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Understanding the anthropogenic influence on formation of biogenic secondary organic aerosols via analysis of organosulfates and related oxidation products

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Abstract

Anthropogenic emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) may affect concentration levels and composition of biogenic secondary organic aerosols (BSOA) through photochemical reactions with biogenic organic precursors to form organosul-

- fates and nitrooxy organosulfates. We investigated this influence in a field study from 19 May–22 June 2011 at two sampling sites in Denmark. Within the study, we identified a substantial number of organic acids, organosulfates and nitrooxy organosulfates in the ambient urban curbside and semi-rural background air. A high degree of correlation in concentrations was found among a group of specific organic acids, organosulfates
- ¹⁰ and nitrooxy organosulfates, which may originate from various precursors, suggesting a common mechanism or factor affecting their concentration levels at the sites. It was proposed that the formation of those species most likely occurred on a larger spatial scale with the compounds being long-range transported to the sites on the days with highest concentrations. The origin of the long-range transported aerosols was inves-
- tigated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model in addition to modeled emissions of related precursors including isoprene and monoterpenes using the global Model of Emissions of Gases and Aerosols from Nature (MEGAN) and SO₂ emissions using the European Monitoring and Evaluation Program (EMEP) database. The local impacts were also studied by examining the correlation
- ²⁰ between selected species which showed significantly enhanced concentrations at the urban curbside site and the local concentrations of various gases including SO_2 , ozone (O_3) , carbon monoxide (CO), NO_x, aerosol acidity and other meteorological conditions. This investigation showed that an inter-play of the local parameters such as the aerosol acidity, NO_x, relative humidity (RH), temperature and global radiation seemed to in-
- fluence the concentration level of those species, via such as wet aerosol chemistry. The local impacts however seemed minor on the concentration levels of the studied compounds. The total concentrations of organosulfates and nitrooxy organosulfates contributed to approximately 0.7 % of PM₁ mass.



1 Introduction

Volatile organic compounds (VOC) are emitted from both biogenic and anthropogenic sources and are oxidized to form lower volatility products partitioning between the gas and particle phase, leading to the formation of secondary organic aerosols (SOA) (Don-

- ⁵ ahue et al., 2006; Kroll and Seinfeld, 2008; Jimenez et al., 2009; Hallquist et al., 2009). In general, the production of biogenic SOA (BSOA) is estimated to be significantly larger than anthropogenic SOA (ASOA) (Goldstein and Galbally, 2007; Heald et al., 2010; Spracklen et al., 2011). For example, Hallquist et al. (2009) estimated a manyfold higher annual global production of BSOA (88 TgC) compared to ASOA (10 TgC),
- ¹⁰ which were however associated with high uncertainties. Other studies suggested that ASOA might have been underestimated (De Gouw and Jimenez, 2009), while some local and regional studies have indicated that ASOA could be more substantial than BSOA (Aiken et al., 2009; Fushimi et al., 2011). It is also thought that a substantial proportion of aerosols is formed through condensation of low-volatility biogenic VOC
- onto existing particles of anthropogenic origin (Carlton et al., 2010), thereby blurring the division between biogenic and anthropogenic SOA. Several studies have indicated that anthropogenic activities could enhance the production of BSOA via different mechanisms, for example by enhancing the incorporation of biogenic VOC products into the condensed phase due to pre-existing organic aerosol from anthropogenic activities;
- affecting the SOA yield by the complex effect of the anthropogenic species NO_x and nitrate (NO₃) radical (a nighttime product of NO₂ and ozone) or affecting new particle formation and growth where sulfuric acid has been identified as having an essential role in new particle formation (Aiken et al., 2009; Carlton et al., 2010; Szidat et al., 2006, 2009; Hoyle et al., 2011; Kulmala et al., 2004a). Further research is thus reguired on the actual impact of anthropogenic emissions on the formation and growth of
- ²⁵ quired on the actual impact of anthropogenic emissions on the formation and growth of SOA formed from biogenic VOC.

Several classes of VOC precursors, which are either reactive or could form oxidation products for SOA formation have been identified, of which cyclic compounds are par-





ticularly important. These include compounds such as cycloalkanes, aromatic hydrocarbons and terpenes, which are typically oxidized by an addition mechanism, yielding oxidation products with more than two polar functional groups, increasing the possibility of forming low-volatility products (Hallquist et al., 2009). A number of studies have focused on the oxidation pathways of monoterpenes by hydroxyl radical (OH), ozone 5 (O_3) or nitrate radical (NO_3) forming organic acids such as pinonic and pinic acid as supposed first generation oxidation products (Glasius et al., 2000; Larsen et al., 2001; Yu et al., 1999; Hoffmann et al., 1997; Librando and Tringali, 2005; Surratt et al., 2008; Calogirou et al., 1999; Yasmeen et al., 2012). The first generation products are further oxidized to form more oxidized products, for example pinonic acid is oxidized by 10 the OH radical to form 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Szmigielski et al., 2007; Müller et al., 2012). Another example is the oxidation and ozonolysis of α -pinene, one of the principal species of the monoterpene class, forming terpenylic acid and diaterpenylic acid acetate (DTAA) (Claeys et al., 2009).

- ¹⁵ Organosulfate formation has recently been demonstrated in both laboratory studies (Surratt et al., 2008, 2007a; linuma et al., 2007b) and ambient samples (Gómez-González et al., 2008, 2012; Kristensen and Glasius, 2011; Worton et al., 2011) as SOA produced from the oxidation of biogenic VOC, such as isoprene, α -pinene, β pinene, limonene in the presence of acidic sulfate particles. In addition to representing
- an interesting link coupling the formation of SOA from biogenic VOC precursors with the impact from anthropogenic pollutants, organosulfates were also estimated to contribute up to 5–10 % of the total organic mass (Tolocka and Turpin, 2012) or even 30 % of the total aerosol mass (Surratt et al., 2008). Organosulfates and nitrooxy organosulfates are also polar compounds, which can thus enhance the ability of aerosols to act
- as cloud condensation nuclei (CCN) with important climate implications (Hallquist et al., 2009; IPCC, 2007).

Here we studied the occurrence, levels and trends of the acidic monoterpene oxidation products (including for example *cis*-pinic acid, pinonic acid, terpenylic acid, MTBCA and DTAA), oxidation products from anthropogenic VOC precursors, typically aromatic





hydrocarbons (benzoic acid and phthalic acid) or cyclic olefins (adipic acid and pimelic acid), organosulfates and nitrooxy organosulfates in aerosols at two different locations in Denmark. These include an urban curbside site and a semi-rural background site. The chemical analysis was performed following an approach adapted from Kristensen

- and Glasius (2011), employing high-performance liquid chromatography (HPLC) coupled with an electrospray ionization inlet (ESI) to a quadrupole time-of-flight mass spectrometer (q-TOF-MS). The impacts of long-range transported SOA were investigated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model assisted by the modeled emissions of the major biogenic precursors including isoprene
- and monoterpene using the global Model of Emissions of Gases and Aerosols from Nature (MEGAN) and the anthropogenic emissions of sulfur dioxide (SO₂) using the long-range chemistry transport model, the DEHM, based on the European Monitoring and Evaluation Program (www.EMEP.int) database. Additional support analyses were also performed, including measurement of major inorganic ions to determine the aerosol additional support analyses of the aerosol additional support analyses.
- acidity level, analysis of local new particle formation events, local concentrations of atmospheric oxidants including ozone (O_3), carbon monoxide (CO), sulfur dioxide (SO_2) and nitrogen oxides NO_x ($NO_x = NO + NO_2$) and other meteorological parameteres including the global radiation level, temperature, relative humidity (RH), wind direction and wind speed.

