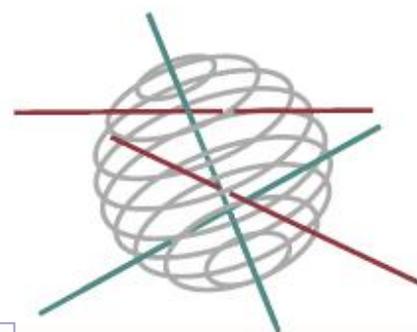


# SSD

SCIENCE FOR A SUSTAINABLE DEVELOPMENT



FORMATION MECHANISMS, MARKER COMPOUNDS AND SOURCE  
APPORTIONMENT FOR BIOGENIC ATMOSPHERIC AEROSOLS

« BIOSOL »

W. MAENHAUT, M. CLAEYS, I. JANSSENS, M. KULMALA



ENERGY



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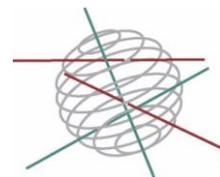


TERRESTRIAL AND MARINE ECOSYSTEMS



TRANSVERSAL ACTIONS





***Atmosphere***

FINAL REPORT

FORMATION MECHANISMS, MARKER COMPOUNDS AND SOURCE  
APPORTIONMENT FOR BIOGENIC ATMOSPHERIC AEROSOLS

« BIOSOL »

SD/AT/02

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## SUMMARY

Biogenic volatile organic compounds (BVOCs) play an important role in atmospheric chemistry and give rise to secondary aerosols, which have effects on climate and human health. Increased temperature and CO<sub>2</sub> concentrations will lead to increased plant photosynthesis and growth rates and higher emissions of BVOCs, which in turn result in a higher aerosol load from natural sources and partly offset the decreased cooling from anthropogenic aerosols. However, a considerable lack of knowledge exists concerning the formation of new particles from BVOCs and the organic chemical composition of natural aerosols.

The objectives of the BIOSOL project included (1) study of the formation mechanisms of secondary organic aerosol (SOA) from isoprene and other BVOCs, assessing their role in particle formation and growth, examining the relative importance of homogeneous photo-oxidation and multi-phase processes, and modelling of the processes involved; (2) identification of particulate-phase oxidation products of isoprene and other BVOCs, which can be used as indicator compounds for source apportionment, and development/deployment of novel analytical techniques thereby; and (3) determination of the contribution from the BVOCs to the organic aerosol for various sites in Europe.

For reaching objective (1), experiments and measurements were performed in the laboratory, at three forested European sites, and during an oceanic cruise in the Atlantic and at a remote island in the southern Indian Ocean. The BVOCs, their volatile organic oxidation products, and critical inorganic trace gases were determined, and aerosol samples were collected and subjected to comprehensive analyses; in addition, in-situ measurements of particle number concentrations and size distributions, of ion spectra, and of the particulate mass (PM) and particulate organic carbon (OC) were made, and radiation and standard meteorological measurements were performed.

In co-operation with Caltech, a study was performed to obtain insights into the formation mechanisms of SOA from isoprene, in particular the mechanisms that result in the formation of 2-methyltetrols, 2-methylglyceric acid (2-MG), and humic-like substances (HULIS). An extensive series of smog chamber experiments was performed under various conditions, in particular at low- and high-NO<sub>x</sub> levels, and with and without seed aerosol. It was found that the chemical nature of the SOA was significantly different between the two NO<sub>x</sub> regimes. At high-NO<sub>x</sub>, the SOA components were acidic and formed upon the further oxidation of methacrolein; no other first-generation gas-phase products contributed to the high-NO<sub>x</sub> SOA. In contrast, the low-NO<sub>x</sub> SOA was neutral owing to the formation of polyols and organic

peroxides. Oligomerisation was an important isoprene SOA formation pathway at both low- and high-NO<sub>x</sub>. The nature of the oligomers was, however, distinctly different in each NO<sub>x</sub> regime. The high-NO<sub>x</sub> oligomers were characterised as oligo-esters involving 2-MG as the key monomeric unit, while the low-NO<sub>x</sub> oligomers were hemiacetal derivatives of the 2-methyltetrols. Based on the results of this study mechanisms could be proposed for the formation of isoprene SOA under both high- and low-NO<sub>x</sub> conditions.

In co-operation with Caltech and US EPA smog chamber experiments were performed in order to study the mechanism and ubiquity of organosulphate formation in biogenic SOA. In addition, archived laboratory-generated isoprene SOA and ambient filter samples from the southeastern US were re-examined for organosulphates and nitrooxy organosulphates. Only SOA compounds that were also detected in ambient PM<sub>2.5</sub> aerosol were selected for structural characterisation. By comparing the mass spectral data collected for both the laboratory-generated and ambient aerosol, previously uncharacterised ambient organic aerosol components were found to be organosulphates of isoprene,  $\alpha$ -pinene,  $\beta$ -pinene, and limonene, thus demonstrating the ubiquity of organosulphate formation in ambient SOA. Several of the organosulphates characterised in this study provide ambient tracer compounds for the occurrence of biogenic SOA formation under acidic conditions. As to the contribution from organosulphates to the total organic mass fraction in ambient aerosols, the calculations for the PM<sub>10</sub> samples from the 2003 K-puszta summer campaign indicated that this contribution can be as high as 30%.

A comprehensive field campaign was held at the forested site of K-puszta, Hungary, from 24 May to 29 June 2006. From the start of the campaign until 11 June, it was unusually cold with daily maximum temperatures between 12 and 23 °C, but from 12 June onward higher temperatures were noted with daily maxima from 24 to 36 °C. From the data for the volatile organic compounds (VOCs) and their oxidation products it was quite clear that much higher levels were observed during the warm period than during the cold one. This difference is to be expected, given that both formation and emission of the VOCs by plants increase with light and temperature. An increase with temperature was also observed for the 24-hr (or day-time or night-time) averaged concentrations of fine PM and fine OC (whereby fine = PM<sub>2.5</sub>) from the in-situ instruments and for the data of a number of components in the filter samples, such as the dicarboxylic acids (DCAs) and the mineral dust elements. The in-situ measurements of particle number concentrations and size distributions and of ion spectra indicated that there were particle production episodes around every second day, which is quite frequent. There seemed to be no relation between the particle production events and the in-situ VOC, fine PM or fine OC levels. Organic matter,

estimated as 1.8 OC, was the major aerosol component in both PM<sub>2.5</sub> and PM<sub>10</sub> and in both the cold and warm periods and accounted for between 40 and 50% of the gravimetric PM. Sulphate was the second component in PM<sub>2.5</sub>, with percentage contributions of 22-24%.

From the results for OC, elemental carbon (EC), and the VOCs that were obtained in the course of 2007 at the forested site "De Inslag", Brasschaat, it appeared that the site is substantially impacted by anthropogenic activities. This is in contrast to the two other forested sites studied in this project. The fine size fraction samples of the Hi-Vol dichotomous sampler (HVDS) were analyzed for inorganic and organic ions by ion chromatography (IC) and for a variety of organic compounds by liquid chromatography/mass spectrometry (LC/MS). Known and new tracers for  $\alpha$ -pinene SOA and a number of organosulphates, including nitrooxy organosulphates with a molecular weight (MW) of 295, were detected and quantified, in addition to the DCAs. Interestingly, rather low concentrations of the MW 295 SOA tracers were found during the first nights of the campaign (with maximum day-time temperatures > 22 °C). These results hint that the latter  $\alpha$ -pinene SOA tracers are formed during nights following days where  $\alpha$ -pinene was not fully consumed by photo-oxidation, leaving a portion of the emitted  $\alpha$ -pinene available for processing by night-time NO<sub>3</sub> chemistry. The combined contribution of the measured organic compounds to the OC was, on average, 5.3% (with 4.1% from the IC compounds and 1.2% from the LC/MS compounds).

From 1 to 31 August 2007, a comprehensive field campaign was held at the SMEAR II forested site in Hyytiälä, Finland. Overall, the weather was nice during the campaign with little rain. The mean daily temperature rose from 13.4 °C on 1 August to around 20 °C in the period of 6-13 August and decreased to 6.1 °C on 31 August, with a secondary maximum of 17 °C on 22-24 August. From the time series of the in-situ data for the BVOCs, it appeared that the highest levels of the monoterpenes were noted in the nights of 7, 8, and 9 August, thus right after the start of the warm period. When looking at daily averages, there was clearly some relation between the concentrations of the BVOCs and temperature, with higher levels at higher temperatures. The time series for in-situ fine PM and fine OC was different from that for the BVOCs. The OC levels (and to a lesser extent also the PM levels) kept increasing from the beginning of the campaign until 13 August and decreased afterwards, with a second maximum on 22 to 24 August. It seemed thus that there was little relation between the local concentrations of the BVOCs and fine OC at the SMEAR II site. It is thought that the levels of fine OC are more related to the total BVOC emissions upwind of the site during the last 5 days or so of air mass transport than to the local BVOC concentrations at SMEAR II itself. The mass size distributions for OC, as measured in cascade

impactor samples collected at ambient relative humidity (RH), peaked in the accumulation size range, but there was also a clear coarse mode with peak at around 3-4  $\mu\text{m}$  aerodynamic diameter. Like during the 2006 summer campaign at K-puszta, there was little EC in the aerosol at SMEAR II and most of the fine OC was water-soluble (i.e., 63%). The PM<sub>2.5</sub> samples of the HVDS were analyzed for inorganic and organic ions by IC. The organic compounds measured accounted, on average, for 2.0% of the OC and 3.1% of the water-soluble OC (WSOC). These percentages are about one third lower than those found at K-puszta. The results from the low-volume filter samples were used to examine to which extent aerosol chemical mass closure could be obtained. Eight aerosol types (components) were considered in the mass closure calculation. Organic matter was clearly the dominant component in both PM<sub>2.5</sub> and PM<sub>10</sub>. It accounted for 73% and 64% of the average gravimetric PM in PM<sub>2.5</sub> and PM<sub>10</sub>, respectively, and was in both cases followed by non-sea-salt sulphate, which represented 25% and 17% of the average gravimetric PM in PM<sub>2.5</sub> and PM<sub>10</sub>, respectively.

The OC and EC data from the oceanic cruise in 2006 in the Northern Hemisphere (NH) indicated that there was a large impact from continental aerosol and from fossil-fuel combustion aerosol. This was in contrast with the OC and EC data from Amsterdam Island in the southern Indian Ocean. At the latter site, EC was below the detection limit and OC was substantially lower than during the NH cruise. A common feature of both marine study areas was that only around 30% of the fine OC was water-soluble. This percentage is similar to that found at urban sites, where most of the OC consists of primary organic aerosol from fossil fuel combustion. It seems that the fine OC for our two oceanic study areas was also mostly primary. It has been suggested that SOA from isoprene may be a large source of cloud condensation nuclei in some oceanic regions. There was clearly no evidence for SOA from isoprene in the samples from the NH cruise nor in these from Amsterdam Island. In both the coarse and fine size fractions of the HVDS samples from Amsterdam Island, sea salt was by far the major aerosol type; organic aerosol made up for less than 10% of the dry aerosol mass. Of the organic species measured, methanesulphonate, a gas-to-particle conversion product from dimethylsulphide, which is emitted by marine phytoplankton, was by far the major contributor to the fine WSOC, with an average contribution of about 17%. Various organosulphates were also present in the fine WSOC (with an average combined contribution of 0.8%); they were attributed to oxidation of primary algal biomass.

With regard to objective (2) of BIOSOL, studies were conducted to structurally characterise major particulate-phase oxidation products of  $\alpha$ -pinene that occur at significant concentrations in ambient fine aerosol. Using mass spectrometric

techniques and synthesis of reference compounds, the structures of two major  $\alpha$ -pinene SOA marker compounds with MWs of 148 and 204 were established as 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), respectively. A formation mechanism for MBTCA was proposed, which involves OH-initiated oxidation in the presence of  $\text{NO}_x$ . Furthermore, major efforts were undertaken to elucidate the structure of a MW 172 compound and related compounds, which are formed upon photo-oxidation and ozonolysis of  $\alpha$ -pinene (and other BVOCs) and are also present in ambient fine aerosol from sites with coniferous vegetation. The MW 172 compound was identified as the lactone-containing terpenylic acid. Terpenylic acid shows unique non-covalent dimer-forming properties upon electrospray ionisation in the negative ion mode [(-)ESI] and is thought to play a role in initial particle formation.

As to objective (3), we determined the contribution from the BVOCs to the organic aerosol for  $\text{PM}_{2.5}$  samples, which had been collected in summer 2003 in a mixed deciduous forest in Jülich, and for the  $\text{PM}_{2.5}$  size fraction of the HVDS samples from the 2003 summer campaign at K-pusztá. We made thereby use of the laboratory-derived tracer mass fractions ( $f_{\text{SOC}}$ ), which were obtained by Kleindienst et al. [2007] with gas chromatography/mass spectrometry (GC/MS). For the K-pusztá samples, isoprene secondary organic carbon (SOC) and  $\alpha$ -pinene SOC accounted, on average, for respectively 6.9% and at least 4.8% of the  $\text{PM}_{2.5}$  OC; for the Jülich samples, the average contributions from isoprene SOC and  $\alpha$ -pinene were 2.5% and at least 2.4%, respectively. Although the data for  $\alpha$ -pinene SOC should be regarded as minimum values because not all molecular tracers necessary to estimate  $\alpha$ -pinene SOC were measured, these percentages are clearly much lower than expected. Although the uncertainty that is associated with our estimates is at least a factor of 2, one may wonder to what extent the values of Kleindienst et al. [2007] are applicable to ambient organic aerosol in various types of environments and different levels of  $\text{NO}_x$ , oxidants, RH, 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 is also suggested that additional techniques, such as LC/MS, are used besides GC/MS in future studies on  $f_{\text{SOC}}$ .

Project valorisation was done through interaction with members of the Follow-up Committee and joint meetings with the SSD project IBOOT, writing of progress reports and scientific publications, conference presentations, and contributions to activities organised within national and international programmes.

**Keywords:** atmosphere, biogenic volatile organic compounds, secondary organic aerosols, indicator compounds, smog chambers, forested sites.



## 1. INTRODUCTION

It is well established that trace gases and atmospheric aerosols are important to the global radiation, cloud formation, and human and animal health and welfare. Trace gases and atmospheric aerosols are tightly connected with each other via physical, chemical, meteorological, and biological processes occurring in the atmosphere and at the atmosphere-biosphere interface. Atmospheric aerosol particles influence the Earth's radiation balance directly by scattering and absorbing solar radiation, and indirectly by acting as cloud condensation nuclei (CCN) [e.g., Charlson et al., 1992; Novakov and Penner, 1993; Andreae et al., 2005; IPCC, 2007]. Progress has been made in evaluating the radiative effects of various aerosol components such as sulphate, organics, black carbon, sea-salt, and crustal species [Penner et al., 2001]. Despite these efforts, substantial uncertainties still remain in quantifying the contribution from each source, particularly to assess the relative contributions of biogenic and natural emissions.

Knowledge of the effects of natural emissions of aerosols on the Earth's radiation balance is necessary in order to accurately predict and understand the true effect of anthropogenic emissions and land-use changes. In its Third Assessment Report (TAR), the Intergovernmental Panel on Climate Change revised its older prediction of the globally averaged surface temperature increase over the period 1990 to 2100 from 1.0-3.5 to 1.4-5.8 K [IPCC, 2001] and the results from the new Fourth Assessment Report [IPCC, 2007] essentially corroborate those given in the TAR. The increase in the upper limit of the prediction is largely due to the role of aerosols in the climate of the Earth: it is believed that reduction of pollution will result in reduced direct and indirect (via clouds) scattering of sunlight back to the space. However, as can be seen from the large uncertainty of the estimated temperature increase, there is insufficient knowledge about the role of natural and anthropogenic aerosols in climate processes. As stated by Andreae et al. [2005], the strong present-day aerosol cooling may imply a hot future. The terrestrial vegetation is a key player in future climate change processes; increased temperature and CO<sub>2</sub> concentrations will lead to increased plant photosynthesis and growth rates and higher emissions of volatile organic compounds (VOCs), which in turn will result in a higher aerosol load from natural sources and partly offset the decreased cooling from anthropogenic aerosols.

Organic material significantly contributes to the total fine aerosol mass, i.e., 20-50% at continental mid-latitudes [Saxena and Hildemann, 1996; Putaud et al., 2004], and a substantial fraction of the organic material results from the oxidation of VOCs and is thus secondary organic aerosol (SOA). However, our knowledge about the organic aerosol and SOA is still rather poor. A large fraction remains uncharacterised [e.g.,

Turpin et al., 2000; Kubátová et al., 2002; Iinuma et al., 2004]. It is recognised that especially the characterisation of multifunctional organic molecules is a major analytical challenge [Brasseur et al., 2003]. Furthermore, organic aerosol has so far been poorly represented in current aerosol global climate models [for a review, see Kanakidou et al., 2005]. The latter models focus mainly on sulphur chemistry, especially when considering the formation of new particles in the troposphere. Nucleation events, that is the formation of "nucleation mode" (3-20 nm diameter) particles, are usually discussed in terms of sulphuric acid nucleation, either as binary ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ) or ternary ( $\text{H}_2\text{SO}_4/\text{NH}_3/\text{H}_2\text{O}$ ) system. However, aerosol formation studies at rural sites indicate a link between new particle formation and oxidation of VOCs. Measurements of nanometer size particles at the SMEAR II station in southern Finland provide an example of particle formation events over a boreal pine forest [Mäkelä et al., 1997; Boy et al., 2004]. Similar observations have been made in other forested regions [Kulmala et al., 2004a]. The observation of nucleation events took place in remote forested areas, where the release of highly reactive VOCs from trees followed by a rapid oxidation to less volatile products has to be considered a potential source of nucleating vapours. Unfortunately, the amount of condensable material needed to form nanometer particles is extremely small and the chemical identification of the nucleating species is therefore rather difficult. According to Kulmala et al. [2004a], organic vapours could, in principle, participate in nucleation, but nucleation mechanisms that involve organics have not yet been identified. It is very likely, however, that organics contribute to growth of nucleated particles into the size range that they efficiently scatter solar radiation and can act as CCN [O'Dowd et al., 2002].

The effort to understand particle formation and growth from biogenic VOC oxidation is driven not only by the field observations mentioned above, but also by certain characteristics of this group of hydrocarbons. First, it is well established that terrestrial vegetation releases into the atmosphere a tremendous amount of organic compounds (e.g., isoprene, monoterpenes, sesquiterpenes, oxygen-containing compounds) [Guenther et al., 1995]. The large quantities of biogenic VOCs (BVOCs) emitted globally exceed the release of anthropogenic VOCs and have stimulated research into the atmospheric chemistry of these compounds. Secondly, the aerosol formation potential of BVOCs with more than six carbon atoms, as measured in smog chamber experiments, is generally high and, for specific biogenics, the major fraction of products can convert to the particle phase [Hoffmann et al., 1997; Griffin et al., 1999]. Based on information regarding fractional aerosol yields and on available emission inventories, the global production of SOA from oxidation of BVOCs is estimated at between 8 and 40 Tg per year [IPCC, 2001]. Since aerosol formation from BVOC oxidation represents a natural source contributing to the continental background aerosol, knowledge of its contribution to the particle burden of the troposphere is crucial in order to determine the

relative importance of anthropogenic versus natural particle production. The gas-phase chemistry in a forest ecosystem, which is driven by high concentrations of reactive precursor compounds and high UV radiation and leads to aerosol formation, is still poorly understood although some recent progress has been made [Holzinger et al., 2005]. Natural VOCs are also tightly linked with the oxidative capacity of the atmosphere, which involves mainly hydroxyl radicals and ozone. Ozone and particulate concentrations are affected by  $\text{NO}_x$  and both biogenic and anthropogenic VOC emissions. With the levels of  $\text{NO}_x$  and anthropogenic VOCs decreasing, it may be expected in the future that the contribution of biogenic VOCs to ozone and the particle burden in the troposphere will become relatively more important. It should be pointed out, however, that quite a number of non-volatile oxidation products considered as key molecules in aerosol formation processes are of minor relevance for the tropospheric ozone production.

There is a general consensus in the atmospheric chemistry community that monoterpenes, aromatic hydrocarbons, and possibly sesquiterpenes are significant contributors to SOA, while the contribution from isoprene, which is emitted in larger amounts than monoterpenes (estimated at 500 Tg vs 125 Tg [Guenther et al., 1995]), has generally been thought to be negligible based on the smog chamber experiments by Pandis et al. [1991]. However, during the past five years, evidence from both field and laboratory experiments has been obtained for isoprene contributing to SOA formation. Polyols (2-methyltetrols), a hydroxycarboxylic acid (2-methylglyceric acid), and  $\text{C}_5$ -alkene triols, which have retained the  $\text{C}_5$ -isoprene skeleton or a part of it, were characterised and detected in significant amounts in natural background  $\text{PM}_{2.5}$  (particulate matter with diameter smaller than 2.5  $\mu\text{m}$ ) aerosol from the Amazon basin, Brazil, from K-pusztá, Hungary, and from Hyytiälä, Finland [Claeys et al., 2004a,b; Wang et al., 2005; Kourtchev et al., 2005]. In addition, a 2003 summer field campaign at K-pusztá revealed that the 2-methyltetrols and 2-methylglyceric acid exhibit a diel pattern with the highest concentrations during day-time, consistent with their formation through fast photo-oxidation of locally emitted isoprene [Ion et al., 2005]. Furthermore, a field experiment carried out at a Japanese boreal forest site showed significant concentrations of carbonyl-containing oxidation products of isoprene in the  $\text{PM}_{2.5}$  aerosol with maxima in the evening [Matsunaga et al., 2003]. Laboratory studies supporting the contribution of isoprene oxidation to the organic fraction of ambient  $\text{PM}_{2.5}$  are the investigations showing that acidic seed aerosol catalysed the SOA-forming ozonolysis reaction of isoprene [Jang et al., 2002], that exposure to isoprene of quartz fibre filters impregnated with sulphuric acid leads to the formation of oligomeric humic-like substances (HULIS) [Limbeck et al., 2003], and that irradiation of isoprene/ $\text{NO}_x$ /air mixtures in the presence of  $\text{SO}_2$  results in the formation of

2-methyltetrols, 2-methylglyceric acid, as well as other unidentified organic compounds, possibly oligomeric HULIS [Edney et al., 2005].

All together, the impact of BVOCs on air quality and the formation of secondary products affecting our climate on a regional and global scale are far from being understood. A considerable lack of knowledge exists concerning the formation of new particles from BVOCs and the organic chemical composition of natural aerosols. As stated in the review by Kanakidou et al. [2005] on organic aerosol and global climate modelling, SOA formation is a complex and not yet sufficiently understood process.

The objectives of the current project include (1) study of the formation mechanisms of SOA from isoprene (and other BVOCs), assessing their role in particle formation and growth, examining the relative importance of homogeneous photo-oxidation and multi-phase processes, evaluating the importance of HULIS formation, and modelling of the processes involved; (2) identification of particulate-phase oxidation products of isoprene (and other BVOCs), which can be used as indicator compounds for source apportionment, and development and deployment of novel analytical techniques and procedures thereby; and (3) determination of the contribution from the BVOCs to the organic aerosol for various sites in Europe.

## 2. METHODOLOGY

### 2.1. Study of the formation mechanisms of SOA from isoprene (and other BVOCs) by laboratory experiments

The methodology and approaches for reaching objective (1) of this project were quite varied. Experiments and measurements were performed in the laboratory (i.e., in smog chambers and plant growth chambers), at three forested European sites (K-puszta, Hungary; Brasschaat, Belgium; and Hyytiälä, Finland), and during an oceanic cruise and at a remote island in the southern Indian Ocean. The BVOCs, their volatile organic oxidation products, and critical inorganic trace gases are determined and aerosol samples are collected and subjected to comprehensive analyses; in addition, in-situ measurements of particle number concentrations and size distributions, of ion spectra, and of the particulate mass (PM) and particulate organic carbon (OC) are made, and radiation and standard meteorological measurements are performed. The data sets are used for modelling the formation and growth of the fine biogenic atmospheric aerosol. In this section 2.1, we present the methods and approaches for the laboratory experiments; the methods and approaches for other activities are presented in the subsequent sections.

The smog chamber experiments were performed in co-operation with the groups of Prof. J.H. Seinfeld (California Institute of Technology (Caltech), U.S.A.), of Dr. T.E. Kleindienst (National Exposure Research Laboratory of the US Environmental Protection Agency (US EPA), U.S.A), of Prof. U. Baltensperger (Paul Scherrer Institute (PSI), Villigen, Switzerland), and of Prof. H. Herrmann (Leibniz Institute for Tropospheric Research (IfT), Leipzig, Germany). The actual smog chamber experiments and all in-situ (on-line) measurements were made by these teams, but samples were collected for chemical analysis by BIOSOL partner 2 (P2). For details on the chambers and the in-situ (on-line) measurements, reference is made to Surratt et al. [2006], Edney et al. [2005], Paulsen et al. [2005], Iinuma et al. [2007], and to references cited in these papers. P2 performed analyses on aerosol (and other) samples collected from these chambers by gas chromatography-flame ionisation detection (GC-FID), gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) techniques. For GC-FID a 800 Top gas chromatograph (Carlo Erba, Milan, Italy) was used, while for GC/MS a TRACE GC2000 gas chromatograph connected with a Polaris Q ion trap mass spectrometer (Thermo Scientific, San Jose, CA, USA) was employed. GC/MS analysis was performed in the electron ionisation (EI) or chemical ionisation (CI) modes. For LC/MS analysis, a Surveyor Plus system (Thermo Scientific) was coupled to an LXQ linear ion trap mass spectrometer

(Thermo Scientific), and electrospray ionisation in the negative ion mode was used [(-)ESI]. Prior to analysis, the samples were extracted with a mixture of methanol and dichloromethane (1:1, v/v) or with methanol. In addition, prior to GC-FID or GC/MS, the sample extracts were derivatised (e.g., trimethylsilylated) to convert the polar compounds into volatile derivatives. The capillary columns used for GC-FID and GC/MS contained a 95% dimethyl, 5% phenyl polysiloxane stationary phase. The reversed phase C<sub>18</sub>-column employed for LC/MS was a dC18 Atlantis column (Waters); this column contains difunctionally bonded C<sub>18</sub> alkyl residues in order to allow the analysis of very polar analytes. Additional details on the GC-FID, GC/MS, and LC/MS methods used by P2 can be found in Surratt et al. [2006, 2007], Szmigielski et al. [2007a], Maenhaut and Claeys [2007], and Gómez-González et al. [2008].

For the plant growth chamber experiments, it was planned to make use of the growth chambers of BIOSOL partner 3 (P3). Unfortunately, these chambers were badly damaged by a storm in January 2007. Therefore, P2 started a co-operation with the group of Dr. J. Joutsensaari (University of Kuopio, Finland), whereby use is made of the Kuopio growth chambers. The actual experiments were made by this team, but samples were collected for LC/MS analysis by P2. Young Scots pine and Norway spruce plants (2-year old) were housed in a plant chamber and BVOC emissions were triggered by methyl jasmonate. Subsequently, the emitted BVOCs were transferred to a 2 m<sup>3</sup> Teflon reaction chamber with a pressurised air stream and oxidised with ozone (200 ppb). Simultaneously, particle formation and growth was monitored by measuring aerosol particle number size distributions using a differential mobility particle sizer (DMPS). After a reaction time of ca. 60 min the SOA formed was collected on a Teflon or quartz fibre filter. The filters were extracted with methanol:dichloromethane (1:1, v/v) under ultrasonic agitation, and the extract was analysed with the LC/(-)ESI-MS technique. Chromatographic separation of the SOA components was achieved with a dC18 Atlantis column (Waters).

## **2.2. Field experiment at the forested site of K-puszta, Hungary**

From 20 May to 1 July 2006, a field campaign was conducted at the K-puszta background station in Hungary. This station is a mixed deciduous/coniferous forest site [Ion et al., 2005] and is located at 46°58'N, 19°35'E, 136 m above sea level. It is about 15 km to the NW of the town of Kecskemét and about 80 km SE of Budapest. The station is one of the 20 high-quality ground-based stations within the European Union (EU) funded project "European Supersites for Atmospheric Aerosol Research" (EUSAAR) and is also involved in the Global Atmospheric Watch (GAW) network and in the European Monitoring and Evaluation Programme (EMEP). The actual field work at the site took place from 24 May to 29 June 2006. Besides the 4 BIOSOL partners also

two Hungarian teams participated in the field work, i.e., the team of Prof. A. Gelencsér from the University of Pannonia (Veszprém) and that of Prof. I. Salma from Eötvös University (Budapest).

Isoprene ( $C_5H_8$ ), other BVOCs including monoterpenes ( $C_{10}H_{16}$ ) and the hemiterpene 2-methyl-3-buten-2-ol (MBO), and their volatile organic oxidation products were determined by proton-transfer reaction - mass spectrometry (PTR-MS) [Lindinger et al., 1998]. Critical inorganic trace gases (i.e.,  $O_3$  and  $NO_x$ ) were determined by instrumentation, which was available at the site. Particle number concentrations and size distributions (in the size range from 10 nm to 1  $\mu m$ ) were measured with a DMPS and ion spectra (for diameter from 0.5 to 40 nm) were determined with an Air Ion Spectrometer (AIS); both the DMPS and AIS were home-built instruments of BIOSOL partner 4 (P4). The PM, aerosol black carbon (BC), and particulate-phase OC and elemental carbon (EC) were determined in situ and in real time with a Rupprecht and Patashnick tapered element oscillating microbalance (TEOM, model 1400A), a Magee Scientific aethalometer (tape-feeder model AE 14U), and an OCEC Field instrument from Sunset Laboratory, respectively. All three instruments were equipped with a PM<sub>2.5</sub> inlet. The TEOM was a standard TEOM, with the filter heated at 50 °C. The OCEC Field instrument was equipped with a parallel plate denuder to remove VOCs from the incoming air stream. The OCEC Field instrument of Sunset Laboratory is based on the same principles as the lab instrument from the same company and makes use of a thermal-optical transmission (TOT) technique to measure total carbon (TC) and to discriminate between thermal EC and thermal OC [Birch and Cary, 1996]. In addition, the Field instrument provides data for optical EC (OptEC), which are obtained from the transmitted laser light (660 nm) intensity through the sampling filter. From the difference between TC and OptEC, optical OC (OptOC) is then deduced. The in-situ measurements with the TEOM and aethalometer were done with a time resolution of 5 min and those with the OCEC Field instrument with a time resolution of one hour.

Aerosol samples (normally separate day and night samples, with start at 7:00 and 19:00, respectively) for comprehensive organic and inorganic analyses were collected with a variety of filter samplers, including low-volume PM<sub>2.5</sub> and PM<sub>10</sub> collectors [Maenhaut and Claeys, 2007] and a Hi-Vol dichotomous sampler (HVDS) [Solomon et al., 1983], which provides two size fractions (fine: <2.5  $\mu m$  aerodynamic diameter (AD) and coarse (>2.5  $\mu m$  AD)), and with a 10-stage microorifice uniform deposit impactor (MOUDI) [Marple et al., 1991] with 3-stage nano-MOUDI extension. In order to restrict and/or to assess the artifacts in the filter sampling for particulate OC, a cylindrical diffusion denuder for VOCs was deployed in front of the filter [Mikuška et al., 2003; Maenhaut et al., 2004] and/or a tandem (double) filter system

with front and back quartz fibre filters [Maenhaut and Claeys, 2007] was used. All together, 3 low-volume PM<sub>2.5</sub> samplers with quartz fibre filters were deployed, all of them with tandem filters, one with normally day/night time resolution, the other two with normally 24-hour time resolution, with one of these (P25DWW) operated with a diffusion denuder for VOCs upstream of the front filter and the other (P25UWW) without such denuder.

Standard meteorological measurements (of, e.g., temperature, relative humidity, and wind speed and direction) were also performed.

Depending upon the sampler type and/or collection surface, the aerosol samples were analysed for the PM, OC and EC, water-soluble OC (WSOC), various individual water-soluble and organic-solvent extractable species, and a suite of elements. The analytical methods include gravimetry (for the PM), a TOT technique (for OC and EC), ion chromatography (IC) for the inorganic components, and GC/MS, LC/MS, and IC for the organic species [Maenhaut and Claeys, 2007, and references therein]. For measuring WSOC, use was made of a Shimadzu TOC-V CPH analyser and the elements were determined by particle-induced X-ray emission spectrometry (PIXE) [Maenhaut and Claeys, 2007]. The analyses for the PM, OC, EC, WSOC, inorganic and organic ionic components, and elements have all been completed, but the detailed analyses for the organic species are still going on.

Prior to the 2006 campaign, a 2003 campaign was conducted at the K-puszta site by the BIOSOL partners C and P2 [Maenhaut and Claeys, 2007]. This earlier campaign was an aerosol measurement and collection campaign only. A HVDS was deployed in the 2003 campaign too and these samples were subjected to additional analyses for detailed organic compounds as part of the current project.

### **2.3. Field experiment at the state forest "De Inslag", Brasschaat, Belgium**

The state forest "De Inslag" is located at 51°18'33"N, 4°35'14"E, 15 m above sea level, in Brasschaat, Belgium. It is a 79-year old mixed pine-oak forest and is situated at about 12 km NE of the center of the city of Antwerp and at about 9 km to the east of the Antwerp harbour area. The field work at this site was done in co-operation with the Flemish Research Institute for Nature and Forest (Ir. J. Neiryneck); it started on 25 April 2007 and ended on 12 November 2007. Three of the 4 BIOSOL partners (C, P2, and P3) participated in the field work. In-situ measurements for OC, EC, and TC (all in PM<sub>2.5</sub>) were done with a Sunset Laboratory OCEC Field instrument from 25 April to 13 July 2007 (1st period) and from 19 September to 12 November 2007 (2nd period); in between 13 July and 19 September 2007, the instrument was shipped off to Finland

and back for use in the field campaign at the SMEAR II site (see section 2.4). The time resolution of the operation with the OCEC Field instrument was 1 hour during the 1st period of the measurements and 2 hours during the 2nd period. From 5 June until 13 July 2007, a HVDS was deployed for separate day and night aerosol collections in two size fractions (fine:  $<2.5 \mu\text{m AD}$ ; coarse:  $>2.5 \mu\text{m AD}$ ). The inlet for the OCEC Field instrument and the HVDS were located on a tower at about 9 m above ground level. For measuring biogenic and other VOCs, a PTR-MS instrument was deployed at the site from 25 April until the end of October 2007. However, because of instrument problems, good accurate data are only available for the period from the end of July until mid-September 2007. Two intakes were installed on the tower for the PTR-MS measurements, one at 24 m above ground level, the other at 40 m above ground. Because of the problems with the PTR-MS instrument, there are unfortunately no overlapping aerosol and PTR-MS measurements for the site. The samples of the HVDS were analysed by C for OC and EC by TOT and also for WSOC. C analysed both the fine front and back filters by IC for cationic and anionic species, including dicarboxylic acids. P2 performed analyses for detailed organic compounds by LC/(-)ESI-MS of the fine front filters.

P3 was not really satisfied with the results from its VOC measurements by PTR-MS in 2007 and decided therefore to make new measurements in the course of 2008. Unfortunately, there were serious problems with the PTR-MS instrument and good data were not acquired. In order to have the 2008 PTR-MS measurements complemented by measurements for organic aerosols, C decided to perform in-situ measurements for OC with its OCEC Field instrument in parallel. The latter instrument was installed at the site on 9 June 2008, but there were during one month serious problems with it. Good data were obtained from 15 July on until 6 November 2008, when the instrument was removed from the site. The time resolution used for the measurements was 2 h.

