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Aerosol composition and sources in the Central Arctic Ocean during ASCOS

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Abstract

Measurements of submicron aerosol chemical composition were made in the Central Arctic Ocean from 5 August to 8 September 2008 as a part of the Arctic Summer Cloud Ocean Study (ASCOS) using an aerosol mass spectrometer (AMS). The median levels of sulphate and organics for the entire study were 0.042 and 0.046 µg m^{-3}, respectively. Positive matrix factorisation was performed on the entire mass spectral time series and this enabled marine biogenic and continental sources of particles to be separated. These factors accounted for 33 % and 36 % of the sampled ambient aerosol mass, respectively, and they were both predominantly composed of sulphate, with 47 % of the sulphate apportioned to marine biogenic sources and 48 % to continental sources, by mass. Within the marine biogenic factor, the ratio of methane sulphonate to sulphate was 0.25 ± 0.02, consistent with values reported in the literature. The organic component of the continental factor was more oxidised than that of the marine biogenic factor, suggesting that it was more processed and had been present longer in the atmosphere than the organics in the marine biogenic factor. The remaining ambient aerosol mass was apportioned to an organic-rich factor that could have arisen from a combination of marine and continental sources.

1 Introduction

The sources and chemical composition of Arctic aerosol are still poorly understood. In a recent intercomparison study of 13 models that predict transported Arctic aerosol sulphate and black carbon mass, the majority of the models did not compare well to aerosol loadings observed at three land sites (Shindell et al., 2008). In general, the models had trouble capturing the seasonality of the observed aerosol mass, underpredicting for the winter months and overpredicting for the summer months.

The observed seasonal behaviour is driven by Arctic haze, which is a phenomenon that takes place during the winter and early spring and has been observed in the northern latitudes of North America and Europe. During this time, aerosol loadings are 10–40 times higher than summertime values, with sulphate and black carbon making up the principal identified components (Barrie, 1986; Heintzenberg and Leck, 1994; Quinn et al., 2007). Models show that these particles are transported from the lower latitudes of Eurasia and North America into the Central Arctic (Gong et al., 2010) and are lost more slowly because strong temperature inversions lead to reduced precipitation. As sunlight returns to the Arctic in the spring, the atmospheric stability is reduced and the particles can be lost with deposition (summarised by Quinn et al., 2007).

In contrast, during the summer, air first passes over open ocean in the North Atlantic and Pacific Oceans before arriving in the Arctic. Because the air is less stable and travels more slowly with more frequent precipitation, aerosol mass transported from lower latitudes is less compared to the winter (Law and Stohl, 2007). Low summertime aerosol number loadings have been observed, for example, over Greenland (Megaw and Flyger, 1973), on Spitsbergen (Heintzenberg and Leck, 1994) and over the Central Arctic Ocean (Covert et al., 1996). Under these conditions, local aerosol sources become much more important because the background concentrations are so low.

A series of three previous international ice-breaker expeditions to the Central Arctic Ocean (north of 85° N) during the summers of 1991 (IAOE-91) (Leck and Persson, 1996), 1996 (AOE-96) (Leck et al., 2001) and 2001 (AOE-2001) (Leck et al., 2004; Tjernström, 2005) has greatly contributed to our knowledge of aerosol sources and composition at these northern latitudes. For example, it was observed during IAOE-91 that submicron sulphur-containing particles over the Arctic pack ice are efficiently scavenged by fogs and low clouds and have average residence times of ≈ 20 h (Nilsson and Leck, 2002). This was corroborated by observations from AOE-96 which found cloud condensation nuclei (CCN) concentrations to decrease as the transport time over pack ice reached 36 h (Bigg and Leck, 2001), consistent with loss due to aerosol scavenging. However, this latter study also observed an increase in CCN concentration in air that had travelled over the pack ice for > 36 h. Transport from the free troposphere was ruled out (Bigg and Leck, 2001) and it has been hypothesised that a local source directly emits water insoluble organic components from the surface microlayer of open leads by bubble bursting (e.g. Bigg et al., 2004; Bigg and Leck, 2008; Leck et al., 2002; Leck and Bigg, 2010). These organics are suggested to be exopolymer secretions which are microcolloids and their gels (Leck and Bigg, 2005). They can be viewed as three-dimensional biopolymer networks containing polysaccharides and/or monosaccharides (carbohydrates), with peptides and proteins attached to the network. These biopolymers are inter-bridged with divalent cations (such as Ca^{2+}) which result in a gel-like consistency (Chin et al., 1998).

Open leads have been observed in the past to be a source of particles in the Canadian Arctic spring (Leaitch et al., 1994). In addition, observations of an organic aerosol fraction originating from the ocean have been made at lower latitudes such as Barrow, USA (71° N, 156° W) and the Arctic Ocean (Hawkins and Russell, 2010; Russell et al., 2010), the North Atlantic Ocean (Ceburnis et al., 2008; Facchini et al., 2008; O'Dowd et al., 2004), as well as the Southeast Pacific (Hawkins and Russell, 2010). Depending on the location and method, these aerosol have been observed to be both water soluble (Hawkins and Russell, 2010; Russell et al., 2010) and insoluble (Bigg and Leck, 2008; Ceburnis et al., 2008; Facchini et al., 2008; Hawkins and Russell, 2010; O'Dowd et al., 2004). The chemical nature of these compounds has been reported to be similar to lipopolysaccharides, based on nuclear magnetic resonance spectra (Facchini et al., 2008); similar to simple biological sugars, based on fourier transform infrared spectra (Russell et al., 2010); and originating from proteins, amino acids and micro-organisms, based on scanning transmission X-ray microscopy with near-edge X-ray absorption fine structure (Hawkins and Russell, 2010). A detailed summary of marine organic aerosol can be found in Hawkins and Russell (2010).

There is also evidence of secondary organic products, with the oxidation products of isoprene identified in aerosol collected at Alert, Canada (83° N, 62° W) (Fu et al., 2009), which could have originated from local marine organisms emitting isoprene. Aerosol growth observed at Summit, Greenland has also been attributed to organics originating from the snow (Ziemba et al., 2010). Overall, the level of scientific understanding of the biological contributions to organic aerosol in the Arctic, as well as aerosol sources in general, is still low due to the limited amount of observational data.

These findings complement the better understood biogenic contributions to marine aerosol, including over the Arctic pack ice, of dimethyl sulphide (DMS) oxidation products. DMS is produced through the planktonic food web and emitted from the ocean into the air where it is oxidised to ultimately form, among other products, sulphuric acid and methane sulphonic acid (Yin et al., 1990b,a), both of which can end up in the condensed phase (Kreidenweis et al., 1991). Local marine biogenic sources of sulphur in aerosol have been observed at various Arctic sites such as over the Arctic pack ice (Kerminen and Leck, 2001; Leck and Persson, 1996), at Alert, Canada (Li and Barrie, 1993a,b; Norman et al., 1999), at Ny-Ålesund, Spitsbergen (79° N, 12° E) (Heintzenberg and Leck, 1994) and at Barrow, USA (as summarised by Quinn et al., 2009). It has been proposed that in the Central Arctic Ocean, after the sulphur-containing particles have been lost to wet deposition (Nilsson and Leck, 2002), DMS oxidation products formed further over the pack ice condense on the locally produced organic particles formed from bubble bursting (Leck et al., 2002).

