Organosulfates and organic acids in Arctic aerosols: Speciation, annual variation and concentration levels

Anne Maria K. Hansen[1], Kasper Kristensen[1], Quynh T. Nguyen[1,2], Azimeh Zare[1,2,3], Federico Cozzi[1], Jacob K. Nøjgaard[2], Henrik Skov[2,4], Jørgen Brandt[2], Jesper H. Christensen[2], Johan Ström[5], Peter Tunved[5], Radovan Krejci[5,6] and Marianne Glasius[1]

[1]Department of Chemistry and iNANO, Aarhus University, Aarhus, Denmark
[2]Department of Environmental Science, Aarhus University, Roskilde, Denmark
[3]Institute of Geophysics, University of Tehran, Iran
[4]University of Southern Denmark, Institute of Chemical Engineering and Biotechnology and Environmental Technology, Odense, Denmark
[5]Department of Applied Environmental Science, Stockholm University, Sweden
[6]Department of Physics, University of Helsinki, Helsinki Finland

Abstract

Sources, composition and occurrence of secondary organic aerosols in the Arctic were investigated at Zeppelin Mountain, Svalbard, and Station Nord, northeast Greenland, during the full annual cycle of 2008 and 2010, respectively. Speciation of three secondary organic aerosol compound groups: organic acids, organosulfates and nitrooxy organosulfates from both anthropogenic and biogenic precursors were in focus. A total of 11 organic acids (terpenylic acid, benzoic acid, phthalic acid, pinic acid, suberic acid, azelaic acid, adipic acid, pimelic acid, pinonic acid, diaterpenylic acid acetate and 3-methyl-1,2,3-butanetricarboxylic acid), 12 organosulfates and one nitrooxy organosulfate were identified in aerosol samples from the two sites using High Performance Liquid Chromatography coupled to a quadrupole Time-of-Flight mass spectrometer. At Station Nord, compound concentrations followed a distinct annual pattern, where high mean concentrations of organosulfates (47±14 ng m^{-3}) and organic acids (11.5±4 ng m^{-3}) were observed in January, February and March contrary to considerably lower mean concentrations of organosulfates (2±3 ng m^{-3}) and organic acids (2.2±1 ng m^{-3}) observed during the rest of the year. At Zeppelin Mountain, organosulfate and organic acid concentrations remained relatively constant during most of the year at a mean concentration of 15±4 ng m^{-3} and 3.9±1 ng m^{-3} respectively. However during four weeks of spring remarkably higher concentrations of total organosulfates (23-36 ng m^{-3}) and total organic acids (7-10 ng m^{-3}) were observed. Elevated organosulfate and organic acid concentrations coincided with the Arctic Haze period at both stations; where northern Eurasia was identified as the main source region. Air mass transport from northern Eurasia to Zeppelin Mountain were associated with a 100% increase in the number of detected organosulfate species compared with periods of air mass transport from the Arctic Ocean, Scandinavia and Greenland. The results from this study suggested that the presence of organic acids and organosulfates at Station Nord was mainly due to long-range transport, whereas indications of local sources were found for some compounds at Zeppelin Mountain. Furthermore organosulfates contributed significantly to organic matter throughout the year at Zeppelin Mountain (annual mean of 13±8%) and during Arctic Haze at Station Nord (7±2%), suggesting organosulfates to be important compounds in Arctic aerosols.

1 Introduction

It is well known that the Arctic environment is sensitive to changes in the radiative balance. Within the last 100 years the atmospheric temperature in the Arctic has increased by 2 to 3 °C, which is twice the global average (IPCC, 2013; ACIA, 2004). This enhancement in temperature has resulted in increased melting of sea-ice and thawing of permafrost, which in turn decrease surface albedo, thereby further impacting the radiative balance of the region through positive feedback processes

(Hudson, 2011). Atmospheric aerosols are key constituents of the climate system, influencing the radiative balance of Earth directly by absorbing and reflecting radiation (Charlson et al., 1992) and indirectly by acting as cloud condensation nuclei (CCN) affecting the formation and lifetime of clouds (Albrecht, 1989). In the Arctic, low-altitude liquid clouds warm the surface during winter as they trap and re-emit outgoing long-wave radiation more efficiently than they reflect the incoming short-wave radiation (Bennartz et al., 2013; Shupe and Intrieri, 2004). Formation of low-altitude liquid clouds thus has a warming effect on the surface throughout most of the year in the Arctic, except a short period in summer, when a net cooling is observed (Intrieri et al., 2002; Walsh and Chapman, 1998). Thus, the presence of aerosols that can act as CCN may have a warming effect on the Arctic environment during winter.

In the Arctic atmosphere, the aerosol loading is highly seasonal as recently shown by Tunved et al. (2013) in a study investigating Arctic aerosol life cycle based on a ten year dataset from Zeppelin Mountain, Svalbard. Authors found an increased mass loading during late winter and spring, coinciding with the period of Arctic haze. Arctic haze has previously been assigned to occur during winter and spring Due to expansion of the polar air dome to include parts of Eurasia and North-America (Ottar, 1989), intensifying the meridional air transport from the mid-latitudes to the Arctic (Iversen and Joranger, 1985; Austin, 1980; Solgaard et al., 1979). In addition, the polar night causes the Arctic atmosphere to stabilize due to strong surface-based temperature inversions. The stable atmosphere inhibits turbulent transfer between the atmospheric layers as well as the major aerosol removal processes, formation of clouds and precipitation (Barrie et al., 1981; Shaw, 1981, 1995; Heintzenberg and Larssen, 1983; Heidam, 1981), thus trapping the pollutants in the Arctic atmosphere for up to 15-30 days (Shaw, 1981, 1995). The primary source regions of Arctic haze have been identified as Northern Eurasia through chemical fingerprint analysis and air transport modelling (Nguyen et al., 2013b; Stohl et al., 2007; Treffeisen et al., 2007; Heidam et al., 2004;

Christensen, 1997; Pacyna et al., 1985; Shaw, 1982; Rahn, 1981). Chemical analyses have shown that the haze aerosols primarily consist of sulfate and organic matter in addition to nitrate, ammonium, dust, trace heavy metals and soot (Fenger et al., 2013; Nguyen et al., 2013b; Heidam et al., 2004; Heidam et al., 1999; Iversen and Joranger, 1985; Pacyna et al., 1985; Barrie et al., 1981; Rahn et al., 1977).The reflection, absorption and CCN properties of aerosols are highly dependent on the chemical composition as well as particle size (Lohmann and Feichter, 2005; Andreae et al., 2004). However, there is a lack of knowledge on the composition of organic aerosols, especially the secondary organic aerosol (SOA) component. Hence, in this study, chemical speciation of three classes of molecular SOA tracers, namely organic acids, organosulfates and nitrooxy organosulfates is in focus. Furthermore the anthropogenic and biogenic contribution to SOA is investigated.

Organic acids, which are often semi-volatile and water soluble, are formed through atmospheric oxidation of volatile organic compounds (VOCs) (Hallquist et al., 2009; Glasius et al., 2000). They contribute to the formation of SOA by condensation onto pre-existing particles and by dissolving in the water film, thereby coating existing particles (Hallquist et al., 2009). Organic acids have previously been quantified in the Arctic atmosphere, with a mean annual concentration of individual species generally below 1 ng m^{-3} (Fu et al., 2009; Kawamura et al., 2005). Organosulfates and nitrooxy organosulfates are low-volatile SOA constituents, most likely formed from acid-catalysed particle phase reactions of epoxides with inorganic sulfate (Lin et al., 2012; Surratt et al., 2010; Minerath and Elrod, 2009). Both smog chamber experiments and ambient aerosol samples show that isoprene and monoterpenes are precursors of organosulfates in the atmosphere (Surratt et al., 2008; Iinuma et al., 2007). Since sulfate in the atmosphere primarily originates from anthropogenic sources (e.g. Zhang et al., 2009) the presence of organosulfates in ambient aerosols suggests an anthropogenic enhancement of the formation of biogenic SOA (BSOA) (Hoyle et al., 2011). Only one previous study has suggested the presence of organosulfates in the Arctic (Frossard et al., 2011) based on observations of organic sulfate functional groups in Arctic aerosol samples. However, no chemical speciation of organosulfates in the Arctic has been made.

This study aims to investigate speciation, occurrence and annual variation in concentrations of organosulfates and organic acids in the Arctic, analysing aerosol samples collected at two Arctic sites: Zeppelin Mountain, Svalbard, during 2008 and Station Nord, northeast Greenland, during 2010.

2 Experimental

2.1 Sampling

The aerosol samples used in this study were collected at two Arctic sites: Station Nord, Greenland (81°36' N 16°40' W, 24 m a.s.l.) and Zeppelin Mountain, Svalbard (78°56' N, 11°53' E, 474 m a.s.l.).

The measurement site at Station Nord is located in the north-eastern part of Greenland in a remote area 924 km from the North Pole, at a small military camp, representing a “natural high-Arctic station” (Nguyen et al., 2013b; Skov et al., 2004). The site is dominated by winds from south-westerly directions and is probably influenced by local topography of katabatic winds from ice caps in the fjord south-west of the station (Nguyen et al., 2013b). Atmospheric monitoring at Station Nord is carried out by Danish Centre for Environment and Energy and the Department of Environmental Science, Aarhus University, as the Danish contribution to the atmospheric part of the Arctic Monitoring and Assessment Program (AMAP). In this study, weekly samples of PM_{10} were collected on quartz fibre filters (Advantec, Toyo Roshi Kaisha, Ltd., diameter 150 mm) every fourth week during the entire year 2010 using a high-volume sampler (HVS) (Digitel DHA-80, Reimer Messtechnik, Switzerland). To avoid problems with the harsh weather, the HVS including the PM_{10} head was placed indoors in a building located within the military station and was furthermore equipped with a heated outdoor sampling head. Each sample corresponds to 5000 m^3 air. After sampling the filters were wrapped in aluminium foil and stored at -20 °C until extraction in 2012.