#### **2.4. Field experiment at the forested site of SMEAR II, Hyytiälä, Finland**

From 29 July to 2 September 2007, a field campaign was conducted at the Station for Measuring Forest Ecosystem-Atmosphere Relations (SMEAR II) in Hyytiälä, Finland. This station is a boreal coniferous forest station [Boy et al., 2004] and is located at  $61^{\circ}51'N$ ,  $24^{\circ}17'E$ , 181 m above sea level. The largest city near the station is Tampere, ca. 60 km S-SW of the measurement site. Similarly as K-pusztá, SMEAR II is a EUSAAR station. The actual field work at the site took place from 1 to 31 August 2007. Three of the 4 BIOSOL partners (C, P2, and P4) participated in the field work.

The field work for the campaign consisted of in-situ measurements on gases and aerosols and of collection of various types of aerosol samples. Isoprene, other BVOCs, and their volatile organic oxidation products were determined by PTR-MS; critical inorganic trace gases (e.g., O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>) were determined by instrumentation available at the site; particle number concentrations and size distributions were measured with DMPS systems; ion spectra were determined with an AIS; the PM, BC, and particulate-phase OC (and EC) were determined in situ and in real time with a TEOM, an aethalometer, and an OCEC Field instrument, respectively. The real-time measurements were thus similar as for the 2006 campaign at K-puszta; however, the ones for trace gases and various auxiliary parameters were much more extensive than at K-puszta. The time resolution for the OCEC Field instrument was 1, 2, or 4 hours, depending upon the OC levels, whereas the time resolution of the other in-situ measurements was 10 min or better.

As far as the aerosol collections were concerned, the same samplers were deployed as for the 2006 campaign at K-puszta (see section 2.2) and in addition also a small deposit area low pressure cascade impactor (SDI) [Maenhaut et al., 1996a]. The latter device was used with quartz fibre filter impaction substrates for OC and EC analyses by TOT and thus for obtaining the detailed mass size distribution of OC and EC. The collections with the various samplers were mostly done with day/night time resolution, with the day-time samplings from 7:30 to 19:40 local time (UTC+3) and the night-time samplings from 20:20 to 6:40 local time.

Depending upon the sampler type and/or collection surface, the aerosol samples were (or will be) analysed for the PM, OC and EC, WSOC, various individual water-soluble and organic-solvent extractable species, and a suite of elements, using the same analytical techniques as for the samples from the 2006 K-puszta campaign (see section 2.2). The analyses for the PM, OC, EC, WSOC, inorganic and organic ionic components, and elements have all been completed, but the detailed analyses for the organic species by MS still have to be started.

Prior to the 2007 campaign, a less comprehensive campaign was conducted in summer 2005 (i.e., from 28 July to 11 August) at SMEAR II by the BIOSOL partners P2, P4, and C. The work of that campaign also forms part of the current project. Details on the measurements, aerosol collections, and chemical analyses of that 2005 campaign are given in Kourtchev et al. [2008a,b].

## 2.5. Field work during an oceanic cruise and at a remote island in the southern Indian Ocean

These experiments were at the same time conducted within the framework of the EU-funded project "Organics over the Ocean Modifying Particles in both Hemispheres" (OOMPH) and were carried out in co-operation with research teams of France (Dr. J. Sciare, Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif-sur-Yvette) and of Greece (Prof. N. Mihalopoulos, University of Crete (UoC), Heraklion). At the outset, it was planned to have aerosol samples collected during two oceanic cruises, one in the Northern and one in the Southern Hemisphere. The cruise in the Northern Hemisphere took place with the F.S. Meteor in the Mauritanian upwelling region of the tropical North Atlantic from 12 July to 6 August 2006. At the request of Prof. Mihalopoulos, Hi-Vol samples on quartz fibre filter substrates were collected during this cruise by the team of Dr. A. Baker (University of East Anglia, U.K.). The sampler was a 3-stage Hi-Vol cascade impactor [Baker, 2004], providing three size fractions ( $>2 \mu\text{m}$ ,  $1.3\text{-}2 \mu\text{m}$ , and  $<1.3 \mu\text{m}$ ), and a total of 21 daily samples were collected. The coarse ( $>2 \mu\text{m}$ ) and medium ( $1.3\text{-}2 \mu\text{m}$ ) size fractions were collected on impaction substrates, and the fine ( $<1.3 \mu\text{m}$ ) fraction on a back-up filter. The three size fractions of all samples from this cruise were analysed for OC and EC, the fine and coarse size fractions also for WSOC, and the fine fractions also by GC/MS and LC/MS.

As far as the cruise in the Southern Hemisphere is concerned: It was decided not to collect Hi-Vol samples on this cruise, but instead at Amsterdam Island ( $37.52^\circ\text{S}$ ,  $77.32^\circ\text{E}$ ), which is located in the southern Indian Ocean about half-way between the southern edge of Africa and the southern edge of Australia. UGent provided a HVDS to LSCE for deployment by LSCE personnel at the site. The sampler was located on the north side of the island at about 30 m above sea level and the horizontal distance of the HVDS from the sea was around 45 m. A total of 18 HVDS collections (of 5 days) were done in two size fractions (fine:  $<2.5 \mu\text{m}$ , and coarse:  $>2.5 \mu\text{m}$ ) on double Gelman Pall quartz fibre filters, i.e., from 3 December 2006 until 4 March 2007. The front and back filters of both size fractions were subjected by C to analyses for OC, EC, TC, WSOC, and water-soluble inorganic and organic species. Besides, the samples were subjected to LC/(-)ESI-MS by P2; with this technique, the front and back filters of the fine size fraction were analysed for methanesulphonate (MSA), sulphate, and organosulphates, whereas the front and back filters of the coarse size fraction were analysed for MSA. As part of the analyses for organosulphates, it was also examined whether isoprene-related organosulphates were present. SOA from the photo-oxidation of isoprene produced by phytoplankton blooms has been proposed as

a marine SOA source, which could be responsible for the increased cloud droplet concentrations over such blooms [Meskhidze and Nenes, 2006]. The isoprene SOA markers targeted were sulphate esters of the 2-methyltetrols (2-methylthreitol and 2-methylerythritol), which have been reported first by Surratt et al. [2007] and can serve as markers for SOA from the photo-oxidation of isoprene in acidic conditions. Our rationale for considering the 2-methyltetrol sulphates was that the 2-methyltetrols are markers for the photo-oxidation of isoprene under low-NO<sub>x</sub> conditions [Surratt et al., 2006] such as found in a pristine marine environment, and that, if formed, they would be converted to sulphates given that fine marine aerosols contain a substantial amount of sulphate.

## **2.6. Data analyses and interpretation for the laboratory and field experiments**

For both the laboratory and field measurements, the relationships between the concentrations of the BVOCs, their volatile oxidation products, critical inorganic trace gases, other atmospheric and radiative parameters, particle (and ion) numbers and sizes, and the aerosol composition as a function of size (in particular the concentration of particulate-phase BVOC oxidation products) are thoroughly examined. This involves approaches as used by Boy et al. [2004] and Edney et al. [2005]. A major aim of this work is to gain improved insights into the relative importance of homogeneous photo-oxidation and multi-phase processes and in the importance of HULIS formation.

## **2.7. Modelling of the formation and growth of the fine particles and of the fine biogenic atmospheric aerosol**

The data sets obtained are used for modelling the formation and growth of the fine particles and of the fine biogenic atmospheric aerosol. For this purpose, extensive use is made of the modelling capabilities of the Finnish partner (i.e., partner 4), and especially of aerosol dynamics and atmospheric chemistry models, such as the University of Helsinki Multicomponent Aerosol (UHMA) model [Pirjola 1999; Lehtinen and Kulmala, 2003; Laakso et al., 2004; Korhonen et al., 2004]. In these models, aerosol formation and growth, including aerosol dynamics to evaluate sink terms for condensable molecules and gas-phase chemistry to include source terms for these molecules, will be used. Furthermore, process models are coupled with dispersion models. In the chemistry part of the models, the chemistry of O<sub>3</sub>, NO<sub>x</sub>, VOC, and other relevant species are related to aerosol formation. The effects of meteorological dynamics on aerosol processes are studied by applying the aerosol dynamic models in a Lagrangian approach including wave motions and atmospheric mixing. The

concentrations of non-measured critical species, such as the OH and HO<sub>2</sub> radicals, are hereby estimated, as done by Boy et al. [2005].

The characteristics of new particle formation events and cluster ions were examined for the 2006 summer campaign at K-puszta.

## **2.8. Identification of particulate-phase oxidation products of isoprene (and other BVOCs), which can be used as indicator compounds for source apportionment**

For the identification of particulate-phase oxidation products of isoprene (and other BVOCs) useful for source apportionment, archived and newly collected aerosol samples from both laboratory experiments and field campaigns were examined. Unknown compounds, which occur at important levels in gas or liquid chromatograms of the sample extracts, were structurally characterised. For the structural elucidation of unknown compounds, use was made of GC/MS in combination with derivatisation and ion trap MS<sup>n</sup> techniques as well as of LC/MS employing electrospray ionisation and the ion trap MS<sup>n</sup> capability. The latter technique is also used to elucidate the complex chemical structures of the HULIS, which represent an important fraction of natural biogenic aerosol [Zappoli et al., 1999]. On the basis of the results, it is deduced which oxidation products (besides the 2-methyltetrols) are sufficiently stable to serve as marker compounds for the determination of the SOA contribution, which is derived from isoprene. Although the emphasis in this work was placed on oxidation products of isoprene, other unknown compounds, which occur at important levels and which, for example, might be formed by photo-oxidation of other BVOCs, such as the mono- and sesquiterpenes, were characterised as well. Besides advanced multidimensional MS approaches, also nuclear magnetic resonance (NMR) is used for the structural elucidation [Claeys et al., 2007; Szmigielski et al., 2007a].

On the basis of the results obtained from the field campaign samples and those from the various laboratory measurements, it is attempted to construct appropriate source profiles (that is with percentages of the appropriate indicator compounds in the OC generated from the BVOCs), which can be useful for source apportionment, including Chemical Mass Balance receptor modelling.

## **2.9. Determination of the contribution from the BVOCs to the organic aerosol for various sites in Europe**

So far, this work was performed for the PM<sub>2.5</sub> size fraction of the HVDS samples from the 2003 summer campaign at K-puszta [Kourtchev et al., 2009] and for PM<sub>2.5</sub>

samples, which had been collected in summer 2003 in a mixed deciduous forest in Jülich [Kourtchev et al., 2008c]. The secondary organic carbon (SOC) contributions of isoprene and  $\alpha$ -pinene and the OC contributions from wood smoke and fungal spores (and for K-pusztá also from the dicarboxylic acids (DCAs)), were calculated. The SOC contributions from isoprene and  $\alpha$ -pinene were estimated using our measured tracer concentrations and the laboratory-derived tracer mass fractions ( $f_{\text{SOC}}$ ) reported by Kleindienst et al. [2007]. Three isoprene SOA tracers (i.e., the two 2-methyltetrols and 2-methylglyceric acid) and 9  $\alpha$ -pinene SOA tracers were included by these authors in the determination of the  $f_{\text{SOC}}$  data and the  $f_{\text{SOC}}$  data and associated uncertainties reported were  $0.155 \pm 0.039$  for isoprene and  $0.231 \pm 0.111$  for  $\alpha$ -pinene. We used the same set of 3 tracers for isoprene SOA, but our set of tracers for  $\alpha$ -pinene SOA was limited to 3 of the 9 tracers of Kleindienst et al. [2007], i.e., to 3 of the 4 following compounds: *cis*-pinonic acid, *cis*-pinic acid, 3-hydroxyglutaric acid (3-HGA), and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA); as a consequence, our estimate of SOC from  $\alpha$ -pinene has to be considered as a lower limit of the true contribution from  $\alpha$ -pinene. The DCAs, which were measured by us and included in the contribution calculations (for K-pusztá) were oxalic acid, malic acid, succinic acid, glutaric acid, and 2-hydroxyglutaric acid. It was hereby assumed that the short-chain diacids do not form part of the isoprene and  $\alpha$ -pinene SOA in the laboratory experiments of Kleindienst et al. [2007]. Levoglucosan was used as indicator for wood burning and arabitol for fungal spores. For estimating the wood burning OC, use was made of the levoglucosan/OC ratio of 0.179 for Austrian wood smoke, as deduced from Schmidl et al. [2008]. Fungal spores OC was estimated using the arabitol/OC ratio for fungal spores of 0.092, as derived from the data given by Bauer et al. [2008].

### **3. RESULTS**

#### **3.1. Study of the formation of biogenic SOA through smog chamber experiments**

##### **3.1.1. Formation mechanisms of SOA from isoprene**

In co-operation with Caltech, a study was performed to obtain insights into the formation mechanisms of SOA from isoprene, in particular the mechanisms that result in the formation of 2-methyltetrols, 2-methylglyceric acid (2-MG), and HULIS. An extensive series of smog chamber experiments was performed under various conditions, in particular at low- and high-NO<sub>x</sub> levels, and with and without seed aerosol. The results from the chamber experiments were compared with results for fine aerosol that had been collected in the Amazon forest.

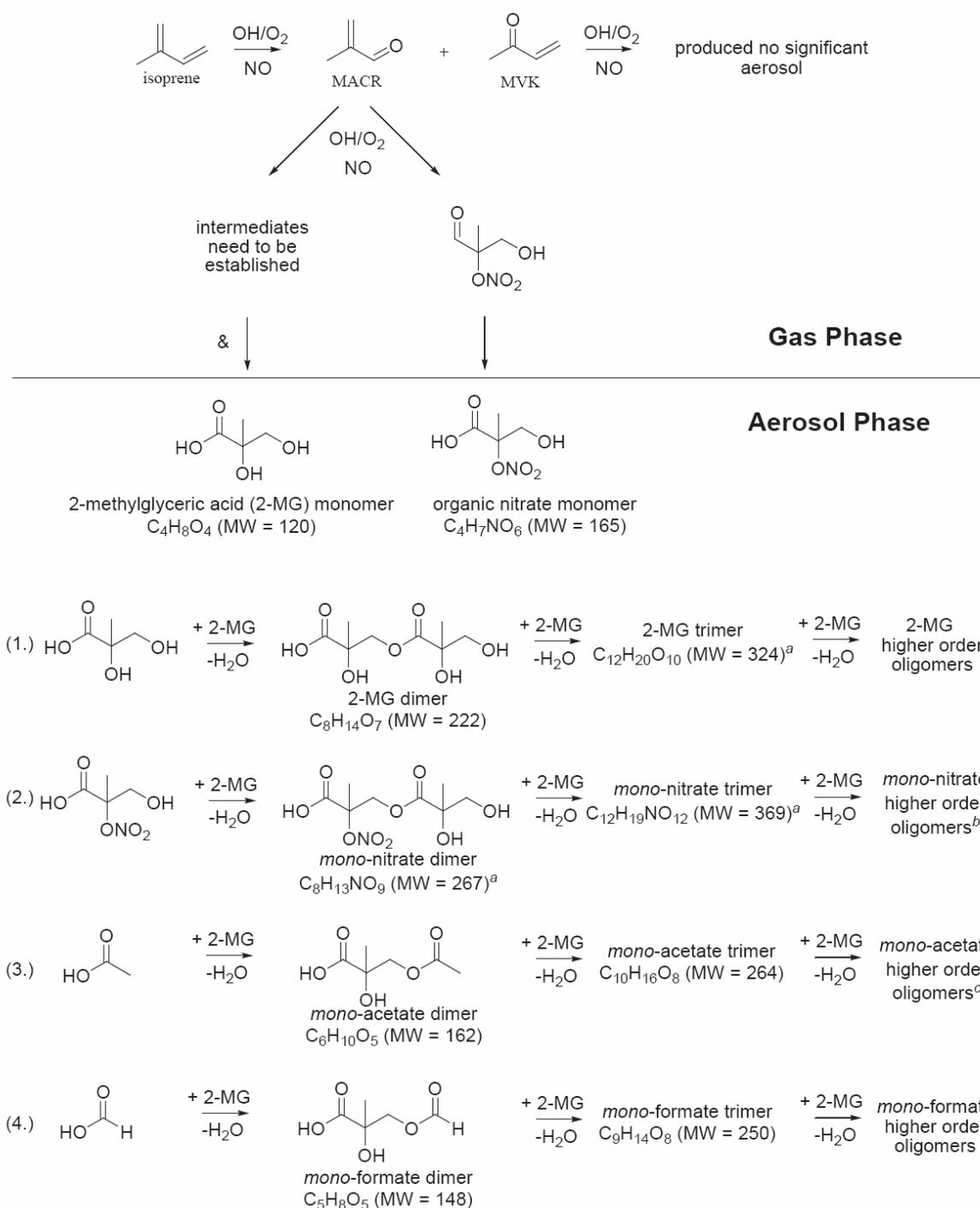
It was found that the chemical nature of the smog-chamber SOA was significantly different between the two NO<sub>x</sub> regimes. For the high-NO<sub>x</sub> conditions, the SOA components were acidic and formed upon the further oxidation of methacrolein (MACR), where currently no other first-generation gas-phase products appear to contribute to SOA formation. The low-NO<sub>x</sub> SOA was found to be neutral in nature owing to the formation of polyols and organic peroxides. MACR was found not to contribute to SOA formation under low-NO<sub>x</sub> conditions, which is likely due to hydroperoxide formation. Based on SOA growths, acid-catalysis seemed to play a larger role under low-NO<sub>x</sub> conditions. By using a conventional iodometric-spectroscopic method, it was found that organic peroxides (likely dominated by hydroperoxides) contributed significantly to the low-NO<sub>x</sub> SOA mass [~61% for nucleation experiments (these are experiments without seed aerosol) and ~25% and 30% for dry seeded and acid seeded experiments, respectively].

Oligomerisation was observed to be an important isoprene SOA formation pathway for both low- and high-NO<sub>x</sub> conditions. The nature of the oligomers, however, was distinctly different in each NO<sub>x</sub> regime. The high-NO<sub>x</sub> oligomers have an obvious monomeric unit, where observable 102 Da differences were detected with the on-line and off-line mass spectrometry techniques. These high-NO<sub>x</sub> oligomers were characterised as oligo-esters, where their formation could be explained by particle-phase esterification reactions involving 2-methylglyceric acid as the key monomeric unit. These oligo-esters accounted for a substantial fraction (~22-34%) of the SOA mass formed from isoprene oxidation under high-NO<sub>x</sub> conditions.

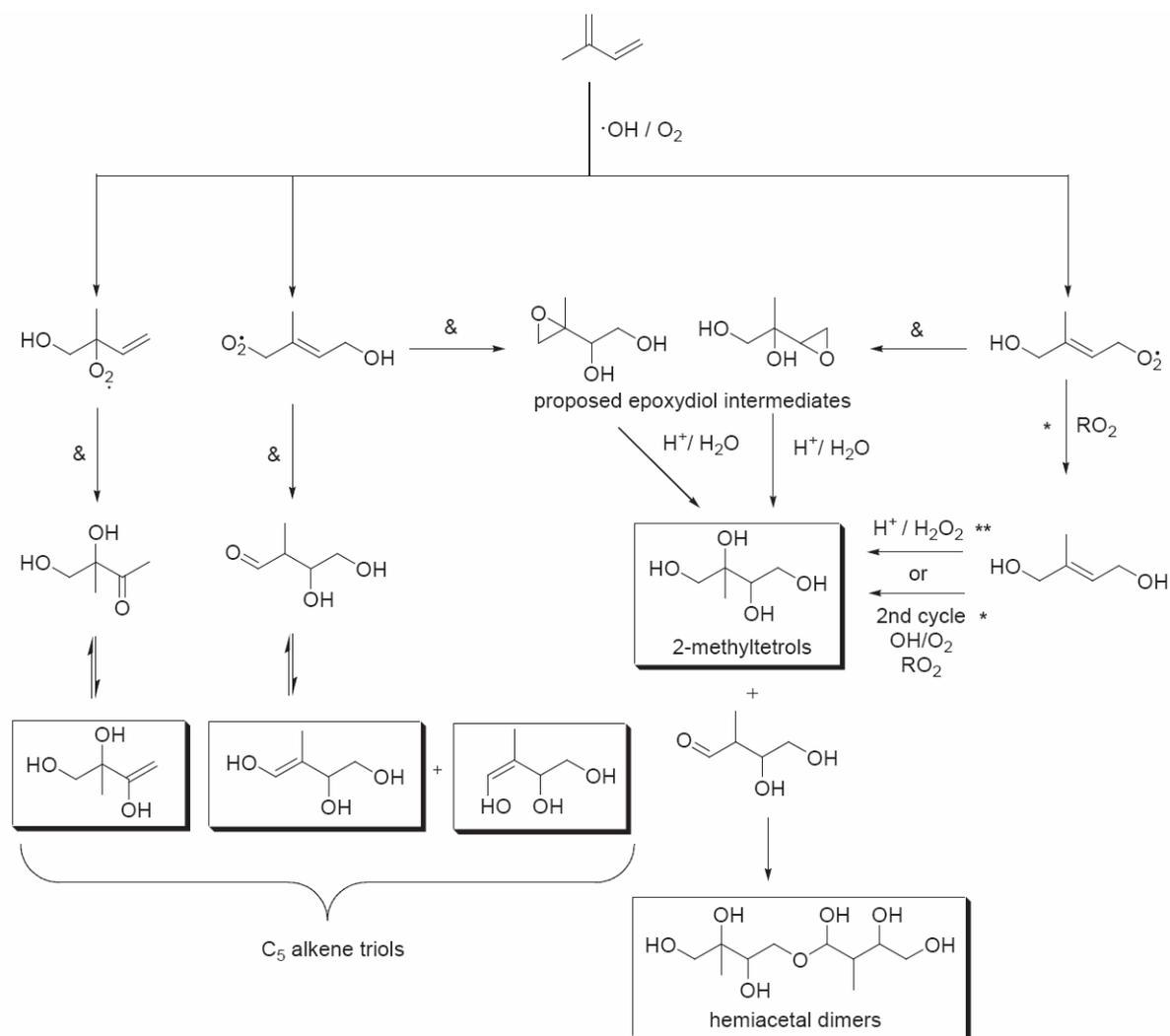
Tracer compounds for isoprene oxidation in the ambient atmosphere, which had been detected for samples from the Amazon Basin, were detected in the low-NO<sub>x</sub> chamber experiments with isoprene. They included C<sub>5</sub>-alkene triols and hemiacetal dimers, which were detected for the first time in a controlled laboratory experiment, suggesting that the oxidative conditions used in these experiments are relevant to remote regions of the world. It was elucidated that the hemiacetal dimers formed in these low-NO<sub>x</sub> chamber experiments result from the reaction of 2-methyltetrols and C<sub>5</sub>-alkene triols (a pathway that is likely relevant to the real atmosphere). Higher mass hemiacetals (and acetals) evaded detection using the GC/MS derivatisation technique, owing to the possible thermal decomposition of these higher mass oligomers and/or being permanently retained on the GC/MS column. The detection of C<sub>5</sub>-alkene triols and the unstable products, tentatively characterised as 2-methyltetrol performate derivatives, provides evidence for the rearrangement of hydroxyperoxy radicals or the decomposition/rearrangement of hydroperoxides, formed from the initial oxidation (OH/O<sub>2</sub>) of isoprene, into C<sub>5</sub>-alkene triols and epoxydiols. Besides the formation of hemiacetal (acetal) oligomers in low-NO<sub>x</sub> SOA, it is speculated (despite lack of spectroscopic evidence) that peroxyhemiacetal oligomers could also form, owing to the large amounts of peroxides measured in the particle phase.

Based on the results of this study mechanisms could be proposed for the formation of isoprene SOA under both high- and low-NO<sub>x</sub> conditions (Schemes 1 and 2).

More details on this isoprene smog chamber study and the structural characterisation of isoprene SOA compounds can be found in two comprehensive published articles [Surratt et al., 2006; Szmigielski et al., 2007a].



**Scheme 1.** Proposed mechanism for SOA formation from isoprene photo-oxidation under high- $\text{NO}_x$  conditions. Symbol used: &, further study needed in order to understand the formation (in gas/particle phase) of 2-MG.  
<sup>a, b and c</sup>Elemental compositions confirmed by accurate mass ESI-MS.



**Scheme 2.** Low- $\text{NO}_x$  SOA formation pathways as elucidated by GC/MS. Symbols used: &, further study needed for the formation of the hypothetical carbonyl diol and epoxydiol intermediates which may result from the rearrangements of  $\text{RO}_2$  radicals and/or hydroperoxides.

### 3.1.2. Formation mechanism of 2-methyltetrols from gaseous precursors

In co-operation with PSI, a smog chamber study was performed to gain insights into the formation mechanism of 2-methyltetrols from gaseous precursors and to identify relatively polar gas-phase oxidation products of isoprene. Photo-oxidation experiments were conducted with isoprene (2 ppm) in the presence of  $\text{NO}_x$  (NO, 500 ppb;  $\text{NO}_2$ , 500 ppb) in a 27- $\text{m}^3$  Teflon chamber. The oxidation reaction was initiated by UV irradiation and after a reaction time of 3.5 h, the filtered chamber content containing gaseous photo-oxidation products of isoprene was passed through a quartz fibre filter that was impregnated with sulphuric acid or a non-treated filter.

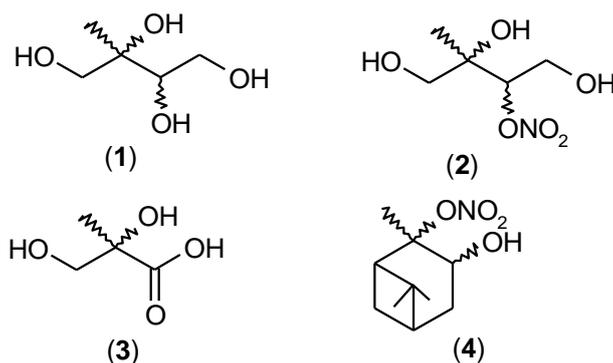
It was found that the 2-methyltetrol concentration is significantly increased in the sulphuric acid-treated filter compared to the non-treated filter. These results support that formation of 2-methyltetrols in SOA from the photo-oxidation of isoprene involves acid-catalysed hydrolysis of gaseous precursors, as proposed in previous work. More specifically, the formation of 2-methyltetrols can be readily explained by acid-catalysed degradation of methylnitrooxybutanetriols and methyl dinitroxybutanediols, which are known to form in the presence of  $\text{NO}_x$ . In addition, a relatively polar photo-oxidation product of isoprene was collected on the sulphuric acid-treated filter. This compound was tentatively identified as a novel  $\text{C}_5$ -hydroxydicarbonyl compound (molecular weight (MW): 116; 4-hydroxy-1,3-diketo-2-methylbutane) based on its chromatographic behaviour and detailed interpretation of electron and chemical ionisation mass spectral data. The formation of 4-hydroxy-1,3-diketo-2-methylbutane can be explained through acid-catalysed degradation of methylnitrooxybutanetriols and methyl dinitroxybutanediols but also involves acid-catalyzed loss of the tertiary hydroxyl group and formal loss of nitrous acid (HONO).

### 3.1.3. Structure of marker compounds for the photo-oxidation of $\alpha$ -pinene

In co-operation with US EPA, a smog chamber study was carried out to elucidate the structures of marker compounds for the photo-oxidation of  $\alpha$ -pinene, which were also detected in fine aerosol that had been collected during the 2003 summer campaign in K-puszta, Hungary. The results of this study are presented in section 3.8.

### 3.1.4. Studies on organosulphates

P2 collaborated in the interpretation of results on organosulphates which were obtained by Caltech and US EPA in smog chamber experiments with isoprene and  $\alpha$ -pinene. In this study, experiments were done under different  $\text{NO}_x$  conditions in the absence and presence of sulphuric acid seed aerosol. Over the full range of  $\text{NO}_x$  conditions, resultant sulphate esters in isoprene and  $\alpha$ -pinene SOA were identified and structurally elucidated. Sulphate esters were found to account for a larger fraction of the SOA mass with increased acidity of seed aerosol, providing an explanation for the "acid-effect" in SOA formation. Many of the isoprene and  $\alpha$ -pinene sulphate esters identified in the chamber experiments were also found in aerosol collected from the southeastern US and K-puszta, Hungary, demonstrating the atmospheric relevance of these particle-phase reaction products. The isoprene and  $\alpha$ -pinene photo-oxidation products of which organosulphate derivatives were identified include (Scheme 3): 2-methyltetrols (**1**), 2-methyltetrol *mono*-nitrate derivatives (**2**), 2-methylglyceric acid (**3**), and  $\alpha$ -pinanediol hydroxynitrate (**4**).



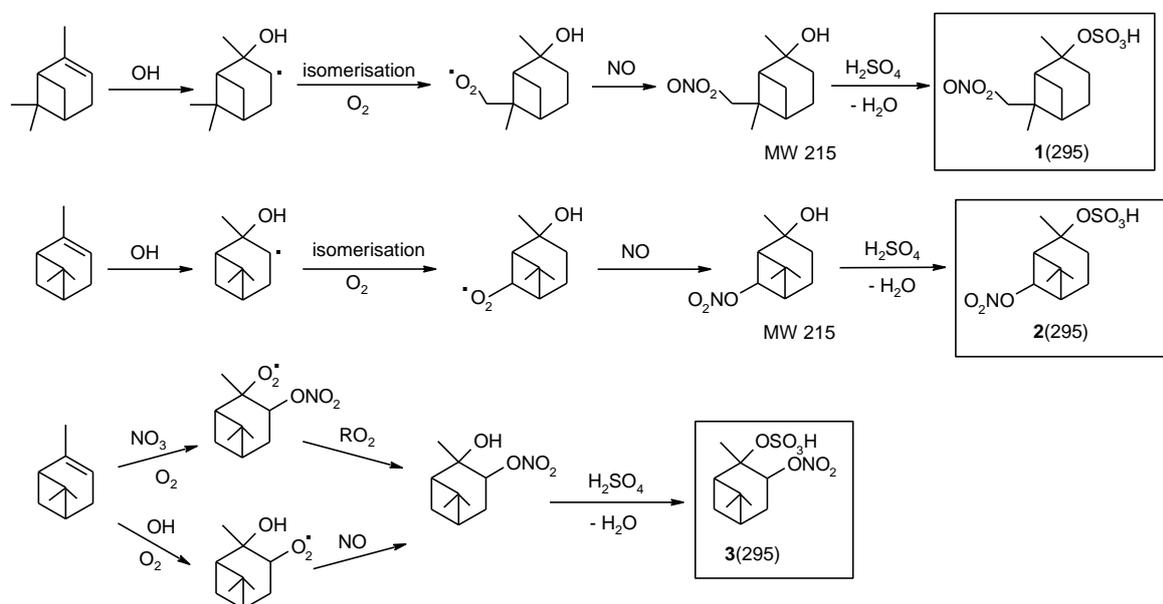
**Scheme 3.** Photo-oxidation products of isoprene and  $\alpha$ -pinene for which sulphate derivatives were identified.

Further details on this study can be found in a published article [Surratt et al., 2007].

P2 also contributed to a smog chamber study performed by the IfT with interpretation of results and interpretation of mass spectral data. This study dealt with the characterisation of an organosulphate from the ozonolysis of  $\beta$ -pinene and of other organosulphates from the photo-oxidation of monoterpenes. Organosulphates were only found in SOA from  $\beta$ -pinene ozonolysis in the presence of acidic sulphate seed particles. One of the detected organosulphates also occurred in ambient aerosol samples that were collected at a forest site in northeastern Bavaria, Germany.  $\beta$ -Pinene oxide, an oxidation product in  $\beta$ -pinene/ $O_3$  and  $\beta$ -pinene/ $NO_3$  reactions, is identified as a possible precursor for the  $\beta$ -pinene-derived organosulphate. Furthermore, several nitrooxy-organosulphates originating from monoterpenes were found in the ambient samples. These nitrooxy-organosulphates were only detected in the night-time samples suggesting a role for night-time chemistry in their formation. Their LC/MS chromatographic peak intensities suggest that they represent an important fraction of the organic mass in ambient aerosols, especially at night. More details on this study are given in Iinuma et al. [2007].

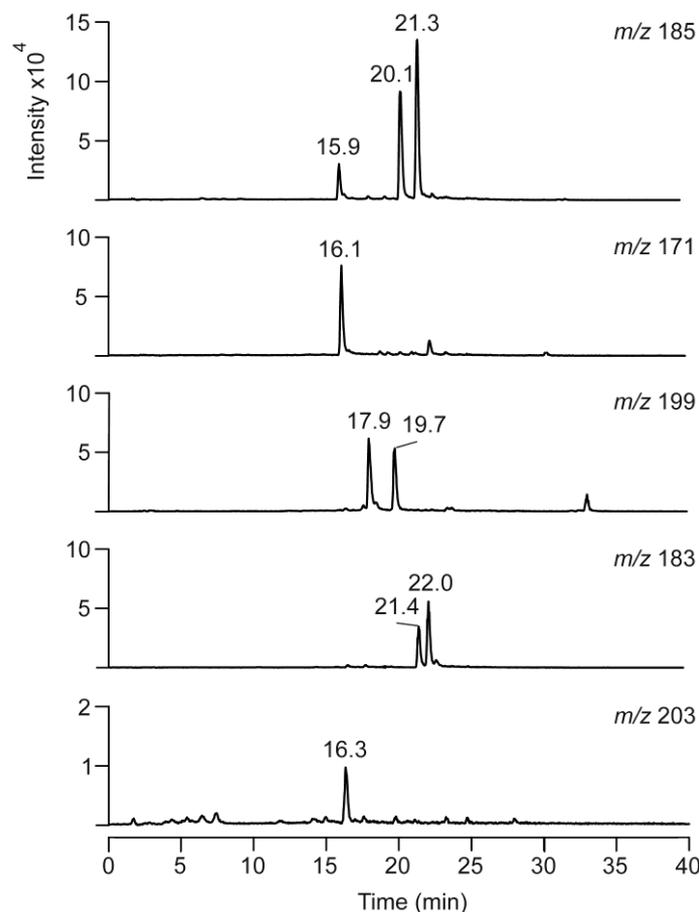
In cooperation with Caltech and EPA, the mechanism and ubiquity of organosulphate formation in biogenic SOA was comprehensively investigated by a series of laboratory photo-oxidation and night-time oxidation experiments using isoprene and monoterpenes ( $\alpha$ - and  $\beta$ -pinene, *d*- and *l*-limonene,  $\alpha$ -terpinene,  $\gamma$ -terpinene, and terpinolene). In addition, archived laboratory-generated isoprene SOA and ambient filter samples from the southeastern US were re-examined for organosulphates and nitrooxy organosulphates. Only SOA compounds that were also detected in ambient PM<sub>2.5</sub> aerosol from the southeastern USA were selected for structural characterisation. In addition, C estimated for PM<sub>10</sub> samples of K-pusztá, Hungary, which contain the same organosulphates as the samples from the southeastern USA,

for which a fraction of the OM may be due to organosulphates. In these calculations, C made use of its sulphur data obtained by particle-induced PIXE and of its sulphate data obtained by IC for the samples from the 2003 summer campaign at K-puszt. It was found that the organosulphates were formed only when monoterpenes were oxidised in the presence of acidified sulphate seed aerosol, a result consistent with prior work. By comparing the tandem MS and accurate mass data collected for both the laboratory-generated and ambient aerosol, previously uncharacterised ambient organic aerosol components were found to be organosulphates of isoprene,  $\alpha$ -pinene,  $\beta$ -pinene, and limonene, thus demonstrating the ubiquity of organosulphate formation in ambient SOA. Several of the organosulphates of isoprene and of the monoterpenes characterised in this study provide ambient tracer compounds for the occurrence of biogenic SOA formation under acidic conditions. Furthermore, the night-time-oxidation experiments conducted under highly acidic conditions revealed one viable mechanism for the formation of previously identified nitrooxy organosulphates found in ambient night-time aerosol samples. It was estimated that the contribution from organosulphates to the total organic mass fraction for the PM10 samples from the 2003 K-puszt summer campaign can be as high as 30%. Based on this study, reaction mechanisms for the formation of the MW 295 nitrooxy organosulphates related to  $\alpha$ -pinene were proposed (Scheme 4). For isomers **1** and **2**(295), it remains unclear how the  $\text{NO}_3$ -initiated oxidation produces these products in the presence of highly acidified sulphate seed aerosol. Further work is recommended to address this issue. A comprehensive article on this study was published [Surratt et al., 2008].



