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# OBSERVATIONS ON SOME POLAR ORGANIC COMPOUNDS IN RURAL AEROSOLS

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In the present work, we examined rural background aerosols, which were collected during a 2003 summer field campaign. Emphasis was given to the chemical analysis of polar organic compounds, *i.e.*, polyols, mono- and dihydroxydicarboxylic acids and saccharidic compounds. Valuable information could be obtained on secondary organic aerosol (SOA) components as well as on primary organic aerosol components. Fine size aerosols (<2.5 μm) collected on quartz fibre filters were extracted with an organic solvent mixture. Trimethylsilyl derivatives were obtained and analysed by gas chromatography with flame ionisation detection (GC-FID) and gas chromatography/mass spectrometry (GC/MS).

## INTRODUCTION

Aerosols are of climatic interest because they act as cloud condensation nuclei[1] and scatter and absorb solar radiation.[2] Atmospheric aerosols are suspended liquid or solid particles in the ambient air, airborne particles having natural and anthropogenic sources and spanning a large range of sizes.[3,4] Ambient aerosols particles can be primary or secondary in origin, primary particles being emitted directly from their respective sources, whereas secondary particles (SOAs) are formed in the atmosphere from gaseous precursors.[5] For SOAs formed from volatile organic precursors, a clear understanding of the processes linking emissions and their contributions to the particle phase is missing. However, it has been assumed that the much larger emissions of isoprene do not result in secondary organic aerosol (SOA) formation in the atmosphere. A considerable interest in water-soluble (and hygroscopic) aerosol fraction exists, because of its role as cloud condensation nuclei (CCN) and the associated effects on cloud formation and cloud properties and the indirect effects of aerosols on climate.

In recent research,[6] emphasis has been given to the chemical characterisation and quantitative determination of polar water-soluble organic compounds in the fine size fraction (<2.5 μm) of natural aerosols.[7] Two novel previously unidentified polar organic compounds could be characterised as the diastereoisomeric 2-methyltetrols, 2-methylthreitol and 2-methylerythritol. The 2-methyltetrols have retained the isoprene skeleton and can be explained by photo-oxidation of isoprene which is emitted in large quantities by the rain forest vegetation. Other polar organic compounds identified in the Amazonian aerosols included mono- and dihydroxydicarboxylic acids, as malic acid and 2,3-dihydroxymethacrylic acid. The last one was not observed previously and it seems to be an important secondary organic aerosol component in the forest aerosol examined.

In the present work, we examined rural background aerosols, which were collected during a 2003 summer field campaign. Emphasis was given to the chemical analysis of polar organic compounds, *i.e.*, polyols, mono- and dihydroxydicarboxylic acids and saccharidic compounds. Valuable information could be obtained on SOA components as well as on primary organic aerosol components. Fine size aerosols (<2.5 μm) collected on quartz fibre filters were extracted with an organic solvent mixture. The extract was derivatised into trimethylsilyl derivatives and analysed by gas chromatography

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with flame ionisation detection (GC-FID) and gas chromatography/mass spectrometry (GC/MS), according to previously developed analytical procedures.[8,9]

The following polar organic compounds were identified: the 2-methyltetrols, 2-methylthreitol and 2-methylerythritol, which are unique molecular markers for the photo-oxidation of isoprene;[10] the hydroxydicarboxylic acid, malic acid, which has been proposed to be a late product in the photochemistry of unsaturated fatty acids;[11] levoglucosan, which is a marker for biomass smoke;[12] the sugar alcohols, arabitol and mannitol, which are markers for fungal spores;[13] the mono- and dihydroxydicarboxylic acids: malic acid and 2,3-dihydroxymethacrylic acid.[14,15]

## EXPERIMENTAL

**Chemicals.** Standards of levoglucosan (1,6-anhydro- β-D-glucopyranose) D(+)-arabitol and D(+)-mannitol were obtained from Sigma (St. Louis, MO, USA). N-methyl-N-trimethylsilytrifluoroacetamide (MSTFA) containing 1% trimethylchlorosilane (TMCS) and anhydrous pyridine used for trimethylsililation were obtained from Pierce (Rockford, IL, USA). Dichloromethane (Supra Solv grade) was supplied by Merck and methanol (Super grade) by Lab-Scan (Dublin, Ireland). Deuterated ($D_3$)-malic acid used as internal standard for malic acid was purchased from Sigma (St. Louis, MO, USA). For 2-methylglyceric acid no reference was available, the response factor of malic acid being used. As surrogate standard for 2-methyltetrols, 2-methylthreitol and 2-methylerythritol, meso-erythritol was used.

