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Characterization of Atmospheric Aerosols at a Forested Site in Central Europe

IVAN KOURTCHEV,[†]
LUCIAN COPOLOVICI,[‡] MAGDA CLAEYS,[†]
AND WILLY MAENHAUT*,[‡]

Department of Pharmaceutical Sciences, University of Antwerp (Campus Drie Eiken), Universiteitsplein 1, BE-2610 Antwerp, Belgium, and Department of Analytical Chemistry, Institute for Nuclear Sciences, Ghent University, Proeftuinstraat 86, BE-9000 Gent, Belgium

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Mass concentrations, mass size distributions, time series, and diel variations for organic tracers and major inorganic ions in aerosols from K-puszta, Hungary, during a 2003 summer period are reported. Emphasis was placed on α-/β-pinene secondary organic aerosol (SOA) tracers comprising *cis*-pinic acid, 3-hydroxyglutaric acid, and 3-methyl-1,2,3-butanetricarboxylic acid. Only *cis*-pinic acid and the *d*-limonene SOA tracer 3-carboxyheptanedioic acid exhibited diel variations with highest concentrations at night. Malic acid was fairly well correlated with succinic and oxalic acid, pointing to a similar SOA formation process. No day-night variations were observed for the latter acids, suggesting that they are formed over relatively long time scales. Of the ionic species sulfate, ammonium, and nitrate, only nitrate showed clear diel variations with highest concentrations at night. As to the size-segregated samples, the 2-methyltetrols were present in both the fine and coarse modes, while the C_5-alkene triols and the α-/β-pinene SOA tracers were only associated with the fine mode. The ionic species sulfate, ammonium, and nitrate made up for, on average, 24, 10, and 2.6% of the $PM_{2.5}$ mass, while organic matter was responsible for 47% of that mass. Isoprene and α-pinene secondary organic carbon (SOC) accounted, on average, for, respectively, 6.8 and at least 4.8% of the $PM_{2.5}$ organic carbon, but the contribution of isoprene SOC was more pronounced during daytime (9.6%), whereas that of α-pinene SOC was largest at night (at least 6.0%).

Introduction

The fine aerosol from K-puszta, Hungary, a rural forest site with a mixed deciduous/coniferous vegetation, has been intensively studied during the past decade because it contains a large fraction of water-soluble organic carbon (WSOC) compounds (e.g., ref *1*, and references therein). These compounds are of interest owing to their climatic effects, including their ability to alter cloud properties (*2*). Emphasis has been placed on the characterization of humic-like substances (HULIS), which represent a large fraction of the organic carbon (OC), with 24% at the K-puszta site (*3*). Recently, substantial progress has been made with the molecular characterization of water-soluble organic compounds; in particular, it has been shown that fine summer aerosol from forested sites contains organosulfates and nitrooxy organosulfates of photooxidation products of isoprene, α-/β-pinene, and unsaturated fatty acids (*4–7*). The latter tracers have a mixed biogenic/anthropogenic origin since sulfuric acid and NO_x which participate in their formation mainly have an anthropogenic origin.

Previous work from our laboratories on the organic speciation of $PM_{2.5}$ (particulate matter with an aerodynamic diameter (AD) <2.5 μm) K-puszta aerosol (*1*) dealt with sources and time series of selected polar tracers that can be measured with gas chromatography/mass spectrometry (GC/MS) and prior derivatization. These compounds comprised isoprene secondary organic aerosol (SOA) tracers (i.e., the 2-methyltetrols, 2-methylthreitol and 2-methylerythritiol (*8–10*), and 2-methylglyceric acid (*9–11*); levoglucosan, a tracer for biomass combustion (*12*); malic acid, an oxidation product of unsaturated fatty acids (*13–15*); and the polyols arabitol and mannitol, tracers for fungal spores (*16, 17*). In addition, recent work led to the structure elucidation of novel SOA tracers for α-/β-pinene that occur at significant concentrations in $PM_{2.5}$ K-puszta aerosol, i.e., 3-hydroxyglutaric acid (3-HGA) (*18, 19*) and 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA) (*18, 20*), which are higher-generation photooxidation products.

The main objectives of the present work are to discuss time series, mass size distributions, and diel variations of polar organic tracers and to assess the biogenic secondary organic carbon (SOC) from α-/β-pinene and isoprene. With regard to the latter contributions, estimates were made based on the measured SOA tracer concentrations and the laboratory-derived tracer mass fractions reported by Kleindienst et al. (*21*). Aerosol samples collected during a 2003 summer field campaign were re-examined. Emphasis is placed on α-/β-pinene SOA tracers, but to evaluate correlations between tracers for aerosol sources and/or processes, other polar tracers and inorganic ions were included. The isoprene SOA tracers comprised, in addition to the 2-methyltetrols and 2-methylglyceric acid, the C_5-alkene triols (2-methyl-1,3,4-trihydroxy-1-butene (*cis* and *trans)* and 3-methyl-2,3,4-trihydroxy-1-butene) (*9, 22*). Polar tracers other than α-/β-pinene and isoprene SOA tracers were a *d*-limonene SOA tracer (i.e., 3-carboxyheptanedioic acid (*23*)) and short-chain (C_2-C_6) dicarboxylic acids, including oxalic, malic, succinic, glutaric, and 2-hydroxyglutaric acid. C_2-C_6 dicarboxylic acids are formed through photochemical oxidation of hydrocarbons and unsaturated fatty acids, and can also arise through direct emissions from biomass and fossil fuel combustion (*24–27*).

