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Polar organic compounds in rural PM$_{2.5}$ aerosols from K-puszta, Hungary, during a 2003 summer field campaign: Sources and diel variations

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Abstract. In the present study, we examined PM$_{2.5}$ continental rural background aerosols, which were collected during a summer field campaign at K-puszta, Hungary (4 June–10 July 2003), a mixed coniferous/deciduous forest site characterized by intense solar radiation during summer. Emphasis was placed on polar oxygenated organic compounds that provide information on aerosol sources and source processes. The major components detected at significant atmospheric concentrations were: (a) photo-oxidation products of isoprene including the 2-methyltetrols (2-methylthreitol and 2-methylerythritol) and 2-methylglyceric acid, (b) levoglucosan, a marker for biomass burning, (c) malic acid, an intermediate in the oxidation of unsaturated fatty acids, and (d) the sugar alcohols, arabitol and mannitol, markers for fungal spores. Diel patterns with highest concentrations during day-time were observed for the 2-methyltetrols, which can be regarded as supporting evidence for their fast photochemical formation from locally emitted isoprene. In addition, a diel pattern with highest concentrations during day-time was observed for the fungal markers, suggesting that the release of fungal fragments that are associated with the PM$_{2.5}$ aerosol is enhanced during that time. Furthermore, a diel pattern was also found for levoglucosan with the highest concentrations at night when wood burning may take place in the settlements around the sampling site. In contrast, malic acid did not show day/night differences but was found to follow quite closely the particulate and organic carbon mass. This is interpreted as an indication that malic acid is formed in photochemical reactions which have a much longer overall time-scale than that of isoprene photo-oxidation, and the sources of its precursors are manifold, including both anthropogenic and natural emissions. On the basis of the high concentrations found for the isoprene oxidation products during day-time, it can be concluded that rapid photo-oxidation of isoprene is an important atmospheric chemistry process that contributes to secondary organic aerosol (SOA) formation at K-puszta during summer.

1 Introduction

The fine aerosol at K-puszta, Hungary, has been widely studied during recent years because it contains a large fraction of water-soluble organic compounds (WSOC). Characterization of the latter compounds is of climatic relevance since they enhance the ability of the aerosol to act as cloud condensation nuclei (Novakov and Penner, 1993) and may as such affect cloud processes (e.g., Shulman et al., 1996; Facchini et al., 1999; Kiss et al., 2005). With regard to the studies dealing with the K-puszta fine aerosol, emphasis has been formerly placed on the characterization and origin of hemic-like substances which represent a large fraction of the WSOC (Zappoli et al., 1999; Gelencsér et al., 2000; Gelencsér et al., 2002; Kiss et al., 2002; Kiss et al., 2003).

In the present study we focus on the characterization of small polar organic molecules that are marker molecules for aerosol sources and source processes and can be measured using gas chromatography/mass spectrometry (GC/MS) after suitable sample preparation. The sample workup consisted of extraction with methanol and trimethylsilylation which converts hydroxyl and carboxylic acid groups into trimethylsilyl ether and ester derivatives, respectively. A summer field campaign was conducted at K-puszta with a main objective to characterize rural biogenic aerosol. Emphasis was
The sampling station is situated in the clearing of a mixed coniferous/deciduous forest on the Great Hungarian Plain during a field campaign between 4 June and 10 July 2003. The aerosol samples were collected at K-puszta, Hungary, which had been prebaked for 24 h at 550 °C to remove organic contaminants, were used to collect each of the two size fractions. In parallel with the Hi-Vol sampler a Gent PM10 stacked filter unit (SFU) sampler was operated (Maenhaut et al., 1994). In this sampler a Pall Teflo filter was used for collection of the fine (≤2 μm AD) size fraction and a Nuclepore polycarbonate filter for collecting the coarse (2–10 μm AD) particles. Separate day-time and night-time samples were collected with both samplers until 2 July. From this day on, 24-h samples were collected. The day-time samples were taken from 07:00 to 18:30 local time, the night-time samples from 19:00 to 06:30 the next day; for the 24-h samples collections were done from 07:00 to 06:30 the next day. A total of 63 samples were collected. The loaded filters from both samplers were stored in the dark in a freezer at −25 °C until analysis.