**Aerosol collections**. The collection devices included a total filter sampler, several Gent PM10 stacked filters unit (SFU) samplers and different types of cascade impactors. The open-faced samplers used a 47-mm diameter Whatman QM-A quartz fiber filter. They were equipped with a cylindrical intake tube facing downward and were operated at a flow-rate of 150 $Lmin^{-1}$. The Hi-Vol dichotomous sampler used was designed by Solomon *et al.*[16] It separates the aerosol into two size fractions, coarse and fine, with the separation between the two fractions at about 2-3 μm equivalent aerodynamic diameter (EAD). Pallflex quartz fiber filters were used to collect both size fractions. The Gent PM10 SFU samplers[17] operates at a flow rate of 17 L $min^{-1}$ and provides two size fractions, coarse (2.5-10) μm EAD and fine (<2.5 μm EAD). The coarse filter is a 47 mm diameter filter, 8 μm pore size, Apiezon-coated Nuclepore polycarbonate filter, whereas virtually any type of 47 mm diameter filter with high collection efficiency can be used as fine filter. All filters, except those from Hi-Vol were weighed before and after sampling to determine the particulate mass (PM). The weighing was done at 20°C and 50% relative humidity and the filters were pre-equilibrated at those conditions for at least 24 hours before the actual weighing. Furthermore, all quartz filters were subjected to analysis for organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission (TOT) technique. This technique delivers OC and EC results in μg (C) $m^{-3}$. To convert the measured OC values to organic aerosol mass, one needed to account for the other atoms in the OC molecules and multiplying factors ranging from 12 to 18 are used.

**Analyses for organic compounds.** Fine size aerosols (<2.5 μm AD) collected on quartz fibre filters were used. For each sample (10 samples), 1/16 of the whole filter was placed in a 25 mL bottle and spiked with 50 μL (10.35 ng/μL) of methyl-β-D-xylopyranoside (Sigma, St. Louis, MO, USA) and 20 μL (37.41 ng/μL) deuterated malic acid (CDN isotopes, Canada), then 20 mL of methanol were added. The mixture was shaken for 15 minutes under ultrasonic agitation. The filters were extracted twice more with 20 mL of $CH_3OH$ following a protocol that was established previously.[18-20] The combined filtrates were then concentrated to 1 mL at 35°C using a rotary evaporator, then transferred to a 1 mL reaction glass vial and blown to dryness with a gentle stream of pure nitrogen. The dried residue was derivatized by adding 40 μL of a trimethylsilylation mixture containing N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) with 1% trimethylchlorosilane (TMCS) and 500 μL anhydrous pyridine, capping the vial and heating at 70°C for 60 minutes.

**Instrumentation and materials.** After cooling at room temperature, samples were analyzed using a Polaris Q GC/ ion trap MS instrument, equipped with an external ionization source (ThermoFinnigan, San Jose, CA, USA). X-calibur version 1.2 software was used for data acquisition and processing. The chromatographic system consisted of a deactivated fused-silica precolumn (2 m x 0.25 mm i.d.) (Alltech) and a low-bleed Rtx-5MS(cross-bond 5% diphenyl-95% dimethyl polysiloxane) fused-silica capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness) (Restek, USA).

The following temperature program was applied: the temperature was kept at 50°C for 5 minutes, was then increased to 200°C at a rate of 3°C/min and kept at this temperature for a further 2 min and then raised to 310°C at a rate of 30°C/min. The total analysis time was 62 min. The ion trap analyzer was operated in the EI mode at 200 and 140°C. The temperature of the transfer line was 280°C. The electron energy was 70 eV for electron ionization. First-order mass spectra were recorded in the mass range m/z 45 - 450. 1 μL of the samples was injected in the splitless mode (splitless time 0.5 min). The temperature of the injector was 250°C.