Experimental Procedures

Aerosol Sampling and Analysis. The aerosol samples were collected at K-puszta (46°58′N, 19°33′E), Hungary, during a 2003 summer campaign, which was exceptionally dry, sunny, and warm. A detailed description of the sampling site and the meteorological conditions during the campaign were reported in previous studies (*1, 28*). Briefly, the sampling station is situated in the clearing of a mixed coniferous/deciduous forest and is located approximately 80 km SE of Budapest on the Great Hungarian Plain. The largest city nearby (Kecskemét with about 108 000 inhabitants) is at a distance of 15 km.

A dichotomous high-volume (Hi-Vol) sampler was used to collect samples in two size fractions, fine or $PM_{2.5}$ (<2.5

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* Corresponding author phone: +32 9 264 65 96; fax: +32 9 264 66 99; e-mail: willy.maenhaut@ugent.be.
[†] University of Antwerp.
[‡] Ghent University.

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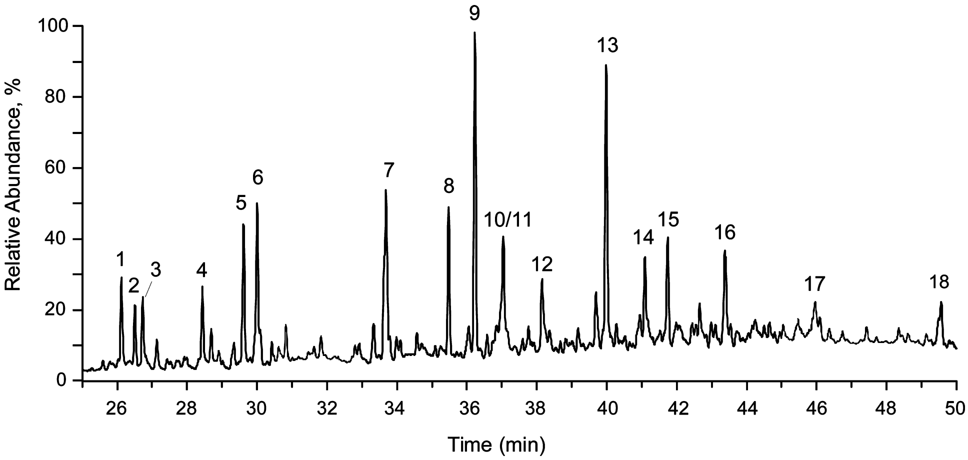

FIGURE 1. GC/MS total ion chromatogram obtained for a nighttime sample collected on 11 June 2003. Peak attributions: (1) succinic acid; (2) 2-methylglyceric acid; (3) glyceric acid; (4) *cis*-2-methyl-1,3,4-trihydroxy-1-butene; (5) 3-methyl-2,3,4-trihydroxy-1-butene; (6) *trans*-2-methyl-1,3,4-trihydroxy-1-butene; (7) malic acid; (8) 2-methylthreitol; (9) 2-methylerythritol; (10) 2-hydroxyglutaric acid; (11) 3-hydroxyglutaric acid; (12) octadecanoic acid; (13) *cis*-pinic acid; (14) levoglucosan; (15) arabitol; (16) 3-methyl-1,2,3-butanetricarboxylic acid; (17) 3-carboxyheptanedioic acid; and (18) mannitol.

μm AD) and coarse (>2.5 μm AD) (*29*). Double Pallflex quartz fiber filters of 102 mm diameter (prefired for 24 h at 550 °C) were used to collect each of the two fractions. Parallel to the Hi-Vol sampler, a microorifice uniform deposit impactor (MOUDI) (model 110, MSP Corporation, Minneapolis, MN) (*30*) was used to collect size-segregated aerosol samples. The 50% aerodynamic cutoff diameters of the preimpaction stage (stage 0) and the 10 regular stages were 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, and 0.056 μm. Preheated aluminum foils of 37 mm diameter were employed as impaction surfaces in the MOUDI. Furthermore, a Gent PM10 stacked filter unit (SFU) sampler was operated (*31*). In this sampler a Nuclepore polycarbonate filter was used for collecting the coarse (2−10 μm AD) particles and a Pall Teflo filter for collection of the fine (<2 μm AD) size fraction. Separate day- and nighttime samples were collected with all samplers from 4 June to 2 July 2003. During the period from 2 to 10 July 2003, 24-h samples were collected. The daytime samples were taken from 07:00 to 18:30 local time, the nighttime samples from 19:00 to 06:30 the next day; for the 24-h samples, collection was done from 7:00 to 6:30 the next day.

