**Atmospheric
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Discussions**

Source apportionment of particles at Station Nord, North East Greenland during 2008–2010 using COPREM and PMF analysis

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Abstract

In order to develop strategies for controlling and reducing Arctic air pollution, there is a need to understand the basic mechanisms for determining the fate of air pollution in the Arctic. Sources of atmospheric particles at Station Nord (81°36′ N, 16°40′ W) in North East Greenland were evaluated for a two-year period from March 2008 to February 2010. Source apportionment using Positive Matrix Factorization (PMF) and COnstrained Physical Receptor Model (COPREM) was based on measurements of black carbon, elements (Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Zr, Pb) and inorganic ions (SO_2, SO_4^{2-}, Na^+, NH_4^+, NO_3^-, Cl^-). In general, source apportionment results by PMF and COPREM showed good agreement. Five sources adequately explained the measurements, which included a *Marine* and a *Soil* source of natural origin and three additional anthropogenic sources, which were all influenced by metal industries. One anthropogenic source was dominated by Zn of which air mass back trajectories using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model suggested a Canadian Arctic origin, despite certain influences from southern and eastern origins. Another anthropogenic source was characterised by high concentrations of Pb and As, which has been historically referred to as a *Combustion* source at Station Nord. The impacts of large-scale industry in Siberia, Russia were evident through high Cu concentrations in both the *Combustion* source and an additional Cu/Ni source.

Br correlated well with the anthropogenic species S and Pb though the elements are unlikely to have a common origin. More likely, sulphuric acid aerosols serve as transport containers for Br species of marine or local origin. Of particular relevance to climate, sources of black carbon were identified to be mainly anthropogenic and most probably of Siberian origin (80–98 %).

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1 Introduction

The global temperature increase has been primarily well-attributed to anthropogenic emissions of carbon dioxide. However, the temperature in the Arctic has increased at a rate twice as high as the rest of the world (IPCC, 2007), which has been partly explained by the compositional change of short-lived pollutants including methane, tropospheric ozone and black carbon (Quinn et al., 2008; ACIA, 2004). Black carbon (BC) contributes significantly to Arctic warming through direct absorption of incoming light and indirectly by reducing the albedo of especially snow and ice-covered surfaces (Hansen and Nazarenko, 2004; Flanner et al., 2007, 2009).

Investigations over the past decades have shown that a considerable part of Greenlandic, Norwegian, Russian, Northern USA and Canadian Arctic troposphere is significantly influenced by atmospheric pollution of distant latitude origin (Heidam et al., 1999, 2004; Flyger et al., 1980; Barrie et al., 1981; Pacyna et al., 1984; Bourgeois and Bey, 2011). The phenomenon which is known as Arctic haze is widespread throughout the Arctic during wintertime. Most notable identified sources include the industrial and other anthropogenic activities in the Eurasian region, particularly Northern Russia, Central Europe and North America (Heidam et al., 1999; Shindell et al., 2008; Bourgeois and Bey, 2011). Arctic haze aerosols contain a mixture of sulphate (SO_4^{2-}), organic matter (OM), BC and dust, nitrogen compounds, heavy metals and other elements (e.g. Li and Barrie, 1993; Quinn et al., 2002). The Arctic haze phenomenon results in a typical annual variation with elevated concentrations of such elements during Arctic winter while removal by deposition is slow (Quinn et al., 2007; Heidam et al., 1999, 2004; Barrie et al., 1981). Arctic haze may also generally add to the warming trend of the Arctic through its potential to absorb thermal infrared radiation and also incoming solar radiation when present on top of snow and ice-covered surfaces.

During the Arctic haze phenomenon, the air in the Arctic lower troposphere is partially isolated from other layers of the atmosphere by the so-called "Arctic Front" barrier, resulting in low potential temperatures at the ground surface (Klonecki et al., 2003;

Stohl, 2006). A transported polluted air mass originating from outside the Arctic must have a similar low potential temperature (Barrie, 1986; Carlson, 1981; Iversen, 1984; Quinn et al., 2011; Stohl, 2006), which thus emphasizes relatively colder regions such as Northern Eurasia as a major mid-latitude pollution source region in comparison to

5 other regions further south where the air masses are too warm to reach the Arctic lower troposphere (Barrie, 1986; Eckhardt et al., 2003; Heidam et al., 2004; Klonecki et al., 2003).

Emissions from sources within the Arctic must also be considered to obtain a complete picture of the particle burden in this region. The non-ferrous metal smelters on the

10 Kola Peninsula (Nikel, Monchegorsk and Zapolyarnyy) and Norilsk in Northern Siberia were identified as major sources of anthropogenic pollution within the Arctic (Heidam et al., 1999, 2004; Christensen, 1997) in addition to other anthropogenic emissions from the industrial sector, power generation and transport activities in the Arctic cities of Russia. Furthermore, there are also direct and indirect emissions resulting from ex-

15 ploitation of oil and gas in the region (Gautier et al., 2009) as well as ship emissions including cargo transport, tourist cruise and fishing vessels (Odemark et al., 2012).

In order to develop strategies for controlling and reducing Arctic air pollution, there is a need to understand the basic mechanisms for determining the fate of Arctic air pollution, such as long-range transport, transformation of gaseous and particulate species

20 and their partitioning between the gas and particle phase. In addition, the nature and source origin of anthropogenic compounds contributing to Arctic air pollution must be investigated. This study presents analyses of data from 2008–2010 at the high Arctic site Station Nord in North East Greenland using two statistical receptor models; Positive Matrix Factorization (PMF) and the COnstrained Physical REceptor Model

25 (COPREM). The measured concentrations can be considered as a remote indicator from which the average emissions of a massive emission region in the eastern part of Europe and Russia can be followed (Heidam et al., 2004).