**Scheme 4.** Proposed mechanisms for formation of the isomeric MW 295 nitrooxy organosulphates related to  $\alpha$ -pinene.

### 3.2. Study of the formation of biogenic SOA through plant growth chamber experiments



**Figure 1.** LC/(-)ESI-MS extracted ion chromatographic data obtained for SOA produced from BVOCs emitted by Scots pine.

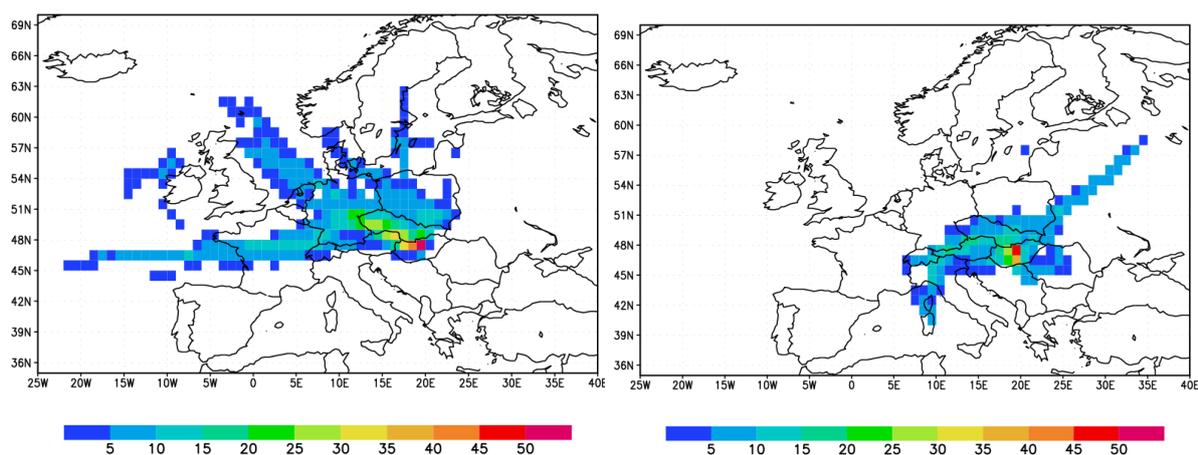
As indicated in section 2.1, the plant growth chamber experiments were carried out at the University of Kuopio. Figure 1 shows LC/(-)ESI-MS data obtained for SOA produced from BVOCs emitted by Scots pine after triggering the plant with methyl jasmonate. Several terpenoic acids could be detected in their deprotonated form at  $m/z$  185, 171, 199, 183, and 203. Similar results were obtained for SOA from BVOCs emitted by Norway spruce. Some of the detected compounds could be identified using available reference standards, i.e., *cis*-pinic acid ( $m/z$  185 compound with retention time (RT) 20.1 min) and *cis*-pinonic acid ( $m/z$  183 compound with RT 21.4 min), which are known ozonolysis products of  $\alpha$ -pinene. The mass spectra obtained for the  $m/z$  185 compound (RT 21.3 min) and the  $m/z$  183 compound (RT 22.0 min) were similar to those obtained for *cis*-pinic acid and *cis*-pinonic acid, respectively, and were tentatively attributed to analogues of  $\Delta^3$ -carene, which was found to be a major monoterpene emitted from the Scots pine foliage.

The  $m/z$  199 compounds were tentatively assigned to 10-hydroxy-*cis*-pinonic acid (RT 17.9 min) and its  $\Delta^3$ -carene analogue (RT 19.7 min). The  $m/z$  203 compound (RT 16.3 min) showed features similar to 3-methyl-1,2,3-butanetricarboxylic acid, which has been reported as a stable end-oxidation product of  $\alpha$ -pinene [Szmigielski et al., 2007b]. The  $m/z$  185 (RT 15.9 min) compound was found to correspond to an unknown compound, while the  $m/z$  171 (RT 16.1 min) compound was attributed to terpenylic acid, a recently identified  $\alpha$ -pinene SOA tracer [Claeys et al., 2009].

### 3.3. Comprehensive studies during the 2006 summer campaign at the forested site of K-pusztá, Hungary

#### 3.3.1. Meteorology and air mass origin

The field campaign took place from 24 May to 29 June 2006. From the start of the campaign until 11 June, it was unusually cold with daily maximum temperatures between 12 and 23 °C, but from 12 June onward higher temperatures were noted with daily maxima from 24 to 36 °C. The air mass origin, as calculated with HYSPLIT [Lupu and Maenhaut, 2002], was also quite different during the two periods (see Figure 2). During the cold period (24 May – 11 June 2006), the air masses came from the northwest and often originated over the North Sea and/or the Atlantic Ocean. In contrast, during the warm period (12-29 June 2006), the air masses had essentially a continental character and were more stagnant.



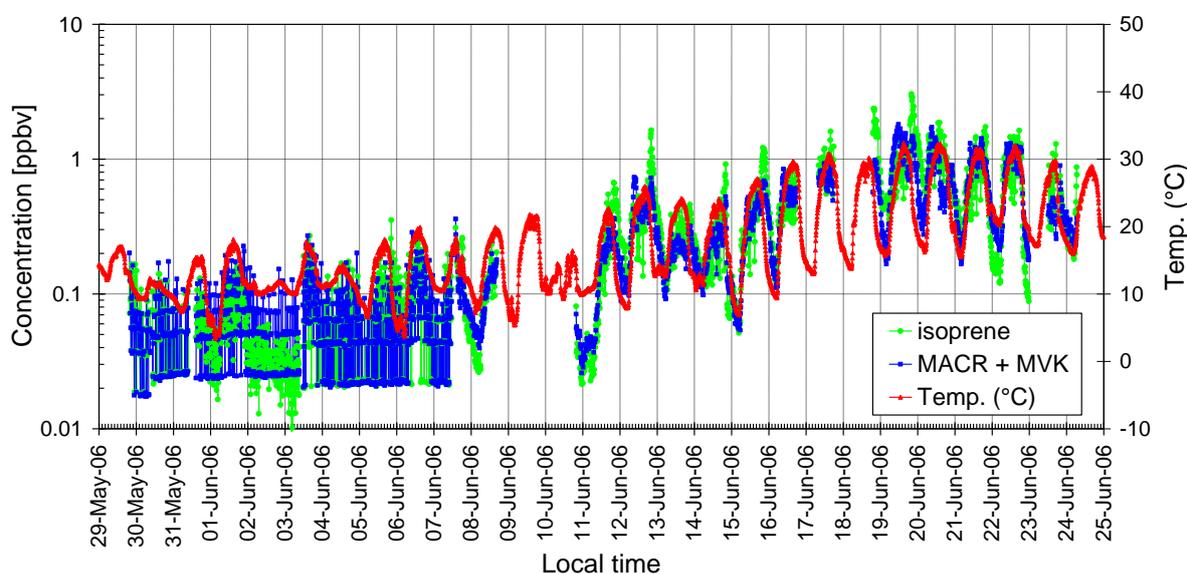
**Figure 2.** Air mass origin for the cold (left) and warm (right) periods of the 2006 summer campaign at K-pusztá. The plots show the number of trajectory crossings per grid cell (2.5° x 2.5° grid) in colour code for each of the two periods (only numbers of crossings of 4 and higher are depicted). The trajectories used were 5-day 3-dimensional back trajectories, calculated for every 6 hours and for an arrival level of 100 m above ground (The results for an arrival level of 300 m above ground were fairly similar).

### 3.3.2. VOC data and relation to temperature

From the data for the VOCs and their oxidation products, as obtained by PTR-MS, it was quite clear that much higher levels were observed during the warm period than during the cold one (Table I). This difference is to be expected, given that both formation and emission of the VOCs by plants increase with light and temperature.

**Table I.** Interquartile atmospheric concentration ranges for selected VOCs under different weather conditions. 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.

Weather period	Interquartile concentration ranges for selected compounds (ppbv)						
	Isoprene ( <i>m/z</i> 69)	MACR and MVK ( <i>m/z</i> 71)	Mono- terpenes ( <i>m/z</i> 137)	Nopinone ( <i>m/z</i> 139)	Pinonal- dehyde ( <i>m/z</i> 151)	MBO ( <i>m/z</i> 87)	Benzene ( <i>m/z</i> 79)
Cold (cloudy)	0.028 - 0.090	0.026 - 0.093	0.019 - 0.044	0.0039 - 0.0079	0.0029 - 0.0063	0.046 - 0.074	0.038 - 0.066
Warm (sunny, clear sky)	0.24 - 0.82	0.24 - 0.71	0.089 - 0.63	0.028 - 0.062	0.011 - 0.036	0.12 - 0.21	0.049 - 0.086

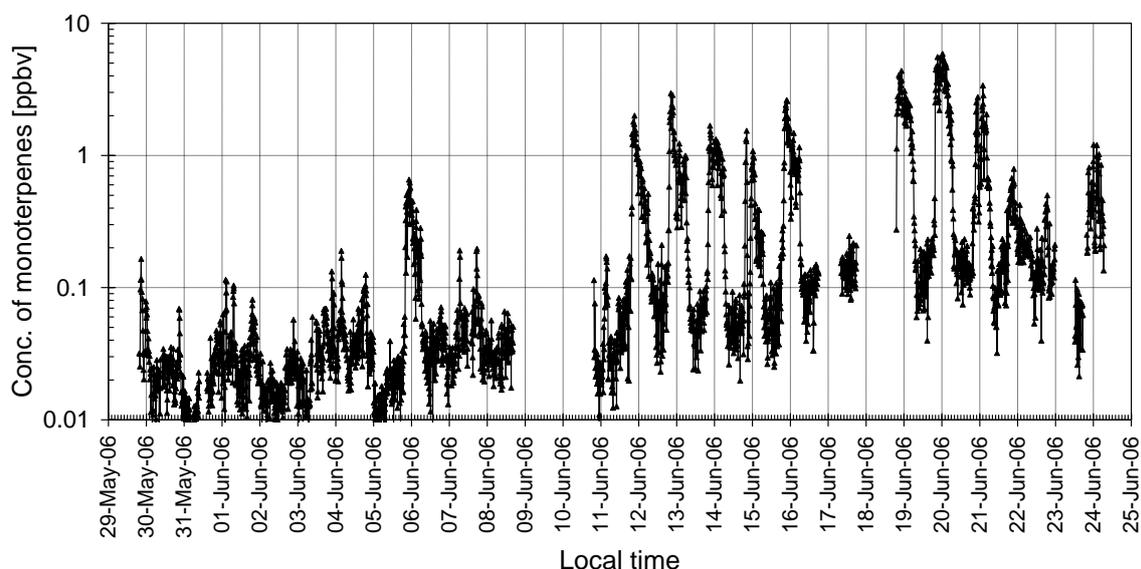


**Figure 3.** Time series of the atmospheric concentrations of isoprene (*m/z* 69), its oxidation products (*m/z* 71) [i.e., methacrolein (MACR) and methyl vinyl ketone (MVK)], and of the air temperature at K-pusztá for the period from 29 May to 25 June 2006. Note that a log scale is used for the VOCs and a linear scale for the temperature. The vertical dashed lines are at 00:00 h.

When looking at the data with high-time resolution (10-15 min) (see Figure 3), 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 of the order of 1 hr, this behaviour is not surprising.

The regression equation of the high-time resolution data for isoprene (in ppbv) as a function of air temperature (in °C) for the period from 29 May to 25 June 2006 was  $y = 0.014 * e^{0.140x}$  [ $R^2 = 0.63$ ]. This equation can also be written as  $y = 0.014 * 4.06^{x/10}$ ; this indicates that there is a factor of 4 increase in isoprene concentration per 10 °C increase in temperature. This is much higher than the value typically observed for biological reactions (which is about 2). For comparison, Lappalainen et al. [2009] found a lower dependence on air temperature for the day-time isoprene concentration at the SMEAR II station in Hyytiälä, Finland, during the period 6 June, 2006 - 31 August, 2007. Their equation was  $y = 0.033 * e^{0.085x}$  [ $R^2 = 0.65$ ], which corresponds to  $y = 0.033 * 2.34^{x/10}$ .

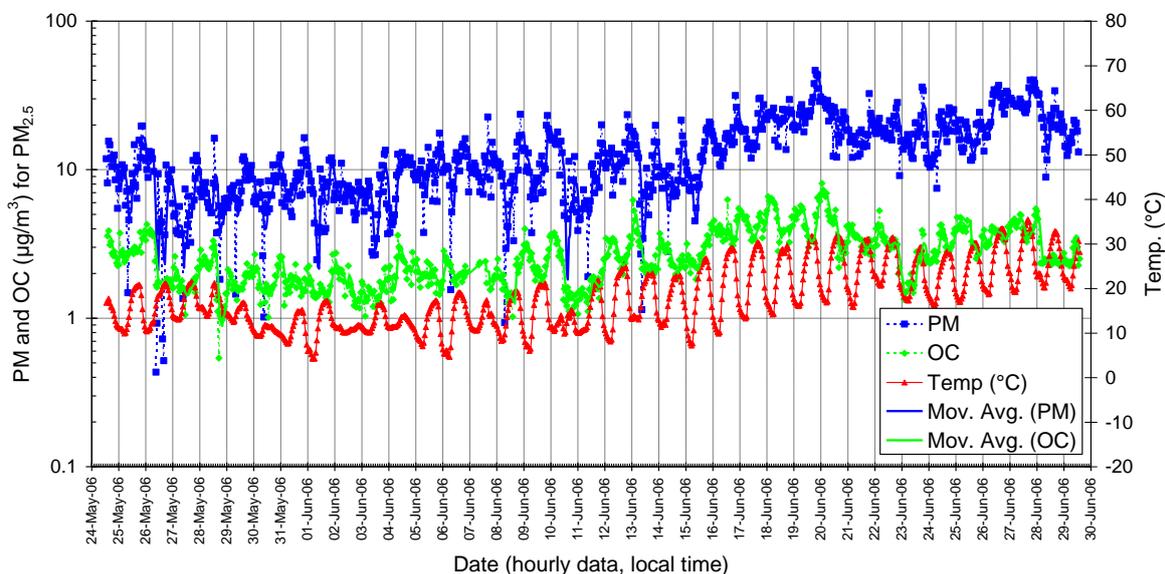


**Figure 4.** Time series of the atmospheric concentration of monoterpenes ( $m/z$  137) at K-pusztá for the period from 29 May to 25 June 2006. The vertical dashed lines are at 00:00 h.

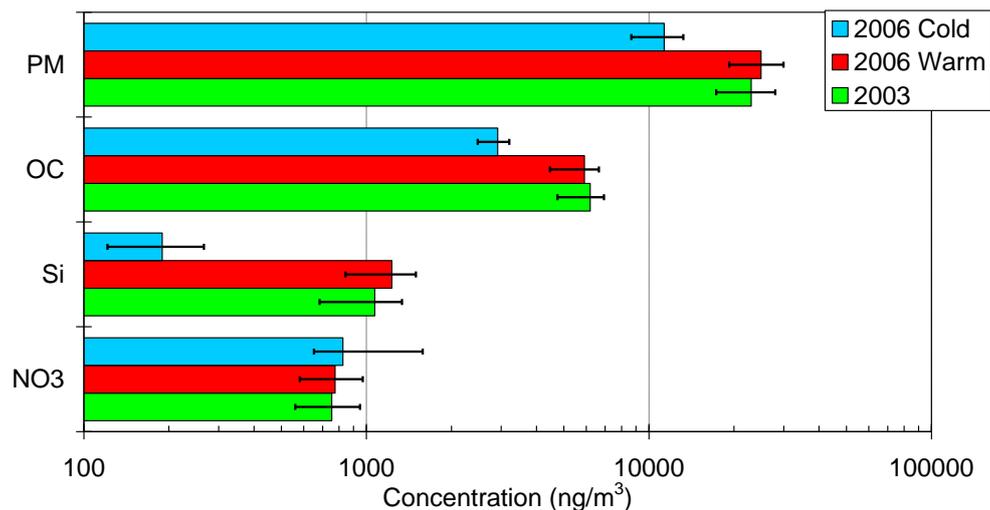
The concentrations of the monoterpenes ( $m/z$  137) also followed the temperature when examining these data with low time resolution (such as daily averages) or the separate high-resolution day-time and night-time data. For example, a similar regression on temperature as for isoprene for the day-time monoterpene data indicated that  $y = 0.008 * 2.46^{x/10}$  [ $R^2 = 0.56$ ]. However, when looking at the combined day-time and night-time data (Figure 4), it appears that the concentration of the monoterpenes is about an order of magnitude higher during the night than during the day. The difference in behaviour between the monoterpenes and isoprene is in part explained by the longer atmospheric lifetime of the monoterpenes.

### 3.3.3. Relation of the data for the PM and various aerosol components to temperature

An increase with temperature was also observed for the 24-hr (or day-time or night-time) averaged concentrations of fine PM and fine OC (whereby fine = PM<sub>2.5</sub>) from the in-situ instruments (TEOM and OCEC Field instrument) and for the data of a number of components in the filter samples. The relationship between air temperature and the hourly fine PM (TEOM) and fine OC (OCEC Field instrument) data is shown in Figure 5. Although there is clearly an increase in fine PM and fine OC when going from the cold to the warm period, the high-time resolution dependence of the two components on temperature seems to be quite complicated. For example, during the warm period (from 12 June on) there is clearly a tendency for opposite diurnal variation of OC and temperature. This behaviour is similar to that for the monoterpenes, be it that it is much less pronounced. The higher OC levels during night than during the day may be due to a combination of several reasons, including the build-up of a shallow atmospheric boundary layer during the night, the larger partitioning of semi-volatile organic compounds towards the vapour phase during the warm day, increased formation of SOA from condensable compounds during the cool night, and/or specific night-time chemistry resulting in SOA formation.



**Figure 5.** Time series (hourly data) of PM<sub>2.5</sub> PM and OC and of the air temperature during the 2006 summer K-pusztá campaign (the vertical dashed lines are at 00:00 h). Full lines for the PM and OC are 4-point moving averages.



**Figure 6.** Median concentrations (and interquartile ranges) for the PM, OC, Si, and nitrate in PM<sub>10</sub> aerosol in the separate cold and warm periods of the 2006 summer campaign at K-pusztá and for the entire 2003 summer campaign at the same site. All data were obtained from filter samplers, which were operated with mostly 12-h time resolution.

The median concentrations (and interquartile ranges) for the PM, OC, Si (an indicator for the mineral dust or crustal component), and nitrate in PM<sub>10</sub> during the separate cold and warm periods of the 2006 summer campaign are shown in Figure 6, together with the overall medians (and interquartile ranges) for the same aerosol components in the 2003 summer campaign at the same site. It was very hot and dry during the entire 2003 campaign, similar as during the warm period of the 2006 campaign. Clearly, higher levels are noted for PM, OC, and especially Si during the warm period than during the cold one of the 2006 campaign. In contrast, for nitrate, the levels are highest during the cold period. Overall, the data from the 2003 campaign are quite similar to those from the 2006 warm period.

The relationships between the PM<sub>10</sub> data of the crustal component (obtained as explained below) and OC (each in  $\mu\text{g}/\text{m}^3$ ) and the air temperature (in  $^{\circ}\text{C}$ ) for the 2006 summer day-time samples were  $y = 0.097 * e^{0.150x}$  [ $R^2 = 0.84$ ] and  $y = 1.094 * e^{0.059x}$  [ $R^2 = 0.87$ ], respectively. The higher concentrations of OC at elevated temperature are attributed to higher emissions of primary organic matter by the vegetation and of biogenic SOA precursors, such as isoprene and monoterpenes, followed by fast SOA formation. As to the steep increase of crustal matter with temperature, this is likely due to much more intense soil dust mobilisation on the local and regional scale, probably because of the combination of a drier soil and increased agricultural activities in warm weather.

As indicated above in relation to Figure 6, aerosol nitrate levels (expressed per  $\text{m}^3$  of air) were higher during the cold period than during the warm one. When expressing

nitrate as concentration in the aerosol (instead of in the ambient air), the dependence on temperature was even more pronounced. The relationship between the  $\text{NO}_3/\text{PM}$  ratio in  $\text{PM}_{2.5}$  and the air temperature over all filter samples (thus day-time + night-time) was  $y = 0.305 * e^{-0.117x}$  [ $R^2 = 0.66$ ]. It should be indicated that there was sufficient ammonium in the fine aerosol to fully neutralise the fine sulphate and nitrate to  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$ . The  $\text{NO}_3/\text{PM}$  ratio in  $\text{PM}_{2.5}$  increased with increasing air relative humidity (RH), which is not surprising considering that RH was inversely related to temperature. It is well known that the equilibrium between  $\text{NH}_4\text{NO}_3$  and the gas-phase species  $\text{NH}_3$  and  $\text{HNO}_3$  depends on temperature and RH [e.g., Stelson and Seinfeld, 1982]. At higher temperature particulate  $\text{NH}_4\text{NO}_3$  dissociates into the gas-phase species. On the other hand, artifacts during the aerosol collection may also have played a role.

### 3.3.4. Examination of the VOC data set by Principal Component Analysis

To better understand the relationships between the compounds measured by PTR-MS, Principal Component Analysis (PCA) was applied to the full data set from 29 May to 25 June. This full data set contained 2901 observations for 59 variables (atmospheric concentrations of 59  $m/z$  values). Seven components were found to explain more than 1 unit of variance. These 7 components explained 84% of the total variance in the data set. Each component represents an independent group of strongly correlated  $m/z$  values, as is indicated by the loadings of the  $m/z$  values on the components. When certain  $m/z$  values exhibit a high loading on a component, this suggests that their release from the vegetation (or from anthropogenic activity in the case of non-biogenic VOCs) and/or their formation/destruction in the atmosphere is correlated in time. It does not necessarily mean that these  $m/z$  values reflect fragments or compounds that are truly interdependent (such as isoprene and its oxidation products), although this could be the case. Correlation between independent compounds in time could, for example, occur if the release or production of these compounds is controlled by the same driver, such as stomatal conductance or irradiance. The results presented here only show the observed correlations, not the potential drivers.

The variables ( $m/z$  values) that were highly loaded ( $> 0.7$ ) on the first 4 principal components were:

Component 1: 43, 61, 69, 70, 71, 85, 87, 99, 101, 111, 113, 115, 117, 123, 125, 127, 141, 143, 145, 155, 157, 159, 163, 167, 169, 171, 173. The species associated with this component include acetic acid ( $m/z$  43 and 61), isoprene ( $m/z$  69 and 70), methacrolein ( $m/z$  71) and methyl vinyl ketone ( $m/z$  71), and a wide range of other compounds.

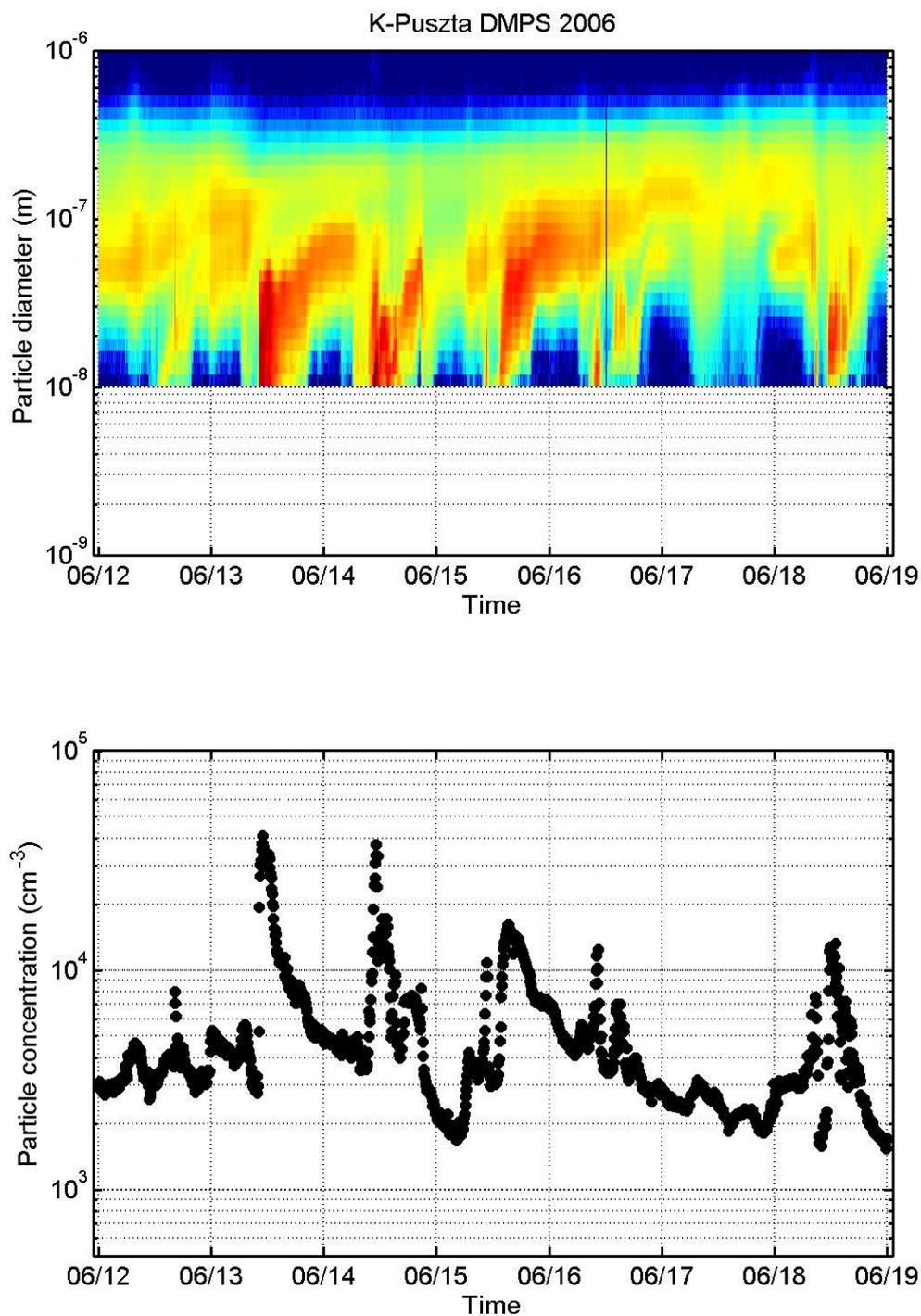
Component 2: 81, 93, 95, 135, 137, 139, 151. The species associated with this component include  $\alpha$ -pinene ( $m/z$  81 and 137),  $\beta$ -pinene,  $\Delta^3$ -carene, myrcene ( $m/z$  81, 93, 137, 139),  $\alpha$ -humulene ( $m/z$  81 and 95),  $\beta$ -caryophyllene, nopinone ( $m/z$  139), and pinonaldehyde ( $m/z$  151).

Component 3: 30, 31, 32, 33, 34. Component 3 includes signals that are related to  $\text{NO}^+$  ( $m/z$  30, 31), and  $\text{O}_2^+$  ( $m/z$  32).

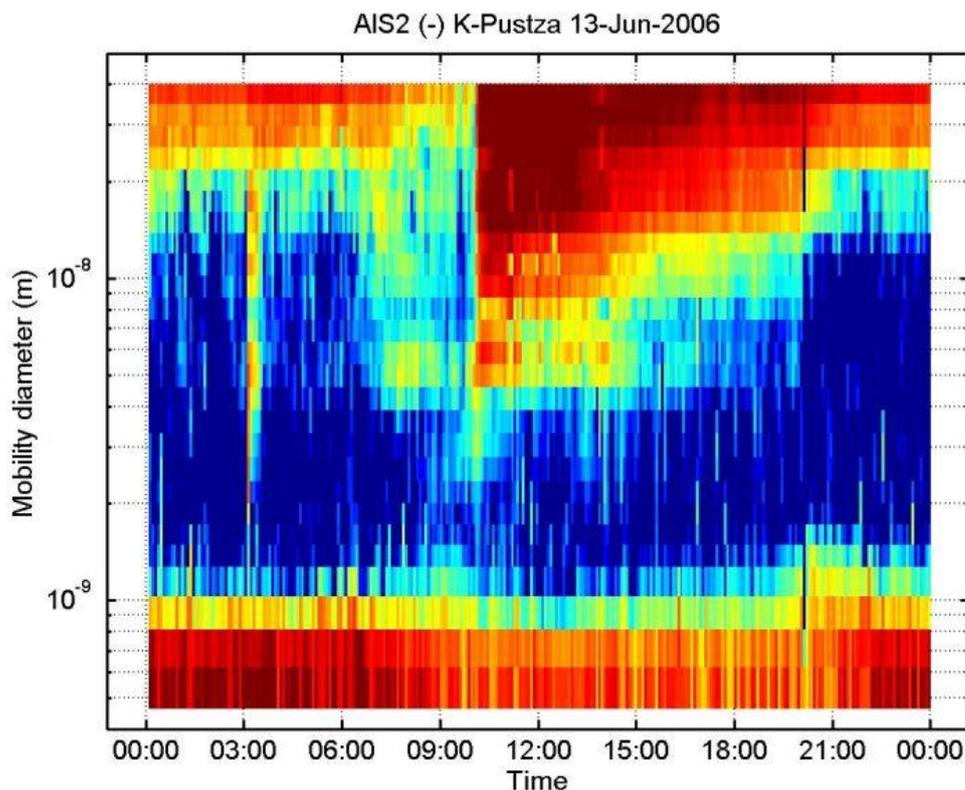
Component 4: 29 (negative loading), 37, 38, 39, 55. The species associated with this component include a cluster of protonated water ( $\text{H}_3\text{O}\cdot\text{H}_2\text{O}^+$ ) ( $m/z$  37).

### 3.3.5. Physical aerosol data

The physical aerosol measurements (DMPS and AIS) for the 2006 summer K-pusztá campaign were worked up by P4. During the measurement period particle production episodes were detected around every second day, which is quite frequent. During these episodes the total particle concentration in the 10 nm – 1  $\mu\text{m}$  size range, as measured with the DMPS, rose from the background concentration of some thousand particles to tens of thousands particles per  $\text{cm}^3$ . The lowest concentration detected was around 800  $\text{cm}^{-3}$  and the highest concentration was noted during the production event of 13 June, with over 40,000  $\text{cm}^{-3}$ . The AIS detected the same episodes as the DMPS. Episodes initiated typically some time during the morning. Figure 7 shows the DMPS size distributions for the week from 12 to 19 June. During each day of this week some particle production was detected and during five days the particle concentration reached 10,000  $\text{cm}^{-3}$  over the measurement range. In Figure 8, the negative air ion size distribution is presented over the strongest production day 13 June. The air ion concentration increased suddenly around 10:00 in the morning. The ion peak below 1 nm is a so called cluster ion peak, it consists of charged molecules or molecular clusters. It is worth noting that the strong particle production event was not associated with high VOC levels, as measured by PTR-MS (Figures 3, 4) or with high PM or OC levels (Figure 5).



**Figure 7.** Particle size distribution and total concentration measured at the K-pusztta site with the DMPS during the week from 12 to 19 June 2006. The vertical dashed lines are at 00:00 h.



**Figure 8.** AIS air negative ion size distribution at the K-pusztza site during the day of 13 June 2006.

### 3.3.6. Assessment of artifacts in the collection of particulate OC

All aerosol filter samplers for subsequent analyses for OC and EC (and also for organic compounds) had tandem quartz fibre filters in an attempt to assess the artifacts in the collection of particulate OC (and particulate organic compounds). The average ratio (OC on the back filter)/(OC on the front filter) and associated standard deviation for the undened 12-hour samples (N=68 for each sampler type) were  $0.15 \pm 0.04$  for the PM<sub>2.5</sub> size fraction of the HVDS, and  $0.15 \pm 0.06$  and  $0.09 \pm 0.05$  for the low-volume PM<sub>2.5</sub> and PM<sub>10</sub> samplers. For the undened and denuded 24-hour low-volume PM<sub>2.5</sub> filter samplers (P25UWW and P25DWW) the average ratio (OC on the back filter)/(OC on the front filter) and associated standard deviation were  $0.18 \pm 0.05$  for P25UWW and  $0.02 \pm 0.03$  for P25DWW. In the 2003 summer campaign the corresponding ratios were very similar, i.e.,  $0.16 \pm 0.05$  for P25UWW and  $0.02 \pm 0.04$  for P25DWW. These results clearly show that the diffusion denuder for VOCs has an effect on the back to front filter ratio for OC. If we assume that the OC on the back filter is essentially due to the collection of VOCs (positive artifacts) in an undened set-up and to the loss of semi-volatile VOCs from the front filter (negative artifacts) in a denuded set-up, "artifact-free" particulate OC data can be obtained as  $OC(\text{front filter}) - OC(\text{back filter})$  for the undened set-up and as  $OC(\text{front filter}) + OC(\text{back filter})$  for the

denuded set-up [Mader et al., 2003]. Moreover, when a denuded and undenuded set-up are operated in parallel, the corrected OC data from the two set-ups should be the same. Applying the correction to the OC data from the parallel undenuded and denuded 24-hour low-volume PM<sub>2.5</sub> filter samplers resulted in an average ratio (corrected OC from P25UWW)/(corrected OC from P25DWW) of  $0.97 \pm 0.28$ , which indicates that the above assumptions were valid for these samples [In the 2003 campaign a poorer ratio of  $1.16 \pm 0.11$  was obtained]. We assumed that the above assumptions were also valid for the undenuded 12-hour samplers, and corrected OC were calculated for these samples as OC(front filter) – OC(back filter). The OC data listed and used for the K-pusztta site in this report are such corrected data, except when indicated otherwise.

