**Atmospheric
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Chemical characterisation of atmospheric aerosols during a 2007 summer field campaign at Brasschaat, Belgium: sources and source processes, time series, diel variations, and temperature dependencies

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Chemical characterisation of atmospheric aerosols

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Abstract

Measurements of organic marker compounds and inorganic species were performed on $PM_{2.5}$ aerosols from a Belgian forest site that is severely impacted by urban pollution ("De Inslag", Brasschaat, Belgium) during a 2007 summer period within the framework of the "Formation mechanisms, marker compounds, and source apportionment for biogenic atmospheric aerosols (BIOSOL)" project. The objectives of this study were to determine sources, source processes, time series, and diel variations of the organic species, and to explore the relationships between their concentrations and those of trace gases (O_3, NO_2, SO_2, and CO_2) or meteorological parameters (temperature, relative humidity, wind speed, and rain fall). The measured organic species included (i) low-molecular weight (MW) dicarboxylic acids (LMW DCAs), (ii) methanesulfonate (MSA), and (iii) terpenoic acids originating from the oxidation of α-pinene, β-pinene, d-limonene and Δ^3-carene, and (iv) organosulfates related to secondary organic aerosol (SOA) from the oxidation of isoprene and α-pinene. The measurements of MSA, the LMW DCAs and selected inorganic species were done with ion chromatography (IC), while those of the terpenoic acids and organosulfates were performed using liquid chromatography with negative ion electrospray ionisation mass spectrometry [LC/($-$)ESI-MS]. The organic tracers explained, on average, 5.3 % of the organic carbon (OC), of which 0.7 % was due to MSA, 3.4 % to LMW DCAs, and 1.2 % to organosulfates and terpenoic acids. The highest atmospheric concentrations of most species were observed during the first five days of the campaign, which were characterised by maximum day-time temperatures >22 °C. Most of the terpenoic acids and the organosulfates peaked during day-time, consistent with their photochemical origin, except the MW 295 α-pinene-related nitrooxy organosulfates and the terpenoic acids, *cis*-pinic, caric, and limonic acid. High concentrations of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) and low concentrations of *cis*-pinonic acid were noted during the first five days of the campaign, indicative of an aged biogenic aerosol. Several correlations between organic species were very high (r>0.85), high (0.7<r<0.85), or substantial

(0.5 < r < 0.7). Substantial correlations with temperature were found for OC, water-soluble OC, MBTCA, and several other organic species; the exceptions were *cis*-pinonic, *cis*-pinic, caronic, limonic, and caric acid, and the MW 295 nitrooxy organosulfates. The temperature dependency of species that were highly correlated with temperature (r > 0.7) was examined in more detail, and it was found that MBTCA and terebic acid showed an Arrhenius-type relationship.

1 Introduction

A comprehensive chemical characterisation was carried out of $PM_{2.5}$ aerosols collected at a Belgian forest site ("De Inslag", Brasschaat, Belgium) that is severely impacted by urban pollution within the frame of the "Formation mechanisms, marker compounds, and source apportionment for biogenic atmospheric aerosols (BIOSOL)" project. The objectives of this study were to determine sources, source processes, time series, and diel variations of the organic species, and to explore the relationships between their concentrations and those of trace gases (O_3, NO_2, SO_2, and CO_2) or meteorological parameters (temperature, relative humidity, wind speed, and rain fall). Comprehensive organic chemical characterisation of fine ambient aerosols has mainly been performed for forest sites, which are little perturbed by urban emissions, such as Hyytiälä, Finland (e.g., Kourtchev et al., 2005, 2008a; Parshintsev et al., 2010) and K-puszta, Hungary (e.g., Ion et al., 2005; Kourtchev et al., 2009), but studies for vegetated areas in Europe that are affected by urban pollution are rather limited (e.g., Kourtchev et al., 2008b, 2011; Zhang et al., 2010). The measured organic species included (i) methane-sulfonate (MSA), (ii) low-molecular weight (MW) dicarboxylic acids (LMW DCAs), (iii) terpenoic acids originating from the oxidation of α-pinene, β-pinene, d-limonene and Δ^3-carene, and (iv) organosulfates related to secondary organic aerosol (SOA) from the oxidation of isoprene, α-pinene, and unsaturated fatty acids. The measurements of MSA, LMW DCAs, and selected inorganic species were done with ion chromatography (IC), while those of the terpenoic acids and the organosulfates, including nitrooxy

organosulfates, were performed using liquid chromatography with negative ion electrospray ionisation mass spectrometry [LC/(−)ESI-MS].

Special emphasis was given in this study to the measurement of organosulfates and nitrooxy organosulfates, a new class of SOA tracers from the oxidation of isoprene, monoterpenes, and unsaturated fatty acids that have only been recently discovered (Surratt et al., 2007, 2008, 2010; Iinuma et al., 2007a, b; Gómez-González et al., 2008) and have a mixed biogenic/anthropogenic origin. More specifically, the formation of these compounds involves the participation of sulfuric acid which is of anthropogenic origin. In addition, emphasis was given to the measurement of terpenoic acids, including species that have only been recently reported such as 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Szmigielski et al., 2007), and terpenylic acid and related lactone-containing compounds (Claeys et al., 2009; Iinuma et al., 2009; Yasmeen et al., 2010, 2011). MBTCA has been proposed as a higher-generation oxidation product of α-pinene formed by OH radical-initiated oxidation of *cis*-pinonic acid (Szmigielski et al., 2007), which has been confirmed in a recent laboratory study (Müller et al., 2011). In addition, a recent field study has revealed that MBTCA shows a strong Arrhenius-type temperature dependency and serves as a suitable tracer for "aged" biogenic SOA (Zhang et al., 2010). Inspired by the latter study, we have examined in detail the temperature dependency of the organic species that showed a high correlation with temperature.