2 Methods

2.1 Measurement site

The measurement hut "Flygers Hut" at Station Nord (81°36′ N, 16°40′ W, 30 m a.s.l.)
is located 2.5 km south east of the Danish military Station at North East Greenland
(Fig. 1). At this latitude, the polar day prevails from mid-April to the beginning of
September, and the polar night lasts from mid-October to the end of February. Fly-
gers Hut is the main site for the Danish contribution to the atmospheric part of the
Arctic Monitoring and Assessment Programme (AMAP). It is supplied by electricity
from a local JET A-1 fuel generator at Station Nord. The location was selected due to
the insignificant contribution from local air pollution and has been described elsewhere
(Skov et al., 2004). Only a few episodes of waste burning from the military camp were
identified to influence the measurements in the summertime (Heidam et al., 2004).
Measurements at Station Nord have been conducted since 1990 and since 1994 as
part of the official AMAP programme. The local wind is dominated by south west direc-
tions, with highest wind velocities originating from north west and south west (Fig. 2).
The analysis is based upon one year wind data obtained from a sonic anemometer
(METEK, USA-1, heated) from 31 May 2011 to 1 June 2012, but the data coverage is
less in the winter month due to frost on the anemometer. An analysis of winter data
(November–March), however, also reveals dominating south-westerly winds (Fig. 2).
The wind flow is probably influenced by regional topography with katabatic winds from
the ice caps flowing out along the fjord located south west of Station Nord.

2.2 Instrumentation

At Station Nord, a comprehensive list of different compounds is measured and de-
scribed elsewhere (Heidam et al., 2004). Additionally, a custom-built Particle Soot
Absorption Photometer (PSAP) was set up in 2008 to measure black carbon mass
concentrations based on measurements of the absorption coefficient of the ambient

aerosol. While the calibration of the PSAP is on-going, a preliminary specific absorption coefficient is applied in the present study. The specific absorption coefficient was found via a comparison between the PSAP and Elemental Carbon (EC) measurements in field at Station Nord.

Filter pack sampler (FPS) collects total suspended particles with an approximate cut-off diameter of 20 µm depending on wind speed. The sampler consists of a sequence of 3 filters, of which the first collects particulate matters. The subsequent filters are impregnated to collect specific gases, notably SO_2. The particle filters are analysed for the sulphate (SO_4^{2-})-, ammonium (NH_4^+)- and nitrate (NO_3^-)- ions by ion chromatography. Elements with atom number higher than Al (Table 1), including particulate sulphur S, particle bound Br (see Skov et al., 2004) were analysed using Proton Induced X-ray Emission (PIXE), albeit with the exception of Cl and Hg which evaporate from the particle filter. Gas filters also collect ammonia (NH_3) if present and nitric acid (HNO_3). These nitrogen species may evaporate from the particle filter onto the gas filters, for which reason the sum of the particulate and gaseous fractions, are reported. Sampling runs from Monday 00:00 UTC for one week, equivalent to approximately 400 m^3.

Uncertainties are listed in Table 1.

2.3 Receptor modelling

In general, two types of models are used for source apportionment of aerosols, including source-oriented models and receptor models (Schauer et al., 1996). The source-oriented models employ emission data inventories and calculate transportation modes (such as dispersion, deposition and trajectories) to estimate the emission, formation, transformation, transport and deposition of aerosols at receptor sites (Eldering and Cass, 1996). Although the models can be very useful especially in scenario studies where emission abatement strategies are evaluated, the use of this type of models is often limited by the availability and reliability of the emission inventories (Viana et al., 2008). In contrast, the receptor models assume that the observed concentrations can be adequately explained by a linear combination of a number of sources with fixed

source profiles and variable source strengths in time. In this work, we use two different source apportionment models, i.e. Positive Matrix Factorization (PMF) and the COnstrained Physical REceptor Model (COPREM) to evaluate the sources to Arctic particulate matter at Station Nord over a period of two years from March 2008 to February 2010. The obtained factors of the PMF solution and the obtained sources of the COPREM solution will be both referred to as "source" in this work.

2.3.1   2.3.1 PMF

PMF is a multivariate factor analysis tool, which derives a source contribution matrix **g**, and a source strength matrix **f** (Paatero, 1997) based on measured mass concentrations of selected species and weighted by analytical uncertainty.

$$x_{ij} \cong \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}, \tag{1}$$

where x_{ij} is the observed mass concentration of compound i in sample j, p is the number of sources that contribute to x_{ij}, g_{ik} is the source contribution (or source score), f_{kj} is the mass fraction (or source loading), and e_{ij} is the residual or error (Hopke, 2003). The results are constrained to physically possible solutions, which imply that a sample cannot have a negative contribution from a source. Moreover, each data point can be weighted individually, e.g. by regulating the uncertainty of the corresponding measured values below the detection limit so that they have less influence on the resulting solution. The PMF solution minimizes the function Q:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right], \tag{2}$$

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where u_{ij} is the analytical uncertainty of x_{ij}. Hence, this is a least square problem to identify the matrices **g** and **f** (Xie et al., 1999). The uncertainty of the PMF solution can be estimated by generating new data sets, which are consistent with the original one. Each data set is then decomposed to a **g** and **f** matrix, which are compared with the base run (Eberly, 2005).

In this study we used PMF 3.0 provided by the US EPA, which is based on the second version of the Multi linear Engine (ME-2).

2.3.2 COPREM

The data was also analysed using the multivariate receptor model COPREM (Wåhlin, 2003; Heidam et al., 2004; Skov et al., 2006). Like any receptor model, COPREM is based on the assumption that the observed mass concentrations at the receptor site can be explained by contributions from a number of sources with constant source profiles, but variable source strengths in time.

$$x_{ij} \cong \sum_k a_{ik} f_{kj}, \tag{3}$$

where x_{ij} is the measured mass concentration of compound i in sample j. k is the number of sources, which are required to adequately describe the observations. a_{ik} is the fixed profile, and f_{kj} is the source strength in the individual samples. COPREM may be perceived as a hybrid receptor model between PMF and chemical mass balance (CMB), where COPREM resembles PMF or CMB dependent on the number of constraints. If COPREM is operated with a minor number of constraints, the model will resemble PMF, which requires no prior knowledge of the sources (Baltensperger and Prevot, 2008). As a result, x_{ij} in Eq. (3) is the only necessary input though a substantial amount of data is required to infer the sources. In contrast, the sources can be attributed to even small data sets in CMB, as the user can apply constraints and define the source profiles in the receptor model.