EC represented only a minor fraction of the TC (with TC = OC + EC), indicating that the K-pusztta site was not influenced much by automotive emissions or other fossil fuel combustion. For the hourly PM<sub>2.5</sub> OCEC data presented in Figure 5, the average ratio and associated standard deviation for OptEC/TC were  $0.15 \pm 0.05$ . For the filter samples even lower EC/TC ratios were obtained. For example, based on the 68 HVDS samples for the 2006 campaign, the average ratios and associated standard deviations for EC/TC (using uncorrected OC data) were  $0.063 \pm 0.030$  for the fine front filters and  $0.026 \pm 0.038$  for the coarse front filters. The corresponding data for the 2003 campaign were similar, i.e.,  $0.049 \pm 0.014$  for fine and  $0.036 \pm 0.013$  for coarse. Most of the PM<sub>10</sub> OC was in the fine (PM<sub>2.5</sub>) size fraction during the 2006 campaign, on average  $72 \pm 10\%$  [N=68]. For comparison, of the PM<sub>10</sub> PM, on average,  $67 \pm 8\%$  [N=68] was in the PM<sub>2.5</sub> size fraction (based on the PM data from the samplers with Nuclepore polycarbonate filters). The data from the MOUDI/nano-MOUDI combination indicated that there was very little mass in the ultrafine (<0.1 µm) size fraction, i.e., on average, only 3% of the PM<sub>10</sub> PM. It also appeared from the detailed mass size distributions for the PM that no real separate Aitken or nucleation mode could be discerned; rather the mass size distribution in the ultrafine size range appeared to be a tail of the accumulation mode. The WSOC analyses of the HVDS samples indicated that most of the fine OC was water-soluble. Using uncorrected OC data,  $57 \pm 9\%$  [N=68] of the OC was WSOC for the fine front filters and  $73 \pm 12\%$  [N=68] for the fine back filters during the 2006 campaign. The corresponding percentages for the 2003 campaign were  $61 \pm 9\%$  for the fine front filters and  $87 \pm 15\%$  for the fine back filters.

### 3.3.7. Chemical aerosol data from the HVDS samples

The median concentrations and interquartile ranges for TC, OC, EC, WSOC, MSA, DCAs, and water-soluble inorganic species, as derived from the PM<sub>2.5</sub> size fraction front filters of the HVDS samples from the 2006 summer campaign, are given in

**Table II.** Median concentrations and interquartile ranges for TC, OC, EC, WSOC, MSA, DCAs, and water-soluble inorganic species, as derived from the PM<sub>2.5</sub> size fraction front filters of the HVDS samples from the 2006 summer campaign at K-pusztá. The medians obtained for the PM<sub>2.5</sub> size fraction front filters of the HVDS samples from the 2003 summer campaign at K-pusztá are also included.

Species	2006 Cold period (N = 33)		2006 Warm period (N = 34)		2003 (N = 63) Front filter
	Front filter conc. (ng/m <sup>3</sup> ) median	interq. range	Front filter conc. (ng/m <sup>3</sup> ) median	interq. range	(ng/m <sup>3</sup> ) median
TC	2100	1730 – 2500	4600	3700 – 5300	4400
OC	1960	1540 – 2300	4500	3400 – 4900	4200
EC	143	124 – 192	176	130 – 250	195
WSOC	970	770 – 1130	2900	2200 – 3200	2600
NH <sub>4</sub> <sup>+</sup>	840	580 – 1040	1530	1130 – 2000	1520
SO <sub>4</sub> <sup>2-</sup>	1790	1170 – 2400	3600	2600 – 4400	3500
NO <sub>3</sub> <sup>-</sup>	410	300 – 750	360	197 – 500	310
Na <sup>+</sup>	30	13.8 – 47	35	22 – 51	48
Mg <sup>2+</sup>	2.3	1.14 – 3.9	6.8	4.6 – 13.8	14.7
K <sup>+</sup>	48	39 – 81	81	64 – 127	67
Ca <sup>2+</sup>	22	14.5 – 32	88	57 – 210	198
MSA <sup>-</sup>	29	12.2 – 44	29	22 – 36	
Oxalate	73	56 – 85	210	154 – 250	196
Malonate	33	24 – 37	65	50 – 76	
Succinate	32	26 – 38	142	100 – 166	41
Glutarate	7.1	4.9 – 9.0			7.8

Table II. Separate medians and ranges for the cold and warm periods are given in the Table. A comparison is also made with the medians obtained for the PM<sub>2.5</sub> size fraction front filters of the HVDS samples from the 2003 summer campaign. For most species, the median concentrations are substantially larger during the warm period than during the cold one of the 2006 campaign and the warm period medians are similar to the overall medians of the 2003 campaign. This feature was already observed for other samples and other species and/or elements. The organic species listed in Table II follow the overall trend of higher concentrations in the warm period, with the exception of MSA. The higher levels for OC in the warm period were attributed to higher emissions of primary organic matter by the vegetation and of biogenic SOA precursors, such as isoprene and monoterpenes, followed by fast SOA formation. The DCAs are both of primary and secondary origin and are attributed to a multitude of sources. It seems that the primary emissions for these species, the emissions of their gaseous precursors, and/or their secondary formation processes were more pronounced in the warm period than in the cold one. The difference in air

mass origin between the two periods (with more maritime air in the cold period and continental air in the warm period) may also have played a role. As to MSA, this is a particulate phase oxidation product of dimethylsulphide (DMS), which is mainly emitted by marine phytoplankton. It is thus not surprising that the MSA levels of the cold period (with maritime air) were equally high as those observed in the warm period. The organic compounds measured by IC accounted, when averaging over all samples, for 2.9% of the OC and 5.2% of the WSOC and there was little difference between the means of the cold and the warm periods.

It is well known that the collection of carbonaceous aerosols on quartz fibre filters is prone to both positive and negative artifacts [e.g., Turpin et al., 2000]. A simple way to assess the importance of the artifacts is to make use of a tandem filter set-up with front and back quartz fibre filters in series. In studies on artifacts, one normally concentrates on OC as a whole or occasionally on WSOC. It is rare that studies are carried out on individual organic species. One example of the latter type of study is that by Limbeck et al. [2001], who used a tandem filter set-up at a rural background site in South Africa and measured DCAs and other polar organic species on the front and back filters. Substantial amounts were found on the back filter; the mean back/front filter ratios for oxalate, malonate, succinate, and glutarate were 0.14, 0.01, 0.26, and 0.38, respectively. The authors' interpretation was that the DCA concentrations on the back filters were caused by the adsorption of gaseous organic species and that DCAs have a semivolatile behaviour. Low-volume TSP samplers were used in that study, the face velocity across the filter was about 22 cm/s, and the collection time per sample was around one week. From the results of the fine size fraction of our HVDS samples we first calculated the back/front filter ratio for each species in each individual sample and from these data the interquartile ranges in the back/front ratios were then obtained for each species (for the 2006 campaign, the data from the cold and warm periods were kept separate). The resulting data for the carbonaceous species, organic compounds, and selected inorganic species are given in Table III. Our back/front ratios for oxalate and succinate are low and clearly lower than those obtained by Limbeck et al. [2001]; malonate was nearly absent on the back filter in the earlier study, whereas we found larger back/front ratios than for oxalate and succinate; of the four DCAs studied by us, glutarate has the largest back/front ratio, but Limbeck et al. [2001] found an even greater back/front ratio for this species. It should be noted that there were substantial differences in sampling between our HVDS samplings at K-pusztta and the samplings in the study of Limbeck et al. [2001]. In our HVDS samplings the collection time per sample was generally only 12 h (occasionally 24 h) versus one week in the earlier study; besides, the face velocity through the PM<sub>2.5</sub> filters of the HVDS was 80 cm/s, which is almost a factor of 4 larger than that in the TSP samplings of Limbeck et al. [2001]. It is clear that

results from one site and sampler cannot be generalised to all sites and sampler types. Therefore, it was decided to examine the back/front ratios also in our DCA analyses for the HVDS samples from the two other forested BIOSOL sites.

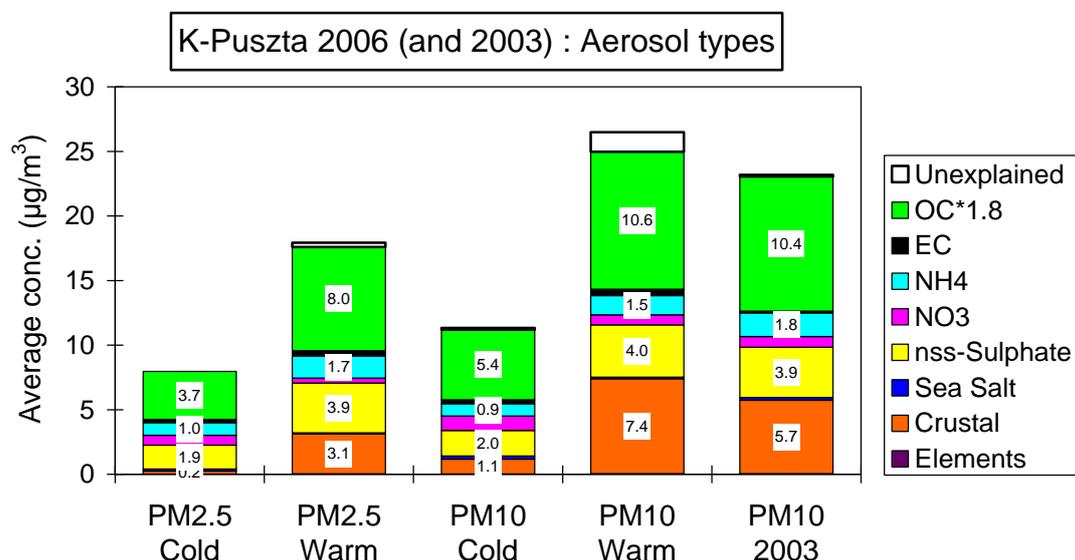
**Table III.** Interquartile ranges of the back/front filter ratio for the carbonaceous species, organic compounds, and selected inorganic species in the PM<sub>2.5</sub> size fraction of the HVDS samples from the 2006 summer campaign at K-pusztá. The data for the PM<sub>2.5</sub> size fraction of the HVDS samples from the 2003 summer campaign at K-pusztá are also included.

Species	2006 Cold period (N = 33)	2006 Warm period (N = 34)	2003 (N = 63)
	Interq. range for back/front ratio	Interq. range for back/front ratio	Interq. range for back/front ratio
TC	0.09 – 0.17	0.12 – 0.16	0.10 – 0.13
OC	0.10 – 0.18	0.12 – 0.17	0.10 – 0.13
EC	0.00 – 0.00	0.00 – 0.00	0.00 – 0.01
WSOC	0.17 – 0.26	0.13 – 0.19	0.15 – 0.19
NH <sub>4</sub> <sup>+</sup>	0.05 – 0.16	0.00 – 0.00	0.01 – 0.03
SO <sub>4</sub> <sup>2-</sup>	0.00 – 0.00	0.00 – 0.00	0.00 – 0.01
Mg <sup>+</sup>	0.00 – 0.00	0.00 – 0.00	0.01 – 0.04
Ca <sup>2+</sup>	0.00 – 0.00	0.00 – 0.00	0.02 – 0.06
MSA <sup>-</sup>	0.01 – 0.13	0.01 – 0.08	
Oxalate	0.01 – 0.02	0.01 – 0.03	0.01 – 0.03
Malonate	0.03 – 0.13	0.01 – 0.13	
Succinate	0.02 – 0.08	0.01 – 0.05	0.01 – 0.03
Glutarate	0.17 – 0.35		0.15 – 0.22

### 3.3.8. Aerosol chemical mass closure

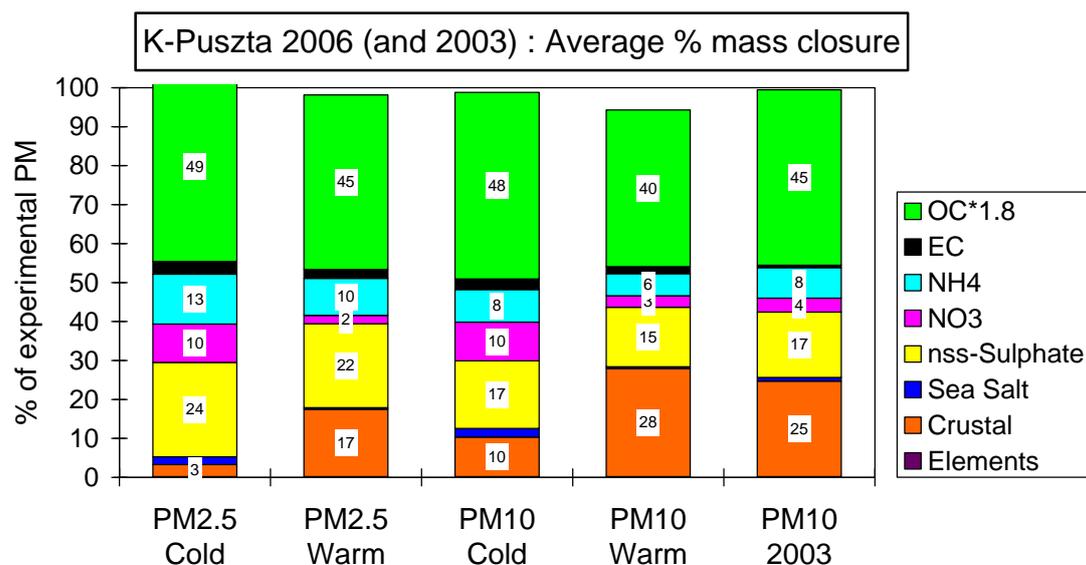
The data from the 12-hour low-volume PM<sub>2.5</sub> and PM<sub>10</sub> samplers of the 2006 summer campaign at K-pusztá were used for aerosol chemical mass closure calculations, that is to assess to what extent the gravimetrically measured PM agreed with the sum of the measured chemical components [Maenhaut et al., 2008]. As gravimetric PM data we adopted the results from the samplers with Nuclepore polycarbonate filters. The following eight components (aerosol types) were used in the mass closure work: (1) organic aerosol (organic matter, OM), which was estimated as 1.8 OC; (2) EC; (3) non-sea-salt (nss) sulphate; (4) ammonium; (5) nitrate; (6) sea salt, estimated as Cl + 1.4486 Na, whereby 1.4486 is the ratio of the concentration of all elements except Cl in sea water to the Na concentration in sea water; (7) crustal matter = 1.16 (1.90 Al + 2.15 Si + 1.41 Ca + 1.67 Ti + 2.09 Fe), where the factor 1.16 is to compensate for the exclusion of MgO, Na<sub>2</sub>O, K<sub>2</sub>O, and H<sub>2</sub>O from the crustal

mass calculation; and (8) elements, which is the sum of the mass of all non-crystal/non-sea-salt elements measured by PIXE (S and K were excluded from this sum). The average concentrations of the various aerosol types (and of the unexplained gravimetric PM) are shown in Figure 9, and this separately for the PM2.5 and PM10 aerosol and for the cold and warm periods. For 6 of the 8 components, higher average levels are observed in the warm period than in the cold one. The two exceptions are nitrate and sea salt. The lower levels of nitrate during the warm period are attributed to transfer of nitrate from the particulate to the vapour phase at elevated temperature, as indicated above in section 3.3.3. For sea salt, the difference is due to difference in air mass origin (more maritime air during the cold period versus continental air during the warm one, see Figure 2). It also appears from Figure 9 that the data for most of the aerosol types in PM10 are quite similar for the overall 2003 campaign and the warm period of the 2006 campaign.



**Figure 9.** Average concentrations of 8 aerosol types during the 2006 summer campaign at K-pusztá, and this separately for the PM2.5 and PM10 aerosol and for the cold and warm periods. The data for the PM10 aerosol during the 2003 summer campaign at the same site are also shown.

The percentage contributions of the various components to the average gravimetric PM are given in Figure 10. Noteworthy here are the much larger percentages of crustal matter during the warm period than during the cold one (both for the PM2.5 and PM10 aerosol). In the PM2.5 aerosol, crustal matter accounted for 17% of the PM during the warm period, but only for 3.1% during the cold period. Of all components, OM contributed by far the most to the PM2.5 PM, and its percentage contributions were rather similar in both periods. For PM10, the data of the overall 2003 campaign are quite similar to those of the warm period of the 2006 campaign.

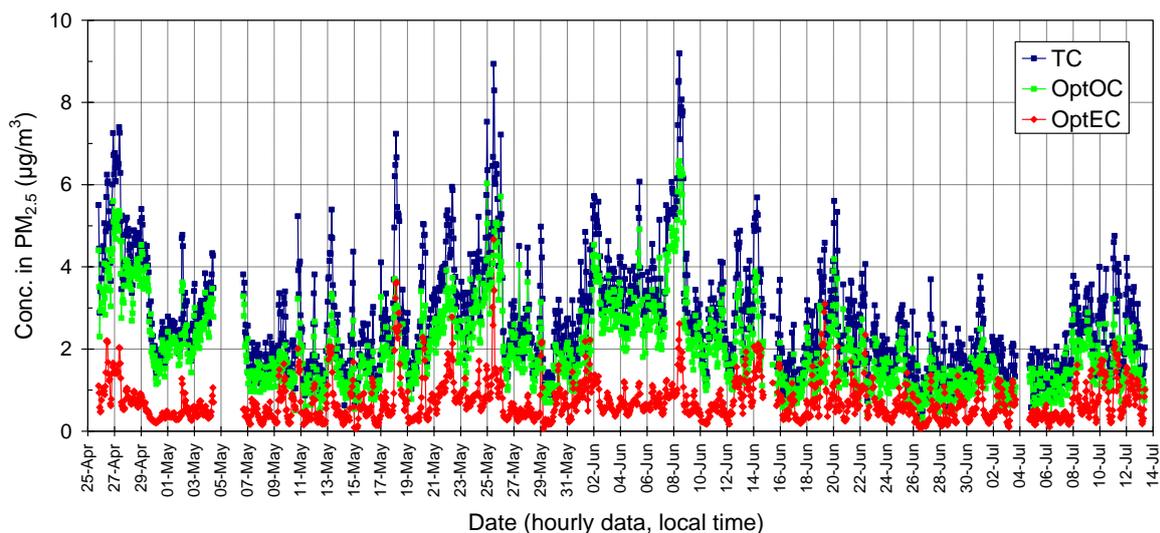


**Figure 10.** Percentage contributions of the various components to the average gravimetric PM for the 2006 summer campaign at K-pusztza, and this separately for the PM<sub>2.5</sub> and PM<sub>10</sub> aerosol and for the cold and warm periods. The data for the PM<sub>10</sub> aerosol during the 2003 summer campaign at the same site are also shown.

### 3.4. Studies during 2007 at the state forest "De Inslag", Brasschaat, Belgium

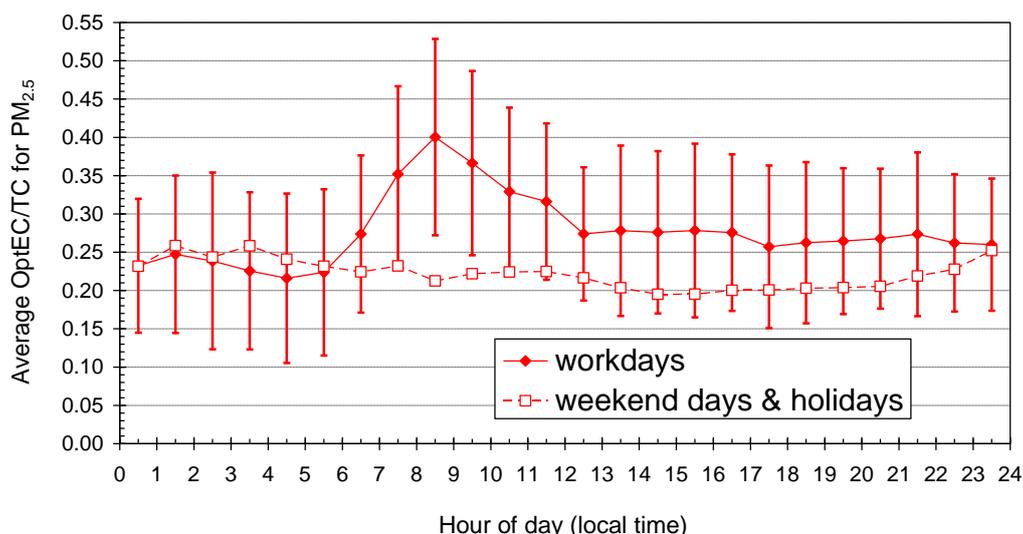
#### 3.4.1. In-situ data for particulate OC and EC

As already indicated in section 2.3, the OCEC Field instrument was deployed at the site in 2007 from 25 April until 13 July (1st period) and from 19 September to 12 November (2nd period), and during the year 2008 good data were obtained from 15 July until 6 November (3rd period); the time resolution of the measurements was 1 h during the first period and 2 h in the other two periods. For the first period, TC ranged from 0.3 to 9.2  $\mu\text{g}/\text{m}^3$  (median 2.5  $\mu\text{g}/\text{m}^3$ ) and the OptEC/TC ratio was, on average,  $0.26 \pm 0.11$  [N = 1769]; for the second period, the range in TC was 0.4 – 15  $\mu\text{g}/\text{m}^3$  (median 3.4  $\mu\text{g}/\text{m}^3$ ) and the OptEC/TC ratio was, on average,  $0.36 \pm 0.12$  [N = 611]; for the third period, TC ranged from 0.6 to 16  $\mu\text{g}/\text{m}^3$  (median 2.8  $\mu\text{g}/\text{m}^3$ ) and the OptEC/TC ratio was, on average,  $0.38 \pm 0.11$  [N = 1303]. These OptEC/TC ratios are about a factor of 2 larger than those, which were obtained with the same instrument during the 2006 campaign at K-pusztza (see section 3.3.6), indicating that the Brasschaat site is much more impacted by fossil fuel combustion (including traffic) aerosols than the K-pusztza site. The EC/TC ratio at Brasschaat is actually similar to that observed at Ghent and other urban sites in Europe [e.g., Viana et al., 2007]. Note that EC should be absent in both primary and secondary aerosols that are derived from the vegetation.



**Figure 11.** Time series of TC, OptOC, and OptEC (with TC = OptOC + OptEC) at the state forest "De Inslag" in Brasschaat for the period from 25 April until 13 July 2007 (the vertical dashed lines are at 00:00 h).

The individual hourly data of TC, OptOC, and OptEC for the first period at Brasschaat are shown in Figure 11. There is quite some variability in the data, which to a large part is a reflection of the variability in weather conditions (temperature and the occurrence of precipitation). The ratio of OptEC/TC was examined as time of the day by calculating for each hour (or every 2 h) the average (over the entire period) and associated standard deviation and plotting these data as a function of hour of the day. The results for the 1st period, and this separately for workdays and weekend days & holidays, are shown in Figure 12. The OptEC/TC ratio is for most hours in the range 0.20-0.28, but on workdays there is a clear maximum in the morning, with a peak ratio



**Figure 12.** Means and standard deviations of the OptEC/TC ratio as function of hour of the day for the first period of OCEC measurements at the state forest "De Inslag" in Brasschaat.

of 0.40 at around 8:30, which illustrates the effect of the morning rush hour traffic. A similar maximum was also observed for the other two periods of the OCEC measurements.

The relationships between the OptOC, OptEC, and TC data and the meteorological and inorganic trace gas data were examined. This was done for the measurement periods of 2007 and also that of 2008. The data for the several meteorological parameters and inorganic trace gases were provided by the Flemish Research Institute for Nature and Forest (INBO); they included pressure (P), temperature (T), relative humidity (RH), wind speed (WS), wind direction (WD), sunshine, precipitation, and concentrations of SO<sub>2</sub>, O<sub>3</sub>, NO, NO<sub>2</sub>, and CO<sub>2</sub>. For the 2007 data (combination of periods 1 and 2), OptEC was highly correlated with NO ( $r = 0.75$ ) and NO<sub>2</sub> ( $r = 0.66$ ), but even better with NO<sub>x</sub> ( $r = 0.83$ ). This is clearly a reflection of the common origin of OptEC and these trace gases, which is the combustion of fossil fuels and in particular automotive exhaust emissions. OptOC, OptEC, and TC were also highly correlated with CO<sub>2</sub> (all  $r$  around 0.7). Furthermore, there was a clear tendency for the particulate carbonaceous species, NO, NO<sub>2</sub>, NO<sub>x</sub>, and CO<sub>2</sub> to be negatively correlated with wind speed. This is rather logical as low wind speeds are common during periods of stagnation, when the levels of pollutants can build up. As to the relationship between the particulate carbonaceous species and wind direction, this was examined by making polar plots (wind roses) for OptOC and OptEC. OptOC was highest for winds from the east; periods of easterly winds are frequently periods of air mass stagnation and low wind speeds. OptEC, in contrast, showed highest levels for the wind direction range from 112.5° to 270°, which corresponds roughly with the sector where the center of Antwerp and the harbour are located. There was, however, a clear peak in OptEC for winds from the SSE. Incidentally, in this direction, a major highway (i.e., the E19/A1) passes within 1.5 km from our sampling site.

### 3.4.2. Data from the HVDS aerosol samples

The HVDS samplings for separate day-time and night-time collections in two size fractions (fine: <2.5 µm, and coarse: >2.5 µm) took place from 5 June until 13 July and overlapped thus with the last five weeks of OCEC Field instrument measurements of the first period at the site. The fine fraction (PM<sub>2.5</sub>) front filter EC/TC ratio was, on average, 0.21±0.09, whereas the OptEC/TC for the OCEC instrument data taken in parallel was somewhat higher (i.e., 0.29±0.09). Of the fine front filter OC, 51±9% was, on average, WSOC, which is intermediate between the percentages observed for urban sites and pure forested sites [Chi and Maenhaut, 2008]. The mean back/front filter percentage ratio for fine OC was 18±5%, which is on the high side, but not much higher than summer values for other sites in Europe, and the mean back/front

percentage ratio for fine WSOC was 24±9%. Of the total front filter OC (sum of fine + coarse), 60±12% was, on average, in the fine size fraction, whereas the percentage for EC was 86±11%. It further appeared that the back/front filter percentage ratio for coarse OC was generally quite low, i.e., below 5% for 90% of the samples taken.

**Table IV.** Median concentrations and interquartile ranges for TC, OC, EC, WSOC, MSA, DCAs, and water-soluble inorganic species, as derived from the PM<sub>2.5</sub> size fraction front filters of the HVDS samples from the 2007 summer campaign at Brasschaat [N = 71]. The medians and interquartile ranges for the back/front ratio in the PM<sub>2.5</sub> size fraction are also included.

Species	Front filter conc. (ng/m <sup>3</sup> )		Back/front filter ratio	
	median	interq. range	median	interq. range
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 <sub>4</sub> <sup>+</sup>	1080	650 – 2100	0.04	0.00 – 0.07
SO <sub>4</sub> <sup>2-</sup>	2700	1840 – 3900	0.00	0.00 – 0.00
NO <sub>3</sub> <sup>-</sup>	650	400 – 2200	0.24	0.15 – 0.34
Cl <sup>-</sup>	40	15.7 – 93		
Na <sup>+</sup>	108	65 – 210	0.01	0.00 – 0.06
Mg <sup>2+</sup>	2.7	1.42 – 6.7	0.00	0.00 – 0.00
K <sup>+</sup>	38	18.7 – 93		
Ca <sup>2+</sup>	27	14.7 – 36	0.00	0.00 – 0.01
MSA <sup>-</sup>	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 – 54	0.02	0.00 – 0.10
Glutarate	4.7	3.3 – 9.7	0.26	0.17 – 0.57

The fine front and back filters of the HVDS were analysed for water-soluble inorganic and organic ions by IC. A summary of the results is given in Table IV. Also data for TC, OC, EC, and WSOC are included in the Table. When comparing the front filter concentration data of Table IV with those for the 2006 summer campaign at K-puszta (Table II), it appears that for several species the concentrations at Brasschaat are similar to those in the cold period at K-puszta. This is the case for TC, OC, WSOC, oxalate, Mg<sup>2+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>. The levels for sulphate, nitrate, and especially EC are higher at Brasschaat than in the cold K-puszta period, indicating that the Brasschaat site is indeed more impacted by anthropogenic emissions. Also the Na<sup>+</sup> and MSA<sup>-</sup> concentrations are substantially larger in Brasschaat, but this is attributed to the much closer distance to the North Sea and the Atlantic Ocean and thus to a much larger impact from marine emissions. With regard to the four DCAs, whereas the

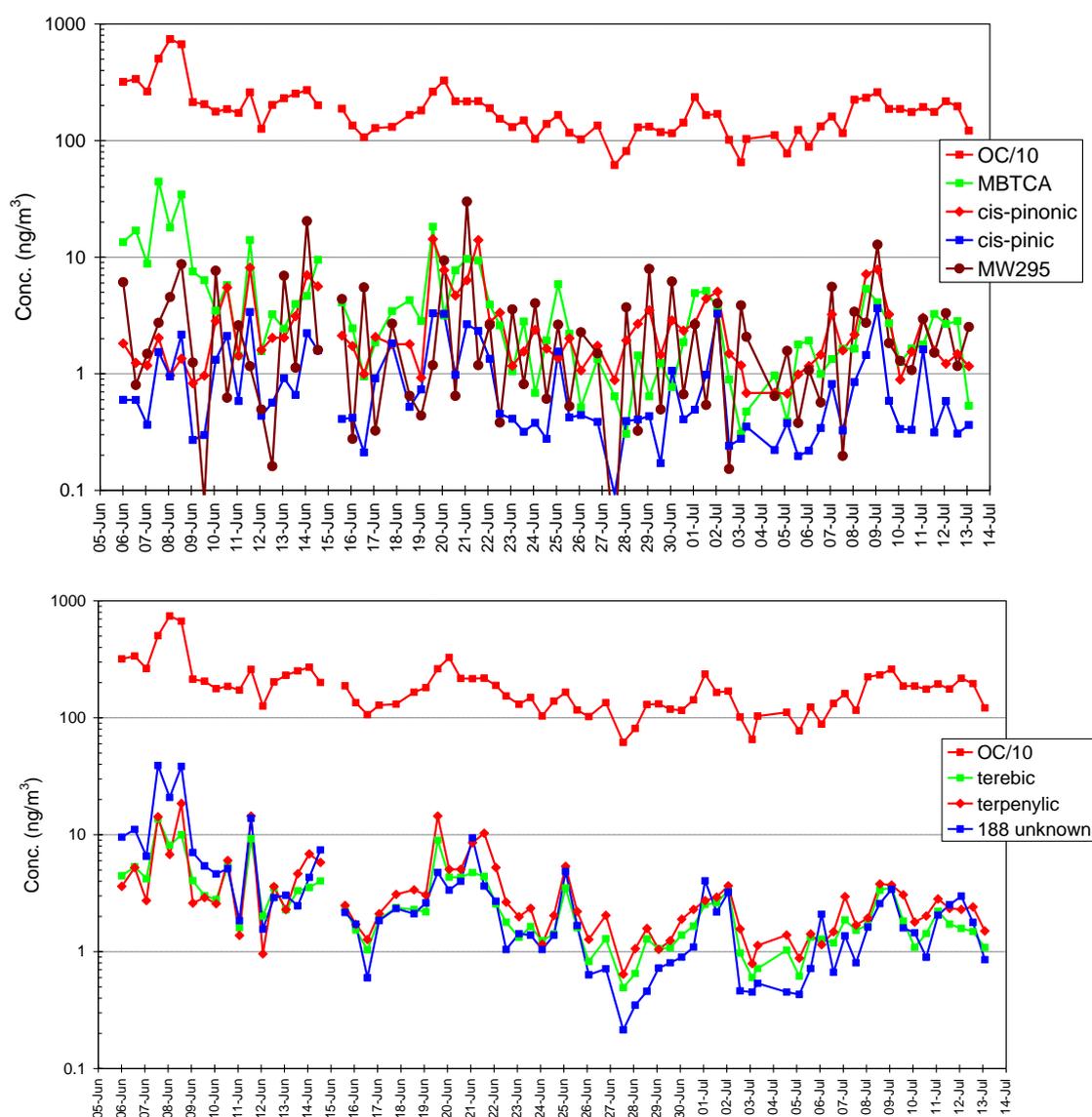
Brasschaat site and the cold K-puszta period exhibited the same levels for oxalate, malonate was substantially more elevated at Brasschaat and succinate and glutarate were substantially less elevated at Brasschaat. The organic compounds measured by IC accounted, on average, for 4.1% of the OC and 8% of the WSOC.

The back/front filter ratios of Table IV were calculated in the same way as for K-puszta, thus on a sample by sample basis, and from these data medians and interquartile ranges for the ratios were then derived. The ratios of Table IV are overall quite similar to those observed at K-puszta (Table III), but there are, however, a few noteworthy exceptions, i.e., for the DCAs. Whereas at K-puszta the ratios for malonate were larger than those for oxalate and succinate, this is not the case at Brasschaat. At both sites, glutarate has clearly the largest back/front filter ratios. However, the concentration of glutarate was near the detection limit in several back filters (particularly for Brasschaat) and had thus a large associated uncertainty.

**Table V.** Median concentrations and interquartile ranges for the species measured by LC/(-)ESI-MS, as derived from the PM<sub>2.5</sub> size fraction front filters of the HVDS samples [N= 71] from the 2007 summer campaign at Brasschaat.

Species (MW)	Formula	Front filter conc. (ng/m <sup>3</sup> )	
		median	interq. range
MBTCA (204)	C <sub>8</sub> H <sub>11</sub> O <sub>6</sub>	2.7	1.33 – 5.0
<i>cis</i> -pinonic acid (184)	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	1.79	1.23 – 3.1
<i>cis</i> -pinic acid (186)	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	0.49	0.35 – 1.19
terebic acid (158)	C <sub>7</sub> H <sub>10</sub> O <sub>4</sub>	1.87	1.31 – 3.5
terpenylic acid (172)	C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>	2.4	1.57 – 3.7
unknown compound (188)	C <sub>8</sub> H <sub>12</sub> O <sub>5</sub>	2.1	0.90 – 3.8
diaterpenylic acid acetate (232)	C <sub>8</sub> H <sub>16</sub> O <sub>6</sub>	0.27	0.13 – 0.64
caronic acid (184)	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	0.30	0.19 – 0.47
caric acid (186)	C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	0.60	0.31 – 1.50
ketolimonic acid (186)	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	0.41	0.27 – 0.57
limonic acid (186)	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	0.85	0.45 – 1.69
homoterpenylic acid (186)	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	0.57	0.39 – 0.88
2,3-dihydropentane-1,5-dialdehyde OS [∑2 isomers] (212)	C <sub>5</sub> H <sub>8</sub> O <sub>7</sub> S	6.5	0.64 – 81
2-methyltetrol OS [∑2 isomers] (216)	C <sub>6</sub> H <sub>10</sub> O <sub>7</sub> S	6.4	0.47 – 64
2-hydroxy-6-ketohexanoic acid OS (226)	C <sub>5</sub> H <sub>8</sub> O <sub>8</sub> S	4.6	0.48 – 66
2- & 3-hydroxyglutaric acid OS (228)	C <sub>5</sub> H <sub>12</sub> O <sub>7</sub> S	3.4	0.12 – 51
2-methyltetrol mononitrate OS [∑2 isomers] (261)	C <sub>5</sub> H <sub>11</sub> O <sub>9</sub> SN	0.76	DL – 27
pinanediol mononitrate OS [∑5 isomers] (295)	C <sub>10</sub> H <sub>17</sub> O <sub>7</sub> SN	1.51	0.63 – 3.6
2-methyltetrol dinitrate OS [∑4 isomers] (306)	C <sub>5</sub> H <sub>10</sub> O <sub>11</sub> SN <sub>2</sub>	6.6	DL – 40

Table V gives a summary of the results obtained by P2 [using LC/(–)ESI-MS] for the fine front filters of the HVDS samples. All species listed in the Table, with the exception of *cis*-pinonic acid and *cis*-pinic acid, were identified and structurally characterised as part of the BIOSOL project; they include pure organic species (i.e., containing only C, H, and O) and organosulphates (OS), with among the latter also nitrooxy organosulphates. The MWs and gross formulas of the various compounds are also included in the Table. More information on the pure organic species, which were structurally characterised as part of BIOSOL, and on some of the organosulphates is given in section 3.8. The time series for selected LC/MS species and OC throughout the 2007 campaign at Brasschaat is shown in Figure 13. Of the LC/MS species shown, MBTCA, terebic acid, terpenylic acid, and an unknown MW188 compound exhibited the highest concentrations during the first days of the



**Figure 13.** Time series for selected LC/MS species and OC, as derived from the PM<sub>2.5</sub> front filters of the HVDS samples, for the 2007 summer campaign in Brasschaat.

campaign that were characterised by high maximum temperatures ( $> 22\text{ }^{\circ}\text{C}$ ), while *cis*-pinonic acid showed the lowest concentrations, a result consistent with the formation of MBTCA through further oxidation of *cis*-pinonic acid [Szmigielski et al., 2007b]. MBTCA and *cis*-pinonic acid (expressed as %C of OC) showed diel variations with maxima mostly during day-time, while *cis*-pinic acid mainly peaked at night. The MW 295 nitrooxy organosulphates exhibited clear diel variations with maxima at night, consistent with observations first reported by Iinuma et al. [2007] and night-time  $\text{NO}_3$  radical chemistry as supported by Surratt et al. [2008]. Interestingly, rather low concentrations of the MW 295 SOA tracers were found during the first nights of the campaign (with maximum day-time temperatures  $> 22\text{ }^{\circ}\text{C}$ ). These results hint that the latter  $\alpha$ -pinene SOA tracers are formed during nights following days where  $\alpha$ -pinene was not fully consumed by photo-oxidation, leaving a portion of the emitted  $\alpha$ -pinene available for processing by night-time  $\text{NO}_3$  chemistry. The 19 LC/MS compounds listed in Table V accounted, on average, for 1.2% of the OC and 2.3% of the WSOC.

