Norsk institutt for luftforskning
Norwegian Institute for Air Research

SHIPMATE - SHIp traffic Particulate MATter Emissions

Final Project Report

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NILU report 1/2016

NILU report 1/2016	ISBN: 978-82-425-2814-8 ISSN: 2464-3327	CLASSIFICATION: A- Unclassified (open report)
DATE 10.03.2016	SIGNATURE OF RESPONSIBLE PERSON Kari Nygaard, Managing Director (sign.)	NUMBER OF PAGES 27
TITLE SHIPMATE - SHIp traffic Particulate MATter Emissions		PROJECT LEADER Susana Lopez-Aparicio
		NILU PROJECT NO. O-114049
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REPORT PREPARED FOR Svalbard Miljøvernfond		CONTRACT REF.

ABSTRACT

In the SHIPMATE project, we have carried out measurements of a large number of pollutants and aerosol components at the Mt. Zeppelin observatory during 2014 and 2015, with focus on the summer period (April to September). The aims were 1) identification of the particulate matter (PM) contribution from ship emissions by source apportionment and 2) isolation of data records influenced by local ship emissions in order to preserve the usefulness of the observatory for regional trends of atmospheric constituents. A total of 8 potentially ship-influenced 3-day sampling intervals were found in the analysis of the wind direction record and the harbour calls from Ny-Ålesund (2014 and 2015). The local shipping pollution contributed significantly (≥50%) to the concentration levels of certain heavy metals such as Cu, Ni, Zn and Cd during the two summers. This is supported by the enrichment factors analysis. However, the influence of local pollution from shipping on the measurements carried out at the Mt. Zeppelin observatory is rather infrequent.

SHIPMATE - svevestøvutslipp fra skipstrafikk

KEYWORDS

The Zeppelin Observatory | Aerosols and particles | Coastal zone management

ABSTRACT (in Norwegian)

I SHIPMATE-prosjektet er det gjennomført målinger av en rekke forurensningskomponenter og aerosoler på Mt. Zeppelin observatoriet i løpet av 2014 og 2015. Målet for prosjektet var 1) å kartlegge hvor mye skipstrafikken bidrar til de observerte svevestøv-nivåene og 2) identifisere tidsrom i eksisterende tidsserier som i betydelig grad er påvirket av lokale utslipp fra skipstrafikken. Det siste er viktig for at tidsserien skal kunne benyttes for å studere regionale trender for ulike forurensningskomponenter i atmosfæren. Basert på en vurdering av gunstig vindretning mot målestasjonen med samtidige skipsanløp til Ny-Ålesund, er det identifisert alt åtte 3-dagers episoder hvor utslipp fra skipsfart påvirker datagrunnlaget. I disse episodene bidro utslipp fra skipstrafikken med ca. 50% av konsentrasjoner av følgende tungmetaller: Cu, Ni, Zn og Cd. Disse resultatene understøttes av en berikelsesfaktoranalyse av prøvene. Forekomst av episoder hvor skipstrafikk påvirker målingene ved målestasjonen på Mt. Zeppelin forekommer derimot sjeldent.

PUBLICATION TYPE: Digital document (pdf)	COVER PICTURE: Source: NILU

Preface

This scientific report is the final report of the project SHIPMATE "Ship Traffic Particulate Matter Emissions". The project is funded by Svalbard Miljøvernfond, starting in September 2014 and finalizing in December 2015. The project is a collaboration between NILU – Norwegian Institute for Air Research and the Department of Meteorology at Stockholm University (MISU).

SHIPMATE aims at determining the contribution of ship emissions to particulate matter (PM) measured at Mt. Zeppelin station by source apportionment methods. The project aimed at identifying days that were influenced by local ship emissions in order to preserve the usefulness of the observatory for regional trends of atmospheric constituents.

The work has been led at NILU by Matthias Karl until August 2015 and thereafter by Susana López-Aparicio. Are Bäcklund from NILU has led the work regarding sample collection. Caroline Leck from the department of Meteorology (MISU) at the University of Stockholm (Sweden) has been responsible for the analysis of Black Carbon (BC) and polysaccharides. Thanks to Marit Vadset from the Environmental Chemistry department at NILU for leading the work regarding the chemical analysis of PM filters. Internal quality control at NILU has been carried out by Claudia Hak.

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Summary

In the SHIPMATE project, we have carried out measurements of a large number of pollutants and aerosol components at the Mt. Zeppelin observatory during 2014 and 2015, with focus on the summer period (April to September). The aims were 1) identification of the particulate matter (PM) contribution from ship emissions by source apportionment and 2) isolation of data records influenced by local ship emissions in order to preserve the usefulness of the observatory for regional trends of atmospheric constituents.

The chemical components analysed act as markers of different local / regional anthropogenic and biogenic PM. Data analysis based on Enrichment Factor (EF) analysis and Positive Matrix Factorization (PMF) analysis identify the time series (record) of the ship-related PM source. EF analysis is a classical approach for use in data screening and to support assumptions for PM sources for which little information is available. Soil samples from Kongsfjord (Svalbard) provided the reference crustal material for EF analysis. EF analysis showed enrichment of certain metals typical for a certain (e.g. combustion) source compared to the crustal material. PMF was used for the source identification of ship PM emissions.

The SHIPMATE study identifies the contribution of local ship pollution from cruise boats to PM measurements carried out at the Mt. Zeppelin observatory (78.9°N, 11.9°E). For a ship plume to reach Mt. Zeppelin observatory two conditions have to be met simultaneously; 1) ships with 200 passengers or more in the harbour of Ny-Ålesund and 2) northerly winds at the observatory.

In this study, a total of 8 potentially ship-influenced 3-day sampling intervals were found in the analysis of the wind direction record and the harbour calls from Ny-Ålesund in 2014 and 2015. The local shipping pollution contributed significantly (≥50%) to the concentration levels of certain heavy metals such as Cu, Ni, Zn and Cd during the two summers. This is supported by the enrichment factors analysis. However, the influence of local pollution from shipping on the measurements carried out at the Mt. Zeppelin observatory is rather infrequent.

The analysis developed in this project will be refined to include (1) measurements of BC from MISU Stockholm in the PMF analysis that will identify time series of ship-related sources of particulate matter, (2) hourly-based analysis of wind direction record and Passenger Vessel (PAX) record, and (3) back trajectory analysis for the identified ship events.

SHIPMATE - Ship traffic Particulate Matter Emissions

1 Introduction

The latest prognoses estimate that the Arctic Ocean is going to become nearly ice-free during summer season over the next 30 to 40 years (AMAP,2012, IPCC, 2013). Further diminishing sea-ice in summer will likely lead to increased number of cargo ships that take the shorter passage through the Arctic instead of the current routes. Ship traffic is associated with emissions of a wide range of pollutants, among them Greenhouse Gases (GHGs), nitrogen Oxides (NO_x), black carbon (BC), sulphur dioxide (SO_2), and particulate matter (PM). Primary and Secondary PM from ship traffic emissions have been associated with adverse health effects (e.g. Corbett et al., 2007). This is of specific concern for PM population exposure in coastal areas nearby port activities (Hallquist et al., 2013). PM emissions from ships consist of sulphate, organic carbon (OC), soot (measured as elemental carbon, EC, or as black carbon, BC), and mineral ash (Murphy et al., 2009; Petzold et al., 2008, Moldanova et al., 2013). Fuel quality and operation mode of the engine affect emissions of particulate OC, EC and sulphate (Petzold et al., 2010).