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COPREM requires three input matrices: a $(2 \times n \times N)$ matrix with measurement data including analytical uncertainty, a $(n \times p)$ source profile matrix and a $(n \times p)$ form matrix defining additional constraints. In the source matrix, the user defines the source profiles (columns) by the ratio of the source elements (rows), e.g. as the percentage of particulate matter (PM). In the form matrix, the user can define additional constraints. The form matrix has the same number of rows and columns as the source matrix, and elements are set to either "0" or "1". If the profile elements are set to "0", such elements are fixed in the ratios defined in the source profile, taking the analytical uncertainty into account, whereas if such elements are set to "1", a solution is allowed where the particular elements can be solved different from the values defined in the source profile. The latter is particularly useful, where knowledge of the relevant sources is limited or unknown. Furthermore, specific elements can be excluded from a particular source by setting the concentration to "0" in the source profile and "0" in the form matrix.

Equation (3) is solved by an iterative method to determine a_{ik} and f_{kj}, while taking the uncertainty σ_{ij} of the measurements into account. Chi-square statistics provide the squared difference between measurement and model results.

$$X^2 = \sum_j \sum_i \frac{\left(x_{ij} - \sum_k a_{ik} f_{kj}\right)^2}{\sigma_{ij}^2}, \tag{4}$$

Negative coefficients in the source profile and negative source strengths are excluded by built-in constraints in COPREM. The Chi-square is minimized until it reaches a stagnant minimum value during the iteration process within the constraint limits.

The uncertainty of the fitted source profiles in COPREM is estimated with a specific module using weighted linear regression between the calculated source strengths and the measured data, taking into account the analytical uncertainties of the individual species, which are multiplied by a constant factor $\sqrt{\frac{X^2}{\nu}}$ where ν is the degree of freedom. However, the calculated uncertainty represents a lower estimate, since other

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uncertainties may also influence the fitted source profiles (e.g. constraints which are not correctly assigned or by the use of insufficient number of sources).

COPREM fills up a gap in source apportionment analysis as the user-defined constraints can transform the model from either multivariate to strictly CMB. This property is convenient when the analyst has sound knowledge about the source compositions and wishes to partly control the solution based on this knowledge. Other sources may be less understood and the analyst can loosen the constraints on a particular source profile. In contrast, the possibility of COPREM to resemble CMB may become a true disadvantage, if the source profiles fail to meet the actual ones. By combining PMF and COPREM, the analyst can critically evaluate present knowledge of contributing sources.

Soil and *Marine* profiles corresponding to elemental abundances in igneous rocks (Kaye and Laby, 1959) and seawater (Sverdrup et al., 1942) were used in the COPREM source profiles. The *Soil* profile was fully constrained. The *Marine* profile was also constrained except for Cl, V, S, SO_x, BC and Br (Table S1). No constraints were imposed on the anthropogenic profiles, since the knowledge of these sources is scarce. In this regard, the apportionment of the anthropogenic sources in COPREM and PMF followed a strictly mathematical solution free of constraints imposed by the analyst, though the degrees of freedom were larger in PMF, where the natural sources were not constrained.

3 Results and discussion

Source apportionment on Arctic aerosols is typically confined to a limited number of sources due to scarce numbers of contributing emission sources in the Arctic as well as unique meteorology and transport mechanisms characteristic for these remote regions. Furthermore, low concentrations of species necessitate longer sampling times (e.g. days to weeks depending on sampling and analysis technique), which may disfavour the differentiation between sources during non-stationary conditions. As an example,

four sources were sufficient in a COPREM analysis to account for the sources contributing to the aerosols load at Station Nord from 1991–2001, including a crustal source (soil), a marine source (sea), a metal source (Cu and Ni production within the Arctic region) and a combustion source representing various distant anthropogenic activities (Heidam et al., 2004). In a study by Xie et al. (1999) using PMF, five sources were required to account for the Arctic aerosols measured at Alert, Northwest Territories, Canada, from 1980–1991. Only one anthropogenic factor was identified. In the present study, at least five sources were necessary to adequately explain the measurements of particulate composition at Station Nord from March 2008 to February 2010. Data was analysed with and without Br, S and SO_x. Similar to Cl, Br may evaporate as HBr upon acidification of the aerosol, or partly act as a secondary pollutant (Mcconnell et al., 1992), which may disturb the apportionment of primary sources. In addition, the season-dependent OH oxidation of SO_2 to H_2SO_4 calls for special attention on sulphur species in source apportionment, for which reason we account for the sulphur species by introducing the parameter $SO_x = SO_2 + SO_4^{2-}$. We concluded that inclusion of SO_x and Br supported the source apportionment.

Initially, four sources were fitted to the data with a constrained soil profile, a partially constrained marine profile and two unconstrained profiles in COPREM analysis, following Heidam et al. (2004). However, high Chi^2 numbers (Wåhlin, 2003) and poorly fitted data were also observed, especially with S, As, Pb and Br species. Non-converging solutions and poorly fitted data also resulted from PMF analysis. This indicates that a four-source solution is no longer sufficient. In fact, satisfactory fits were achieved from a five-source solution with two natural sources (*Soil* and *Marine* source) and three anthropogenic sources dominated by the metals Cu/Ni, Zn and Pb/As, respectively (Figs. 3–4, Table S2). Compared to the previous solution proposed by Heidam et al. (1999, 2004) for Station Nord, the Cu/Ni source in our study resembles the previous metal source and our *Combustion* source probably resembles the previous combustion source whereas Zn source is a newly added one. Concentration and standard deviation of the PMF and COPREM profiles are shown in Fig. S1a, b. *Q* (robust) for

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the base run was 7340. In order to check the stability of the solution, 100 bootstrap runs were completed of which all converged. Q (robust) varied from 4441–7537 with 25th quartile: 6031, median: 6382 and 75th quartile: 6780. Fpeak runs of strength 0.1–0.5 resulted in Q-values from 7145–7249. The calculated total Chi^2 statistic for the COPREM solution is 10683 for total 27 species.