The physical and chemical properties of aerosol particles determine whether they can act as CCN and nucleate cloud droplets. As such, the particle sources and aging processes in the Arctic are important since they can affect their CCN-activity. Clouds at low- to mid-latitudes have a net cooling effect. At these locations, an increase in particle number concentration can result in an increase in the number of particles that act as CCN, leading to an increase in cloud droplet concentration and further cooling of the surface (Twomey, 1977). In the Arctic, however, because of high surface albedos and low levels of solar radiation, longwave emissions from clouds can dominate and the clouds instead warm the surface during most of the year (Shupe and Intrieri, 2004; Tjernström, 2005). Furthermore, for thin clouds under pristine conditions, as often found in the Arctic, increased particle concentrations due to pollution can lead to clouds that increase surface warming from longwave emission (Garrett et al., 2002; Garrett and Zhao, 2006; Mauritsen et al., 2011). Whether Arctic clouds have a net warming or cooling effect depends on the time of year and location (Garrett et al., 2002; Garrett and Zhao, 2006; Lubin and Vogelmann, 2007; Sedlar et al., 2011; Shupe and Intrieri, 2004; Tjernström, 2005; Wang and Key, 2003). As such, it is important that cloud forcing, formation and dispersion are well understood such that the effects of future increases in temperature and particle concentration on Arctic low-level clouds and their effects on polar climate can be projected.

This paper presents measurements of aerosol chemical composition made in the Central Arctic Ocean and uses them to elucidate information about aerosol sources to contribute to our understanding of low-level cloud formation over the pack ice. Measurements were made with an aerosol mass spectrometer (AMS), which quantifies chemical composition of the submicron non-refractory component at high time-resolution from mass spectra. This expands on previous studies in the high Arctic and Central Arctic Ocean which relied on filter or impactor measurements collected over hours to weeks (e.g. Hillamo et al., 2001; Li and Barrie, 1993a; Xie et al., 2006), and which do not measure the organic component. Although surface AMS measurements have been made at Eureka, Canada (80° N, 86° W) (Kuhn et al., 2010), this site is primarily influenced by the free troposphere and to our knowledge, this is the first time that AMS measurements have been made in the boundary layer of the Central Arctic Ocean. These boundary layer data can also be compared to free tropospheric measurements made during other International Polar Year campaigns where biomass burning was found to dominate the aerosol loading (Brock et al., 2011).

These measurements were made as a part of the Arctic Summer Cloud Ocean Study (ASCOS), the overall purpose of which was to study the formation, structure, and dispersion of low-level stratiform clouds during the biologically-active period of the Central Arctic summer and transition to autumn freeze-up conditions. This question is multifaceted and the interdisciplinary team included meteorologists, oceanographers, atmospheric chemists, aerosol scientists and marine biologists. ASCOS continues observations made in the Central Arctic Ocean from IAOE-91, AOE-96 and AOE-2001.

2 Description of measurements

2.1 Arctic summer cloud ocean study

The ASCOS expedition (www.ascos.se) took place on the Swedish icebreaker *Oden* from 2 August to 9 September 2008 (day of year, DOY 215–253). The research cruise began at Longyearbyen on Spitsbergen, with an open water station (OW1) on 3 August 2008 00:00 to 12:00 UTC (DOY 216–216.5) (78.2° N, 7.5° E) followed by a 24 h station in the marginal ice zone (MIZ1) starting 4 August 2008 12:00 UTC (DOY 217.5) (79.9° N, 6.1° E). Afterwards, the ship headed north through the Arctic Ocean drifting pack ice as far as 87.4° N, 1.5° W on 12 August 2008 (DOY 225) when an ice camp was established on an ≈ 3 km × 6 km ice floe. The *Oden* drifted with the ice for 21 days and departed on 2 September 2008 (DOY 246) to return southwards. A second marginal ice zone station (MIZ2) took place 6 September 2008 09:00 UTC to 7 September 2008 04:00 UTC (DOY 250.4–251.2) (80.7° N, 8.9° E) immediately followed by a final 12 h open water station (OW2) ending 7 September 2008 16:00 UTC (DOY 251.7) (80.4° N, 10.1° E). All times are reported in co-ordinated universal time (UTC). Overall, the cruise ranged in location from 77.9° to 87.5° N and 11.1° W to 9.6° E. A map of the route with the ice drift magnified is shown in Fig. 1.

2.2 Aerosol mass spectrometer

A compact time-of-flight (C-ToF) aerosol mass spectrometer (Aerodyne Research Inc.) measured the submicron aerosol non-refractory chemical composition. The instrument was located in the aerosol container on the 4th deck of the *Oden* and sampled from an inlet with an impactor whose 50 % cutoff diameter was 10 µm (PM_{10}). The inlet was located ≈ 25 m above sea level and the total flow through this 9 cm inner diameter pipe was ≈ 1100 $\mathrm{l\,min^{-1}}$. This resulted in a residence time of < 1.4 s, while the secondary line from which the AMS sampled (10 mm OD × 7 m) had a residence time of < 4 s. Since the room temperature was at least 20 K warmer than ambient, the RH of the

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measured aerosol was assumed to be < 30 % throughout the study. The PM_{10} inlet was identical to the one used during IAOE-91, AOE-96 and AOE-2001 and details on its position and design on board the *Oden* are further described in Leck et al. (2001).

Particles enter the AMS through a 100 µm critical orifice at 2 torr and pass through a series of aerodynamic lenses which both focus the particles into a beam and accelerate them into a vacuum chamber. Particles impact on a resistively heated ceramic oven, which flash vapourises the non-refractory components of the aerosol at 870 K and 10^{-7} torr. The resulting gaseous compounds are ionised by electron impact (70 eV) and detected with a unit mass resolution time-of-flight mass spectrometer. The results presented here are for the average bulk aerosol composition, which was averaged over 5 min intervals. Further details on the general operation of the AMS can be found in the literature (Canagaratna et al., 2007; Drewnick et al., 2005; Jayne et al., 2000; Jimenez et al., 2003).

The fragmentation table, used to identify the different contributors to the mass spectrum, was modified from the standard table (Allan et al., 2004) according to Langley et al. (2010) to include methane sulphonate (MSA). Furthermore, the airbeam was corrected to the signal at mass-to-charge ratio (*m/z*) 40 due to non-linearities in the signal at *m/z* 28. An ionisation efficiency calibration with ammonium nitrate was performed at least once each week. The sample flow rate was $\approx 100\,\mathrm{cm^3\,s^{-1}}$ (STP) and was calibrated throughout the study with a bubble flow meter. Finally, a filter was put in line twice every day for blank measurements.

A collection efficiency of 0.6 ± 0.2 was used for the mass calculations to correct for particles that bounce in the vaporiser and are not measured. This was the average of values obtained by two methods. The first method compared the total mass measured by the AMS with mass calculated from the number distributions measured by a differential mobility particle sizer, also sampling from the PM_{10} inlet, and correcting them for transmission efficiencies in the AMS according to Liu et al. (2007). A collection efficiency of 0.4 gave the best agreement using this method, assuming that the density of sulphate, nitrate, MSA and organic are 1770, 1730, 1480 and 1500 $\mathrm{kg\,m^{-3}}$, respectively

(Weast et al., 1983; Kostenidou et al., 2007). The second approach compared the AMS measurements of sulphate and MSA with the submicron stages of cascade impactors (Chang et al., 2011), also on the PM_{10} inlet, which resulted in a collection efficiency of 0.8. Note that because the mass comparison between the AMS and the other instruments did not systematically change at any point during the study, the value of the collection efficiency does not affect the factor analysis presented below since only the relative values are important.