2   Experimental

2.1   Description of the site and aerosol sampling

The Brasschaat sampling site (51°19′ N, 4°35′ E, 15 m a.s.l.) is located in the north part of Belgium. The nearest big city is Antwerp (with a population of 500 000). The sampling site is located within the state forest "De Inslag", a 78-yr old mixed pine-oak forest, in which the dominant species are *Pinus sylvestris* L. and *Quercus robur* L. For a

map with the location of the site, see Fig. 1. The site is at about 12 km northeast of the city centre of Antwerp and about 9 km to the east of the highly industrialised Antwerp harbour area; there is a major highway (E19/A1) to the south and in the south-east direction, and the shortest distance between the sampling site and the major highway is about 1.5 km. Hence, local aerosols could be a mixture of anthropogenic emissions from traffic, the city and harbour area of Antwerp, and biogenic emissions from the forest. A summer campaign was conducted from 5 June until 13 July 2007. A high-volume dichotomous sampler (HVDS) was set up on the first level of a tower at around 9 m above ground. Separate day-time (from about 07:15 to 20:15 local daylight saving time, UTC +2) and night-time (from about 20:15 to 07:15) collections were made in two size fractions (fine: <2.5 µm aerodynamic diameter (AD); coarse: >2.5 µm AD) and pre-fired double (front and back) Pall Gelman quartz fibre filters were used for each of the two size fractions. A total of 71 actual samples (34 day-time samples, 34 night-time samples, and 3 24-h samples) and 10 field blanks were taken. All filters were subjected to analyses for organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission (TOT) technique (Birch and Cary, 1996; Chi, 2009), the fine size fraction front and back filters were analysed for water-soluble OC (WSOC) with a total organic carbon analyser as described by Viana et al. (2006) and Chi (2009), and water-soluble inorganic, whereas the fine size fraction front filters were analysed for organic species (including MSA) by IC, and organosulfates, nitrooxy organosulfates and terpenoic acids by LC/(−)ESI-MS. Only the fine size fractions were analysed by LC/(−)ESI-MS.

2.2 Meteorological and trace gas measurements

Meteorological measurements were made on a tower; the data included vertical profiles of air temperature and humidity (HMP 230 dewpoint transmitter and PT100, Vaisala, Finland) at 2, 24, and 40 m and wind speed (LISA cup anemometer, Siggelkow GMBH, Germany) at 24, 32, and 40 m. At the top of the tower, measurements were made of down-welling shortwave radiation (pyranometer, Kipp and Zonen CM6B, The Netherlands), and precipitation (NINA precipitation pulse transmitter, Siggelkow

GMBH, Germany). All meteorological sensors were operated at 0.1 Hz and their data were stored as half hour means on a data logger (Campbell CR1000, UK).

Measurement of gaseous NO_x (chemiluminescence, Ecophysics 700 AL, Switzerland, detection limit 1 ppb), SO_2 (pulsed fluorescence analyser TEI 43C, Thermo Environmental Instruments, USA (detection limit: 1 ppb, precision: 1 ppb)), CO_2 (IRGA, LI-800, LI-COR Inc., Lincoln, NE, USA) and O_3 (UV Photometric Analyser, model TEI 49C, Thermo Environmental Instruments, USA (detection limit: 1 ppb, precision: 0.5 ppb)) were conducted at three inlets above the canopy (24, 32 and 40 m). From each inlet, air is drawn through 54 m-long Teflon sampling tubes with a flow rate of 60 L min^{-1} and led towards an air-conditioned instrument shelter. Prior to transport, air is filtered through 0.5 mm Teflon filter housings, which are covered with a rain shield. The Teflon tubings (external diameter 9.5 mm) are wrapped with 47 mm-isolated housings and heated to 35 °C using an electric heating wire. Each inlet is sampled for 5 min before switching to the next inlet using a PLC controlled valve system. An additional filter of 0.5 µm is placed before the sample inlet from the monitor. Readings of the first minute from every inlet are discarded as sample tubes need to be flushed.

Figure 2 shows the time series for O_3 and some meteorological parameters, i.e., temperature (measured 40 m above ground) and the amount of precipitation during the sampling campaign. The time-resolution for the temperature and O_3 data was 30 min; the precipitation data apply to the duration of the individual samples. During the first 10 sampling days of the campaign, there was less rain, higher temperatures, and higher O_3 concentrations than during the remainder of the campaign. Hence, during the first 10 sampling days the levels of SOA were expected to be the highest. The wind speed was low during the whole campaign, at 40 m it ranged from 0.25 to 7.2 m s^{-1} with an average value of 3.3 m s^{-1}. The wind direction was mainly from the southwest, the direction of the city, and the North Sea.

2.3 Analysis for water-soluble inorganic and organic species by IC

A procedure reported in a recent previous study was followed (Maenhaut et al., 2011). Briefly, a section of each $PM_{2.5}$ quartz fibre filter (1.5 cm^2) was placed in a 15 mL polystyrene tube; 5 mL Millipore Simplicity water was added and the tube was vig-
5   orously hand-shaken during 5 min, after which it was allowed to stand for 30 min. The sample extract was then filtered through a PVDF syringe filter (pore size 0.2 µm) and the filtrate was subjected to IC analysis. A Dionex DX-600 instrument with AG17 guard and AS17 analytical columns and with an ASRS II autosuppressor operating in the external water mode was used for anionic species, and a Dionex ICS-2000 instrument
10 with CG12A guard and CS12A analytical columns and with a CSRS II autosuppressor operating in the recycle mode for cationic species. All columns had 2 mm inner diameter. The Dionex DX-600 instrument was equipped with an EG40 eluent generator. The IC for anions was done with a 0.4–30 mM KOH gradient (0.45 mL min^{-1}) and a duration of 30 min; for cations we relied on a standard Dionex method, with 21.5 mM
15 methanesulfonic acid (isocratic) as eluent (0.25 mL min^{-1}) and a duration of 13 min. The sample loops used were 100 µL for anions and 25 µL for cations. Additional details on the IC analyses can be found in Wang (2010).

2.4 Analysis of organosulfates, nitrooxy organosulfates, and terpenoic acids by LC/(−)ESI-MS

20 The $PM_{2.5}$ samples were prepared as follows: a section (1/4) of each front quartz fibre filter was cut and a methanolic solution (10 µL) of each of the two internal recovery standards was added, i.e., sebacic acid (162 ng for both day- and night-time filters) and decyl sodium sulfate (31 ng for the day-time filters and 310 ng for the night-time filters). After drying, the sample was extracted 3 times for 30 min in an ultrasonic bath
25 with 20 mL of methanol. The extracts were combined and concentrated in a rotary evaporator at 35 °C and 200 mbar to approximately 1 mL and filtered through a Teflon filter (0.45 µm), then evaporated to dryness under a nitrogen stream and redissolved in

200 µL of water. An aliquot of 4 µL was used for LC/MS analysis.