3.1 Natural sources

The source *Soil* was dominated by Al, Si, Ca, Ti, Mn, V and Fe (Fig. 3, Table S2). A crustal source was previously described as peaking in spring and late summer (Heidam et al., 1999). PMF and COPREM solutions for the *Soil* source were highly consistent with maximum concentration also observed in spring/summer 2008, though this spring/summer peaking trend was much less pronounced in 2009 (Fig. 4). PMF and COPREM attributed $33\%_{PMF}$ and $25\%_{COPREM}$ of total V to this source, respectively. V is typically associated with fossil oil combustion, but other Arctic studies have associated V with the crustal source (Heidam et al., 2004; Maenhaut and Cornille, 1989) and V occurs in about 65 different minerals (Wang and Wilhelmy, 2009). Notable differences ($> 20\%$) in the PMF and COPREM solutions for the *Soil* source are seen for Rb ($43\%_{PMF}$; $11\%_{COPREM}$) and Cr ($7\%_{PMF}$; $52\%_{COPREM}$) (Table S2), however, measured concentrations of Rb were low.

Na and Cl are dominating species in the *Marine* source, which in addition also included K, Ca, Sr and V ($28\%_{PMF}$; $33\%_{COPREM}$), small amounts of SO_x ($9\%_{PMF}$; $6\%_{COPREM}$) and BC ($5\%_{PMF}$; $1\%_{COPREM}$). The worldwide increasing ship traffic could explain BC, SO_x and V in the natural *Marine* source. However, V is also relatively abundant in open ocean waters (Wang and Sañudo Wilhelmy, 2009). The *Marine* source shows a clear annual trend with lower summer concentrations and increased contributions in the autumn and winter period (Fig. 4). In the autumn, ocean storms may lead to high productions of sea spray aerosols. During winter, the sea surrounding Station Nord is frozen and thus it is not likely that the aerosols originate from open waters, however it is suggested by Fenger et al. (2012) that large Cl^- containing particles at

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Station Nord can originate from frost flowers torn at high wind speeds. Furthermore a study by Domine et al. (2004) also found that both frost flowers and the marine snow pack can be sources of sea salt.

The PMF and COPREM solutions for the *Marine* source are fairly similar though the former includes low contributions of additional elements, including Al, Si, Ti and Fe (Fig. 3). The time profiles of PMF and COPREM solutions are also highly similar, with slightly higher contribution of the *Marine* source during certain intervals of the PMF solution (Fig. 4). The presence of Al, Si, Ti and Fe in the PMF source (Fig. 3) suggests that the *Marine* source is somehow mixed with a crustal source, probably disturbed by the low (weekly) time resolution or complex long-range transport imprinting of the observed samples. K and Ca are also found in all sources, except for the Zn source. Indeed, unclear or "blurry" source profiles have been observed in other studies in the Arctic region (Xie et al., 1999). The COPREM solution, on the other hand, is constrained with respect to these elements, which may explain small deviations in the time profiles. K, Ca and Sr were assigned to the COPREM input source profile (Table S1), since these elements are abundant in both seawater and aerosols created from sea spray (Maenhaut and Cornille, 1989; Heidam et al., 2004). Except for V, S, SO_x, Br and BC, all elements in the COPREM input profile were constrained to a seawater composition profile (Sverdrup et al., 1942). Notable differences in the PMF and CO-PREM solutions are only observed for Na (21 %). Se has previously been suggested to originate mainly from marine biogenic sources in the Norwegian Arctic (Maenhaut and Cornille, 1989). However, we find only a negligible marine contribution to Se (5 %$_{PMF}$; 0 %$_{COPREM}$) compared to the anthropogenic sources (83 %$_{PMF}$; 100 %$_{COPREM}$).

3.2 Anthropogenic sources

Three sources are characterised by high abundances of the elements Zn, Cu, Ni, Pb and As, which are interpreted as anthropogenic sources or most likely agglomerates of sources. Two sources influenced by metal industry peaked in spring/summer (Cu/Ni source), and winter (*Combustion* source). The Cu/Ni source is probably an