2.3 Proton-transfer-reaction time-of-flight mass spectrometer

DMS, toluene and benzene were measured using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF) built at Innsbruck University. The PTR-MS technique is a well-established method for fast online VOC analysis (Lindinger et al., 1998; de Gouw and Warneke, 2007) in the atmosphere. The instrument used in this study (employing a TOF-MS instead of a quadrupole mass analyser) was described in detail by Graus et al. (2010). The PTR-TOF was calibrated by applying a dynamically diluted VOC gas standard (Apel-Riemer Environmenal Inc); zero-calibrations were performed every 2–6 h using catalytically scrubbed air. The PTR-TOF co-sampled next to the aerosol inlet through a Teflon filter and a heated 6.4 mm Sulfinert® (Restek Performance Coating) tubing with a residence time of < 3 s. The PTR-TOF spectra were analysed as described by Graus et al. (2010) and Müller et al. (2010).

2.4 Radon 222

^{222}Rn is often used as a tracer for air that was in contact with land and was measured every hour on the 7th deck of the *Oden* using a US Department of Homeland Security, Environmental Measurements Laboratory instrument based on the in-growth and subsequent alpha counting of short-lived ^{222}Rn progeny. The sample air was pumped through a HEPA filter which removed all the radionuclides, including short-lived ^{222}Rn progeny attached to aerosol particles. However, ^{222}Rn, being a noble gas, passed through this filter. Next the air entered a 500 l delay chamber where part of the ^{222}Rn decayed to its short-lived daughter nuclides. These nuclides are heavy metals and were trapped by a second filter. The alpha particles emitted by the collected daughter nuclides were then counted with a scintillation detector (Hutter et al., 1995).

2.5 Lead 210

^{210}Pb is a radioactive decay product of ^{222}Rn and can be used to indicate the age of the air since it was last in contact with land. High-volume aerosol samples were collected onto glass fibre filters (Munktell MGA) on the 7th deck of the *Oden*. The sample air flow rate was $\approx 140\,\mathrm{m^3\,h^{-1}}$ and the sampling time 24 h. In the laboratory the exposed filters and the field blanks were assayed for ^{210}Pb six months after the sampling with an automatic alpha/beta analyser (Mattsson et al., 1996). ^{210}Pb activity content of the filters was calculated from the in-grown ^{210}Po activity which was assayed with alpha counting.

2.6 Positive matrix factorisation

Positive matrix factorisation (PMF) is a statistical model that uses weighted least-square fitting for factor analysis (Paatero, 1997; Paatero and Tapper, 1994). It uses a bilinear model $\mathbf{X} = \mathbf{GF} + \mathbf{E}$, where $\mathbf{X}$ is a matrix of the measured values, and $\mathbf{G}$ and $\mathbf{F}$ are matrices computed by the model and represent the scores and loading, respectively. For AMS data, each row in $\mathbf{X}$ is a mass spectrum measured at a given time, with the columns representing the signal at a given *m/z*. In this case, $\mathbf{G}$ represents the time series and $\mathbf{F}$ the profile mass spectrum for the p factors computed by the algorithm. $\mathbf{E}$ is the difference between the measured signal and that reconstructed by the product of $\mathbf{G}$ and $\mathbf{F}$ and is made up of the elements e_{ij}. The model adjusts $\mathbf{G}$ and $\mathbf{F}$ in order to reduce the object function (Q), where

$$Q = \sum_i \sum_j (e_{ij}/\sigma_{ij})^2, \quad (1)$$

and σ_{ij} is the uncertainty for each element in the matrix $\mathbf{X}$.

In continental regions, where the sources of inorganic aerosol are well understood, PMF is typically only performed on the organic aerosol mass spectrum (e.g. Lanz et al., 2007; Ulbrich et al., 2009a) in order to learn more about the sources and transformation processes of organic aerosol. However, in the Arctic, our understanding of both the inorganic and organic aerosol sources are limited. In particular, sulphate, which is an anthropogenic constituent in continental regions, also has a biogenic source in marine areas. PMF was performed on the entire aerosol mass spectrum in order to gain understanding on the sources and processes of the entire aerosol. This also allowed us to associate organic fractions to both anthropogenic and marine biogenic aerosol.

The PMF2 program (Paatero, 1997) was used to analyse these data in robust mode with an outlier distance of 4 and no model error. The PMF evaluation tool kit (PET) (Ulbrich et al., 2009a) was used to prepare the data and error, execute PMF and evaluate the results. The data matrix was calculated by taking the entire aerosol mass spectrum ("All") and subtracting species that were 1) not of interest (i.e. air and water) and 2) unreliable due to high background and low signal (i.e. chloride and ammonium). The error matrix (σ_{ij}) was calculated by adding in quadrature the errors calculated for the entire aerosol mass spectrum with those calculated for the subtracted species (Allan et al., 2003) and a minimum counting error of one ion was applied, as described by Ulbrich et al. (2009a). All of these calculations were done in nitrate equivalent mass. In total, 168 *m/z*, ranging from 13 to 200, were included in the analysis, with peaks removed due to known interference (e.g. 18, 28, 32); being constantly negative, which the algorithm would be unable to fit (e.g. 33, 34); or due to difficulty fitting (e.g. 35, 36).

2.7 FLEXPART

The study of air mass transport to the ship and identification of aerosol source regions was based on simulations with the Lagrangian particle dispersion model FLEXPART (Stohl et al., 1998, 2005) in backward mode. So-called retro-plumes (see Stohl et al., 2003) were initialised at hourly time intervals or when the ship had changed position by more than 0.2° longitude or latitude since the last calculation. The simulations are based on operational data from ECMWF with a horizontal resolution of 0.5° and a time resolution of 3 h. Each simulation consists of the trajectories of 60 000 "virtual" particles released in the volume of air sampled and tracked for 20 days backward in time. Stochastic fluctuations, obtained by solving Langevin equations, are superimposed on the grid-scale winds to represent transport by turbulent eddies (Stohl et al., 2005). A convection scheme is used to represent convective transport (Forster et al., 2007).

The backward simulations yield an emission sensitivity which is proportional to the residence times of the air parcels in a particular 3-D grid cell. It was calculated for a passive tracer and the value of this emission sensitivity is a measure for the simulated mixing ratio in the receptor volume that a source of unit strength in the respective grid cell would produce. The emission sensitivity of the passive tracer can also be used to display the transport history. By multiplying the emission sensitivity near the ground with an emission flux from an appropriate inventory, maps of source contributions are obtained, which can be used to identify pollution sources. Spatial integration of the source contributions yields the simulated mixing ratios of the passive and aerosol-like tracers along the ship track. For emission information, the EDGAR V3.2FT2000 anthropogenic emissions inventory (Olivier and Berdowski, 2001) was used outside of North America and Europe where regional emission information was used. Emissions from biomass burning were modelled as described by Stohl et al. (2007) using fire locations detected by the moderate-resolution imaging spectrometer (MODIS) on the Aqua and Terra satellites and a land-cover vegetation classification.

2.8 Contamination from research activities

Possible contamination events from local emissions (e.g. ship, helicopter, snowmobile) were determined by particle number concentrations measured by an ultrafine condensation particle counter, toluene mixing levels measured by the PTR-TOF, wind direction (contamination suspected if 70° to 290°, relative to the bow) and wind speed (contamination suspected if $<2\,\mathrm{m\,s^{-1}}$ or variable). These are excluded from the general AMS results presented below but included in the PMF analysis. This allowed the PMF algorithm to identify a Ship Emission factor and resulted in clearer separation between the factors than simply deleting suspected contamination times. However, in order to avoid these contamination events from overweighting the solutions, times when the total AMS mass exceeded $1\,\mu\mathrm{g\,m^{-3}}$ were removed.