The Zeppelin station is located on a mountain ridge overlooking the small settlement of Ny Ålesund. Due to its mountain location, Zeppelin station is mostly unaffected by local contamination from Ny Ålesund and can be considered to represent remote Arctic conditions. The Zeppelin station is confined within the boundary layer most of the time, but on occasions the top of the boundary layer is below the station altitude exposing the station to the lowermost free troposphere (Tunved et al., 2013). Local wind is dominated by east-southeast directions due to katabatic flow from the Kongsvegen glacier and additionally influenced by local orography (Hirdman et al., 2010; Beine et al., 2001). The station is owned by the Norwegian Polar Research Institute (NP), with the Norwegian Institute for Air Research (NILU) coordinating the scientific program. At the station the Department of Applied Environmental Science (ITM), Atmospheric Science Unit, Stockholm University, carries out aerosol microphysical and optical properties measurements as well as routinely collecting weekly samples of total suspended particulate matter (TSP) on quartz fibre filters (Munktell & Filtrak GmbH, diameter 47 mm, grade T293) using a Leckel Sequential Sampler SEQ 47/50 (Leckel GmbH, Germany). In this study TSP samples from every second week of year 2008 were selected to keep the number of samples manageable and still obtain information on the annual cycle. Each sample corresponds to 210 m^3 of air. After sampling, the filters were stored in Petri dishes, wrapped in aluminum foil and stored at -20 °C until extraction in 2012.

2.2 SOA analysis

SOA extraction and analysis was based on the method of Kristensen and Glasius (2011). The collected aerosol filters were extracted by sonication in 10 mL 90% acetonitrile/10% milliQ water in a cooled ultrasonic bath for 30 min. Each filter was extracted twice and the resulting extracts were combined, filtered through a Teflon filter (0.45 µm pore size, Chromafil) and evaporated until dryness using a rotary evaporator. Each sample was re-dissolved twice in 0.5 mL MilliQ water with 3% acetonitrile and 0.1% acetic acid. All prepared samples were stored in a refrigerator at 3-5 °C until analysis.

To monitor the efficiency of the extraction of the organic acids, organosulfates and nitrooxy organosulfates, a recovery standard (RSTD) of camphoric acid was added onto each filter before extraction. A mean recovery of 87 (± 13%) was obtained for all samples. Recovery percentages of the internal standard (ISTD) have been included in the calculation of the concentrations of organic acids and organosulfates, the reported concentrations corresponding to a 100% recovery.

All sample extracts were analysed on a Dionex UltiMate 3000 HPLC coupled to a quadrupole Time-of-Flight (qTOF) mass spectrometer from Bruker Daltonics (Bremen, Germany) through an electrospray ionization (ESI) inlet. Data was acquired and processed using Bruker Compass software.

The HPLC stationary phase was an Atlantis T3, 3µm (150 x 2.1 mm) column from Waters and the mobile phase consisted of 0.1 % (v/v) acetic acid (eluent A) and 95 % (v/v) acetonitrile (eluent B). The applied gradient was a 57 min. multistep gradient with the following course: Eluent B increased from 3% to 20% within the first 20 min. B increased to 60% in 10 min, and then to 90% in 5 min. held at 90% B for 10 min then increased to 100% B within 1 min. Held at 100% B in 5 min, and finally decreased to 3% B within 3 min. held at 3% B during the remaining 3 min. The injected sample volume was 10 µL and the flow rate was 0.2 mL min^{-1}. The ESI-q-TOF-MS was operated in negative ionization mode under the following conditions: nebulizer pressure at 3.4 bar, dry gas flow 8.0 L/min, collision energy 6.0 eV, Collision RF 120 and transfer time 50.0 µs.

Organic acids were identified and quantified using authentic standards. Organosulfates and nitrooxy organosulfates were identified from their loss of SO_3^- (*m/z = 80*) or HSO_4^- (*m/z = 97*) and an additional neutral loss of HNO_3 ($m/z = 63$) in the case of nitrooxy organosulfates (Surratt et al., 2007). Organosulfates were quantified using an authentic β-pinene organosulfate standard (synthesized in-house according to a method described by (Iinuma et al., 2009) followed by purification using Medium Pressure Liquid Chromatography (MPLC)), while nitrooxy organosulfates were quantified using a surrogate standard of octyl sulfate (Sigma Aldrich), chosen due to similar chromatographic retention time as the identified nitrooxy organosulfate.

A linear relation between peak area and concentration was established and applied for quantification of pimelic acid, benzoic acid, azelaic acid, suberic acid, *cis*-pinic acid, terpenylic acid, β-pinene (organosulfate standard, OS surrogate) and octyl sulfate (nitrooxy organosulfate standard, NOS surrogate). A quadratic relation between peak area and concentration was established and applied for quantification of adipic acid, phthalic acid, pinonic acid, diaterpenylic acid acetate (DTAA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). The correlation coefficients R^2 of all calibration curves were better than 0.99 (n = 8 data points) and detection limits of all compounds fall within the interval of 0.01 – 0.33 ng m^{-3}.

Regarding uncertainties on the measurements it is estimated that the total uncertainty on the organic acid and organosulfate concentrations is approximately 15 %. This estimate is based upon analytical errors (calibration curve and laboratory equipment), uncertainty on the extraction efficiency and uncertainty on the collected air volume.

2.3 Supplementary analysis

Samples for analysis of organic and elemental carbon (OC/EC) in atmospheric aerosol were collected at Zeppelin station. The OC/EC analysis was carried out with a thermal optical transmittance (TOT) method using a Thermal/Optical Carbon Aerosol Analyser (Sunset Laboratory Inc., USA) following the NIOSH method 5040. Details about the OC/EC analysis can be found in

(Krecl et al., 2007). Non-sea-salt sulfate (nss-sulfate) measurements have been obtained from EBAS and are public available at http://ebas.nilu.no.

Measurements of OC and nss-sulfate were also performed as supporting analyses for the Station Nord samples. OC was measured directly on the collected quartz-fiber samples using a thermal optical transmittance (TOT) method following the EU Standard OC/EC protocol- 2008 European Supersites for Atmospheric Aerosol Research EUSAAR-2 (Cavalli et al., 2010). Non-sea salt sulfate was determined by subtracting sea salt SO_4^{2-}, from total SO_4^{2-}. Sea salt SO_4^{2-} was calculated from the ion ratio SO_4^{2-}/Na^+ in seawater equal to 0.252, assuming that all Na^+ in aerosols originated from sea salt (Sciare et al., 2003; Rankin et al., 2002) . Na^+ and SO_4^{2-} were measured using Ion Chromatography/Dual Ion Chromatography.

2.4 Backwards air-mass trajectory analysis

Air-mass transport and origin was analysed using HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) backwards air parcel model (Draxler and Hess, 1998). Meteorological data from GDAS were used as input for the model. Each filter sample corresponds to seven days of aerosol sampling every fourth week at Station Nord and every second week at Zeppelin Mountain. For each filter sample from both stations, trajectories were calculated 120 h backwards in time every fourth hour for the seven sampling days at 10 m, 1500 m and 3000 m arrival heights (above ground-level) and cluster analyses of the back-trajectories were performed.

2.5 Modelling of biogenic Volatile Organic Compound emissions

In this study, the global Model of Emissions of Gases and Aerosols from Nature (MEGAN) was used to estimate emissions of the biogenic VOC (BVOC) (Guenther et al., 2006) .

The MEGAN model estimates the emission rate of isoprene based on empirical relationships for key drivers of temperature, radiation, soil moisture, leaf area index and foliage age. These activity factors account for the isoprene emission factor response to the environmental conditions. The emission factors are the plant functional type (PFT) dependent isoprene emission rates at the standard conditions. Here, we used the MEGAN v2.04 dataset, which comprises the geographical distribution of both the fractional cover and the emission factor for six PFTs: Broadleaf tree, needle leaf evergreen tree, needle leaf deciduous tree, shrub, and crop. Each area of the Earth's land surface in the model domain is assigned to a fraction of these PFTs. In general, the emission model MEGAN calculates the total flux of isoprene within every grid cell as the sum of emissions from each PFT.

The empirical algorithm of MEGAN is conducted similarly to calculate hourly emission rates of monoterpenes. However, due to the ability of monoterpenes to be stored in the plant, MEGAN describes the effect of radiation on the monoterpene emission rates based on an alternative process (Sakulyanontvittaya et al., 2008). MEGAN uses a light-dependence fraction to take into account the fraction of monoterpene emissions that influenced by light intensity. Furthermore, the response of monoterpene emission rates to the temperature is also parametrized in a simple and different approach from the isoprene one (Sakulyanontvittaya et al., 2008).

The monoterpene emission rates are a summation of calculated emission rates for seven monoterpene compounds (α-pinene, β-pinene, ocimene, limonene, sabinene, myrcene, and delta3-carene) by the MEGAN model.

The required meteorological data for running MEGAN are provided by the mesoscale meteorological model MM5v3.7, using the required initial and boundary conditions, derived from NCEP Final Analyses data (http://rda.ucar.edu/datasets/ds083.2/).

Recently the performance of this emission model with coupling into the chemistry transport model DEHM (Danish Eulerian Hemispheric Model) (Brandt et al., 2012) was evaluated. The results showed a relatively good agreement with available observations at measuring sites in Europe and

North America for simulation of both isoprene and monoterpene concentrations (Zare et al., 2013; Zare et al., 2012).

3 Results and discussion

3.1 Identified compounds

Figure 1 shows a typical chromatogram obtained from HPLC-q-TOF-MS analysis of the aerosol samples. Good separation of chromatographic peaks was obtained for most compounds, and only five of the observed peaks remained unidentified from our analysis. 24 different SOA tracers were identified including 11 organic acids (terpenylic acid, benzoic acid, phthalic acid (given as the sum of phthalic acid and terephathalic acid), pinic acid, suberic acid, azelaic acid, adipic acid, pimelic acid, pinonic acid, DTAA and MBTCA), 12 organosulfates (molecular weight 140, 154, 168, 180, 182, 196a, 196b, 208, 210, 224, 250 and 280) and one nitrooxy organosulfate (MW 295). All of the observed organic acids have previously been reported as atmospheric trace constituents. In this study all organic acids are categorized into anthropogenic (benzoic acid, phthalic acid, adipic acid and pimelic acid) and biogenic (terpenylic acid, DTAA, pinic acid, pinonic acid, MBTCA, suberic acid and azelaic acid) tracers based on previous studies of their atmospheric formation and precursors (Williams et al., 2010; Claeys et al., 2009; Rybka et al., 2007; Ma et al., 2007; Mochida et al., 2003; Bunce et al., 1997; Hatakeyama et al., 1987). However, pimelic acid, here assigned to be an anthropogenic tracer, may be of biogenic origin as well, derived from the oxidation of unsaturated fatty acids (Kawamura and Gagosian, 1987). In Table S1 an overview of the structures and suggested precursors of the carboxylic acids are given. The organosulfates are less studied, this being the first investigation of their speciation in the Arctic. The suggested molecular formulas, structures and precursors of the organosulfates identified in this study are listed in Table 1.