The filters from the SFU sampler and the aluminum foils from the MOUDI were weighted before and after sampling with a microbalance of 1 μg sensitivity. The weightings were done at 20 °C and 50% relative humidity, and the filters and foils were equilibrated at these conditions for 24 h prior to weighing. OC and elemental carbon (EC) data for all Hi-Vol quartz fiber filters, as measured by thermal-optical transmission (TOT) analysis, were available from our previous study (*1*).

The fine front filters of all 63 Hi-Vol samples and the aluminum foils of six selected MOUDI samples (i.e., the day- and nighttime samples of 6, 11, and 27 June) were subjected to analyses by GC/MS and ion chromatography (IC). Details about these analyses are given in the Supporting Information (S1−S2).

Results and Discussion

Figure 1 presents the GC/MS total ion chromatogram for the nighttime $PM_{2.5}$ sample collected on 11 June 2003, in which pinic acid (PA) and 3-MBTCA were present at the highest concentrations (135 ng m^{-3} and 74 ng m^{-3}, respectively), and the *d*-limonene SOA tracer, 3-carboxyheptanedioic acid, was also clearly present (21 ng m^{-3}). Information on the mass spectral characterization of 3-carboxyheptanedioic acid is provided as Supporting Information (S3).

TABLE 1. Median and Mean Mass Concentrations and Concentration Ranges of the PM in $PM_{2.0}$ and of OC, WSOC, EC, and Organic and Inorganic Species in $PM_{2.5}$ for the Period 4 June−10 July, 2003 at K-puszta, Hungary[a]

species	median conc.	mean conc.	conc. range
PM (μg m^{-3})	13.6	14.0	6.3–24
OC (μg m^{-3})	4.2	4.0	1.9–6.8
WSOC (μg m^{-3})	2.6	2.5	1.0–4.7
EC (μg m^{-3})	0.20	0.21	0.08–0.59
Organic Compounds (ng m^{-3})			
oxalic acid (IC)	196	189	91–350
malic+succinic acids (IC)	41	39	10–77
glutaric acid (IC)	7.8	9.6	2.1–35
malic acid	40	40	16.5–78
succinic acid	13.8	15.2	1.2–50
2-hydroxyglutaric acid	5.7	6.2	1.9–19.5
cis-pinic acid	5.3	12.2	0.6–135
3-hydroxyglutaric acid	16.8	19.7	5.4–113
3-methyl-1,2,3-butanetricarboxylic acid	12.3	15.8	1.9–74
3-carboxyheptanedioic acid	1.1	1.8	0–21
Inorganic Species (ng m^{-3})			
NO_3^-	310	400	116–2900
NH_4^+	1520	1700	620–3300
SO_4^{2-}	3500	3800	1790–7700

[a] Concentrations of the PM and of the OC, WSOC, and EC mass are in μg m^{-3}, whereas those of the organic and inorganic species are in ng m^{-3}.

Quantitative Data for α-/β-Pinene SOA Tracers and C_2−C_6 Dicarboxylic Acids in $PM_{2.5}$ Samples. Table 1 summarizes the median concentrations and concentration ranges for the $PM_{2.0}$ particulate mass (PM) and for OC, EC, and detected organic and inorganic species, as derived from the $PM_{2.5}$ Hi-Vol samples. Among the identified terpenoic acids, 3-HGA showed the highest median concentration (16.8 ng m^{-3}), followed by 3-MBTCA (12.3 ng m^{-3}), PA (5.3 ng m^{-3}), and 3-carboxyheptanedioic acid (1.1 ng m^{-3}). Comparable concentrations for 3-HGA and 3-MBTCA were reported for $PM_{2.5}$ samples collected from Research Triangle Park, NC, during a 2003 summer period (ranges of 19.4−91.7 and 15.8−130 ng m^{-3}, respectively), whereas PA was detected at higher concentrations (4.5−15.5 ng m^{-3}) (*32*). Comparison with data from other field sites is provided as Supporting Information (S4). It should be noted that for the two nights of 11 and 12 June (Figure 2) the concentrations of the