3 Results and discussion

3.1 General AMS results

Mass concentrations for the non-refractory components of aerosol measured by the AMS are shown in Fig. 2, with the shaded areas showing the times of the stations. These data have been corrected to STP using room temperature and pressure measurements. Table 1 shows basic descriptive statistics for the study as well as median values for the stations during which the AMS measured. Due to technical difficulties, the AMS was not operational during OW1. Detection limits were calculated for each blank filter measurement as 3 times the standard deviation for each constituent, and the average of these values was used as the detection limit for the entire campaign. These are also included in Table 1. Ammonium is not included since it was below its detection limit of $0.03\,\mu\mathrm{g\,m^{-3}}$ 86 % of the time.

On average, sulphate and organics contributed 45 and 43 % of the aerosol mass detected by the AMS, respectively, with an average MSA contribution of 8 %. The values for sulphate reported in this study are of non-sea salt sulphate, since sodium sulphate, found in sea salt, has a melting point of 1150 K (Weast et al., 1983) and would be refractory (i.e. undetected) in the AMS. In addition, submicron sea salt sulphate concentrations were negligible (Chang et al., 2011), consistent with past studies in the pack ice (e.g. Leck and Persson, 1996). The range of sulphate ($\leq 0.35\,\mu g\,m^{-3}$) and MSA ($\leq 0.07\,\mu g\,m^{-3}$) in this study is generally in agreement with values measured at Alert, Canada which ranged from 0.03–0.22 $\mu g\,m^{-3}$ for summertime sulphate (Norman et al., 1999) and 0.03–0.05 for MSA in August (Li and Barrie, 1993a); Ny-Ålesund, Spitsbergen, which averaged to 0.39 and 0.018 $\mu g\,m^{-3}$ for summertime sulphate and MSA, respectively (Heintzenberg and Leck, 1994); the Antarctic, which ranged up to 0.1 and 0.0001 to 0.065 $\mu g\,m^{-3}$ in the summer at Palmer Station for sulphate and MSA, respectively (Berresheim et al., 1998); and average values of 0.075 and 0.042 $\mu g\,m^{-3}$ at Halley Station in the summer, for non-sea salt sulphate and MSA, respectively (Read et al., 2008). They are also consistent with previous Central Arctic Ocean measurements, 0.0027–0.66 $\mu g\,m^{-3}$ and 0.0002–0.13 for sulphate and MSA, respectively, during IAOE-91 (Leck and Persson, 1996) and 0.0036–1.2 $\mu g\,m^{-3}$ and 0.002–0.10 for sulphate and MSA, respectively, during AOE-96 (Kerminen and Leck, 2001). These values are summarised in Table 2.

In general, the two MIZ stations had higher aerosol loadings in all constituents than both the IF and OW2 stations, consistent with past Arctic Ocean expeditions (Nilsson and Leck, 2002). Aerosol MSA mass was measured during the MIZ2 station at the beginning of September, suggesting that marine biology was still active at this time. Care should be taken in interpreting statistics from the non-ice floe stations since the sampling time at the two MIZ stations and the OW station were limited to ≈ 3 % and 1 % of the total sampling time, respectively.

3.2 PMF results

A four-factor solution was chosen to best represent the variations in the aerosol mass for this data set. The time series and profiles of the factors are shown in Figs. 3 and 4, respectively. In this solution, there are three ambient factors that describe the background air in the Central Arctic Ocean: a Marine Biogenic factor, a Continental factor, and an Organic factor. In addition, a fourth factor describes emissions from contamination. These factors will be described in more detail in subsequent sections.

Finding the best PMF solution for a data set can be subjective. The number of factors in the solution, the robustness of these factors, and rotational ambiguities, all affect how well the variations are represented. The rotational ambiguities will be discussed here, while the details describing other solutions and robustness can be found in the Supplement.

Rotational ambiguity in PMF solutions can be explored by varying the *fPeak* parameter. In this analysis, because the entire mass spectrum is used and because there are few external time traces with which to corroborate the time series for a certain PMF solution, the best *fPeak* can be difficult to determine. Instead, a range of *fPeak* values (−1.5 to 0) was found to give physically reasonable mass spectra and time series, while remaining reasonably robust. As such, the results shown here are for an *fPeak* of −0.75, with the minimum and maximum of this range included to show uncertainties in the solution. In general, this uncertainty was greater than that from the robustness runs, and is considered to be more representative of the overall uncertainties.

The composition of the factors was determined by applying the fragmentation table to the profile mass spectrum of each factor. Values for an *fPeak* of −0.75 are shown in Table 3, and the range due to changes in fPeak from −1.5 to 0 can be found in the Supplement. This calculation was corrected for the relative ionisation efficiencies of the different species but not to STP or for collection efficiency. It also assumes that there are no other components in the aerosol besides organics, sulphate, MSA and nitrate, and does not account for any organonitrogen or organosulphur compounds that may be present. The overall contribution of each factor, excluding the Ship Emission factor, is also given in Table 3. We see that the three ambient factors contributed approximately equally throughout the study. The next sections describe the characteristics of each factor.

3.2.1 Marine Biogenic factor

This factor was dominated by sulphate peaks (*m/z* 48, 64, 80, 81, 98) as well as MSA peaks (*m/z* 79 and 96). Since MSA is only significantly formed via the photo-oxidation of DMS, which mainly originates from biological activity (Chin et al., 1996), and 71 % of the MSA mass was found in this factor, it was attributed to marine biogenic sources. The time series correlates to some degree with that of DMS (see Fig. 5), but it improves if we exclude the last week of the study when the *Oden* neared the marginal ice zone and open waters ($r = 0.36$, inset of Fig. 5). It is not to be expected that the particulate and gas phase products of biological activity correlate very tightly since DMS is a precursor for both sulphate and MSA and the loss processes over the pack ice are expected to be slower for gases ($\tau \approx 3$ d) than particles ($\tau \approx 1$ d) (Nilsson and Leck, 2002). While the concentration of DMS and its oxidation product SO_2 behave similarly on a seasonal and synoptic time scale, correlation on shorter time scales is not necessarily expected (Kerminen and Leck, 2001). Furthermore, previous studies in the Antarctic have found no correlation between DMS and its oxidation products (Berresheim et al., 1998; Read et al., 2008). We speculate that the measured air passed over productive waters that had both gas phase DMS and intermediate species which eventually oxidised to MSA and sulphate by the time they reached the measurement site, but that DMS had insufficient time to entirely react away. This is consistent with DMS concentrations increasing in the last week of the study while the time trace of the Marine Biogenic factor only increases slightly. As the *Oden* neared the open water source region, the particulate MSA and sulphate would not have had enough time to form from recent DMS emissions (Karl et al., 2007; Kerminen and Leck, 2001).

In particular, analysis of 10 and 11 August (DOY 223, 224) showed that the air had passed over the open ocean ≈ 1 d before reaching the *Oden*. Figure 6 shows the footprint potential emission sensitivity from FLEXPART for 11 August (DOY 224) and suggests that the air originated from the Barents sea, which, during August 2008, was ice free and biologically productive (up to 3 mg of chlorophyll-*a* m^{-3} Feldman and McClain, 2008). This was generalised using potential source contribution function (PSCF) analysis for this factor (Fig. S4 in the Supplement), which shows that this factor was high when the air originated from the Barents and Kara Seas.