20 2 Experimental

2.1 Field campaign sites

The campaign was conducted during the period 19 May–22 June 2011 concurrently at two sampling sites in Denmark (Fig. 1). The sampling site HCAB (55°38' N, 12°34' E) is located in central Copenhagen (~ 1.2 million inhabitants) on the curbside of H.C. Andersen's Boulevard with considerable traffic influence (~ 50 000 vehicles per day) (Municipality of Copenhagen, www.kk.dk). The second sampling site Risø





 $(55^{\circ}41' \text{ N}, 12^{\circ}05' \text{ E})$ is a semi-rural background site located approximately 30 km west of Copenhagen and 7 km northeast of Roskilde, which houses about 46 000 inhabitants. The semi-rural background area is characterized by agricultural land, small villages, Roskilde Fjord located about 100 m to the west of the station, and a main road

- (A6) located about 700 m east of the site. PM₁ samples were collected on quartz fiber filters (150 mm diameter, Advantec QR-100) using Digitel DHA-80 High Volume Samplers (HVS) equipped with PM₁ sampling heads. In order to assess the diurnal variation on PM₁ composition, sampling was performed in 12 h daytime and nighttime intervals starting every day at 6.00 a.m. and 6.00 p.m. LT simultaneously at both sites. The sampling flow rate was set to 23.1 m³ h⁻¹ providing a nominal sampling volume of 277.2 m³ per 12 h sample. There were several gaps in the dataset with one major gap at the
- per 12 h sample. There were several gaps in the dataset with one major gap at the Risø site from 3–16 June due to technical problems with the HVS.

2.2 Extraction

Extraction and analysis of the samples followed the procedure of Kristensen and Glasius (2011). Aerosol sample filters were extracted in 75 mL of 90 % v/v acetonitrile by ultra-sonication for 30 min in a water bath, where ice was regularly added to the bath to avoid heating. The extract was filtered through a nylon syringe filter (0.45 µm, VWR or Q-max), evaporated to dryness using a rotary evaporator and re-constituted twice in 500 µL 3 % v/v acetonitrile containing 0.1 % acetic acid. Prepared samples were kept at 3–5 °C prior to analysis. Camphoric acid was used as an internal standard to calculate the recovery. Field blanks were extracted and analyzed using the same procedure as for the samples.

2.3 HPLC-ESI-qTOF-MS analysis and quantification of compounds

 Samples were analyzed using a HPLC system (Dionex Ultimate 3000) coupled through
 an ESI inlet to a qTOF-MS (Bruker Daltonics GmbH, Bremen, Germany). A reversedphase HPLC separation was achieved using a Waters Atlantis T3 C18 column (2.1 ×





150 mm, $3 \mu m$). The mobile phase was comprised of 0.1 % v/v acetic acid (eluent A) and 95 % v/v acetonitrile (eluent B). The injection volume was $10 \mu L$ and the flow rate of the mobile phase was $0.2 \, m L \, min^{-1}$ with the following gradient: the mobile phase was kept at 3 % of eluent B in 10 min prior to injection until 5 min after injection; eluent B was then increased to 20 % (at $20 \, min$), 60 % (at $30 \, min$) and 95 % (at $35 \, min$) where it was kept at a plateau (95 %) until 45 min and increased to 100 % at 46 min; the gradient was kept at 100 % of eluent B until 51 min and decreased to 3 % (at $54 \, min$) where it was further kept at 3 % for $3 \, min$. The MS scan range was set from $50-1000 \, m/z$. The ESI-

qTOF-MS was operated in negative ionization mode with nebulizer pressure at 3.0 bar,
 dry gas flow 8.0 Lmin⁻¹, source voltage 4000 V and transfer time 50 μs. Acquired data was processed using the Bruker Compass software.

All organic acids were quantified using authentic standards with the exception of hydroxy-pinonic acid, which was quantified using pinonic acid standard. The organosulfates and nitrooxy organosulfates were quantified using three different surrogate stan-

¹⁵ dards depending on the retention time of the compound. The surrogate standards included D-mannose sulfate (molecular weight (MW) 260) for compounds eluting in the first 15 min, an in-house synthesized organosulfate from β -pinene (MW 250) for compounds eluting during 15–40 min and octyl sulfate (MW 210) for compounds eluting after 40 min.

20 2.4 Extraction and analysis of ions

A circle punch (28 mm diameter) of the aerosol sample filter was sonicated in 4.00 mL milli-Q water for 1/2 h. The extract was filtered through a polyethersulfone syringe filter (0.45 μm, PALL Life Sciences IC Acrodisc) and analyzed by ion chromatography using a Methom 820 IC separation center (with a Metrosep A Supp5–150 column for anion analysis and a Metrosep C4–150 column for cation analysis) and an 819 IC conductivity detector. For anion analysis, an eluent of 3.2 mM Na₂CO₃/1.0 mM NaHCO₃ was used. For cation analysis, an eluent of 0.7 mM dipicolinic acid/1.7 mM HNO₃ was used. An auto-sampler was used where 100 μL of each sample was introduced into the eluent,





which was kept at a flow rate of 0.7 mLmin^{-1} . The inclusion of ion analysis in this work is mainly to calculate the level of acidity (H⁺) from the charge balance, based on IC data of [SO₄²⁻], [NO₃⁻] and [NH₄⁺] following Zhang et al. (2012b).

2.5 Measurement of particle number size distributions

Particle number size distributions in 15 channels from 6–700 nm were measured using A Differential Mobility Particle Sizer (DMPS), which was composed of a Vienna-type Differential Mobility Analyzer (DMA) (WinkImayer et al., 1991) employing re-circulating sheath air flow (Jokinen and Makela, 1997) and a Condensation Particle Counter (CPC) (TSI Inc. 3010, Shoreview, MN). The data was corrected for reduced counting
 efficiency at the low size end (6–10 nm), multiply charging and losses during sampling following inversion algorithm by Wiedensohler (1988). A ratio of sheath air to aerosol air of 6.8 : 1 was applied, with alternating up- and down-scans of 150 s for each size spectrum. Annual service of the CPC was performed at TSI ensuring correct counting efficiency.

15 2.6 Biogenic VOC and SO₂ emissions

Emissions of biogenic VOCs are estimated by using the global model MEGAN (Guenther et al., 2006; Zare et al., 2013, 2012). The empirical algorithm in MEGAN simulates the emission rates based on relationships between ecosystem dependent emission factors and key drivers that control emissions. The model takes into account the effects of temperature, radiation, leaf area index, foliage age and soil moisture on the estimation of emissions. In MEGAN, plant species are grouped into six plant functional types (PFTs): broadleaf tree, needle leaf evergreen tree, needle leaf deciduous tree, shrub, crop and grass; and the model dataset provides the geographical distribution of the standard emission factor of the six PFTs with high spatial resolution of 1 km². The required meteorological inputs are provided by the MM5v3.7 model (Grell et al., 1994). The initial and boundary conditions for the MM5 model are derived from





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the NCEP FNL (Final Analyses) data with 6 h temporal and $1^{\circ} \times 1^{\circ}$ spatial resolution (http://rda.ucar.edu/datasets/ds083.2/).

Sulfur dioxide emissions were modeled using the long-range chemistry transport model DEHM (Brandt et al., 2012), based on the European Monitoring and Evalua-

tion Program (www.EMEP.int) database in Europe with a resolution of 50 km × 50 km. These European anthropogenic sulfur dioxide emissions are mainly released by fuel combustion (www.ceip.at), dominated by coal fired power plant and emissions from international ship traffic.

2.7 Gas and meteorological data

- ¹⁰ Meteorological data including temperature, RH and global radiation were obtained from a station located on the roof-top of the H.C. Ørsted institute (HCOE, 55°42′ N, 12°33′ E), which represents the urban background conditions of Copenhagen, Denmark. HCOE is located ~ 3.5 km north of HCAB. O₃, NO/NO_x and CO were measured using photometry (Teledyne API 400, San Diego, CA, USA), chemiluminescense (Teledyne API M200
- A, San Diego, CA, USA) and infrared absorbance (Teledyne API 300 E, San Diego, CA, USA), respectively at both field sites HCAB and Risø with 30 min resolution whereas measurement of SO₂ using UV fluorescence (Teledyne API M100E, San Diego, CA, USA) with 30 min resolution was only obtained from HCAB. Gas and meteorological data were collected within the Danish Air Quality Monitoring Program (Ellermann et al., 2012).