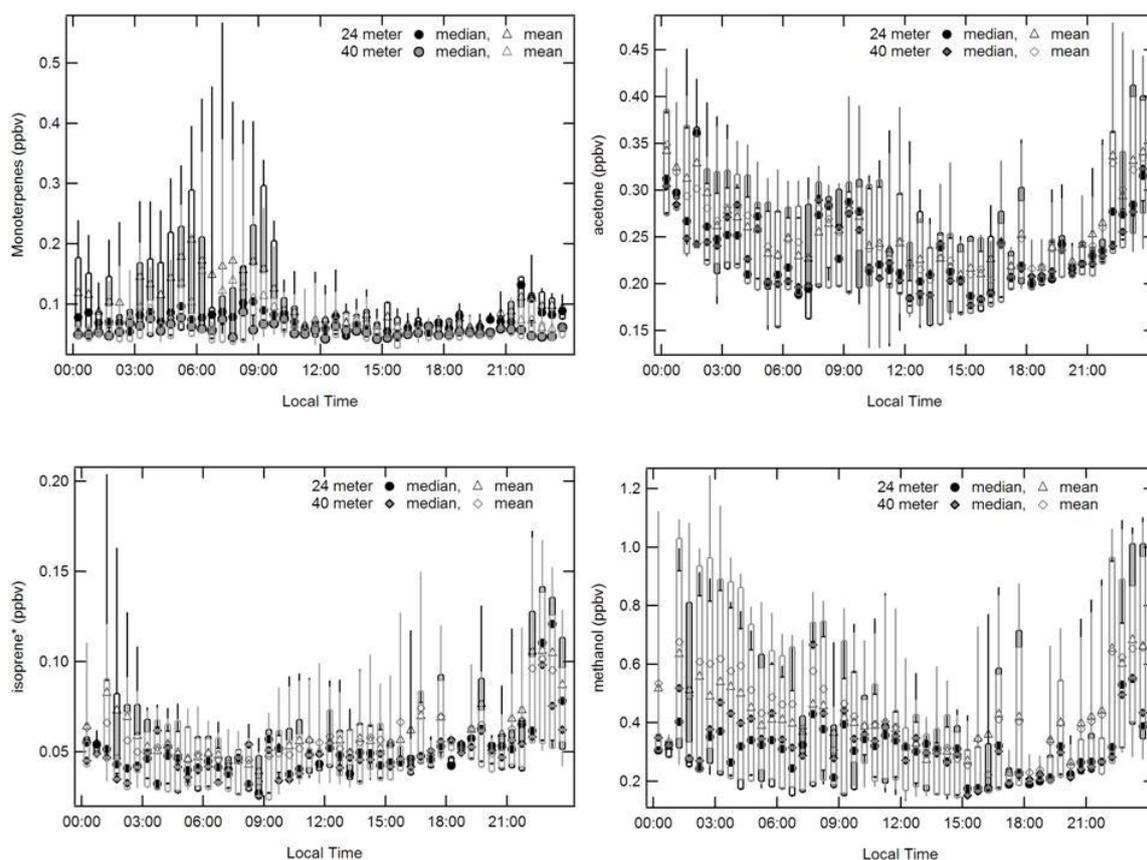
All concentration data available for the fine front filters of the Brasschaat HVDS samples were combined and pairwise correlations between the various species and also between the species and data for several meteorological parameters and inorganic trace gases were calculated. The meteorological and trace gas data included were the same as for the data sets from the OCEC Field instrument. 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. Several correlations were very high ( $r > 0.85$ ) or high ( $0.7 < r < 0.85$ ) or substantial ( $0.5 < r < 0.7$ ). For example, oxalate exhibited very high or high correlations with TC, OC, WSOC, ammonium, nitrate, sulphate, malonate, succinate, MBTCA, terebic, diaterpenylic acid acetate, and the OS with MWs 212, 226, and 228. MBTCA was very highly correlated with TC, OC, WSOC, oxalate, malonate, succinate, terebic, terpenylic, diaterpenylic acid acetate, homoterpenylic acid, and the OS with MWs 212, 216, 226, 228, 261, and 306 (thus all OS with the exception of these with MW 295). As to the correlations for *cis*-pinic, very high, high or substantial correlations were only noted with *cis*-pinonic ( $r = 0.78$ ), terebic ( $r = 0.60$ ), terpenylic ( $r = 0.68$ ), caronic ( $r = 0.73$ ), ketolimonic ( $r = 0.61$ ), limonic ( $r = 0.59$ ), homoterpenylic ( $r = 0.77$ ), and caric acid ( $r = 0.81$ ). For the MW 295 nitrooxy organosulphates correlations were only found between its 5 isomers and with limonic and caric acid. MSA had only high or substantial correlations with  $\text{Na}^+$  ( $r = 0.70$ ),  $\text{Cl}^-$  ( $r = 0.63$ ), and  $\text{Mg}^{2+}$  ( $r = 0.63$ ); these correlations might have been expected considering the importance of marine sources for these species. The correlations between the various species and the meteorological parameters and trace gases were at most substantial. For example, substantial correlations with T were found for TC, OC, WSOC, succinate, MBTCA, and several

other organic LC/MS species (the exceptions were *cis*-pinonic, *cis*-pinic, caronic, limonic, and caric acid, and the MW 295 OS).

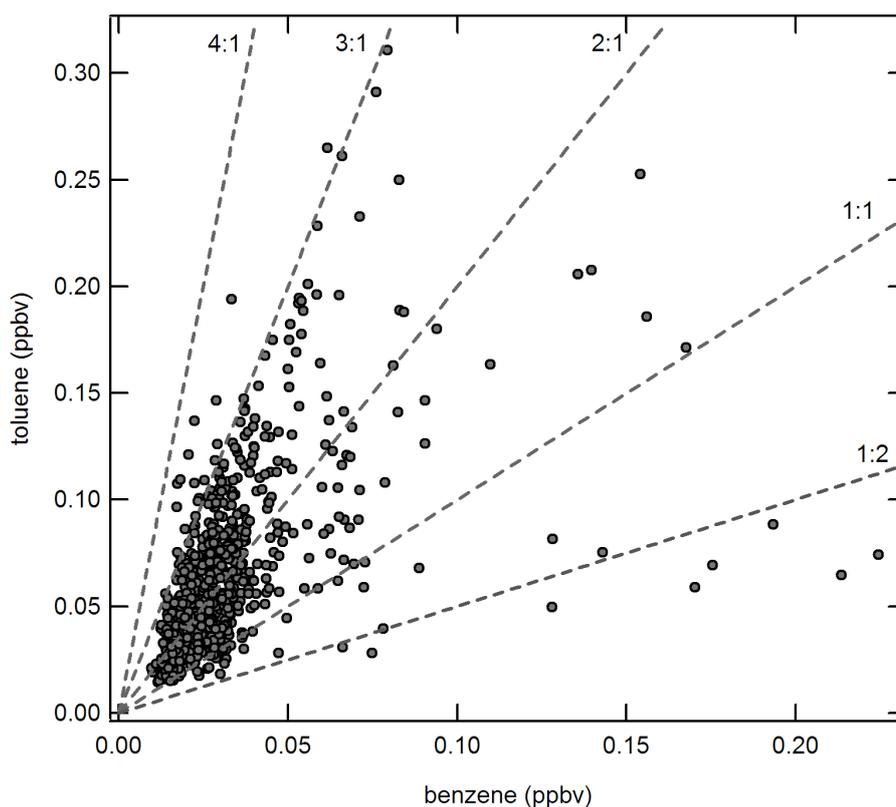
### 3.4.3. VOC data

BVOC concentration measurements at two heights above the forest started on 25 April 2007 and were scheduled to continue until the end of October 2007. However, as already indicated in section 2.3, due to instrument problems, good accurate data are only available from the end of July until mid-September 2007.

The two-months useful data contains nice diel patterns of BVOC concentrations. An average of the diel concentration fluctuations of total monoterpenes, acetone, methanol, and isoprene for the month of August is presented in Figure 14.



**Figure 14.** Average diel profiles of the concentrations of total monoterpenes (upper left panel), acetone (upper right panel), isoprene (lower left panel) and methanol (lower right panel). Mean and median concentrations are given for two measurement heights as determined from the data for August 2007.

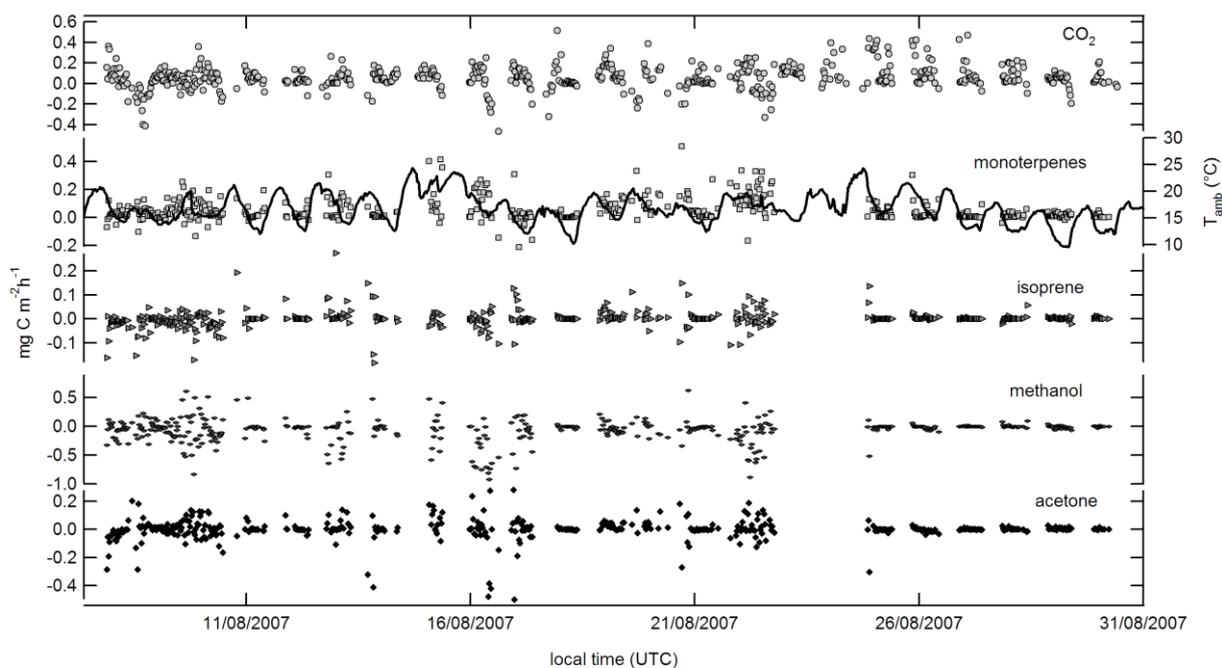


**Figure 15.** Toluene concentrations relative to benzene concentrations. Data above the 1:1 line indicate that fresh pollutants were added to the atmosphere.

The time series of the BVOC concentrations is currently being quality controlled with the view of publishing the most important results. The higher concentrations observed during night-time are related in part to the shallower boundary layer during night, and partly to the reduced oxidation rates. The concentration patterns do, however, differ substantially from those observed during the 2006 K-pusztas campaign. One possible reason could be that the Brasschaat site is located downwind of the harbour of Antwerp with its associated anthropogenic emissions. The PTR-MS instrument does not measure individual compounds but individual masses. Under natural conditions, for example, isoprene dominates the signal at its corresponding mass and hence the PTR-MS results can be interpreted as being representative for isoprene. Under polluted conditions, however, a wide variety of VOCs having the same mass as isoprene, can be present at relatively high concentrations. Hence, the diel concentration patterns at the Brasschaat site may have been affected by the industrial VOC emissions, whereas this was much less the case at the rural K-pusztas site. An indication that fresh pollution was present is given by the ratio of toluene/benzene concentrations. Toluene oxidises much more rapidly than benzene. Hence, air masses where toluene is dominant are indicative for fresh additions of organic pollutants. It is clear that these emissions were important for the Brasschaat site (Figure 15), and therefore that the natural VOCs may have been overshadowed by the anthropogenic

VOCs. Chemical analyses of the collected aerosols for detailed organic compounds indeed revealed that the anthropogenic contribution to the VOCs was reflected in the aerosols; more specifically, nitrophenolic compounds which are due to photo-oxidation of aromatic hydrocarbons could be detected. That the Brasschaat site is much more influenced by anthropogenic emissions than the K-pusztta site appeared also from the EC/OC ratios that were measured with the OCEC Field instrument and derived from the HVDS samples.

Despite observing interesting differences in BVOC concentrations for different meteorological conditions and between day and night, these observations can not be related to the activity of the pine forest because of the presence of fresh pollutants. To overcome this problem, we opted to determine VOC fluxes rather than concentration patterns. The advantage of using flux estimates is that these can be constrained to a small area (1 km<sup>2</sup>) surrounding the measurement tower and thus give information on the VOC release from (or uptake by) the forest. Fluxes can be estimated using the profile-gradient method if concentration measurements are available at minimum two heights and if turbulence was measured simultaneously. Because these were all available, we calculated the net fluxes of the different VOCs. Unfortunately, the concentration differences between the two different measurement heights were often too small (less than the measurement error) to allow emission/uptake estimations. Figure 16 presents a rare period where fluxes could frequently be computed (mid-August), in contrast to a period where fluxes could rarely be computed (end-August).



**Figure 16.** Time series of fluxes calculated with the profile-gradient technique for (from top to bottom): CO<sub>2</sub>, temperature and monoterpenes, isoprene, methanol, and acetone.

### **3.5. Studies at the SMEAR II forest station in Hyytiälä, Finland**

#### **3.5.1. Summer campaign in 2005**

The comprehensive experiments at the SMEAR II site in Hyytiälä took place in August 2007. However, as indicated in section 2.4, already in summer of 2005 a less comprehensive campaign was conducted, for which the work also forms part of the current project. The results are described in detail in Kourtchev et al. [2008a,b]. Here only a brief summary is given. The median total concentration of terpenoic acids [i.e., *cis*-pinic acid, *cis*-norpinic acid, and two novel compounds, 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (this compound was previously and also in Kourtchev et al. [2008a] incorrectly identified as 2-hydroxyl-4-isopropyladipic acid) was  $65 \text{ ng m}^{-3}$ , while that of the isoprene oxidation products (i.e., 2-methyltetrols and  $\text{C}_5$ -alkene triols) was  $17.2 \text{ ng m}^{-3}$ . The 2-methyltetrols exhibited day/night variations with maxima during day-time, while the  $\alpha/\beta$ -pinene oxidation products did not show any diel variation. The sampling period was marked by a relatively high condensation sink, caused by pre-existing aerosol particles, and no nucleation events. In general, the concentration trends of the SOA compounds reflected those of the inorganic trace gases, meteorological parameters, and condensation sink. Both the isoprene and  $\alpha/\beta$ -pinene SOA products were strongly influenced by  $\text{SO}_2$ , which is consistent with earlier reports that acidity plays a role in SOA formation. The results support previous proposals that oxygenated VOCs contribute to particle growth processes above the boreal forest.

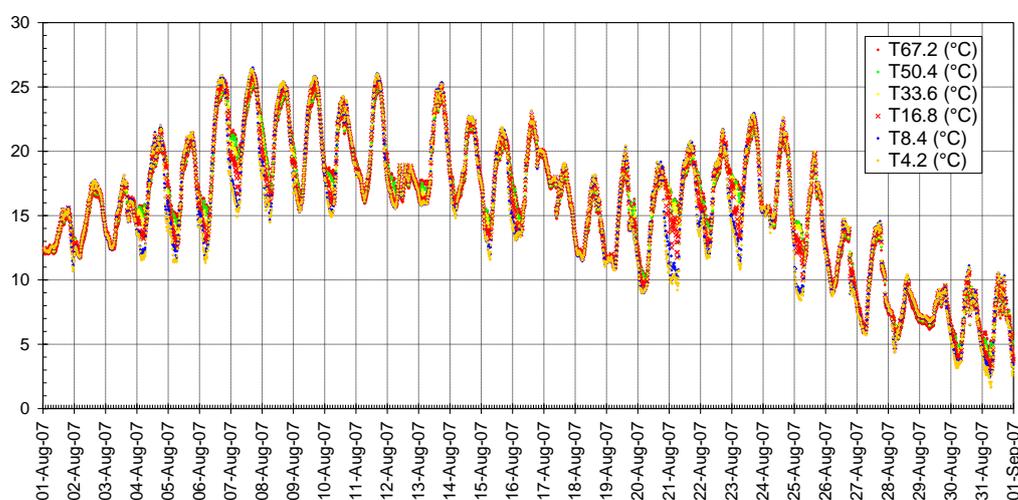
#### **3.5.2. Meteorology, air mass origin, and inorganic trace gases for the 2007 summer campaign**

The field work for the 2007 summer field campaign took place from 1 to 31 August 2007. A summary of selected meteorological and inorganic trace gas data for the month of August is given in Table VI. The data in this Table are based on daily averages (in case of precipitation, daily sums). The temperature and trace gas data in the Table are for a height of 8.4 m above the base of the mast on which the sensors were installed. There were sensors at 7 levels above mast base, ranging from 4.2 to 74 m. The highest sensor level within the forest canopy was at 8.4 m above mast base (near the top of the canopy) and the lowest sensor level above the canopy was at 16.8 m above mast base. The aerosol instruments and collectors of BIOSOL partner C were all installed at about 8 m above mast base on a separate tower. Figure 17 shows the time series of the 15-min averaged temperature data at 6 levels above mast base. There were 14 days with rain throughout the month (i.e., on 1, 3, 12, 15 through 19, and

26 through 31 August). However, on most of these days, the total amount of rain was less than 4 mm; the only exceptions were 28 and 29 August with 8-9 mm. As to the temperature, the mean daily temperature rose from 13.4 °C on 1 August to around 20 °C in the period of 6-13 August and decreased then down to 6.1 °C on 31 August, with a secondary maximum of 17 °C on 22-24 August.

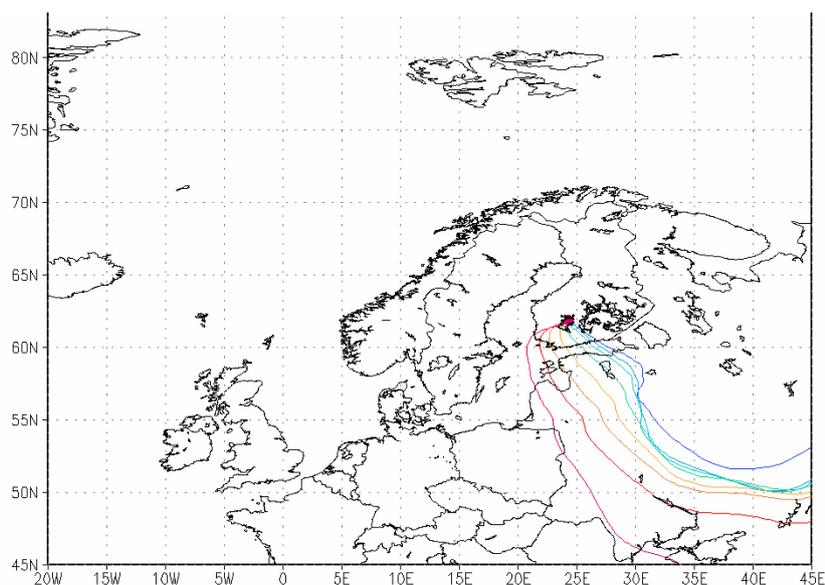
**Table VI.** Averages (and associated standard deviations), medians, and ranges of daily averaged data for temperature, wind speed, relative humidity, and selected inorganic trace gases (O<sub>3</sub>, NO<sub>x</sub>, and SO<sub>2</sub>) during August 2007 at SMEAR II. The data for precipitation are the average, median, and range of the daily summed rainfall.

Parameter	mean ± std.dev.	median	range
Temp. (°C)	15.5 ± 4.4	17.0	6.1 – 21.3
Wind speed (m/s) at 8.4 m	0.67 ± 0.29	0.61	0.34 – 1.45
Wind speed (m/s) at 16.8 m	1.95 ± 0.69	1.71	1.05 – 3.71
Precipitation (mm)	1.2 ± 2.2	0	0 – 8.7
Relative humidity (%)	78 ± 9	79	59 – 98
O <sub>3</sub> (ppbv)	29 ± 4	29	21 – 36
NO <sub>x</sub> (ppbv)	0.76 ± 0.27	0.69	0.30 – 1.56
SO <sub>2</sub> (ppbv)	0.14 ± 0.13	0.10	0.01 – 0.51

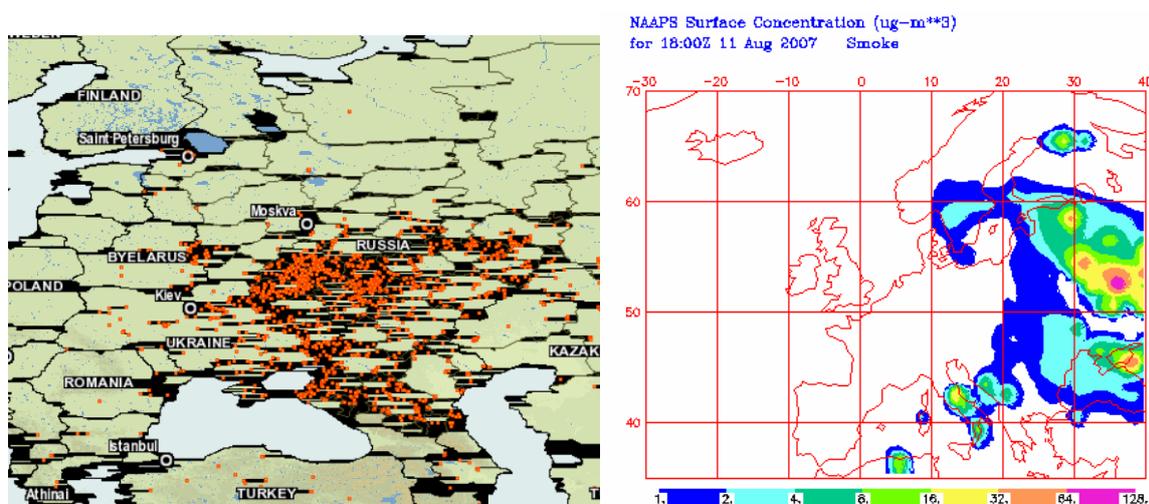


**Figure 17.** Time series of the 15-min averaged temperature as a function of local summer time during August 2007 at SMEAR II.

The air masses came mostly from the West, except in the period from 9 to 14 August, when they first showed a recirculation pattern and on 13 and 14 August came from the South (Figure 18). In the period of 10-13 August there was extensive biomass burning in the southern part of European Russia (Figure 19), which considering the air mass transport could have affected our measurements at SMEAR II.



**Figure 18.** Five-day, 3-dimensional air mass back trajectories, calculated with HYSPLIT [Lupu and Maenhaut, 2002] for every 6 hours and for an arrival level of 100 m above ground at SMEAR II on 13 and 14 August 2007. The trajectories are colour-coded from dark blue to dark red, with the dark blue one for 13 August 0:00 UTC and the dark red one for 14 August 18:00 UTC.

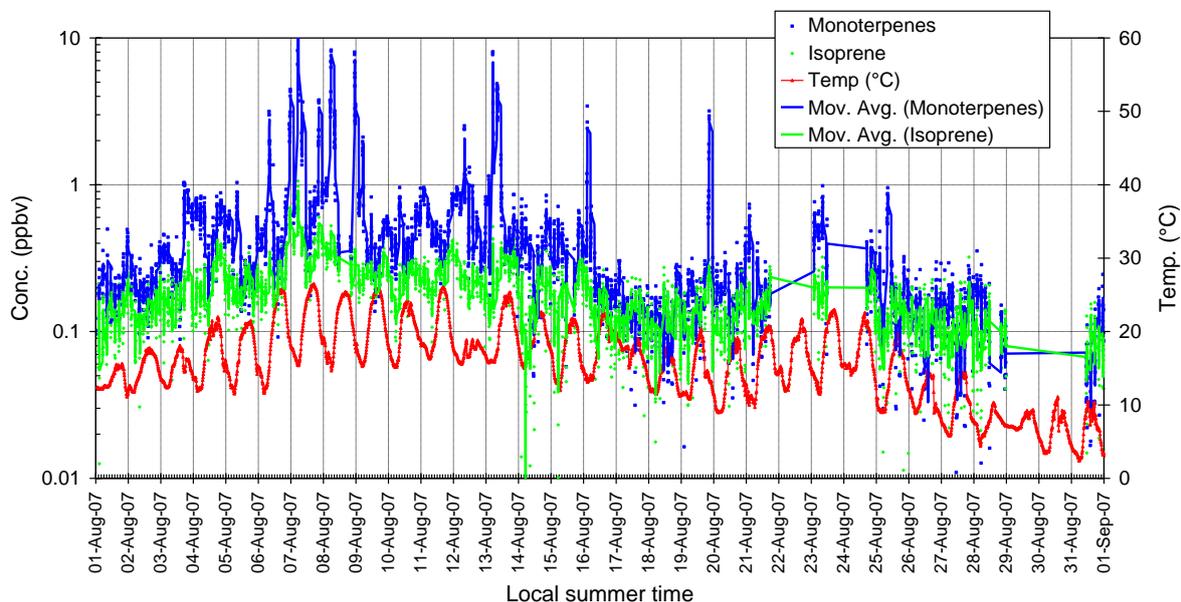


**Figure 19.** Left: MODIS fire map for 11 August 2007 (source: University of Maryland). Right: Navy Aerosol Analysis and Prediction System (NAAPS) surface smoke concentration (in  $\mu\text{g}/\text{m}^3$ ) for 11 August 2007: 18:00 UTC.

### 3.5.3. BVOC data and relation to temperature for the 2007 summer campaign

The time series of the in-situ data for isoprene and the monoterpenes and of the ambient temperature is shown in Figure 20. The highest levels of the monoterpenes are noted in the nights of 7, 8, and 9 August, thus right after the start of the warm period (from 6 to 13 August) when daily averaged temperatures were around 20 °C. Overall, when looking at daily averages, there was some relation between the concentrations of

the two BVOCs and temperature, with higher levels at higher temperatures. However, similarly as during the 2006 K-pusztas campaign (see section 3.3.2), in the high time resolution data, the night-time levels for the monoterpenes are about an order of magnitude level higher than the day-time levels, so that there is an anticorrelation with temperature for these BVOCs.

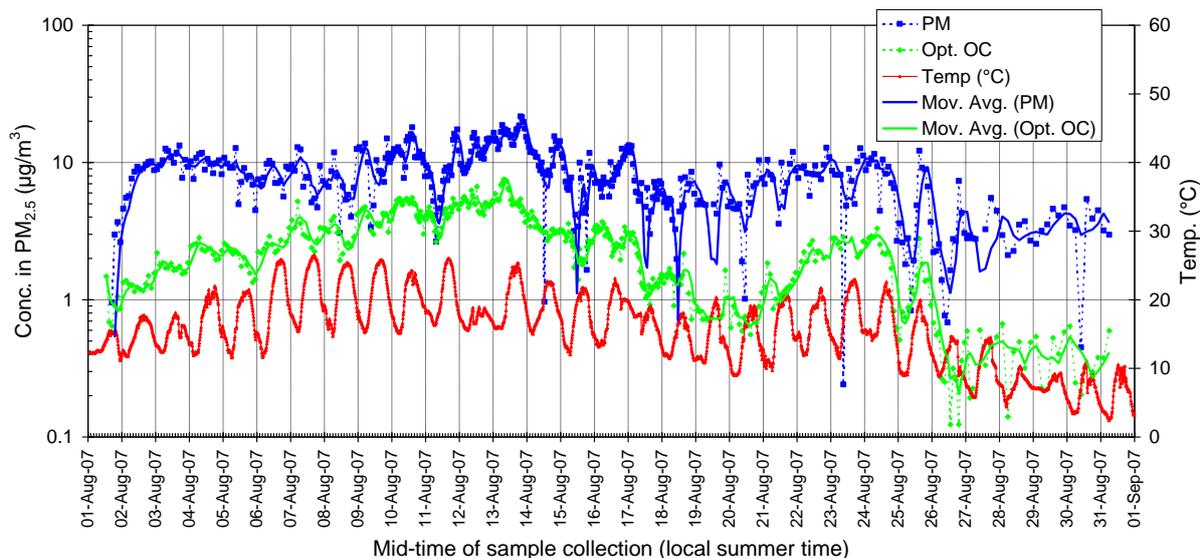


**Figure 20.** Time series of the atmospheric concentrations of monoterpenes ( $m/z$  137) and isoprene ( $m/z$  69), and of the air temperature at SMEAR II for the period from 1 to 31 August 2007. Note that a log scale is used for the BVOCs and a linear scale for the temperature. The vertical dashed lines are at 00:00 h.

### 3.5.4. In-situ data for the PM, BC, and particulate OC and EC during the 2007 summer campaign and their relation to temperature

The PM<sub>2.5</sub> in-situ data for optical OC (OptOC) and optical EC (OptEC), as obtained with the OCEC Field instrument (using 1-hour, 2-hour or 4-hour time resolution, depending on the OC level), varied from 0.1 to 7.9  $\mu\text{g}/\text{m}^3$  (OptOC) and from 0 to 0.82  $\mu\text{g}/\text{m}^3$  (OptEC). The ratio of OptEC to TC (with TC = OptOC + OptEC) was, on average,  $0.083 \pm 0.039$  [N = 425]. Such ratio is fairly logical for a forested site. It is substantially lower than the mean OptEC/TC ratio of  $0.15 \pm 0.05$  that was obtained with the OCEC Field instrument during the 2006 K-pusztas campaign (it should be noted, though, that the EC/TC ratio, as derived from the PM<sub>2.5</sub> front filters of the HVDS during that campaign was, on average, only  $0.063 \pm 0.030$ , see section 3.3.6) and much lower than the OptEC/TC ratios from the OCEC Field instrument and EC/TC ratio from the HVDS obtained for Brasschaat (sections 3.4.1 and 3.4.2). In any case, the low OptEC/TC ratio at SMEAR II indicates that the site was little affected by carbonaceous matter from fossil fuel combustion. PM and BC in PM<sub>2.5</sub> were measured with 10 min time resolution by a TEOM and aethalometer, respectively, but the data were averaged over the time

periods of the OCEC instrument. The averaged data ranged from 0 to 22  $\mu\text{g}/\text{m}^3$  for the PM and from 0 to 0.79  $\mu\text{g}/\text{m}^3$  for BC.



**Figure 21.** Time series of PM<sub>2.5</sub> PM and OC and of the air temperature during the 2007 summer campaign at SMEAR II (the vertical dashed lines are at 00:00 h). Full lines for the PM and OC are 4-point moving averages.

The time series of the PM and OptOC (both in PM<sub>2.5</sub>) and of the ambient temperature is shown in Figure 21. Optical OC and the PM were fairly well correlated with each other, with  $\text{OptOC} = 0.28 * \text{PM} + 0.36$  ( $R^2 = 0.55$ ). The time series for the PM and OC is different from that for the BVOCs. Whereas the highest levels of the monoterpenes were noted in the nights of 7, 8, and 9 August, and high levels were also observed in the nights of 13, 16, and 19 August, the OC levels (and to a lesser extent also the PM levels) kept increasing from the beginning of the measurements until 13 August and decreased afterwards, with a second maximum on 22 to 24 August. It seems thus that there is little relation between the local concentrations of the BVOCs and fine OC at the SMEAR II site. Tunved et al. [2006] found that both particle number concentrations and aerosol mass at three boreal forest sites in Finland (including SMEAR II) in the period from late spring to early fall were related to the integrated passage time of the air masses over the forested areas, where the BVOCs were emitted, and to the total amount of terpenes emission that had occurred during the air mass transport. It is likely that this also holds for our fine OC data and that they are thus related to the total BVOC emissions upwind of the site during the last 5 days or so of air mass transport rather than to the local BVOC concentrations at SMEAR II itself.

### **3.5.5. Mass size distributions for the PM and OC during the 2007 summer campaign and comparison with physical aerosol data**

As part of the activities during the 2007 summer campaign at SMEAR II, size-fractionated aerosol samples were collected with two cascade impactors, i.e., a 12-stage SDI and a 10-stage MOUDI, which was extended with 3 nanoMOUDI stages. Separate collections were made during day-time (from 7:30 to 19:40 local time) and night-time (from 20:20 to 6:40 local time). The two impactors were operated at ambient temperature and RH. The collection surfaces in the SDI consisted of pre-fired Pall quartz fibre filters and the impaction surfaces in the MOUDI of pre-fired aluminium foils. The SDI samples were analysed for OC and EC by TOT, whereas the MOUDI aluminium foils were weighed at 20 °C and 50% RH to obtain the PM. Besides the two cascade impactors, a DMPS was operated with 10-min time resolution to derive the number size distribution from 3 nm to 1 µm mobility diameter. The DMPS was deployed under dry conditions (RH <30%).

The mass of EC on the SDI stages was close to the detection limit of the TOT method and will therefore not be discussed. The mass size distributions for OC and PM peaked in the accumulation size range, but there was also a clear coarse mode for both with peak at around 3-4 µm AD. Two distinct submicrometer modes, with peaks at about 0.3 and 0.7 µm AD, were clearly present for OC in the accumulation size range for the individual day-time SDI samples, whereas in the night-time SDI samples the two modes seemed to have consistently merged into one broad accumulation mode.