The MSA/SO_4^{2-} mole ratio calculated from the Marine Biogenic factor was 0.25 ± 0.02, with the uncertainties calculated from changes in the PMF *fPeak*. Although this ratio has been observed to be dependent on temperature (Bates et al., 1992), Table 2 shows that our value is similar to other summertime values measured in polar regions such as that calculated from submicron filter measurements during IAOE-91 (Leck and Persson, 1996) for marine biogenic times, excluding the influence of fog (0.22). It is also within the lower bounds of uncertainty found by Norman et al. (1999) for Alert, Canada in July and August of 1993 and 1994 (0.39 ± 0.21), although lower than the 10 year record reported by Li and Barrie (1993a) in August also at Alert (0.6 ± 0.3). Finally, it is within the range of values calculated from a box model for conditions from AOE-96 (0.32 mean, Karl et al., 2007), although lower than that predicted by a chemical transport model (0.38–0.65, Gondwe et al., 2004). Higher MSA/SO_4^{2-} ratios have previously been observed in the coarse mode compared to the fine mode in the Antarctic (Jefferson et al., 1998; Read et al., 2008) and in the Pacific (Phinney et al., 2006), which is thought to occur because sulphuric acid nucleates to form the smaller particles, causing methane sulphonic acid, a weaker acid to condense on the neutral coarse mode aerosol (Jefferson et al., 1998). This would be consistent with the higher ratios measured at Alert, which are of total suspended particles, whereas our measurements are for submicron particles. However, some Arctic measurements do not see a size-dependent MSA/SO_4^{2-} (Leck and Persson, 1996). Approximately 50 % of the total sulphate mass was apportioned to this factor, with the remaining 50 %

apportioned to the Continental factor.

It is interesting to note that the Marine Biogenic aerosol had an organic component that was approximately equal in mass to the amount of MSA in the aerosol. Based on this analysis alone, it is unclear whether this organic component is formed from secondary processes (e.g. oxidation of isoprene emitted from phytoplankton) or whether it is emitted directly from the ocean through a mechanism such as bubble bursting. The degree of oxygenation of the organic component of this factor is quite variable, with the fraction of the organic signal at *m/z* 44 (F44) ranging from 0–0.12, depending on the *fPeak* used. Although at continental sites a higher F44 is interpreted as an organic component formed from secondary processes, it is possible that in polar marine environments, this organic mass is emitted as a primary aerosol that is already oxygenated, such as a mono or polysaccharide (Leck and Bigg, 2007; Russell et al., 2010).

3.2.2 Continental factor

The main feature of the time series of this factor is high signal between 26–30 August (DOY 239–243, see Fig. 3) which accounted for $\approx 1/3$ of the entire mass of this factor. This was a period of high pressure and possible mixing from aloft (M. Shupe, personal communication) that coincided with transported air influenced by continental combustion and high particle masses. As seen in Fig. 7, the time series correlates with the ^{210}Pb signal ($r = 0.66$), which is a radioactive decay product of ^{222}Rn, lending strong support that the air originated from a continental source. Furthermore, the composition of this factor, 60 % sulphate and 35 % organic (see Table 3), is similar to typical aerosol measured in continental regions (Zhang et al., 2007). Finally, this factor contains only 3 % MSA, suggesting that it was uninfluenced by marine sources.

There was little correlation between the time series of this factor and ^{222}Rn ($r = -0.05$, data not shown), which has a half-life of approximately 3.8 days (Weast et al., 1983), suggesting that this factor represents air that had not been in contact with land for at least a week. The organic component of this factor is aged, with an F44 of 0.25, which is comparable to the largest value previously reported (Ng et al., 2010), consistent with aerosol that has been extensively oxidised in the atmosphere with a long residence time. In sum, this factor is consistent with very aged continentally-influenced air that has been transported to the Central Arctic in the summer.

3.2.3 Organic factor

This factor was thus named because it is 71–88 % organic. It is robust, being present in the factor solution when there are at least three factors. However, it does not correlate with any measured external tracers, making its source difficult to identify. The mass spectrum of the entire factor, and in particular the organic component (Fig. 8), resembles that of oxygenated organic aerosol (OOA) often found from factor analysis of organic aerosol at continental sites (see Sect. 3.3 for comparisons). OOA typically forms from the chemical aging of gaseous emissions originating from anthropogenic sources (e.g. Ng et al., 2010; Zhang et al., 2007), biogenic sources (e.g. Chen et al., 2009; Slowik et al., 2010) as well as aging of biomass burning aerosol (Capes et al., 2008). In particular, based on the time series of the CO fire tracer from FLEXPART, the signal at the end of the study (4–6 September, DOY 248–250) measured as the ship approached the MIZ was likely due to biomass burning in Europe (see Fig. 9, which illustrates the modelled contribution of biomass burning to the air sampled on 4 September). The agreement is not as good for the remainder of the study, suggesting that this factor does not uniquely represent biomass burning but instead also includes background organic aerosol from a variety of sources that was transported to the Arctic whose original sources can no longer be separated. Similar to the discussion in Sect. 3.2.1, it is also possible that some of this aerosol was emitted directly from the ocean as an oxygenated organic compound and transferred to the atmosphere through processes such as bubble bursting. Similar to the FLEXPART results, PSCF analysis also shows contribution from Northern Europe in addition to contribution from west of the Queen Elizabeth Islands, north of the Beaufort Sea, as well as the area around the Kara Sea (see Fig. S4). Overall, this factor has very little inorganic component, demonstrating that there is a source of Arctic organic aerosol that is not associated with sulphate. The organic component of this factor is fairly oxidised, with an F44 of 0.17, and will be further discussed in Sect. 3.3.

3.2.4 Ship Emission factor

The time series for this factor is characterised by low signals for most of this campaign with intermittent periods of high loading which coincide with times when the pollution record, comprised of toluene, benzene and particle concentrations, indicated that the air was at risk of being contaminated by ship exhaust. The mass spectrum qualitatively resembles that of ship fumigation periods measured by Phinney et al. (2006), as well as hydrocarbon-like organic aerosol from urban sites ($r \geq 0.93$) (Lanz et al., 2007; Ulbrich et al., 2009b; Zhang et al., 2005b) which are thought to be primary aerosol emitted from vehicular traffic and whose mass spectra are similar to that of lubricating oil ($r = 0.98$) (Canagaratna et al., 2004; Ulbrich et al., 2009b). This factor helped identify when the aerosol was affected by ship emissions and by excluding it, allows us to consider the ambient Central Arctic Ocean aerosol without interference. There are some spikes in the Continental and Organic factors that coincide with signal in the Ship Emission factor, showing that the separation between these factors was not perfect. However, given that the signal of the Ship Emission factor was at times 20 times greater than the signal from the ambient factors, the spikes are < 2 % of the mass in either of these factors, and the structure of the time series is still distinct, the impact on the ambient factors was considered insignificant.

3.3 Discussion of organic component

To summarise the nature of the organic aerosol sampled, Fig. 8 shows the organic mass spectra of the four factors. The Continental and Organic factors resemble that of the OOA factor found at continental urban sites (Ulbrich et al., 2009b; Zhang et al., 2005a) (r of 0.73 and 0.85, respectively). They also qualitatively resemble the mass spectrum of aged biomass burning aerosol (Capes et al., 2008). As shown in Table 3, these organic fractions appear quite aged compared to measurements made at continental sites (Ng et al., 2010), with an F44 of 0.25 and 0.17, respectively, corresponding to an atomic oxygen to carbon ratio (O/C) of 1.1 and 0.7, using the relationship in Aiken et al. (2008). Care should be taken in interpreting these numbers, since the fragmentation table is normally applied to a full mass spectrum and not to a PMF factor profile. Nevertheless, the degree of oxygenation of the Continental factor appears to be comparable to the most aged continental aerosol observed (Ng et al., 2010) and is consistent with it being the most aged out of all the factors found in this study.

The organic component of the Marine Biogenic factor also resembles that of OOA from continental urban sites (r of 0.62 Ulbrich et al., 2009b; Zhang et al., 2005a). Although F44 is quite variable depending on the *fPeak* of the solution (see Supplement), it is lower than those of the other factors, suggesting that it is different than the organics found in the other two ambient factors. If the organics in the Marine Biogenic factor were indeed formed from secondary processes, then they would be the least aged of the ambient aerosol observed.

