

Article

# Contribution from Selected Organic Species to PM<sub>2.5</sub> Aerosol during a Summer Field Campaign at K-Pusztá, Hungary

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**Abstract:** A summer field campaign was conducted at the forested background site of K-pusztá in Hungary. The main aim was to assess the contribution of terpene-derived particulate organic compounds to the PM<sub>2.5</sub> organic carbon (OC) and of the secondary organic carbon (SOC) from  $\alpha$ -pinene to the OC. The study lasted from 24 May to 29 June 2006; the first half the weather was cold, while the second half was warm. Separate daytime and night-time PM<sub>2.5</sub> samples were collected with a high-volume sampler and the samples were analysed by several analytical techniques, including ion chromatography (IC) and liquid chromatography–mass spectrometry (LC/MS). The latter technique was used for measuring the terpene-derived species. Ancillary high time resolution measurements of volatile organic compounds (VOCs) were made with proton-transfer reaction–mass spectrometry. The temporal and diurnal variability of the particulate compounds and VOCs and interrelationships were examined. It was found that the monoterpenes and a number of terpene-derived particulate compounds, such as *cis*-pinic and *cis*-caric acid, exhibited a strong day/night difference during the warm period, with about 10 times higher levels during the night-time. During the warm period, the IC compounds and LC/MS compounds accounted, on average, for 3.1% and 2.0%, respectively, of the OC, whereas the contribution of SOC from  $\alpha$ -pinene to the OC was estimated at a minimum of 7.1%.

**Keywords:** liquid chromatography; mass spectrometry; terpene-derived compounds; organic carbon; secondary organic carbon from  $\alpha$ -pinene; forested site

## 1. Introduction

The fine aerosol at the forested site of K-pusztá, Hungary, is dominated by secondary organic aerosol (SOA) in summer. According to Gelencsér et al. [1], non-fossil SOA, which is presumably mostly from biogenic origins in the summer, accounts for 69% of the PM<sub>2</sub> total carbon in that season.

The K-pusztas site is thus an excellent site to study in summer because of the contribution from the main biogenic volatile organic compounds (VOCs), i.e., isoprene and monoterpenes. One can examine in detail what fraction of the organic carbon (OC) can be explained by the particulate organic species that are produced from those VOCs and assess to what extent the OC can be attributed to monoterpene and isoprene secondary organic carbon (SOC). If it is possible to reliably assess the biogenic contribution to the PM at forested sites on the basis of tracer or marker compounds, it should be possible to apply the same approach at polluted sites and thus assist in developing suitable abatement strategies for such sites. Indeed, by assessing the biogenic fraction of the PM, which is virtually impossible to eliminate, one could estimate what fraction of the PM could be reduced by appropriate strategies. In an earlier study [2], we reported on a number of polar organic compounds, including photooxidation products of isoprene, levoglucosan, malic acid, and sugar alcohols, which were measured by gas chromatography/mass spectrometry (GC/MS) for PM<sub>2.5</sub> aerosol collected during a 2003 summer field campaign at the K-pusztas site. In a follow-up study [3],  $\alpha$ -/ $\beta$ -pinene SOA tracers, comprising *cis*-pinic acid, 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), and the *d*-limonene SOA tracer 3-carboxyheptanedioic acid were also measured by GC/MS. Besides those GC/MS compounds, organic and elemental carbon (OC, EC), water-soluble organic carbon (WSOC), and dicarboxylic acids were also measured for the 2003 campaign [2–4]. In 2006 a new summer field campaign was conducted at the K-pusztas site, in which a total of 68 high-volume PM<sub>2.5</sub> samples (again, typically separate daytime and night-time samples) were collected. OC, EC, WSOC, and dicarboxylic acids were again measured but instead of GC/MS, liquid chromatography/mass spectrometry (LC/MS) using electrospray ionisation in the negative ion mode [(-)ESI] was now used for the analyses. The LC/MS analyses were targeted at more oxidation products of monoterpenes than could be measured by GC/MS. Among these products were important terpene-derived substances that were identified in the past decade, such as terpenylic acid and related compounds [5], and 2-hydroxyterpenylic acid isomers [6], which were expected to provide a substantial contribution to the OC. It was also hoped that LC/MS could elucidate a larger fraction of the OC than the 1.75% that was, on average, accounted for in the 2003 campaign by GC/MS [2,3]. The latter method typically suffers from the presence of a large unresolved complex mixture so that only a small fraction of the OC is explained by the molecular organic species that are measured with it (e.g., [7]). Also, in several other aerosol composition studies for forested sites, only a small fraction of the OC could be accounted for by the compounds measured by GC/MS [8–12]. Besides the aerosol samplings, measurements were made of VOCs by proton-transfer reaction–mass spectrometry (PTR-MS) in the 2006 summer campaign at K-pusztas. The aims of the 2006 study were (1) to examine the temporal and day/night variations of the various species measured, (2) to examine the correlations between the various species and the relationships between the particulate species and the important biogenic volatile organic compounds (BVOCs) isoprene and the monoterpenes, (3) to assess how the contribution from the LC/MS compounds to the OC compares with that from the GC/MS compounds, and (4) to determine the contribution from  $\alpha$ -pinene SOC to the OC and to compare it with the contributions from  $\alpha$ -pinene and isoprene SOC, as found for the 2003 campaign [3], for a mixed deciduous forest site in Jülich, Germany [9], and in a number of other studies.