2.2 Meteorological data and ozone

Standard meteorological data (i.e., temperature, wind speed and direction, relative humidity (RH), and amount of precipitation) and ozone concentrations were measured by the Hungarian Meteorological Service with 1-h time resolution. Mean values of the day-time and night-time averaged and maximum data for the period 4 June through 1 July, during which separate day and night samples were collected, are given in Table 1. For precipitation, total data for day-time and night-time of that period are reported. Overall, the campaign can be characterized by stable meteorological conditions. The weather was especially warm and dry. Notable rainfall was only observed during the nights of 9, 15, 16, 28, and 29 June and 3 July (more than 80 mm in each case).

2.3 Analysis of aerosol samples for the particulate mass and for organic, elemental and water-soluble organic carbon

The filters from the SFU sampler were weighed before and after sampling with a microbalance of 1 μg sensitivity. The weighings were done at 20 °C and 50% relative humidity and the filters were equilibrated at these conditions for 24 h prior to weighing. The weighings provided data for the particulate mass (PM) in the fine (≤2 μm AD) and coarse (2–10 μm AD) size fractions. The quartz fibre filters used in the Hi-Vol sampler were too brittle for accurate and precise weighing, and no PM data were thus obtained from the Hi-Vol sampler. All filters from this sampler were analysed for organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission (TOT) technique (Birch and Cary, 1996), using the same analysis temperature program as we used in the aerosol carbon round robin of Schmid et al. (2001). The filters from the fine size fraction (≤2.5 μm AD) were also analysed for water-soluble OC (WSOC). A filter punch of 1.0 or 1.5 cm² was placed in a 15 mL tube, 5 mL Millipore Simplicity water...
was added, and the tube was hand-shaken during 5 min, after which it was allowed to stand for 30 min. The sample extract was then filtered through a PVDF syringe filter (pore size 0.2 \( \mu \)m) and analysed for total organic carbon (TOC), thereby correcting for the inorganic carbon, with a Shimadzu GC-FPD. The following temperature program was applied: the temperature was kept at 50° C for 5 min, was then increased to 200° C at the rate of 3° C min^{-1} and kept at that temperature for a further 2 min and then raised to 310° C at the rate of 30° C min^{-1}; the total analysis time was 62 min. The other GC/MS experimental conditions were the same as reported in Pashynska et al. (2002). Mass spectra were recorded in the mass range m/z 45–450. All compounds were characterized on the basis of their electron ionization (EI) mass spectra and comparison with those of authentic reference compounds or reported mass spectral data (Claeys et al., 2004a; Claeys et al., 2004b; Wang et al., 2005). In the selected ion monitoring mode, the instrument was operated at an ion dwell time of 25 ms. The selected ions were at m/z 204 and 217 for methyl-\( \beta \)-D-xylanopyranoside, m/z 219 and 277 for the 2-methyltetrols, m/z 233 and 307 for malic acid, m/z 236 and 319 for deuterated (D$_3$)-malic acid, and m/z 217 and 319 for arabitol and mannitol.

Taking into account the polar character of the targeted compounds, we evaluated pure methanol for extraction and compared it with dichloromethane-methanol (80:20, v/v) which was used in previous work for polar polyhydroxylated compounds such as levoglucosan (Pashynska et al., 2002). On the basis of this comparison which revealed that methanol was an efficient solvent for extraction of the 2-methyltetrols, levoglucosan, malic acid, 2-methylglyceraldehyde, arabitol, and especially mannitol (the most polar compound among the saccharidic compounds), it was selected in further determinations. The extraction recoveries were estimated by spiking blank filters with known amounts of the analytes and were >65% for the polyhydroxy compounds, the 2-methyltetrols, levoglucosan, arabitol and mannitol, and 72% for malic acid, and are expected to be higher for real samples due to carrier effects (Zd ráhal et al., 2002). Employing D$_3$-malic acid, it was also verified that methylation did not occur with methanol under the sample workup conditions.

For quantitative analysis, calibration curves were constructed in the appropriate concentration ranges by analysing aliquots of stock solutions of standards as reported in

### Table 1. Mean and standard deviation of day-time and night-time averaged and maximum meteorological parameters and ozone concentrations, and total day-time and night-time precipitation for the period 4 June–1 July 2003.