Emissions from shipping have been regulated within the International Maritime Organization (IMO) in the MARPOL Annex VI - Regulations for the Prevention of Air Pollution from Ships. It has been ratified by Norway, thus ships operated on Svalbard have to obey these rules. The EU has implemented the MARPOL rules in their directives 1999/32/EC and 2012/33/EU for the North and Baltic seas, which are sulphur emission control areas (SECAs) and it is also applies to European ports. MARPOL Annex VI includes a limit of 3.5% m/m on the sulphur content of fuel oil from the 1st of January 2012 and warrants progressive reductions in nitrogen oxide (NO_x) emissions from marine engines.

Most cruise ships in the Svalbard region use marine diesel oil (MDO) or marine gas oil (MGO) (Evenset and Christensen, 2011) which contains 0.1-1% of sulphur with average value of 0.35% while the conventional marine residual oil (crude oil, heavy fuel oil (HFO)) has 0.5-4% of sulphur with average values of ca. 2.5% (Corbett and Winebrake, 2008). All ships that travel to the national parks on Svalbard can only use light marine diesel as fuel.

To set the context for SO_2/SO^{2-}_4: The largest source of SO_2 on Svalbard is a coal energy production, contributing 92% to total SO_2 emissions from Svalbard (Vestreng et al., 2010). Coal-fired power plants for the production of electricity and heat are operated in Longyearbyen and Barentsburg. The approximate distance from Ny-Ålesund to Barentsburg and to Longyearbyen is 110 km and 113 km, respectively.

The cruise tourism in Norway is growing at about the same rate as in other European areas. For instance, the number of cruise visitors in Norway has increased from about 200 000 to almost 700 000 the last 15 years, and the number of cruise ship port calls has gone up by approximately 67% (Dybedal et al., 2015). Likewise, sightseeing cruises increased in the archipelago of Svalbard in the last two decades, and the annual number of tourists landing on Svalbard was 100 000 during the period between 2006 and 2010 (Hagen et al., 2012).

Ny-Ålesund is a research town on the island of Spitsbergen in Svalbard situated on the shore of the bay of Kongsfjorden (Figure 1). Ny-Ålesund has an all-year permanent population of 30 to 35 inhabitants, and in summer it reaches 120 inhabitants. Figure 1 shows the accumulated ship tracking lines around the archipelago of Svalbard in 2014. According to Hagen et al. 2012, the activity at the port of Ny-Ålesund accounts for around 15% of all Svalbard ship landings. Based on the information obtained through the Automatic Identification System (AIS; Figure 1) it is possible to establish that a high density of vessels around Svalbard, and specifically around Ny-Ålesund, is associated with passenger-type and fishing vessels.

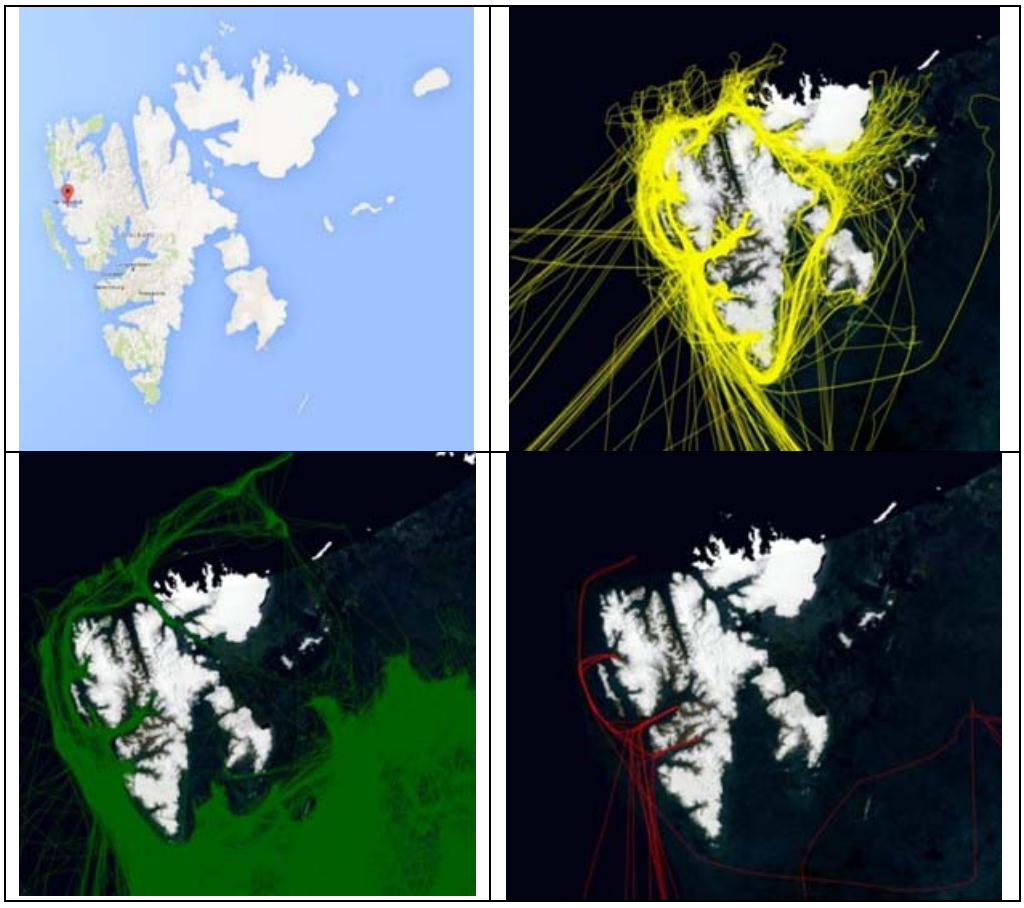

Figure 1: Map of Svalbard with the location of Ny-Ålesund (top-left), accumulated ship tracking lines around Svalbard in 2014 obtained from the Automatic Identification System (AIS) from passenger vessels (top-right), fishing vessels (bottom-left) and chemical tanks (bottom-right).

Previous studies have been carried out to identify the potential impact of shipping activities in Svalbard. For instance Weinbruch et al. (2012) analysed aerosol samples taken at the research station Zeppelin with electron microscopy and suggested that soot is only present when cruise ships harboured in the Kongsfjord area. Eckhardt et al. (2013) showed that local pollution from tourist cruise ships in the Kongsfjord influences observations at Mt. Zeppelin station.

Surveillance of pollutant components at Zeppelin station is currently not complete enough to allow for unambiguous source identification and source attribution by means of statistical analysis. In summer, when long-range transport of pollutants into the Arctic is at a minimum, regional marine biological sources contribute about one third to the sulphate aerosol (Heintzenberg and Leck, 1994). Without knowledge of the (natural) oceanic sources of sulphate and OC, the identification of ship emissions based on measured air pollutants will be biased or wrongly attributed.

The overall aim of the SHIPMATE project is (1) to identify the PM contribution from ship emissions by source apportionment and (2) to isolate data records influenced by local ship emissions in order to preserve the usefulness of the observatory for regional trends of atmospheric constituents. A secondary objective is to increase knowledge of the effect of climate-induced sea-ice changes on levels of marine biogenic airborne components.