agglomerate of sources from Eurasia as evident from the contribution of Cu ($45\%_{PMF}$; $56\%_{COPREM}$) and Ni ($29\%_{PMF}$; $36\%_{COPREM}$). Cu and Ni are present in both the Cu/Ni and *Combustion* sources but virtually absent in the natural sources. The impact of Cu on anthropogenic and natural sources gives evidence that Eurasia, and in particular the Siberian Cu/Ni industry, is a major source of pollutants in the higher Arctic. Previously, Cu has almost exclusively been apportioned to one anthropogenic source with heavy influences from the metal industry, whereas two distinct anthropogenic sources have contributed to Ni in former studies at Station Nord (Heidam et al., 1999, 2004). The highest abundance of primary and secondary combustion products were attributed to the Cu/Ni source by both PMF and COPREM, ie. NO_3^- ($59\%_{PMF}$; $63\%_{COPREM}$), SO_x ($54\%_{PMF}$; $45\%_{COPREM}$) and BC ($54\%_{PMF}$; $37\%_{COPREM}$), which could reflect combustion processes fuelled by coal, as indicated by Se ($19\%_{PMF}$; $21\%_{COPREM}$), and most likely not oil due to the low abundance of V ($3\%_{PMF}$; $0\%_{COPREM}$). Alternatively, the combustion products may originate from power generation and other combustion processes connected to the metal industry near the industrial sites. As mentioned above, we included a parameter SO_x, defined as the sum of SO_2 and SO_4^{2-}. In this way, we take into account the variable oxidation rate of SO_2 to form SO_4^{2-} over the seasons, where the availability of sunlight and thereby OH is highly variable. However, the results should be taken by caution, since differences in the deposition velocities of SO_2 (gas) and SO_4^{2-} (particles) impose an error in the definition of $SO_x = S-SO_2 + S-SO_4^{2-}$. For example, the majority of SO_x ($54\%_{PMF}$; $45\%_{COPREM}$) and NO_3^- ($59\%_{PMF}$; $63\%_{COPREM}$) are apportioned to Cu/Ni. The remaining mass of these species is largely found in the *Zn* source. Although both PMF and COPREM suggest Cu/Ni to be the major source of NO_3^- and SO_4^{2-}, recent findings at Station Nord show that the particle modes of NO_3^- (maximum at 1.2 μm) and SO_4^{2-} particles (maximum at 0.3 μm) are significantly different (Fenger et al., 2012), which suggests different but co-varying sources. The apportionment by PMF and COPREM generally agree well with respect to the abundances of species (Fig. 3 and Table S2) and time profiles (Fig. 4). Notable differences are observed for Si, Cr, Fe, Ga, Pb and NH_4^+. Among these species, NH_4^+ is believed

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to originate from long-range transported husbandry sources and influence all anthropogenic sources.

Also influenced by Cu/Ni is the *Combustion* source, which is characterised by high concentration of Pb (72 %$_{PMF}$; 86 %$_{COPREM}$) and As (63 %$_{PMF}$; 68 %$_{COPREM}$). This *Combustion* source represents typical anthropogenic pollutants which are long-range transported to Station Nord (Heidam et al., 1999, 2004). High abundances of V (27 %$_{PMF}$; 25 %$_{COPREM}$) and Se (44 %$_{PMF}$; 41 %$_{COPREM}$) indicate oil and coal fuelled industry and/or other anthropogenic combustion processes. Primary and secondary combustion products also appear with high abundances (Fig. 3). As and Se have previously been apportioned to sources from the Kola Peninsula (Maenhaut and Cornille, 1989). This *Combustion* source is also characterised with the absence of NO_3, which is the oxidation product of NO_x.

Br (66 %$_{PMF}$; 96 %$_{COPREM}$) is largely apportioned to the *Combustion* source and plays a key-role in ozone depletion during Arctic sunrise, though the activation of bromine is not fully understood (Sumner and Shepson, 1999). It has previously been suggested that sea-salt bromine may be accumulated in the snowpack during the long polar night and is evolved as Br_2 into the atmosphere at polar sunrise (Mcconnell et al., 1992). In the following step, BrO is formed in the reaction with O_3 and Br atoms from photolysis of Br_2, or, e.g. HOBr from the reaction of BrO with the HO_2 radical (Impey et al., 1999). Br may also react with organic compounds to form HBr and organic bromine compounds, all of which are suspected to be scavenged by Arctic aerosols (Mcconnell et al., 1992; Impey et al., 1997, 1999). Furthermore, Br_2 can recycle with or without O_3 (Impey et al., 1999; Simpson et al., 2007) and may photolyse to Br atoms which further deplete O_3. In addition to the *Combustion* source, Br is apportioned to Cu/Ni source (31 %$_{PMF}$; 0 %$_{COPREM}$) and virtually no other sources, though the Br has both natural sources, e.g. sea-salt and marine organisms (Gribble, 2000) and anthropogenic sources, e.g. incineration and chemical industries (Morawska and Zhang, 2002). An anti-correlation is apparent between Br and O_3 in 2009 from about polar sunrise in the beginning of March until beginning of June (Fig. 5), after which Br decreases,

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which is in agreement with previous observations at Station Nord (Skov et al., 2004). Br is only low during summer and increases to $pg\,m^{-3}$ levels from November–December (Fig. 5). We assume that this is due to oceanic storms, since the *Marine* source peaks earlier than bromine concentrations (Figs. 4–5). Br is mainly apportioned (96 %) to *Combustion* using COPREM. Using PMF, this source accounts for 66 % whereas Cu/Ni source accounts for additional 31 % (Table S2). Apparent from Fig. 5, Br resembles the anthropogenic elements Pb and S, which can probably be explained by S acting as a "transport container" in addition to S as H_2SO_4 being a source of H^+. In other words, Br is most unlikely emitted from anthropogenic sources, but probably has local and/or marine sources.

The Zn source appears to have a different origin than Cu/Ni and *Combustion* source, since it is only influenced by Cu to a minor extent. According to Heidam et al. (2004), Zn together with Pb and As were mostly attributed to the combustion source. Compared to the work by Heidam et al. (2004) based on data from 1991–2001, the present work analyses a shorter but more recent data set from March 2008–February 2010 with a larger number of chemical parameters. A separate COPREM analysis is also conducted to investigate whether the inclusion of an additional anthropogenic source is necessary based on previous source results from Heidam et al. (2004). According to this, Zn, Pb and As could no longer be adequately explained using a single common source, which consequently indicates that the sources have changed. The apportionment by PMF and COPREM to Zn source as the largest source of Zn ($69\,\%_{PMF}$; $98\,\%_{COPREM}$) to Station Nord agrees well. Zn source also accounts for Arctic summer periods, where the contribution of anthropogenic elements was high (Fig. 4), which was not observed earlier at Station Nord (Heidam et al., 1999, 2004). In this source, Br is absent whereas SO_x ($10\,\%_{PMF}$; $8\,\%_{COPREM}$) and S ($10\,\%_{PMF}$; $6\,\%_{COPREM}$) are low in comparison with the Siberian sources imprinted with abundant Br and S. While this stresses the difference of this Zn source compared to the other two anthropogenic sources Cu/Ni and *Combustion*, it also supports the hypothesis of S acting as a transport container for Br. Only minor differences in the apportionment of other species to

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this Zn source are observed between PMF and COPREM (Table S2). Finally, all anthropogenic sources are influenced by Se (19–44 %), indicative of coal-fuelled processes (Sholkovitz et al., 2009) (Fig. 3, Table S2).