The standards, surrogate standards, and internal recovery standards were from the following suppliers: *cis*-pinic acid: Sigma-Aldrich (purity: >98 %); *cis*-pinonic acid: Sigma-Aldrich (purity >98 %); sebacic acid: Sigma-Aldrich (purity 99 %); ethanesulfonic acid: Acros Organics (purity 95 %); sodium octanesulfate: Merck (purity: HPLC grade); decyl sodium sulfate: Acros Organics (HPLC grade). The following standards were available from previous studies: 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Szmigielski et al., 2007); terpenylic acid and diaterpenylic acid acetate were prepared at the Leibniz Institute for Tropospheric Research (Leipzig, Germany) (Claeys et al., 2009; Iinuma et al., 2009) and were obtained through the courtesy of Y. Iinuma.

The separation of the terpenoic acids was achieved using a T3 Atlantis C18 (Waters) column, which contains trifunctionally bonded C_{18} alkyl chains and shows polar retention. The mobile phase consisted of acetic acid 0.1 % (v/v) (A) and methanol (B). The applied gradient elution program for the analyses performed was as follows: the concentration of eluent B was kept at 3 % for 2 min, then increased to 90 % in 18 min, kept at 90 % for 43 min, then decreased to 3 % in 5 min and kept at 3 % for 12 min. The separation of the isomeric α-pinene-related nitrooxy organosulfates with MW 295 (five peaks) was achieved using a Hypersil Gold C18 (Thermo Scientific, San Jose, USA) column and acetonitrile as organic modifier. The elution gradient applied was exactly the same as for the analyses performed with the T3 Atlantis column.

The LC/MS instrument consisted of a Surveyor Plus LC system (pump and autosampler) and an LXQ linear ion trap mass spectrometer (Thermo Scientific). Electrospray was used as ionisation technique in the negative ion mode. The operating conditions of the LXQ instrument were as follows: sheath gas flow (nitrogen), 50 arbitrary units ($0.75\,L\,min^{-1}$); auxiliary gas flow (nitrogen), 5 arbitrary units ($1.5\,L\,min^{-1}$); source voltage, $-4.5\,kV$; capillary temperature, 350 °C; and maximum ion injection time, 200 ms. The $[M-H]^-$ signal optimisation was done by introducing a $50\,\mu g\,mL^{-1}$ malic acid standard solution.

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The quantification of the terpenoic acids and the polar organosulfates (see also Results and discussion) was based on an internal standard calibration procedure employing sebacic acid as internal recovery standard and pure reference compounds, if available, or surrogate standards. The quantification of the nitrooxy organosulfates with MW 295 was based on an internal standard calibration procedure employing sodium octanesulfate as surrogate standard and sodium decylsulfate as internal recovery standard. Extracted ion chromatography using specific ions was utilised to obtain clear chromatographic peaks and derive the peak areas used as input for the quantitative determinations. The concentrations in the extracts of the actual samples were obtained by relating the peak area (analyte/internal recovery standard) ratio data for the extracts to linear or quadratic calibration lines that were obtained with unweighted regression from the calibration curve data. For performing the unweighted regressions and the calculations of the concentration, use was made of Excel, running under Microsoft Windows on PCs. The day-to-day precision (RSD) was found to be better than 10 %; the precision of the measurements accounting for imprecision of sample flow control (Decesari et al., 2006) is therefore estimated to be better than 20 %. Field blanks were prepared and analysed in the same way as the samples; they proved to be free of the compounds of interest.

3 Results and discussion

3.1 Measurement of terpenoic acids and organosulfates

Forest fine aerosol has a very complex composition of organic compounds, which have only been partially elucidated. Table S1 of the supplement lists the terpenoic acids, organosulfates, and nitrooxy organosulfates that have been considered in this study, as well as some additional compounds that were used as surrogate or internal recovery standards. The terpenoic acids include SOA tracers formed from the photooxidation of α-pinene, β-pinene, d-limonene, Δ^3-carene, and 1,8-cineole. Details about the

structural characterisation of terpenoic acids in fine forest aerosol have been previously reported (Szmigielski et al., 2007; Claeys et al., 2009; Yasmeen et al., 2011). The organosulfates include the sulfate esters of the 2-methyltetrols, and their *mono-* and *di*nitrates (MWs 216, 261, and 306), of 2- and 3-hydroxyglutaric acid (MW 228), and unknown organosulfates with MW 212 and 226. The nitrooxy organosulfates include the α-pinene-related MW 295 compounds, which occur as five isomers, consistent with the formation of three positional isomers of which two have two enantiomeric forms (Surratt et al., 2008). Details about the structural characterisation of the isoprene-related organosulfates and nitrooxy organosulfates (MW 216, 261, and 306), and the α-pinene-related organosulfates (MW 228) and nitrooxy organosulfates (MW 295) can be found in Gómez-González et al. (2008) and Surratt et al. (2008). The group of the organosulfates and nitrooxy organosulfates are of particular interest because they have a mixed biogenic and anthropogenic origin due to the fact that their formation requires sulfuric acid (Surratt et al., 2007, 2008, 2010; Iinuma et al., 2007a, b; Gómez-González et al., 2008), which is formed by oxidation of SO_2, a product of anthropogenic origin that is present in polluted environments at high concentrations. As expected for the Brasschaat site, the sulfate concentrations were high during the whole campaign, and had a median concentration of $2700\,\mathrm{ng\,m^{-3}}$ (see Table 1 below). The median SO_2 concentration was 1.30 ppb (range 0–29 ppb), part of which may originate from the petrochemical industry in the harbour of Antwerp or from the E19/A1 highway, suburban traffic, and heating from contiguous buildings.

Quantitative aspects, including the choice of the surrogate standard in the case a reference standard was not available and the choice of the internal recovery standard, are presented in Table S2 of the supplement. The surrogate standards were selected taking into account structural and functional similarities with the target compounds and aiming at a similar molar response and retention times during LC/(−)ESI-MS analysis in order to minimise the possible effect of the mobile phase composition on the ionisation process. Selected LC/(−)ESI-MS chromatographic data obtained for real samples and calibration mixtures are illustrated in the Supplement (Figs. S1–S3).