2.8 Statistical analysis

Statistical analysis was performed on the data set to analyze the intraday variability between daytime and nighttime samples as well as the possible inter-site variation between the two sites HCAB and Risø. As the data was not normally distributed, the U

²⁵ Mann–Whitney test was used instead of a two-way ANOVA to assess the intraday and inter-site variability (Wilks, 2011).





3 Results and discussion

3.1 Detection and characterization of organic acids, organosulfates and nitrooxy organosulfates

During the field campaign, a total of 39 species including 12 organic acids, 17 organosulfates (OS) and 9 nitrooxy organosulfates (NOS) were detected as summarized in Tables 1–3. The organic acids were identified using their authentic standards, with the exception of hydroxy-pinonic acid where the identification was based on the characteristic mass-to-charge (m/z) fragments of the compound. The organic acids included those of anthropogenic origin (i.e. benzoic acid, adipic acid, pimelic acid and phthalic acid) and biogenic origin, specifically suberic acid and azelaic acid originating from unsaturated fatty acids in addition to terpenylic acid, pinonic acid, pinic acid, hydroxy-pinonic acid, DTAA and MTBCA originating from α -/ β -pinene (Table 1). Among the anthropogenic organic acids, benzoic acid is a photochemical degradation product of aromatic hydrocarbons, which originate from anthropogenic automobile emissions

- (Suh et al., 2003), while adipic acid and pimelic acid have been identified as photooxidation products from the ozonolysis of cyclic olefins (Hatakeyama et al., 1985; Grosjean et al., 1978; Koch et al., 2000) and phthalic acid could be the oxidation product of naphthalene and other polycyclic aromatic compounds (Fine et al., 2004). The biogenic dicarboxylic acids with relatively long carbon chains including suberic acid
- $_{20}$ (C₈) and azelaic acid (C₉) are believed to originate from the oxidation of unsaturated fatty acids (Mochida et al., 2003) which are rich in marine phytoplankton and leaves of terrestrial higher plants though some contribution may originate from anthropogenic meat cooking (Rogge et al., 1991) or wood burning (Rogge et al., 1998). The other biogenic organic acids (terpenylic acid, pinonic acid, pinic acid, hydroxy-pinonic acid and
- ²⁵ DTAA) are oxidation products of α -/ β -pinene (Claeys et al., 2009; Ma et al., 2007), with MBTCA being the second generation oxidation product of pinonic acid which indicates aging by OH (Müller et al., 2012; Szmigielski et al., 2007). The identified organic acids were all detected at both sites.





The organosulfates were identified using the characteristic fragment of m/z 97 (bisulfate anion HSO₄⁻) and possibly m/z 80 (sulfur trioxide anion SO₃⁻). The nitrooxy organosulfates were identified based on a neutral loss of m/z 63 (HNO₃) in addition to the characteristic fragments of HSO₄⁻ and SO₃⁻. Many organosulfates and nitrooxy organosulfates species which were detected in this study (Tables 2–3) have also been identified in previous smog chamber (Surratt et al., 2007a, 2008, 2010) and field studies (Gómez-González et al., 2008, 2012; Kristensen and Glasius, 2011). Most organosulfates, which were identified based on the literature, probably originated from isoprene (OS molecular weight (MW) 154, 156, 170, 200, 212, 214, 216 and 334) and monoterpenes including α - and β -pinene precursors (OS 248, 250, 280 and 298) whereas a large share of the detected nitrooxy organosulfates could be the oxidation products from limonene (NOS 297, 311, 313, 327 and 329). The structures of several organosul-

a large share of the detected nitrooxy organosulfates could be the oxidation products from limonene (NOS 297, 311, 313, 327 and 329). The structures of several organosulfates (OS 182, OS 208, OS 210) and one nitrooxy organosulfate (NOS 331) were not identified.

3.2 Concentration levels

The ranges of concentration levels of the detected species are shown in Table 4. In general, a higher number of valid measurements (*N*) were available from HCAB, mostly due to the gap in the set of samples collected from the semi-rural background site Risø. The total concentrations of the detected organic acids averaged per sampling interval (12 h) during the sampling period was 23 ± 15 ngm⁻³ and 19 ± 13 ngm⁻³ at HCAB and

- (12 h) during the sampling period was 23 ± 15 ngm ° and 19 ± 13 ngm ° at HCAB and Risø, respectively, with the second generation product MBTCA accounting for approximately 21 % of total organic acids at HCAB and 20 % at Risø. The median value of MBTCA was 2.3 ngm⁻³ at HCAB and 2.0 ngm⁻³ at Risø, which are in range of the overall median value of 2.7 ngm⁻³ reported by Gómez-González et al. (2012) from a study at a Palaian forest site with source urban pollution impact. Among the orthogonal control of the control of t
- a study at a Belgian forest site with severe urban pollution impact. Among the anthropogenic organic acids, adipic acid and phthalic acid seemed to dominate at both sites,





whereas azelaic acid (4.0 ng m⁻³ average) and pinonic acid (2.2 ng m⁻³ average) were the dominant first generation biogenic organic acid at HCAB and Risø, respectively.

The organosulfates were detected in most samples from both sites (Table 4). The major organosulfates detected in high concentrations at both HCAB and Risø mostly

- originated from isoprene, such as OS 154, OS 156, OS 200 and OS 212 (Surratt et al., 2007a, 2008). The total organosulfate concentration averaged per sampling interval (12 h) during the sampling period was 59 ± 43 ngm⁻³ at HCAB, whereas at Risø a slightly lower total concentration value of 47 ± 28 ngm⁻³ was obtained. Nitrooxy organosulfates were detected in lower concentrations compared to organosulfates, with
 a total concentration of 4 ± 1 ngm⁻³ at HCAB and 3±1 ngm⁻³ at Risø. NOS 297, which
- was possibly an oxidation product from limonene (Surratt et al., 2008) was the major nitrooxy organosulfate found at both sites.

The concentration levels of the detected compounds were compared with an earlier study performed at a forest site in Denmark by Kristensen and Glasius (2011) ¹⁵ during spring 2008, in which fewer species (six organic acids, five organosulfate, five nitrooxy organosulfates) were included. The comparison was thus only targeted at similar compounds. In general, the levels of most organic acids were higher in the present study, except *cis*-pinic acid and pinonic acid, which were more abundant at the for-

est site. The concentration levels of the organosulfates and nitrooxy organosulfates in

- this study were many-fold higher compared to the previous study, especially with regards to the organosulfate species. This, in addition to the differences among the sites and years could be caused by differences in quantification standards, as Kristensen and Glasius (2011) used camphor sulfonic acid as a surrogate standard, as opposed to the three different standards including D-mannose sulfate, an in-house synthesized
- organosulfate from β -pinene and octyl sulfate used in this study (as described above). This highlights the analytical challenge of quantifying organosulfates and comparing concentrations among different studies.

The total concentration of organic acids and organosulfates are significantly higher in our samples compared to the Arctic, where a total concentration of 3 (± 1) ngm⁻³





for organic acids and 12 (\pm 2) ngm⁻³ for organosulfates (quantified using the same organosulfate from β -pinene used in the present study) were measured at Zeppelin Mountain, Svalbard during summer of 2008 (Hansen et al., 2014). However, during late winter and early spring, total concentration levels up to 70 ngm⁻³ and over 45 ngm⁻³ were detected for all organic acid, organosulfate and nitrooxy organosulfate compounds respectively at Station Nord, northeast Greenland and at Zeppelin (Hansen et al., 2014). These values are in range with our concentration values. It must be noted that a total of 11 organic acids, 12 organosulfates and one nitrooxy organosulfate were detected by Hansen et al. (2014).