In order to investigate the origin of the Zn source, the HYSPLIT model is used to generate air mass back trajectories. Back trajectories are calculated for arrival at 50 m and 500 m a.s.l. every 24 h during the Arctic summer periods where there was sudden elevation of Zn concentration or consistently high Zn concentrations. As the back trajectories are calculated 10 days backwards due to the remote location of Station Nord whereas the associated uncertainty increases dramatically with time, implications of back trajectory results must be interpreted with caution. Calculated air masses from the back trajectories seem to arrive from various directions, including west of Station Nord (Canadian Arctic, North America and West Greenland), north of Station Nord (the North Pole and Siberia) and south of Station Nord (North Atlantic over Greenland) (Fig. 6). However it was revealed that a change in air mass direction to westerly origins of Station Nord (Canadian Arctic, North America, and West Greenland), especially from Canadian Arctic is often accompanied with an elevated concentration of Zn, thereby indicating a Zn source from this region. Zn smelters within the Canadian Arctic region are thus a possible candidate for Zn source though a recent study which also recognized a high concentration of Zn over the Canadian Arctic has excluded Canadian Arctic Zn smelters as a contributing source (Li and Cornett, 2011). In addition, there are also high Zn concentrations associated with air masses arriving from other directions, including the North Atlantic over Greenland and Siberia which are observed less frequently than air masses originated from westerly directions of Station Nord.

BC is mainly apportioned to anthropogenic sources (80 %$_{PMF}$; 98 %$_{COPREM}$), and predominantly found to have Siberian origin. Whereas COPREM assigns a higher percentage of BC to *Combustion* source (61 %$_{COPREM}$) and a lower percentage to Cu/Ni source (37 %$_{COPREM}$), the PMF solution suggests a lower percentage to *Combustion* (26 %$_{PMF}$) compared to Cu/Ni source (54 %$_{PMF}$). PMF also apportioned a certain higher amount of BC (10 %$_{PMF}$) to Zn source compared to COPREM (1 %$_{COPREM}$). Despite

such differences between PMF and COPREM, the high contribution from Siberian metal industries to BC at Station Nord is inevitable, which agrees with other recent findings (Hirdman et al., 2010; Wang et al., 2011).

3.3 Comparison of PMF and COPREM

Using a combination of PMF and COPREM in analysing the same data set provides certain advantages. First, we are able to achieve fairly reliable solutions of the better-defined natural *Soil* and *Marine* sources using COPREM. Such solutions also serve to identify the corresponding *Soil* and *Marine* sources from the PMF solution among the initially unidentified sources. Second, the anthropogenic sources of COPREM can be compared with the remaining PMF sources to determine the corresponding match of COPREM and PMF sources, though it should be expected that the solution for the anthropogenic sources using COPREM in principle should fairly resemble PMF, since no constraints were applied to such sources. Third, using COPREM with some knowledge on the possible number of sources could also serve to limit the number of PMF sources, especially as PMF tends to find more sources, than what is actually present in order to provide the best fit.

PMF in return can be used to validate existing COPREM profile knowledge. The general agreement between PMF and COPREM solutions increases the confidence in apportionment results, especially with our limited 2-yr data set of weekly samples. Meanwhile, as the solutions of COPREM and PMF are not always comparable, which is presumably due to the set constraints of COPREM, certain species can be apportioned very differently such as Cr (of *Soil* source) and Na (of *Marine* source) (Table S1a).

Current data evaluated by PMF and COPREM failed to apportion biomass combustion, which is an important source where K and the sugar anhydride levoglucosan are typically chosen as markers. K is almost evenly distributed among the sources with no clear dominating source and the approximately 10 % difference between PMF and COPREM in the apportionment of K to Cu/Ni is probably a consequence of K being constrained in the *Soil* source profile (Table S1). In a previous study at the Canadian

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Arctic site Alert, K was apportioned to Marine, Biogenic, Anthropogenic and Photo-chemistry influenced sources in comparable abundances but not apportioned to *Soil* (Xie et al., 1999). At Station Nord, K has previously been apportioned to mainly *Soil* and *Marine* and to a minor extent to the copper smelters but not to *Combustion* (Hei-dam et al., 2004). K is a well-known qualitative tracer for biomass burning (Cachier et al., 1995; Lewis et al., 1988); however it may not be applicable to use this species as a tracer for biomass burning in the Arctic, where long-range transport favour atmo-spheric degradation, as suggested from the present findings.

4   Conclusions

In this work, two different source apportionment models were used to explain the chem-ical observations at Station Nord, Northern Greenland during a two-year period from March 2008 to February 2010. PMF and COPREM produced highly comparable solu-tions with similar source profiles and source time series. Differences in abundance of particular compounds are evident in particular sources as a consequence of the con-straints on the natural sources (*Marine* and *Soil*) in COPREM. In addition to the natural sources, we identified three anthropogenic sources which are all highly influenced by metal industries. Cu/Ni and *Combustion* sources are subjected to influences from the Cu and Ni industry which is most likely of Siberian origin. As expected, the majority of BC originated from these sources (80–98 %). A third source, Zn source, was only influenced by Cu to a minor extent and explained a significant fraction of Zn, which could not be apportioned to the other anthropogenic sources. HYSPLIT back trajecto-ries indicated that this source is probably influenced by the Canadian Arctic, though southern and even eastern air mass origin also exerted influence on this source. Br is mainly apportioned to Siberian sources though it is most likely sulphuric acid from these sources that acts as transport containers for Br species, which themselves have local/marine origin.