## 2. Experiments

The study site of K-pusztas in Hungary (46°58' N, 19°33' E, 136 m a.s.l.) is a forested site situated on the Great Hungarian Plain, 80 km southeast of Budapest (1.9 million inhabitants). The largest nearby town (Kecskemét, 110,000 inhabitants) is located 15 km southeast from the site. The sampling site is surrounded by forest (62% coniferous trees) interspersed with clearings. The aerosols collected here may be representative of forested rural background for the Central–Eastern European region. The site was selected as an air monitoring station by EMEP (European Monitoring and Evaluation Programme) and GAW (Global Atmospheric Watch) and is one of 20 European supersites within the

EU project EUSAAR (European Super-sites for Atmospheric Aerosol Research). More information on the site can be found in [2,13–15].

The 2006 sampling campaign at K-puszta lasted from 24 May until 29 June. Aerosol collections were performed with a variety of samplers, including with a dichotomous high-volume sampler [16], which separates the aerosol into two size fractions, coarse ( $>2.5\ \mu\text{m}$ ) and fine ( $\text{PM}_{2.5}$ ). Separate daytime (from 7:15 to 18:00 local time, UT + 2) and night-time (from 18:30 to 6:40 local time) collections were typically made with the several samplers, and a total of 68 parallel collections were made. The filters used in the high-volume sampler were double Pallflex quartz fibre filters (of 102 mm diameter), which had been prebaked for 24 h at 550 °C to remove organic contaminants. Here, only data for the front filters of the  $\text{PM}_{2.5}$  size fraction of the high-volume sampler are presented.

Isoprene ( $\text{C}_5\text{H}_8$ ), other BVOCs including monoterpenes ( $\text{C}_{10}\text{H}_{16}$ ) and the hemi-terpene 2-methyl-3-buten-2-ol (MBO), their volatile organic oxidation products, and other VOCs were determined by PTR-MS [17,18] with a time resolution of 10 min. Critical inorganic trace gases (i.e.,  $\text{O}_3$  and  $\text{NO}_x$ ) and meteorological parameters, including ambient temperature, relative humidity, wind speed, and direction, were measured by instrumentation that was available at the site.

The  $\text{PM}_{2.5}$  high-volume samples from the 2006 campaign were analysed for OC and EC with a thermal-optical method, using a NIOSH-like protocol [19]. WSOC was determined as described in [20]. Methanesulphonate ( $\text{MSA}^-$ ), oxalate, malonate, and succinate were measured by ion chromatography (IC) [4]. Fifteen organic acids (e.g., MBTCA, *cis*-pinonic, *cis*-pinic, terebic, terpenylic), and 5 isomeric  $\alpha$ -pinene-related pinanediol mono-nitrate organosulphates (OSs) with a molecular weight (MW) of 295 were determined by LC/MS, as described in [21].

All concentration data for the actual samples were corrected for field blanks.

### 3. Results and Discussion

#### 3.1. Concentrations, Time Series, and Correlations

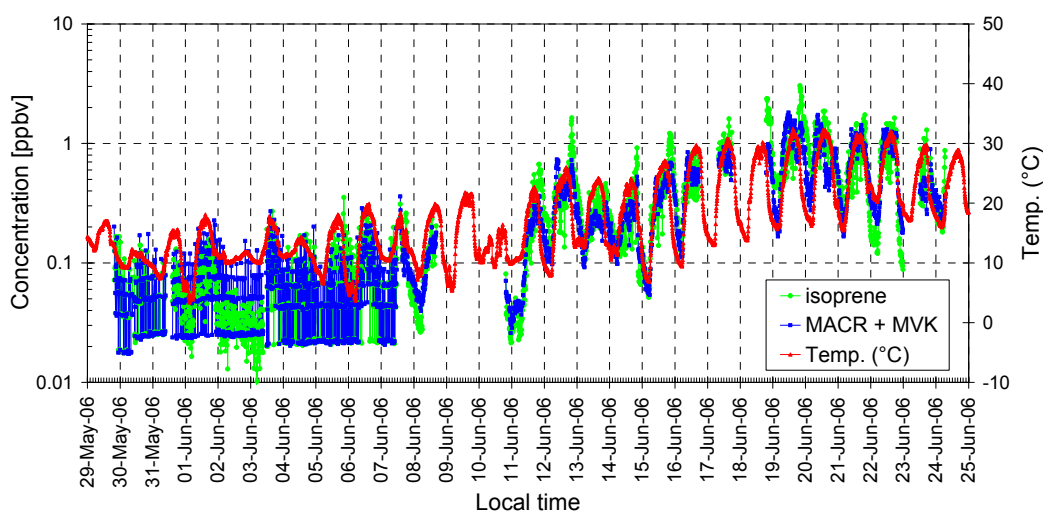
Whereas it was very hot and dry during the entire 2003 campaign, the 2006 campaign was characterised by two distinct periods, with the first half of the campaign (24 May–11 June) unusually cold and the second half (12–29 June) warm. The average temperatures and associated standard deviations during the cold period were  $16.9 \pm 2.6\ ^\circ\text{C}$  and  $11.3 \pm 2.4\ ^\circ\text{C}$  during the daytime and night-time samplings, respectively, and during the warm period  $27.4 \pm 3.1\ ^\circ\text{C}$  and  $18.5 \pm 3.5\ ^\circ\text{C}$ , respectively. The air masses often originated over the North Sea and/or the Atlantic Ocean during the cold period, whereas during the warm period they had a continental character and were more stagnant [22].