The average F44 for the entire study, as calculated from the bulk mass spectrum, was 0.18 ± 0.05. PMF was also performed on only the organic mass spectrum and compared to the solutions from the entire mass spectrum. However, because the organic components of the ambient factors tend to resemble OOA, the results did not yield as much information and the solution is generally in agreement with the results from PMF of the entire mass spectrum.

4 Conclusions

From 5 August to 8 September 2008, non-refractory submicron aerosol particles in the Central Arctic Ocean were composed of approximately equal amounts of organic and sulphate components. These particles were influenced by both marine biogenic and continental sources (33 % and 36 % of the sampled ambient aerosol mass, respectively), as determined using PMF. Aerosol from both of these sources were predominantly composed of sulphate, and 47 % of the total sulphate was apportioned to marine biogenic sources while 48 % was apportioned to continental sources. There also appears to be aerosol that was almost purely organic (31 % of the sampled ambient aerosol mass), although it was not possible to identify a single source for this aerosol at this time. These results show that up to 1/3 to 2/3 of the Arctic submicron aerosol mass is formed from marine sources in the Central Arctic basin including the pack ice, MIZ and surrounding open ocean, and that Arctic models that only include aerosol transport from anthropogenic sources could be neglecting a significant mass. These findings can be contrasted to the Arctic free troposphere which at times can be heavily influenced by biomass burning (Brock et al., 2011).

In general, the organic components of all ambient aerosol measured were as oxidised as, if not more than, the OOA component from ground-based continental sites. The organic component of air influenced by continental sources was also found to be more oxidised than that of marine biogenic sources. This is consistent with long range transport of these particles. Although the degree of oxygenation of the organic component of the Marine Biogenic and Organic factors would normally be interpreted as being atmospherically processed, it is possible that in polar marine environments, primary oxygenated organic aerosol particles are emitted directly into the atmosphere, as suggested by previous findings over the pack ice (Leck and Bigg, 2005). In contrast to previous analyses of AMS observations, this study used PMF on the entire mass spectrum, which allowed the inorganics from different sources to be separated, along with their associated organic component.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/14837/2011/ acpd-11-14837-2011-supplement.pdf.

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Table 1. 1st, 2nd and 3rd quartiles of AMS measurements, median concentrations for the four stations (see text) and detection limits. All units in µg m^{-3}.

	Q_1	Q_2	Q_3	MIZ1	IF	MIZ2	OW2	Det. Lim.
Organic	0.015	0.046	0.081	0.11	0.036	0.087	0.036	0.02
Sulphate	0.016	0.042	0.082	0.070	0.037	0.099	0.050	0.006
MSA	0.0031	0.0069	0.012	0.016	0.006	0.015	0.008	0.008
Nitrate	0.0019	0.0036	0.0060	0.005	0.003	0.008	0.005	0.006

Table 2. Summertime sulphate and MSA concentrations at various polar locations.

Location or study	Sulphate ($\mu g m^{-3}$)	MSA ($\mu g m^{-3}$)	MSA/SO_4^{2-} (mol/mol)	Reference
IAOE-91	0.0027–0.66	0.0002–0.13	0.22	Leck and Persson (1996)
AOE-96	0.0036–1.185	0.002–0.104		Kerminen and Leck (2001)
Alert, Canada		0.03–0.05	0.6 ± 0.3	Li and Barrie (1993a)
	0.03–0.22		0.39 ± 0.21	Norman et al. (1999)
Ny-Ålesund, Spitsburgen	0.39	0.018		Heintzenberg and Leck (1994)
Palmer Station	≤ 0.1	0.0001–0.065	0.61	Berresheim et al. (1998)
Halley Station	0.075	0.042	0.65 ± 0.13	Read et al. (2008)
ASCOS	≤ 0.35	≤ 0.07	0.25 ± 0.02	This study

Table 3. Composition and % contribution of factors by mass from the four-factor solution for an *fPeak* of −0.75. See Figs. S2 and S3 for uncertainties. O/C calculated using the equation from Aiken et al. (2008).

	F1:Marine Biogenic	F2: Continental	F3: Organic	F4: Ship Emission
Organic (%)	15	35	88	97
Sulphate (%)	65	60	5	1
MSA (%)	16	3	3	2
Nitrate (%)	4	2	5	< 1
F44	0.09	0.25	0.17	< 0.01
O/C	0.42	1.1	0.71	< 0.08
% of ambient air	33	36	31	–

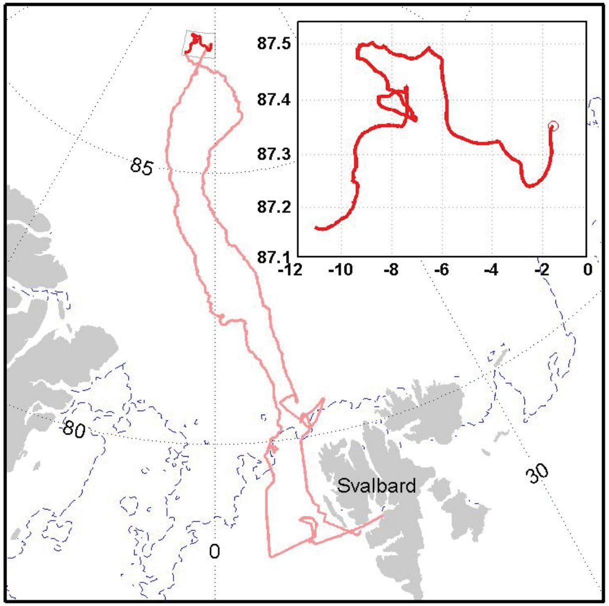

Fig. 1. Map of the ASCOS cruise track (pink) with ice-drift period highlighted (red) and shown in detail with the start of the drift marked by the circle (inset). The ice edge for the start of the drift period on 12 August 2008 is shown in the dashed blue line (courtesy of I. Brooks).

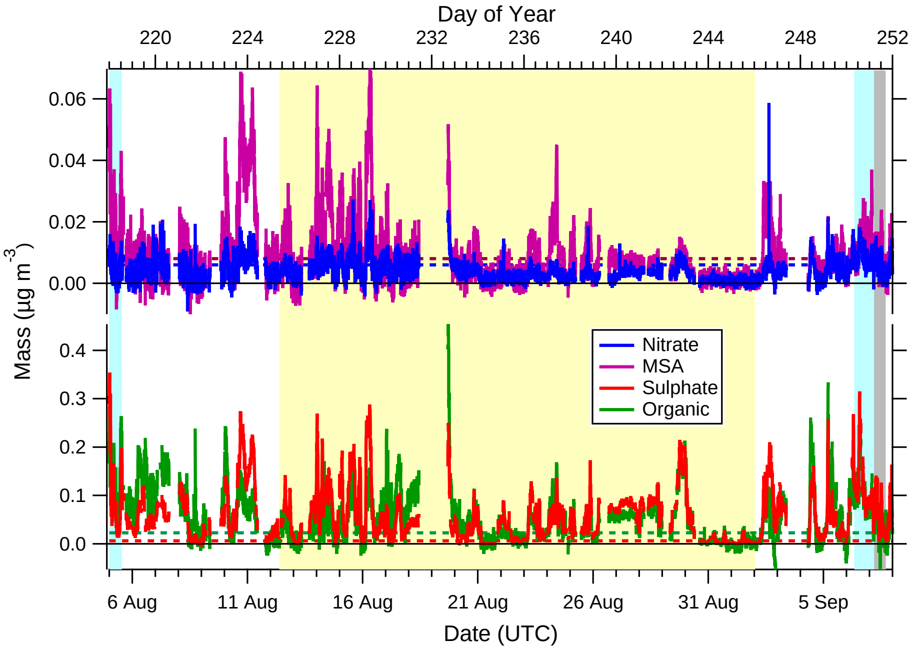

Fig. 2. Organic, sulphate, methane sulphonate (MSA) and nitrate mass concentrations (solid lines) and detection limits (dashed lines) during ASCOS. Blue, yellow and gray regions represent marginal ice zone (MIZ), ice floe (IF) and open water stations (OW), respectively.