<table>
<thead>
<tr>
<th></th>
<th>Day-time averaged data (N=27)</th>
<th>Night-time averaged data (N=28)</th>
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</thead>
<tbody>
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<td>Temperature (°C)</td>
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<td>Mean±std.dev.</td>
</tr>
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<td>Wind speed (m/s)</td>
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<td>2.1±1.0</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>41±11</td>
<td>77±10</td>
</tr>
<tr>
<td>Ozone (ppbv)</td>
<td>68±10</td>
<td>41±8</td>
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<tr>
<td>Day-time maximum (N=27)</td>
<td>Mean±std.dev.</td>
<td>Mean±std.dev.</td>
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<td>Temperature (°C)</td>
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<td>24.1±3.1</td>
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<tr>
<td>Wind speed (m/s)</td>
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<td>3.3±1.5</td>
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<tr>
<td>Relative humidity (%)</td>
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<tr>
<td>Ozone (ppbv)</td>
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<tr>
<td>Precipitation (mm)</td>
<td>9.7</td>
<td>764</td>
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</table>
and (β-methyl-1808 A. C. Ion et al.: Polar organic compounds in rural PM
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monocarboxylic acid, 2-methylglyceric acid (1) (Fig. 1). alcohols, arabitol (7) and mannitol (8), and the dihydroxy-
carboxylic acid, malic acid (2), levoglucosan (6), the sugar
methylthreitol (3) and 2-methylerythritol (4), the hydroxydi-
major identified compounds include the 2-methyltetrols, 2-
drosugars and hydroxycarboxylic acids could be identified
ing GC/MS a range of polyols, sugars, sugar alcohols, anhy-
duration blanks. Duplicate analyses showed that the precision
ance was available, the response factor of malic acid was
acid), whereas for 2-methylglyceric acid, for which no ref-
and deuterated (D$_3$-malic acid (IS)), (3) 2-methylthreitol, (4) 2-methylerythritol, (5)
methyl-β-D-xylanopyranoside (IS), (6) levoglucosan, (7) arabitol and (8) mannitol.

Pashynska et al. (2002). The quantification of 2-
methyltetrols, levoglucosan, arabitol and mannitol as well as
that of malic acid was based on the use of selected ion mon-
itoring data and an internal standard calibration procedure
employing methyl-β-D-xylanopyranoside (internal standard
for 2-methyltetrols, levoglucosan, arabitol, and mannitol)
and deuterated (D$_3$)-malic acid (internal standard for malic
acid), whereas for 2-methylglyceric acid, for which no ref-
rence was available, the response factor of malic acid was
used. All reported concentrations were corrected for proce-
dural blanks. Duplicate analyses showed that the precision
was about 10%.

3 Results and discussion
3.1 Characterisation and sources of polar organic com-
pounds in the PM$_{2.5}$ aerosol

Figure 2 shows GC/MS selected ion monitoring data ob-
tained for the trimethylsilylated extracts of the fine size fraction
of a typical day- and night-time aerosol sample. Using
gc/MS a range of polyols, sugars, sugar alcohols, anhy-
drosugars and hydroxycarboxylic acids could be identified
and measured in the derivatised PM$_{2.5}$ aerosol extracts. The
major identified compounds include the 2-methyltetrols, 2-
methylthreitol (3) and 2-methylerythritol (4), the hydroxidy-
carboxylic acid, malic acid (2), levoglucosan (6), the sugar
alcohols, arabitol (7) and mannitol (8), and the dihydroxy-
monocarboxylic acid, 2-methylglyceric acid (1) (Fig. 1).
The 2-methyltetrols have been first reported in the PM$_{2.5}$
size fraction of Amazonian rain forest aerosols (Claeys et al.,
2004a) but have since been detected in the fine aerosol of dif-
ferent rural and semi-rural locations, including the K-puszta
site (Claeys et al., 2004b), diverse sites in the Eastern United
States (Edney et al., 2005) and a boreal forest site in Fin-
lnd (Kourtchev et al., 2005). The dihydroxymonocarboxylic
acid, 2-methylglyceric acid, has been found for the first time
in the K-puszta PM$_{2.5}$ aerosol, has been explained by further
aerosol-phase oxidation of methacrolein and methacrylic
acid, which are gas-phase oxidation products of isoprene
(Claeys et al., 2004b), and has recently also been reported
in PM$_{2.5}$ aerosol from the Great Smoky Mountain National
Park, Tennessee, USA (Yu et al., 2005). Recent laboratory
smog chamber experiments with irradiated isoprene/NO$_x$/air
mixtures in the presence and absence of SO$_2$ established that
the 2-methyltetrols and 2-methylglyceric acid can be gener-
ated from isoprene and that sulfuric acid (generated by oxida-
tion of SO$_2$) plays a crucial role in their formation (Edney
et al., 2005).