Table 1 shows the medians and interquartile concentration ranges (in ppbv) for selected VOCs for the daytime and night-time periods of the cold and warm periods. The concentration of the anthropogenic VOC benzene showed little variability between daytime and night-time and between the cold and warm periods. In contrast, for the BVOCs and their oxidation products substantial differences are observed. The daytime and night-time isoprene medians for the warm period are 7.8 and 8.1 times larger, respectively, than the corresponding medians for the cold period. For the monoterpenes, the (warm median)/(cold median) ratios for the daytime and night-time are 3.4 and 22, respectively. The higher levels for the BVOCs during the warm period are to be expected, given that the emission of VOCs by plants increases with light and temperature [23]. When looking at the data with high time resolution (10 min) (see Figure 1), it appears that the individual concentrations of isoprene and its first-order gas-phase oxidation products (MACR + MVK) followed the temperature quite closely and the concentrations of the three compounds are highly correlated with each other. Considering that the emission of isoprene increases exponentially with temperature and that this compound has an atmospheric lifetime on the order of 1–2 h [24], this behaviour is not surprising. For the monoterpenes, the temporal profile was substantially different from that for isoprene and MACR + MVK. They typically showed the highest levels in the late evening (around 21:00–22:00) and

lowest levels, which were nearly two orders of magnitude lower, at noon. The atmospheric lifetime of monoterpenes is on the order of minutes to hours due to their fast reaction with hydroxyl radicals (OH), nitrate radicals (NO<sub>3</sub>), and ozone (O<sub>3</sub>) [23,25,26], so the large temporal variation is not unexpected. The night/day difference for the monoterpenes was particularly pronounced during the warm period. From the median data in Table 1, night/day ratios of 1.06 and 7.0 are calculated for the monoterpenes in the cold and warm periods, respectively.

**Table 1.** Medians and interquartile atmospheric concentration ranges (in ppbv) for selected VOCs for the daytime and night-time of the cold and warm periods. MACR = methacrolein, MVK = methyl vinyl ketone, and MBO = 2-methyl-3-buten-2-ol. The data for the cold period pertain to the period 29 May–11 June 2006 (there are no data for the earlier days), those for the warm period to the period 12–25 June 2006. The daytime and night-time hours of the high-volume samplings were adopted.

Species	Cold Period—Day	Cold Period—Night	Warm Period—Day	Warm Period—Night
	Median (Interq. Range)	Median (Interq. Range)	Median (Interq. Range)	Median (Interq. Range)
isoprene ( <i>m/z</i> 69)	0.074 (0.042–0.125)	0.041 (0.025–0.065)	0.58 (0.34–0.90)	0.33 (0.179–0.69)
MACR and MVK ( <i>m/z</i> 71)	0.072 (0.042–0.123)	0.047 (0.025–0.075)	0.60 (0.36–0.91)	0.29 (0.168–0.50)
monoterpenes ( <i>m/z</i> 137)	0.028 (0.0190–0.041)	0.030 (0.0192–0.047)	0.095 (0.062–0.140)	0.66 (0.29–1.35)
nopinone ( <i>m/z</i> 139)	0.0057 (0.0040–0.0085)	0.0054 (0.0038–0.0075)	0.036 (0.022–0.052)	0.044 (0.033–0.077)
pinonaldehyde ( <i>m/z</i> 151)	0.0039 (0.0025–0.0053)	0.0049 (0.0034–0.0072)	0.0143 (0.0077–0.022)	0.035 (0.022–0.065)
MBO ( <i>m/z</i> 87)	0.062 (0.049–0.078)	0.056 (0.044–0.072)	0.172 (0.131–0.21)	0.150 (0.110–0.20)
benzene ( <i>m/z</i> 79)	0.046 (0.034–0.059)	0.055 (0.042–0.072)	0.056 (0.043–0.073)	0.075 (0.058–0.097)



**Figure 1.** Time series of the atmospheric concentrations of isoprene (*m/z* 69), its oxidation products (*m/z* 71) (i.e., methacrolein (MACR) and methyl vinyl ketone (MVK)), and of the air temperature at K-pusztá for the period from 29 May to 25 June 2006. Note that a log scale is used for the VOCs and a linear scale for the temperature. The vertical dashed lines are at 00:00 h.

During the warm period, the median night-time concentration was twice as large for the monoterpenes as for isoprene, whereas the median daytime concentration is six times lower (Table 1). The overall median (daytime and night-time combined) for the warm period, with the interquartile range between parentheses, was 0.45 (0.24–0.82) ppb for isoprene and 0.175 (0.089–0.63) for monoterpenes, whereas the average concentrations were 0.58 and 0.56 ppb, respectively. There was thus a clear tendency for lower concentrations for the monoterpenes than for isoprene during the warm period (incidentally, this was also the case during the cold period). It is hard to estimate the relative production of SOA from those two species types, as the SOA formation depends on many complicated factors, including temperature, relative humidity, NO<sub>x</sub> and hydrocarbon mixing ratios, and UV intensity [27]. In their 2015 paper, Jokinen et al. [28] adopted, when assuming no SOA formation from NO<sub>x</sub> oxidation, total SOA yields of 15% and 5% for monoterpenes and isoprene,

respectively. By combining these yields with the relative median concentrations of the monoterpenes and isoprene in the warm period, it is estimated that the SOA masses from both species types would be rather similar.