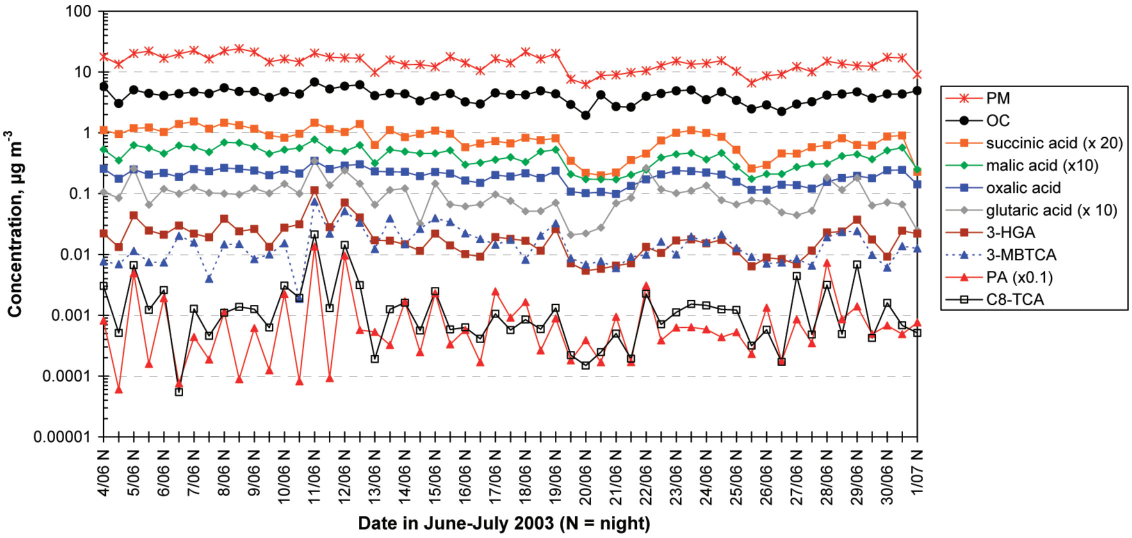

FIGURE 2. Time series for the fine ($PM_{2.0}$ or $PM_{2.5}$) mass concentrations of the PM, OC, selected short-chain diacids, 3-hydroxyglutaric acid (3-HGA), 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA), *cis*-pinic acid (PA), and 3-carboxyheptanedioic acid (C_8-TCA).

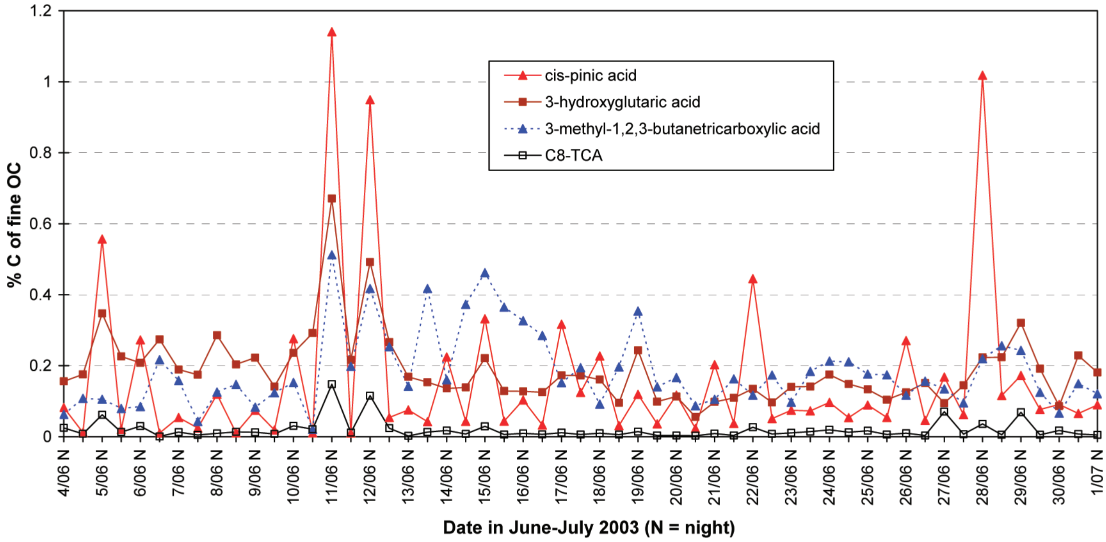

FIGURE 3. Time series of the percentage carbon of the $PM_{2.5}$ OC mass attributable to *cis*-pinic acid, 3-hydroxyglutaric acid, 3-methyl-1,2,3-butanetricarboxylic acid, and 3-carboxyheptanedioic acid (C_8-TCA).

terpenoic acids were elevated and reached (on 11 June) 135 ng m^{-3} for PA, 113 ng m^{-3} for 3-HGA, and 74 ng m^{-3} for 3-MBTCA. In addition, during those nights the terpenoic acids provided a notable contribution to the OC mass (Figure 3), with a maximum of 1.1% for PA, 0.7% for 3-HGA, and 0.5% for 3-MBTCA. The elevated concentrations of PA at K-puszta during the nights of 11, 12, and 28 June suggest that photooxidation of α-/*β*-pinene was less complete than on other days, considering that PA is a lower-generation photoxidation product of α-/*β*-pinene compared to 3-HGA and 3-MBTCA (Supporting Information, S5). It is noteworthy that there were three days during the 2003 campaign with daytime maximum temperatures of more than 35 °C and ozone levels of more than 90 ppb (i.e., 11, 12, and 13 June) and that the two nights with highest PA (i.e., 11 and 12 June) followed such hot and high ozone days.