3.2 Concentrations and time series of LMW DCAs and selected ionic species

The median concentrations and interquartile ranges for the carbonaceous components and the various ionic species measured, as derived from the PM$_{2.5}$ front filters of the HVDS, are given in Table 1. No clear diel variations were observed for MSA and the LMW DCAs, suggesting that they are aged products formed over a relatively long time scale. The time series for OC and four selected ionic species in the PM$_{2.5}$ front filters is shown in Fig. 3. There is a tendency for all five components to exhibit higher concentrations during the first 10 sampling days (which were dry, warm, and with high O$_3$ concentrations) than in the remainder of the campaign. This tendency is especially clear for sulfate, ammonium, and oxalate. The five components were well correlated with each other. The correlation coefficient between sulfate and ammonium was 0.95 and those between OC and oxalate and malonate were 0.79 and 0.75, respectively. OC was also highly correlated with WSOC ($r = 0.95$), succinate ($r = 0.83$), and glutarate ($r = 0.72$). It is evident from Table 1 that SO$_4^{2-}$, NH$_4^+$, and NO$_3^-$ are the major inorganic species at Brasschaat, with median concentrations of 2700 ng m^{-3}, 1080 ng m^{-3}, and 650 ng m^{-3}, respectively. The data for SO$_4^{2-}$ and NH$_4^+$ are intermediate between those from the cold and warm periods of the 2006 campaign at K-puszta (Maenhaut et al., 2011), but the median for NO$_3^-$ is larger than at K-puszta. The higher NO$_3^-$ level is likely due to the impact from automotive emissions from the nearby highway and to various anthropogenic emissions from the city of Antwerp and the Antwerp harbour. Nitrate is a dominant component of fine PM in western and central Europe, but low ambient concentrations are typical during summer (Schaap et al., 2004).

Consistent with the impact from maritime air is the high median for MSA (79 ng m^{-3}), which is about 2.5-fold higher than that found at K-puszta during the 2006 campaign (medians of 29 ng m^{-3} during the cold and warm periods) (Maenhaut et al., 2011) and almost twice the median of 45 ng m^{-3} during the 2007 summer campaign at Hyytiälä (Maenhaut et al., 2011). It is noteworthy that the median at Brasschaat is even higher than the median of 47 ng m^{-3}, which was obtained for the pristine marine site of Am-

sterdam Island (Claeys et al., 2010). The high value at Brasschaat suggests that the source regions of the MSA precursors (dimethylsulfide, dimethylsulfoxide, etc.) are nearer to the sampling site of Brasschaat than to that of Amsterdam Island, and/or that the source strengths of the precursor emissions were larger, and/or that the conversion to MSA was more efficient, and/or that there was less removal by wet deposition. The median concentration for oxalate at Brasschaat is 75 ng m^{-3}, which is nearly identical to the 73 ng m^{-3} for the 2006 cold period at K-puszta, but much lower than the medians for the 2006 warm period (210 ng m^{-3}) (Maenhaut et al., 2011) and the 2003 campaign at K-puszta (196 ng m^{-3}) (Kourtchev et al., 2009). Our median for Brasschaat is comparable with the mean value (95 ng m^{-3}), which was obtained for weekly low-volume Teflon filter samples that were collected in summer 2004 at a rural site (Lannemezan) in France (Legrand et al., 2005). When the samples are separated into two groups on the basis of temperature, the median concentration of oxalate rises to 230 ng m^{-3} for the first 10 sampling days, while it is 59 ng m^{-3} for the remainder of the campaign. The median concentrations of malonate, succinate, and glutarate for the full campaign are 49 ng m^{-3}, 11.0 ng m^{-3}, and 4.7 ng m^{-3}, respectively. The data for malonate and glutarate are comparable with those at K-puszta (for malonate 33 ng m^{-3} and 65 ng m^{-3} in the 2006 cold and warm periods and for glutarate 7.1 ng m^{-3} and 7.8 ng m^{-3} in the 2006 cold period and in the 2003 campaign) (Maenhaut et al., 2011). The medians for malonate and succinate at Brasschaat are comparable to the means of 48 ng m^{-3} (malonate) and 20 ng m^{-3} (succinate) observed at Lannemezan by Legrand et al. (2005). The time series of succinate was similar to that for oxalate (with $r = 0.97$), but the medians for the first 10 days (97 ng m^{-3}) and for the remainder of the campaign (8.4 ng m^{-3}) differ much more than was the case for oxalate. Incidentally, also during the 2006 campaign in K-puszta, there was a larger difference between the warm and cold periods for succinate than for oxalate. The succinate median for the first 10 days at Brasschaat is comparable to the median of 142 ng m^{-3}, which was obtained for the warm period of the 2006 campaign at K-puszta. Thus, the concentrations of the LMW DCAs, especially succinate, but also oxalate at Brasschaat were strongly affected by the local

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weather conditions, such as temperature and O_3 concentration. High temperatures and high O_3 levels lead to enhanced emissions of biogenic precursors of the DCAs and to enhanced photo-oxidant formation of SOA (Legrand et al., 2007).

Overall, MSA and the LMW DCAs corresponded on average to 0.7 % and 3.4 % of the OC, respectively. It is noted that the value for the LMW DCAs is substantially higher than that found for the sum of the terpenoic acids and the organosulfates, which contributed with 1.2 % to the OC (see Sect. 3.3).

3.3 Concentrations and time series of terpenoic acids and organosulfates

The median concentrations and interquartile ranges of the terpenoic acids and organosulfates, as derived from the $PM_{2.5}$ front filters of the HVDS, are given in Table 2. Most of the analytes peaked during day-time, indicating that they are formed through photooxidation processes. Only a few species, i.e., *cis*-pinic acid, caric acid, limonic acid, and the α-pinene-related MW 295 nitrooxy organosulfates peaked during night-time, which may be interpreted by dark ozonolysis, enhanced gas-to-particle partitioning at the cooler night-time temperatures or formation through night-time chemistry. For the α-pinene-related MW 295 nitrooxy organosulfates it has been demonstrated that they can be formed by photooxidation in the presence of NO_x as well as by NO_3 radical-initiated oxidation, which is a specific night-time oxidation process (Surratt et al., 2008). An alternative explanation is that their intermediate photooxidation products, the pinanediol nitrates (Aschmann et al., 1998; Surratt et al., 2008), are too volatile and need cooler night-time to partition to the particle phase where they are subsequently sulfated. A possible explanation for the night-time prevalence of the terpenoic acids, *cis*-pinic, caric and limonic acid, is dark ozonolysis of α-/β-pinene (Jaoui and Kamens, 2003; Winterhalter et al., 2003; Presto et al., 2005), Δ^3-carene, and *d*-limonene, respectively. Another factor that can contribute to the night-time prevalence of the terpenoic acids, *cis*-pinic, caric and limonic acid, is enhanced gas-to-particle partitioning at the cooler night-time temperatures. In this context, Kamens and Jaoui (2001) demonstrated that a 10 °C increase in ambient temperature results in a de-

crease of the SOA concentration in the α-pinene/ozone system by as much as a factor of two. Similar higher night-time concentrations of *cis*-pinic acid were observed for a German coniferous forest site, i.e., the Thuringer Wald (Plewka et al., 2006), and at K-puszta, Hungary (Kourtchev et al., 2009). Furthermore, it is also possible that *cis*-pinic, caric, and limonic acid are not stable during day-time and are converted to higher-generation oxidation products through OH radical-initiated reactions; additional research to test this hypothesis is warranted.