Tables 2 and 3 present median concentrations (and interquartile ranges) for the particulate compounds in the daytime and night-time PM<sub>2.5</sub> samples of the cold and warm periods. The 15 organic acids, measured by LC/MS, are all believed to predominantly originate from the oxidation of  $\alpha$ -pinene and other monoterpenes [29], whereas the five isomeric  $\alpha$ -pinene-related pinanediol mono-nitrate OSs can be formed by photooxidation in the presence of NO<sub>x</sub> as well as by NO<sub>3</sub> radical-initiated oxidation, which is a specific night-time oxidation process [30]. For EC, which is a primary aerosol component that originates from the incomplete combustion of fossil fuels and biomass [31], there is little difference between daytime and night-time and between the cold and warm periods. The same is true for MSA<sup>-</sup>, which is a photooxidation product of dimethylsulfide, which is emitted by marine phytoplankton [32] and thus originates from long-range transport to the K-puszta site. The concentrations of virtually all other compounds are larger in the warm period than in the cold one; for OC, there is a difference of a factor of 2; the only exception is formed by the OSs. For OC, EC, WSOC, the dicarboxylic acids, MBTCA, and *cis*-pinic acid, the data from the 2006 campaign can be compared with those from the 2003 campaign [3,4]. The warm period medians and interquartile ranges for OC, EC, WSOC, and oxalate for the warm period of the 2006 campaign are quite similar to those of the 2003 campaign, which was very hot and dry. For succinate, concentrations about three times lower were found in 2003 (see Table 2 of [4]) and malonate was not determined in the 2003 campaign. For MBTCA, the levels of the 2003 campaign compare better with those of the cold period of the 2006 campaign than with those of the warm period, whereas the 2003 levels of *cis*-pinic acid are only slightly lower than those of the warm period of the 2006 campaign. For most of the compounds of Tables 2 and 3, only a moderate difference was noted between the daytime and night-time levels, but, as will be indicated below, there were some notable exceptions.

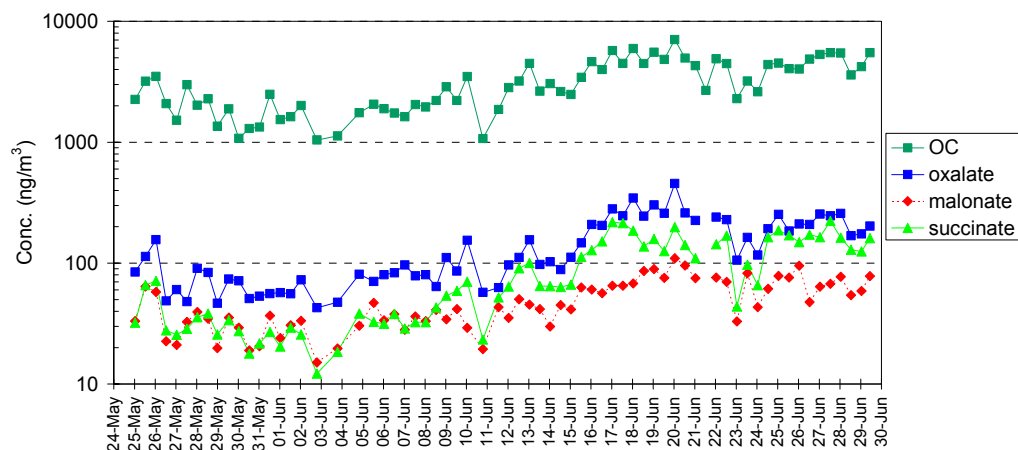
**Table 2.** Median concentrations (and interquartile ranges), in ng/m<sup>3</sup>, for the daytime and night-time PM<sub>2.5</sub> samples of the cold period.

Compound (MW)	Day (N = 14) Median (Interq. Range)	Night (N = 15) Median (Interq. Range)
EC	144 (129–180)	165 (127–230)
OC	2100 (1870–2300)	1960 (1530–2500)
WSOC	960 (860–1150)	1050 (740–1330)
MSA <sup>-</sup>	37 (15.1–53)	23 (15.2–36)
oxalate	67 (56–82)	80 (66–97)
malonate	36 (33–42)	33 (26–34)
succinate	33 (29–42)	32 (26–45)
MBTCA (204)	7.3 (5.8–13.9)	5.8 (4.1–12.4)
<i>cis</i> -pinonic acid (184)	9.2 (7.4–12.4)	4.1 (2.5–5.4)
<i>cis</i> -pinic acid (186)	2.8 (2.1–3.7)	1.51 (1.02–7.4)
terebic acid (158)	3.6 (2.7–4.3)	1.96 (1.26–4.0)
terpenylic acid (172)	4.9 (3.4–6.2)	2.7 (2.0–6.5)
diaterpenylic acid acetate (232)	0.82 (0.72–1.51)	0.74 (0.55–1.34)
<i>cis</i> -caronic acid (184)	1.11 (0.72–2.3)	0.27 (0.21–0.52)
<i>cis</i> -caric acid (186)	0.73 (0.63–0.89)	0.72 (0.63–3.1)
ketolimonic acid (186)	0.92 (0.71–1.19)	0.54 (0.41–0.69)
limonic acid (186)	1.31 (1.02–1.62)	1.71 (1.36–2.5)
homoterpenylic acid (186)	1.75 (1.23–2.1)	1.22 (0.82–2.1)
4-hydroxyterpenylic acid (188)	1.15 (0.72–2.1)	1.19 (0.88–2.5)
(2 <i>R</i> ,3 <i>R</i> )-2-hydroxyterpenylic (188)	4.0 (2.5–7.7)	3.2 (3.0–8.7)
(2 <i>S</i> ,3 <i>R</i> )-2-hydroxyterpenylic (188)	1.97 (1.53–4.0)	2.3 (1.48–4.7)
unknown (188)	2.0 (1.39–3.3)	1.23 (1.15–2.9)
pinanediol mono-nitrate OSs [ $\Sigma$ 5 isomers] (295)	3.6 (2.3–4.4)	13.7 (9.3–25)