In order to achieve the objectives of the SHIPMATE project, we conducted a large number of measurements of pollutants and aerosol components (receptor constituents) at Zeppelin during summer (April - September) 2014 and 2015. Among the components analysed were trace metals, major inorganic components, BC, dimethyl sulphide (DMS) and methane sulfonic acid (MSA). The analysed components act as markers of different local/regional anthropogenic and biogenic PM sources. For instance, trace metals are excellent source markers for anthropogenic activities. Vanadium (V) and ratios of V/Ni and V/EC (or V/BC) are specific for ship emissions and different ship types (Viana et al., 2009). On the other hand, OC has multiple sources and originates from primary emissions or from secondary photochemical reactions. OC from combustion sources is usually associated with certain heavy metals. Polysaccharides are prevalent building blocks of the marine gels and help to quantify the oceanic microgel source (Leck et al., 2013). In the Svalbard region, the melting ice edge gives rise to a spring bloom of phytoplankton (April-June), leading to the release of dimethyl sulphide (DMS) to the atmosphere from the uppermost ocean layer (Park et al., 2013). Methane sulfonic acid (MSA) is a main oxidation product of DMS present in marine aerosols.

In addition, soil samples from Kongsfjord were collected and analysed as reference material of crustal composition and for Enrichment Factor (EF) analysis. EF analysis is a classical approach for use in data screening and to support assumptions for PM sources for which little information is available. The EF analysis shows, for instance, enrichment of certain metals typical for a certain source compared to the crustal material, for instance a combustion source versus crustal origin. The full set of analysed components is used as input data for Positive Matrix Factorization (PMF) analysis for the source apportionment of PM, and specifically for the identification of ship PM emissions.

2 Methodology

2.1 Soil sample collection and evaluation

The area of interest is around Ny-Ålesund, a research town located on the island of Spitsbergen in Svalbard, on the Brøgger peninsula, and on the shore of the bay of Kongsfjorden (Figure 1). For the analysis of soil, 15 samples were collected in June 2014 on the south-east of Ny-Ålesund, in Kongsfjord area, along the transect indicated in Figure 2. Samples were collected after removing the most superficial level of soil (*Figure 3*).

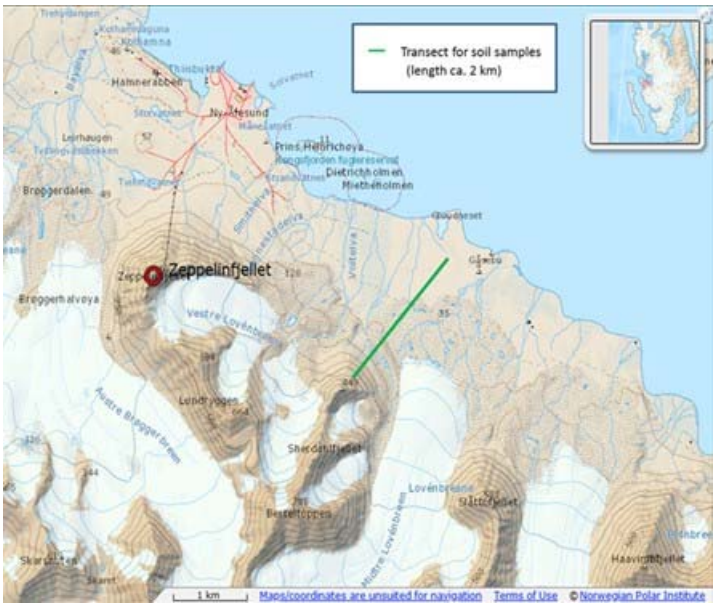

Figure 2: Location of Ny-Ålesund, the transverse along which the soil samples were collected (green line) and the Zeppelin observatory (red circle).

A complete extraction of soil samples and subsequent metal analysis were carried out at NILU. The analysis included aluminium (Al), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), molybdenum (Mo), cadmium (Cd) and lead (Pb). The metal analysis of soil sample will be used to evaluate the enrichment of certain component in the PM based on Enrichment Factors (EF) and on a reference crustal material represented by the soil sample. EF analysis is a classical approach in data screening and to support assumptions for PM sources for which little information is available. EF analysis shows enrichment of certain metals typical for a certain activity or source (e.g. combustion) compared to the crustal material. The EF is calculated according to:

$$(EF_X) = \frac{\left(\frac{C_X}{C_R}\right)_{aerosol}}{\left(\frac{C_X}{C_R}\right)_{crust}}$$

where, EFx is the enrichment factor of the element of interest (X); CX is the concentration of X in an aerosol sample (aerosol subscript) and soil material (crust subscripts). CR represents

the concentration of a crustal reference element. In our study, we have selected aluminium (Al) as crustal reference element, as for instance, Zhan et al., (2014).

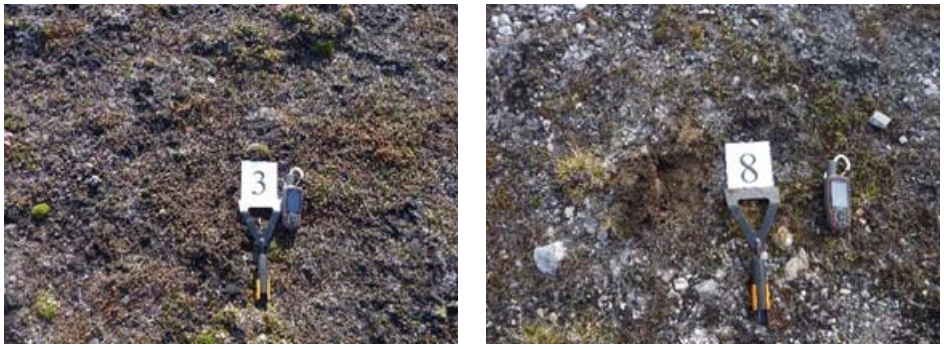

Figure 3: Example of soil samples collected.

2.2 PM sample collection

The PM_{10} samples are collected at the Zeppelin observatory at Svalbard on sampling intervals of about 72 or 96 hours long. The observatory is located at 79° N on Zeppelin Mountain (Figure 2), in an undisturbed arctic environment. Influence from local pollution sources, such as from the nearby community of Ny-Ålesund is considered to be limited because of the observatory's location at 474 metres a.s.l. However, as Eckhardt et al. (2013) showed, local pollution from tourist cruise ships in the Kongsfjord area influences observations at Zeppelin mountain station.

MISU used an air inlet with cut-off at 1 µm to collect 1-day or 2-day PM_1 samples on polycarbonate membrane (PCMB) for MSA and BC analysis, and on Millipore membrane filters for polysaccharides. The smaller size-fraction (PM_1) is required to eliminate local crustal material, which would otherwise dominate the samples. The use of PCMB filters avoids high chemical blanks common for the typically used glass fibre filters.

2.3 PM Chemical Analysis

As part of the surveillance program at Mt. Zeppelin observatory, 1-day air filter samples for PM_{10} are taken to analyse for major inorganic components of the aerosol: SO_4^{2-} (total), NO_3^- (+ HNO_3), NH_4^+ (+ NH_3), Cl-, Na+, K+, Mg2+, and Ca2+. Moreover 2-day air filters (PM_{10}) are taken for the analysis of metals (Ni, Cr, Cu, Zn, As, Cd, Pb, V, Mn, Zn, Se, Al, Mo, Fe). These measurements are part of the national monitoring programme conducted by NILU on behalf of the Norwegian Environment Agency (for more detail we refer to Aas, W., et al. 2014).