Throughout the campaign, oxalic acid was the most abundant short-chain dicarboxylic acid with a median concentration of 196 ng m^{-3}, followed by malic acid (40 ng m^{-3}), succinic acid (13.8 ng m^{-3}), glutaric acid (7.8 ng m^{-3}), and 2-hydroxyglutaric acid (5.7 ng m^{-3}). The sum of malic and succinic acids measured by IC was 41 ng m^{-3} and is comparable to that determined by GC/MS and with data from other field sites (Supporting Information, S4).

Diel Variations of the Mass Concentrations of the PM, OC, α-/*β*-Pinene SOA Tracers, C_2−C_6 Dicarboxylic Acids, and Inorganic Ions. Figure 2 shows the time series for fine ($PM_{2.0}$ or $PM_{2.5}$) PM, OC, α-/*β*-pinene SOA tracers, and selected short-chain diacids. It can be seen that the mass concentrations of oxalic acid, succinic acid, malic acid, 3-HGA, and 3-MBTCA follow closely those of the PM and OC. In contrast, PA and 3-carboxyheptanedioic acid do not show the same pattern and exhibit strong diel variations with highest concentrations at night. The nocturnal increase in the concentrations of PA is especially apparent in its percent carbon to the fine OC mass (Figure 3). The median (and 10−90% ranges) of the percentage contribution of PA to the OC were 0.17 (0.08−0.67) during the night versus 0.04 (0.01−0.07) during the day. Possible explanations for the nighttime prevalence of PA at K-puszta are fresh formation such as dark ozonolysis of α-pinene and/or enhanced gas-to-particle partitioning at the cooler nighttime temperatures (Supporting Information, S6). In contrast, diel variations were not seen for 3-HGA and 3-MBTCA; the median (and 10−90%