In addition to the isoprene oxidation products, other polar
organic molecules detected with GC/MS at significant con-
centrations in the K-puszta PM$_{2.5}$ aerosol were malic acid,
levoglucosan, arabitol and mannitol. Malic acid is gener-
ally considered as an intermediate in the oxidation of unsat-
urated fatty acids (Kawamura and Ikushima, 1993; Kaw-
amura and Sakaguchi, 1999; Neusüss et al., 2000; Yu et al.,
2005). However, in addition to unsaturated fatty acids, malic
acid is believed to have other biogenic sources that remain
to be identified (Claeys et al., 2004a). Levoglucosan (6) is an
anhydro derivative of glucose formed through pyroly-
sis of cellulose at temperatures above 300°C (Shafizadeh,
1984), is an excellent indicator compound for biomass smoke
(Simoneit, 2002), and has been extensively used to moni-
tor biomass smoke in tropical environments that are affected
by deforestation (Zdráhal et al., 2002; Graham et al., 2002;
Graham et al., 2003; Schkolnik et al., 2005) as well as in ur-
ban and rural environments where wood burning is important
during winter (Zdráhal et al., 2002; Pashynska et al., 2002;
Pio et al., 2004). The sugar alcohols, arabitol (7) and man-
nitol (8), are fungal marker compounds (Lewis and Smith,
1967; Bialeski, 1982). Other minor compounds identified but
not measured were the monosaccharides, fructose and glu-
cose, which are believed to originate from plant pollen that
may be rich in fructose and glucose (Pacini, 2000), as well
the anhydrosugars, mannosan and galactosan, which accom-
pany the emission of levoglucosan during biomass burning
(Zdráhal et al., 2002; Graham et al., 2002). In addition, C$_5$
alkene triol derivatives of isoprene that are related to the 2-
methyltetrols (i.e., 2-methyl-1,3,4-trihydroxy-1-butene (cis
and trans) and 3-methyl-2,3,4-trihydroxy-1-butene) (Wang
et al., 2005) could be detected in low concentrations (<10%
of the 2-methyltetrols) in most samples.

While the 2-methyltetrols, levoglucosan and malic acid
have been shown to be associated with the fine size fraction
(<2.5 μm AD), the sugar alcohols, arabitol and mannitol,
have been found to be mainly confined to the coarse size frac-
tion (>2.5 μm AD) of aerosols collected above the Amazon

Fig. 2. GC/MS selected ion monitoring data for (a) a day- and (b) night-time PM$_{2.5}$ aerosol sample collected on 19 June 2003. Peak
identifications: (1) 2-methylglyceric acid, (2) malic acid [+ D$_3$-
malic acid (IS)], (3) 2-methylthreitol, (4) 2-methylerythritol, (5)
methyl-β-D-xylanopyranoside (IS), (6) levoglucosan, (7) arabitol and (8) mannitol.
3.2 Time trends and diel variations of polar organic compounds in the PM$_{2.5}$ aerosol

Figure 3 shows the time trends for the PM$_2$ particulate mass concentration and for the PM$_{2.5}$ concentration of OC, malic acid, the 2-methyltetrols (sum of 2-methylthreitol and 2-methyerythritol) and the sugar alcohol mannitol.