BC is analysed at MISU by a Photometer measuring light transmission and scattering at 528 nm (Engström and Leck, 2011), and corrected for effects of non-absorbing or low-absorbing particles by chemical quantification of the inorganic fraction on the PCMB filters. Polysaccharides are quantified after hydrolysis to their subunit monomers (monosaccharides) using Liquid Chromatography coupled with tandem Mass Spectrometry (LC/MS/MS). Biogenic sulphate in the samples gap to be inferred using the ratio non-sea salt sulphate/MSA from previous field measurements (i.e. 0.22; Leck and Persson, 1996). Microgels and soot particles were in addition sampled on microscope grids during 24 hours once per week for later Electron Microscope analysis by MISU. Based on Coz and Leck, 2011 both microgels and BC

particles will be mapped. The analysis of MSA is an ongoing process at the moment of writing this report. In this report we therefore only show the record of BC during the period from 29th December 2014 to 29th June 2015.

2.4 Black carbon measurements

Filter-based optical measurements of particulate black carbon in air have been determined during the period from 29th December 2014 to 29th June 2015 at Zeppelin station on Svalbard.

The collection of aerosol particles was operated with a Nuclepore® polycarbonate membrane (PCMB) based sampler using a filter cassette and subsequent post sampling determinations with a soot photometer instrument at the Department of Meteorology, Stockholm University, MISU.

The PCMB filter (0.4 µm pore size, 37 mm diameter) samples were taken for 1-2 days through isokinetic take off lines from the main inlet pipe. Sampling flow was 2.0 dm3 min-1. A cyclone with a size cut of Dp50 = 1 µm was mounted upstream of the sampler. After sampling, the PCMB filters were stored in filter cassettes, which were sealed with parafilm until post-sampling determinations.

For post-sampling determinations of the light absorption coefficient of BC (σap) a soot photometer instrument was used. To optimize the analytical conditions (increase the signal to noise ratio) in the BC determinations, the exposed PCMB Nuclepore® filter surface was masked to 8 mm sampling diameter (0.5 cm2 area).
The soot instrument used a 528 nm LED light source. A sensor behind the PCMB Nuclepore® filter measured the transmitted light intensity through the BC sample spot on the filter. A second sensor measured the transmitted light through an unexposed part of the filter. The difference in intensity of transmitted light between exposed and unexposed filter surface was used to calculate the optical density (Od). σap is defined as Od per meter air column and is calculated by multiplying Od with the PCMB filter sample spot area and dividing by the volume of air sampled. BC mass concentrations were subsequently derived using a mass absorption cross-section of $10\pm1 m^2 g-1$.

2.5 Positive Matrix Factorization (PMF)

Data analysis using Positive Matrix Factorization (PMF) is carried out for source identification of ship-related PM. The PMF is a type of factor analysis where the underlying covariability of many variables, such as sample to sample variation in PM species, is described by a set of factors to which the original variables are related. The method is based on a weighted least-squares method that uses the uncertainty for each measurement as the data point weights. The output from the PMF analysis is source profiles (factors) and time profiles (temporal variation of the factors). In this study, we have used US EPA PMF version 5.0.

A previous PMF study at Greenland by Nguyen et al. (2013) demonstrated the applicability of this method for Arctic stations. Based on own practical experience, PMF has three important requirements: (1) the data record (time series) has to be long enough, (2) a rather extensive

number of receptor species is needed, and (3) the uncertainties of the species measurements have to be assessed in a proper manner.

3 Results and Discussion

3.1 Chemical composition of soil samples

Table 1 shows the chemical composition of the soil samples expressed as trace metals. The 15 samples show similar chemical composition, characterized by high concentration of aluminium and iron, typical of crustal elements.

Table 1: Concentration of elements in soil samples at Ny-Ålesund. Unit: mg.kg^{-1} dried material.

	Al	V	Cr	Mn	Fe	Co	Ni
SM1	16 406	25.1	18.2	177.2	15 889	5.21	8.5
SM2	22 590	29.8	20.5	352.9	18 610	6.83	12.1
SM3	23 583	31.7	22.7	222.1	18 099	6.28	11.0
SM4	19 775	27.7	21.2	334.1	18 628	6.22	11.9
SM5	27 412	36.2	26.1	232.2	19 478	6.94	12.2
SM6	26 761	38.2	28.0	407.4	22 709	8.36	14.7
SM7	33 762	41.1	30.8	486.0	25 127	10.87	18.4
SM8	30 998	42.7	29.8	409.9	21 863	8.65	14.5
SM9	20 452	26.9	20.7	366.9	18 884	7.55	12.6
SM10	23 592	30.4	22.6	408.7	21 032	7.94	13.9
SM11	39 764	52.0	37.1	428.2	27 783	11.63	19.4
SM12	27 785	39.9	28.7	296.2	23 045	9.16	15.5
SM13	30 993	43.2	29.8	398.8	20 991	8.51	14.4
SM14	26 464	30.6	20.3	289.2	17 333	6.93	11.6
SM15	42 924	21.8	17.1	207.8	14 058	6.12	11.0

Table 2: Continuation from Table 1 (Unit: mg.kg^{-1} dried material)

	Cu	Zn	As	Mo	Cd	Pb
SM1	5.47	37.2	2.01	0.30	0.10	15.3
SM2	9.76	42.2	2.88	0.30	0.09	14.6
SM3	10.82	40.7	3.57	0.27	0.13	19.4
SM4	15.70	45.4	3.05	0.25	0.11	17.2
SM5	17.61	44.9	4.13	0.20	0.14	20.4
SM6	14.55	58.7	3.82	0.27	0.12	18.9
SM7	20.02	72.5	4.75	0.19	0.10	19.5
SM8	16.60	55.8	4.01	0.31	0.16	20.9
SM9	12.07	43.4	5.83	0.32	0.15	18.9
SM10	12.68	49.0	5.37	0.77	0.15	22.1
SM11	17.96	84.8	5.12	0.25	0.13	22.3
SM12	15.87	64.8	3.50	0.21	0.15	19.8
SM13	13.75	58.2	3.10	0.20	0.13	20.5
SM14	14.47	43.4	3.19	0.30	0.17	18.8
SM15	9.71	37.3	5.92	0.36	0.21	22.9

The comparison between the results from soil analysis obtained in our study and those reported by Zhan et al. (2014) shows reasonable similitudes (Table 3). Both average chemical compositions represent soil samples rich in aluminium and iron. Our average sample is analysed to be higher in vanadium (V) and nickel (Ni), whereas the soil sample reported by Zhan et al., (2014) shows higher chromium (Cr) and zinc (Zn) content.

The chemical composition of soil samples was used as crustal reference material to determine the enrichment factor of some compounds in the PM_{10} fraction (Chapter 3.2).

Table 3: Comparison between average results obtained in this study and published by Zhan et al., (2014). Units: mg kg^{-1}.

Elements	This Work (SHIPMATE)	Zhan et al. (2014)
Al	27 551	20 900
V	34.5	23.5
Cr	24.9	51.0
Mn	334.5	247
Fe	20 235	19 900
Co	7.8	5.1
Ni	13.5	7.69
Cu	13.8	17.0
Zn	51.9	115
As	4.0	3.82
Mo	0.3	n.a.
Cd	0.14	0.112
Pb	19.4	35.7

3.2 Chemical analysis of Particulate Matter and Enrichment Factors

The elemental composition of PM_{10} samples in summer 2015 is shown in tables from Table 4 to Table 8, along with the corresponding EF considering Al as reference element. Following the study of Zhat et al. (2014), we consider EF values below five as crustal origin, and those above five as non-crustal sources. Based on this evaluation, it is estimated that Cu, Zn, As and Cd are mainly of non-crustal sources, and V, Cr and Ni are estimated to be non-crustal for some of the sampling days.