3.1.1 OS 140, OS 154, OS 168 and OS 182

Of the organosulfates observed in Arctic aerosols, four have previously been identified as isoprene tracers, namely OS 140, OS 154, OS 168 and OS 182. Smog chamber studies of photochemical oxidation of isoprene in the presence of acidic sulfate aerosols showed formation of multiple organosulfates including OS 140, OS 154, OS 168 and OS 182, which have been hypothesized to originate from the isoprene degradation products: glycolaldehyde, hydroxyacetone, methacrolein and 2-methylglyceric acid, respectively (Surratt et al., 2007; Szmigielski et al., 2007).

In order to investigate potential sources, emissions of isoprene during each month of 2008 were modelled using the MEGAN model (Figure 2). The model results show negligible emissions in the Arctic and the mid-latitudes in the period November to March (< 1.0 mg/m^2/week) compared to June to August (approximately 100-300 mg/m^2/week). The low winter and spring emissions of isoprene at mid-latitudes obtained by the MEGAN model are in very close agreement with results of Hakola et al. (2009), who studied emissions from scots pine, and Guenther (1997) reviewing measurements of isoprene from deciduous trees. The highest concentrations of OS 140, OS 154, OS 168 and OS 182 are however observed during winter and spring at both Station Nord (section 3.2) and Zeppelin Mountain (section 3.3).

As considerable isoprene emissions occur in the tropics during winter and spring, it is possible that transport from the tropics with uplift outside the Arctic followed by descent into the Arctic through the upper troposphere/lower stratosphere (Stohl, 2006) could account for the observation of OS 140, OS 154, OS 168 and OS 182 from isoprene degradation at the Arctic sites. However, during winter and spring the Arctic troposphere is very stratified and this source is not likely to explain concentrations observed at the surface and lower part of the troposphere. Backwards air-mass trajectory analysis using the HYSPLIT model (See Supplementary) was performed to study vertical mixing across the boundary layer for specific periods. The results showed no considerable difference in the degree of vertical mixing during the sampling periods with high concentrations of OS 140, OS 154, OS 168 and OS 182 and during weeks when none of the isoprene organosulfates were present, indicating that transport from the tropics through the upper troposphere/lower stratosphere is an unlikely source. If OS 140, OS 154, OS 168 and OS 182 observed in the Arctic aerosols were solely from isoprene degradation a relatively constant ratio between them would furthermore be expected, this was however not the case. The ratio between the four organosulfates varied over three orders of magnitude between the different samples, thus other sources of OS 140, OS 154, OS 168 and OS 182 are expected.

Several studies suggest that glycolaldehyde, hydroxyacetone, methacrolein and 2-methylglyceric acid originate from biomass burning, field burning of agriculture wastes and anthropogenic sources such as automobiles and fossil fuel combustion as well as photooxidation of isoprene (Myriokefalitakis et al., 2008; Surratt et al., 2008; Hakola et al., 2009; Biesenthal and Shepson, 1997; Tuazon and Atkinson, 1990; Zhang et al., 2012; Kawamura et al., 2013). Considering the relatively low emissions of isoprene (Figure 2) during winter and early spring in the Arctic and in the northernmost part of Eurasia (the main source region for Arctic haze), the variability of the ratios between OS 140, OS 154, OS 168 and OS 168, and the lack of indication for transport from the tropics, we propose that OS 140, OS 154, OS 168 and OS 182 in the Arctic aerosols primarily originate from anthropogenic emissions from combustion of fossil fuels and biomass burning.

3.1.2 OS 250, OS 280 and NOS 295

Smog chamber studies of photooxidation of α-/β-pinene and limonene have identified monoterpenes as important precursors of OS 250, OS 280 and NOS 295 (Surratt et al., 2007; Iinuma et al., 2007; Surratt et al., 2008). Recently residential wood combustion has also been suggested as a source of NOS 295 and organosulfates during winter (Kahnt et al., 2013). In the chamber experiments other organosulfates and nitrooxy organosulfates were identified as well, three of which were also detected in our Arctic aerosol samples (OS 238, OS 265, NOS 310), however, all three compounds were below the detection limit and will not be mentioned further.

Emissions of monoterpenes were modelled during summer, autumn, winter and spring using the MEGAN model. In contrast to isoprene, emissions of monoterpene are not only confined to the growing season but occur throughout the year (Hakola et al., 2009). The model results showed emission rates of up to 20 mg/m^2/week during winter and early spring (November to April) at mid-latitudes, which is approximately one fifth of the emission rates observed during summer and autumn (May to October; 40-60 mg/m^2/week). The regions with adequately high monoterpene emissions are also common source regions for air masses arriving at the sites during Arctic winter and early spring.

3.1.3 OS 180, OS 196a, OS 196b, OS 208, OS 210 and OS 224

Six of the Arctic organosulfates, namely OS 180, OS 196a, OS 196b, OS 208, OS 210 and OS 224, have not been previously reported in either smog chamber or ambient studies.

Until now, smog chamber experiments have focused on formation of organosulfates from isoprene, monoterpenes and sesquiterpenes, which all generate multiple organosulfates (Iinuma et al., 2007; Surratt et al., 2008; Gómez-Gonzàlez et al., 2008; Chan et al., 2011). Isoprene and monoterpenes have especially been identified as the dominant precursors of organosulfates in atmospheric aerosols during summer periods in temperate and sub-tropical areas (Kristensen and Glasius, 2011; Stone et al., 2012; Surratt et al., 2008).

Based on the fact that the unknown organosulfates have not been identified in smog chamber experiments with isoprene, limonene and α-/β-pinene it is unlikely that these compounds are the unidentified precursors.

Possible precursors could be of anthropogenic origin or from marine sources (which have not yet been studied), but further studies are needed to elucidate this matter.

Based on the measured masses of the compounds we have included the most likely molecular formulas of OS 180, OS 196a, OS 196b, OS 208, OS 210 and OS 224 in Table 1, while structures and precursors are not listed for these six compounds as they are not identified yet.

3.2 Station Nord

Figure 4 shows the annual variation in concentrations of organic acids, organosulfates and nitrooxy organosulfates at Station Nord in 2010. A distinct annual pattern, especially in concentration levels of the organosulfates, was identified. From week 4 (January) to week 12 (March) the mean concentration of total organosulfate compounds was 47.4 (±14) ng m^{-3}, a concentration two orders of magnitude higher than that observed during the rest of the year (mean concentration of 2.1 (±3) ng m^{-3}). The organic acids showed the same seasonal trend, but with less clear differences in concentration levels, with a mean concentration of total organic acids of 11.5 (±4) ng m^{-3} from week 4 to 12 (January-March) and 2.2 (±1) ng m^{-3} from week 16 to 48 (April-December).

Elevated concentrations of organic matter (OM) were observed at Station Nord in week 4, 8 and 12 (January - March), 2010, while nss-sulfate showed elevated concentrations during January and March – May (weeks 4 and 8 to 20) (Nguyen et al., 2013a). Increases in the atmospheric concentration of OM, nss-sulfate and several elements of anthropogenic origin have long been used as indicators of Arctic haze (Heidam et al., 2004; Heidam et al., 1999; Iversen and Joranger, 1985; Pacyna et al., 1985; Heidam, 1981; Barrie et al., 1981; Rahn et al., 1977) and high levels of organic acids and organosulfates thus overlap with Arctic haze at Station Nord.

In week 4, 8 and 12 (January-March) the organosulfates and nitrooxy organosulfates accounted for 7 (± 3) % of OM and in addition organic acids contributed on average with 2 (±0.6) %. Furthermore, the organosulfates contributed to 5 (±5) % of water-soluble sulfate at Station Nord during these weeks.

3.2.1 Analysis of air mass back trajectories

Provided that accurate modelling of air mass trajectories in the Arctic is challenging due to sparse meteorological data and long distances to the source regions, back trajectories were calculated every fourth hour during each week of aerosol sampling. The trajectories were calculated 5 days back in time, arriving at 10 m above ground level at Station Nord and the trajectories for each week were subsequently clustered to identify major source regions.

Figure 5 shows the cluster analysis of trajectories for the sampling weeks of 2010 at Station Nord. Four main cluster maps were identified, representing the air mass transport routes for all twelve sampling weeks. Two of the identified air mass transport routes, Nord 1 (week 4 - January) and Nord 3 (week 12 - March), showed considerable transport from the Yakutsk area and the Norilsk area, respectively. Yakutsk and Norilsk have previously been identified as anthropogenic source regions in Russia, contributing to Arctic air pollution (Nguyen et al., 2013b; Heidam et al., 2004; Heidam et al., 1999; Christensen, 1997; Ottar, 1989; Pacyna et al., 1985), which could account for the high concentrations of organosulfates and anthropogenic acids observed in week 4 and 12 (January and March).

Nord 2 (week 8 (February), 24 (June), 44 and 48 and (November – December)) represent air mass transport routes, where some of the back trajectories arrived from the coastal areas of Russia close to Yakutsk, but not directly from any identified pollution sources. For week 8 (February) almost half (48%) of the back trajectories originated from the coastal area of Yakutsk which is in line with the observed lower concentration levels compared to week 4 (January) and 12 (March), but higher concentrations compared to the rest of the sampling period. Transport from the Russian coastal areas is also observed for weeks 24 (June), 44 (November) and 48 (December) (14-20% of trajectories).

Back trajectories for the rest of the sampling weeks at Station Nord (represented as Nord 4 (week 16 (April), 20 (May) and 32-40 (August – October)) showed significant transport from the Arctic Ocean as well as the north-western coast of Greenland and the northern coast of Canada, correlating with the observation of very low concentrations of organosulfates and organic acids. A small peak in the concentration of biogenic organic acids as well as OM and the biomass burning tracer levoglucosan (Nguyen et al., 2013a) was detected for week 28 (July). Nguyen et al. (2013a) suggested that during this week aerosols at Station Nord could be influenced by biomass burning aerosols; however the source region was unclear.