**Quantitative analysis**. Calibration curves were constructed by analyzing aliquots of stock solutions of standards that have been evaporated and derivatized in the fashion described above. All glassware was deactivated with 5% DMDCS in toluene (Sylon CT). All reported concentrations are corrected for procedural blanks.

The quantification of 2-methyltetrols, levoglucosan, arabitol and mannitol as well as that of malic acid was based on an internal standard calibration procedure employing methyl-β-D-xylopyranoside (internal standard for 2-methyltetrols, levoglucosan, arabitol and mannitol) and deuterated malic acid (internal standard for malic acid), whereas that of 2,3-dihydroxymethacrylic acid was based on the use of the response factor of malic acid relative to deuterated malic acid. For assessing the amounts of compounds for which no pure reference compounds were available, the response factor of meso-erythritol was used for 2-methyltetrols.

The selected ions were at m/z 217 and 204 for levoglucosan and for the internal recovery standard methyl-β-D-xylopyranoside, m/z 219 and 277 for the 2-methyltetrols,

m/z 217 and 319 for arabitol and mannitol, m/z 233 and 307 for malic acid and m/z 236 and 310 for deuterated ($d_3$) malic acid.

## RESULTS AND DISCUSSION

With regard to derivatization, the procedure developed by Pashynska *et al.*[14] using MSTFA +1% TMCS-pyridine, which was shown to yield a single TMS derivative for each of the studied compounds, was followed. While one derivative was observed for methyl β-L-xylopyranoside, 2-methyltetrols, levoglucosan arabitol and mannitol, multiple peaks were observed for glucose (two) and for fructose (three) in agreement with literature data.

In particular, the mass concentration of aerosol with AD < 2.5 μm (fine fraction) was found to be consistently higher during days than during nights (Fig. 2). The higher daytime concentration is likely due to lowered relative humidity during day. Organic carbon (OC) measurements performed on the Hi-Vol filters indicated that organic matter accounted for only 3.2% of the OC. SOA formed via the gas-to-particle conversion of biogenic gases from the rainforest would be also expected to have made a sizeable contribution to the fine OC concentration.

Using the proposed GC/MS technique it was possible to identify and quantify a range of sugars, sugar alcohols, anhydrosugars and carboxylic acids in the sample. Taking into account the polar character of studied compounds, $CH_2Cl_2$-$CH_3OH$ (75:25 v/v) was selected as suitable solvent mixture for extraction. The extraction recovery for this mixture was estimated to 95.0 ± 2.0% (n = 3) at 100 ng level.

**Tetrols**: Fig.1 shows a typical GC/MS total ion chromatogram obtained for the trimethylsilylated extract of the fine size fraction of a day time and a night time aerosol sample.