10 3.3 Inter-site, day/night variability and inter-species correlation

The non-parametric U Mann–Whitney test was performed on the data sets to analyze the inter-site variability between HCAB and Risø during the overlapping period (19 May–1 June and 17–22 June) where data from both sites were available. The 90 % confidence interval was used for evaluation of the statistical significance to account for the passible field sampling filter extraction and guantification upcartaining. The test

- ¹⁵ the possible field sampling, filter extraction and quantification uncertainties. The test results showed that 14 parameters out of the 41 tested parameters were statistically different between the two sites at 90 % confidence interval (p < 0.1) (Table 5). These 14 parameters included six organic acids (benzoic acid, pimelic acid, phthalic acid, suberic acid, pinonic acid, and azelaic acid), the concentrations of total first generation organic
- acids, five organosulfates (OS 182, OS 200, OS 210, OS 248 and OS 298), one nitrooxy organosulfate (NOS 297) and the concentration of total nitrooxy organosulfates. The species with statistically higher concentrations were mostly from HCAB (12 out of 14) with the exception of benzoic acid and pinonic acid, which showed significantly higher concentrations at Risø. While a higher occurrence of benzoic acid at the semi-
- ²⁵ rural background site Risø was unexpected, it seems that the urban curbside site HCAB was associated with enhanced concentrations of both biogenic (suberic acid and aze-laic acid) and anthropogenic (pimelic acid and phthalic acid) compounds in addition to





the anthropogenic-biogenic coupling species (OS 182, OS 200, OS 210, OS 248, OS 298 and NOS 297), which probably indicated some local anthropogenic enhancement impacts on the concentration levels of the compounds. In fact, the total concentrations of organic acids and nitrooxy organosulfates were also found at significantly higher

- ⁵ levels at HCAB. In contrast, the second generation product of pinonic acid, MBTCA, which has been regarded as an indicator of photochemical aging of pinonic acid by OH (Müller et al., 2012) was statistically indifferent at the two sites. The fact of a statistically higher level of the pinonic acid precursor at Risø and the indifferent concentration of its product MBTCA at the sites probably suggest that the degree of photochemical aging was not directly governed by the concentrations of the precursor at the semi-rural
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background site Risø.

The variability between daytime and nighttime samples at each site during the whole field study was also analyzed using a non-parametric U Mann-Whitney test at 90% confidence interval. The test results showed statistically indifferent daytime and nighttime concentrations for most species (Tables S1 and S2), with the exception of higher daytime concentrations of phthalic acid (p = 0.0385), OS 210 (p = 0.0622) and NOS 343 (p = 0.0825) at HCAB and higher nighttime concentrations of NOS 297 at both sites (p = 0.0011). Phthalic acid, OS 210 and NOS 297 were associated with high numbers of valid measured daytime or nighttime concentrations ($N \ge 30$) whereas NOS 343 was associated with a lower number of valid N ($N_{dav} = 10$; $N_{night} = 13$).

Phthalic acid is widely used in plasticizer substrates and could be primarily emitted to the atmosphere from off-gassing of plasticizers from plastics (Fraser et al., 2003), though previous studies have also suggested that it correlated with SOA in ambient samples (Fraser et al., 2003; Fine et al., 2004; Schauer et al., 2002). A recent study

of the photooxidation of naphthalene has also indicated the link between phthalic acid 25 formation and photochemistry, while pointing towards negligible primary emissions of the compound based on laboratory and field measurements (Kleindienst et al., 2012). The findings support our observation of higher daytime concentration of phthalic acid at HCAB, though phthalic acid was not necessarily formed directly at the site. Meanwhile



the indifferent daytime and nighttime concentrations of phthalic acid at Risø were probably governed by a generally lower concentration level of the species at the site (Table 5). The other compound with significantly higher daytime concentrations at HCAB was OS 210, which has recently been reported in aerosols in the Arctic (Hansen et al., 5 2014).

The compound NOS 297 (m/z fragments 296, 233, 177, 163 and 97) showed significantly higher nighttime concentration at both sites, though its concentrations were statistically higher at HCAB compared to Risø (Table 5). This species was previously detected in ambient aerosols (Gao et al., 2006; Reemtsma et al., 2006; Kristensen and Glasius, 2011) and has been suggested as an oxidation product of limonene-like

monoterpene precursors (Surratt et al., 2008). In this study, NOS 297 was identified as the major nitrooxy organosulfate (Table 4), accounting for 36% and 34% of the total concentrations of nitrooxy organosulfates detected at HCAB and Risø, respectively. The higher nighttime occurrence of NOS 297 could indicate the impacts of local or re-

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- gional nighttime chemistry on the concentration level of the compound. In fact, the formation of nitrooxy organosulfates has been suggested to involve nighttime nitrate (NO₃) radical chemistry (linuma et al., 2007a, b; Surratt et al., 2008). In contrast, NOS 343 showed significantly higher daytime concentrations at HCAB, though the statistical calculation was associated with a lower number of measurements, as mentioned above.
- Too few measurements of NOS 343 were available at Risø to compare its daytime and nighttime concentrations. Overall, significantly higher nighttime concentrations were observed for total nitrooxy organosulfates at both sites (Tables S1 and S2), which was attributed to the predominant contribution from the nighttime important species NOS 297.
- As a majority of the detected species did not show any immediate evidence of local site impacts on their concentration levels according to the U Mann–Whitney test results, the relations among the compounds were furthermore investigated using R^2 correlation coefficients to unveil any potentially driving mechanisms or factors influencing their formation. The correlation coefficients were calculated for each pair of species at each site





and subsequently averaged for both sites. The averaged R^2 correlation coefficients are presented in Fig. 2, with each organic acid, organosulfate and nitrooxy organosulfate compound (lines) correlating with other species (x-axis). Relative standard deviations (RSD, %) for the corresponding averaged R^2 correlation coefficient are shown in Table S1. Only 36 out of the total 38 species were used to calculate the R^2 correlation coefficient values as those with very few measurement values were excluded. The re-

sults in Fig. 2 were divided into panels of organic acids (top), organosulfates (middle) and nitrooxy organosulfates (bottom).

Figure 2 shows a clear correlating group with high R^2 correlation coefficient values (> 0.5) among the species in the group, which is comprised of certain organic acids, organosulfates and nitrooxy organosulfates. The correlating group included three organic acids, namely terpenylic acid, MBTCA and DTAA (dark blue), a vast number of 12 organosulfates (red) and four nitrooxy organosulfates (green). These organosulfates and nitrooxy organosulfates among others included species closely related in molec-

- ¹⁵ ular weight, such as the groups of OS (154, 156), OS (212, 214, 216), OS (252, 254) and NOS (327, 329, 331). The organic acids pinonic and pinic acid (light blue) and OS 248 (purple) seemed to only partly follow the correlation pattern as the degree of correlation was somewhat lower, especially with regards to the correlation between these species and organosulfates.
- The degree of correlation (calculated as the R^2 values) among the mentioned specific compounds was persistent at both study sites, as evident by the generally lower deviation with small RSD values (%) associated with averaging the *R*-squared values from both sites as opposed to the uncorrelated species (Table S3). The organosulfates correlated consistently well with the organic acids and the other organosulfates
- within the correlating group, with RSD ranging from typically a few to over 20 % between sites. Correlation coefficients between the nitrooxy organosulfates and the other species showed larger discrepancies between the two sites, with RSD ranging from a few percent (NOS 313) to considerably higher percentages (NOS 327, 329 and 331), mostly due to a higher correlation level of these species at Risø compared to HCAB.





Concentrations of pinonic acid, pinic acid and phthalic acid, which only partly followed the correlation pattern showed larger deviations between the two sites. In contrast, OS 248 which also partly followed the pattern (with slightly lower R^2 coefficient ~ 0.5) showed a highly consistent correlating tendency at both sites with low RSD values.

⁵ The consistent correlation pattern among the group of organic acids, organosulfates and nitrooxy organosulfates of different precursors detected at both sites probably indicate a common source for the species at both sites.