3.2.2 Anthropogenic and biogenic contribution to SOA at Station Nord

Of the SOA species analyzed in this study, unknown organosulfates contributed the most to Arctic haze aerosols followed by the identified anthropogenic organosulfate compounds, anthropogenic acids, biogenic acids and finally the biogenic organosulfates. The small contribution of biogenic SOA compounds observed in week 4 (January) through 12 (March) is not surprising, since emission of monoterpenes is limited in the Arctic and the Russian source regions (see Figure 3). Interestingly, maximum concentrations of the identified BSOA tracers were observed during the Arctic haze period and not during summer, when emissions of BVOCs are expected to be highest. This result suggests that long-range transport and inefficient removal processes during winter and spring are possibly more important factors affecting concentrations of BSOA at Station Nord than emissions in the region during summer.

The molar ratio of C_6(azelaic acid)/C_9(adipic acid) organic acids can be used to estimate the anthropogenic to biogenic contribution to SOA, as suggested by Ho et al. (2006). A value above 1 could indicate anthropogenic dominance, whereas a value below 1 could indicate biogenic dominance. The three samples with high concentrations of organosulfates and organic acids (Week 4 – 12 (January – March)) showed a high C_6/C_9-values (5-12) supporting a strong anthropogenic contribution. During the rest of the year, the C_6/C_9-ratio was close to 1, indicating equal contributions from anthropogenic and biogenic precursors. The drop in C_6/C_9-value between week 12 (March) and 16 (April) was due to a combination of a rise in the C_9 concentration from ~0.3 ng m^{-3} in week 4 to 12 (January - March) to ~0.7 ng m^{-3} in week 16 to 48 (April – December) and a drop in the C_6 concentration from ~1.5 ng m^{-3} in week 4 to 12 (January - March) to ~0.4 ng m^{-3} in week 16 to 48 (April – December).

3.3 Zeppelin Mountain

Figure 6 shows the annual variation in concentrations of organic acids and organosulfates at Zeppelin station in 2008. In general, the total concentration of organosulfate and organic acid species showed a quite constant concentration throughout the year with mean concentrations of 14.7 (±4) ng m^{-3} and 3.9 (±1) ng m^{-3}, respectively. Though four weeks (week 7, 9, 13 and 17) showed a clear increase in concentrations of both organosulfates and organic acids, where the mean total concentration of organosulfates reached 27.8 (±6) ng m^{-3} whereas the mean total concentration of organic acid was 8.6 (±2) ng m^{-3}. These four weeks occured within late winter and early spring, coinciding with elevated levels of organic matter and nss-sulfate observed in week 9, 13 and 17 (Figure 6), and as for Station Nord, the increased levels of SOA tracers are thus confined within the Arctic haze period.

An explanation for the observed trend in organosulfate concentration (high during Arctic haze and very low during the remaining part of the year) is related to the Arctic aerosol seasonality observed by Tunved et al. (2013). Based on a ten-year dataset of particle mass and number size distributions at Zeppelin Mountain the authors observed a distinct and repeating pattern in the Arctic aerosol life cycle. During Arctic haze, transport of pollution into the Arctic was effective and precipitation and wet removal was at a minimum, resulting in a high concentration of particles in the accumulation mode. New particle formation was limited due to low photochemistry during Arctic spring. In summer precipitation and cloudiness increased, resulting in more efficient removal in the Arctic as well as during transport of air masses to the Arctic.

During Arctic haze the measured organosulfates contributed 4±1% of OM and 3.7±1% of nss-sulfate at Zeppelin Mountain, whereas during the remaining part of the year the contribution is 15±9% and 9±5% to organic matter and nss-sulfate, respectively. These results are in line with a previous study by Frossard et al. (2011), where organosulfates contributed to 6% of total sulfate and 9-11% of submicron organic aerosol mass over the Arctic Ocean close to Svalbard during spring 2008. Frossard et al. (2011) estimated the organosulfate contribution to aerosol mass and total sulfate from the organic functional group contribution, quantified using Fourier-transform infrared (FTIR) spectroscopy. Contrary to our HPLC-qTOF-MS method, the FTIR method does not provide information on the organosulfate speciation, but only the presence of the functional group; hence concentration levels of individual organosulfates and variations in the organosulfate composition were not obtained.

The considerably larger contribution of organosulfates to OM and nss-sulfate outside the Arctic haze period, discovered in this study, is interesting and can be caused by multiple factors. One possibility is that the organic aerosols transported to Zeppelin during Arctic haze contained a smaller mass fraction of organosulfates compared to aerosols from local and sub-Arctic regions. Even though long-range transport also occurs during summer and autumn, removal processes are thought to be more efficient possibly resulting in local emissions and emissions from sub-Arctic regions to gain a higher relative weight in the aerosol composition compared to long-range transport.

According to our results Arctic haze persisted further into spring at Zeppelin Mountain in 2008 than at Station Nord in 2010. It was expected that Arctic haze would also last until April at Station Nord, as was observed in other studies (Heidam et al., 2004). The short Arctic haze period at Station Nord in 2010 might be caused by either an unrepresentative sample from week 16 (April) giving a low concentration of the measured species, or by meteorological differences between the two sampling years, causing the polar air dome to contract earlier in 2010 and shortening the period of Arctic haze.

Even though the seasonal variation in organic acid and organosulfate concentrations at Station Nord and Zeppelin Mountain are very different, the concentration ranges of the observed compounds are comparable in magnitude (Table 2), Station Nord however experiences both the maximum and minimum summed concentration of organic acids and of organosulfates. In general the organosulfates are more abundant at both stations compared to the organic acids, OS 154, OS 184, OS 196b and OS 210 being most abundant at Zeppelin Mountain and OS 182 and OS 196b being most abundant at Station Nord. The most pronounced organic acids are azelaic acid and adipic acid. The concentrations of the individual organic acids are in the range of previous studies in the Arctic and in Mainz, Germany but approximately a magnitude lower than concentrations measured in Tokyo and in Chinese cities (Zhang et al., 2010; Ho et al., 2007; Kawamura and Yasui, 2005; Kawamura et al., 1996).

3.3.1 Connection between source region and organosulfate complexity at Zeppelin Mountain

In Figure 7 the relative composition of the organosulfate species observed at Zeppelin Mountain in 2008 are shown. A clear distinction between the samples was recognized: The organosulfate composition showed increased complexity from week 1 to 15 and from week 47 to week 51, compared to week 17 to week 39. Hence, during the winter-spring period, when transport from the mid-latitudes is most pronounced and aerosol sinks are least active, the number of different organosulfates contributing to aerosol particles was much higher (7-10 species) than during the summer and autumn (2-4 species). The increased complexity is due to three additional organosulfates identified as anthropogenic (OS 140, OS 168 and OS 182) and two unknown (OS 180 and OS 224).

Based on HYSPLIT trajectories (see Figure 8), it was recognized that the increased number of identified organosulfates correlated with air masses transported from Russia or the coastal area of Russia in all studied weeks during the Arctic haze period with the exception of W5 and W7. In contrast, during the summer and autumn periods (week 17-39), air masses primarily originated from locations within the high-Arctic, Greenland and the coastal areas of the Scandinavian countries. Russian areas as Norilsk and Yakutsk as have long been known as source areas of atmospheric pollution due to metal smelting and coal combustion (Hirdman et al., 2010; Ottar, 1989; Pacyna et al., 1985). Our observations of a higher organosulfate complexity when air was transported from these areas compared to less polluted regions, such as ocean regions, Greenland and Scandinavian coastal areas, implies a connection between organosulfate complexity and the level of air pollution. This is in line with chamber studies pointing out the importance of acidic sulfate aerosols for organosulfate formation (Gómez-Gonzàlez et al., 2008; Iinuma et al., 2007).

One organosulfate (OS 210) was found in relative high concentrations (> 4 ng m^{-3}) in all the samples from Svalbard, possibly indicating a regional source. To our knowledge OS 210 has not been reported before in neither field investigations nor smog chamber studies.

The correlations between the observed organosulfates were investigated. A high correlation coefficient ($R^2 > 0.95$, $n > 13$) was found between OS 168, OS 180, OS 182 and OS 224, implying common precursors or common source areas. As the source areas (identified from the back trajectories) changed between the samples, where OS 168, OS 180, OS 182 and OS 224 are observed a common precursor is more likely. As mentioned in section 3.1, methacrolein and 2-

methylglyceric acid, a photooxidation product of methacrolein (Zhang et al., 2012) are suggested precursors of OS 168 and 182, respectively. Methacrolein or an oxidation product of methacrolein could be precursors of OS 180 and OS 224. Correlations between OS compounds were also computed for the Station Nord Samples, showing a good correlation between the same four organosulfates, but with only few available data points ($n < 6$) no final conclusions could be drawn. Regarding the organosulfate concentration levels at Zeppelin Mountain (Figure 6), the stable concentration observed during most weeks (week 1 to 5, 11, 15 and 19 to 51) remains unexplained. The specific organosulfate composition showed a distinct variation during the annual cycle (Figure 7) suggesting changes in sources and emissions, which were supported by the trajectory analysis as well as the emission maps (Figure 2 and 3). The stable concentration level may possibly be caused by large-scale recirculation of air masses within the Arctic area.

4 Conclusions

At the two Arctic sites investigated in this study (Station Nord and Zeppelin Mountain), organosulfates and organic acids were detected throughout the year, with observed maximum concentrations overlapping with the Arctic haze period. Organic acids and organosulfates from anthropogenic precursors dominated the SOA collected at the two sites, with biogenic organosulfates being almost negligible throughout the year. Both the anthropogenic and the biogenic species reached their maximum concentrations during the Arctic haze period, suggesting that long-range transport is the main source of SOA in the Arctic. The transport pattern and source regions of the sampled aerosols were investigated by modelling backwards air mass trajectories using the HYSPLIT model. The model results indicated Russian areas, especially Norilsk and Yakutsk as potential source regions of Arctic haze and organosulfates at both sites. Furthermore, at Zeppelin station it was observed that the complexity (i.e. number) of organosulfate species was highly dependent on source area. When Russian areas were involved as source regions, the organosulfates showed a 100% increase in complexity compared to source areas such as Greenland, coastal areas of Scandinavia and the Arctic Ocean.