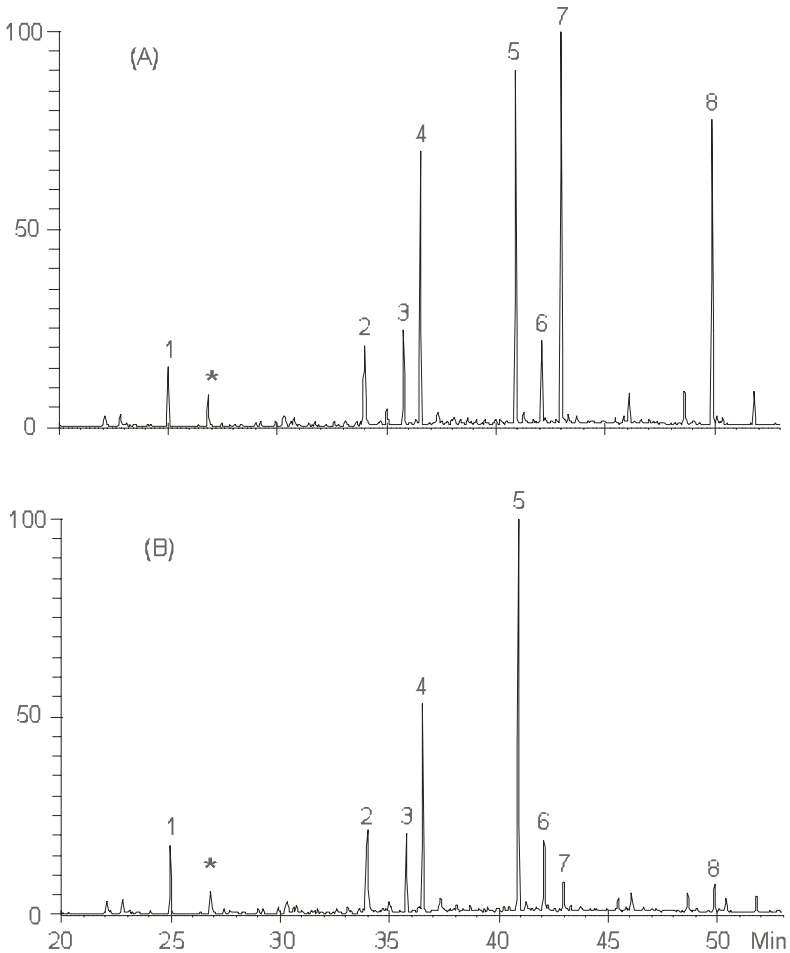


Fig. 1 – GC/MS TIC obtained for (A) a day- and (b) night time fine aerosol sample; **1**, 2,3-dihydroxymethacrylic acid; **2**, malic acid (+$D_3$-malic acid); **3**, 2-methylthreitol; **4**, methylerythritol; **5**, methylxylopyranoside; **6**, levoglucosan; **7**, arabitol; **8**, mannitol.

Major peaks in the chromatogram correspond to the 2-metyhltetrols, 2-metylthreitol (3) and 2-methylerythritol (4). These polyols have been reported for the first time in forest aerosols from Amazonia and have been explained by gas-phase photo-oxidation of isoprene.[15] Fig. 2 shows the time trends for the PM2 particulate mass (PM derived from a separate filter sample) and for PM2.5 OC, malic acid, the tetrols sum and the sugar alcohol mannitol. These are mainly confined to the coarse size fraction (> 2.5 μm AD) of aerosols at this site, with an average in the PM 2.5 fine size fraction of 0.05 and 0.04 (N = 10) respectively. There is clearly more variation in the time trend of the tetrols, for these compounds appearing a tendency for higher concentrations during the day than during the night. Average atmospheric concentrations of 9.6 and 4.5ngm$^{-3}$ were measured for 2-methylerythritol and 2-methylthreitol, respectively. The calibration curve for the sum of tetrols was obtained using meso-erythritol and it has the following regression parameters: y = 0.0018x -0.0109, $r^2$ = 0.9999, where y represents peak area, x represents concentration ( as ngm$^{-3}$).