In order to evaluate possible influences of ship emissions at Ny-Ålesund, we have examined the samples collected when ship events occurred. These events are identified based on analysis of passenger records at Ny-Ålesund and wind records at Mt. Zeppelin. From the sampling in summer 2015, we have identified four main ship events which have been highlighted in Table 6 and Table 7. On 22th of June and 15th July for instance, samples are evaluated as enriched in non-crustal components as Cr, Mn, Ni, Cu, Zn, As and Cd, whereas samples from 29th June and 8th of July, also characterized by ship events, seem to show lower levels of enrichment, and even several compounds are below detection limit. These differences may be explained by different meteorological conditions, resulting in variable level of impact of ship emissions at the sampling locations.

Table 4: PM chemical composition (April 2015) and EF for each element. EF values higher than 5 (red) are considered as non-crustal source. Empty cells: below detection limit. Unit ng.m^{-3}

Date	06.04.15		12.04.15		24.04.15		27.04.15	
	PM	EF	PM	EF	PM	EF	PM	EF
Al (ref)	31,79	1,00	69,00	1,00	36,67	1,00	19,71	1,00
V	0,22	5,56	0,05	0,62	0,04	0,97	0,03	1,25
Cr	0,29	10,20	0,19	2,99	0,07	2,09		
Mn	0,94	2,44	0,63	0,75	0,34	0,77	0,21	0,87
Fe	21,86	0,94	15,55	0,31	12,43	0,46	8,02	0,55
Co	0,03	2,86	0,01	0,40	0,01	0,62	0,00	0,71
Ni	0,32	20,64	0,09	2,75	0,06	3,54	0,03	3,33
Cu	0,49	30,96	0,22	6,22	0,07	3,59	0,11	11,56
Zn	6,46	107,90	1,21	9,34	0,62	8,98	0,44	11,85
As	0,92	198,25	0,06	5,63	0,04	7,08	0,05	17,68
Mo			0,03	43,74				
Cd	0,10	648,48	0,01	25,41	0,01	36,00	0,01	75,75
Pb	2,24	99,71	0,23	4,80	0,17	6,46	0,19	13,94

Table 5: PM chemical composition (May 2015) and EF for each element. EF values higher than 5 (red) are considered as non-crustal source. Empty cells: below detection limit. Unit ng.m^{-3}

	04.05.15		11.05.15		18.05.15		25.05.15	
	PM	EF	PM	EF	PM	EF	PM	EF
Al (ref)	72,74	1,00	35,22	1,00	38,73	1,00	7,31	1,00
V	0,06	0,68	0,04	0,83	0,05	0,94	0,03	2,99
Cr	0,15	2,24	0,07	2,34	0,17	4,87		
Mn	0,45	0,50	0,29	0,67	0,34	0,73	0,12	1,35
Fe	20,71	0,39	10,29	0,40	12,38	0,44	4,40	0,82
Co	0,01	0,52	0,00	0,49	0,01	0,55		
Ni	0,07	1,92	0,05	2,71	0,10	5,31	0,05	12,63
Cu	0,32	8,81	0,23	13,29	0,23	11,77		
Zn	0,99	7,23	0,69	10,33	0,79	10,81		
As	0,03	2,87	0,03	5,90	0,03	5,65	0,03	29,82
Mo								
Cd	0,004	10,89	0,005	27,62	0,004	22,88	0,005	130,79
Pb	0,12	2,32	0,12	4,64	0,13	4,88	0,11	21,21

Table 6: PM chemical composition (June 2015) and EF for each element. EF values higher than 5 (red) are considered as non-crustal source. Empty cells: below detection limit. Unit ng.m^{-3}. Yellow sample date: date with high ship events at Ny-Ålesund.

	01.06.15		08.06.15		15.06.15		22.06.15		29.06.15	
	PM	EF	PM	EF	PM	EF	PM	EF	PM	EF
Al (ref)	15,83	1,00	15,29	1,00	13,37	1,00	26,09	1,00	7,87	1,00
V	0,02	1,10	0,02	1,28	0,06	3,61	0,03	0,98	0,01	0,89
Cr					0,07	6,11	0,16	6,59		
Mn	0,17	0,86	0,12	0,64	0,16	0,96	1,93	6,08	0,09	0,93
Fe	7,97	0,69	5,97	0,53			6,37	0,33		
Co	0,00	0,90	0,00	0,65	0,01	2,15	0,01	1,84		
Ni	0,03	3,53	0,04	5,95	0,27	40,88	0,18	14,05		
Cu					0,22	33,41	2,94	224,70		
Zn							11,28	229,57		
As	0,02	8,66	0,02	7,04	0,04	19,24	0,02	5,88	0,01	8,92
Mo										
Cd	0,002	19,83	0,001	19,30	0,003	39,62	0,011	82,28	0,0004	12,40
Pb	0,04	3,53	0,04	3,68	0,07	7,28	0,05	2,60	0,01	2,64

Table 7: PM chemical composition (July 2015) and EF for each element. EF values higher than 5 (red) are considered as non-crustal source. Empty cells: below detection limit. Unit ng.m^{-3}. Yellow sample dates: dates with high ship events at Ny-Ålesund.

	08.07.15		15.07.2015		22.07.2015		29.07.2015	
	PM	EF	PM	EF	PM	EF	PM	EF
Al (ref)	21,96	1,00	9,99	1,00	17,62	1,00	4,41	1,00
V	0,02	0,81	0,05	4,31	0,02	1,08	0,03	6,13
Cr	0,06	3,14	0,05	5,43	0,08	4,97	0,15	36,42
Mn	0,20	0,74	0,16	1,33	0,18	0,85	0,07	1,25
Fe	8,78	0,54	4,83	0,66	8,68	0,67	3,56	1,10
Co	0,00	0,68				0,89	0,00	2,77
Ni	0,03	2,37	0,05	10,57	0,04	4,53	0,07	34,13
Cu	0,10	8,78	0,30	59,73	0,06	6,86	0,09	41,89
Zn			0,92	48,82	0,45	13,50		
As	0,01	3,77	0,02	11,93	0,01	5,64	0,02	38,66
Mo								
Cd	0,001	10,18	0,006	114,14	0,004	45,31	0,003	115,69
Pb	0,03	1,74	0,03	3,63	0,03	2,47	0,04	13,10

Table 8: PM chemical composition (August-September 2015) and EF for each element. EF values higher than 5 (red) are considered as non-crustal source. Empty cells: below detection limit. Unit ng.m^{-3}

	03.08.15		01.09.15		16.09.15		21.09.15		28.09.15	
	PM	EF	PM	EF	PM	EF	PM	EF	PM	EF
Al (ref)	10,18	1,00	14,02	1,00	27,09	1,00	6,51	1,00	27,54	1,00
V	0,02	1,35	0,02	0,98	0,03	0,85	0,01	0,74	0,03	0,83
Cr	0,05	5,01	0,07	5,29			0,05	9,04	0,21	8,49
Mn	0,16	1,28	0,15	0,90	0,22	0,67	0,06	0,75	0,29	0,85
Fe	5,92	0,79	6,40	0,62	11,51	0,58	1,95	0,41	8,29	0,41
Co		0,00	0,00	0,87	0,01	0,72				0,52
Ni		0,00	0,03	4,30		0,00			0,09	6,77
Cu	0,04	7,26	0,07	10,33	0,05	3,94	0,04	12,80	0,15	10,77
Zn	0,75	39,26							0,31	5,88
As	0,02	15,45	0,01	3,25	0,02	6,13			0,01	1,83
Mo						0,00				
Cd	0,01	119,71	0,0004	5,13	0,002	16,60	0,0003	8,98	0,001	7,94
Pb	0,04	5,32	0,01	1,17	0,05	2,41	0,01	1,21	0,02	1,07

3.3 Black carbon measurements results

Monthly numbers of collected and determined samples at the station are given in Table 1.The geographical location of the Zeppelin station and the local facilities (Figure 2) gave crucial conditions in the implementation phase of the instruments. This resulted in a delay of the full operation of the particulate BC sampling, and there were no measurements in all December 2014. The monitoring finalized in December 31st 2015. Filters stored at the station are still waiting to be shipped to MISU for subsequent analyses.