The atmospheric concentrations of the 2-methyltetrols are the highest during day-time consistent with the emission of isoprene which is both light- and temperature-dependent (Sharkey and Yeh, 2001) in the area around the sampling site as well as with a rapid photochemical formation mechanism which follows from the high reactivity of isoprene and its intermediates (Claeys et al., 2004a; Claeys et al., 2004b). The day-time-averaged temperature was quite high and fairly constant during the campaign, with mean and associated standard deviation of 28.2±3.2°C (Table 1). Also the day-time averaged ozone concentration was high, with a mean of 77±10 ppbv. This is indicative of high concentrations of photo-oxidants and favorable conditions for fast oxidation of and aerosol formation from isoprene, which was most likely predominantly emitted in the fairly close vicinity of the sampling site. Enhanced day-time concentrations have been previously reported for $\alpha$-pinene oxidation products and are generally seen as evidence for a photochemical source (Kavouras et al., 1998). The mass concentration ratio 2-methylthreitol/2-methyerythritol was 0.36 and the excellent correlation ($R^2=0.95$) found between the mass concentrations of the two diastereoisomers is consistent with their formation through the same aerosol source process, i.e., photo-oxidation of isoprene (Fig. 4). The diel cycle of mannitol revealing its highest atmospheric concentrations during day-time contrasts with observations made for the coarse aerosol fraction ($>2.5\mu m$ AD) in the Amazon forest where the highest concentrations were found at night (Graham et al., 2003). A possible explanation for this phenomenon could be that emission of smaller-sized fungal fragments, known to be released together with spores from moldy surfaces (Görrny et al., 2002), at K-puszta is more pronounced during day-time, which is generally characterized by stronger winds and convective activity compared to night-time (Table 1). Furthermore, hygroscopic particle
growth due to a higher relative humidity during night-time (Table 1) may shift some of the smaller particles that contain mannitol and arabitol to the coarse size fraction during night. The day/night differences for 2-methylerythritol and the sugar alcohol, mannitol, are also very apparent in the trends of their percentage carbon contributions to the fine OC (Fig. 5). The diel pattern of 2-methylthreitol is similar to that of 2-methylerythritol, while that of arabitol is similar to that of mannitol (data not shown). The percentage carbon contributions to the fine OC are thought to provide better an insight into the time-dependent formation of the targeted compounds than the atmospheric concentration data, since the latter depend on meteorological conditions and are, e.g., affected by day/night variations in the mixing height of the tropospheric boundary layer. A diel pattern is also observed for 2-methylglyceric acid (Fig. 6), consistent with its formation through rapid photo-oxidation of locally emitted isoprene. The 2-methyltetrols and 2-methylglyceric acid contributed on average 2 times more to the OC during the day than at night (Figs. 5 and 6), while the sugar alcohols, arabitol and mannitol, accounted, on average, 4 times more to the OC during the day than at night (Fig. 5). It is pointed out that the latter compounds, unlike the isoprene oxidation products, are primary aerosol components that are associated with fungal fragments. The levoglucosan concentrations were quite variable and indicate that wood burning takes place at or close to the K-puszta site, likely for household purposes or agricultural waste burning. A consistent day-night variation in the levoglucosan contribution to the OC is noted (Fig. 6), accounting, on average, 2 times more at night than during the day. This phenomenon was also clearly observed during the LBA-SMOCC 2003 biomass burning experiment in Rondônia, Brazil, and has been explained by a different combustion stage with flaming combustion dominating during day-time and smoldering combustion (a less complete combustion resulting in higher yields of levoglucosan) prevailing at night (Schkolnik et al., 2005; Claeys et al., unpublished results). However, in this case it is more likely that in the summer many people around in the villages, farms and summer lodges use wood for barbecue and even for cooking especially in the evenings. This may show up in the records, especially at night when the mixing height of the boundary layer is low and inversion frequently occurs.

In contrast to the isoprene oxidation products, arabitol and mannitol, and levoglucosan, malic acid does not show day/night differences but is found to follow quite closely the particulate and organic carbon mass (Fig. 3). This behavior indicates that malic acid likely forms from precursors which have multiple and widely distributed sources, both anthropogenic and natural. This is reasonable to assume since unsaturated fatty acids are ubiquitous compounds in the atmosphere, emitted from cooking operations as well as by vegetation (Rogge et al., 1991; Limbeck and Puxbaum, 1999). Furthermore, it can be assumed that the conversion of unsaturated fatty acids to malic acid has a relatively large over-all time-constant, which further dampens diel fluctuations. Our observation mirrors the results obtained by Brook et al. (2004) on urban aerosols from Toronto, Canada, who have found that the concentrations of malic acid were correlated with those of the SOA.