Overall, the sum of the terpenoic acids and organosulfates corresponded on average to 1.2 % of the organic carbon (OC) with a maximum in the night of 20 June of 4.3 %; this was the night after one of the warmest days of the campaign. The sum of the 12 terpenoic acids investigated ranged from $4\,\mathrm{ng\,m}^{-3}$ to $129\,\mathrm{ng\,m}^{-3}$ and in total represented 0.6 % of the OC. MBTCA, the unknown MW 188 terpenoic acid, and *cis*-pinonic acid were the most abundant with average concentrations of $4.9\,\mathrm{ng\,m}^{-3}$, $4.1\,\mathrm{ng\,m}^{-3}$, and $2.8\,\mathrm{ng\,m}^{-3}$. The sum of the 7 organosulfates and nitrooxy organosulfates analysed ranged from $3\,\mathrm{ng\,m}^{-3}$ to $431\,\mathrm{ng\,m}^{-3}$ and represented, on average, 0.6 % of the OC.

Figures 4 and 5 show time series for selected species and WSOC, which can be regarded as a proxy for SOA, throughout the 2007 campaign at Brasschaat. Of the organic species shown in Fig. 4, MBTCA and terebic, terpenylic, and the unknown MW 188 terpenoic acids exhibited the highest concentrations during the first days of the campaign that were characterised by high maximum temperatures ($>22\,°\mathrm{C}$), while *cis*-pinonic acid showed the lowest concentrations, a result consistent with the formation of MBTCA through further OH radical-initiated oxidation of *cis*-pinonic acid (Szmigielski et al., 2007; Müller et al., 2011). It can be seen that MBTCA and the unknown MW 188 terpenoic acid (Fig. 4 – top) closely follow each other; this could suggest that the unknown MW 188 terpenoic acid, tentatively assigned to a hydroxynorpinic acid (Yasmeen et al., 2011), is as MBTCA a further OH radical-initiated reaction product of *cis*-pinonic acid and a higher-generation photooxidation product of α-pinene. Except for the first days of the campaign the concentrations of *cis*-pinonic acid were compa-

rable with those of MBTCA (and the unknown MW 188 terpenoic acid), which reflects that the biogenic fine aerosol is relatively fresh or non-aged. It can be seen for the lactone-containing terpenylic, terebic and homoterpenylic acids (Fig. 4 – bottom), that they closely follow each other and the WSOC. Furthermore, it appears that the lactone-containing terpenoic acids are quite stable during the first days of the campaign that were characterised by the highest day-time temperatures. The time series for organic species that maximise at night, i.e., the MW 295 α-pinene-related nitrooxy organosulfates, limonic acid, and *cis*-pinic acid, and for WSOC, is presented in Fig. 5 (top). The most pronounced diel variations were observed for the MW 295 α-pinene-related nitrooxy organosulfates, but the diel differences for the first days of the campaign that were characterised by the highest day-time temperatures were less clear. A possible explanation for this behaviour during these first days is that their precursors, the pinanediol nitrates (Surratt et al., 2008), were not stable during day-time and could thus not partition to the particle phase during night-time where they are subsequently sulfated. It is worth mentioning that the night-time prevalence of the MW 295 α-pinene-related nitrooxy organosulfates was first reported by Iinuma et al. (2009) for $PM_{2.5}$ aerosol samples collected from the Fichtelgebirge mountain range in northern Bavaria, Germany. Furthermore, it can be seen in the bottom graph of Fig. 5 that the highest concentrations of the 2-methyltetrol (MW 216) and the unknown MW 212 organosulfates were observed during the first warm days of the campaign, and that they follow quite closely the WSOC.

3.4 Correlations among species and between species and meteorological and trace gas data

All concentration data available for the fine front filters of the Brasschaat High-Vol samples were combined and pairwise correlations among the various species and also between the species and data for several meteorological parameters and inorganic trace gases were calculated. In addition, a day-night (D_N) parameter was included; this was set equal to 1 for the day-time samples and equal to 0 for the night-time samples. The

correlations obtained between OC, WSOC, the terpenoic acids, the organosulfates, T_40 m, ozone, and CO_2, and the D_N parameter, are given in Table S3 of the supplement. Several correlations were very high ($r > 0.85$) or high ($0.7 < r < 0.85$) or substantial ($0.5 < r < 0.7$). For example, MBTCA was very highly correlated with OC, WSOC, terebic acid, terpenylic acid, the unknown MW 188 terpenoic acid, diaterpenylic acid acetate, and homoterpenylic acid, and very highly or highly with the organosulfates (OSs) with MW 212, 216, 226, 228, 261, and 306 (thus all OSs with the exception of the MW 295 OSs). As to the correlations for *cis*-pinic acid, very high, high or substantial correlations were only noted with *cis*-pinonic ($r = 0.78$), terebic ($r = 0.60$), terpenylic ($r = 0.68$), caronic ($r = 0.73$), ketolimononic ($r = 0.61$), limonic ($r = 0.60$), homoterpenylic ($r = 0.77$), and caric acid ($r = 0.81$). For the MW 295 nitrooxy organosulfates correlations were only found among its five isomers and with limonic and caric acid. The correlations between the various species and the meteorological parameters and trace gases were at most substantial. For example, substantial to high correlations with temperature were found for OC, WSOC, MBTCA, and several other organic species (the exceptions were *cis*-pinonic, *cis*-pinic, caronic, limonic, and caric acid, and the MW 295 OSs).

The correlations between the fine front filter data and the data for several meteorological parameters and inorganic trace gases were also examined by principal component analysis (PCA) with Varimax rotation. The loadings for the 8-component solution are given in Table S4. TC (with TC = OC + EC), OC, WSOC, malonate, succinate, and 11 of the 19 LC/MS compounds are very highly (>0.85) or highly ($0.7 < r < 0.85$) loaded on the first component, whereas oxalate, glutarate, ammonium, sulfate, three other LC/MS species, and the temperature show substantial ($0.5 < r < 0.7$) loadings on this component. *Cis*-pinic, *cis*-pinonic, and caronic acids are very highly loaded on the second component, and four other LC/MS species, exhibit substantial loadings on this component. The MW 295 OSs exhibit a loading of 0.46 on the second component, but a higher one (i.e., of 0.56) on component 4. Caric acid is also substantially loaded on this component 4, but more interesting, are the high positive loading of the relative humidity (RH) and the high negative loadings of the amount of sunshine and the D_N

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parameter, which are all consistent with the night-time formation of the MW 295 OSs.