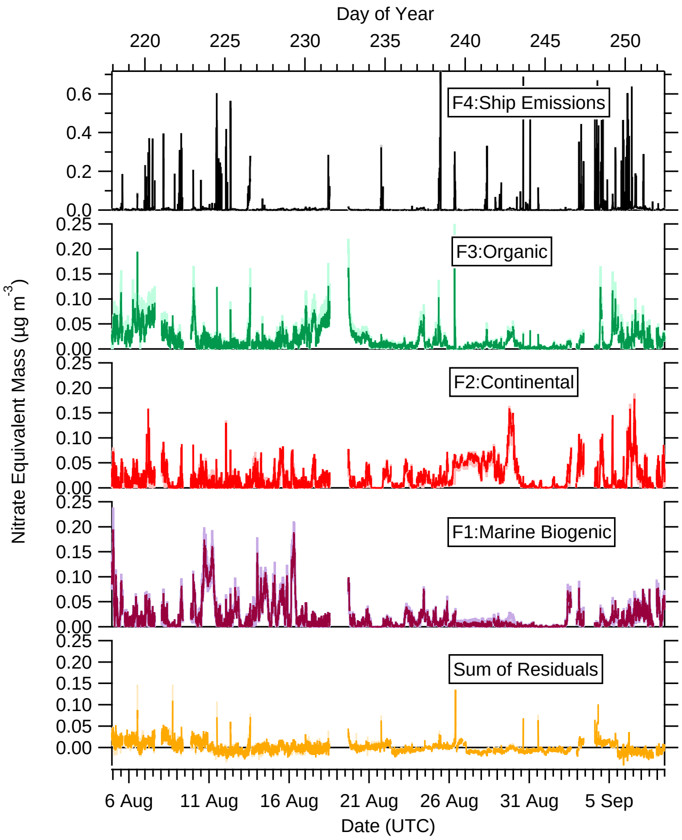

Fig. 3. Time series of the PMF factors. The solid trace is the solution for an *fPeak* of −0.75 and the shaded regions the range for *fPeaks* of −1.5 to 0.

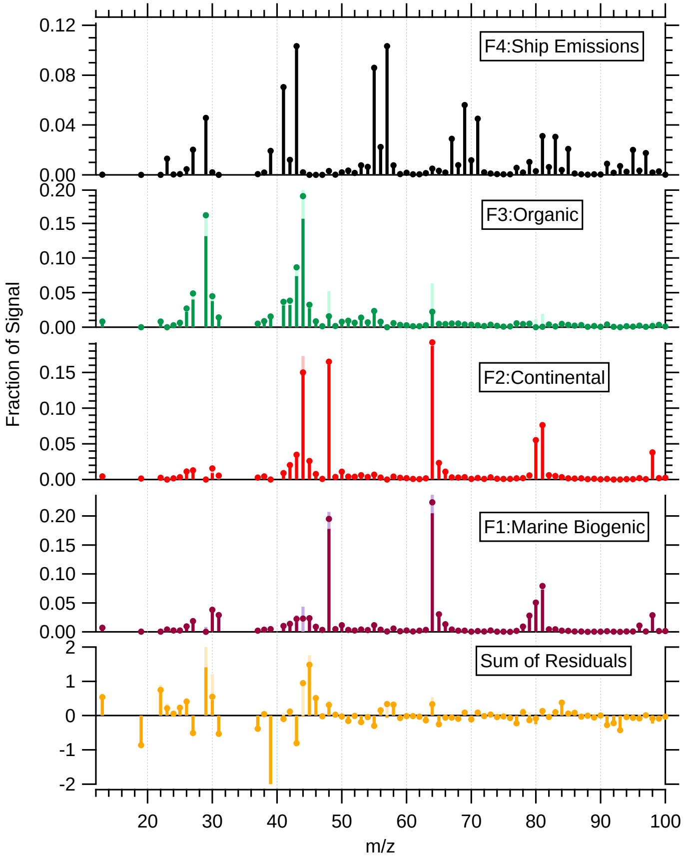

Fig. 4. Mass spectra of the PMF factors. The circle represents the solution for an *fPeak* of −0.75, and the light and solid bars the range for *fPeaks* of −1.5 to 0. The signal is adjusted so that the sum of the signal for each mass spectrum is one.

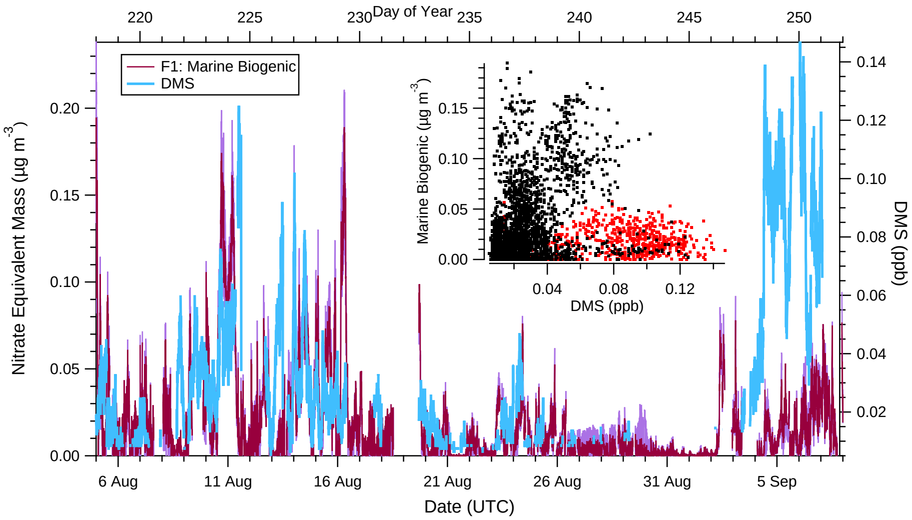

Fig. 5. Time series of the Marine Biogenic factor and DMS. The inset is a scatter plot of these two quantities excluding (black) and including (red) the last week of the study.

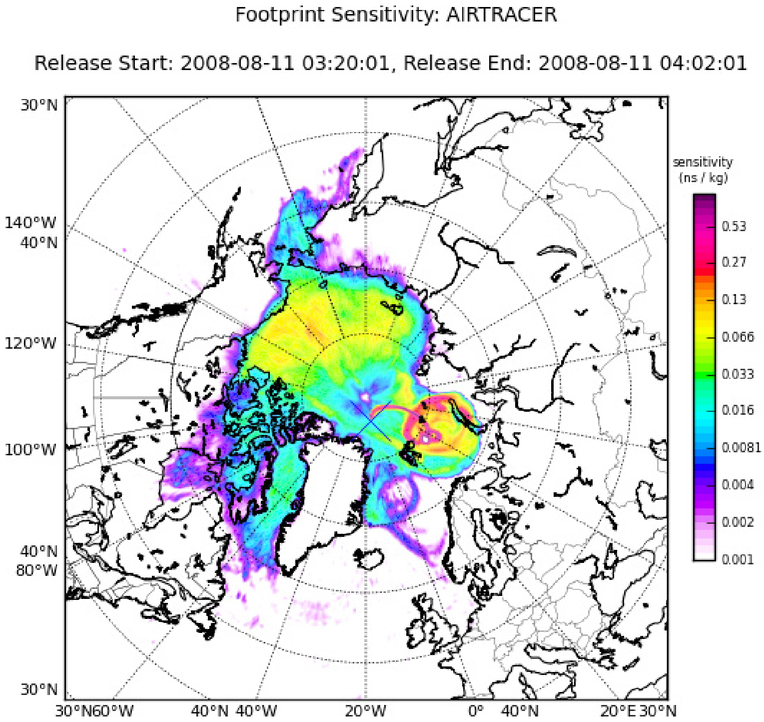

Fig. 6. FLEXPART modelled footprint potential emission sensitivity for 11 August 2008 03:20 UTC (DOY 224.14). The *Oden*'s position is marked by the blue cross and the sensitivity shows that the air was influenced by the Barents sea.