Six organosulfates (OS180, OS 196a, OS 196b, OS 208, OS 210 and OS 224), which to our knowledge have not been reported before, were observed at both sites. OS 180 and OS 224 correlated perfectly with OS 168 and 182, which have been suggested to form from methacrolein, indicating that methacrolein could be the precursor of these two organosulfates as well. Based on this study it has not been possible to deduce structures or to account for precursors for the other four organosulfates. It is, however, suggested that the precursors are of anthropogenic or marine origin as the organosulfate formation from major terrestrial BVOCs, isoprene and monoterpenes, have been studied thoroughly in smog chamber studies.

As organosulfates binds inorganic sulfate, their presence in the Arctic atmosphere may affect the formation and lifetime of clouds. Despite the knowledge obtained in the present paper there is still a lack of knowledge concerning time tends, source regions, atmospheric formations and sinks of organosulfates in the Arctic so further studies are needed.

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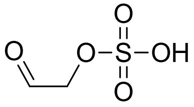
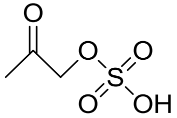
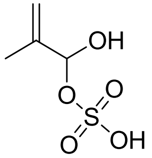
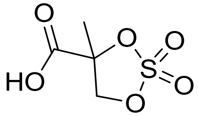
Table 1: The observed organosulfates and nitrooxy organosulfates. Measured m/z, molecular weight, retention time, MSMS fragments, molecular formula, possible structure and suggested precursor are given. a) (Surratt et al., 2007), b) (Surratt et al., 2008)

	Measured m/z	**MW (Da)**	**RT (min.)**	**MSMS fragments**	**Molecular formula**	**Possible structure**	**Suggested precursor**
OS 140	139.002	140.010	6.2; 7.3	96.96; 79.96	$C_2H_4O_5S$ Exact mass: 139.978		glycolaldehyde[a,b]
OS 154	153.020	154.028	13.4	96.96; 79.96	$C_3H_6O_5S$ Exact mass: 153.994		hydroxyacetone[a,b]
OS 168	167.043	168.051	21.7; 23.2	121.02 96.96; 79.96	$C_4H_8O_5S$ Exact mass: 168.009		Methacrolein[a]
OS 180	179.023	180.031	24.0;	96.95; 79.96	$C_5H_8O_5S$ Exact mass: 180.009	Unknown	Unknown
OS 182	181.043	182.052	29.1; 30.3	96.95; 79.96	$C_5H_{10}O_5S$ Exact mass: 182.025		2-methylglyceric acid[a]
OS 196a	195.029	196.037	12.8; 15.0	96.96	$C_6H_{12}O_5S$ Exact mass: 196.041	Unknown	Unknown
OS 196b	195.064	196.078	35.5; 38.7	96.96; 79.96	$C_6H_{12}O_5S$ Exact mass: 196.041	Unknown	Unknown
OS 208	206.996	208.004	29.4; 30.2	96.96; 79.96	$C_6H_8O_6S$ Exact mass: 208.004	Unknown	Unknown
OS 210	209.090	210.098	42.5	96.96	$C_7H_{14}O_5S$ Exact mass: 210.056	Unknown	Unknown

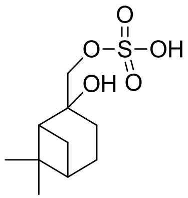
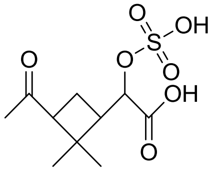
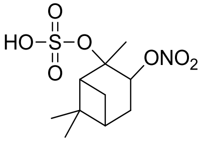
OS 224	223.110	224.118	45.1	96.96	$C_8H_{16}O_5S$ Exact mass: 224.072	Unknown	Unknown
OS 250	249.073	250.081	32.4	96.96	$C_{10}H_{18}O_5S$ Exact mass: 250.087	 More isomers	α-/β-pinene[b]
OS 280	279.050	280.058	22.2;27.7	199.093; 164.982; 96.96; 79.96	$C_{10}H_{16}O_7S$ Exact mass: 280.062		α-/β-pinene[b]
NOS 295	294.063	295.071	41.4; 44,7	247.056; 231.06; 96.96	$C_{10}H_{17}O_7NS$ Exact mass: 295.073	 More isomers	α-/β-pinene[b]

Table 2: Concentration ranges, median concentrations and mean concentrations of the individual and summed organic acids and organosulfates observed at Station Nord and at Zeppelin Mountain. Anthropogenic compounds are marked with (A), unknown compounds are marked with (U), biogenic compounds from fatty acids with (BF) and biogenic compounds from monoterpenes with (BM). All values are in ng m^{-3}. BLD denotes values below detection limit.

[1] Diaterpenylic acid acetate. [2] 3-methyl-1,2,3-butanetricarboxylic acid.

[ng m^{-3}]	**Station Nord**			**Zeppelin Mountain**		
	Range	**Median**	**Mean**	**Range**	**Median**	**Mean**
Adipic acid (A)	0.13 – 1.96	0.31	0.61	0.39 – 2.91	1.11	0.77
Pimelic acid (A)	0.01 – 0.38	0.13	0.18	0.05 – 0.57	0.20	0.15
Benzoic acid (A)	–	–	–	BDL – 1.14	0.42	0.37
Phthalic acid (A)	0.05 – 8.29	0.17	2.22	0.02 – 1.45	0.28	0.20
Suberic acid (BF)	0.01 – 0.53	0.12	0.21	0.07 – 1.68	0.43	0.37
Azelaic acid (BF)	0.10 – 1.43	0.65	0.58	0.05 – 1.46	0.69	0.70
Pinic acid (BM)	BDL – 1.81	0.10	0.35	0.09 – 1.28	0.31	0.24
Pinonic acid (BM)	0.02 – 0.18	0.06	0.06	0.07 – 0.97	0.36	0.26
Terpenylic acid (BM)	0.05 – 1.83	0.14	0.32	0.07 – 2.88	0.40	0.21
DTAA (BM)[1]	0.01 – 0.05	0.02	0.03	0.03 – 0.16	0.09	0.08
MBTCA (BM)[2]	0.02 – 1.05	0.14	0.25	0.09 – 0.67	0.28	0.27
Sum organic acids	0.39 – 17.50	1.83	4.82	0.93 – 15.19	4.57	3.63
OS 140 (A)	0.01 – 2.08	0.10	0.38	0.03 – 1.62	0.36	0.13
OS 154 (A)	BDL – 2.72	0.11	0.54	1.27 – 9.56	3.36	3.09
OS 168 (A)	0.01 – 5.44	0.13	1.31	0.02 – 5.47	0.97	0.52
OS 180 (U)	0.01 – 1.81	0.05	0.47	0.01 – 2.06	0.42	0.27
OS 182 (A)	0.16 – 11.14	1.04	3.72	0.03 – 8.54	1.78	0.82
OS 196a (U)	BDL – 1.64	0.35	0.58	0.32 – 5.68	2.38	2.14
OS 196b (U)	0.04 – 17.55	1.59	5.26	–	–	–
OS 208 (U)	–	–	–	0.04 – 4.46	0.68	0.32
OS 210 (U)	0.01 – 13.99	0.38	2.89	4.13 – 11.06	6.26	5.80
OS 224 (U)	0.01 – 9.39	0.26	1.79	0.01 – 5.34	0.73	0.13
OS 250 (BM)	BDL – 0.99	0.07	0.18	0.01 – 4 87	0.60	0.08
OS 280 (BM)	BDL – 0.69	0.05	0.19	0.01 – 0.16	0.04	0.03
NOS 295 (BM)	BDL – 0.18	0.03	0.06	BDL – 0.05	0.03	0.03
Sum organosulfates	0.25 – 67.63	4.15	17.42	5.88 – 58.87	17.61	13.36

Figure 1: Chromatogram of the SOA sample from Station Nord Week 8 (in green). A blank filter sample is shown in black. The SOA products giving rise to each peak are identified as follows: 1. Sulphate dimer, 2 and 3. OS 140, 4. OS 154, 5. OS 196a, 6. Terpenylic acid, 7. Phthalic acid, 8. Terephathalic acid, 9. Pimelic acid, 10. Unknown, 11 and 13. OS 168, 12 and 24. Pinic acid, 14. OS 180, 15. DTAA, 16. Unknown, 17. Suberic acid. 18. Unknown, 19. Internal standard, 20. Azelaic acid, 21 and 23. OS 182, 22. OS 208, 25. OS 250, 26 and 28. OS 196b, 27 and 29. Unknown m/z 293, 30. OS 196b. 31. NOS 295, 32. OS 210.

