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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 diurnal 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. Analysis was performed using gas chromatography/mass spectrometry (GC/MS) after suitable sample workup consisting of extraction with methanol and derivatisation into trimethylsilyl (TMS) derivatives. 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 end-oxidation product of unsaturated fatty acids, and (d) the sugar alcohols, arabitol and mannitol, markers for fungal spores. Diurnal patterns with highest concentrations during day-time were observed for the isoprene oxidation products, i.e., the 2-methyltetrols and 2-methylglyceric acid, which can be regarded as supporting evidence for their fast photochemical formation from their locally emitted precursor. In addition, a diurnal pattern with highest concentrations during day-time was observed for the fungal markers, arabitol and mannitol, suggesting that the release of fungal fragments that are associated with the $PM_{2.5}$ aerosol is enhanced during that time. Furthermore, a diurnal 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, i.e., the 2-methyltetrols (28.5 ng m^{-3}) and 2-methylglyceric acid (7.6 ng m^{-3}),

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 humic-like substances which represent a large fraction of the WSOC (Zappoli et al., 1999; Gelencsér et al., 2000a, b; Kiss et al., 2002, 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 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 establish the sources and diurnal variations of major polar organic molecules. Emphasis was placed on the recently discovered photo-oxidation products of isoprene, i.e., the 2-methyltetrols (2-methylthreitol and 2-methylerythritol) and 2-methylglyceric acid. 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 different 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[1]) and forest sites in Germany and Finland (Kourtchev et al., unpublished results). The dihydroxymonocarboxylic acid, 2-methylglyceric acid, has been found for the first time in the K-puszta $PM_{2.5}$ aerosol and 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). 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 generated from isoprene and that sulfuric acid (generated by oxidation of SO_2) plays a crucial role in their formation (Edney et al., 2005[1]). In addition to the isoprene oxidation products, other polar organic molecules detected with our GC/MS method at significant concentrations in the K-puszta $PM_{2.5}$ aerosol were malic acid, levoglucosan, arabitol and mannitol. Of these compounds, malic acid is believed to be an end-product of the oxidation of unsaturated fatty acids (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Neusüss et al., 2002), levoglucosan is a well-established tracer for pyrolysis of cellulose in biomass smoke (Simoneit, 2002), while arabitol and mannitol are molecular markers for fungal cells (Lewis and Smith, 1967; Bieleski, 1982).

This paper describes our efforts to determine the sources and diurnal variations of the particulate mass (PM), organic carbon (OC), WSOC, isoprene oxidation products (2-methylthreitol, 2-methylerythritol, and 2-methylglyceric acid), malic acid, levoglucosan, and arabitol and mannitol (Fig. 1), during summer when the emissions of biogenic volatile organic compounds and the intensity of solar radiation are known to be at their maximum and the forest ecosystem also shows an increased biological activity involving the emission of primary biological particles such as fungal spores and plant pollen. This integrated approach may provide insights into novel photochemical

[1]Edney, E. O., Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Wang, W., and Claeys, M.: Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary aerosol from laboratory irradiated isoprene/NO_x/air mixtures and their detection in ambient $PM_{2.5}$ samples collected in the Eastern United States, Atmos. Environ., submitted, 2005.

and biological processes that contribute to the fine organic aerosol at K-puszta.