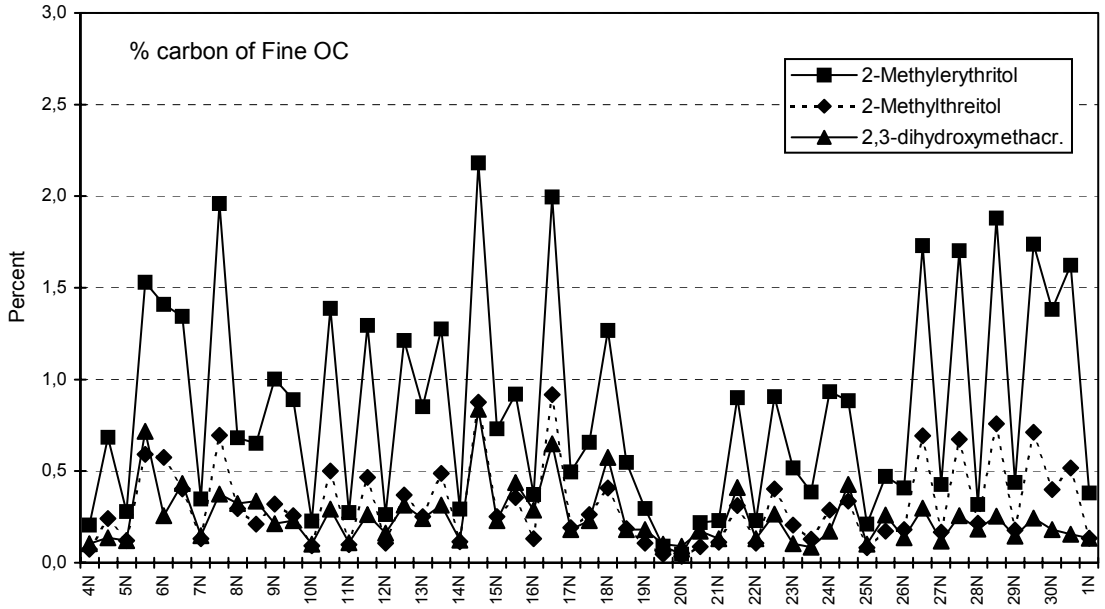


Fig. 2 – Time trends for the PM2 particulate mass (PM derived from a separate filter sampler) and for PM2.5 OC, malic acid, the tetrols (sum of 2-methylthreitol and 2-methylerythritol) and the sugar alcohol mannitol.

The day/night differences for the two tetrols and the two sugar alcohols were also very apparent in the trends of the percent carbon the fine OC (Fig. 3). From Table 1 it could be noticed that the contribution of the 2-metyltetrols to the PM2.5 OC is on average 1%, which is half that found for natural Amazonian aerosols.[17] The tetrols and 2,3-dihydroxymethacrylic acid accounted, on average 2 times more to the OC during the day than during the night.

*Table 1*

Median concentrations and concentrations ranges, as derived from the PM2.5 Hi-Vol samples (n = 10).
Data for PM, OC, WSOC and EC are in μg.m$^{-3}$, for all other species in ng.m$^{-3}$

| Species | Median conc. | Conc. Range |
|---|---|---|
| OC (μg.m$^{-3}$) | 4.2 | 1.94 – 6.8 |
| WSOC | 2.6 | 0.98 – 4.7 |
| EC | 0.20 | 0.077 – 0.59 |
| Malic acid (ng.m$^{-3}$) | 38 | 11.5 – 79 |
| Levoglucosan | 12.3 | 3.5 – 95 |
| Arabitol | 4.8 | 0.69 – 25 |
| Mannitol | 5.3 | 0.62 – 29 |
| 2-methylthreitol | 7.5 | 0.79 – 34 |
| 2-methylerythritol | 21 | 1.03 – 85 |
| 2,3-dihydroxymethacrylic acid | 7.6 | 2.2 – 18.3 |

**Sugars and sugar alcohols**: of the various compounds identified the sugars (glucose and fructose) and sugar alcohols (arabitol and mannitol) were found. All these compounds have been previously identified in samples from dry season, in fruits, flowers and tissues of plants. They are mainly confined to the coarse size fraction (>2.5 μm AD) of aerosols at this site, with an average in the PM 2.5 fine size fraction of 0.050 and 0.040 (N = 10), arabitol and mannitol, respectively.

For the quantification of arabitol and mannitol calibration curves were constructed by analysing aliquots stock solutions of authentic standards processed in the same way described in experimental. The calibration curves have the following regression parameters: y = 0044x – 0.0184, $r^2$ = 0.9980 for arabitol and y = 0.0017 – 0.0566, $r^2$ = 0.9980 for mannitol.

Based on similar observations recorded at a diverse range of locations, it seems reasonable to conclude that there must exist two generic sources of sugars and sugar alcohols. Since arabitol and mannitol are well-known constituents of fungal spores, the enhanced daytime concentration of these compounds could be mainly associated with a diurnal increase of yeast's and other small fungal spores. On the other hand, the higher glucose and fructose levels during day coincide with higher pollen, fern spores and insect counts recorded for the day samples. Fungal spores cover a wider size range (spores were also observed in the fine aerosol samples by electron microscopy), which might explain the significant levels of arabitol and mannitol that were observed in this fraction. Fungal fragments may also contribute to the fine aerosol fraction. In rural aerosols the sugar alcohols (arabitol and mannitol) accounted on average 4 times more to the OC during the day than during the night. (Fig. 3).