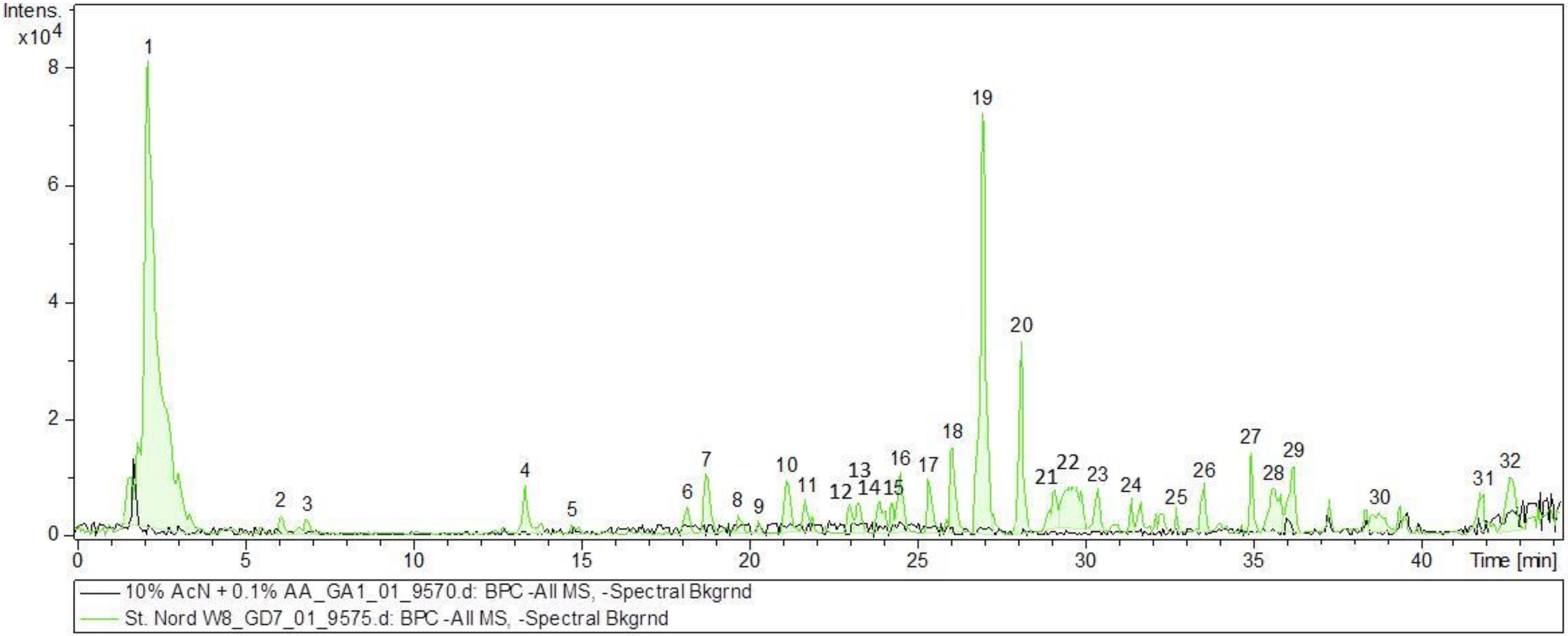


Figure 2: Spatial distribution of the simulated isoprene emission from the MEGAN model the year 2008. Months with similar emissions are represented with the same map.

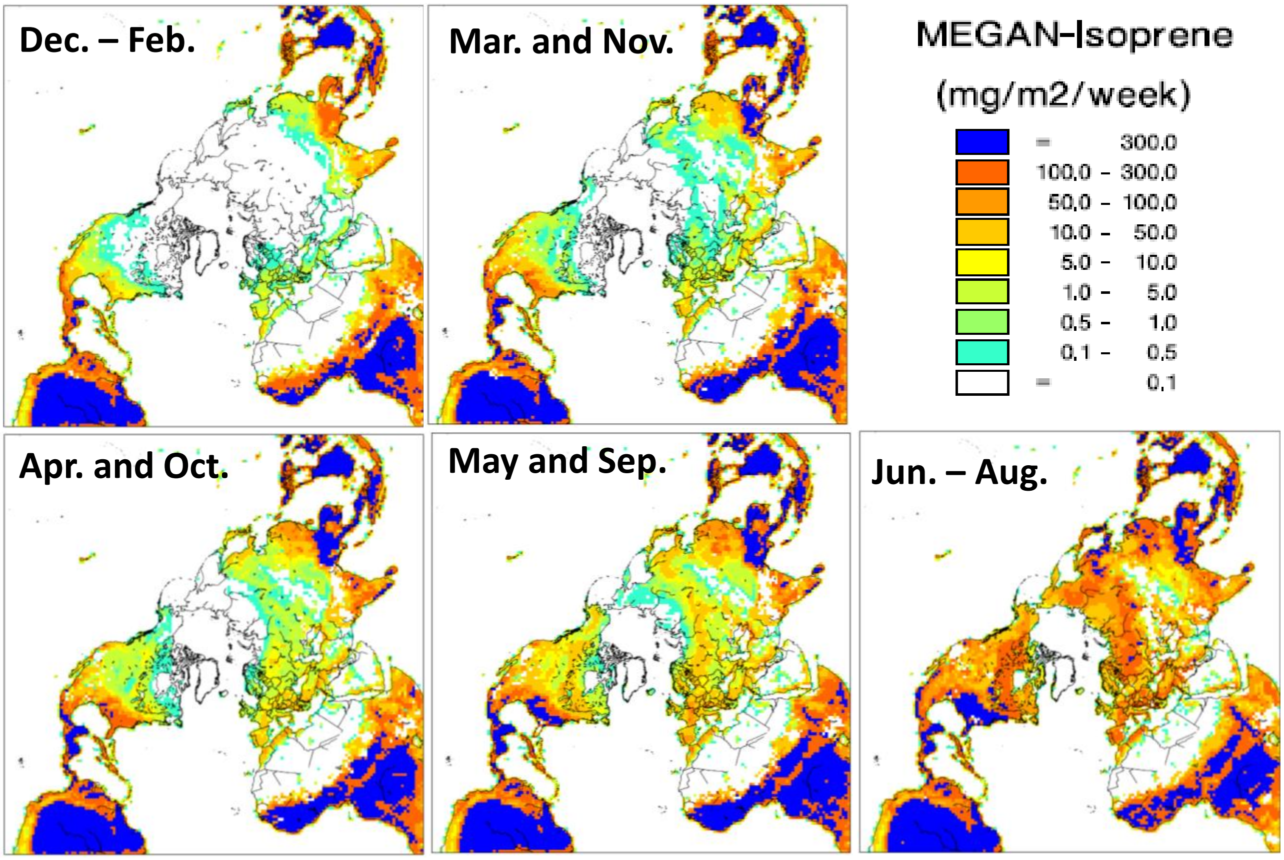


Figure 3: Spatial distribution of the simulated monoterpene emission from the MEGAN model during the year of 2008.

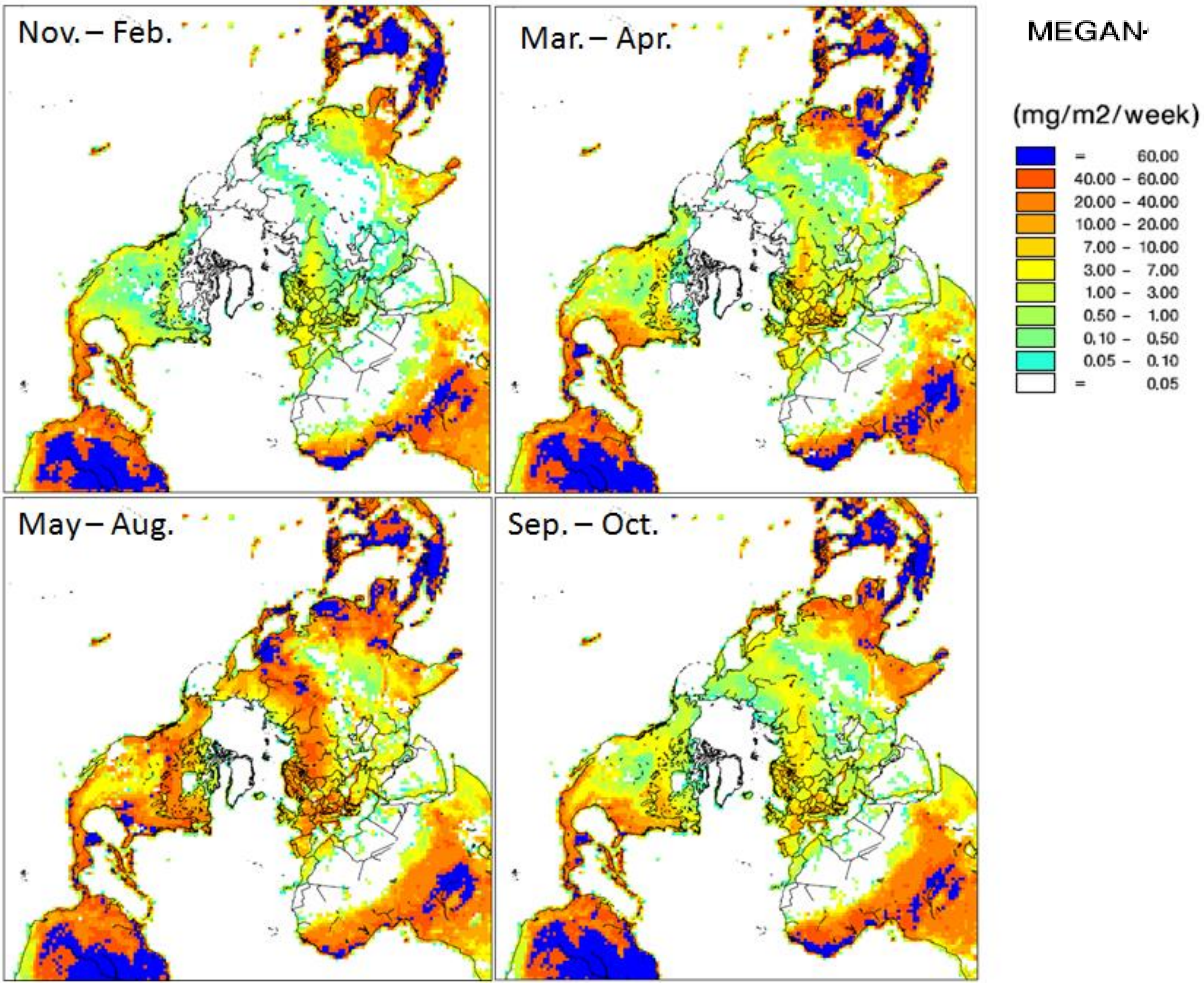


Figure 4: Variation in total air concentration (ng m^{-3}) of observed acids and organosulfates from anthropogenic (A), biogenic (B) and unknown (U) precursors every fourth week of 2010 at Station Nord. W4 corresponds to January, W8 to February, W12 to March and so on. The secondary axis shows the molar ratio of adipic acid (C_6) to azelaic acid (C_9) estimating the anthropogenic to biogenic influence. The error bars show the estimated error of 15%.