3.5 Temperature dependency of selected organic species

In a recent study by Zhang et al. (2010) the temperature dependency of MBTCA was examined in detail for aerosol samples collected weekly during a whole year in Mainz, Germany. MBTCA was found to show a strong Arrhenius-type relationship with temperature, consistent with its formation through OH radical-initiated reactions and indicating that it is a useful tracer for aged biogenic SOA. Model calculations suggested that the temperature dependency observed for MBTCA can be explained by enhanced photochemical production due to an increase of the OH radical concentration with increasing temperature. It is worth noting in our study that high correlations with the temperature ($r \geq 0.7$) were found for MBTCA, terebic acid, terpenylic acid, diaterpenylic acid acetate, and ketolimononic acid (Table S3 in the Supplement). Interestingly, the best correlation with the temperature was found for terebic acid ($r = 0.74$), which is consistent with its proposed formation through further OH radical-initiated reactions (aging) of terpenylic acid (Yasmeen et al., 2010), which itself is a photooxidation product of α-pinene (Claeys et al., 2009). The high correlations with temperature found for terpenylic acid and the related diaterpenylic acid acetate support their proposed formation pathway involving OH radical chemistry (Claeys et al., 2009). The temperature dependency was examined for several organic species that showed a high correlation with temperature; the day-time correlations of MBTCA and terebic acid are presented in Fig. 6. For both MBTCA and terebic acid high day-time correlations were obtained, in contrast to *cis*-pinonic acid (not shown; $R^2 = 0.27$); the activation energies (E_a) calculated from the day-time samples ($N = 34$) were 260±30, 189±24, and 118±35 kJ mol^{-1}, for MBTCA, terebic, and *cis*-pinonic acid, respectively. When including all samples ($N = 71$), the E_a values were 230±30, 149±17, and 88±23 kJ mol^{-1}, for MBTCA, terebic, and *cis*-pinonic acid, respectively, with R^2 of 0.53, 0.53, and 0.18, respectively. Our E$_a$ values for MBTCA and *cis*-pinonic acid (obtained for summer PM$_{2.5}$ samples) are higher (by

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about a factor 2) than the values reported in the study by Zhang et al. (2010) (obtained for weekly fine, coarse, and TSP (total suspended particles) samples and over a whole year) but follow the same trend in that the E_a value for MBTCA is more than twice larger than that for *cis*-pinonic acid. For *cis*-pinic acid, there was a large difference between

5 the E_a values derived from our day-time samples only and from all samples; the E_a values were 210±30 and 106±27 kJ mol^{-1}, respectively (with R^2 of 0.58 and 0.19, respectively. The smaller of our two E_a values is in reasonable agreement with the E_a values of Zhang et al. (2010) for *cis*-pinic acid.

4 Conclusions

10 Based on the results of this study it is clear that temperature was a main driver in biogenic SOA formation at the study site. Substantial to high correlations with temperature were found for OC, WSOC, MBTCA, and several other organic species. An Arrhenius-type temperature dependency was found for several organic species including MBTCA, pinic acid, and terebic acid, consistent with their formation through OH-initiated oxida-

15 tion reactions. More research is warranted on the temperature dependency of the terpenoic acids to determine whether Arrhenius parameters such as the activation energy can provide useful information on biogenic SOA aging. It is also evident that the terpenoic acids and the organosulfates only explain a small portion of the organic carbon at the study site (on average 1.2 %); nevertheless, they allow one to obtain detailed

20 insights into biogenic SOA formation processes. For example, during the first days of the campaign, which were characterised by day-time temperatures >22 °C, the highest concentrations of MBTCA and the lowest ones for pinonic acid were measured, consistent with pinonic acid serving as a gas-phase precursor for MBTCA. Another interesting finding was that the unknown MW 188 compound, tentatively assigned to

25 a hydroxynorpinic acid, also reached the highest concentrations during the first warm days of the campaign, suggesting that it is as MBTCA a useful tracer for SOA formed through OH-initiated oxidation reactions. Based on their diel behaviours the organic

species can be divided in three distinct groups: a first group (comprising MSA and the LMW DCAs), which did not reveal clear diel variations, suggesting that they are aged products formed over a relatively long time scale, a second group (comprising terpenoic acids and organosulfates) which showed day-time maxima, suggesting that their forma-
tion involves OH-initiated oxidation reactions, and a third group (comprising terpenoic acids and nitrooxy organosulfates) which revealed night-time maxima, suggesting that their formation involves different and/or additional chemical processes. More research is also warranted to obtain more detailed insights into the latter processes.

Supplement related to this article is available online at:
http://www.atmos-chem-phys-discuss.net/11/23541/2011/
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Table 1. Front filter median concentrations and interquartile ranges (in $ng\,m^{-3}$) of TC, OC, EC, WSOC, low-MW dicarboxylic acids and selected inorganic species for the $PM_{2.5}$ size fraction of the HVDS samples. Also given are the medians and interquartile ranges for the back/front filter ratio of the various species.

Species	Front filter conc. ($ng\,m^{-3}$)	Back/front filter ratio
TC	2100 (1660–2800)	0.13 (0.12–0.16)
OC	1730 (1270–2200)	0.17 (0.15–0.20)
EC	400 (280–620)	0.00 (0.00–0.00)
WSOC	810 (570–1170)	0.21 (0.18–0.25)
NH_4^+	1080 (650–2100)	0.04 (0.00–0.07)
SO_4^{2-}	2700 (1840–3900)	0.00 (0.00–0.00)
NO_3^-	650 (400–2200)	0.24 (0.15–0.34)
Cl^-	40 (16–93)	0.26 (0.14–0.48)
Na^+	108 (65–210)	0.01 (0.00–0.05)
Mg^{2+}	2.7 (1.42–6.7)	0.00 (0.00–0.00)
K^+	38 (18.7–93)	0.04 (0.00–0.22)
Ca^{2+}	27 (14.7–36)	0.00 (0.00–0.01)
MSA^-	79 (46–119)	0.03 (0.01–0.08)
oxalate	75 (50–140)	0.01 (0.01–0.01)
malonate	49 (28–82)	0.02 (0.00–0.04)
succinate	11.0 (5.7–4)	0.02 (0.00–0.10)
glutarate	4.7 (3.3–9.7)	0.26 (0.17–0.57)

Table 2. PM$_{2.5}$ front filter median concentrations and interquartile ranges of terpenoic acids and organosulfates (ng m^{-3}).