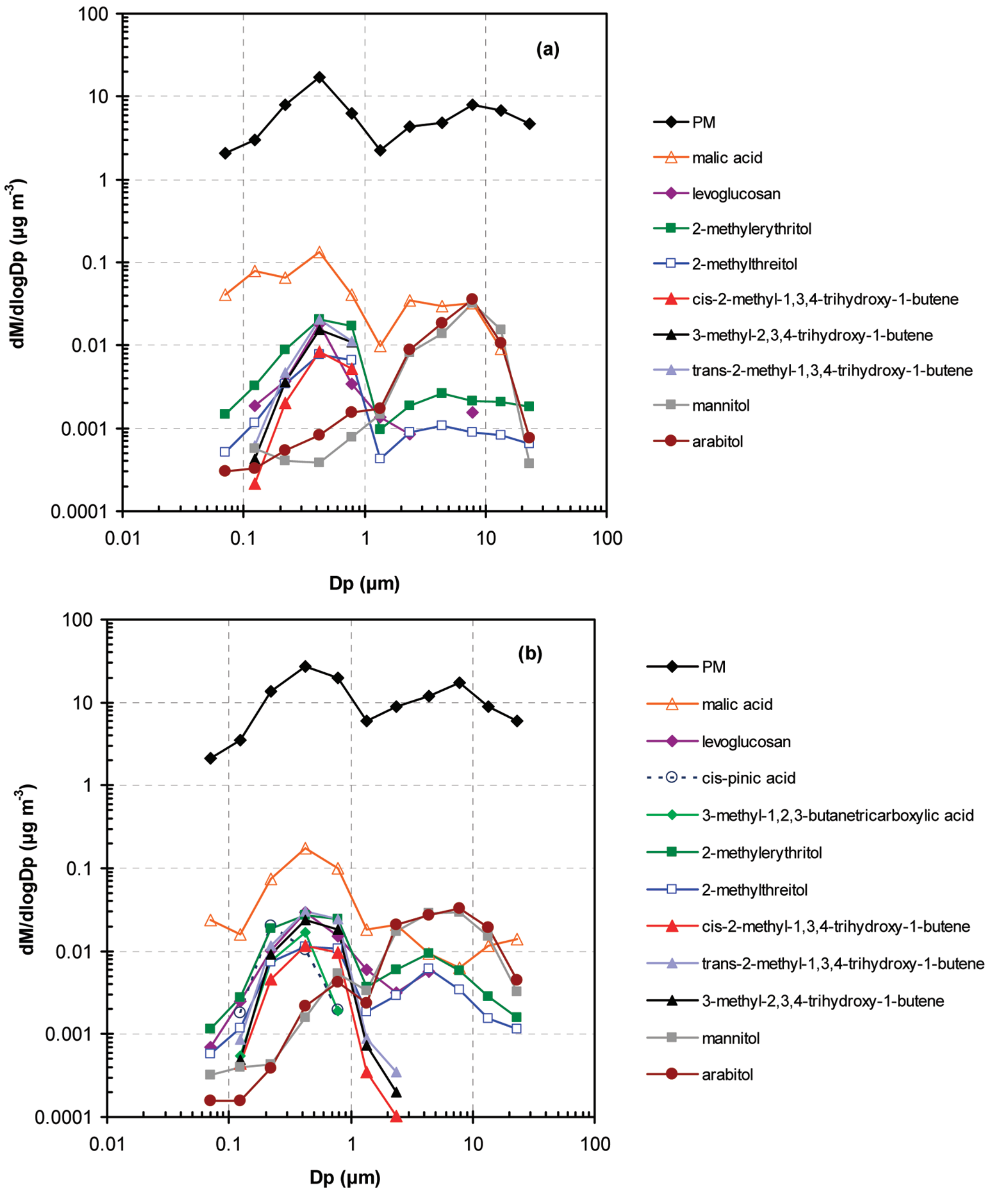

FIGURE 4. Mass size distributions of the PM and organic species detected by GC/MS (malic acid, levoglucosan, *cis*-pinic acid, 3-methyl-1,2,3-butanetricarboxylic acid, 2-methylerythritol, 2-methyltreitol, *cis*- and *trans*-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, mannitol, and arabitol) for MOUDI samples collected on 11 June 2003 during (a) day- and (b) nighttime.

ranges) of the percentage contribution of 3-HGA to the OC were 0.17 (0.11−0.33) during the night versus 0.15 (0.10−0.25) during the day, the corresponding data for 3-MBTCA were 0.15 (0.08−0.37) during the night versus 0.17 (0.08−0.32) during the day. This indicates that the time scales at which 3-HGA and 3-MBTCA are formed are larger than those of PA, consistent with higher-generation oxidation products of α-pinene (Supporting Information, S5). The two species were fairly well correlated with each other ($R^2 = 0.6$), but no correlation between PA and 3-HGA or 3-MBTCA was found.

Malic acid was well correlated with succinic acid ($R^2 = 0.85$) and oxalic acid ($R^2 = 0.78$), pointing to a close relationship and thus consistent with a similar aerosol formation process, i.e., photooxidation of unsaturated fatty acids (*13*). Furthermore, it can be noted that malic, succinic, and oxalic acid do not reveal diel variations, indicating that the time scales at which these products are formed are relatively large, thus consistent with higher-generation photooxidation products.

The diel variations of the inorganic ions are discussed in the Supporting Information (S7).

Mass Size Distributions of the PM, Isoprene and α-/β-Pinene SOA Tracers, C_2−C_6 Dicarboxylic Acids, and Inorganic Ions. Figure 4 shows the mass size distributions of the PM and polar organic compounds measured by GC/MS for the day- and nighttime samples of 11 June; the figures for the samples of 6 and 27 June are provided as Supporting Information (S8). Only two α-/β-pinene SOA tracers were detected in the MOUDI samples, i.e., PA and 3-MBTCA, which, moreover, could only be detected for the nighttime sampling of 11 June. Size distributions of the OC and EC mass were not determined because of difficulties associated with TOT analysis for aluminum foils. During both day- and nighttime, the PM exhibits a bimodal size distribution with higher concentration in the fine mode than in the coarse one.

Malic acid was the most dominant GC/MS species. During both day and night, it exhibits a bimodal distribution with a major fine mode, which peaks at 0.4 μm. Predominance of malic acid in the fine mode is consistent with its secondary origin, i.e., photooxidation of unsaturated fatty acids (*13*−*15*), while its presence in the coarse mode can be explained by