2. Experimental

2.1. Site description and aerosol sampling

The aerosol samples were collected at K-puszta, Hungary, during a field campaign between 4 June and 10 July 2003. The sampling station is situated in the clearing of a mixed coniferous/deciduous forest on the Great Hungarian Plain (46°58′ N, 19°33′ E, 136 a.s.l.) about 80 km SE of Budapest. The location is believed to be representative for a rural site, to be free from local anthropogenic pollution and is characterized by intense solar radiation during summer. The station is involved in the Global Atmospheric Watch (GAW) network and the European Monitoring and Evaluation Programme (EMEP). A dichotomous high-volume (Hi-Vol) sampler (about 7 m above ground level) was used to collect samples in two size fractions, a fine (<2.5 μm aerodynamic diameter (AD)) and a coarse (>2.5 μm AD) fraction (Solomon et al., 1983). Double Pallflex quartz fibre filters (of 102 mm diameter), which had been prebaked for 24 h at 550°C to remove organic contaminants, were used to collect each of the two size fractions. Loaded filters were stored in the dark in aluminium foil, which had also been prebaked at 550°C, in a freezer at −25°C until analysis. Separate day-time and night-time samples were collected during most days. The day-time samples were taken from 7:00 to 18:30 local time, the night-time samples from 19:00 to 6:30 the next day. A total of 63 samples were collected. The samples were analysed for organic carbon (OC) and elemental carbon (EC) by a thermal-optical (TOT) technique (Birch and Cary, 1996). The PM_2 mass data were derived from the fine (<2 μm AD) size fraction of a Gent PM10 stacked filter unit (SFU) sampler that was operated in parallel with the Hi-Vol sampler. A Pall Teflo filter was used as fine filter in the SFU sampler and the PM_2 mass data were obtained by weighing these filters 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.

2.2. Analyses for polar organic marker compounds

Only the fine size fractions (<2.5 μm AD) of the Hi-Vol samples were analysed. All glassware used for sample workup was deactivated with 5% dimethyldichlorosilane in toluene in order to minimize adsorption and loss of polar acidic compounds. For each sample, 1/16 of the whole filter was placed in a 25 mL Pyrex glass bottle and spiked with solutions of internal recovery standards (IS), i.e., 50 μL (10.4 ng/μL) of methyl-β-D-xylanopyranoside (Sigma, St. Louis, MO, USA) and 20 μL (37.4 ng/μL) deuterated (D_3)-malic acid (CDN isotopes, Canada); then 20 mL of methanol was added as extraction solvent and the mixture was shaken for 15 min under ultrasonic agitation. The filters were extracted two more times with 20 mL of methanol following a protocol that was established previously (Pashynska et al., 2002). The combined filtrates were 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 nitrogen. The dried residue was derivatised by adding 40 μL of a trimethylsilylation mixture containing *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) with 1% trimethylchlorosilane (TMCS) (Pierce, Rockford, IL, USA) and anhydrous pyridine (2:1, v/v), and heating at 70°C for 60 min. After cooling to room temperature, samples were analysed 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×0.25 mm i.d.) (Alltech, Deerfield, IL, USA) and a low-bleed Rtx-5MS (crossbond 5% diphenyl – 95% dimethyl polysiloxane) fused-silica capillary column (30 m×0.25 mm i.d., 0.25 μm film thickness) (Restek, Bellafonte, PA, USA). 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 ion source was operated at 200°C in the electron ionization (EI)

mode with an electron energy of 70 eV. The temperature of the transfer line between the gas chromatograph and the ion source was 280°C. Mass spectra were recorded in the mass range m/z 45–450. Aliquots of 1 μL of the derivatised extracts were injected in the splitless mode (splitless time: 0.5 min) at a temperature of 250°C.

For quantitative analysis, calibration curves were constructed by analysing aliquots of stock solutions of standards that were evaporated and derivatised according to the procedure described above. The quantification of 2-methyltetrols, levoglucosan, arabitol and mannitol as well as that of malic acid was based on the use of mass chromatographic data and an internal standard calibration procedure employing methyl-β-D-xylopyranoside (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 reference was available, the response factor of malic acid was used. All reported concentrations were corrected for procedural blanks. Duplicate analyses showed that the precision was about 10%.

3. Results and discussion

3.1. Method development for analysis of polar organic compounds

In preliminary experiments, the $PM_{2.5}$ Hi-Vol samples were extracted with dichloromethane-methanol (80:20, v/v), a solvent mixture found to be suitable for a polar compound such as levoglucosan (Pashynska et al., 2002). However, for the final analyses of which the results are reported in the present study, methanol was used for extraction of the filter samples. It was shown in previous work from our laboratory (G. Vas, unpublished results) that methanol is a much better extractant than the solvent mixture dichloromethane-methanol (80:20, v/v) for extraction of polar hydroxycarboxylic acids such as malic acid. Taking into account the polar character of the other compounds detected in the derivatised extracts, we evaluated pure methanol and compared it with dichloromethane-methanol (80:20, v/v). On the basis of this com-