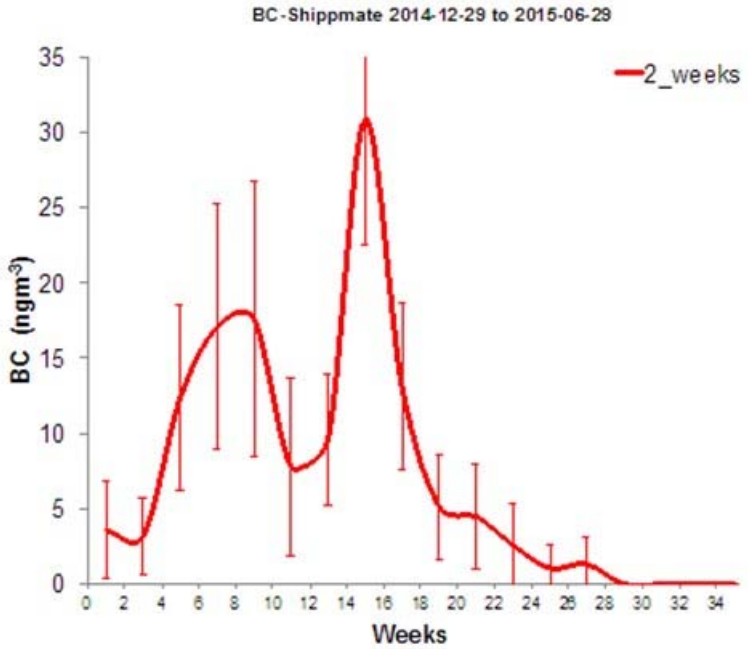

Figure 4: Black carbon time series (averaged over 2 weeks) from 29th December 2014 to 29th June 2015.

Black carbon measurements in Svalbard are shown in *Figure 4*. BC data, with elevated concentrations during week 5-9 and week 14 – 18, showed the typical Arctic haze seasonality established by Rahn et al. (1980). This seasonality is based on a generally strong import of polluted lower-latitude air during the period November – April into a source free Arctic. According to this concept, the annual minimum pollution import is reached during June – August. Maritime transportation is the biggest contributing sector to black carbon emissions in Svarbard, followed by landbased transportation which is mainly represented by heavy duty vehicles (diesel). Within maritime transportation, international cruises and marine coal transportation are the biggest subsectors (*Figure 5*). It is important to point it out that fishing vessels are not considered in this inventory. As it will be highlighted at the end of this report, a factor determined by PMF analysis (Factor 4) also shows high contribution in April and beginning of May, similarly to the black carbon measurements.

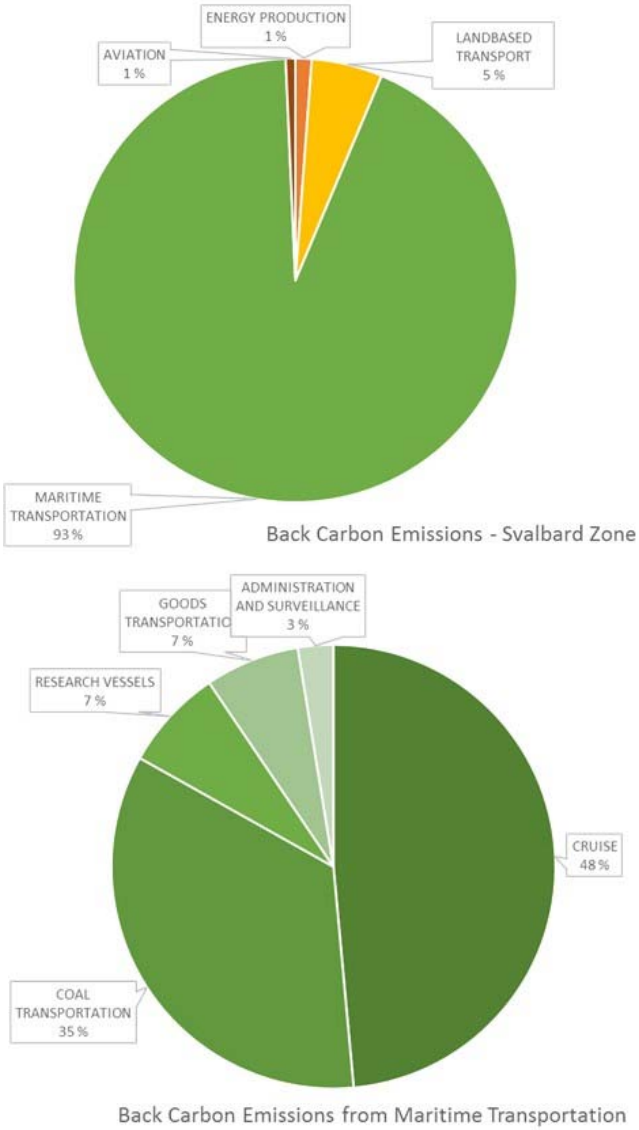

Figure 5: Distribution of Black Carbon Emissions in Svalbard in 2007 according to sectors (top) and subsectors within the Maritime Transportation (bottom). Data from Vestreng et al. (2010).

3.4 Positive Matrix Factorization

Concentration values of metals and inorganic compounds analysed on air filters by NILU together with estimated uncertainty for each chemical species from summer 2014 and 2015 were combined in an Excel data-sheet prepared for the PMF analysis. A base run with PMF was performed using the default number of 20 runs for 6 factors. The found 6-factor solution appears to be rather robust (Figure 6). Run 17 was selected, but all other 19 runs showed similar factors as no. 17. The interpretation of the resulting factor profiles is:

- **Factor 1:** Biomass burning, from long- or medium-range transport;
- **Factor 2:** Secondary regional or long-range transport, ammonium nitrate aerosol;
- **Factor 3:** Crustal, wind-blown soil, mineral dust;
- **Factor 4:** V-Pb-As, secondary sulphate aerosol;
- **Factor 5:** Sea-salt aerosol;
- **Factor 6:** Industrial emission, fuel combustion without sulphate;

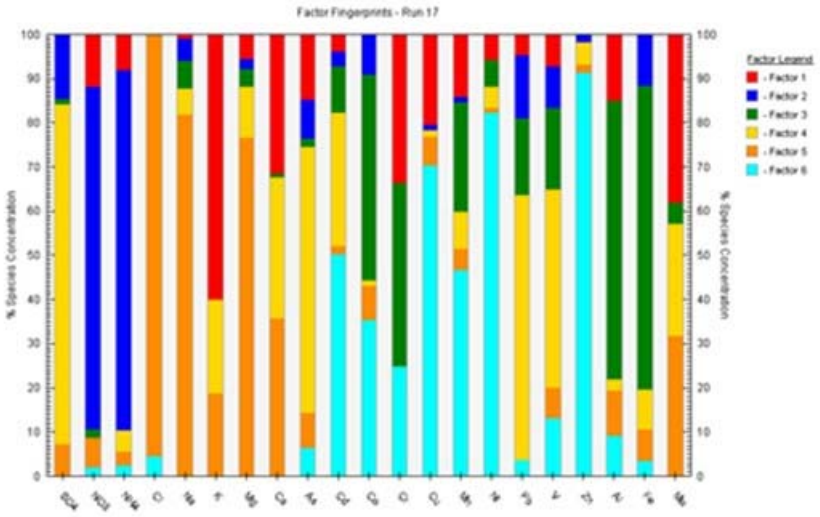

Figure 6: Factor fingerprints obtained from PMF analysis.