Compound (MW)	Overall ($n = 71$) median (interq. range)	Day ($n = 34$) median (interq. range)	Night ($n = 34$) median (interq. range)
MBTCA (204)	2.7 (1.33–5.0)	3.0 (1.68–6.2)	2.2 (1.10–4.1)
cis-pinonic acid (184)	1.79 (1.23–3.1)	1.90 (1.46–3.3)	1.88 (1.17–2.9)
cis-pinic acid (186)	0.49 (0.35–1.19)	0.42 (0.31–0.98)	0.59 (0.40–1.25)
terebic acid (158)	1.87 (1.31–3.5)	1.81 (1.42–3.9)	1.95 (1.29–3.5)
terpenylic acid (172)	2.4 (1.57–3.7)	2.6 (1.77–5.0)	2.3 (1.41–3.5)
unknown (188)	2.1 (0.90–3.8)	1.94 (0.83–3.9)	2.1 (1.38–3.9)
diaterpenylic acid acetate (232)	0.27 (0.13–0.64)	0.33 (0.17–1.04)	0.20 (0.10–0.43)
caronic acid (184)	0.30 (0.19–0.47)	0.30 (0.18–0.55)	0.30 (0.19–0.47)
caric acid (186)	0.60 (0.31–1.50)	0.36 (0.24–(0.74)	0.78 (0.47–2.5)
ketolimononic acid (186)	0.41 (0.27–0.57)	0.51 (0.35–0.79)	0.30 (0.21–0.43)
limonic acid (186)	0.85 (0.45–1.69)	0.62 (0.42–1.02)	1.38 (0.68–2.2)
homoterpenylic acid (186)	0.57 (0.39–0.88)	0.51 (0.37–0.83)	0.61 (0.39–0.97)
unknown OSs [$\sum$2 isomers] (212)	6.5 (3.5–11.3)	5.9 (3.5–12.1)	6.8 (3.7–11.3)
2-methyltetrol OSs [$\sum$2 isomers] (216)	6.4 (3.0–9.0)	6.4 (3.2–9.5)	6.4 (3.0–10.0)
unknown OS (226)	4.6 (2.0–6.2)	4.6 (2.5–6.3)	4.6 (1.81–6.1)
2- and 3-hydroxyglutaric acid OSs (228)	3.4 (1.67–9.4)	2.8 (1.37–9.2)	4.4 (1.92–11.5)
2-methyltetrol mono-nitrate OSs [$\sum$3 isomers] (261)	0.76 (0.14–2.3)	1.05 (0.31–3.9)	0.58 (DL–1.94)
pinanediol mono-nitrate OSs [$\sum$5 isomers] (295)	1.51 (0.63–3.6)	0.66 (0.50–1.18)	3.4 (1.75–6.0)
2-methyltetrol di-nitrate OSs [$\sum$4 isomers] (306)	6.6 (2.6–9.2)	8.4 (2.8–13.6)	5.9 (2.6–8.1)
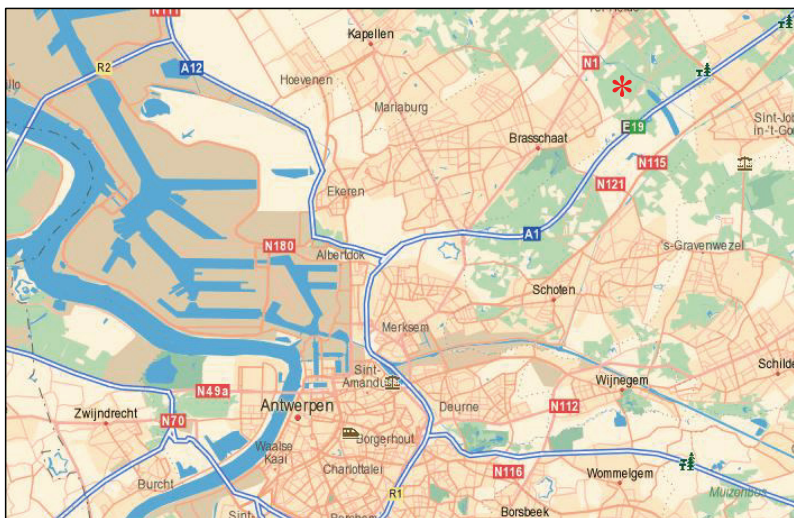
Fig. 1. Map of Antwerp, Belgium, and surroundings with the location of the Brasschaat sampling site indicated with a red asterisk.
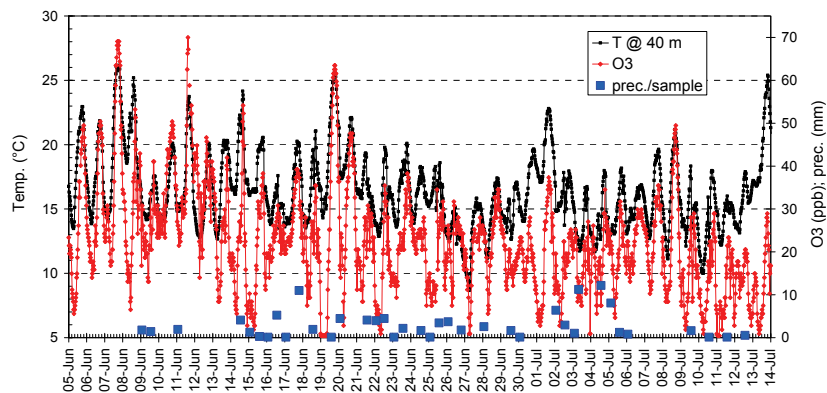