Two submicrometer submodes have been observed earlier for particulate sulphate, ammonium, and nitrate [Hering and Friedlander, 1982; John et al., 1990; Hering et al., 1997; Ricard et al., 2002]; the one with lower diameter was termed "condensation" mode and the other one "droplet" mode. The formation of the "droplet" mode is explained by activation of condensation mode particles to form fog or cloud drops followed by aqueous-phase chemistry in fogs or clouds and subsequent fog or cloud evaporation [Meng and Seinfeld, 1994; Kerminen and Wexler, 1995]. This formation process of the "droplet" mode can only be invoked for water-soluble (or at least hydrophilic) species. As indicated below in section 3.5.6, it appeared from the analysis of the PM<sub>2.5</sub> HVDS filter samples that a very large fraction of the PM<sub>2.5</sub> OC was water-soluble, on average, 63±7%. As to the broad accumulation mode during the night, this is likely due to hygroscopic growth of the OC. The RH increased to 80-100% during the night, whereas it generally decreased to well below 60% during day-time. In the MOUDI size distributions for the PM, no

distinct submicrometer modes could be discerned, but this is attributed to the fewer number of submicrometer stages than in the SDI [Salma et al., 2005]. Both during day and night, the PM exhibited a broad submicrometer size distribution, but with peak at slightly larger diameter during night than during the day (i.e., at 0.45  $\mu\text{m}$  AD versus 0.40  $\mu\text{m}$  AD). For the dry volume size distributions derived from the DMPS there was no difference between the average day-time and night-time distributions; both peaked at 0.25  $\mu\text{m}$  mobility diameter. This is fully consistent with the difference between day and night mass size distributions for OC and the PM being caused by hygroscopic growth during the night.

### **3.5.6. Filter data for the PM, OC, EC, and WSOC during the 2007 summer campaign and assessment of artifacts in the collection of particulate OC**

The medians (and ranges) for the PM, as derived from 12-hour low-volume PM<sub>2.5</sub> and PM<sub>10</sub> samplers with Nuclepore filters, were 7.2 (0.7 – 15)  $\mu\text{g}/\text{m}^3$  for PM<sub>2.5</sub> and 10.2 (1.5 – 29)  $\mu\text{g}/\text{m}^3$  for PM<sub>10</sub>. The PM<sub>2.5</sub> to PM<sub>10</sub> mass ratio for the PM, was, on average,  $0.64 \pm 0.11$  [N=51]. The medians (and ranges) for "artifact-free" (i.e., back-filter corrected) OC, as derived from undenuded 12-hour low-volume PM<sub>2.5</sub> and PM<sub>10</sub> samplers with tandem quartz fibre filters, were 2.8 (0 – 6.0)  $\mu\text{g}/\text{m}^3$  for PM<sub>2.5</sub> and 3.4 (0 – 8.6)  $\mu\text{g}/\text{m}^3$  for PM<sub>10</sub>. The PM<sub>2.5</sub> to PM<sub>10</sub> mass ratio for OC, was, on average,  $0.72 \pm 0.23$  [N=50]. On the basis of the individual OC and PM data from the samplers just mentioned, average OC/PM ratios of  $0.41 \pm 0.12$  and of  $0.37 \pm 0.10$  were calculated for PM<sub>2.5</sub> and PM<sub>10</sub>, respectively, indicating that the PM was dominated by organic aerosol. If we apply an OC-to-OM conversion factor of 1.8, as done for K-pusztá (section 3.3.8), this would lead to a concentration of OM in the PM of 74% for PM<sub>2.5</sub> and 67% for PM<sub>10</sub>.

As far as artifacts for the particulate OC are concerned, the average ratios (OC on the back filter)/(OC on the front filter) for the undenuded 12-hour samples were  $0.17 \pm 0.04$  for the PM<sub>2.5</sub> size fraction of the HVDS, and  $0.09 \pm 0.08$  and  $0.11 \pm 0.09$  for the low-volume PM<sub>2.5</sub> and PM<sub>10</sub> samplers. For the undenuded and denuded 24-hour low-volume PM<sub>2.5</sub> filter samplers (F25UWW and F25DWW) the average ratios and associated standard deviations of (OC on the back filter)/(OC on the front filter) were  $0.11 \pm 0.06$  for F25UWW and  $0.05 \pm 0.02$  for F25DWW. All these ratios are fairly similar to those obtained for the 2006 summer campaign at K-pusztá (see section 3.3.6), be it that there was a tendency for the undenuded samplers to exhibit slightly higher ratios in that campaign. From the data for F25UWW and F25DWW an average ratio (corrected OC from F25UWW)/(corrected OC from F25DWW) of  $1.11 \pm 0.10$  was obtained, indicating that like for the 2006 K-pusztá campaign, the assumptions of Mader

et al. [2003] were valid and that it was appropriate to calculate "artifact-free" particulate OC for the undenuded samplers as the difference between front and back filter OC.

As indicated above in section 3.5.4, the average ratio of OptEC/TC in PM<sub>2.5</sub>, as obtained from the OCEC Field instrument, was 0.083±0.039. Like at K-pusztá, from the filter samplers somewhat lower EC/TC ratios were obtained, be it that the difference was smaller now. For example, in the HVDS samples from the 2007 campaign at SMEAR II, the average ratios and associated standard deviations for EC/TC (using uncorrected OC data) were 0.060±0.020 for the fine front filters and 0.027±0.015 for the coarse front filters. The WSOC analyses of the HVDS samples indicated that most of the fine OC was water-soluble. Using uncorrected OC data, 63±7% [N=51] of the OC was WSOC for the fine front filters and 70±12% [N=51] for the fine back filters during the 2007 campaign. The corresponding percentages for the HVDS samples of the 2006 K-pusztá campaign were 57±9% for the fine front filters and 73±12% for the fine back filters.

### 3.5.7. Results from the IC and elemental analyses, impact from biomass burning, correlations with meteorological and trace gas data, and aerosol chemical mass closure for the 2007 summer campaign

**Table VII.** Median concentrations and interquartile ranges for TC, OC, EC, WSOC, MSA, DCAs, and water-soluble inorganic species, as derived from the PM<sub>2.5</sub> size fraction front filters of the HVDS samples from the 2007 summer campaign at SMEAR II [N = 71]. The medians and interquartile ranges for the back/front ratio in the PM<sub>2.5</sub> size fraction are also included.

Species	Front filter conc. (ng/m <sup>3</sup> )		Back/front filter ratio	
	median	interq. range	median	interq. range
TC	2600	1650 – 3400	0.15	0.13 – 0.19
OC	2400	1540 – 3300	0.16	0.14 – 0.20
EC	164	101 – 191	0.00	0.00 – 0.00
WSOC	1570	870 – 2100	0.17	0.11 – 0.28
NH <sub>4</sub> <sup>+</sup>	520	280 – 1880	0.00	0.00 – 0.01
SO <sub>4</sub> <sup>2-</sup>	1640	930 – 2300	0.00	0.00 – 0.00
NO <sub>3</sub> <sup>-</sup>	71	45 – 106	0.25	0.13 – 0.36
Na <sup>+</sup>	55	35 – 84	0.00	0.00 – 0.06
Mg <sup>2+</sup>	3.5	1.91 – 5.0	0.00	0.00 – 0.00
K <sup>+</sup>	47	14.2 – 77		
Ca <sup>2+</sup>	22	15.1 – 37	0.00	0.00 – 0.00
MSA <sup>-</sup>	45	31 – 58	0.06	0.02 – 0.10
Oxalate	104	67 – 132	0.01	0.01 – 0.02
Malonate	19.8	10.0 – 33	0.09	0.02 – 0.17
Succinate	12.6	4.4 – 23	0.02	0.01 – 0.06
Glutarate	7.0	5.0 – 8.8	0.07	0.00 – 0.15

The fine front and back filters of the HVDS were analysed for water-soluble inorganic and organic ions by IC. The results are summarized in Table VII. Also data for TC, OC, EC, and WSOC are included in the Table. When comparing the front filter concentration with those for the 2006 summer campaign at K-pusztá (Table II), it appears that for most species the concentrations at SMEAR II are similar to those in the cold period at K-pusztá. Only for nitrate are the levels substantially lower at SMEAR II than in the cold K-pusztá period. With regard to the DCAs, whereas oxalate has somewhat higher concentrations at SMEAR II than in the cold K-pusztá period, an opposite pattern is noted for malonate and succinate. The organic compounds measured by IC accounted, on average, for 2.0% of the OC and 3.1% of the WSOC. These percentages are about one third lower than those found at K-pusztá.

The back/front filter ratios of Table VII were calculated in the same way as for K-pusztá, thus on a sample by sample basis, and from these data medians and interquartile ranges for the ratios were then derived. The ratios of Table VII are overall quite similar to those observed at K-pusztá (Table III).

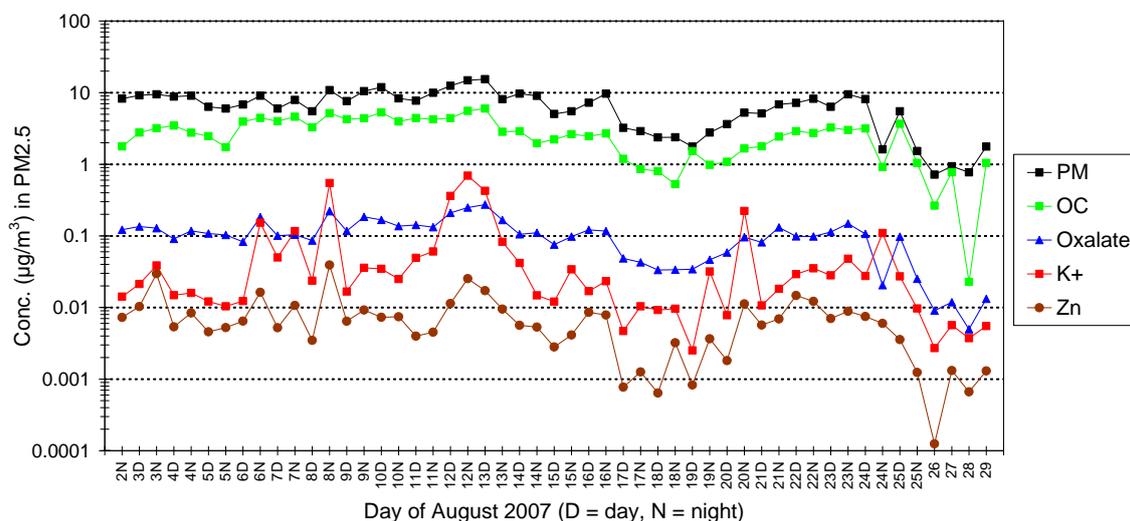
**Table VIII.** Median concentrations and interquartile ranges for the PM, OC, EC, and water-soluble inorganic species, as derived from the PM<sub>2.5</sub> and PM<sub>10</sub> low-volume filter samples with Nuclepore polycarbonate or Whatman QM-A quartz fibre filters. DL indicates detection limit.

	PM <sub>2.5</sub> (ng/m <sup>3</sup> )		PM <sub>10</sub> (ng/m <sup>3</sup> )		PM <sub>2.5</sub> /PM <sub>10</sub>
	median	interq. range	median	interq. range	ratio median
PM	7200	4300 – 9100	10200	7400 – 12400	0.67
OC	2800	1590 – 4000	3400	2100 – 4700	0.73
EC	72	34 – 107	49	12 – 104	
NO <sub>3</sub> <sup>-</sup>	37	13.1 – 95	187	92 – 480	0.21
SO <sub>4</sub> <sup>2-</sup>	1520	910 – 2300	1690	1070 – 2500	0.92
nss-SO <sub>4</sub> <sup>2-</sup>	1500	890 – 2300	1620	1030 – 2400	0.94
Cl <sup>-</sup>	2.4	0.62 – 10.2	5.5	2.73 – 44	0.19
Br <sup>-</sup>	0.16	DL – 0.28	0.13	DL – 0.34	
MSA <sup>-</sup>	135	66 – 171	145	98 – 181	0.90
NH <sub>4</sub> <sup>+</sup>	580	360 – 920	570	350 – 790	1.10
Na <sup>+</sup>	49	33 – 85	116	57 – 270	0.39
Mg <sup>2+</sup>	1.87	0.02 – 5.0	25	12.5 – 39	0.08
K <sup>+</sup>	24	11.4 – 45	52	33 – 80	0.48
Ca <sup>2+</sup>	9.9	2.6 – 20	57	33 – 131	0.10

The filters from the 12-hour PM<sub>2.5</sub> and PM<sub>10</sub> Nuclepore filter samplers were analysed for inorganic ions by IC and for elements by PIXE [Maenhaut et al., 2011]. The median concentrations and interquartile ranges for the PM, OC, EC, and water-soluble inorganic species, as derived from the PM<sub>2.5</sub> and PM<sub>10</sub> low-volume filter samples with Nuclepore polycarbonate or Whatman QM-A quartz fibre filters, are presented in Table VIII. For PM<sub>2.5</sub>, the data can be compared with those derived from the HVDS (Table VII). The two sets of PM<sub>2.5</sub> data are in reasonable agreement. For MSA<sup>-</sup> there is a difference of a factor of 3 between the two medians; the MSA<sup>-</sup> data from the HVDS are thought to be more reliable because of a much better peak separation in the IC of the HVDS samples than in the IC of low-volume PM<sub>2.5</sub> samples. As to EC, NO<sub>3</sub><sup>-</sup> and the cationic species Mg<sup>2+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>, there is clearly a tendency for lower levels in the low-volume samples than in the HVDS. For NO<sub>3</sub><sup>-</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>, the low-volume data (which were derived from Nuclepore polycarbonate filters) are expected to be more reliable because of positive artifacts in the case of NO<sub>3</sub><sup>-</sup> and high blank levels for Mg<sup>2+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> with the quartz fibre filters used in the HVDS. As to EC, the data from the HVDS are expected to be more reliable than those from the low-volume samples. Table VIII also gives the median PM<sub>2.5</sub>/PM<sub>10</sub> ratios for various species, as derived from the low-volume samples. When looking at Table VIII, for both PM<sub>2.5</sub> and PM<sub>10</sub>, OC is clearly the major component, followed by sulphate and ammonium. These major species are mostly associated with the fine size fraction, and as a result also the PM is mostly in this fraction. Also MSA, which is a gas-to-particle conversion product of marine DMS is mostly fine. For K<sup>+</sup>, which had important contributions from biomass burning in a number of samples (see below), the median PM<sub>2.5</sub>/PM<sub>10</sub> ratio is 0.48; for Na<sup>+</sup>, which is mostly attributable to sea salt, it is 0.39, and NO<sub>3</sub><sup>-</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> are clearly predominantly associated with the coarse particles. The Cl<sup>-</sup>/Na<sup>+</sup> ratio in PM<sub>10</sub> exhibited a median of 0.08 and an interquartile range of 0.02-0.26. All these ratios are much lower than the Cl/Na ratio in sea water, indicating that the sea salt was quite aged and had been subjected to substantial Cl loss processes.

Figure 22 shows the time series for the PM, OC, oxalate, K<sup>+</sup>, and Zn (all in PM<sub>2.5</sub>) during the 2007 summer campaign at SMEAR II (the data for OC in the Figure come from an undenuded low-volume sampler with quartz fibre filters, those for the PM, K<sup>+</sup>, and Zn from the PM<sub>2.5</sub> sampler with Nuclepore polycarbonate filter, and those for oxalate from the HVDS). It is clear that the time series for K<sup>+</sup> substantially differs from that for the PM and OC. The time series for Zn shows good resemblance to that of K<sup>+</sup> and also oxalate has a tendency to be elevated in the samples where K<sup>+</sup> is high. Fine K<sup>+</sup>, Zn, and oxalate are all indicators for biomass burning [e.g., Andreae, 1983; Maenhaut et al., 1996b; Kuokka et al., 2007]. Particularly striking is that there are 3 samples in a row (i.e., the day-time samples of 12 and 13 August and the night-time

sample of 12 August) that exhibit high  $K^+$ , Zn, and oxalate levels. Considering the intensive biomass burning in the southern part of European Russia (Figure 19), when the air masses passed over there, it is quite likely that the high levels of fine  $K^+$  and Zn in those 3 samples were to a large extent due to the biomass burning in that region. Consistent with the attribution of fine  $K^+$  in the 3 samples in a row to biomass burning was that K was fully water-soluble as could be concluded from the excellent agreement between the PIXE K and IC  $K^+$  data in these samples; in the remaining samples typically only about 50% of the  $PM_{2.5}$  K was water-soluble. Furthermore, the  $PM_{2.5}/PM_{10}$  ratio for PIXE K in the 3 samples was around 0.8, whereas in the other samples the ratio was typically only around 0.5. This all emphasizes the large impact from fine biomass burning K, which was presumably present as KCl in those 3 samples. Although part of the oxalate was likely also derived from biomass burning for those 3 samples, it seems that most of the fine oxalate and also most of the fine OC are derived from other sources.

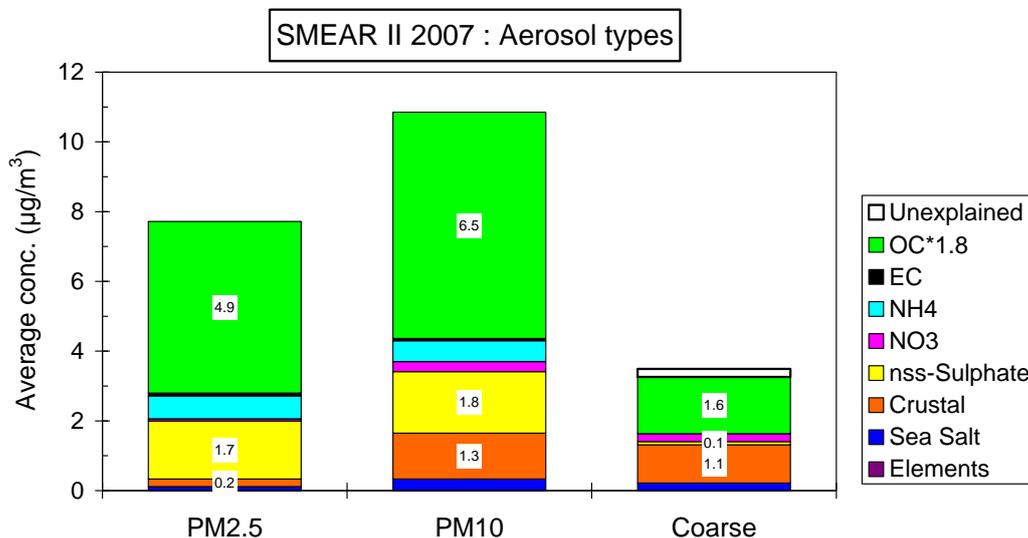


**Figure 22.** Time series of the PM, OC, oxalate,  $K^+$ , and Zn (all in  $PM_{2.5}$ ), as derived from filter samplers during the summer campaign at SMEAR II.

For both the low-volume  $PM_{2.5}$  and  $PM_{10}$  data, the correlations among the various species and of the particulate species with a number of meteorological parameters and trace gases were examined. The meteorological data included T, RH, and WS, whereas the trace gases were  $H_2O$ ,  $CO_2$ , CO,  $SO_2$ , NO,  $NO_x$ ,  $O_3$ , isoprene, and monoterpenes. For  $PM_{2.5}$  also the data from the HVDS were included in the correlation calculations. In both  $PM_{2.5}$  and  $PM_{10}$  OC was highly correlated ( $r > 0.7$ ) with the PM,  $H_2O$ , CO, and isoprene and substantially ( $0.5 < r < 0.7$ ) with the monoterpenes and  $K^+$ . In  $PM_{2.5}$ , OC was also highly correlated with WSOC and oxalate, malonate, and succinate, as derived from the HVDS, and substantially with glutarate (also derived from the HVDS). The correlations between the PM and OC in  $PM_{2.5}$ , as obtained from the in-situ instruments (and thus with much higher time

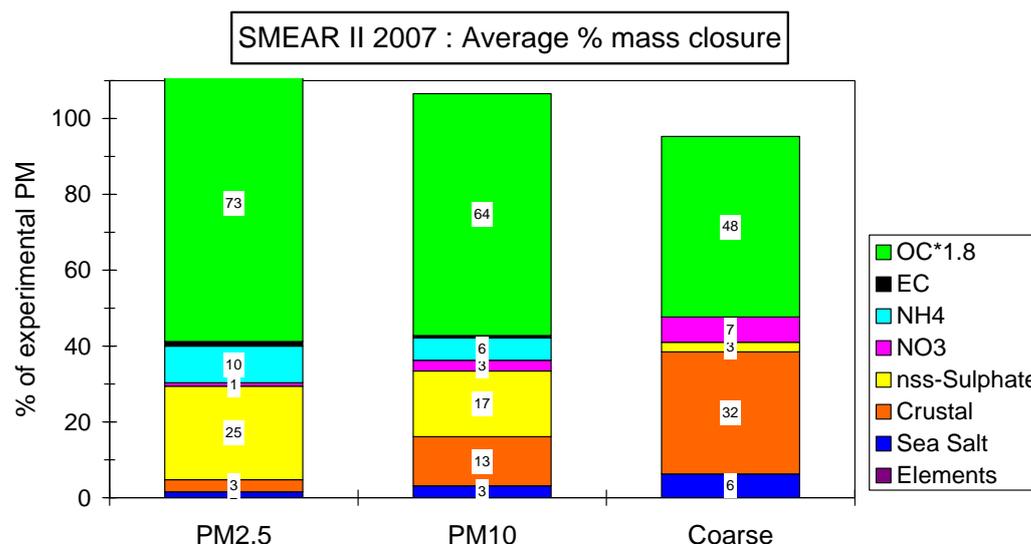
resolution than from the filter measurements), and the meteorological parameters and trace gas data were also examined. OC was highly correlated with the PM, H<sub>2</sub>O, and CO, substantially with T ( $r = 0.52$ ) and isoprene ( $r = 0.53$ ) and somewhat less with the monoterpenes ( $r = 0.43$ ). That there is no very strong correlation between the in-situ data of OC and the BVOCs is attributed to the fact that the biogenic SOA at the SMEAR II site is not so much related to the BVOC concentrations at the site itself, but rather to the total BVOC emissions upwind of the site during the last 5 days or so of air mass transport. The correlations of in-situ OC (in  $\mu\text{g}/\text{m}^3$ ) with H<sub>2</sub>O (in ppthv) and CO (in ppbv) were  $y = 0.463x - 3.7$  [ $R^2 = 0.63$ ] and  $y = 0.072x - 6.0$  [ $R^2 = 0.79$ ], respectively. Although the correlations were strong, the regression lines did not pass through the origin at all; instead there was clearly an offset (constant background) of around 7 ppthv H<sub>2</sub>O and of about 90 ppbv CO for zero OC concentration. The constant background for CO is likely due to CO formation processes (such as fossil fuel combustion) which have virtually no impact on (and are not related to) the OC levels at the SMEAR II site. Why the additional CO (thus that in excess of that offset) is then so very highly correlated with the OC is not so clear. First, the question arises whether the excess CO is due to oxidation of BVOCs or whether there is a substantial contribution from the biomass burning in the southern part of European Russia. Although there was a substantial correlation ( $r = 0.58$ ) between PM<sub>2.5</sub> K<sup>+</sup>, which was shown to be a useful indicator for the biomass burning, and CO, there was much less variability in the CO levels than in the levels of PM<sub>2.5</sub> K<sup>+</sup>, suggesting that the biomass burning CO was not very important. The average of the CO data points was 119 ppbv; thus, after subtraction of the 90 ppbv background, 29 ppbv of excess CO remains. According to modelling calculations by Granier et al. [2000], the CO levels arising from the oxidation of isoprene and monoterpenes are around 5 ppbv each for the month of July in Finland, thus about 10 ppbv combined (Incidentally, Granier et al. [2000] attributed about 20 ppbv to CH<sub>4</sub> oxidation, but most of this may form part of our 90 ppbv background). Although the concentration of 10 ppbv is about a factor of three lower than our excess CO, it may well be that a substantial (if not major) fraction of our excess CO at SMEAR II is due to oxidation of BVOCs, whereby the latter is expected to be the major source process for the OC. The strong correlation between CO and OC may be coincidental and their concurrent increase in concentration may just be a reflection of the more intense (photo-)oxidation processes, which will give rise to both higher CO levels and higher concentrations of biogenic SOA. As to the observed relationship between OC and H<sub>2</sub>O, investigations on this type of relations are generally made in terms of OC versus RH and in smog chamber experiments both positive and negative relations have been found, depending on the VOC and reaction studied. Our in-situ OC data were not related at all to RH ( $r = 0.12$ ), but there was clearly a high positive correlation between OC and the absolute concentration of H<sub>2</sub>O vapour in the air. It

seems thus that the higher the H<sub>2</sub>O vapour concentration the higher the levels of OC and presumably of biogenic SOA. Further studies are suggested to examine whether there is any causal relationship between H<sub>2</sub>O and biogenic SOA and if so, which processes are behind it.



**Figure 23.** Average concentrations of 8 aerosol types during the 2007 summer campaign at SMEAR II, and this separately for the PM<sub>2.5</sub>, PM<sub>10</sub>, and coarse (PM<sub>10-2.5</sub>) aerosol.

The data of the PM and of a number of particulate species and elements in the PM<sub>2.5</sub> and PM<sub>10</sub> low-volume filter samples were used to examine to which extent aerosol chemical mass closure could be obtained. This exercise was done for each individual sample and for both PM<sub>2.5</sub> and PM<sub>10</sub> and also for the coarse (PM<sub>10-2.5</sub>) aerosol, whereby the data for the latter were obtained by subtracting the PM<sub>2.5</sub> data from the PM<sub>10</sub> data. The calculations were done in the same way as for the 2006 campaign at K-pusztá (section 3.3.8) and the same eight aerosol types (components) were considered. The average concentrations of the various aerosol types (and of the unexplained gravimetric PM) are shown in Figure 23, and this separately for the PM<sub>2.5</sub>, PM<sub>10</sub>, and coarse aerosol. The percentage contributions of the various components to the average gravimetric PM are given in Figure 24. OM is clearly the dominant component in both PM<sub>2.5</sub> and PM<sub>10</sub>. It accounts for 73% and 64% of the average gravimetric PM in PM<sub>2.5</sub> and PM<sub>10</sub>, respectively, and is in both cases followed by nss-sulphate, which represents 25% and 17% of the average gravimetric PM in PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. In the coarse aerosol, OM is still the most important component (with 48%), but now followed by crustal matter (with 32%).

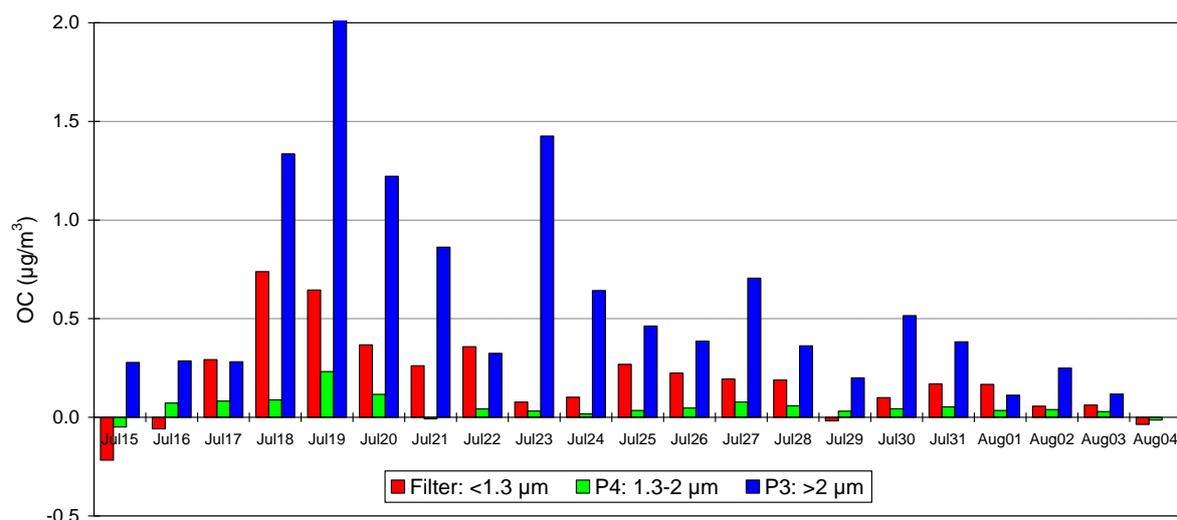


**Figure 24.** Percentage contributions of the various components to the average gravimetric PM for the 2007 summer campaign at SMEAR II, and this separately for the PM<sub>2.5</sub>, PM<sub>10</sub>, and coarse (PM<sub>10-2.5</sub>) aerosol.

### 3.6. Studies during an oceanic cruise and at a remote island in the southern Indian Ocean

#### 3.6.1 Aerosol study during an oceanic cruise in the Northern Hemisphere

As indicated in section 2.5, 21 daily Hi-Vol samples (with 3 size fractions per sample) were collected in summer 2006 during an oceanic cruise with the F.S. Meteor in the Mauritanian upwelling region of the tropical Atlantic of the Northern Hemisphere (NH). There was a large variability in the atmospheric OC, EC, and TC concentrations over the 21 samples, indicating that air masses of very different compositions and/or origins were sampled throughout the cruise track. From 18 to 31 July the ship was much closer to the African continent (between 50 and 500 km away) than during the remainder of the cruise. The total TC concentration (summed over the 3 size fractions) varied from 0.0 to 5.7  $\mu\text{g}/\text{m}^3$  (with median of 0.9  $\mu\text{g}/\text{m}^3$ ); for OC (sum of the 3 size fractions) the concentration range was 0.0 to 5.3  $\mu\text{g}/\text{m}^3$  (with median of 0.7  $\mu\text{g}/\text{m}^3$ ). The OC concentration in the 3 size fractions in the individual samples is shown in Figure 25. Most of the OC was in the coarse (>2  $\mu\text{m}$ ) size fraction (around 69%), followed by the fine (<1.3  $\mu\text{m}$ ) with 23%, and the medium (1.3-2  $\mu\text{m}$ ) size fraction with 8%.



**Figure 25.** OC concentrations in 3 size fractions during the NH cruise. The samples are labeled according to the start date of the 24-h collection. P3 stands for the stage, which collected the coarse particles, and P4 for the stage, which collected the medium size fraction.

Large EC/TC ratios were generally observed for the fine and medium size fractions (typically, around 0.4 and 0.3, respectively). In contrast, in the coarse fraction, there was generally no EC detected. The high fine EC/TC ratios clearly indicate that the samples were substantially impacted by emissions from fossil fuel combustion. The EC/TC ratio in the total aerosol (sum of the 3 size fractions) of the individual samples showed substantial variability, with low ratios being observed in the samples collected from 31 July onward, when the ship was more than 500 km away from the African continent; the median ratio (over all samples) was 0.19.

The percentage OC, which was water-soluble (thus WSOC), was rather variable over the 21 samples; the median percentages were 27% for the fine size fraction and 14% for the coarse fraction.

Sections of the back-up filters (size fraction <1.3 µm) of the Hi-Vol samples were analysed in an effort to detect photo-oxidation products of BVOCs [Claeys et al., 2004a,b; Ion et al., 2005], dicarboxylic acids [e.g., Kawamura and Sakaguchi, 1999], and methanesulphonic acid (MSA) [e.g., Saltzman et al., 1986]. In total, back-up filters from 21 samples and three blanks were analysed. An extraction method similar to that used in previous studies [e.g., Kourchev et al., 2005] was applied. Briefly, a part (10 cm<sup>2</sup>) of the quartz fibre filter was placed in a 25 mL Pyrex glass flask and spiked with two internal recovery standards, i.e., 0.5 µg methyl-β-D-xylanopyranoside (m-XP) and 0.5 µg deuterated (D<sub>3</sub>)-malic acid. The samples were extracted (3 x 20 mL) with a mixture of CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (50:50, v/v) under ultrasonic agitation for 30 min. The extracts were combined and reduced by volume with a rotary evaporator (213 hPA, 30

°C) to approximately 1 mL and filtered through a Teflon filter (0.45 µm). Subsequently, the filtrate was dried under a gentle stream of nitrogen and dissolved in 200 µL of a mixture of CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (50:50, v/v). The final solution was divided into two parts. One part was refrigerated at 4 °C for eventual further analysis. The other part was transferred to a 2 mL silylation vial and evaporated under a gentle stream of pure nitrogen. The dry residue was derivatised with 25 mL of N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA + 1% trimethylchlorosilane (TMCS)) and 15 mL pyridine, and heated for 1 h at 70 °C. The derivatised sample was cooled down to room temperature and immediately analysed by GC/MS. For qualitative analysis the full scan (FS) mode was used in the mass range *m/z* 50-650, while for quantitative analysis the instrument was operated in the selected ion monitoring (SIM) mode. Base ion fragments occurring at *m/z* 204 and 217 were used for monitoring m-XP and levoglucosan; *m/z* 219 and 277 for 2-methyltetrols; *m/z* 231 for C<sub>5</sub>-alkene triols; *m/z* 233 and 307 for malic acid; *m/z* 236 and 310 for (D<sub>3</sub>)-malic acid; *m/z* 171 and 315 for *cis*-pinic acid; *m/z* 349 for 3-hydroxyglutaric acid; *m/z* 405 for 3-methyl-1,2,3-butanetricarboxylic acid and *m/z* 217 and 319 for arabitol and mannitol. The GC/MS analysis results in both the FS and SIM modes did not reveal the presence of the targeted polar organic compounds in the analysed samples.

An attempt was made to detect water-soluble dicarboxylic acids using a procedure described in previous studies [Kawamura, 1993; Kawamura and Ikushima, 1993]. Briefly, a part (10 cm<sup>2</sup>) of five selected back-up filters with the highest OC loadings was cut in small pieces and spiked with an internal recovery standard, i.e., 0.5 µg deuterated (D<sub>3</sub>)-malic acid. The filters were subsequently extracted with organic-free water (3 x 10 mL), which was prepared by oxidising the organic impurities in Milli-Q water with UV light. The extracts (water-soluble organics) were passed through a Teflon filter (0.45 µm) to remove filter debris and then concentrated to 100 µL using a rotary evaporator. The residue was further dried under a nitrogen stream and reacted with 14% BF<sub>3</sub>/n-butanol at 100 °C in order to convert carboxyl groups to n-butyl esters and aldehyde groups to di-n-butoxy acetals. The derivatives were extracted with n-hexane after adding pure water and then analysed with GC/MS in the EI mode and using the FS mode in the mass range *m/z* 50-650. As in the analyses described above, no evidence could be obtained for the presence of dicarboxylic acids in the filter samples. This is in contrast to previous studies conducted in marine environments, e.g., over the Pacific Ocean [Kawamura and Sakaguchi, 1999], where dicarboxylic acids were found at relatively large concentrations contributing up to 13% to the total aerosol carbon. The discrepancy with our study could be explained by the rather low loading of the filters for the NH cruise. While in the Pacific Ocean study [Kawamura and Sakaguchi, 1999] the air volume, aerosol deposit area, and area used for an extraction were 4300 m<sup>3</sup>, 500 cm<sup>2</sup>, and 60 cm<sup>2</sup>, respectively, these

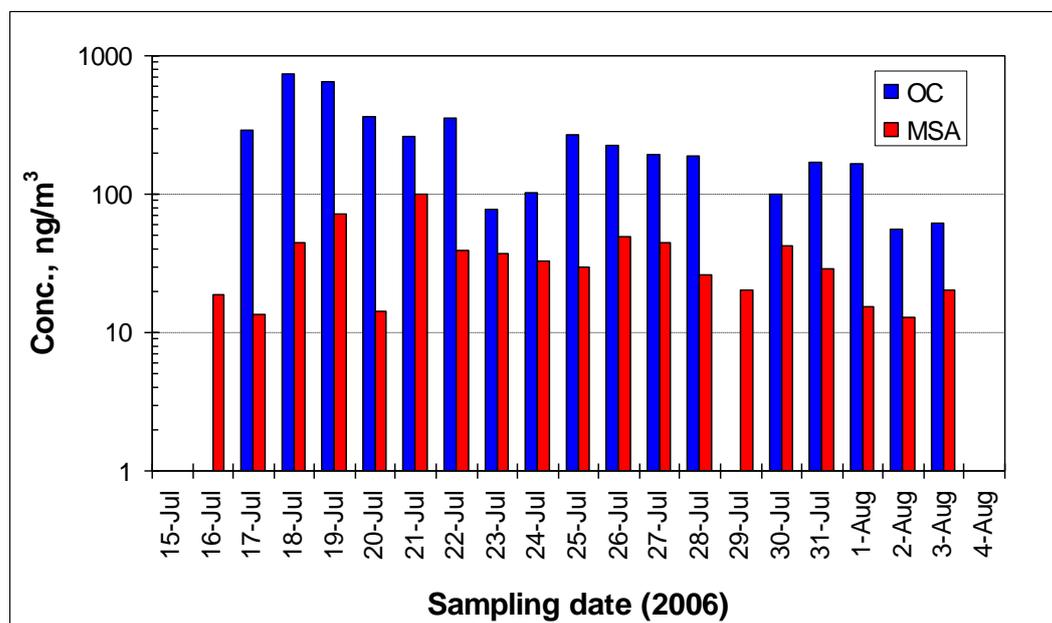
values were much lower in the present study, and were 1300 m<sup>3</sup>, 330 cm<sup>2</sup>, and 10 cm<sup>2</sup>, respectively.