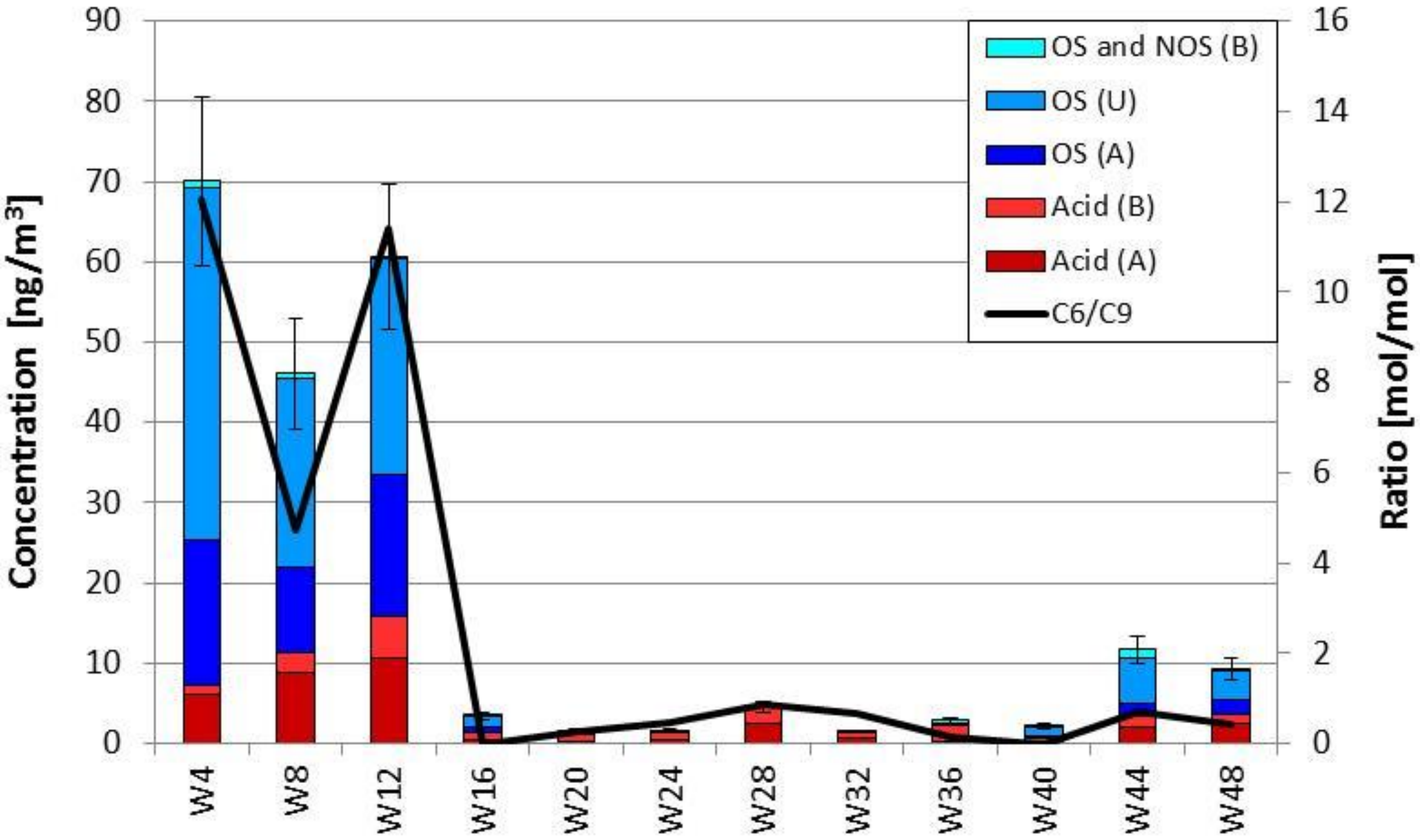


Figure 5: 5-days backward air trajectories ending at Station Nord at 10 m height above ground level, calculated using the HYSPLIT model. Backward air trajectories were made for every 4th hour and clustered for each sampling week of 2010 (each coloured trajectory represent a cluster mean). Sampling weeks with similar trajectory patterns are represented by one map in the following manner: Nord 1 weeks 4, Nord 2 weeks 8, 24, 44 and 48, Nord 3 week 12 and Nord 4 weeks 16, 20 and 32-40. 1 marks the location of the Yakutsk area and 2 marks the location of the Norilsk area, two anthropogenic source regions contributing to air pollution in the Arctic (Ottar, 1989; Pacyna et al., 1985).

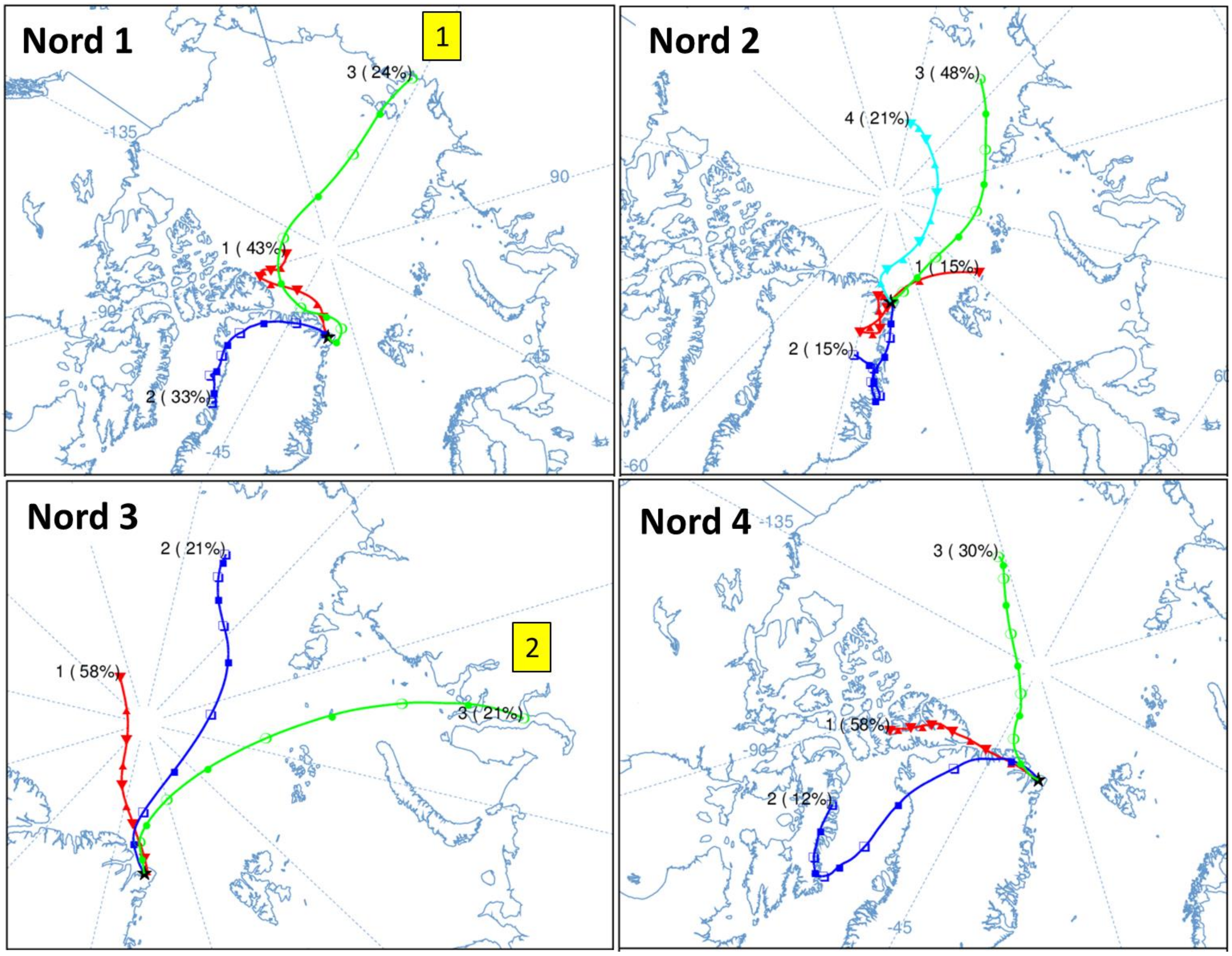


Figure 6: Variation in total air concentration (ng m^{-3}) of observed acids and organosulfates from anthropogenic (A), biogenic (B) and unknown (U) precursors during a full annual cycle at Zeppelin Mountain, Svalbard 2008. Approximately two samples are collected for each month, W1 and W3 from January, W5, W7 and W9 from February, W11 and W13 from March W15 and W17 from April, W19 from May, W23 and W25 from June, W27 and W29 from July, W31, W33 and W35 from August, W37 and W39 from September, W47 from November and W49 and W51 from December. nss-sulfate and OM (µg m^{-3}) are depicted on the secondary axis. The error bars show the estimated 15% uncertainties on the concentrations.