Table 2 presents the median concentrations and concentration ranges for the PM$_2.5$ particulate mass (PM) and for OC, WSOC, EC, and the major identified organic compounds, as derived from the PM$_{1.5}$ Hi-Vol samples, while Table 3 gives the mean percentages of the OC attributable to the WSOC and to the carbon of the organic compounds. It is noted that the median concentration for the sum of the 2-methyltetrols at K-puszta (28.5 ng m$^{-3}$) is comparable to that found during the LBA-CLAIRE 1998 wet season campaign in Balbina, Brazil, where the concentration (in the total aerosol) was 31 ng m$^{-3}$ (Claeys et al., 2004a), as well as to that found during a 2004 summer period in Hyytiälä, Finland, where the mean concentration (in the PM$_1$ aerosol) was 26 ng m$^{-3}$ (Kourtchev et al., 2005). Malic acid is the most abundant single compound detected in the PM$_{2.5}$ aerosol at K-puszta with a median concentration of 38 ng m$^{-3}$, contributing to the OC with 0.4%, and its concentration is about a factor of 1.5 higher than that observed during the LBA-CLAIRE 1998 wet season campaign in Balbina, Brazil (i.e., 22 ng m$^{-3}$, in the total aerosol).

Overall, the carbon content of the polar organic species quantified by GC/MS accounted for 1.2% of the OC in the PM$_{2.5}$ aerosol (Table 3). The remaining part of the organic compounds that were insoluble in methanol or not amenable to GC/MS analysis constitute a significant fraction of the unidentified organic material. The latter fraction likely includes humic-like substances, which are known to
Table 2. Median concentrations and concentration ranges for the PM$_{2.5}$ particulate mass (PM) and for the PM$_{2.5}$ concentrations of OC, WSOC, EC, and polar organic compounds at K-puszta, Hungary, during summer 2003 (N=63). Data for PM, OC, WSOC and EC are in $\mu$g m$^{-3}$, for all other species in ng m$^{-3}$.

<table>
<thead>
<tr>
<th>Species</th>
<th>All samples (N=63)</th>
<th>Day-time samples (N=27)</th>
<th>Night-time samples (N=28)</th>
</tr>
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<tbody>
<tr>
<td>PM ($\mu$g m$^{-3}$)</td>
<td>14.1</td>
<td>6.3–28</td>
<td>14.1</td>
</tr>
<tr>
<td>OC ($\mu$g m$^{-3}$)</td>
<td>4.2</td>
<td>1.94–6.8</td>
<td>4.3</td>
</tr>
<tr>
<td>WSOC ($\mu$g m$^{-3}$)</td>
<td>2.6</td>
<td>0.98–4.7</td>
<td>2.7</td>
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<tr>
<td>EC ($\mu$g m$^{-3}$)</td>
<td>0.20</td>
<td>0.077–0.59</td>
<td>0.20</td>
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<tr>
<td>Malic acid (ng m$^{-3}$)</td>
<td>38</td>
<td>11.5–79</td>
<td>39</td>
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<tr>
<td>Levoglucosan</td>
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<tr>
<td>Arabitol</td>
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<td>Mannitol</td>
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<td>2-methylglyceric acid</td>
<td>7.6</td>
<td>2.2–18.3</td>
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Table 3. 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 PM$_{2.5}$ Hi-Vol samples, at K-puszta, Hungary, during summer 2003.