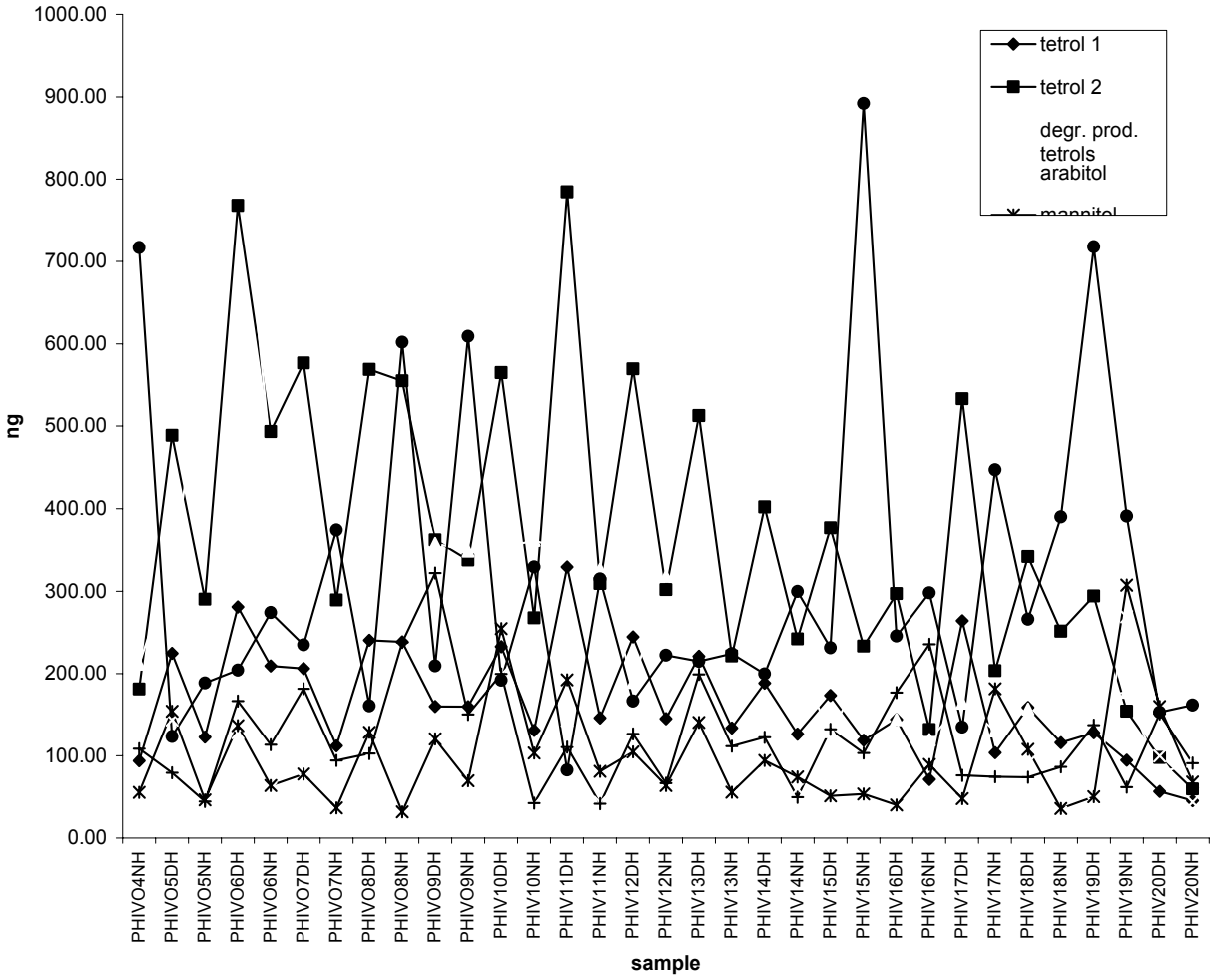


Fig. 3 – The day/night differences for the two tetrols and the two sugar alcohols, apparent in the trends of the percent carbon in the fine OC.

**Anhydrosugars:** important levels of levoglucosan were found in the samples (Table 1). This compound is a derivative of glucose and it is formed through the pyrolysis of cellulose and hemicelluloses present in the biomass. It has been previously identified as a major compound of organic particulate matter in areas impacted by wood smoke and it is an excellent source-specific tracer for biomass burning. For the quantification of levoglucosan, calibration curve was constructed by analysing aliquots of stock solutions of levoglucosan with the following regression parameters: $y = 0.0028x - 0.0566$, $r^2 = 0.9980$. A consistent day-night variation in concentration was observed (levoglucosan accounted, on average, 2 times more to the OC during the night than during the day). The average fine-fraction concentration of levoglucosan (the major anhydrosugar) was found to be 350 ng $m^{-3}$, which represents almost 0.54% of fine OC.

