of the speciation methods sometimes apparently contradict those of the functional group analysis. A first point to discuss concerns the relative constancy of H NMR composition of daytime and nighttime samples. This observation is in contrast with the results of evolved gas analysis, GC/MS and liquid chromatographic analysis (Hoffer et al., 2005; Claeys et al., 2005<sup>1</sup>; Schkolnik et al., 2005; Decesari et al., 2006), which provided fairly distinct chemical compositions for day and night samples, probably due to the different prevalent combustion processes active in daytime (more flaming) and at nighttime (more smoldering). Apparently, the combustion type does not affect the relative contribution of the main functional groups identified by H-NMR. This unexpected outcome calls for the presence of some compensation of the reduced concentration of polyhydroxylated neutral compounds (NC) in daytime samples found in IC analysis, from polyhydroxylated carboxylic acids (either MDA and PA). Gao et al. (2003) reported the presence of polyhydroxy-acids in high concentrations in smoke particles from savannah fires.

A second aspect for discussion is related to the differences between samples collected in the different periods of the campaign. In this respect, if submicrometer aerosols are by far dominated by biomass burning products in the dry period, the composition of the wet period samples should reflect the natural background. The gradual substitution of the markers of biomass burning with biogenic tracer compounds throughout the experiment is confirmed by GC/MS analysis (Claeys et al., 2005<sup>1</sup>). Looking at the data presented in Tables 3 and 6, fine aerosol samples from the wet period contain significantly more oxygenated carbons, either in the form of OH, OR or CO<sub>2</sub>H groups. Nevertheless, the observed changes are minor in comparison with what was a priori expected: percentage variations in the functional group budget from the dry to the wet period add up to only ca. 25% both on a H or a C basis (Tables 3 and 7). Such data are in agreement with other aerosol measurements (Fuzzi et al., 2006), indicating that the burning activity was still active in the wet period and strongly affected the composition of the submicrometer aerosol particles. Indeed, tracer analysis by GC/MS indicates that biomass burning products were only partly replaced by

**Table 9.** Carbon percentages in IC fractions of sample HVDS17NF.

| IC Fraction | R-H      | =C-C-H   | O-C-H    | C content (moles%) <sup>a</sup> |        |                   | Unaccounted (moles%) <sup>b</sup> |
|-------------|----------|----------|----------|---------------------------------|--------|-------------------|-----------------------------------|
|             |          |          |          | O-CH-O and =C-H                 | Arylic | CO <sub>2</sub> H |                                   |
| NC          | 12.0±0.7 | 13.1±0.7 | 24.1±1.1 | 2.5±0.4                         | ≤25.7  | ≤3.4              | 29.6±10.6                         |
| MDA         | 20.0±0.6 | 17.7±0.7 | 17.8±0.6 | ≤0.4                            | ≤8.3   | 11.8±4.3          | 17.4±2.5                          |
| PA          | 10.8±0.5 | 13.4±0.5 | 8.3±0.7  | ≤0.6                            | ≤9.5   | 13.2±2.5          | 35.1±4.0                          |

<sup>a</sup> Uncertainty is estimated from the variability of noise in the NMR spectra. Other error sources are believed to be of minor importance. When concentrations fall below the detection limit (D. L.), the value of the D. L.F is reported.

<sup>b</sup> Percentage difference between the amount of C calculated in the previous column and the WSOC amount obtained by TOC measurement reported in Table 5.

biogenic compounds at the end of the campaign. An unambiguous tracer of biomass burning – levoglucosan – was found in significant concentrations in the wet period samples also by H NMR analysis (Fig. 1).

Another possible reason for the relatively small changes in the functional group composition of fine aerosol samples during the experiment is that biomass burning products were replaced by biogenic compounds having similar chemical structures, as in the case of sugar-alcohols compared to anhydrosugars.

## 5 Conclusions

Functional group analysis by H NMR (Decesari et al., 2000) was extensively performed on aerosol samples collected in Rondônia, during the transition from the dry to the wet period. A new insight in the functional group composition of WSOC was provided by the development and application of a new methodology for the direct measurement of the amount of carboxylic groups through chemical derivatization and H NMR spectroscopic determination. Carboxylic acids are the most important oxygenated functional group in the organic aerosol fraction. In this way, the potential of the analytical protocol proposed a few years ago has been greatly enhanced.

The analysis of the aerosol samples according to the new analytical protocol results in CO<sub>2</sub>H molar contents ranging from 12 to 20% of the total carbon depending on sampling period and aerosol size fraction. Sensitivity and contamination are still a problem in this procedure but, by exploiting HiVol sampling techniques, it was possible to determine the CO<sub>2</sub>H groups also in aerosol particles collected under the semi-clean conditions encountered at the end of the campaign.

The overall set of data provided by H NMR analysis indicates significantly different functional groups compositions between the fine and the coarse size fractions of the aerosol, and also between very fine particles (<0.1 μm) and accumulation mode particles (approximately 0.2–1 μm) for the sam-

ples of the dry season. The IC fractions of WSOC also show distinct compositions, especially with regard to their CO<sub>2</sub>H content. In contrast, only limited differences in the functional group composition of fine aerosol samples were found between the dry, transition and the wet periods. This could be due to the persistence of biomass burning sources also in the wet period, and/or to the replacement of biomass burning products by biogenic compounds showing an analogous functional group composition. The main distinguishing features of the wet season samples are a less aromatic character, a slightly higher content of hydroxyl-alkoxyl functionalities and a lower content of alkylic C-H groups. An increase in the number of CO<sub>2</sub>H groups per mole of water-soluble carbon was also observed from the dry to the wet period, indicating a progressive increase of the oxidation state of the aerosol WSOC throughout the campaign.

The problem of “missing carbon” amounting to 25%, on average, is still to be solved and calls for further research, although the present work is believed to represent a significant step towards carbon mass balance closure.

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