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Table 1. Analytical methods and sample frequency of measured parameters.

Parameter	Analytical method	Time resolution	Uncertainty
40 mm FP nitro cellulose filters			
Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Zr, Pb	Proton Induced X-ray Emission (PIXE)	7 days	18 %
SO_2, SO_4^{2-}, Na^+, NH_4^+, NH_3, NO_3^-, HNO_3, Br^-, Cl^-	Ion Chromatography	7 days	20 %
PSAP filters			
Black carbon	Particle Soot Absorption Photometer (PSAP)	15 min	20 %
On-line gas monitors			
O_3, NO_x, SO_2	Gas monitor	30 min	20 %

Detection limits are $9\,ng\,m^{-3}$ for $S–SO_4^{2-}$, $8\,ng\,m^{-3}$ for $N–NH_4^+$, $11\,ng\,m^{-3}$ for $N–NO_3^-$, $5\,ng\,m^{-3}$ for S, $0.06\,ng\,m^{-3}$ for Pb, $0.08\,ng\,m^{-3}$ for Cu, $0.10\,ng\,m^{-3}$ for Ni and $0.05\,ng\,m^{-3}$ for As.

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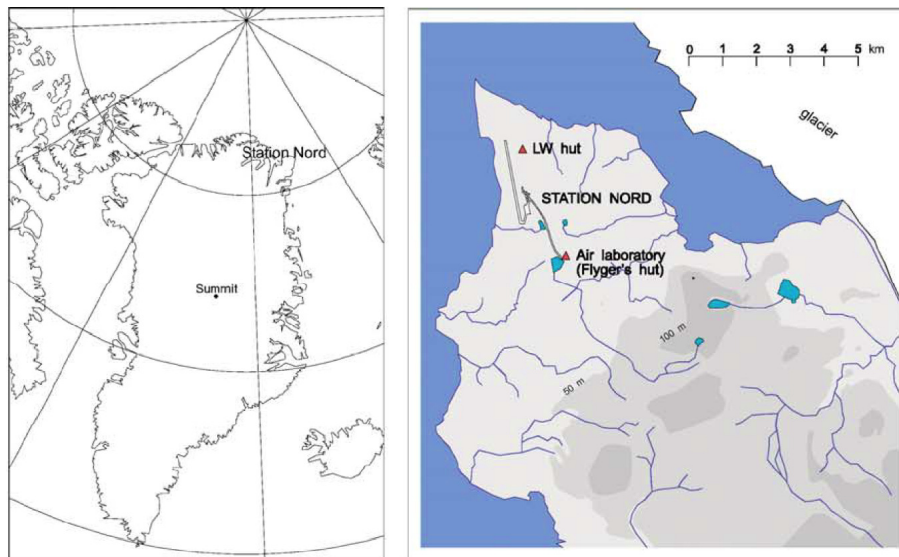
Fig. 1. The Arctic measurement site Station Nord in North East Greenland (81°36′ N, 16°40′ W).
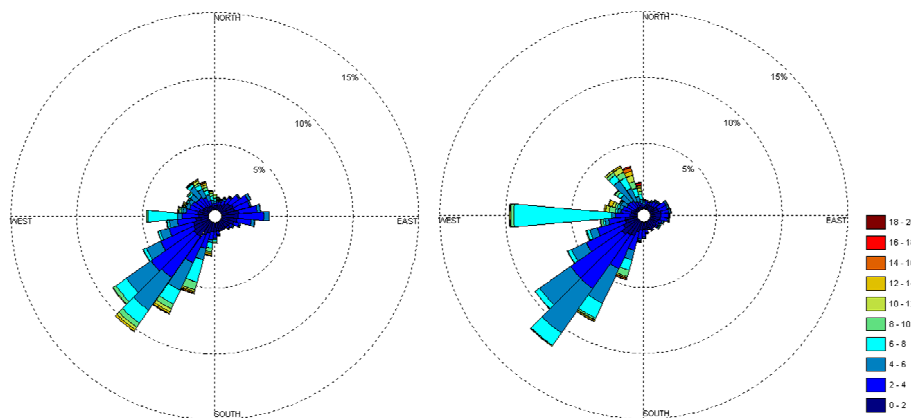
Fig. 2. Windrose showing local wind direction from 31 May 2011 to 1 June 2012 (left) and winter, (November–March 2012) (right).
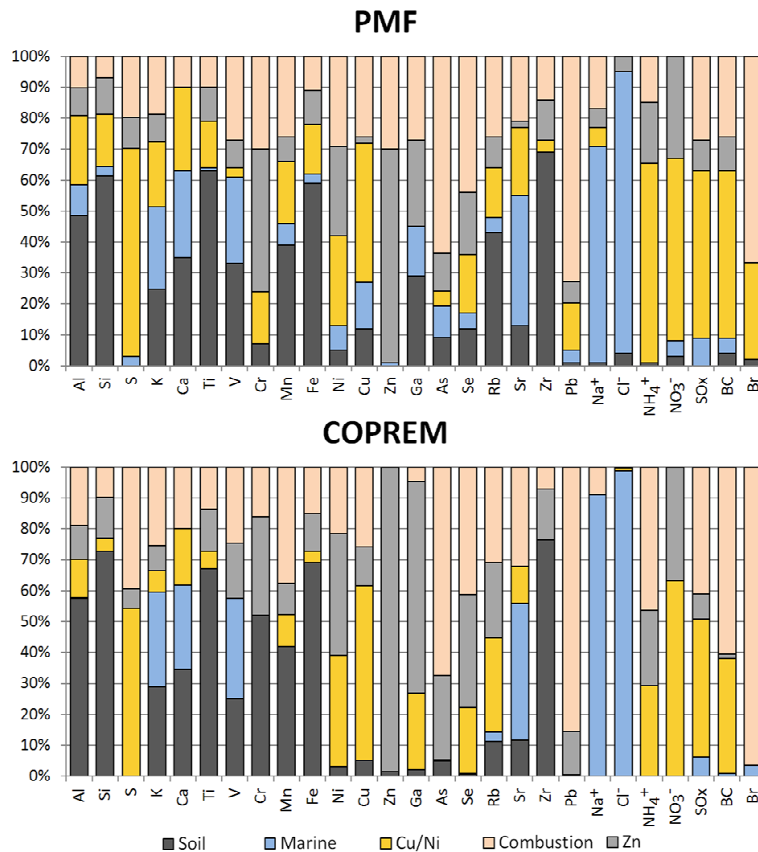
Fig. 3. Source origin of chemical species apportioned by PMF and COPREM.
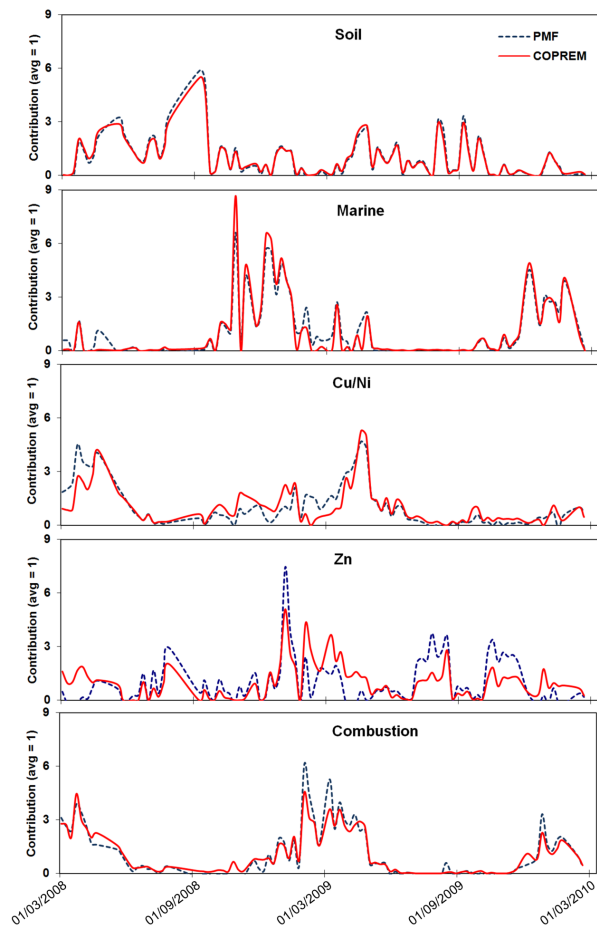
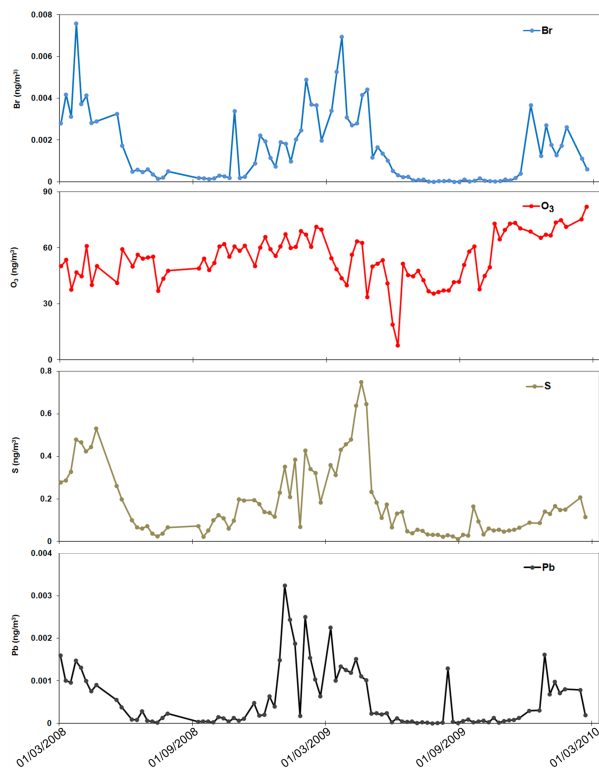**Fig. 4.** Time profiles of PMF and COPREM sources.