**Short-chain carboxylic acids**: another group of compounds that were quantified in the samples were 2,3-dihydroxymethacrylic acid and malic acid. It should be noticed that the extraction efficiency of organic acids into methanol is high when they are present in their neutral form. For avoiding the loss of these acids in their less soluble salt form, all glassware was deactivated. Acidification of the samples to improve the extraction efficiency of the acids was not attempted because of the risk of forming methyl esters. The dihydroxymonocarboxylic acid 2,3-dihydroxymethacrylic acid was not observed previously and it seems to be an important secondary organic aerosol component in the forest aerosol examined. This compound can be formed from methacrolein and methacrylic acid, both volatile gas-phase oxidation products of isoprene by acid-catalysed reaction with $H_2O_2$ in aqueous medium. Unlike malic acid (the other important acid we detected), 2,3-dihydroxymethacrylic acid has retained the key structural features of isoprene. Malic acid is the most abundant single compound detected in the PM 2.5 aerosol with a median concentration of 30 $ngm^{-3}$ based on a calibration curve with the following regression parameters; $y = 0.0028x - 0.0105$, $R^2 = 0.9999$. Regarding the mean percent carbon (and associated standard deviation) of the PM2.5 OC that is attributed to WSOC and the polar organic compounds, malic acid is the dominant organic species measured and it accounts for 0.97% $\pm$ 0.49 of the OC and 2,3-dihydroxymethacrylic acid for 0.23% $\pm$ 0.15 (Table 2). The day/night difference of the organic compounds in the attribution of the OC was also examined: for malic acid there was no difference (Fig. 2), but 2,3-dihydroxymethacrylic acid accounted on average 2 times more to the OC during the day than during the night. Anyway, the average night time-to-day time concentration measured for these compounds exhibited higher concentrations in the daytime samples. This indicates that these acids may have been largely associated with biogenic SOA derived from from the photo-oxidation of VOCs emitted from the forest.

Based on data obtained in this study (Table 1 and Table 2), it is difficult to conclude about the fraction of the SOA that is due to the photo-oxidation of isoprene. These compounds have a high chemical complexity and they could serve as marker compounds for isoprene photo-oxidation after further studies.

Overall, the carbon content of the organic species quantified by GC/MS accounted for an average of only 3.2% of the OC in the fine aerosol fraction. Individual organic compounds insoluble in $CH_3OH$ or not amenable to GC/MS analysis due to their low volatility (including naturally occurring humic acids) would constitute a significant fraction of the unidentified material.

*Table 2*

Mean percentages (and associated standard deviations) of the OC attributable to the WSOC and to the carbon in the organic compounds, as derived from the PM2.5 Hi-Vol samples (n = 10)

| Species | Mean % $\pm$ std.dev. |
|---|---|
| WSOC | 61 $\pm$ 9 |
| Malic acid | 0.97 $\pm$ 0.49 |
| Levoglucosan | 0.54 $\pm$ 0.66 |
| Arabitol | 0.19 $\pm$ 0.17 |
| Mannitol | 0.21 $\pm$ 0.22 |
| 2-methylthreitol | 0.28 $\pm$ 0.22 |
| 2-methylerythritol | 0.76 $\pm$ 0.57 |
| 2,3-dihydroxymethacrylic acid | 0.23 $\pm$ 0.15 |
| Sum (compounds) | 3.2 $\pm$ 1.6 |

## CONCLUSION

The data set presented indicates that the continental rural background aerosols, collected during summer, are a complex mixture of polar organic compounds as polyols, mono- and dihydroxycarboxylic acids and saccharidic compounds, derived primarily from biomass burning. The individual compounds identified by GC-FID and GC/MS analysis were: malic acid (the dominant organic species measured) which accounts for 0.97% of the OC and 2-methyltetrols, whose contribution to the PM2.5 OC is on average 1%, which is half that found for natural Amazonian aerosols in the same group. All compounds together account for only 3.2% of the OC.

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