parison which revealed that methanol was an efficient solvent for the extraction of the 2-methyltetrols, levoglucosan, arabitol, and especially mannitol (the most polar compound among the saccharidic compounds), malic acid and 2-methylglyceric acid, 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. Using D_3-malic acid, it was also verified that methylation did not occur with methanol under the sample workup conditions. GC/MS analysis of the derivatised extracts obtained with dichloromethane-methanol (80:20, v/v) also revealed for about 50% of the samples the presence of trimethylsilylated sulfuric acid, which is hard to explain given the polarity of sulfuric acid, and severely affected the GC/MS analysis. The latter interference disappeared upon use of methanol as extractant. With regard to derivatisation, the procedure developed by Zdráhal et al. (2002) using MSTFA +1% TMCS-pyridine, which was shown to yield a single TMS derivative for most of the studied compounds, was followed; while one derivative was observed for methyl β-L-xylanopyranoside (IS), the 2-methyltetrols, malic acid, 2-methylglyceric acid, levoglucosan, arabitol and mannitol, multiple peaks were found for glucose (two) and fructose (three) in agreement with literature data (Bartolozzi et al., 1997).

3.2. Characterisation, sources and diurnal variations of polar organic compounds in the $PM_{2.5}$ aerosol

Figure 2 shows GC/MS total ion chromatograms (TICs) obtained 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, anhydrosugars 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 hydroxydicarboxylic acid, malic acid (2), levoglucosan (6), the sugar alcohols, arabitol (7) and mannitol (8), and the dihydroxymono-

carboxylic acid, 2-methylglyceric acid (1) (Fig. 1). Other minor compounds identified but not measured were the monosaccharides, fructose (□) and glucose (■), as well the anhydrosugars, mannosan and galactosan, which accompany 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 (i.e., <10% of the 2-methyltetrols) in most samples. All compounds were characterized on the basis of their EI mass spectra and comparison with those of authentic reference compounds or reported mass spectral data (Claeys et al., 2004a, b; Wang et al., 2005). The dihydroxymonocarboxylic acid, 2-methylglyceric acid (1), has been reported in a previous study (Claeys et al., 2004b) where it was wrongly denoted by 2,3-dihydroxymethacrylic acid, and has been explained by further aerosol-phase oxidation of methacrolein and methacrylic acid, which are gas-phase oxidation products of isoprene. Therefore, this compound can be regarded as a higher-order photo-oxidation product of isoprene. The hydroxydicarboxylic acid, malic acid (2), is generally considered as an end-oxidation product of unsaturated fatty acids (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Neusüss et al., 2002). 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 pyrolysis 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 monitor biomass smoke in tropical environments that are affected by deforestation (Zdráhal et al., 2002; Graham et al., 2002, 2003; Schkolnik et al., 2005) as well as in urban and rural environments where wood burning is important during winter (Zdráhal et al., 2002; Pashynska et al., 2002; Pio et al., 2004). The 2-methyltetrols, 2-methylthreitol (3) and 2-methylerythritol (4), have first been reported in $PM_{2.5}$ aerosols from the Amazonian rain forest (Claeys et al., 2004a) and are explained through photo-oxidation of isoprene, which is emitted in by far the largest amounts

among all VOCs by terrestrial vegetation, i.e., about 500 Tg per year on a global scale (Guenther et al., 1995). The sugar alcohols, arabitol (7) and mannitol (8), are fungal marker compounds (Lewis and Smith, 1967; Bieleski, 1982), while the monosaccharides, fructose (□) and glucose (■), are believed to originate from plant pollen which may be rich in fructose and glucose (Pacini, 2000). The latter sugar alcohols and monosaccharides have been shown to be mainly associated with the coarse size fraction (>2.5 μm AD) of aerosols collected above the Amazon forest (Graham et al., 2003). Similar results were obtained for arabitol, mannitol, and glucose for size-fractionated aerosols collected at a rural (meadow) site in Melpitz, Germany; in contrast, arabitol and mannitol were found to be mainly associated with the fine size mode for aerosols collected at a boreal forest site, Hyytiälä, Finland (Carvalho et al., 2003).