Subsequently, the back-up filter samples were analysed by LC/(–)ESI-MS using a C18 Hypersil™ column (Thermo Fisher) in an effort to determine other organic species that could have escaped detection by GC/MS. By LC/(–)ESI-MS non-polar and moderately polar analytes, including acids, neutrals, and lipophilic compounds, were targeted. Prior to LC/MS analysis the filter samples were extracted (3 x 20 mL) with a mixture of CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (50:50, v/v) under ultrasonic agitation for 30 min. The extracts were combined and reduced by volume with a rotary evaporator (213 hPA, 30 °C) to approximately 1 mL and filtered through a Teflon filter (0.45 µm). The filtrate was dried under a gentle stream of nitrogen, redissolved in 100 µL of CH<sub>3</sub>OH and analysed by LC/(–)ESI-MS in the FS mode. The mobile phases of the LC system consisted of acetic acid 0.1% (v/v) (A) and methanol (B). The applied 45-min gradient elution program 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 10 min, then decreased to 3% in 5 min, and kept at 3% for 10 min. The injection volume and flow rate were 5 µL and 0.2 mL min<sup>-1</sup>, respectively. The detailed analysis of the extracts demonstrated the presence of MSA which co-eluted with H<sub>2</sub>SO<sub>4</sub>. For the further quantification of MSA an effort was made to optimise the method. In order to achieve an increased retention of MSA on the C18 reversed-phase column and separation from H<sub>2</sub>SO<sub>4</sub>, various gradient elution programs were used, but without success. Finally, an ion-pairing agent (dibutylammonium acetate (0.5 mol/L)) was added to mobile phase A in order to decrease the polarity of the ionic species.

Addition of dibutylammonium acetate to the mobile phase increased the retention time and enabled separation between MSA and H<sub>2</sub>SO<sub>4</sub>. In a subsequent step, an appropriate internal recovery standard was selected for the estimation of MSA. n-Ethanesulphonic acid (ESA), n-propanesulphonic acid (PSA), and n-butanesulphonic acid (BSA) were tested as possible internal recovery standards; of these, ESA was selected, since both PSA and BSA were found to co-elute with H<sub>2</sub>SO<sub>4</sub>.

Once the methodology for the MSA determination was developed, the concentration of MSA and its contribution to the OC were determined. Figure 26 shows the MSA and OC levels in the fine (<1.3 µm) size fraction for the NH cruise from 15 July to 4 August 2006. During two days (15 July and 4 August) the concentrations of MSA were below detection limit. The average concentration of MSA in the fine (<1.3 µm) size fraction over all aerosol samples was 33 ng/m<sup>3</sup> and the concentration in the

individual samples reached up to  $100 \text{ ng/m}^3$ . MSA contributed on average 2.6% to the fine OC and was up to 6% in some samples.

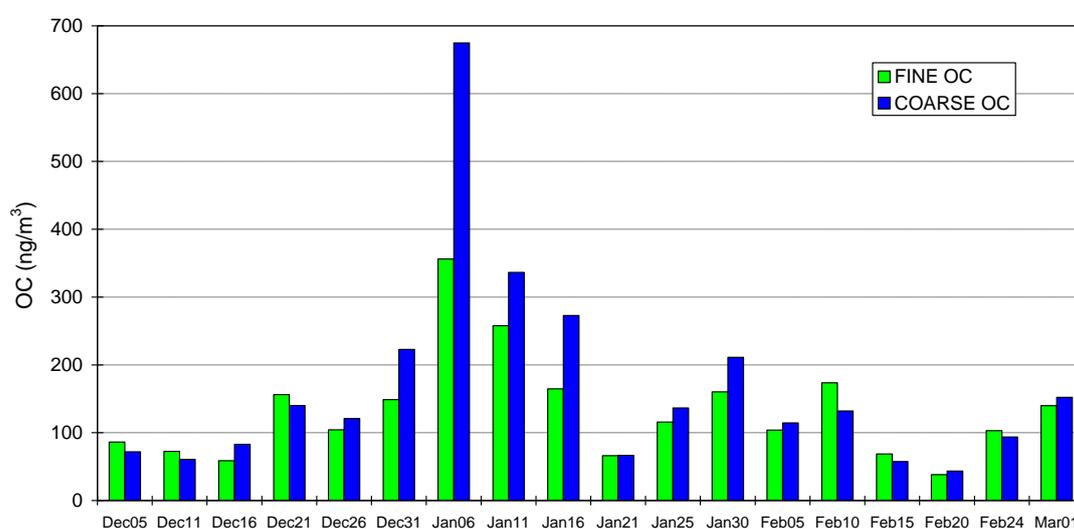


**Figure 26.** Time series for the OC and MSA concentrations in the fine ( $<1.3 \mu\text{m}$ ) size fraction of the aerosol samples collected during the NH cruise.

### 3.6.2. Aerosol study at Amsterdam Island

From 3 December 2006 until 4 March 2007, a total of 18 HVDS collections (of 5 days) were made in two size fractions (fine:  $<2.5 \mu\text{m}$ , and coarse:  $>2.5 \mu\text{m}$ ) on double quartz fibre filters. As to the purpose of double filters for each of the two size fractions, this was to assess artifacts in the collection of particulate OC. The EC levels were all very low, actually below the detection limit (which was of the order of  $10 \text{ ng/m}^3$ ), indicating a negligible impact from fossil fuel combustion. The concentrations of the isoprene SOA markers in the examined fine size fractions were also below detection limit (DL), which was in the order of  $1 \text{ ng/m}^3$ . It was found that the back/front filter ratios for fine OC were puzzlingly high, on average 0.4 (even higher back/front ratios were found for fine WSOC); also for the coarse size fraction, unexpectedly high back/front ratios were observed. Fortunately, the IC data shed light on this issue. It was found that also species, for which artifacts during sampling should be absent, such as the inorganic cations  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ , exhibited high back/front filter ratios. It is evident that positive artifacts, such as those typically observed for OC, cannot be invoked to explain the high back/front filter ratios for the inorganic cations  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ , and that artifact-free data for these species should not be calculated by subtracting the back filter data from the front filter data. It should be indicated here that the HVDS was deployed quite close to the sea (the horizontal distance was around 45 m); as a

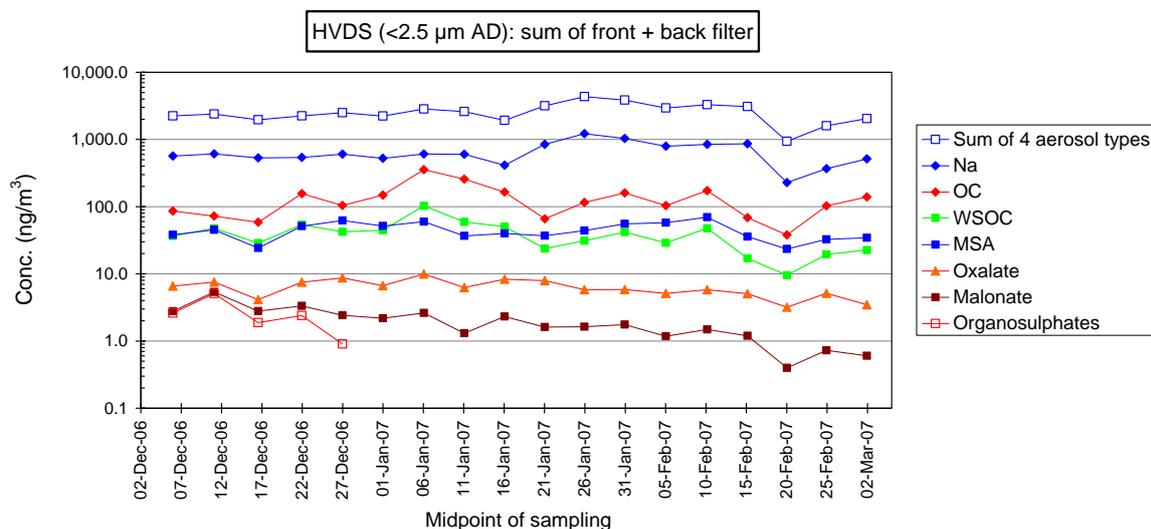
consequence, the relative humidity of the air at the sampler was fairly high and the collected aerosol was presumably rather wet. Besides, each individual HVDS sample was collected over a 5-day period, whereas the collection time at continental sites is usually restricted to 12 or 24 hours. Furthermore, the front and back filter touched each other inside the HVDS. It is thought that the filters became fairly wet during the 5-day collection period and that the continuous drawing of air through the filters had the effect that water-soluble species (including  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ ) could migrate from the front filter to the back filter. Consequently, the double filters acted as one single thick filter and the data of the back and front filters should be combined to obtain the actual concentration data. This approach was adopted for all species measured and for both the fine and coarse size fractions. All data reported from now on for the HVDS samples from Amsterdam Island are thus always the sum of the data of the front+back filters.



**Figure 27.** Time series of fine and coarse OC for the HVDS samples from Amsterdam Island. The samples are labeled according to the mid-point date of the 5-day collection.

The time series of fine and coarse OC is presented in Figure 27. OC peaks in the period from 29 December 2006 to 18 January 2007, which presumably corresponds with the maximum in biogenic activity. WSOC followed OC closely (the correlation coefficient between both parameters was 0.88 for the fine size fraction and 0.97 for the coarse one). The medians and ranges for OC and WSOC in the total aerosol (sum of fine + coarse) were 240 (82 – 1040)  $\text{ng/m}^3$  and 60 (16 – 280)  $\text{ng/m}^3$ , respectively. Of the total OC,  $47 \pm 6\%$  was in the fine size fraction; of the total WSOC,  $61 \pm 11\%$  was fine. The percentage of OC that was WSOC was, on average,  $32 \pm 12\%$  for the fine size fraction,  $18 \pm 6\%$  for the coarse one, and  $25 \pm 8\%$  for the total aerosol. These percentages are very similar to those observed for the NH cruise. As to the median for total OC, this is about a factor of 3 lower for this campaign at Amsterdam Island than in the NH cruise. Another substantial difference between the two studies was in the EC levels and in the EC/TC ratios. For the NH cruise, the median EC/TC ratio for the

total aerosol was 0.19; at Amsterdam Island, EC was below the detection limit. The high EC/TC ratios for many samples of the NH cruise indicate that there was a substantial impact from fossil fuel combustion.



**Figure 28.** Time series of OC, WSOC, Na<sup>+</sup>, MSA (measured by IC), oxalate, malonate, and the organosulphates in the fine size fraction of the HVDS samples. Also included is the time series of the sum of the 4 aerosol types in the fine size fraction. The samples are labelled according to the mid-point date of the 5-day collection.

Figure 28 shows the time series of OC, WSOC, Na<sup>+</sup>, selected organic acids, and the organosulphates in the fine size fraction of the HVDS samples. Also included in the Figure is the time series for the sum of 4 aerosol types (see details below), which can be considered as the mass of the fine dry aerosol. The data for the organosulphates were obtained by P2 (more information on these compounds is given below), all other data come from C. As already indicated above, OC peaks in the period from 29 December 2006 to 18 January 2007 and WSOC follows OC closely. MSA, which is derived from the oxidation of DMS that is released by phytoplankton and is thus also associated with biogenic activity, shows a somewhat different pattern. It exhibits maximum levels in the period from 18 December 2006 to 8 January 2007 and in the period from 28 January to 12 February 2007. Ten-day isentropic air mass back trajectories, calculated with HYSPLIT [Lupu and Maenhaut, 2002] for every 6 hours and for an arrival at 100 m above ground level at our site, indicated that the air masses generally came from the southwest and passed over highly productive waters of the Southern Ocean. However, there was some variability in the trajectories for the individual samples. For the samples with midtimes of 6 and 11 January, which exhibited the highest OC and WSOC levels, the 10-day air mass trajectories started usually North of Amsterdam Island, often at less than 1000 km, showed some recirculation, and remained close to the surface. In contrast, for the samples with midtimes of 27 December and 10 February, which had the highest MSA levels, the 10-day air mass trajectories started normally from the far South-west in the middle

troposphere, often at more than 1000 km from Amsterdam Island. The ratio MSA/nss-sulphate in the fine size fraction (averaged over all 18 samples) was  $0.18 \pm 0.05$ . This ratio is intermediate between the measured MSA/nss-sulphate ratios of, on the one hand, the Indian Ocean and the South Pacific and, on the other hand, austral summertime data for the Southern Ocean and Antarctic [Gondwe et al., 2004]. Since non-DMS derived nss-sulphate should be negligible for most of these earlier data (particularly for the austral summertime data for the Southern Ocean and Antarctic), this suggests that the nss-sulphate during austral summer at Amsterdam Island is like MSA indeed derived from DMS. Oxalate shows somewhat less variability than MSA throughout the sampling period. The concentration of malonate shows a decrease with time and the organosulphates were only above DL in the first 5 samples. According to Wang et al. [2006], the dicarboxylic acids (including oxalate and malonate) and other water-soluble organics in marine aerosols over the Southern Ocean may mainly be produced through in-situ photochemical reactions and their precursors over the Southern Ocean may be predominately derived from sea-to-air emissions of biogenic organic compounds including unsaturated fatty acids, phenolic compounds, and olefins.

Table IX presents a summary of the total concentrations (sum of coarse+fine) for the period of HVDS samplings and of the percentage that was in the fine size fraction. Most data in the Table were obtained by C. For data obtained by P2, P2 is given in brackets after the name of the species. Nss-sulphate was calculated for each individual sample as  $[\text{SO}_4^{2-}] - 0.252 [\text{Na}^+]$ , whereby 0.252 is the  $\text{SO}_4^{2-}/\text{Na}^+$  ratio in bulk sea water [Riley and Chester, 1971]. As expected, the total aerosol is dominated by sea salt ( $\text{Cl}^-$  and  $\text{Na}^+$ ). Slightly less than 50% of these sea-salt ions is in the fine fraction; for nss-sulphate and the organic species ( $\text{MSA}^-$ , oxalate, malonate) around 90% is in the fine fraction and for WSOC and nitrate, intermediate percentages (means of 61 and 74%, respectively) are observed. The fairly high fine percentages for the sea-salt ions are surprising. It is possible that the true cut-point between fine and coarse for our HVDS operating conditions was somewhat larger than the nominal  $2.5 \mu\text{m}$ . According to Solomon [2008], it could be around 3 to  $3.5 \mu\text{m}$ . On the other hand, the fact that our HVDS was at some distance from and at some altitude above the sea may have had the effect that many coarse particles were removed from the sea-salt aerosol by particle settling (dry deposition) before they could reach the HVDS.

**Table IX.** Medians and concentration ranges ( $\text{ng m}^{-3}$ ) in the total aerosol (sum of coarse+fine) and percentage that was in the fine size fraction. Note that organosulphates were not measured for the coarse size fraction, so that the organosulphate data refer to the fine size fraction. DL indicates detection limit. The data are based on the analyses of 18 HVDS samples.

Species	Median conc. ( $\text{ng m}^{-3}$ )	Concentration range ( $\text{ng m}^{-3}$ )	Mean $\pm$ std. dev. for % Fine of Total
OC	240	82 – 1040	47 $\pm$ 6
WSOC	60	16 – 280	61 $\pm$ 11
MSA <sup>-</sup>	47	25 – 78	91 $\pm$ 4
MSA <sup>-</sup> [P2]	56	31 – 89	91 $\pm$ 5
Oxalate	7.0	3.6 – 12	86 $\pm$ 6
Malonate	2.0	0.5 – 5.4	85 $\pm$ 8
Organosulphates [P2]		DL – 5.1	
Cl <sup>-</sup>	2300	920 – 4600	40 $\pm$ 10
NO <sub>3</sub> <sup>-</sup>	17	3.9 – 30	74 $\pm$ 13
NO <sub>2</sub> <sup>-</sup>	4.5	0.6 – 7.9	32 $\pm$ 20
SO <sub>4</sub> <sup>2-</sup>	650	300 – 880	66 $\pm$ 6
nss-SO <sub>4</sub> <sup>2-</sup>	260	157 - 390	93 $\pm$ 6
Br <sup>-</sup>	2.7	0.8 – 6.0	35 $\pm$ 13
Na <sup>+</sup>	1350	570 – 2700	46 $\pm$ 9
K <sup>+</sup>	48	20 – 105	50 $\pm$ 14
Mg <sup>2+</sup>	155	59 – 320	44 $\pm$ 8
Ca <sup>2+</sup>	34	13 – 70	46 $\pm$ 8

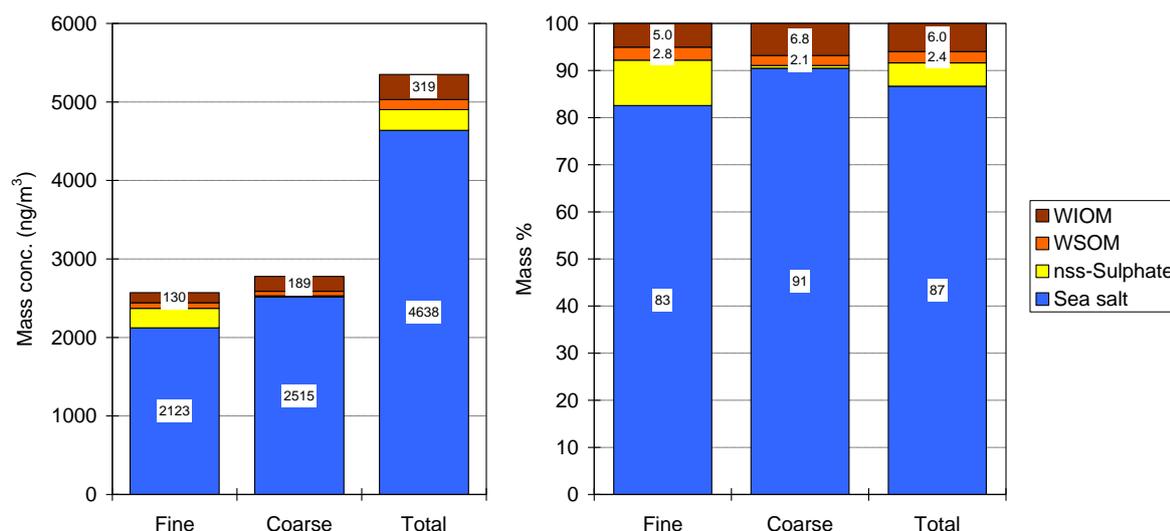
Table X gives for the separate fine and coarse size fractions what fraction of the OC was water-soluble (WSOC) and to what extent the WSOC is accounted for by the carbon in the measured organic species. It is clear that the coarse OC is less water-soluble than the fine one (on average 18% versus 32%). The percentage of fine OC that is water-soluble resembles percentages obtained at urban locations in Europe, where about 50% of the submicrometer OC is of primary origin according to Aerosol Mass Spectrometer (AMS) measurements [Zhang et al., 2007]. It is substantially lower than the percentages of around 60% obtained at forested sites, where a large fraction of the OC is made up by SOA [Chi and Maenhaut, 2008]. This suggests that most of the OC at Amsterdam Island is primary (even during the period of high biogenic activity). For the fine size fraction, a substantial fraction of the WSOC is accounted for by the carbon in the measured compounds (around 25% in total), but for the coarse size fraction only around 5% of the WSOC is explained by these compounds. The composition of the unaccounted WSOC is unclear. This fraction is likely made up of higher molecular weight compounds (MW > 500), which escape detection in the analyses performed by the teams of C and P2. Possibly, the fraction consists of partially oxidised primary OC, which has become water-soluble and/or of

water-soluble primary OC. This is also consistent with another observation, i.e., that SOA (i.e., organosulphates, see below) is found that can be explained through oxidation of primary algal biomass. More specifically, oxidation of unsaturated fatty acid residues in the latter biomass will afford polar and complex higher MW bio-organic macromolecular compounds that are refractory and are not targeted in our analyses.

**Table X.** Percentage of the OC that was water-soluble (WSOC) and percentages of the WSOC that are accounted for by the carbon in the measured organic compounds (based on 18 HVDS samples). Note that the organosulphates were not measured for the coarse size fraction.

	Fine Mean $\pm$ st.dev	Coarse Mean $\pm$ st.dev	Total Mean $\pm$ st.dev
WSOC % of OC	32 $\pm$ 12	18 $\pm$ 6	25 $\pm$ 8
MSA C [P2] % of WSOC	21 $\pm$ 8	3.6 $\pm$ 2.4	14 $\pm$ 6
MSA C % of WSOC	17 $\pm$ 6	2.8 $\pm$ 1.7	11 $\pm$ 5
Oxalate C % of WSOC	5.0 $\pm$ 2.0	1.2 $\pm$ 0.8	3.5 $\pm$ 1.5
Malonate C % of WSOC	1.8 $\pm$ 0.9	0.5 $\pm$ 0.4	1.4 $\pm$ 0.7
Organosulphate C [P2] % of WSOC	0.8 $\pm$ 1.5		0.5 $\pm$ 1.0

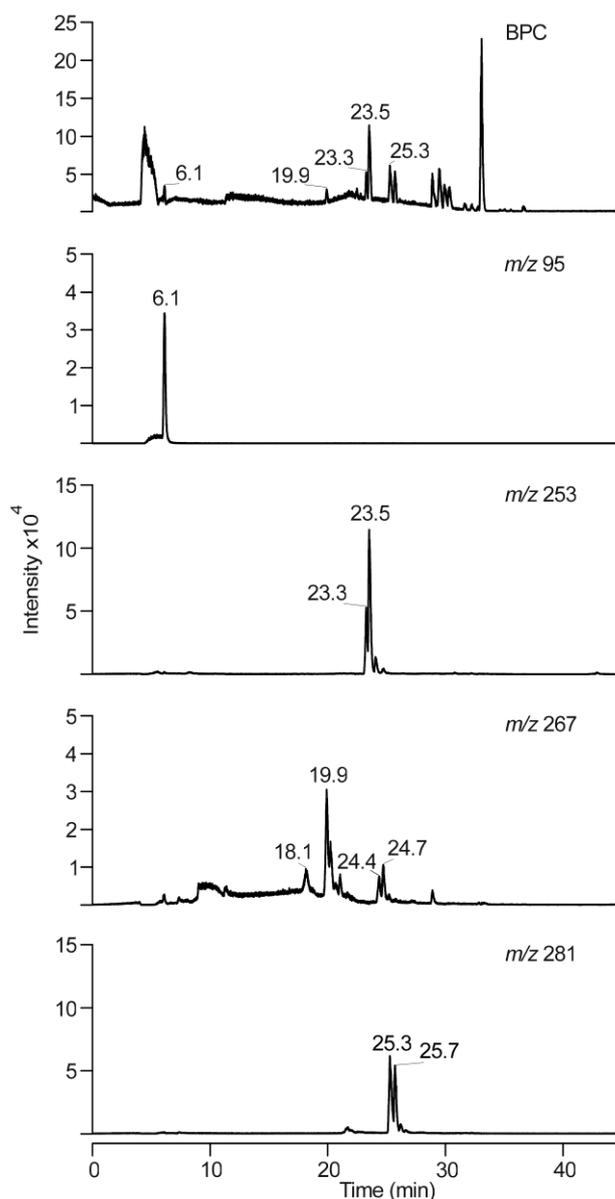
It was indicated above that the total aerosol is dominated by sea salt ( $\text{Cl}^-$  and  $\text{Na}^+$ ). In order to examine this more closely and also for the separate fine and coarse size fractions, the concentrations of 4 aerosol types, i.e., sea salt, nss-sulphate, water-soluble organic matter (WSOM), and water-insoluble organic matter (WIOM), were calculated and it was assumed that the sum of these 4 aerosol types was a reasonable proxy for the dry aerosol mass. A potentially major aerosol type missing from this sum is crustal matter (mineral dust), but it is thought that its contribution is not larger than 10% of the dry aerosol mass. Ezat and Dulac [1995] found an atmospheric mineral dust concentration of 120 ng m<sup>-3</sup> at Amsterdam Island; this is actually less than 2% of the sum of our 4 aerosol types for the total aerosol. Sea salt was calculated as 3.256 [ $\text{Na}^+$ ], whereby the factor is the mass ratio of sea salt to  $\text{Na}^+$  in sea salt, nss-sulphate was estimated as explained above, WSOM was obtained as 1.8 WSOC and WIOM as 1.4 (OC – WSOC). The factors 1.8 and 1.4 are identical to those used by Facchini et al. [2008] in a similar recent exercise. Figure 29 (left part) shows the average concentrations of the 4 aerosol types (averaged over the 18 HVDS samples) for the separate fine and coarse size fractions and for the total aerosol (sum of fine+coarse); in Figure 29 (right part) the percentage contributions of the 4 aerosol types, expressed as percent of the mean concentration of the sum of the 4 types, is given. Organic aerosol (sum of WIOM + WSOM) makes up for less than 10% of the sum of the 4 aerosol types. This is even the case for the fine size fraction, which is clearly dominated by sea salt.



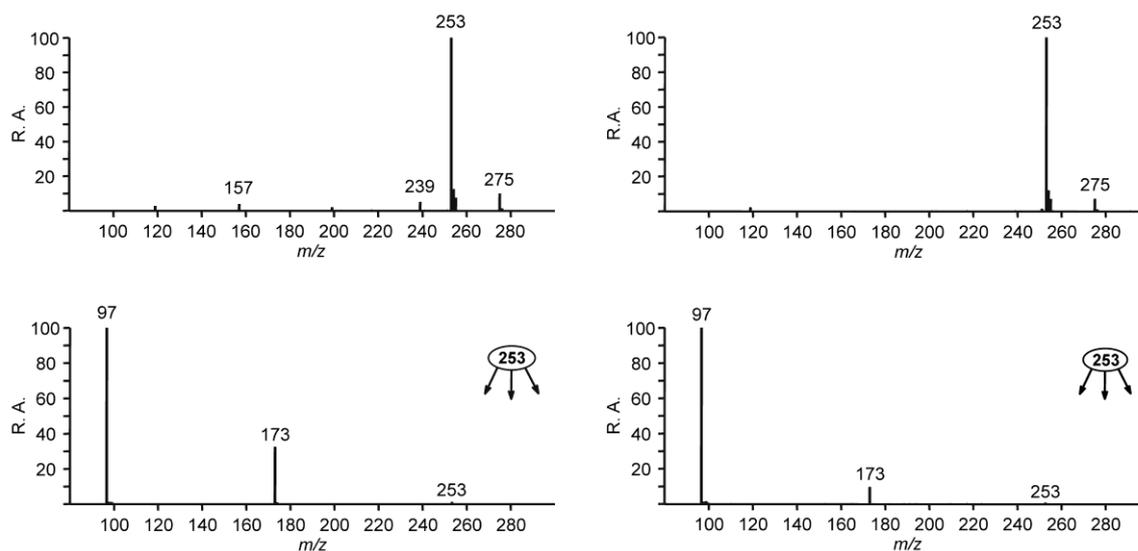
**Figure 29.** Average concentrations of 4 aerosol types in the separate fine and coarse size fractions and in the sum of both (left part of Figure) and percentage contributions of the 4 aerosol types, expressed as percent of the mean concentration of the sum of the 4 types (right part of Figure). The numeric data for WIOM and sea salt are also given for both parts of the Figure, and the right part of the Figure also provides the numeric data for WSOM.

In addition to MSA and sulphate the LC/(–)ESI-MS method also revealed the presence of organosulphates with MWs 212, 254, 268, 282, 296, and 310. Organosulphates are SOA components that only have been recently discovered and are formed by reaction of SOA constituents containing a hydroxyl or a keto/aldehyde group with sulphuric acid [Surratt et al., 2007]. Figure 30 shows LC/(–)ESI-MS chromatographic data obtained without ion-pairing for the fine front filter collected from 8 to 13 December 2006. The most prominent signals were observed for  $m/z$  253 and 281, corresponding to MW 254 and 282 compounds, respectively. In addition to MW 254, 268, and 282 organosulphates, minor signals were also observed for organosulphates with MWs 212, 296, and 310. Similar profiles were obtained for the other fine samples (front and back) but since the signals were quite weak except in the first five samples, quantitative calculations were only done for these five samples. Figure 31 presents mass spectral data obtained for the two major isomers of the MW 254 compound. On the basis of these data, the compounds were identified as organosulphates of  $C_9$  hydroxy fatty acids. Characteristic organosulphate ions in the  $MS^2$  spectra include the loss of  $SO_3$  (80 u) and the bisulphate ion  $[HSO_4]^-$  ( $m/z$  97). In addition, accurate mass measurements performed on the  $m/z$  253 ion allowed to confirm the elemental compositions as  $C_9H_{17}O_6S$ . Mass spectral data sets (not shown) were also obtained for the other organosulphates with MWs 212, 268, 282, 296, and 310. The MW 268, 282, 296, and 310 compounds were characterised as  $C_{10}$ ,  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  homologues of the major  $C_9$  (MW 254) compounds. The MW 212 compound was characterised as an organosulphate of a neutral compound, i.e., a  $C_6$  dihydroxyaldehyde. The  $m/z$  211  $MS^2$  spectrum only revealed the bisulphate ion

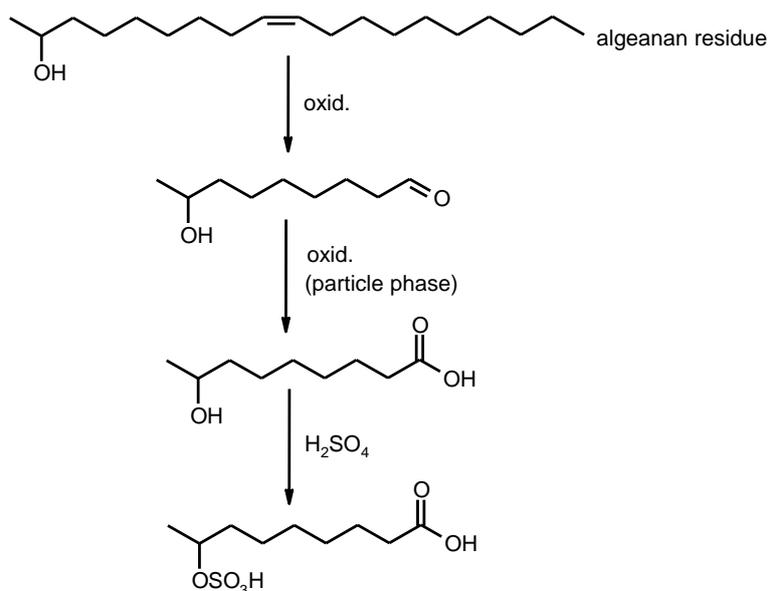
$[\text{HSO}_4]^-$  ( $m/z$  97) and the accurate mass data indicated an elemental composition of  $\text{C}_6\text{H}_{11}\text{O}_6\text{S}$  for the  $m/z$  211 ion.



**Figure 30.** LC/(-)ESI-MS chromatographic data obtained without ion-pairing for the fine front filter collected from 8 to 13 December 2006. The top chromatogram is a base peak chromatogram (BPC), while the other chromatograms are extracted ion chromatograms at the  $m/z$  value of  $[\text{M} - \text{H}]^-$  ions of MSA ( $m/z$  95) and selected organosulphates ( $m/z$  253, 267, and 281) where the  $m/z$  253 and 281 compounds are the most abundant ones.



**Figure 31.** Mass spectral data for the two major MW 254 compounds eluting at 23.3 (left) and 23.5 min (right) (Figure 30). The top spectra are first-order spectra, while the bottom spectra are  $m/z$  253  $MS^2$  spectra.



**Figure 32.** Proposed formation pathway leading to an organosulphate with MW 254 containing a  $C_9$  ( $\omega$ -1)-hydroxy fatty acid part in a marine environment. The hydroxyl group can also be located at the terminal  $\omega$ -position. The higher  $C_{10}$ - $C_{13}$  homologues can be explained from fatty acid residues containing a double bond at  $\omega_{10}$ - $\omega_{13}$  positions.

To our knowledge, no information is available in the literature on the presence of  $C_9$ - $C_{13}$  hydroxy fatty acids in SOA. However, it is known that algal cell membrane lipids (denoted by the term algeanan) and lake sediments contain long-chain hydroxylated/unsaturated fatty acids with hydroxyl groups at the  $\omega$ - (terminal) and ( $\omega$ -1)-positions [Matsumoto et al., 1988; Blokker et al., 2006]. A plausible formation pathway for the formation of organosulphates in marine fine aerosol is presented in Figure 32. It is proposed that upon atmospheric oxidation of algal biomass by the

action of ozone and/or enzymatic degradation, hydroxy alkanals are released, which are trapped on acidic fine aerosol where they are further converted to hydroxy fatty acids. Subsequently, these hydroxy fatty acids may react with sulphuric acid resulting in organosulphates. The formation of the MW 212 compound can be explained via a similar pathway where the C<sub>6</sub> dihydroxyaldehyde is formed through oxidation of bis-unsaturated fatty acid moieties of algal cell membrane lipids.

Unlike organosulphates found in continental fine aerosol, which have a mixed biogenic/anthropogenic origin and where the sulphate part is mainly from anthropogenic origin, the organosulphates in remote marine fine aerosol have a sulphate part from biogenic origin and are thus mainly biogenic.

Our results indicate that organic aerosol for samples collected at Amsterdam Island during the austral summer of 2006-2007, a period of high biological activity, makes up less than 10% of the mass in both the fine and coarse size fractions. Our percentage in the fine size fraction is much less than the 65% of OC (sum of WIOC + WSOC) found for submicrometer-sized aerosol during a high biological activity period at the Atlantic Ocean site of Mace Head [O'Dowd et al., 2004]. On a mass basis, sea salt followed by nss-sulphate dominate and WIOC is relatively more important than WSOC at Amsterdam Island, comparable with results obtained in a recent aerosol characterisation study for size-segregated samples during a phytoplankton bloom in the North Atlantic [Facchini et al., 2008]. The percentage of fine OC that is water-insoluble resembles percentages obtained at urban locations in Europe, where much of the OC is of primary origin. The WIOC is attributed to primary marine biomass produced during phytoplankton blooms, considering that electron microscopic evidence from prior studies is available that marine aerosol particles contain fragments and secretions of algae and bacteria [Leck and Bigg, 2005a; 2005b; 2008].