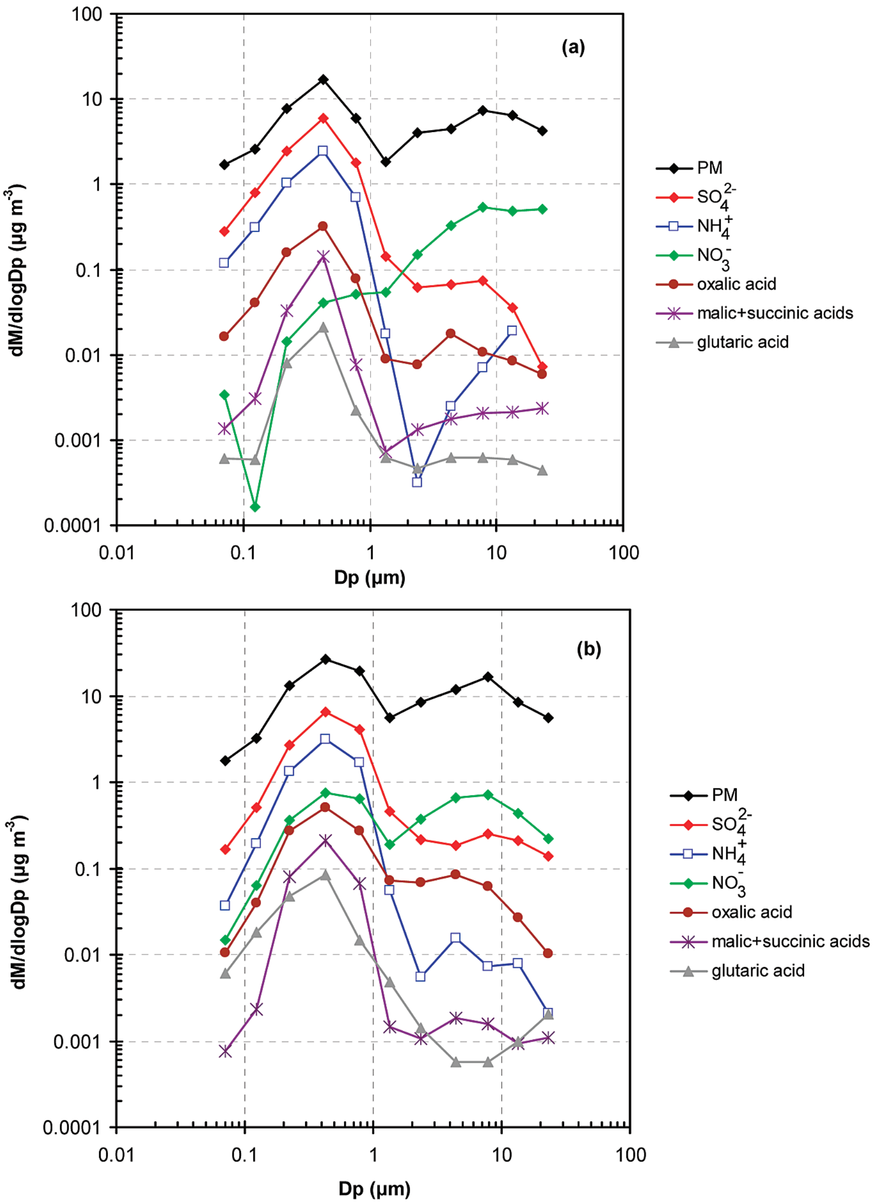

FIGURE 5. Mass size distributions of the PM and species detected by IC (SO_4^{2-}, NH_4^+, NO_3^-, oxalic acid, malic+succinic acids, glutaric acid) for MOUDI samples collected on 11 June 2003 during (a) day and (b) night.

condensation onto the surface of pre-existing particles. Comparison with data from other field sites is provided as Supporting Information (S8).

The oxidation products of α-/β-pinene were only detected in the accumulation mode (0.1−0.8 µm) with a maximum for PA and 3-MBTCA at 0.2 and 0.4 µm, respectively. The mass size distribution data for PA are in agreement with data reported for other field studies (Supporting Information, S8). To our knowledge, the mass size distribution of 3-MBTCA is reported here for the first time.

The mass size distributions of the isoprene SOA tracers were found to be different for the 2-methyltetrols and C_5-alkene triols. While the 2-methyltetrols were detected in both modes, the C_5-alkene triols were only detected in the accumulation mode. No straightforward explanation can be given for this difference in association behavior. Both the 2-methyltetrols and C_5-alkene triols show a maximum concentration at 0.4 µm, in agreement with their secondary origin (*8*−*11*, *22*). It is worth noting that the 2-methyltetrols are also present in the supermicrometer mode at night; again, an obvious reason for this diel difference could not be provided.

Mannitol and arabitol exhibited mass size distributions with a single mode in the supermicrometer size range and peaked at 8 µm during both day- and nighttime. The concentrations of these compounds were very well correlated with each other (R^2 = 0.90 in the $PM_{2.5}$ Hi-Vol samples), consistent with the same primary aerosol source, i.e., fungal spores (*16*, *17*).

The mass size distributions of species detected by IC for 11 June are shown in Figure 5 a (day) and b (night); the figures for the samples of 6 and 27 June are provided as Supporting Information (S8). Malic and succinic acids are presented as the sum of both compounds since they coeluted during IC analysis. The dicarboxylic acids as well as NH_4^+ and SO_4^{2-} were mostly associated with submicrometer particles and essentially showed a unimodal pattern during both day- and nighttime. The presence of dicarboxylic acids in the fine mode is consistent with their aerosol formation mechanism through gas-to-particle partitioning, by surface reactions on gas-particle interfaces, or by liquid-phase reactions in aqueous aerosol particles or in cloud or fog droplets, while their presence in the supermicrometer mode may be explained by condensation onto the surface of pre-existing particles, reaction of gaseous dicarboxylic acids or their precursors with crustal particles or may be due to primary emissions (*33*). No significant differences in the concentrations and size distributions of dicarboxylic acids were found between day and night samples. This is in contrast to findings reported for size-segregated aerosols from Waldstein, Germany (*34*), for which a 10-fold higher concentration of oxalic acid in the size range 0.14−0.42 μm was found at night. Discussion on the size distributions for the inorganic ions is given in the Supporting Information (S8).

Contributions of the Ionic Components and Organic Matter to the PM and of Biogenic SOC to the OC. $PM_{2.5}$ mass data could not be obtained from the Hi-Vol samples. From comparing the $PM_{2.0}$ mass data of the SFU samples with the 24-h $PM_{2.5}$ mass data obtained from $PM_{2.5}$ quartz fiber filter samples that were also taken during the campaign, it followed that the $PM_{2.5}$ mass was, on average, 15% larger than the $PM_{2.0}$ mass. Therefore, the $PM_{2.5}$ data from the Hi-Vol were related to the $PM_{2.0}$ mass data of the SFU samples after multiplying the latter by 1.15. By doing so, it could be calculated that the $PM_{2.5}$ mass contained, on average, 24% sulfate, 10% ammonium, and 2.6% nitrate. These percentages are in good agreement with the 27% sulfate, 13% ammonium, and 2% nitrate in the $PM_{2.0}$ mass, as derived from the SFU samples (*28*). Organic matter, derived by multiplying OC by a conversion factor of 1.8 (*35*), was responsible for 47% of the $PM_{2.5}$ mass.