The correlation between the total concentration level of organosulfates and the concentration of SO_4^{2-} ion measured by IC was also examined. A relatively high correlation

- ¹⁰ coefficient value ($R^2 = 0.6$) was obtained between the total organosulfates and sulfate at the HCAB site with the episodes of highest concentrations of organosulfates coinciding with peak concentrations of the $SO_4^{2^-}$ ion, which is in line with previous observations of aged continental aerosols over the southeast Pacific Ocean (Hawkins et al., 2010). This observation probably indicates a common formation mechanism of the organosul-
- fates and the sulfate ion, such as particle phase formation by reaction with condensed SO_4^{2-} or by means of acid catalysis. It should be noted that the correlation was only visible at the urban curbside site HCAB, while such correlation was not found at Risø (R^2 correlation coefficient = 0.3).

Although the formation of nitrooxy organosulfates could involve nighttime nitrate radical chemistry as discussed above, no direct correlation was found between the total concentration level of nitrooxy organosulfate and the concentration of NO₃⁻ measured by IC. This could be attributed to decoupling of long-range transported nitrate ion and nitrate radical, which is formed in-situ from NO₂ and O₃. In addition, the sampling of NO₃⁻ is associated with some uncertainty as ammonia (NH₃) and nitric acid (HNO₃) could evaporate from the particle filter.





3.4 The regional impacts

Figure 3 shows the temporal variation of the total concentrations of organic acids, organosulfates and nitrooxy organosulfates detected at HCAB and Risø during the field study. It is apparent that the temporal trends are very similar regarding the different cat-

- ⁵ egories of the compounds explored in addition to a similar spatial variation between the two sites, which were attributed to the large contribution of compounds belonging to the correlating group affecting both sites. The observations strongly indicated a regional influence on the total concentration levels of the compounds. Elevated total concentrations of organic acids, organosulfates and nitrooxy organosulfates seemed to occur
- at both sites during the same daytime or nighttime interval, exemplified by the daytime samples on 22 May, 31 May and 18 June or the nighttime sample on 23 May. Several other concentration maxima occurring on 6 June (daytime) and 8 June (nighttime) were observed at HCAB (data from Risø was unavailable for these days).

In order to investigate the regional impacts on the concentration levels of the detected compounds, 5-days air mass back trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model for every 12 h sample (Draxier and Hess, 1998). As HCAB and Risø are relatively close with a distance of ~ 30 km, HYSPLIT calculations were only performed for the HCAB site. The results revealed a dominating westerly origin of air masses during most of the campaign period.

- However a clear dominance of the south-easterly air masses was found to be associated with the daytime or nighttime episodes of elevated concentrations, including the daytime samples on 22, 26 and 31 May, and 6 and 18 June and the nighttime sample on 8 June. The travelling path of the south-easterly air masses probably involved the region around the borders between Germany, Poland and Czech Republic (Figs. 1 and 1).
- 4). It must be noted that the air masses following the south-easterly direction could have different origins (3–5 days backwards) but all passed the south-easterly region 1–2 days immediately before arrival at the sampling site. An example of the impacts of air masses arriving from the south-easterly direction is shown for three consecutive





days on 30 May (nighttime), 31 May (daytime with elevated concentrations) and 1 June (daytime) where data from both HCAB and Risø were available (Fig. 4). To support the interpretation of the HYSPLIT calculations, emissions of isoprene and monoterpenes (daily) calculated using the MEGAN model and SO₂ (monthly) calculated using the 5 DEHM model, are also shown in Figs. 4 and 5 to illustrate the magnitude of biogenic

and anthropogenic emissions in the region.

Figure. 4 shows a sudden change of air mass origin from westerly (30 May) to southeasterly (31 May) back to westerly (1 June), which was coupled with a major episode on 31 May with elevated concentrations of the organic acids, organosulfates and nitrooxy

- organosulfates (Fig. 3). As can be seen from the modeled isoprene and monoterpene daily emissions for the corresponding days (Fig. 4), emissions from the westerly direction affecting 30 May seemed slightly lower than emissions in the region along the southeasterly back trajectories affecting 31 May. Meanwhile, emissions from the westerly direction affecting 1 June were comparable to emissions from the southeasterly direction affecting the previous day. This indicated that VOC emissions were probably
- not the limiting factor in the formation of the investigated compounds.

Figure 5 shows an average of SO_2 emission over the two months May–June 2011. Though the SO_2 emission map could not be used to evaluate the daily change in anthropogenic emissions to further investigate the observed elevated concentrations

on 31 May, it however indicated strong SO₂ emissions from hotspots in the region that were passed over by the south-easterly air mass shown in the trajectories. This could probably influence the formation of the organosulfates and nitrooxy organosulfates during long-range transport to Denmark. The accompanying organic acids, which were also found at high concentrations correlating to the organosulfates and nitrooxy organosulfates, could also be long-range transported to the sampling sites.

3.5 The local impacts

The possible local anthropogenic impacts were investigated by examining the species of significantly higher concentrations at HCAB, which did not belong to the correlating





group, including OS 182 (m/z fragments 181, 97), OS 210 (m/z fragments 209, 153, 137, 97 and 79) and NOS 297 (m/z fragments 233, 177, 163 and 97). As displayed in Fig. 6, the varying patterns of OS 182 and OS 210 concentrations in May were considerably similar, with a few episodes of high daytime concentrations especially

- ⁵ during the period 20–25 May with a lower concentration on Sunday 22 May (daytime). Such observation stands in contrast to the varying trend of the total organosulfate concentrations during the same period, where a generally lower concentration level was observed except from elevated daytime concentrations on Sunday 22 May (Fig. 3). Assuming that the varying trend of the total detected species in Fig. 3 was mostly gov-
- erned by long-range transported compounds belonging to the highly correlated group, the varying trend of OS 182 and OS 210, which did not belong to the correlated group could probably reflect some local impact on the concentration levels of these species. However, while OS 182 and OS 210 seemed to correlate well in May, concentrations of the species deviated towards the end of the field study (Fig. 6), which could be partly
- attributed to the suppressing long-range transported concentration of the species to the site. For example, elevated daytime concentration of OS 182 was observed on 16 June, which is one of the characteristic days of air masses arriving from south-east associated with higher total concentrations of the detected species (Fig. 3).

It was attempted to investigate the local impacts that possibly led to the significantly

- ²⁰ higher concentrations of OS 182, OS 210 and NOS 297 at HCAB by studying the temporal variation of the gases (O₃, NO, NO_x, SO₂, CO) and the aerosol acidity level at HCAB calculated from charge balance using $[SO_4^{2^-}]$, $[NO_3^-]$ and $[NH_4^+]$ at HCAB following Zhang et al. (2012b) during the campaign period (Fig. 7). Analysis of the meteorological conditions including RH, temperature (*T*) and global radiation (GR) at the urban
- ²⁵ background site HCOE, which was located in close proximity to HCAB (Fig. 8) was also included. As can be seen from Fig. 7, the period 20–25 May was accompanied by a generally higher level of aerosol acidity which decreased on 22 May (daytime). Such variation of the aerosol acidity level perfectly matched the trend of the varying concentrations of OS 182 and OS 210 during the same period (Fig. 6). In fact, the





aerosol acidity level has been suggested as an essential parameter in the formation of organosulfates (Zhang et al., 2012b). At the same time, the concentration level of the organosulfates might rather be affected by an inter-play between the aerosol acidity level and other factors, such as the global radiation and temperature. For example

- the 20 and 21 May (daytime) samples showed high concentrations of OS 182 and OS 210, which was comparable to the concentrations on 24 or 25 May (daytime) samples (Fig. 6), whereas the aerosol acidity level on 20 or 21 May was considerably lower compared to the other days (Fig. 7). 20–21 May were however accompanied with a higher level of global radiation, especially on 21 May (579 Wm⁻²) compared to other latter
- days 24–25 May (daytime) (Fig. 8). While a higher level of global radiation could probably enhance the oxidation of SO₂ by the OH radical and thereby resulted in higher concentrations of SO₄²⁻ as observed with the 20–21 May (daytime) samples, NH₄⁺ was also detected at higher concentrations with these samples, resulting in an overall lower aerosol acidity calculated based on ion charge balance on the days. In addition, the higher temperature observed on 20–21 May compared to 24–25 May may also have
- contributed to enhance the formation of supposed local organosulfates in the former samples.