<table>
<thead>
<tr>
<th>Species</th>
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<th>Day-time samples (N=27)</th>
<th>Night-time samples (N=28)</th>
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<td></td>
<td>Mean %±std.dev.</td>
<td>Mean %±std.dev.</td>
<td>Mean %±std.dev.</td>
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<tr>
<td>WSOC</td>
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<td>Malic acid</td>
<td>0.35±0.11</td>
<td>0.36±0.12</td>
<td>0.35±0.11</td>
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<tr>
<td>Levoglucosan</td>
<td>0.19±0.16</td>
<td>0.118±0.056</td>
<td>0.25±0.21</td>
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<tr>
<td>Arabitol</td>
<td>0.070±0.056</td>
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<tr>
<td>Mannitol</td>
<td>0.078±0.073</td>
<td>0.110±0.066</td>
<td>0.033±0.028</td>
</tr>
<tr>
<td>2-methylthreitol</td>
<td>0.105±0.077</td>
<td>0.148±0.088</td>
<td>0.077±0.052</td>
</tr>
<tr>
<td>2-methylerythritol</td>
<td>0.28±0.20</td>
<td>0.39±0.21</td>
<td>0.21±0.16</td>
</tr>
<tr>
<td>2-methylglyceric acid</td>
<td>0.083±0.034</td>
<td>0.104±0.037</td>
<td>0.068±0.024</td>
</tr>
<tr>
<td>Sum (compounds)</td>
<td>1.15±0.29</td>
<td>1.33±0.33</td>
<td>1.02±0.32</td>
</tr>
</tbody>
</table>

be significant at K-puszta (Zappoli et al., 1999), as well as biological structures, such as fragments or constituents of fungi, pollen, algae, bacteria, leaves and insects (Matthias-Maser and Jaenicke, 1995; Bauer et al., 2002a; Bauer et al., 2002b). Because a major fraction of the OC consists of large biomacromolecules such as proteins (Miguel et al., 1999), cellulose (Puxbaum and Tenze-Kunit, 2003) and phospholipids (Womiloju et al., 2003), which are embedded in biomembrane structures, techniques such as GC/MS cannot be expected to explain more than a small fraction of the organic aerosol mass. However, in contrast to humic-like substances, which make up a large fraction of the fine OC mass and are hard to characterize on the molecular level notwithstanding their relatively low average molecular mass (<300 Da) (Kiss et al., 2003), the highly polar, multifunctional compounds identified and measured by GC/MS in the present study are useful marker compounds for source identification of the organic carbon mass.

4 Conclusions

Novel insights have been obtained in the atmospheric chemistry of isoprene which is emitted by forest vegetation and leads to secondary organic aerosol formation. The diel patterns observed for the marker compounds, the 2-methyltetrols and 2-methylglyceric acid, showing maxima during day-time, are consistent with a rapid photochemical formation process from locally emitted isoprene. The latter compounds should be regarded as qualitative marker compounds for secondary aerosol formation through photooxidation of isoprene and more research is warranted to explore their potential usefulness for aerosol source apportionment. On the basis of the data obtained in the present study, it is not possible to draw conclusions about the fraction of the secondary organic aerosol that is due to photo-oxidation of isoprene. Based on laboratory experiments with isoprene (Limbeck et al., 2003), it is very likely that photo-oxidation of isoprene significantly contributes to the large fraction of...
Fig. 5. The day/night differences for 2-methylerythritol and mannitol, apparent in the trends of the percent carbon in the fine OC.

Fig. 6. The day/night differences for levoglucosan and 2-methylglyceric acid, apparent in the trends of the percent carbon in the fine OC.

the fine aerosol that contains humic-like substances during summer. However, in view of the high chemical complexity and polarity of these compounds, it remains to be seen in the future whether they can serve as marker compounds for photo-oxidation of isoprene. Novel insights have also been obtained in the fungal activity of the forest ecosystem in that diel patterns with maxima during day-time were observed for arabitol and mannitol, indicating a higher release of fungal fragments during that time. As the isoprene oxidation products, arabitol and mannitol should be regarded as qualitative...
marker compounds, and research is currently underway in our laboratory to determine their fraction of the organic carbon mass due to fungal bioaerosol (a primary source) with the aim to use these data for source apportionment. Further, the time trends of levoglucosan allow to conclude that the sampling site is occasionally affected by biomass smoke, which is most pronounced during night-time, probably as a result of wood burning during the evening. Finally, the observations made on malic acid, an intermediate in the oxidation of unsaturated fatty acids, whose concentrations are high and follow quite closely those of the particulate and organic carbon mass, are worth noting, suggest that oxidation of unsaturated fatty acids is also an important atmospheric chemistry process and warrant more detailed investigation.

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