Fig. 5. Time profiles for Br, O_3, S and Pb. Br correlates with S and Pb throughout the observation period. Br anti-correlates with O_3 from about polar sunrise in the beginning of March until beginning of June in 2009, after which Br decreases.

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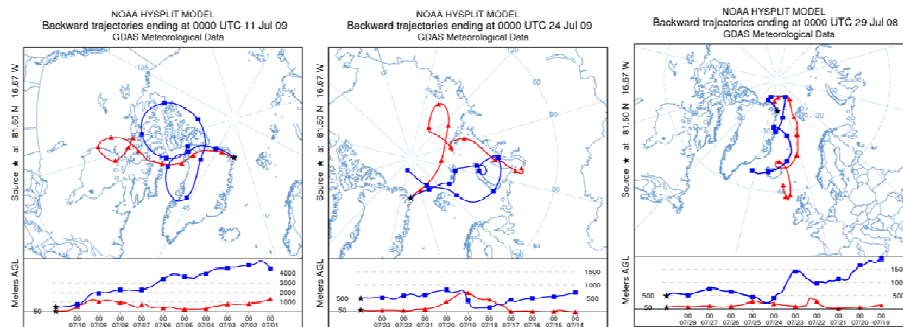
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Fig. 6. Air mass back trajectories calculated for arrival at 50 m and 500 m a.s.l. every 24 h during summer from the period March 2008–February 2012 using the model HYSPLIT. The trajectories are shown for three typical cases: (left) west of Station North (Canadian Arctic, North America and West Greenland); (middle) The North Pole and Siberia and (right) south of Station North (North Atlantic over Greenland).