Figure 3 shows the time trends for the PM_2 particulate mass (PM derived from a Gent SFU filter sampler) and for $PM_{2.5}$ OC, malic acid, the sum of the 2-methyltetrols and the sugar alcohol mannitol. It can be seen in the Figure that the mass concentrations of OC and malic acid follow quite closely that of the PM. In contrast to malic acid, diurnal variations with the highest concentrations during day-time are observed for the 2-methyltetrols and mannitol. A diurnal variation similar to that of mannitol was observed for arabitol (not shown). 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 region 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., 2000b). Enhanced day-time concentrations have been previously reported for α-pinene oxidation products and are generally seen as evidence for a photochemical source (Kavouras et al., 1998). The concentration ratio 2-methylthreitol/2-methylerythritol was 0.37 and the excellent correlation (R^2=0.95) found between the two diasteroisomers expressed as a % C of the OC is consistent with their formation through the same aerosol source process, i.e., photo-oxidation of isoprene (Fig. 4). The diurnal cycle of mannitol revealing its highest atmospheric concentrations during

day-time contrasts with observations made for the coarse aerosol fraction (>2.5 μm 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 release of smaller-sized fungal fragments at K-puszta is more pronounced during day-time, which is generally characterized by stronger winds and convective activity compared to night-time. In this respect, it has also been demonstrated that smaller-sized fungal fragments are released together with spores from moldy surfaces (Górny et al., 2002). The day/night differences for the 2-methyltetrols and the sugar alcohols, arabitol and mannitol, are also very apparent in the trends of their percentage carbon contributions to the fine OC (Fig. 5). Furthermore, a diurnal pattern could be observed for the dihydroxy-monocarboxylic acid, 2-methylglyceric acid, consistent with its formation through rapid photo-oxidation of isoprene (Fig. 6). 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). 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 concentrations was noted (Fig. 6), accounting, on average, 2 times more to the OC 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 levoglu-

cosan, malic acid did not show day/night differences but was found to follow quite closely the particulate and organic carbon mass (Fig. 3). The significant correlation found between the concentrations of OC and malic acid (R^2=0.54) suggests that malic acid can serve as a reasonably good general indicator compound for the organic carbon mass in the $PM_{2.5}$ aerosol (Fig. 7). This fact together with the lack of diurnal variations point out 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 overall time-constant, which further dampens diurnal fluctuations and establishes a significant correlation with the OC of which a substantial fraction is thought to be of secondary origin. In other terms, malic acid could be regarded as a tracer for global SOA, though this aspect clearly requires further evaluation. 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 well correlated with those of the SOA and proposed malic acid as a marker for SOA. It is also worth mentioning that the latter study demonstrated that the concentrations of malic acid are dependant on the aerosol acidity.

Table 1 summarizes the median concentrations and concentration ranges for OC, WSOC, EC, and the major identified organic compounds, as derived from the $PM_{2.5}$ Hi-Vol samples, while Table 2 gives the corresponding 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). 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 1%, and about a factor of 1.5 higher compared to the concentration 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 3.2% of the OC in the $PM_{2.5}$ aerosol. 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 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, b). 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, the highly polar, multifunctional compounds identified and measured by GC/MS in the present study are useful marker compounds for source identification and apportionment of the organic carbon mass. 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 the fine aerosol that contains humic-like substances during summer.

4. Conclusions

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. Analysis was per-

formed using gas chromatography/mass spectrometry (GC/MS) after suitable sample workup consisting of extraction with methanol and derivatisation into trimethylsilyl (TMS) derivatives. 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 smoke, (c) malic acid, an end-oxidation product of unsaturated fatty acids, and (d) the sugar alcohols, arabitol and mannitol, markers for fungal biomass. Diurnal patterns with the highest concentrations during day-time were observed for the isoprene oxidation products, i.e., the 2-methyltetrols and 2-methylglyceric acid, which can be regarded as supporting evidence for their rapid photochemical formation. In addition, a similar diurnal pattern was noted for the fungal markers, arabitol and mannitol, suggesting that the release of fungal fragments that are associated with the $PM_{2.5}$ aerosol is enhanced during day-time. Furthermore, a diurnal pattern was also found for levoglucosan, a marker for biomass smoke, with highest concentrations during night-time when sporadic wood burning may take place. In contrast, malic acid did not show day/night differences but was found to follow quite closely the particulate and organic carbon mass. On the basis of the high concentrations found for the isoprene oxidation products, i.e., the 2-methyltetrols (28.5 ng m^{-3}) and 2-methylglyceric acid (7.6 ng m^{-3}), it can be concluded that photo-oxidation of isoprene is likely an important atmospheric chemistry process that contributes to secondary organic aerosol formation at K-puszta during summer.