Higher daytime concentrations of OS 210 were also observed on 7 June (Tuesday) and 8 June (Wednesday) (Wednesday) (Fig. 6), whereas the aerosol acidity reached its highest level of 46 nmol m⁻³ on 7 June (nighttime) with interestingly almost neutral conditions on the adjacent 7 June (daytime) and 8 June (daytime) (Fig. 7). At the same

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- time, during these two daytime intervals, episodes of elevated concentrations of the anthropogenic gases SO_2 , CO, NO and NO_x were also observed at HCAB, with the most notable increase of NO and NO_x concentrations (Fig. 7). Meanwhile, the O₃ level
- ²⁵ was in the lowest concentration range presumably due to the lower level of sunlight in addition to titration by NO_x (Fig. 8). A close examination revealed that the NO and NO_x were highest during the early morning and late afternoon hours which are attributed to traffic emissions, though during the day course both NO and NO_x remained at a higher level compared to the other days during the campaign period. This observation could





be partially attributed to lower wind speed during daytime on 7 June (2.0 ms⁻¹) and on 8 June (2.9 ms⁻¹), which was considerably lower than the average wind speed of 4.1 ms⁻¹ for the whole campaign period. It must also be noted that this period was coupled with the highest RH range during the campaign period (Fig. 8), which resulted from the corresponding very low global radiation during the days. The observations indicated an inter-play between the anthropogenic gases, especially NO, NO_x and probably wet aerosol chemistry, leading to the occurrence of higher concentrations of OS 210 in these samples. A previous study by Dommen et al. (2006) on the effect of RH under high NO_x conditions indicated that more substantial volatile SOA were

- observed at higher RH rather than at lower RH. Additionally, SOA formation including carboxylic acids and organosulfur compounds in cloud and fog droplets have been hypothesized as plausible by Blando and Turpin (2000) while a recent smog chamber study by Zhang et al. (2012a) suggested that elevated RH values could mediate the formation of organosulfates, thereby emphasizing the role of wet sulfate aerosols in
- forming organosulfates in ambient aerosols. At the same time, though aerosol acidity has been found to enhance isoprene SOA formation under low initial NO conditions (Surratt et al., 2010, 2007b; Jaoui et al., 2010), seed aerosol acidity on SOA formation from isoprene showed a negligible effect under high initial NO conditions (Surratt et al., 2006), which implied the less important role of seed aerosol acidity on the formation of OS 210 on 7 and 8 June (daytime) where both NO and RH were high.

Further investigation of the meteorological conditions during the period where data from both sites were available (19 May–1 June and 17–22 June, see Fig. 8) revealed a possible coupling between higher temperature and global radiation (508 Wm⁻²) with the occurrence of concentration maxima observed on days with the highest tempera-

ture 31 May (daytime) and 6 June (daytime) (Fig. 3). While the concentration maxima were probably due to long-range transport as discussed above, such observations may also indicate that the concentrations of the long-range transported species became more enhanced by the local/regional factors such as high temperature and global radiation.





The third species used to study the local impacts was NOS 297, which showed significantly higher nighttime concentration as discussed above, though some possible long-range transport contribution to its concentration at HCAB could not be completely eliminated, as shown by its elevated concentration also on peak concentration days 31 May and 16 June. However with the exception of these days, elevated concentrations of NOS 297 were only observed at nighttime on 19 May, 20, 22, 26 and 6 June, 8 and 10. In fact, nighttime concentration maxima of NO_x (69, 70 and 75 µg m⁻³) were also observed on 19 May, 20 and 10 June, respectively, compared to an average nighttime NO_x concentration of 47 µg m⁻³, which could contribute to formation of the nitrate

- ¹⁰ (NO₃) radical via the reaction between O₃ and NO₂. The corresponding nighttime RH was also in the lower concentration range (~ 64 % RH) compared to the average night-time RH of 70 % for the whole campaign period, which probably reduced the available condensation sink for particle precursors and facilitated the formation of NOS 297 by nighttime NO₃ radical chemistry. In contrast, during the other nights (22, 26 May and
- 6, 8 June) where high concentrations of NOS 297 were also found, the RH was considerably higher (~ 79%) whereas the gas concentrations were low. Investigation of air mass back trajectories using HYSPLIT also revealed that the 22, 26 May and 6 June nighttime were affected by air masses arriving from the south-south-easterly direction whereas on 8 June air masses arrived from easterly direction. Such observations sug-
- gest that the detected concentrations of NOS 297 could be governed by both the local formation and the degree of long-range transport of the compound to the site. This poses a classical challenge in determining the sources and driving factors affecting the formation and concentrations of ambient SOA compounds. Nevertheless, it seems probable that occurrence of NOS 297 was favored by nighttime chemistry, regardless of whether the species were formed in-situ or long-range transported to the site.

It can be seen that the local impacts could affect the concentration levels of the specific compounds as discussed above. Meanwhile their impacts on the concentration levels of the compounds belonging to the long-range transported group may be not statistically noticeable, as those compounds were most likely formed at a distant site.





However it must be noted that the magnitude of the local impacts on the detected species seemed rather modest in general.

Local new particle formation (NPF) events were also examined using the DMPS data following Dal Maso et al. (2005) to investigate whether the local formation of organosul-

- fates could be associated with particle nucleation at the sites. A limited number of NPF events were found occurring on the same days at the semi-rural background site Risø, the urban background site HCOE and the urban curbside site HCAB, though HCAB is heavily influenced by traffic emissions resulting in generally short nucleation bursts rather than allowing a classic "banana" formation and growth. The NPFs how-
- ever seemed to occur on the days with low concentrations of most species, including the possible local compounds OS 182 and OS 210, which agree with previous indications that NPF may occur more frequently in cleaner environments (Lyubovtseva et al., 2005; Kulmala et al., 2004b). Our observations indicate that the concentrations of our detected organic acids, organosulfates and nitrooxy organosulfates are dominated by
- the accumulation mode and any correlation to NPF should be investigated with sizesegregated samples.

Particle mass concentrations were calculated based on integration of the calculated particle mass size distributions (from DMPS data), which were further based on measured particle number size distributions assuming particle sphericity, using a SOA particle density of 1.05 measured^{-3} (Coetheff et al. 2002) as most semicover large variables.

- ticle density of 1.25 g cm⁻³ (Saathoff et al., 2003) as most compounds were long-range transported to the site and therefore the air masses are expected to be quite aged. The detected and quantified organosulfates and nitrooxy organosulfates accounted for approximately 0.7 % of PM₁ mass, which is considerably lower than previous estimates, including 30 % (Surratt et al., 2008) or 5–10 % contribution of organosulfates to total organic mass (Teleska and Turpin, 2012).
- ²⁵ organic mass (Tolocka and Turpin, 2012).





4 Conclusions

A field study was conducted from 19 May to 22 June 2011 at two sites in Denmark, including the urban curbside site HCAB and the semi-rural background site Risø to investigate the anthropogenic impacts on the formation of biogenic SOA via analysis of organosulfates and related oxidation products using HPLC-qTOF-MS. A substantial range of anthropogenic and biogenic organic acids, organosulfates and nitrooxy organosulfates were detected, identified and quantified. Isoprene oxidation products comprised a large fraction of the detected organosulfates whereas a majority of the detected nitrooxy organosulfates may originate from limonene. The U Mann–Whitney

- statistical test showed significantly higher concentrations of specific biogenic and anthropogenic species at HCAB, whereas an intraday statistical test only revealed significantly higher daytime concentrations of phthalic acid and OS 210 and significantly higher nighttime concentrations of NOS 297. Many detected compounds including a mix of organic acids, organosulfates and nitrooxy organosulfates of various precur-
- ¹⁵ sors were found belonging to a common highly correlated group, consistently affecting their concentration levels at both sites, suggesting a common source region. The analysis of HYSPLIT back trajectories together with isoprene and monoterpene emissions calculated by the MEGAN model and SO₂ emission based on the EMEP monitoring database indicated that the border region among Germany, Poland and Czech Republic on the couth conterly oir more priving direction could probably relate to the source of the s
- ²⁰ public on the south-easterly air mass arriving direction could probably relate to the corresponding episodes of the elevated total concentrations at the sites, implying the importance of the regional impacts on the occurrence of the compounds.