About 23% of the fine WSOC could be attributed to methanesulphonate, dicarboxylic acids, and organosulphates, with methanesulphonate providing the largest fraction (17%). A large fraction of the fine WSOC escaped our analysis and likely corresponds to oxidised marine biomass that became water-soluble. It was found that the temporal variation of WSOC closely followed that of OC, while methanesulphonate, the dicarboxylic acids, and the organosulphates showed a different time series, pointing to different biogenic origins and/or source regions.

A novel group of SOA tracers, i.e., organosulphates, which occurred in low concentrations and represented only 0.8% of the fine WSOC, were structurally elucidated as sulphate esters of C<sub>9</sub>-C<sub>13</sub> hydroxyl acids and a C<sub>6</sub> dihydroxyaldehyde, and explained by oxidation of hydroxylated/unsaturated fatty acid residues of

algal/bacterial cell membrane lipids and subsequent oxidation/sulphation on pre-existing particles. The organosulphates characterised here can be considered as tracers for a SOA formation process that is specific for the marine environment, i.e., oxidation of primary marine biomass. To our knowledge, this is a novel SOA source process that has not been previously reported.

No evidence could be found for SOA from the photo-oxidation of isoprene, which is consistent with recent model estimates indicating that isoprene has an insignificant role in forming marine organic aerosol by secondary processes [Arnold et al., 2009], and thus further supporting a primary source of OC in the remote marine atmosphere.

### 3.7. Modelling of the formation and growth of the fine particles and of the fine biogenic atmospheric aerosol

This work is carried out by BIOSOL partner P4, but experimental data input is provided by all partners.

P4 performed preparatory work to apply the UHMA model to the data sets from K-pusztá (section 3.3) and Hyytiälä (section 3.5). The basic idea is to look at the connection between different vapours and aerosol production and to see how different hypotheses are able to explain particle formation and growth. This has been explained, e.g., by Kulmala et al. [2006] and Sihto et al. [2006].

If we look at the formation rate of 1 nm particles,  $J_1$  is the particle formation rate at 1 nm, corresponding to the size region at which the atmospheric nucleation is generally assumed to take place. In particular, the values  $n_{J_1} = 1$  or  $n_{J_1} = 2$  in the correlation between  $J_1$  and  $[H_2SO_4]^{n_{J_1}}$  would imply the activation of pre-existing clusters ( $n_{J_1} = 1$ ) or kinetic nucleation of sulphuric acid ( $n_{J_1} = 2$ ) to be the dominating mechanisms for atmospheric new particle formation, as proposed by Kulmala et al. [2006]. In these cases the new particle formation rate (i.e., the atmospheric nucleation rate) can be simply written as:

$$J_1 = A [H_2SO_4]$$

or

$$J_1 = K [H_2SO_4]^2$$

where  $A$  and  $K$  are now coefficients containing the details of the nucleation processes. According to Sihto et al. [2006], these nucleation mechanisms seem to be the best candidates for the atmospheric nucleation observed in Hyytiälä. Exponents larger than 2, on the other hand, may indicate that the atmospheric nucleation is thermodynamically limited.

Atmospheric particle and ion data measured during 39 days in the 2006 summer campaign at K-pusztá, Hungary, were analysed and related to meteorological and trace gas data [Yli-Juuti et al., 2009]. It was found that there were many new particle formation event days during that period; formation of new nucleation mode particles and subsequent growth was observed on more than half the days and also during most of the other days some kind of particle formation was observed. Based on the results, it is reasonable to assume that the production rate of condensable vapours able to form particles was high. The chemical production of these vapours is likely to be intense, since K-pusztá is characterised by intensive solar radiation in summertime. The ambient SO<sub>2</sub> concentration was not significantly higher than, e.g., in Hyytiälä [Lyubovtseva et al., 2005]. This suggests that the cause for the high event frequency at K-pusztá might not be a significantly high sulphuric acid concentration - presumably the presence of condensable organic vapours, and their clear contribution to new particle formation and growth [e.g., Kulmala et al., 2004b].

None of the measured trace gases or meteorological variables was solely able to explain the new particle formation events since no clear differences in these data were found between event and non-event days. However, the condensation sink reached, as expected, higher values on non-event days than on average, which is in line with other studies [Dal Maso et al., 2005].

The observed formation rates of 10 nm particles were higher than the formation rates observed at Hyytiälä, Finland. As a summary, we can state that the formation rate is at the upper end of formation rates observed in the continental boundary layer [see Kulmala et al., 2004a]. The growth rates of atmospheric nucleation mode particles during new particle formation events were strongly size-dependent and in the same range as those obtained in other studies at other sites [Kulmala et al., 2004a]. The size-dependency in growth rates is in line with findings in previous observational [Hirsikko et al., 2005; Suni et al., 2008] and phenomenological studies [Kulmala et al., 2004c] and suggests that different factors are affecting the growth of different sized particles. Since the growth and formation rates of particles were not exceptionally high at K-pusztá the high new particle formation event frequency probably cannot be explained by the high concentration of condensable vapours but possibly by the high production rate of these vapours. The high event frequency might also be connected to the intensive solar radiation at K-pusztá.

0.5-1.8 nm ion cluster concentrations were found to correlate clearly with ambient conditions: during the warm period with continental air masses the diurnal maximum cluster concentrations were significantly higher than during the period with colder and

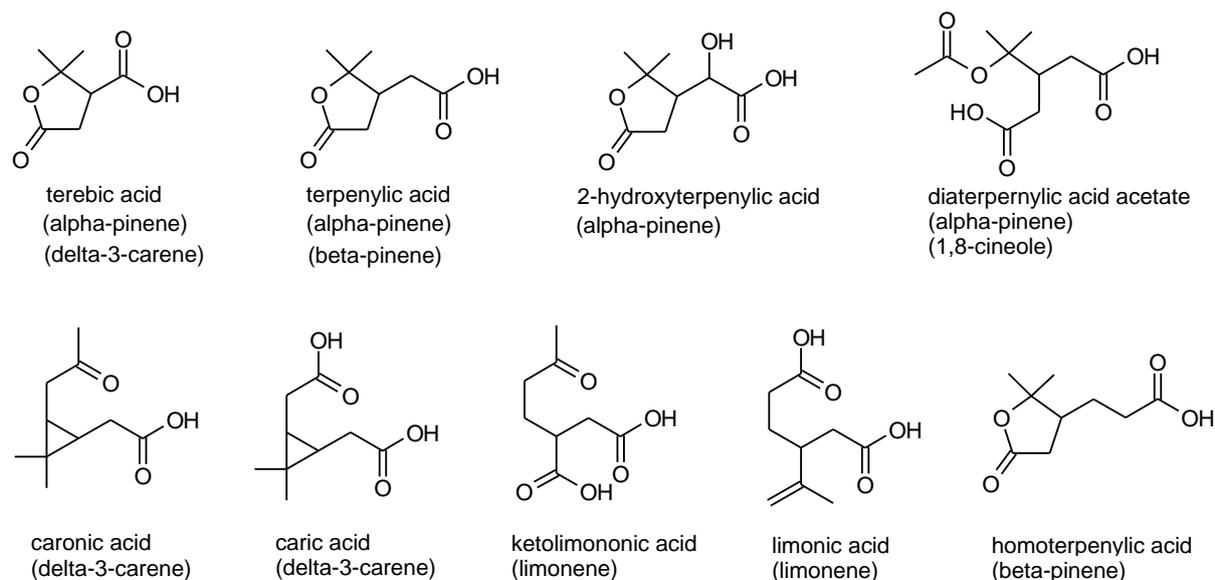
cleaner air masses from the North Sea or the Atlantic Ocean. This could be partly explained by lower wind speed during the warmer period resulting in a weaker boundary layer mixing. It might also point to the role of gaseous precursors in forming atmospheric clusters, since the concentrations of both BVOCs and inorganic trace gases were higher during the warm period. Interestingly, the diurnal variation of the cluster ions was similar to that for the ambient monoterpene concentrations. This could partly be explained by the effect of boundary layer dynamics, but could also point to monoterpenes as a possible source of atmospheric clusters.

### **3.8. Particulate-phase oxidation products of isoprene (and other BVOCs), which can be used as indicator compounds for source apportionment**

The studies mentioned in sections 3.1 and 3.2 also relate to this task. In addition, studies were performed aimed at the characterisation of particulate-phase oxidation products of isoprene,  $\alpha$ -pinene, and unsaturated fatty acids that are present in significant concentrations in ambient fine aerosol and can serve as SOA marker compounds.

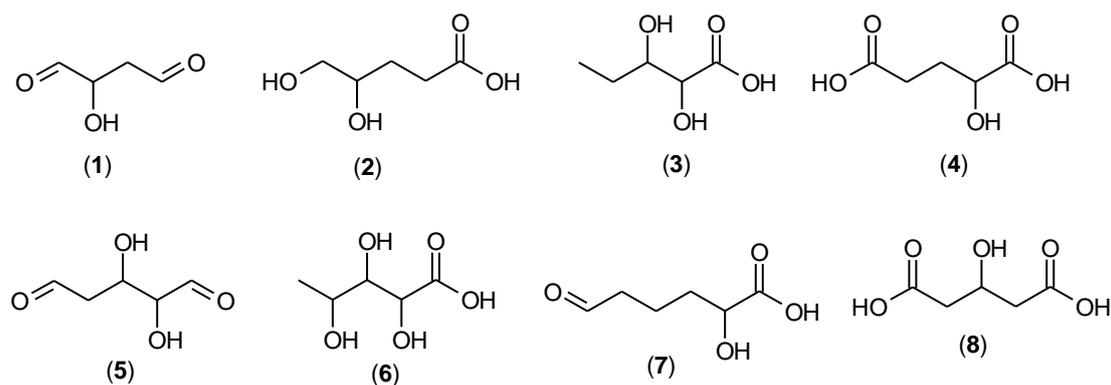
In close collaboration with US EPA, Caltech, and IfT, P2 conducted studies to structurally characterise major particulate-phase oxidation products of  $\alpha$ -pinene that occur at significant concentrations in ambient fine aerosol. It has been firmly established that *cis*-pinic, *cis*-norpinic, and *cis*-pinonic acid are major products formed from  $\alpha$ -pinene by reaction with O<sub>3</sub>. However, several ambient aerosol studies have shown that the atmospheric concentrations of major  $\alpha$ -pinene SOA products (i.e., *cis*-pinic and *cis*-pinonic acid) are rather low during summer episodes, while evidence was obtained that highly oxygenated products are formed that could also be generated by irradiating  $\alpha$ -pinene in the presence of NO<sub>x</sub> through reactions that involve O<sub>3</sub> and OH radicals. Using GC/MS with prior derivatisation to volatile derivatives and LC/(–)ESI-MS, detailed interpretation of the MS data, and synthesis of reference compounds, the structures of two major  $\alpha$ -pinene SOA marker compounds with MWs of 148 and 204 were firmly established as 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), respectively. The proposed formation mechanism for MBTCA is given in Scheme 5. It involves participation of the OH radical, but it cannot be ruled out that ozone is also involved. With the pathway of Scheme 5 it is possible to explain the smog chamber observations reported by Claeys et al. [2007], which suggested that the MW 204 compound was formed at the expense of *cis*-pinic acid. The observations can be explained with *cis*-pinonic acid following two routes; namely, a short one leading to *cis*-pinic acid, and a longer one, leading to MBTCA. The formation of MBTCA likely takes place in the particle phase, but further work is required to confirm this





**Scheme 6.** Structures and trivial names of terpenoic acids that are present in ambient fine aerosol from forested sites. Their BVOC precursor(s) is (are) indicated between parentheses.

A detailed MS characterisation was carried out on organosulphates from isoprene SOA (i.e., 2-methyltetrols, 2-methylglyceric acid, 2-methyltetrol *mono*-nitrate derivatives, glyoxal, and methylglyoxal) and on unknown organosulphates that were present in ambient PM<sub>2.5</sub> aerosol collected at K-pusztá and Brasschaat. LC in combination with linear ion trap MS using (–)ESI was employed. A major fragmentation pathway for the deprotonated molecules of the sulphate esters of 2-methyltetrols and 2-methylglyceric acid and of the sulphate derivatives of glyoxal and methylglyoxal is the formation of the bisulphate [HSO<sub>4</sub>]<sup>–</sup> anion, while the deprotonated sulphate esters of 2-methyltetrol *mono*-nitrate derivatives preferentially fragment through loss of nitric acid. Rational interpretation of MS<sup>2</sup>, MS<sup>3</sup>, and accurate mass data led to the structural characterisation of unknown polar compounds in K-pusztá and Brasschaat fine aerosol as organosulphate derivatives of photo-oxidation products of unsaturated fatty acids (Scheme 7), i.e., 2-hydroxy-1,4-butanedialdehyde (**1**), 4,5- and 2,3-dihydroxy-pentanoic acids (**2** and **3**), 2-hydroxyglutaric acid (**4**), 2,3-dihydroxypentane-1,5-dialdehyde (**5**), 2,3,4-trihoxypentanoic acid (**6**), 2-hydroxy-6-ketohexanoic acid (**7**), and of  $\alpha$ -pinene, i.e., 3-hydroxyglutaric acid (**8**). The deprotonated molecules of the sulphated hydroxyacids (e.g., 2-methylglyceric acid, 4,5- and 2,3-dihydroxypentanoic acid, and 2- and 3-hydroxyglutaric acids) showed in addition to the [HSO<sub>4</sub>]<sup>–</sup> ion (*m/z* 97) neutral losses of water, CO<sub>2</sub>, and/or SO<sub>3</sub>, features that are characteristic of humic-like substances.



**Scheme 7.** Photo-oxidation products of unsaturated fatty acids and  $\alpha$ -pinene for which sulphate derivatives were structurally elucidated.

The polar organosulphates characterised are of climatic relevance because they may contribute to the hydrophilic properties of fine ambient aerosol. In addition, these compounds likely serve as ambient marker compounds for the occurrence of SOA formation under acidic conditions. More details on the organosulphates from isoprene are given in Surratt et al. [2007; 2008], while details on some of the other organosulphates are given in Gómez-González et al. [2008].

### 3.9. Determination of the contribution from the BVOCs to the organic aerosol for various sites in Europe

As indicated in section 2.9, this work was done for the PM<sub>2.5</sub> size fraction of the HVDS samples from the 2003 summer campaign at K-puszta [Kourtchev et al., 2009] and for PM<sub>2.5</sub> samples, which had been collected in summer 2003 in a mixed deciduous forest in Jülich [Kourtchev et al., 2008c]. For K-puszta, the SOC contribution from isoprene was estimated at  $0.28 \mu\text{gC m}^{-3}$ . Expressed as percentage contribution to the PM<sub>2.5</sub> OC, isoprene SOC represented, on average, 6.9%; the day-time mean was 9.6% and the night-time mean 5.2%. The SOC contribution from  $\alpha$ -pinene was, on average,  $0.21 \mu\text{gC m}^{-3}$ . This represented, on average, 4.8% of the PM<sub>2.5</sub> OC; the day-time mean was 3.8% and the night-time mean 6.0%. It is noted that the data for  $\alpha$ -pinene SOC should be regarded as minimum values because not all molecular tracers necessary to estimate  $\alpha$ -pinene SOC were measured. For the Jülich samples, the contribution from isoprene was estimated at, on average, 2.5% of the OC and that of  $\alpha$ -pinene SOA at at least 2.4%. Our percentages for K-puszta and Jülich can be compared to those obtained with the same approach for Research Triangle Park, southeastern USA, during the months May-July of 2003 [Kleindienst et al., 2007], for 5 midwestern US cities during the months June-August of 2004 [Lewandowski et al., 2008], and for Hong Kong during a 2006 summer period [Hu et al., 2008]. The contributions from isoprene SOC to the PM<sub>2.5</sub> OC in these 3 cases

were 23%, 29%, and 3.6%, respectively, while those from  $\alpha$ -pinene SOC were 15%, 13%, and 10%, respectively. The US percentages for isoprene SOC are more than a factor of 3 larger than our percentage for K-pusztá. This may in part be due to the larger isoprene emissions at the US sites. However, it should be noted that the quantification of the isoprene and also the  $\alpha$ -pinene SOA tracers in the US studies was done in a different way than by us and in the Hong Kong study. Because of this, Hu et al. [2008] estimated the quantification uncertainty in their Hong Kong study to be within a factor of 3. Considering that also various other uncertainties are associated with the approach, as indicated by Kleindienst et al. [2007], we estimate that the uncertainty that is associated with our isoprene and  $\alpha$ -pinene SOC percentages is at least a factor of 2.

Combined together, isoprene and  $\alpha$ -pinene SOC make thus up for at least 11.7% of the PM<sub>2.5</sub> OC for K-pusztá. If we assume that the short-chain diacids do not form part of the isoprene and  $\alpha$ -pinene SOA in the laboratory experiments of Kleindienst et al. [2007], we can add to our biogenic SOC percentage the OC accounted for by the various diacids. Oxalate, malonate, succinate, glutarate, 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 [Ion et al., 2005] and of the conversion factors of these compounds to wood combustion OC and fungal spores OC of Schmidl et al. [2008] and Bauer et al. [2008], we can attribute 2.4 and 1.7% of our PM<sub>2.5</sub> 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<sub>2.5</sub> OC attributed. Clearly, this is a rather low percentage and the question remains which compounds and/or sources are responsible for the remaining OC mass. According to Feczko et al. [2007], HULIS represent 24% of the OC at the K-pusztá site. It was also found that organosulphates and nitrooxy organosulphates were important constituents of the OC at K-pusztá during the 2003 campaign [Gómez-González et al., 2008], but their concentrations could not be quantified. By making use of data of total sulphur, measured by PIXE, and of inorganic sulphate, as obtained by IC, it is estimated that up to 22% of the OC at K-pusztá during the 2003 campaign may be attributable to organosulphates (Maenhaut, unpublished results). Thus, the 18% of PM<sub>2.5</sub> OC attributed by our tracers, the 24% of HULIS, and the up to 22% of organosulphates, 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. As to the samples from Jülich, the average contribution from wood smoke to the OC was estimated at

3.3%, while the contribution from fungal spores to the OC was estimated at 3.6%. The summed contribution of isoprene and  $\alpha$ -pinene SOC, wood combustion, and fungal spores to the PM<sub>2.5</sub> OC of the Jülich samples was thus at least 12%. It is clear that most of the OC remained unaccounted. Organosulphates, HULIS, and other primary biogenic aerosol besides fungal spores probably made up for a substantial fraction of the unexplained OC.

It was found for the 2003 summer campaign at K-pusztá that isoprene SOC and  $\alpha$ -pinene SOC accounted, on average, for respectively 6.9% and at least 4.8% of the PM<sub>2.5</sub> OC; for the PM<sub>2.5</sub> samples, which had been collected in summer 2003 in Jülich, the average contributions from isoprene SOC and  $\alpha$ -pinene were 2.5% and at least 2.4%, respectively. Although the data for  $\alpha$ -pinene SOC should be regarded as minimum values because not all molecular tracers necessary to estimate  $\alpha$ -pinene SOC were measured, these percentages are clearly much lower than expected. It was noted above that the uncertainty that is associated with our estimates is at least a factor of 2. The laboratory-derived tracer mass fractions ( $f_{\text{SOC}}$ ) reported by Kleindienst et al. [2007] have a large associated uncertainty and these authors did their quantification of the tracers in a different manner than was done by us. It is recommended that the effect of this different quantification is studied in detail. One may also wonder to what extent the  $f_{\text{SOC}}$  values of Kleindienst et al. [2007] are applicable to ambient organic aerosol in various types of environments and different levels of NO<sub>x</sub>, oxidants, RH, 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. [2007] only performed GC/MS analyses for measuring the tracers. By performing analyses by LC/MS of both laboratory-generated SOA and field samples various new tracers for isoprene and terpene SOC were discovered by us in international cooperation with the US EPA, Caltech, and IfT. It is therefore advisable that besides GC/MS, also LC/MS and possibly other analyses are performed in future studies on  $f_{\text{SOC}}$ .

Additional work on the contribution to the organic aerosol for various sites in Europe was done by P2, who was invited by the Technical University of Vienna (Prof. H. Puxbaum) to co-operate in a manuscript on research that was carried within the EU-funded project CARBOSOL. The manuscript [Puxbaum et al., 2007] dealt with the impact of biomass burning along a trajectory from West to East (from the Azores to K-pusztá) in Europe. As part of this work P2 also contributed to the development of a new method for saccharides (including levoglucosan) in aerosol samples. A manuscript on this work was published [Caseiro et al., 2007]. Furthermore, P2 co-operated with the Vienna group in assessing the contribution from primary biogenic

(biological) particles (i.e., fungal spores) to the organic aerosol. A manuscript on this work was also published [Bauer et al., 2008].

#### 4. POLICY SUPPORT

The project deals with biogenic atmospheric aerosols, their formation mechanisms, marker compounds for source apportionment, and assessment of the contribution from the BVOCs to the organic aerosol. Aerosols have both direct and indirect effects on climate through their scattering and absorption of solar and terrestrial radiation and through their effects on the formation and lifetime of clouds. It is believed that the net effect of aerosols (and definitely that of biogenic aerosols) is cooling so that aerosols counteract to some extent the global warming which results from the greenhouse gases. However, aerosols also affect human health and welfare and as a consequence their concentrations should be reduced, at least on local and regional scales where the population is exposed to the aerosols. The fact that aerosols have both beneficial and harmful aspects gives rise to a dilemma. Some aerosol types, such as elemental carbon (black carbon, soot), lead to warming and are also harmful to humans, so that the concentrations of these aerosols should be reduced. On the other hand, most biogenic aerosols give rise to cooling and are thought to be not so harmful, so that their concentrations should not be reduced. In order to take appropriate measures and to reduce the harmful biosol types, detailed aerosol characterisation (also as a function of size) and assessment of the contribution of the various aerosol types are needed on local, regional, and global scales. Consequently, the work performed within this project contributes to the objectives of policy advisers and policy makers who deal with climate and human health.

As indicated in a recent SOA status paper, to which C and P2 contributed [Hallquist et al., 2009], the chemical and physical processes associated with SOA formation are complex and varied, and, despite considerable progress in recent years, a quantitative and predictive understanding of SOA formation does not exist and therefore represents a major research challenge in atmospheric science. Several emerging issues pose challenges which need to be addressed via a combination of laboratory, field, and modelling studies. These key issues are briefly discussed below and in more detail in Hallquist et al. [2009]. It is pointed out that many of the items on the list require faster and more accurate analytical tools which may open avenues for exploring a wider range of phenomena. Other major challenges include an improved understanding of the fundamental processes responsible for SOA formation and how they affect composition and the design of simulation experiments which more closely reflect the conditions and complexity of the real atmosphere.

A first issue is that there is large uncertainty associated with the SOA budget. It is plausible that large sources of organic compounds are yet to be identified. There is also a need for improved quantification of biogenic SOA (BSOA) in the field. Future highly

time-resolved studies should be performed at locations that are expected to be dominated by BSOA to evaluate the biogenic signal more clearly. Biomass burning is an important contributor to the organic aerosol on a global scale and has generally been thought to mainly give rise to primary aerosol. Very recent results indicate that SOA formation from biomass burning emissions can be very important under some circumstances and minor in others. Additional field studies are needed to characterise this potentially important SOA source. With regard to the relative contributions of modern and fossil fuel sources to the carbonaceous aerosol, there is a discrepancy between the results from  $^{14}\text{C}$  and highly time-resolved studies, whereby the  $^{14}\text{C}$  studies attribute most SOA to modern sources and the highly time-resolved studies point to anthropogenic pollution as the dominant source. New field studies should strive to include both types of measurements to allow a more direct comparison and to address the possibility that the different findings are due to different geographical locations or times. The potential enhancement of BSOA by anthropogenic pollution needs to be evaluated in the field by analyzing BSOA formation during periods of high and low pollution. Bottom-up estimates of SOA formation fluxes rely on data generated from simulation chamber experiments. However, the yields of SOA from individual precursors appear to be highly dependent on experimental conditions. Further work is clearly required to establish the most appropriate parameters for inclusion in global models. The potential importance of additional sources of SOA (newly discovered and previously unconsidered precursors, such as acetylene and oxygenated BVOCs) should be explored.

As a second issue, there is a need for improved understanding of VOC oxidation. The atmospheric degradation mechanisms for many established SOA precursors (e.g., monoterpenes, aromatics) contain a high level of uncertainty, particularly in relation to the reactivity of certain oxidation products. The role of  $\text{NO}_3$ -initiated chemistry in SOA formation has largely been neglected and the chemical mechanisms for the atmospheric degradation of other potential SOA precursors, such as sesquiterpenes, long-chain alkanes and oxygenated BVOCs, also require improvement. The link between the fundamental understanding of gas-particle partitioning and its application to atmospheric or laboratory-generated SOA is complex. Further improvements in the use of gas-particle partitioning theory to interpret experimental data, obtained in both laboratory and field studies, are required. The wide range of higher-MW products detected in laboratory-generated SOA have resulted in many proposed reactions occurring in the condensed phase. Further work is required to investigate the key processes (e.g., oligomerization, organosulfate formation) under conditions relevant to the atmosphere. Chemical and photochemical processes in the atmospheric aqueous phase may lead to the formation of polyfunctional organic compounds in diluted droplets, which play an important role in condensation reactions leading to oligomers

and SOA when the organic concentrations increase during cloud evaporation. However, the scientific knowledge of photochemical processes of organics, especially polyfunctional compounds, in the atmospheric aqueous phases is still quite limited and needs further investigation. Nucleation of new particles is recognized as a widespread phenomenon but the exact mechanisms of initiation and growth are not well known. A major challenge is posed by the minute mass of the nucleation mode particles. Standing issues include identification of the main nucleating agents, the possible role of organics in nucleation, and the contribution of organics to the growth mechanism. New instrumentation dedicated to these issues is urgently required. The missing parameters need to be studied in different environments (urban, rural, remote locations) in order to be able to include nucleation in a meaningful manner in models.

A third issue deals with measurements of aerosol composition. Organic aerosol contains both WSOM and WIOM. WIOM is left mostly under-characterised. Tools for isolation, characterisation and process studies of this important fraction are therefore encouraged. Recent field and chamber studies suggest that complex organic matter may consist of organosulfates, amines, organic nitrates, oligomers, and other higher-MW compounds. Many of these species remain poorly characterised. Missing information includes the identity, concentration, formation pathways, and possible roles in affecting surface tension, optical properties, reactivity, and CCN activity of SOA. New analytical methods should be developed to extract, identify and quantify these compounds. While the formation of oligomers has been firmly established in laboratory experiments, it is still uncertain whether they are formed under ambient conditions. There are still abundant unknown SOA constituents, even first-generation products detected in laboratory chamber studies, which are present in ambient and plant chamber aerosol and need to be structurally elucidated. Given their chemical complexity, efforts should be made to isolate and purify key species and to establish their chemical structures, where use could be made of available advanced multidimensional MS and NMR techniques. The development of measurement techniques with high time-resolution would be very beneficial especially for mobile platforms by providing fast measurements of more components, e.g., tracers or functional groups.

The fourth issue deals with complexity. Many laboratory studies employ simplified experimental conditions which neglect the environmental complexity. Important factors often overlooked are presence of water, complex reactant mixture and composition, and temperature dependence. This limits the ability to extrapolate laboratory-based data to the atmosphere. With regards to simulation chambers, more complex VOC mixtures could be employed. An important future development would be to describe the effect on SOA formation when going from the oxidation of a single precursor to the

oxidation of complex mixtures. In the field, SOA from different precursors are mixed. The laboratory allows for the analysis of specific precursors and thus SOA detection by different methods can be tested. The laboratory studies should be better linked to the ambient measurements in future.

A fifth and important issue is the modelling of SOA. It is obvious that modelling activities must follow experimental and mechanistic understanding, and the most basic problem regarding modelling of SOA is therefore the uncertainty surrounding the main formation mechanisms. However, the mechanistic details obtained from experimental and theoretical work need to be tested in models against ambient data in order to be considered reliable. It is essential that models reflect the latest findings as well as possible, and it can be noted that much of the understanding that has emerged over the past several years concerning the formation of SOA still needs to be incorporated in the SOA models embedded in atmospheric chemical transport models. The new developments that need to be reflected in any class of models include sufficiently detailed gas-phase chemistry, especially the role of NO<sub>x</sub> level, leading to formation of semi-volatile products, particulate-phase chemistry, identification of the volatility range of oxidation products, and the roles of organic aerosol level in determining aerosol water content. It is evident that laboratory data should preferably reflect conditions either as close to ambient as possible or which allow confident extrapolation to ambient conditions. Ambient data must provide information which can be used for source-apportionment, to evaluate the models emissions, and chemical processing, which will require some combination of chemical speciation, radiocarbon data and/or functional group analysis.

The sixth issue deals with the impacts of SOA on health and climate. A recent epidemiological study reveals a stronger association between daily mortality and fine particulate air pollution in summer than in winter [Nawrot et al., 2007]. As high PM levels in summer are typically associated with the production of SOA, this finding suggests that SOA may substantially contribute to the observed effect on mortality. However, there are very few studies of the health effects of SOA. Several studies strongly suggest that BVOCs may be involved in new particle formation in forested environments. This phenomenon has important implications for climate-biosphere interactions, and should be further investigated, including the application of recently developed nanoparticle composition techniques in forested areas. The optical properties (scattering and absorption) of fresh and aged SOA (pure or in combination with other species) are not well constrained, hindering assessment of their possible contribution to the aerosol direct effect. New sensitive techniques should be sought to measure these missing properties. The complex interaction and influence of SOA in the formation of clouds could be essential. One crucial point is to establish the influence of

SOA on the kinetics and thermodynamics of water uptake. In addition, ice nucleation and evaporation of water are two processes where the complex mixtures of SOA are expected to have an impact.

The six issues discussed can be seen as recommendations to policy advisers and makers for future research on atmospheric aerosols and in particular SOA. Furthermore, several of the activities mentioned in Chapter 5 below were (and are) actually contributions to Policy Support.



## 5. DISSIMINATION AND VALORISATION

Dissimination and valorisation of the results of the BIOSOL project was (and is being done) through various channels, including publications in peer-reviewed international scientific journals, presentations at national and international workshops and conferences, organisation of workshops, Follow-up Committee meetings, and joint meetings with the SSD project IBOOT (Impact of Biogenic emissions on Organic aerosols and Oxidants in the Troposphere), and other activities.

For the peer-reviewed publications we refer to Chapter 6 below. Here, we only like to mention that C and P2 co-authored a major overview article entitled "The formation, properties and impact of secondary organic aerosol: current and emerging issues" [Hallquist et al., 2009]. With regard to presentations at international conferences and workshops, many oral and poster presentations on the BIOSOL work were given, including at the Joint IGAC/CACGP Symposia in 2006 and 2010, the Seventh and Eighth International Aerosol Conferences (IAC 2006 and IAC 2010), the Aerosols - Properties, Processes and Climate INTROP-ESF Conference in 2007, the European Geosciences Union (EGU) General Assemblies of 2007 and 2008, the International Conferences on Nucleation and Atmospheric aerosols (ICNAA) of 2007 and 2009, the 4th Gordon Research Conference on Biogenic Hydrocarbons in 2007, the European Aerosol Conferences (EACs) of 2007, 2008, and 2009, the VOCBAS-INTROP meeting "Biogenic volatile organic compounds. Sources and fates in a changing world" in 2007, the 9th International Conference on Carbonaceous Particles in the Atmosphere (ICCPA) in 2008, and several workshops of the EU project OOMPH. Some of the presentations were on invitation. As to national meetings, C presented BIOSOL at the Kick-off meeting of the Belgian Federal Science Policy Office Programme "Science for Sustainable Development (SSD) (2005-2009)" in March 2007 and at the SSD Encounter "Health and ambient air quality" – Balance of the actions - dialogue between the parties in June 2009.

C and P2 organised an OOMPH workshop in Ghent in 2007 and P4 (co-)organised several workshops on research that is related to BIOSOL. As to the BIOSOL Follow-up Committee meetings, 4 such meetings took place (all at the University of Antwerp), i.e., on 20 March and 22 November 2007, on 26 November 2008, and 19 November 2009. These meetings were only attended by the Belgian members of the Committee (LNE, VMM, and BIRA-IASB), but with the 4 non-Belgian members (from Greece, Germany, Finland, and Austria) there were interactions by E-mail, at international conferences or on other occasions. In July 2007, C and P2 visited IFT (the home institution of the German Committee member) and in August 2007 C and P2 visited the Finnish

Meteorological Institute (the home institution of the Finnish Committee member) and they had discussions then with the German and Finnish Committee members.

In addition to the Follow-up Committee meetings, there were also formal and other meetings (and interactions by E-mail) with the partners of the SSD project IBOOT. On 21 November 2006, a technical meeting of the SSD projects BIOSOL and IBOOT was held at the University of Antwerp, a second BIOSOL-IBOOT meeting took place on 22 November 2007, a third on 26 November 2008, and a fourth on 19 November 2009.

C and P2 gave invited seminars on BIOSOL at the IfT (July 2007) and the University of Florence (November 2009). In August 2007 and July 2008, C also gave invited seminars at the University of Helsinki and Desert Research Institute in Reno, Nevada.

Furthermore, C provided input for the MIRA-T 2006 report and contributed to the EMEP/TFMM PM Assessment report. C also wrote the national contribution from Belgium for the EMEP/TFMM PM Assessment report [Maenhaut, 2007; see: <http://tarantula.nilu.no/projects/cccr/reports/cccr8-2007.pdf>]. On the invitation of the journal Atmospheric Environment C wrote a New Directions article for this journal [Maenhaut, 2008]. C provides advice to the VMM with regard to its chemical aerosol characterisation work and performs analyses for OC and EC on samples from these activities. C also provides advice to the European Commission with regard to OC and EC analyses of aerosol samples and he is an expert member of the Belgian Institute for Normalisation (NBN) and the European Committee for Standardisation, Working group CEN/TC 264/WG 35; the aim of the Working group is to arrive at a standard method for measurement of EC and OC deposited on filters.

P2 contributed to (and appeared in) a scientific programme for the Czech TV on applications of mass spectrometry in environmental and global change research (see: <http://www.ceskatelevize.cz/ivysilani/206411058200032-planeta-veda/>). P2 also provided input for the July 2009 issue of the Science, Technology and Innovation Projects magazine of British Publishers (see: <http://www.projects.eu.com/>). On pages 24-25 there is an article on the EU project SOAMASS, which dealt with research that formed part of BIOSOL.

P2 and P3 taught for doctoral students in an ISONET-VOCBAS Short Course, entitled "Stable Isotopes, Plant VOCs and Secondary Organic Aerosols in Biosphere-Atmosphere Carbon Exchange", which was held in Kuopio, Finland, in November 2006.

In May 2007, a Website was activated for the BIOSOL project. The URL for it is: <http://www.analchem.ugent.be/BIOSOL/>

## 6. PUBLICATIONS

Only the articles, which appeared in peer-reviewed international scientific journals are listed here.

### 6.1. Publications of the teams

For the team of C

W. Maenhaut.

New Directions: Future needs for global monitoring and research of aerosol chemical composition.

Atmospheric Environment, 42 (2008) 1070-1072, doi:10.1016/j.atmosenv.2007.11.038.

**PUBLI 1\_maenhaut\_AE2008.pdf]**

W. Maenhaut, N. Raes, X. Chi, J. Cafmeyer and W. Wang.

Chemical composition and mass closure for PM<sub>2.5</sub> and PM<sub>10</sub> aerosols at K-puszta, Hungary, in summer 2006.

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