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Table 1. Median concentrations and concentrations ranges, as derived from the $PM_{2.5}$ Hi-Vol samples, at K-puszta, Hungary, during summer 2003 (n=63). 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-methylglyceric acid	7.6	2.2–18.3

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 $PM_{2.5}$ Hi-Vol samples, at K-puszta, Hungary, during summer 2003.

Species	All samples (N=63) Mean %±std.dev.	Day-time samples (N=27) Mean %±std.dev	Night-time samples (N=28) Mean %±std.dev
WSOC	61±9	62±10	62±8
Malic acid	0.97±0.49	1.11±0.55	0.94±0.45
Levoglucosan	0.54±0.66	0.38±0.30	0.74±0.92
Arabitol	0.19±0.17	0.29±0.18	0.074±0.047
Mannitol	0.21±0.22	0.33±0.23	0.079±0.061
2-methylthreitol	0.28±0.22	0.43±0.24	0.19±0.12
2-methylerythritol	0.76±0.57	1.15±0.58	0.52±0.37
2-methylglyceric acid	0.23±0.15	0.32±0.18	0.18±0.10
Sum (compounds)	3.2±1.6	4.0±1.5	2.7±1.4

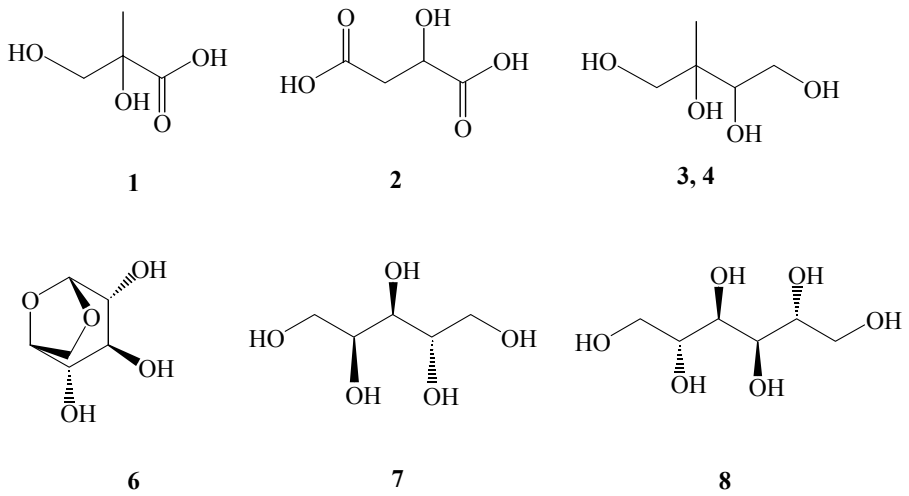

Fig. 1. Chemical structures of the major polar organic marker compounds characterized in the K-puszta $PM_{2.5}$ aerosol. (1) 2-methylglyceric acid, (2) malic acid, (3) 2-methylthreitol, (4) 2-methylerythritol, (6) levoglucosan, (7) arabitol, and (8) mannitol.