The local impacts were also investigated for several selected species which showed significantly higher concentrations at HCAB compared to Risø and did not belong to ²⁵ the correlating group, including OS 182, OS 210 and NOS 297. The results showed that the local factors including aerosol acidity, RH, NO and probably some wet aerosol chemistry could possibly lead to a higher occurrence of the organosulfates, whereas the NO₃ radical chemistry could be important for the formation of the major nitrooxy





organosulfate NOS 297, in addition to temperature and global radiation, which could also enhance the concentrations of the long-range transported species at the sites. As only very few compounds were deemed as affected by the local conditions, the analysis of the local impacts was restricted to a modest number of compounds. In general, the regional impacts seemed to considerably exceed the local impacts. It was estimated that organosulfates and nitrooxy organosulfates contributed to approximately 0.7 % of PM_1 mass.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/2449/2014/

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The anthropogenic

influence on

formation of biogenic

SOA

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Title Page

Abstract

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Table 1. Detected organic acids during the ABSOA campaign. Related references on suggested precursors are cited in the text.

Organic acid	[M-H] [−] ion (<i>m/z</i>)	Retention time (min)	Proposed molecular formula	Proposed structure	Suggested precursors
Benzoic acid	121.022	27.5	C ₇ H ₆ O ₂	OH	Aromatic hydrocarbons
Adipic acid	145.058	14.9	C ₆ H ₁₀ O ₄	но	Cyclic olefins
Pimelic acid	159.061	20.3	C ₇ H ₁₂ O ₄	ности	Cyclic olefins
Phthalic acid	165.123	19.0	$C_8H_6O_4$	С	Aromatic hydrocarbons
Terpenylic acid	171.058	18.3	C ₈ H ₁₂ O ₄	острон	<i>a</i> -pinene
Suberic acid	173.074	25.4	$\mathrm{C_8H_{14}O_4}$	но	Fatty acids
Pinonic acid	183.100	27.5	C ₁₀ H ₁₆ O ₃	но	α/β -pinene
Pinic acid	185.077	23.0; 24.0	C ₉ H ₁₄ O ₄	но у он	α-/β-pinene
Azelaic acid	187.091	28.1	$\mathrm{C_9H_{16}O_4}$	но стран	Fatty acids
Hydroxy-pinonic acid	199.092	29.0	$C_{10}H_{16}O_4$	CHLCH	<i>α-/β</i> -pinene
3-Methyl-1,2,3-butanetricarboxylic acid MBTCA	203.050	16.2	C ₈ H ₁₂ O ₆	ностон	<i>α-/β</i> -pinene
Di-terpenylic acid acetate (DTAA)	231.220	24.3	C ₁₀ H ₁₆ O ₆		α-pinene

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Table 2. Detected organosulfates (OS) during the ABSOA campaign. Included references were ¹ Surratt et al. (2007a); ² Surratt et al. (2008); ³ Surratt et al., (2010); ⁴ Gómez-González et al., (2008); ⁵ Kristensen and Glasius, (2011). ⁶ OS 250 can be found in synthesis of both α and β -pinene derived organosulfates; however with different retention times. The OS 250 detected in this study was assigned to β -pinene precursor based on the corresponding retention time.

Organosulfate	[M-H] [−] ion (<i>m/z</i>)	Retention time (min)	Proposed molecular formula	Proposed structure	Suggested precursors
OS 154 ^{1,2}	152.981	3.6;6.7	$C_3H_6O_5S$	O S OH	hydroxyacetone (isoprene)
OS 156 ¹	154.957	2.8	$C_2H_4O_6S$	OH OF OH	glyoxal (isoprene)
OS 170 ^{1,2}	169.047	3.4	$C_3H_6O_6S$	- сн	methylglyoxal (isoprene)
OS 182	181.063	34.8	$C_5H_{10}O_5S$	unknown	unknown
OS 200 ¹	199.038	3.3	$C_4H_8O_7S$	но он	2-methylglyceric acid (isoprene)
OS 208	207.101	28.4; 29.5	C ₆ H ₈ O ₆ S	unknown	unknown
OS 210 OS 212 ²	209.086 210.983	28.0; 30.5 4.8	C ₇ H ₁₄ O ₅ S C ₅ H ₈ O ₇ S	unknown	isoprene
OS 214 ^{2,4,5}	213.001	3.5	C ₅ H ₁₀ O ₇ S	unknown osoart	isoprene ^{2,5}
				HO	fatty acid ⁴

Organosulfate [M-H] Proposed Proposed structure Suggested precursors Retention ion (m/z)time (min) molecular formula OS 216^{1,2} C5H12O7S 2-methyltetrols (isoprene) 215.018 2.9 óн ċ⊾ OS 248² 247.061 C₁₀H₁₆O₅S 32.2 unknown a-pinene OS 250² C₁₀H₁₈O₅S 249.074 β -pinene⁶ 31.6 loso+ $C_9H_{16}O_6S$ OS 252² 251.017 15.3 limonene OS 254² 253.158 C₈H₁₄O₇S unknown 21.3 α -terpinene OS 268² .OSO₁H 267.225 19.7 C₉H₁₆O₇S limonene óн OS 280² 22.5; 25.2 C₁₀H₁₆O₇S α -/ β -pinene 279.046 но ,OSO3H 0 OS 298² C₁₀H₁₈O₈S 297.079 25.5 a-pinene OS 334² C₁₀H₂₂O₁0S 333.071 38.0 Isoprene

Table 2. Continued.

Table 3. Detected nitrooxy organosulfates (NOS) during the ABSOA campaign. References include ¹ Surratt et al., (2007a); ² Surratt et al., (2008); ³ Surratt et al., (2010); ⁴ Gómez-González et al., (2008); ⁵ Kristensen and Glasius, (2011).

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Table 4. Concentration range (ng m⁻³) of the detected species at HCAB and Risø, reported as mean, standard deviation (stdev.), median, max and the number of detected samples (*N*) at each site.