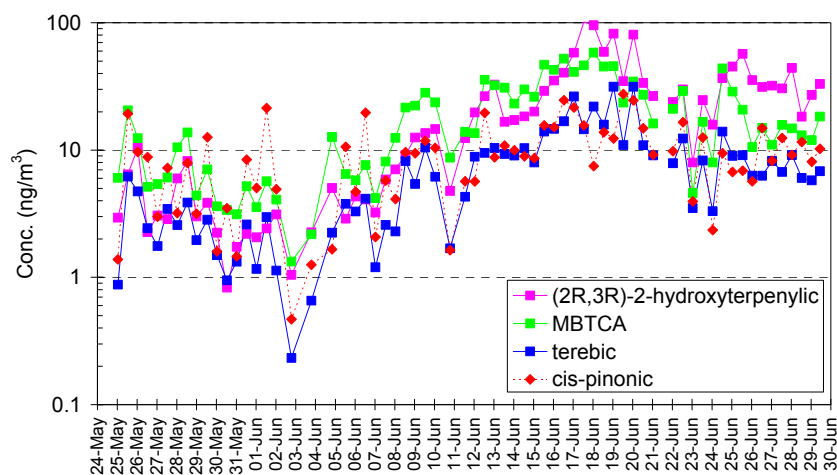
**Table 3.** Median concentrations (and interquartile ranges), in ng/m<sup>3</sup>, for the daytime and night-time PM<sub>2.5</sub> samples of the warm period.

Compound (MW)	Day (N = 17) Median (Interq. Range)	Night (N = 17) Median (Interq. Range)
EC	162 (131–250)	179 (122–230)
OC	4200 (3300–4800)	4500 (4000–5500)
WSOC	2900 (2100–3200)	3000 (2400–3100)
MSA <sup>−</sup>	32 (25–35)	24 (19.4–37)
oxalate	200 (163–240)	230 (156–260)
malonate	65 (54–76)	65 (45–77)
succinate	141 (113–169)	143 (100–164)
MBTCA (204)	29 (18.3–44)	23 (12.0–34)
<i>cis</i> -pinonic acid (184)	13.8 (10.8–15.6)	8.8 (7.5–10.0)
<i>cis</i> -pinic acid (186)	4.5 (3.9–7.4)	14.6 (8.6–33)
terebic acid (158)	10.3 (8.3–13.9)	9.0 (7.9–14.7)
terpenylic acid (172)	12.9 (9.0–14.3)	11.9 (8.4–24)
diaterpenylic acid acetate (232)	4.4 (3.9–6.5)	3.8 (2.9–6.0)
<i>cis</i> -caronic acid (184)	1.70 (1.42–2.5)	1.24 (1.06–1.87)
<i>cis</i> -caric acid (186)	1.21 (1.16–1.46)	9.0 (4.2–15.7)
ketolimonic acid (186)	1.88 (1.58–2.1)	1.26 (1.09–1.84)
limonic acid (186)	1.87 (1.70–2.5)	3.1 (2.1–3.9)
homoterpenylic acid (186)	3.1 (3.0–3.7)	4.8 (3.5–9.4)
4-hydroxyterpenylic acid (188)	5.4 (3.8–5.9)	6.1 (4.6–13.5)
(2 <i>R</i> ,3 <i>R</i> )-2-hydroxyterpenylic (188)	31 (26–37)	33 (24–34)
(2 <i>S</i> ,3 <i>R</i> )-2-hydroxyterpenylic (188)	7.1 (4.8–12.1)	11.5 (7.5–23)
unknown (188)	8.0 (6.5–9.2)	5.5 (4.7–8.0)
pinanediol mono-nitrate OSs [ $\Sigma$ 5 isomers] (295)	1.23 (0.57–1.93)	2.7 (1.83–3.3)

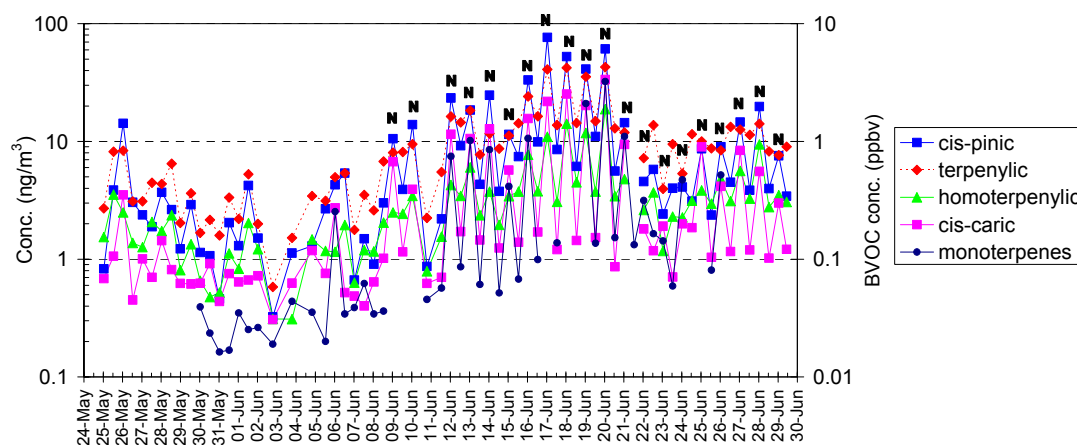
The time series for several compounds are shown in Figures 2–4. Figure 4 also shows the time series for the monoterpenes, as obtained by PTR-MS, whereby the high time resolution data were averaged over the sampling times of the high-volume samples. For a number of LC/MS compounds strong day/night differences were noted, especially during the warm period, with concentrations that were up to a factor of 10 higher during the night-time than during the daytime. This was the case for *cis*-pinic, terpenylic, homoterpenylic, and especially *cis*-caric acid (see Figure 4); this is partly explained by transfer from the vapor to the particulate phase for these compounds during the cool night. Incidentally, the concentration of monoterpenes also shows a similar diurnal pattern, with about 10 times higher levels during the night during the warm period. For some of the SOA compounds in Figure 4 (e.g., *cis*-pinic acid, which is a first-generation oxidation product of  $\alpha$ -pinene [33]), fast oxidation from the monoterpenes may also have contributed to the observed day/night difference. Incidentally, *cis*-pinic acid showed a similar day/night difference, with enhanced night-time levels during the 2003 campaign at K-pusztá [3]. A day/night difference with enhanced night-time levels during both the cold and warm periods of the 2006 campaign was also seen for the OSs (see data in Tables 2 and 3, time series not shown); enhanced night-time levels for these OSs were also observed at a forested site in Brasschaat, Belgium [21].