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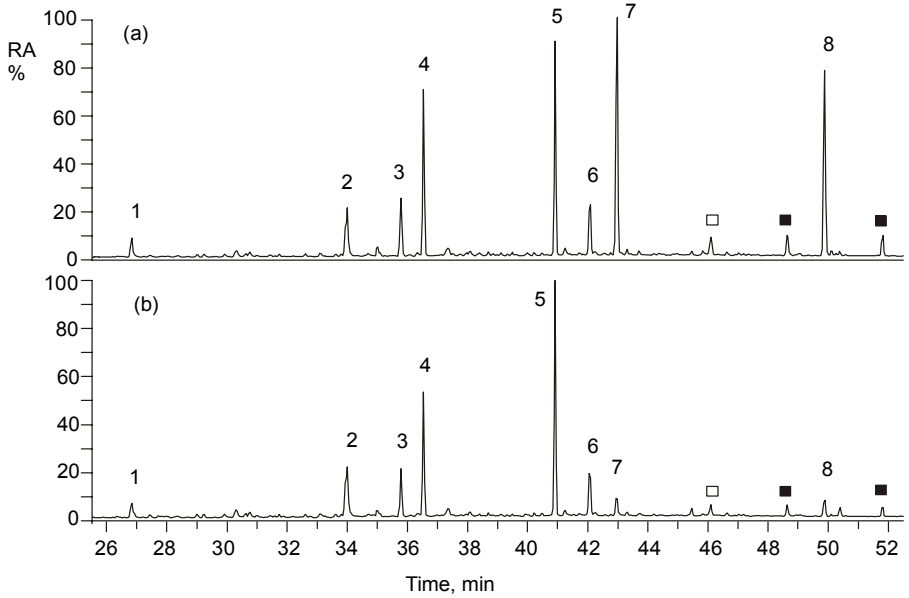

Fig. 2. GC/MS total ion chromatograms for **(a)** a day- and **(b)** nighttime $PM_{2.5}$ aerosol sample collected on 19 June 2003. Peak identifications: (1) 2-methylglyceric acid, (2) malic acid [+ D_3-malic acid (IS)], (3) 2-methylthreitol, (4) 2-methylerythritol, (5) methyl-β-D-xylanopyranoside (IS), (6) levoglucosan, (7) arabitol, (8) mannitol, (□) fructose (3 peaks), and (■) glucose (2 peaks).

ACPD
5, 1863–1889, 2005

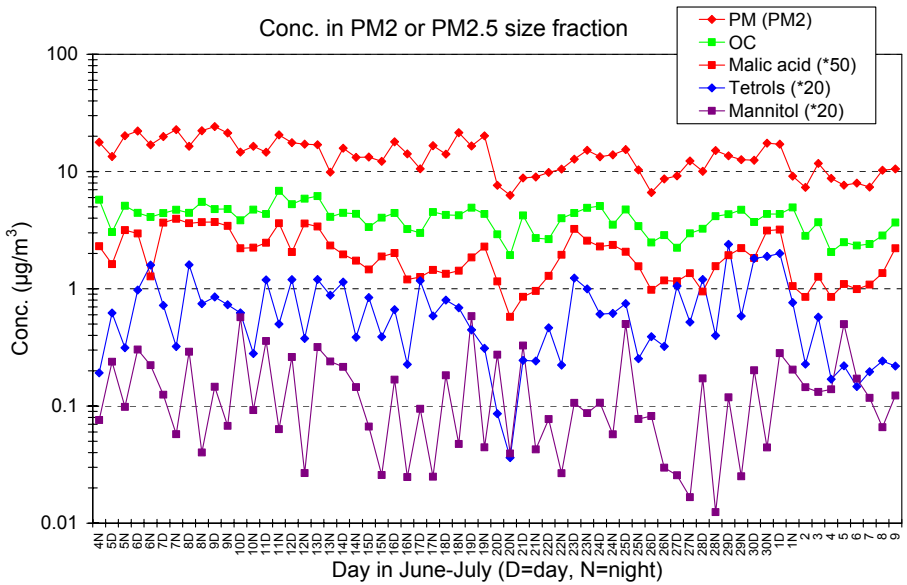

Fig. 3. Time trends for the PM_2 particulate mass and for $PM_{2.5}$ OC, malic acid, the 2-methyltetrols (sum of 2-methylthreitol and 2-methylerythritol) and the sugar alcohol mannitol.