The SOC contributions from isoprene and α-pinene in $PM_{2.5}$ were estimated using measured tracer concentrations and the laboratory-derived tracer mass fractions (f_{soc}) reported by Kleindienst et al. (*21*). The same set of tracers for isoprene SOA (i.e., 2-methyltetrols and 2-methylglyceric acid) were used as those in the latter study. Using the average tracer concentrations (*1*) and the laboratory-derived f_{soc} value (0.155 ± 0.039), the SOC contribution from isoprene was estimated at 0.28 μgC m^{-3}. Expressed as percentage contribution to the $PM_{2.5}$ OC, isoprene SOC represented, on average, 6.9%; the daytime mean was 9.6% and the nighttime mean 5.2%. The SOC contribution from α-pinene using the laboratory-derived f_{soc} value (0.231 ± 0.111) was, on average, 0.21 μgC m^{-3}. This represented, on average, 4.8% of the $PM_{2.5}$ OC; the daytime mean was 3.8% and the nighttime mean 6.0%. It is noted that the data for α-pinene SOC should be regarded as minimum values because not all molecular tracers necessary to estimate α-pinene SOC were measured. Our percentages can be compared to those obtained with the same approach for Research Triangle Park, southern U.S., during the months May−July of 2003 (*21*), for five midwestern U.S. cities during the months June−August of 2004 (*36*), for Hong Kong during a 2006 summer period (*37*), and for a 2003 summer period at a mixed forest site in Jülich, Germany (*38*). The contributions from isoprene SOC to the $PM_{2.5}$ OC in these four cases were 23, 29, 3.6, and 2.5%, respectively, whereas those from α-pinene SOC were 15, 13, 10, and 2.4%, repectively. The U.S. percentages for isoprene SOC are more than a factor of 3 larger than our percentage for K-puszta. This may in part be due to the larger isoprene emissions at the U.S. sites. However, it should be noted that the quantification of the isoprene and also the α-pinene SOA tracers was done in a different way than done by us and in the Hong Kong study. Because of this, Hu et al. (*37*) estimated the quantification uncertainty in their Hong Kong study to be within a factor of 3. Considering also the various other uncertainties that are associated with the approach, as indicated by Kleindienst et al. (*21*), we estimate that the uncertainty that is associated with our isoprene and α-pinene SOC percentages is at least a factor of 2.

Combined together, isoprene and α-pinene SOC make thus up for at least 11.7% of the $PM_{2.5}$ OC. If we assume that the short-chain diacids do not form part of the isoprene and α-pinene SOA in the laboratory experiments of Kleindienst et al. (*21*), we can add to our biogenic SOC percentage the OC accounted for by the various diacids. Oxalic acid, malic acid, succinic acid, glutaric acid, and 2-hydroxyglutaric acid, contributed, on average, with 1.26, 0.36, 0.16, 0.11, and 0.06%, respectively, or in total with 1.94%. By making use of the levoglucosan and arabitol data from our previous analyses (*1*) and of the conversion factors of these compounds to wood combustion OC and fungal spores OC of Schmidl et al. (*39*) and Bauer et al. (*17*), we can attribute 2.4 and 1.7% of our $PM_{2.5}$ OC to wood burning and fungal spores, respectively. If we add these percentages to those from the diacids and the biogenic SOC, we arrive at a total percentage of about 18% of our $PM_{2.5}$ OC attributed. Clearly, this is a rather low percentage and the question remains what compounds and/or sources are responsible for the remaining OC mass. According to Feczko et al. (*3*), HULIS represent 24% of the OC at the K-puszta site. It was also found that organosulfates and nitrooxy organosulfates were important constituents of the OC at K-puszta during the 2003 campaign (*6*), but their concentrations could not be quantified. By making use of data of total sulfur, measured by particle-induced X-ray emission spectrometry (PIXE), and of inorganic sulfate, as obtained by IC, it is estimated that up to 22% of the OC at K-puszta during the 2003 campaign may be attributable to organosulfates (Maenhaut, unpublished results). Thus, the 18% of $PM_{2.5}$ OC attributed by our tracers, the 24% of HULIS, and the up to 22% of organosulfates, if taken as independent, which may not be justified, would sum up to 64%, which would mean that 36% of the OC remains unaccounted. Considering the substantial uncertainties that are associated with the various attributions, it is hard to tell how significant this 36% of unaccounted OC is. It is clear that further work on the sources and closure of the OC is needed.

Acknowledgments

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Supporting Information Available

Additional details and analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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