**Figure 2.** Time series of organic carbon (OC) and three carboxylic acids for the 2006 summer campaign at K-puszta, Hungary.



**Figure 3.** Time series of four monoterpene marker compounds for the 2006 summer campaign at K-puszta, Hungary.



**Figure 4.** Time series of four other monoterpene marker compounds (with concentration scale on the left ordinate axis) and of the monoterpenes (concentration scale in the right ordinate axis) for the 2006 summer campaign at K-puszta, Hungary. The night data from 8 June onward (which includes the entire warm period) are marked with “N” above the *cis-pinonic* data points.

As a consequence of the pronounced day/night differences for *cis*-pinic, terpenylic, homoterpenylic and *cis*-caric acid, these compounds were highly correlated with each other (all  $R > 0.8$ ). Many more good ( $R > 0.7$ ) and high ( $R > 0.8$ ) correlations were observed. This was, for example, the case among the three IC diacids and between OC and WSOC, the three IC diacids, terebic, terpenylic, ketolimonic, homoterpenylic, MBTCA, diaterpenylic acid, and (2R,3R)-2-hydroxyterpenylic, suggesting that a substantial fraction of the three IC diacids was like the terpene-derived compounds also from biogenic origin. A possible biogenic origin of the diacids is in line with the year-round study of Legrand et al. [34] on diacids in the European atmosphere along a west–east transect, wherein the easternmost site was the K-pusztá site. These authors stated that in summer biogenic emissions from vegetation (unsaturated fatty acids, isoprene, oxygenated VOCs, and eventually monoterpenes) likely represent the major precursors of the diacids. Our observed correlations are also in line with the results of Mochizuki et al. [35] for their 2012 summer study in a larch forest in Japan. These authors observed similar variations for oxalic acid and biogenic secondary organic aerosols derived from isoprene and  $\alpha$ -pinene and concluded that the forest ecosystem is an important source of oxalic acid and other dicarboxylic acids in the atmosphere. In their review paper Chebbi and Carlier [36] indicated that carboxylic acids, including diacids, have several sources including biogenic and anthropogenic ones. To assess what fraction of the diacids originates from biogenic sources at forested sites, further research is warranted. Isoprene and its first-order gas-phase oxidation products (MACR + MVK) were well ( $R > 0.7$ ) or highly ( $R > 0.8$ ) correlated with the temperature, OC, WSOC, the three IC diacids, and diaterpenylic acid, whereas isoprene was also highly correlated with terebic, terpenylic, and (2R,3R)-2-hydroxyterpenylic acid. The monoterpenes were well ( $R > 0.7$ ) or highly ( $R > 0.8$ ) correlated with oxalate, *cis*-pinic, terebic, terpenylic, *cis*-caric, homoterpenylic, 4-hydroxyterpenylic, and (2R,3R)-2-hydroxyterpenylic acid. The latter correlations are consistent with a monoterpene origin of at least several of the LC/MS compounds, as was indicated for some of them in [5,6]; the good correlation of the monoterpenes with oxalate suggests that part of this latter compound also originated from the oxidation of monoterpenes.

### 3.2. Contribution of the Measured Organic Compounds and $\alpha$ -Pinene Secondary Organic Carbon to the OC

The four IC organic compounds measured (i.e.,  $\text{MSA}^-$ , oxalate, malonate, and succinate) together accounted, on average, for 2.5% of the OC during both daytime and night-time of the cold period of the 2006 campaign; during the warm period their contribution was somewhat larger (i.e., 3.1%). For the 20 LC/MS compounds, the contribution to the OC was 1.5% during both daytime and night-time of the cold period and 2.0% during the warm period. Of the LC/MS compounds, MBTCA and *cis*-pinonic, *cis*-pinic, and terpenylic acid were the major contributors to the OC. During the 2003 campaign, the three IC compounds measured (i.e., oxalate, succinate, and glutarate) together accounted, on average, for 1.8% of the OC [37], which is thus lower than the contributions in the 2006 campaign. However, for oxalate, the percentage contribution in the 2003 campaign (i.e., 1.3%) was very similar to the percentages of 1.0% and 1.3% in the cold and warm periods, respectively, of the 2006 campaign. The polar organic compounds measured by GC/MS in [2] and the  $\alpha$ -/ $\beta$ -pinene and *d*-limonene GC/MS SOA compounds of [3] accounted for 1.2% and 0.55%, respectively, of the OC during the 2003 campaign. Their collective contribution of 1.75% is very similar to the 2.0% contribution from the LC/MS compounds in the warm period of the 2006 campaign. If we assume that the contributions of the GC/MS compounds, which were found for the 2003 campaign [2,3], would be a good approximation of the same compounds during the warm period of the 2006 campaign, then the IC compounds, LC/MS compounds, and GC/MS compounds, which were not measured by LC/MS, represented together only 6.5% during that warm period. It is evident that a very large fraction of the molecular composition of the OC at K-pusztá remains unexplained by the IC, LC/MS, and GC/MS analyses that we used. Similar low explained fractions were found in several other studies at forested sites. For example, the same IC and LC/MS methods as in the current study were used for high-volume  $\text{PM}_{2.5}$  samples from a 2007 summer campaign in the forested site in Brasschaat [21].