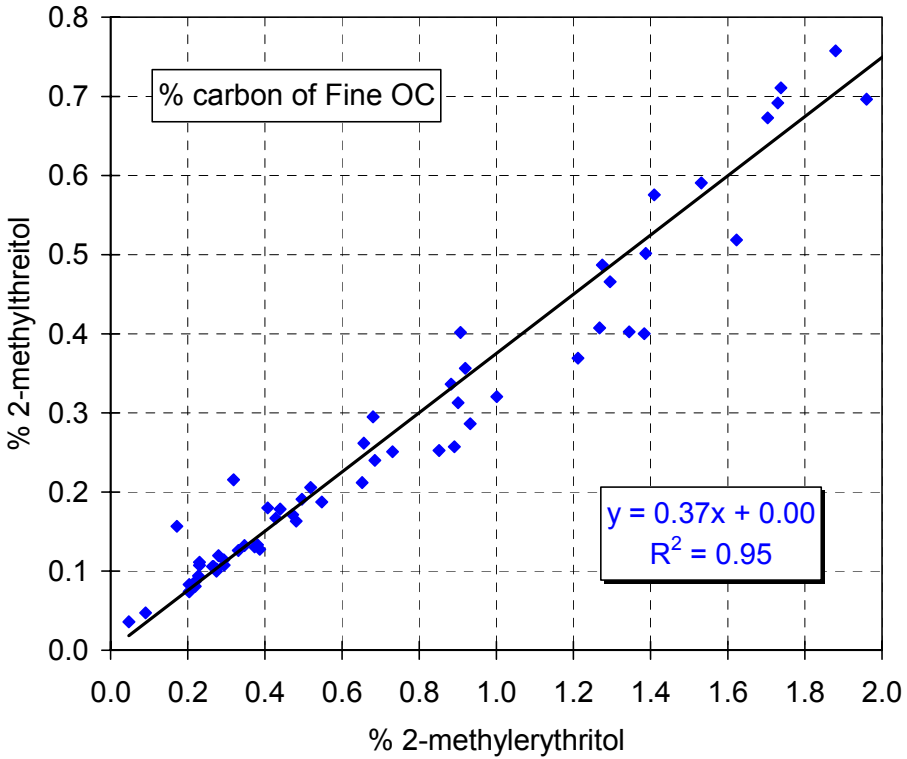

Fig. 4. Scatter plot 2-methylthreitol/2-methylerythritol.

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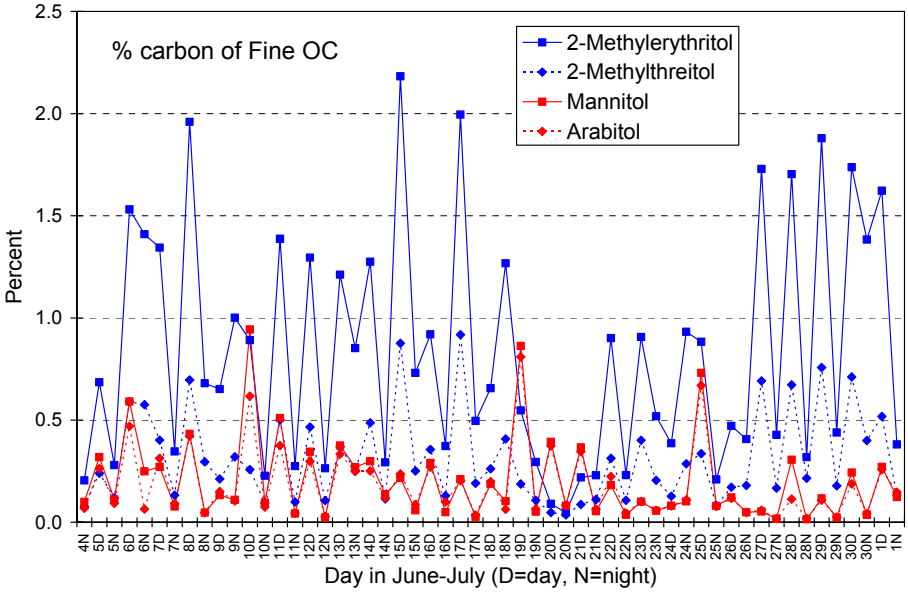

Fig. 5. The day/night differences for the 2-methyltetrols, 2-methylthreitol and 2-methylerythritol, and the two sugar alcohols, arabitol and mannitol, apparent in the trends of the percent carbon in the fine OC.