Fig. 2. Time series for O_3 and selected meteorological data during the 2007 summer campaign in Brasschaat.
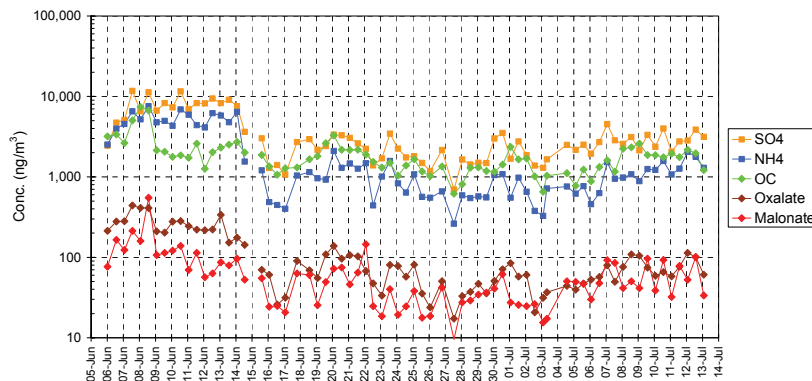
Fig. 3. Time series for OC and selected ionic species, as derived from the PM$_{2.5}$ front filters of the HVDS, in the 2007 summer campaign at Brasschaat.
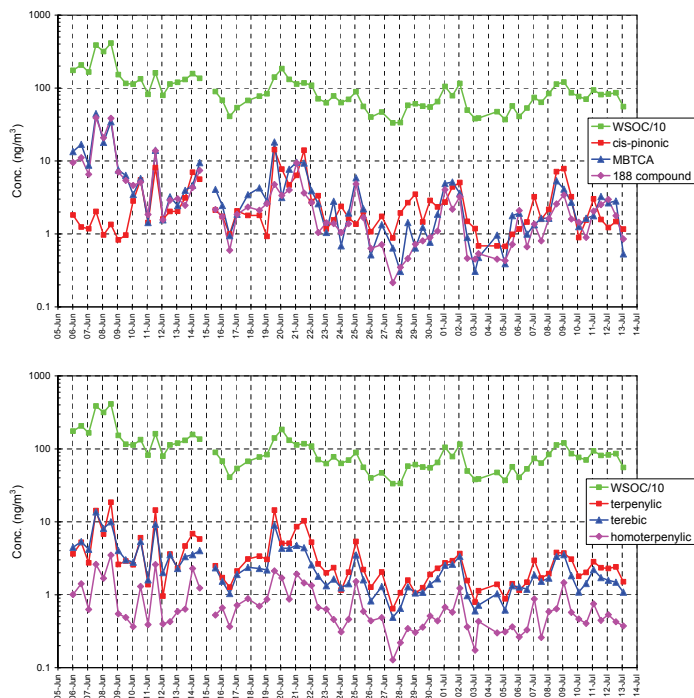
Fig. 4. Time series for (top): *cis*-pinonic acid, MBTCA, and the unknown MW 188 terpenoic acid; and (bottom) the lactone-containing terpenoic acids, terpenylic acid, terebic acid, and homoterpenylic acid, as derived from the $PM_{2.5}$ front filters of the HVDS, for the 2007 summer campaign in Brasschaat. For comparison, the time series of WSOC, which is a proxy for SOA, is also presented, and for clarity it is repeated in each of the graphs.
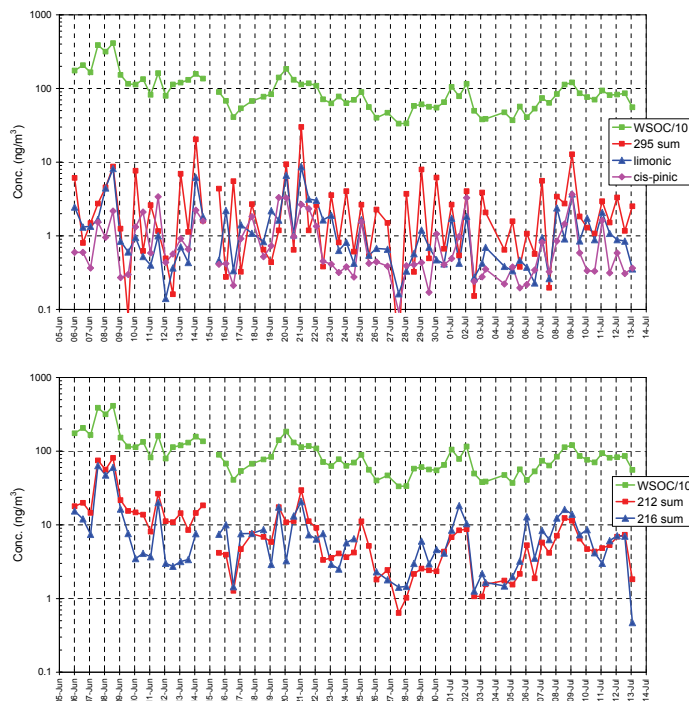
Fig. 5. Time series for (top): the organic species that maximise at night, i.e., the MW 295 α-pinene-related nitrooxy organosulfates, limonic acid, and *cis*-pinic acid; and (bottom) the 2-methyltetrol (MW 216) and the unknown MW 212 organosulfates, as derived from the PM$_{2.5}$ front filters of the HVDS, for the 2007 summer campaign in Brasschaat. For comparison, the time series of WSOC, which is a proxy for SOA, is also presented, and for clarity it is repeated in each of the graphs.
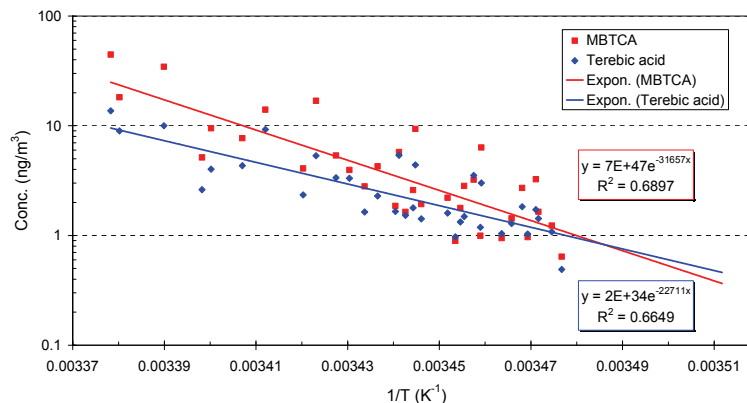
Fig. 6. Arrhenius-type temperature dependencies observed for α-pinene oxidation products: mass concentrations of 3-MBTCA and terebic acid in $PM_{2.5}$ plotted against inverse absolute temperature. The data points represent individual day-time samples ($N = 34$) and the full lines are exponential fits. The corresponding Arrhenius parameters for MBTCA are: A (pre-exponential factor) = 7.0×10^{47} ng m^{-3} and $E_a = 260 \pm 30$ kJ mol^{-1}; those for terebic acid are: A = 2.0×10^{34} ng m^{-3} and $E_a = 189 \pm 24$ kJ mol^{-1}.