The organic tracers explained, on average, 5.3% of the OC, of which 4.1% was due to the IC compounds and 1.2% to the LC/MS compounds. Oliveira et al. [8] measured 200 compounds by GC/MS in their weekly PM<sub>2</sub> samples from the K-pusztá site for a one-year period (July 2002 to September 2003) and only 4% of the OC was explained. In the study of Kourtchev et al. [9] at a forested site in Jülich, only around 2.5% of the OC was explained by the GC/MS compounds measured for PM<sub>2.5</sub> samples from a warm and dry period in summer 2003. Similar percentages, i.e., of around 1.5% of the OC, were explained by the GC/MS analysis of summer 2004 and 2005 PM<sub>1</sub> samples collected at a forested site in Hyytiälä, Finland [10,11]. Also, for summer samples taken in a coniferous forest in eastern Germany and analysed by GC/MS [12], it was found that the detected terpene and isoprene oxidation products accounted for only a small part of the measured organic carbon; oxalic acid accounted for the major fraction of the speciated organic carbon, but even this compound made up only around 1% of the OC. In contrast, much higher percentages were found with GC/MS by Cahill et al. [38] in their 2003 summer study in the Blodgett Forest, California; about 23% of the organic matter was identified and at least 8.6% was oxidised BVOCs.

The SOC contribution from  $\alpha$ -pinene to the OC was estimated using some of our measured tracer concentrations and laboratory (i.e., smog chamber)-derived tracer mass fractions ( $f_{\text{SOC}}$ ) reported by Kleindienst et al. [39]. Nine  $\alpha$ -pinene SOA tracers were included by these authors in the determination of the  $f_{\text{SOC}}$ , which represents the ratio of the sum of the tracers to the OC for the SOA from the chamber experiments; the  $f_{\text{SOC}}$  value and associated uncertainty reported were  $0.231 \pm 0.111$  for  $\alpha$ -pinene. Our set of tracers for  $\alpha$ -pinene SOA was, however, limited to four of the nine tracers of [39], i.e., to *cis*-pinonic acid, *cis*-pinic acid, MBTCA (the latter compound was in those days incorrectly termed 2-hydroxy-4-isopropyladipic acid, see [40]), and terpenylic acid (it was assumed that the MW 172 compound of [39] was actually terpenylic acid; see the arguments for this in [5]). As a consequence, our estimate of SOC from the  $\alpha$ -pinene monoterpene (SOC<sub>M</sub>) has to be considered as a lower limit for the true contribution from  $\alpha$ -pinene. Furthermore, it was assumed that the short-chain diacids do not form part of the  $\alpha$ -pinene SOA in the laboratory experiments of Kleindienst et al. [39]. It was found that SOC<sub>M</sub> made up 5.3% of the OC during the cold period and 7.1% during the warm period. For the 2003 campaign at K-pusztá, on average, 4.8% of the PM<sub>2.5</sub> OC was attributed to  $\alpha$ -pinene SOC [3], but it should be noted that only two of the nine tracers of [39], i.e., *cis*-pinic acid and 3-hydroxyglutaric acid, were included here, so that one may not conclude that the contribution was lower than in the 2006 campaign.

For the 2003 campaign the contribution from isoprene SOC to the OC (SOC<sub>I</sub>) was also estimated [3]. Use was thereby made of the laboratory-derived  $f_{\text{SOC}}$  fraction of  $0.155 \pm 0.039$  reported in [39] and the same three isoprene SOA tracers used in [39] (i.e., the two 2-methyltetrols and 2-methylglyceric acid). SOC<sub>I</sub> represented, on average, 6.9% of the OC. Assuming that this percentage can be used as a proxy for the contribution from isoprene SOC to the OC of the warm period of the 2006 campaign, SOC from both isoprene and  $\alpha$ -pinene together would make up at least 14% of the OC during that warm period. The 2003 SOC<sub>I</sub> percentage of 6.9% is very similar to the SOC<sub>M</sub> percentage of 7.1% obtained for the warm period of the 2006 campaign, so it is expected that the BVOCs isoprene and  $\alpha$ -pinene provided quite comparable contributions to the OC during that warm period, which is in accordance with the rough conclusion made in Section 3.1 that the SOA masses formed from isoprene and monoterpenes are expected to be rather similar in the warm period. It is hereby noted that  $\alpha$ -pinene is by far the major compound of the monoterpenes emitted [41].

For comparison, the approach of Kleindienst et al. [39] was also employed for PM<sub>2.5</sub> samples that had been collected in summer 2003 in the forested site in Jülich [9]. SOC<sub>M</sub> represented, on average, 2.4% of the PM<sub>2.5</sub> OC, whereas the SOC<sub>I</sub> contribution was, on average, 2.5%. In our 2009 paper on K-pusztá [3], we indicated that the approach of Kleindienst et al. [39] was also used in a few other studies (i.e., in [42,43]). We refer to [3] for a presentation and brief discussion of the results from those earlier studies. Since 2010, several more applications of the approach of Kleindienst et al. [39] have been published. El Haddad et al. [44] applied it to data from a 2008 summer campaign in Marseille