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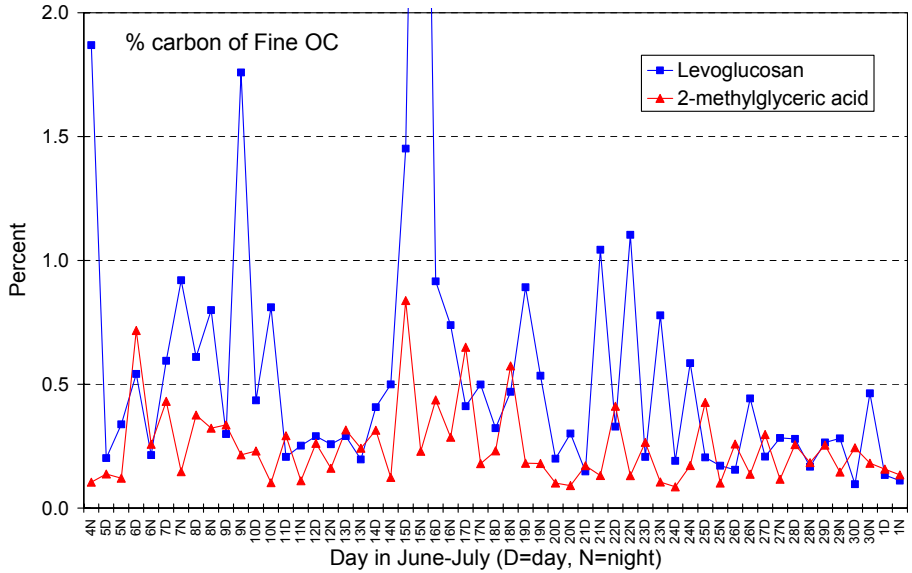

Fig. 6. The day/night differences for levoglucosan and 2-methylglyceric acid, apparent in the trends of the percent carbon in the fine OC.

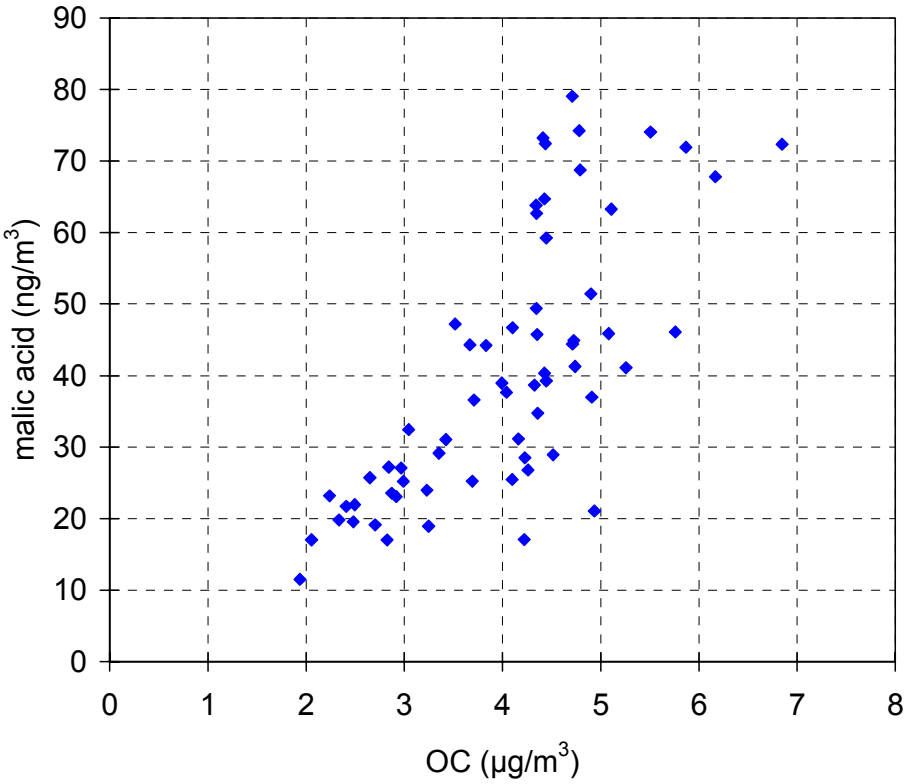

Fig. 7. Scatter plot malic acid/OC.