Solely based on the PMF analysis, Factor 4 and 6 (Figure 7) could both represent the "shipping emission" factor. One of them could be from the coal-fired power plant in Barentsburg. A clarification about the shipping factor can be obtained from a combined analysis of PMF factor contributions, harbour call records (KingsBay) and wind direction measurements at Zeppelin.

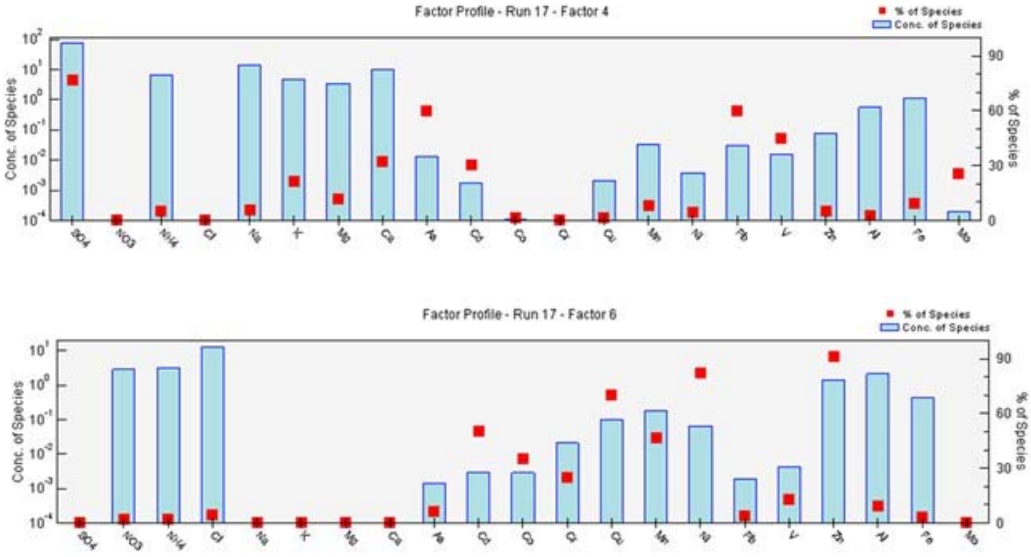

Figure 7: Factor profile of Factor 4 (upper plot) and Factor 6 (lower plot) showing concentration of species in ng m-3 (blue bars) and the percentage of chemical species attributed to this factor (red markers).

Variability due to chemical transformations or process changes can cause significant differences in factor profiles among PMF runs. Two error estimates were applied in the PMF analysis of the air filter measurements at Mt. Zeppelin observatory: Bootstrap (BS) analysis and Displacement (DISP) analysis. BS analysis is used to identify whether there are small sets of observations that can influence the solution more than expected based on their proportion. DISP is an analysis method that helps to understand the selected solution in finer detail, including its sensitivity to small changes. DISP error intervals include effects of rotational

ambiguity but do not include effects of random errors in the data. DISP analysis revealed that a 6-factor solution is sufficient to explain Mt. Zeppelin data unambiguously. BS with 100 runs was performed. Based on BS results, the relative standard deviation of the concentration of main constituents of the factor profiles in Factor 4 and 6 was 50-90%. The estimated error from BS for main constituents was higher than from DISP (Figure 8).

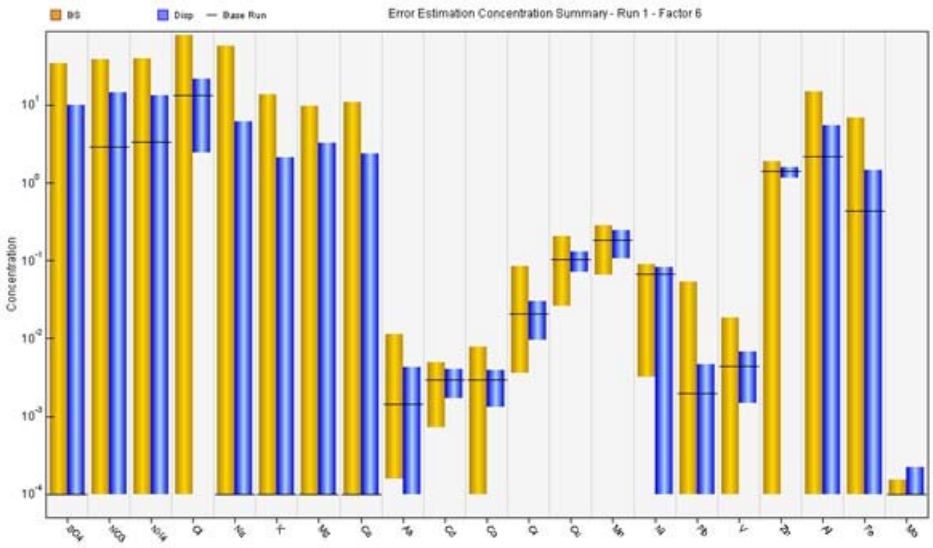

Figure 8: Error estimate by BS and DISP method for Factor 6.

Results from Combined Analysis

From the analysis of 40 air filter samples (metals and inorganic compounds) taken during the summers of 2014 and 2015, a total of 8 ship events, i.e. potential ship-influenced samples, were determined. A sampling interval was defined as ship event when the total number of passengers (PAX) of all ships at harbour of Ny-Ålesund (at berth, peer or anchored) during the period was ≥200 (Figure 9) and at the same time the frequency of northerly winds (sectors NNW: 330°-360° to NNE: 1°-30°) was ≥20% (Figure 10).

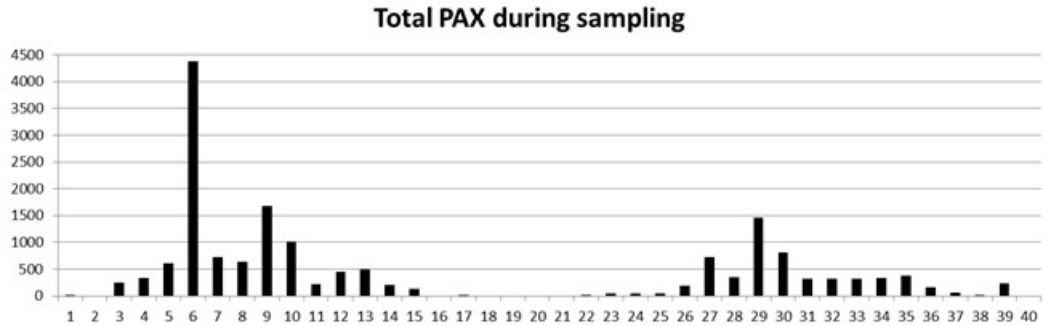

Figure 9: Total number of passengers (PAX) of all ships at Ny-Ålesund harbour during the 40 sampling intervals.

A ship event was defined as detected by a PMF factor when the normalized factor contribution for the respective sampling period (normalization of the factor contribution was done over the measured time series with average value of 1.0) was ≥ 1.0, most often corresponding to a clear peak in the factor contribution time series (Figure 11). According to this criterion, 3 of

the 8 ship events were detected in the contribution time series of Factor 6. Factor 6 included only one false-positive detection.