Compound	НСАВ			Risø						
	Mean	Stdev.	Median	Max	Ν	Mean	Stdev.	Median	Max	Ν
Benzoic acid	0.4	0.6	0.1	2.0	14	1.4	1.9	0.4	7.2	26
Adipic acid	3.3	1.4	2.8	8.4	64	2.9	1.1	2.8	5.9	38
Pimelic acid	0.6	0.3	0.5	2.1	64	0.4	0.2	0.4	1.2	38
Phthalic acid	5.6	2.3	5.1	13.0	64	4.3	1.8	4.4	10.4	38
Terpenylic acid	1.6	1.6	1.1	8.9	64	1.4	1.7	0.9	8.5	38
Suberic acid	1.1	0.6	1.0	3.7	64	0.9	0.5	0.8	2.9	38
Pinonic acid	1.3	1.5	0.9	10.8	64	2.2	2.9	1.3	16.4	38
<i>cis</i> -Pinic acid	0.5	0.5	0.4	3.9	64	0.6	0.9	0.4	5.6	37
Azelaic acid	4.0	3.3	3.0	19.6	58	1.6	0.8	1.6	4.3	35
Hydroxy-pinonic acid	0.1	0.1	0.1	0.2	12	0.1	0.0	0.1	0.1	4
MBTCA	4.7	5.7	2.3	23.8	64	3.9	5.1	2.0	24.4	38
DTAA	0.4	0.5	0.2	2.0	64	0.2	0.3	0.1	1.4	34
Total organic acids	22.8	14.9	18.7	76.7	64	19.3	13.3	15.7	69.8	38
OS 154	6.6	6.0	4.5	25.7	63	5.3	4.6	4.3	24.6	38
OS 156	5.3	3.8	4.3	23.1	64	4.3	3.1	3.5	19.8	38
OS 170	3.5	2.3	2.7	10.3	63	3.1	2.0	2.5	11.5	37
OS 182	1.4	0.8	1.2	3.4	55	0.6	0.4	0.6	1.6	37
OS 200	7.1	6.7	4.4	33.1	64	4.5	3.9	3.0	22.2	37
OS 208	5.0	3.3	5.7	14.2	63	4.1	0.8	4.1	5.6	38
OS 210	2.8	2.4	2.0	8.4	63	1.8	1.0	1.9	4.3	38
OS 212	7.4	6.0	5.0	32.2	64	6.2	4.7	4.6	27.8	38
OS 214	5.1	4.5	3.6	22.3	64	4.4	3.1	3.8	17.9	38
OS 216	5.0	6.8	2.8	36.9	60	3.2	3.3	2.4	20.8	34
OS 248	0.8	0.4	0.8	2.3	57	0.6	0.3	0.6	1.7	37
OS 250	2.3	1.1	2.1	6.8	64	2.4	2.1	1.9	12.4	38
OS 252	1.2	1.2	0.6	5.2	53	0.9	0.9	0.6	4.1	33
OS 254	1.3	1.5	0.8	7.9	63	1.1	1.2	0.8	7.4	38
OS 268	2.5	2.3	1.6	13.1	64	2.2	2.2	1.6	13.9	38
OS 280	2.6	2.5	1.8	11.5	60	2.2	2.0	1.6	10.3	38
OS 298	1.3	1.1	0.8	4.1	28	0.8	1.0	0.5	3.9	16
OS 334	0.6	0.3	0.6	1.0	8	0.8	-	0.8	0.8	1
Total organosulfates	59.2	42.0	43.8	130.6	64	46.5	27.7	36.3	144.0	38
NOS 295	0.5	0.6	0.3	4.2	46	0.4	0.3	0.4	1.2	15
NOS 297	1.4	0.7	1.3	3.7	64	0.9	0.6	0.7	3.4	38
NOS 311	0.9	0.8	0.4	2.4	7	0.5	0.5	0.4	1.8	8
NOS 313	0.7	0.7	0.5	3.4	56	0.6	0.6	0.5	3.0	30
NOS 327	0.9	0.7	0.7	3.6	48	0.6	0.6	0.5	2.8	29
NOS 329	0.8	0.9	0.4	3.6	19	0.5	0.6	0.3	2.6	17
NOS 331	0.3	0.2	0.2	1.2	41	0.3	0.3	0.2	1.5	26
NOS 340	0.2	0.1	0.2	0.2	3	-	-	-	-	-
NOS 343	0.8	0.4	0.8	1.4	24	0.4	0.4	0.4	1.0	4
Total nitrooxy organosulfates	3.9	1.3	2.8	3.7	64	2.8	1.2	2.1	1.8	36

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Table 5. Statistical results of *U* Mann–Whitney test performed on the organic acids, organosulfates and nitrooxy organosulfate detected at the two sampling sites H.C. Andersen Boulevard (HCAB) and Risø. 14 out of 41 tested parameters are statistically different with *p*-level < 0.1 (bold).

Parameter	p-level	Statistically different?	Valid N (HCAB)	Valid N (Risø)
Benzoic acid	0.0014	Yes	11	26
Adipic acid	0.3226	No	37	37
Pimelic acid	0.0016	Yes	37	37
Phthalic acid	0.0029	Yes	37	37
Terpenylic acid	0.7335	No	37	37
Suberic acid	0.0099	Yes	37	37
Pinonic acid	0.0006	Yes	37	37
Pinic acid	0.6352	No	37	36
Azelaic acid	0.0000	Yes	31	34
Hydroxy-pinonic acid	0.3938	No	6	4
MBTCA	0.5131	No	37	37
DTAA	0.1218	No	37	33
Total first generation organic acids	0.0286	Yes	37	37
Total organic acids	0.1108	No	37	37
OS 154	0.7911	No	37	37
OS 156	0.7828	No	37	37
OS 170	0.9551	No	36	36
OS 182	0.0000	Yes	28	36
OS 200	0.0837	Yes	37	35
OS 208	0.4269	No	36	37
OS 210	0.0736	Yes	37	37
OS 212	0.8162	No	37	37
OS 214	0.5061	No	37	37
OS 216	0.6790	No	34	33
OS 248	0.0074	Yes	32	36
OS 250	0.7745	No	37	37
OS 252	0.8474	No	31	32
OS 254	0.7662	No	37	37
OS 268	0.9011	No	37	37
OS 280	0.8415	No	37	37
OS 298	0.0437	Yes	13	16
Total organosulfates	0.7253	No	37	37
NOS 295	0.9138	No	26	15
NOS 297	0.0010	Yes	37	37
NOS 311	0.4142	No	3	8
NOS 313	0.6733	No	31	29
NOS 327	0.1891	No	27	28
NOS 329	0.1565	No	12	17
NOS 331	0.7998	No	21	25
NOS 343	0.1822	No	12	4
Total nitrooxy organosulfates	0.0837	Yes	37	35

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Fig. 1. Locations of the urban curbside station H.C. Andersen Boulevard (HCAB) and the semirural background station (Risø) (map.krak.dk and map.google.dk). HCAB is located in the city centre of Copenhagen close nearby a busy street. Risø is located approximately 30 km west of HCAB.

Fig. 2. Correlation of organic acids (top panel), organosulfates (middle panel) and nitrooxy organosulfates (bottom panel) with each detected species (excluding those with too few measurements). The displayed results are average correlation coefficients (R^2) from both sites. High R^2 values (> 0.5) were found among specific organic acids (dark blue), organosulfates (red) and nitrooxy organosulfates (green), suggesting common sources. A few other species including pinonic acid, pinic acid and phthalic acid (light blue) and OS 248 (purple) also partly followed the correlation pattern.

Fig. 3. Temporal trends of total concentrations of organic acids (dark blue), organosulfates (red) and nitrooxy organosulfates (green) at the urban curbside site H. C. Andersen Boulevard (solid line) and the semi-rural background site Risø (broken line). The figure shows a strong correlation between the two sites and among the three categories of compounds examined.

Fig. 4. A sudden change in air mass back trajectories on 31 May to the south-easterly direction which was coupled with elevated concentrations of organosulfates, nitrooxy organosulfates and organic acids at both HCAB and Risø (HCAB is marked at the bottom tip of the black triangle), while modeled isoprene and monoterpene emissions were higher on 1 June. Emissions of the VOCs were estimated using the global Model of Emissions of Gases and Aerosols from Nature (MEGAN) using fine-scale legends to visualize the generally lower emissions of Denmark.

Fig. 5. SO₂ emission based on the European Monitoring and Evaluation Program (EMEP) database (May–June 2011 average). HCAB is marked at the bottom tip of the black triangle.

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Fig. 6. Time profiles of selected species of significantly higher concentration levels at HCAB, including OS 182, OS 210 and NOS 297. The overlapping periods where data from both sites were available were used in the *U* Mann–Whitney statistical test.

Fig. 7. Temporal variation of gas concentrations (NO_x, O₃, SO₂ and CO) of 30 min resolution and aerosol acidity (12 h resolution) at HCAB during the campaign period. The red and blue lines at the bottom indicate the period where the samples were available at HCAB and Risø, respectively.

Fig. 8. Temporal variation of the local meteorological parameters at the urban background site HCOE, including relative humidity (RH), global radiation (GR) and temperature (T). The red and blue lines at the bottom indicate the period where the samples were available from HCAB and Risø, respectively.