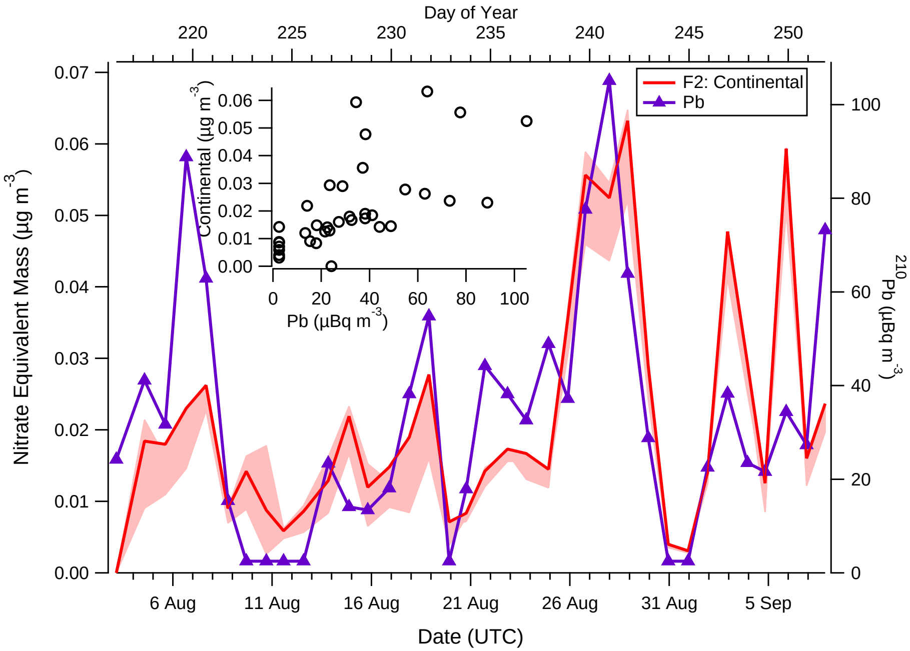

Fig. 7. Time series of the Continental factor and ^{210}Pb. Inset shows scatterplot of these two quantities.

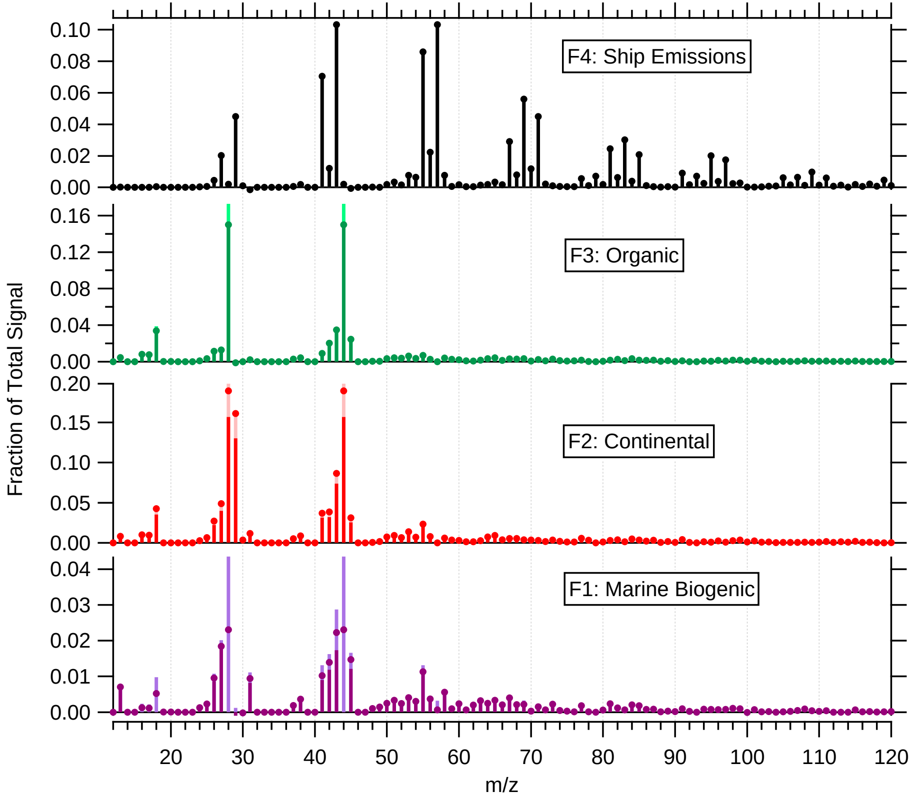

Fig. 8. Mass spectra of the organic components of the PMF factors. The circle represents the solution for an *fPeak* of −0.75, and the light and solid bars the range for *fPeak*s of −1.5 and 0. The signal is adjusted so that the sum of the entire signal for each mass spectrum, not only the organics, is one.

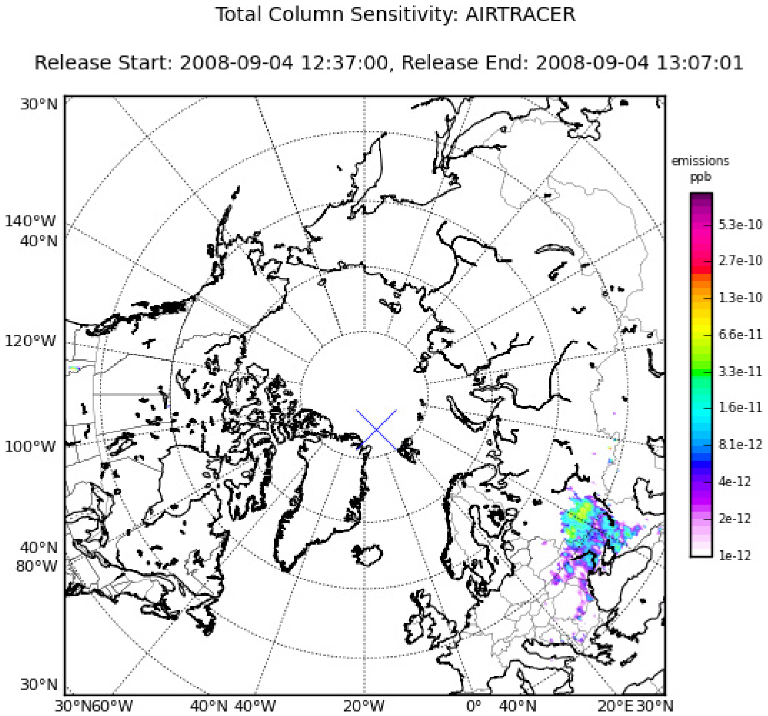

Fig. 9. CO from biomass burning arriving at the ship on 4 September 2008 12:37 (DOY 248.5) as modelled by FLEXPART.