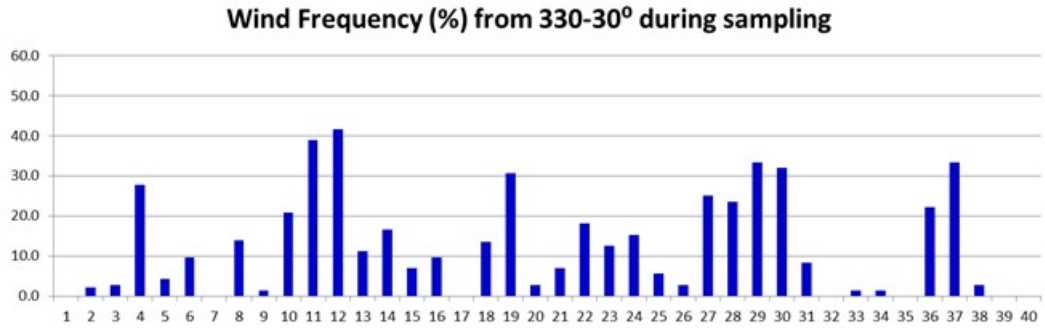

Figure 10: Frequency of northerly winds (NNW and NNE) during the 40 sampling intervals.

The other combustion factor, Factor 4, detected one ship event, and displayed much false-positive detection. The reason why 5 ship events were not found in Factor 6 was most probably that the analysis was based on sampling intervals (72 or 96 hours long) and not on hourly values. The onset of northerly winds may have occurred just before or after the ship stay in the harbour of Ny-Ålesund. This was most probably the case for sample no. 28 (06/29/2015 to 07/01/2015). Another reason might be that the ship plume did not reach the altitude of the Mt. Zeppelin observatory or that winds experienced at Ny-Ålesund were not from north. A previous study by Beine et al. (2001) already concluded that only when both Ny-Ålesund and Mt. Zeppelin station observe northerly air flow there is risk that the Mt. Zeppelin station could be influenced by the polluted air from the village.

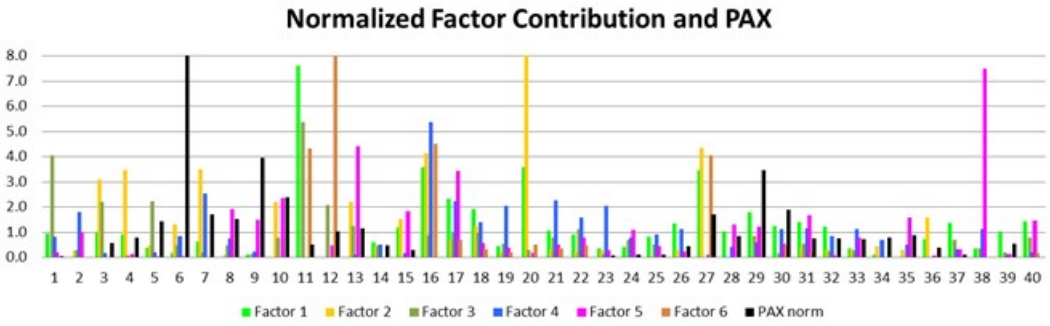

Figure 11: Normalized factor contributions and normalized PAX (normalization over time series with average value of 1.0) during the 40 sampling intervals.

4 Conclusions

This is the first report that unambiguously identifies the contribution of local ship pollution from cruise boats to measurements carried out at the Mt. Zeppelin observatory. For a ship plume to reach Mt. Zeppelin observatory two conditions had to be met simultaneously; 1) ships with 200 passengers or more in the harbour of Ny-Ålesund and 2) northerly winds at the observatory.

Northerly winds had a total frequency of less than 10% between January and October in the years 2014 and 2015. However, occasionally during a period of 3-4 weeks in summer the simultaneous presence of large vessels and northerly winds was found. A total of 8 potentially ship-influenced 3-day sampling intervals were found in the analysis of the wind direction record and the harbour calls from Ny-Ålesund in 2014 and 2015. Only three of these ship events were identified by the PMF Factor 6, which clearly is a result from combustion of marine gas oil or marine diesel oil on ships in Kongsfjord.

The local shipping pollution contributed significantly (≥50%) to the concentration levels of certain heavy metals such as Cu, Ni, Zn and Cd during the two summers. This feature is also observed based on the evaluation of enrichment factors determined from the PM elemental composition and the chemical composition of the local soil as crustal reference material. However, the influence of local pollution from shipping on the measurements carried out at the Mt. Zeppelin observatory is rather infrequent. It is likely that more remote ships which use crude oil are a contribution to the other fuel combustion factor found in the PMF analysis, such as Factor 4.

Factor 4 can be labelled as “secondary sulphate aerosol”. Coal-fired power plants on Svalbard (Longyearbyen and Barentsburg) are very likely the main contributors to this source. It is quite evident that the source is from a mesoscale range (10-300 km) of emissions on Svalbard and its surrounding sea, with frequent pollution peaks at Mt. Zeppelin. Figure 12 shows the normalized contribution of Factor 4 and Factor 6 in calendar weeks of 2015. High contribution of Factor 4 in April/May (weeks 15-22) coincides with measured peak concentrations of BC.

The analysis developed in this project will be refined to (1) include measurements of BC particle filters from MISU Stockholm in the PMF analysis, (2) hourly-based analysis of wind direction record and PAX record, and (3) back trajectory analysis for the identified ship events. Back-trajectories calculated by HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) would be an essential additional input to the study, as they inform about air mass origin.

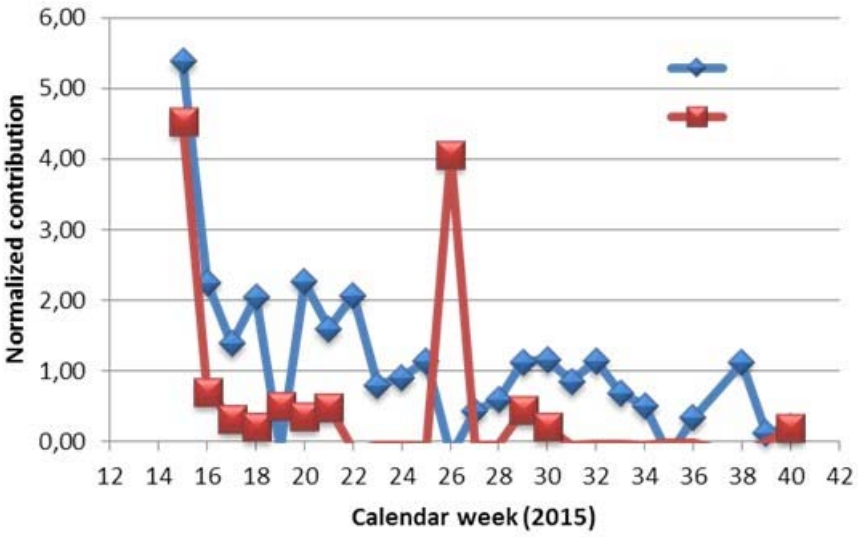

Figure 12: Normalized contribution of Factor 4 ("secondary sulphate aerosol") and Factor 6 ("cruise ships") for calendar weeks in 2015, starting 6th April and ending 30th September.

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ISBN: 978-82-425-2814-8
ISSN:

Norsk institutt for luftforskning
Norwegian Institute for Air Research