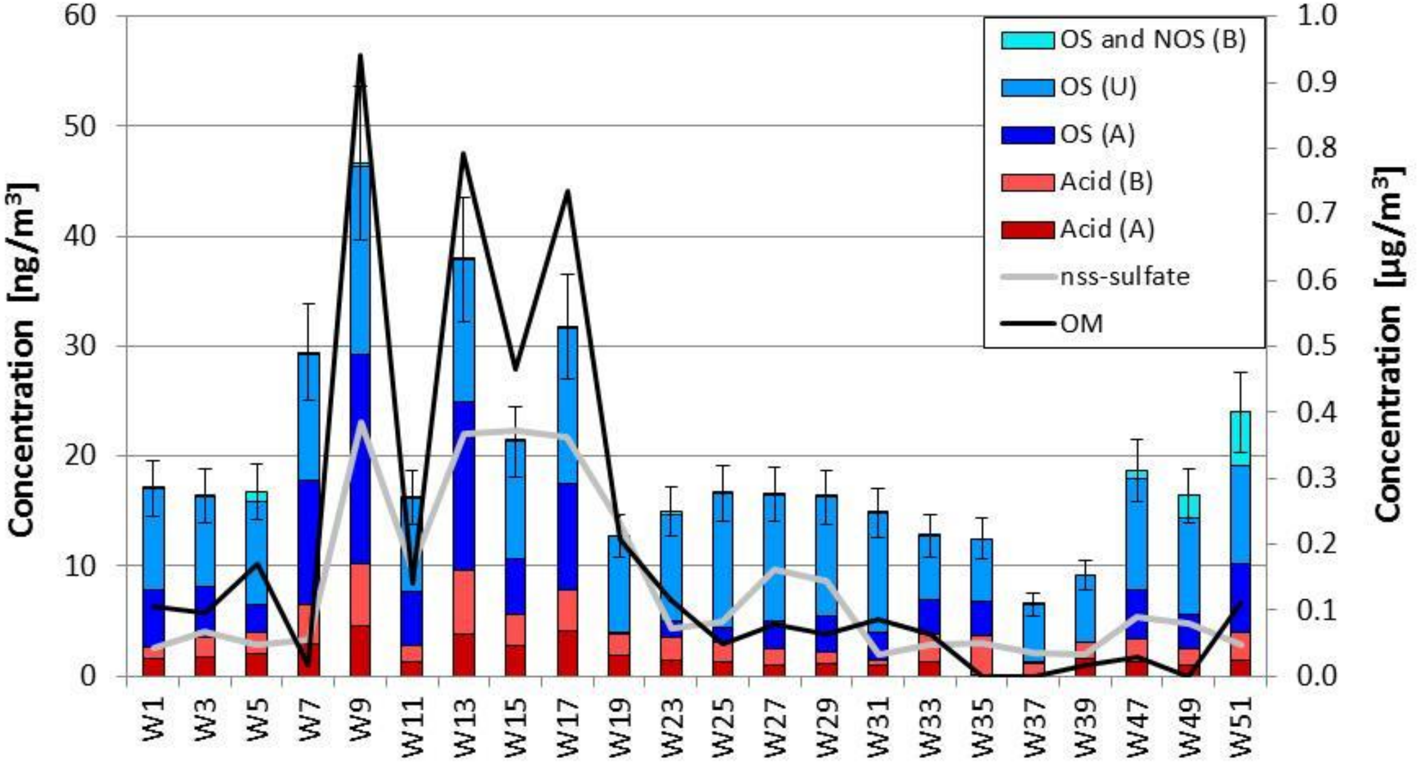


Figure 7: Relative composition of organosulfates from monoterpene (M), anthropogenic (A), and unknown (U) precursors observed at Zeppelin Mountain, Svalbard 2008. Approximately two samples are collected for each month, W1 and W3 from January, W5, W7 and W9 from February, W11 and W13 from March W15 and W17 from April, W19 from May, W23 and W25 from June, W27 and W29 from July, W31, W33 and W35 from August, W37 and W39 from September, W47 from November and W49 and W51 from December.

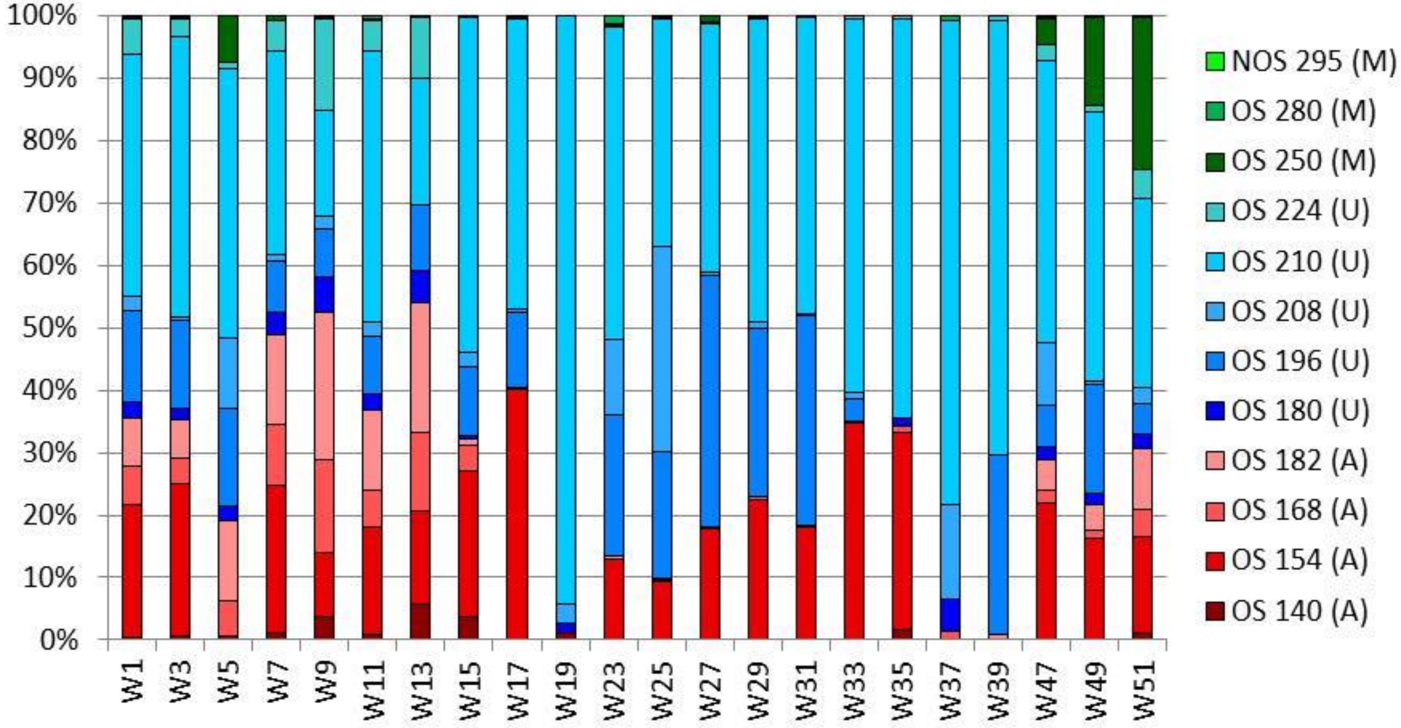
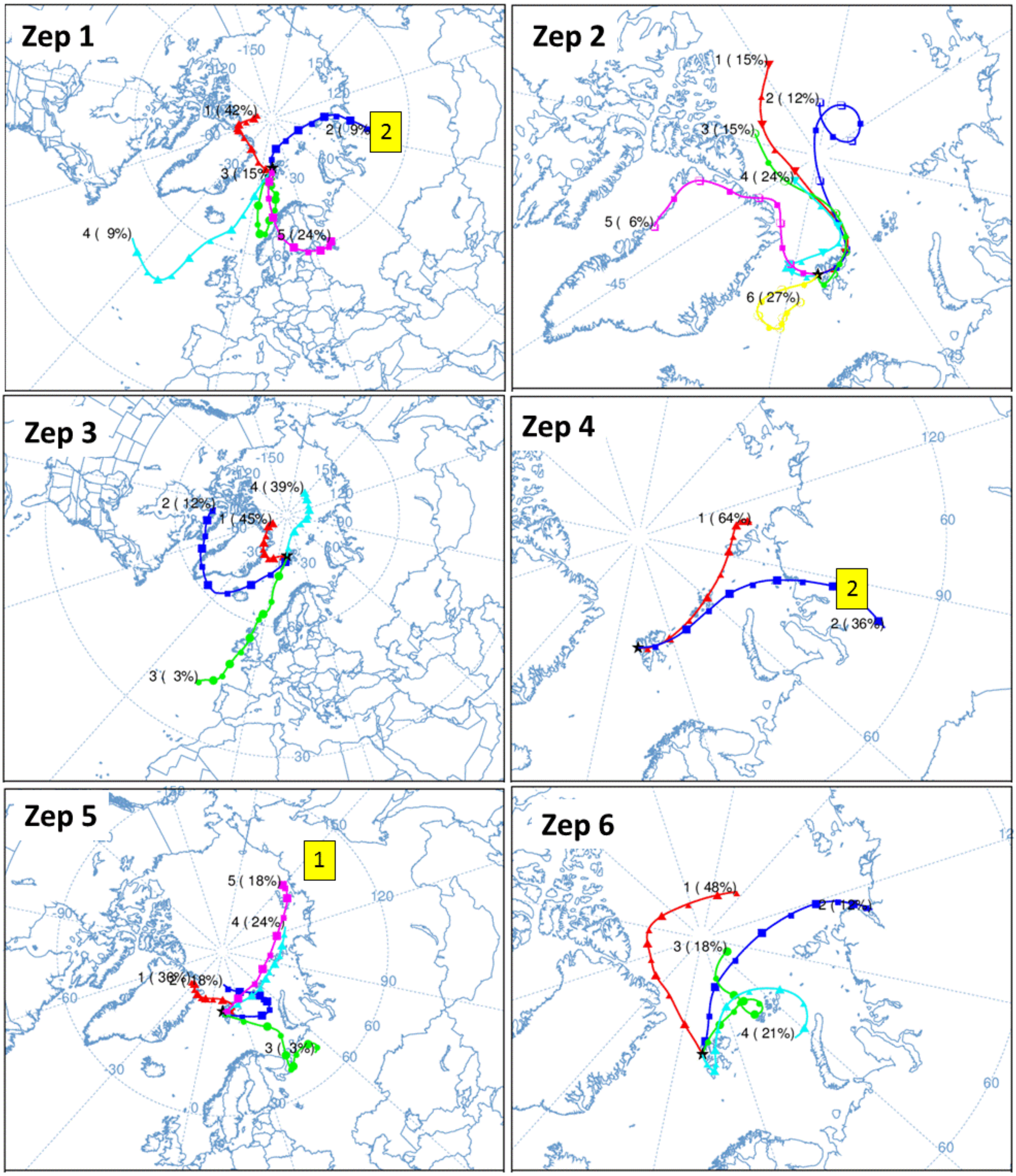


Figure 8: 5-days backwards air mass trajectories ending at Zeppelin Mountain at 10 m height above ground level, calculated using the HYSPLIT model. Backwards air mass trajectories were made for every 4th hour and clustered for each sampling week of 2008 (each coloured trajectory represent a cluster mean). Sampling weeks with similar trajectory patterns are represented by one map in the following manner: Zep1 weeks 1 and 3, Zep 2 weeks 5, 19-35 and 39, Zep 3 weeks 7 and 37, Zep 4 week 9, Zep 5 weeks 11 and 15 and Zep 6 weeks 13, 17 and 47-51. 1 marks the location of the Yakutsk area and 2 marks the location of the Norilsk area, two anthropogenic sources contributing to air pollution in the Arctic (Ottar, 1989; Pacyna et al., 1985).


Zep 1
1 (42%)
2 (9%)
2
3 (15%)
4 (9%)
5 (24%)
Zep 2
1 (15%)
2 (12%)
3 (15%)
4 (24%)
5 (6%)
6 (27%)
Zep 3
2 (12%)
1 (45%)
4 (39%)
3 (3%)
Zep 4
1 (64%)
2
2 (36%)
Zep 5
1
5 (18%)
4 (24%)
1 (36%)
2 (18%)
3 (3%)
Zep 6
1 (48%)
2 (13%)
3 (18%)
4 (21%)