and found that  $\text{SOC}_M$  accounted, on average, for 3.4% of the OC, while  $\text{SOC}_I$  represented 0.58%. They concluded that these estimates are much too low and indicated that the underprediction could be associated with (1) uncertainties underlying the marker-based approach, (2) the presence of other SOC precursors, and (3) further processing of fresh SOC, as indicated by organosulphates ( $\text{RSO}_4\text{H}$ ) and HUmic Like Substances (HULIS) measurements. The team of Kleindienst applied its approach to  $\text{PM}_{2.5}$  samples taken in spring–summer during the years 2003–2010 at 15 field sites across the USA [45]. From the concentration data presented in Tables 6 and 7 of [45], a mean (and interquartile range) of 12% (5–15%) can be calculated for the  $\text{SOC}_M$  contribution to the OC; the corresponding data for  $\text{SOC}_I$  are 33% (20–55%). As was already the case for the earlier publications from the Kleindienst team [39,42], these percentages are substantially larger than those obtained by us for the K-pusztasite, though the difference for  $\text{SOC}_M$  remained limited to a factor of 2. Also, for some recent studies in China, use was made of the Kleindienst et al. [39] approach. For their one-year study at 12 sites across six regions of China, Ding et al. [46] found average annual concentrations of 0.17 to 0.83  $\mu\text{gC}/\text{m}^3$  for  $\text{SOC}_M$  and 0.03 to 0.63  $\mu\text{gC}/\text{m}^3$  for  $\text{SOC}_I$ . Considering that the annual average OC at the 12 sites ranged from 22 to 54  $\mu\text{gC}/\text{m}^3$ , this means that the percentages of  $\text{SOC}_M$  and  $\text{SOC}_I$  in OC were only around 1% each. Ding et al. [46] also noted that biogenic SOC was elevated from April to September and was lowest in January and February, and that its composition changed dramatically from a monoterpene majority in fall–spring to an isoprene majority in summer. The authors further stated that the relative standard deviations were 53% for  $\text{SOC}_M$  and 47% for  $\text{SOC}_I$  and that because of various other uncertainties involved in the approach, their results should have underestimated the total amount of biogenic SOC in the air in China. For a 2015 summer study on  $\text{PM}_{2.5}$  at an agricultural site in the North China Plain, Li et al. [47] found that  $\text{SOC}_M$  and  $\text{SOC}_I$  contributed to the OC with 1.4% and 5.8%, respectively. Also, these percentages, especially for  $\text{SOC}_M$ , are on the low side.

Considering that various uncertainties are associated with the approach of Kleindienst et al. [39], as also indicated by these authors and in other publications since then [3,43,44,46], we estimate that the uncertainty that is associated with the  $\text{SOC}_M$  and  $\text{SOC}_I$  contributions to the OC is at least a factor of 2.

#### 4. Conclusions

The BVOCs, OC, the dicarboxylic acids, and the LC/MS compounds (with the exception of the OSs) all showed higher levels during the warm period than during the cold period of the campaign. The concentrations of isoprene and its first-order gas-phase oxidation products (MACR + MVK) followed the air temperature quite closely. For the monoterpenes, a substantially different temporal profile was noted; they showed the highest levels typically in the late evening (around 21:00–22:00) and the lowest levels, which were nearly two orders of magnitude lower, at noon. Furthermore, good and high correlations between several compounds and the monoterpenes were observed and similar diurnal patterns for the monoterpenes and a number of LC/MS compounds during the warm period, with significantly elevated levels during the night-time, were noted. This all points to a clear link between the monoterpenes and those compounds and indicates that a number of them are formed by fast oxidation from  $\alpha$ -pinene. There was also some correlation between the major dicarboxylate (i.e., oxalate) and the monoterpenes, suggesting that part of the oxalate at the K-pusztasite is derived from the oxidation of monoterpenes. However, further research is needed to assess what fraction of the oxalate and the other diacids originates from the BVOCs at forested sites.

As indicated above, a very large fraction of the OC (actually more than 90%) of the  $\text{PM}_{2.5}$  OC remains unexplained by the IC, GC/MS, and LC/MS analyses that we used. This calls for improved analysis methods for the molecular characterisation of the organic aerosol. As indicated in recent review papers [29,48], important challenges remain in the analysis of aerosols for organic compounds. In recent years, extremely low volatile compounds (ELVOCs) [49], which are currently referred to as highly oxygenated molecules (HOMs) [50], have been observed in biogenic organic aerosols from both the field and chamber experiments, and one may wonder to what extent they contribute to the  $\text{PM}_{2.5}$  OC. HOMs were, in any case, not included in our chemical analyses.

Using the approach of Kleindienst et al. [39], the  $\text{SOC}_M$  contribution to the  $\text{PM}_{2.5}$  OC was estimated to be at least 7.1% during the warm period, and for the warm 2003 campaign at K-pusztá, the contribution from  $\text{SOC}_I$  to the OC was, on average, 6.9%. Although the uncertainty that is associated with our  $\text{SOC}_M$  and  $\text{SOC}_I$  estimates is at least a factor of 2 and our  $\text{SOC}_M$  estimates have to be considered as lower limits, as not all nine  $\alpha$ -pinene SOA tracers of [39] were measured by us, our percentages for K-pusztá are lower than one would expect for this forested site in summer. Kleindienst et al. [39] did their quantification of the tracers in a different manner than was done by us. It might be that there is some effect of this different quantification. One may also wonder to what extent the  $f_{\text{SOC}}$  values of Kleindienst et al. [39] are applicable to ambient organic aerosol in various types of environments and with different levels of  $\text{NO}_x$ , oxidants, relative humidity, and other ambient parameters. More laboratory studies of the  $f_{\text{SOC}}$  values under various conditions (and also for additional BVOCs) are therefore recommended. It should also be indicated that Kleindienst et al. [39] only performed GC/MS analyses for measuring the tracers. By performing analyses by LC/MS of both laboratory-generated SOA and field samples, we discovered various new tracers for isoprene and terpene SOA [13]. It is therefore advisable that LC/MS and possibly other analyses, besides GC/MS, are also performed in future studies on  $f_{\text{SOC}}$ .

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