Positive Matrix Factorization of 47 Years of Particle Measurements in Finnish Arctic

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ABSTRACT

Forty seven years of weekly total suspended particle filters collected at Kevo, Finland from October 1964 through 2010 by the Finnish Meteorological Institute were analyzed for near-total trace elements, soluble trace elements, black carbon, major ions and methane sulfonic acid (MSA). The chemical composition dataset was analyzed by Positive Matrix Factorization using EPA PMF5. The entire dataset (1964–2010) was modeled as well as three separate time periods, 1964–1978, 1979–1990, and 1991–2010. The dataset was split in 1979 due to a change from Whatman 42 cellulose filters to a glass fiber filters, and in 1990 due to drops in concentrations related to the economic collapse of the Soviet Union. Two factors representing non-ferrous metal smelters were found for all time periods. One factor was dominated by Cu and the other by Ni and Co. Each of the time periods contained a factor describing stationary fuel combustion with high percentages of V, BC, and nss-SO\textsubscript{4}\textsuperscript{2-}; a ferrous metal factor dominated by Fe and some Mn; a biogenic sulfate factor; a factor containing the majority of Mo and W; and a factor dominated by Sn. The 1979–1990, 1991–2010, and 1964–2010 results contained a factor for As and Re, and a factor with the majority of Mn and Cd, which were not observed in 1964–1978. The 1964–1978 time period results contain three unique factors, a factor dominated by Ag, a factor dominated by Au, and a sea salt factor characterized by a high percentage of Na and Mg. The 1964–2010 period contains an Ag and Au factor as well. Ag and Au both have high concentrations in the late 1960s that decrease dramatically starting in the early 1970s. The increased uncertainty due to the high blanks in the glass fiber filters may account for the inability to determine a sea salt factor in the later time periods.

Keywords: Arctic aerosol; PMF5; Source identification; Potential Source Contribution Function.

INTRODUCTION

Particulate matter (PM) in the Arctic has been extensively studied, but there are a limited number of long-term datasets available to explore trends and changing patterns of sources. There is now data from forty-seven years of PM measurements at Kevo that are the longest available Arctic dataset. Previous work on these data have detailed chemical composition and solubility (Laing et al., 2014a), black carbon concentrations (Dutkiewicz et al., 2014), anthropogenic and biogenic sulfate concentrations (Laing et al., 2013), and determined long-range trends and source identification of individual species (Laing et al., 2014b). Kevo is heavily influenced by the industrial areas on the Kola Peninsula in Russia. The largest point sources are the Cu-Ni-Co ore roasting and smelting facilities, the Severonickel plant in Monchegorsk and the Pechenganickel plant in Zapolyarnyy/Nikel. The apatite mines at Apiatity and Kirovsk, the aluminium smelter at Kandalaksha, the iron ore mines and mills at Kovdor and Olengorsk, the Kirken's iron mine and mill in northern Norway, and industrial port city of Murmansk are also large sources of emissions close to Kevo.

Positive Matrix Factorization (PMF) analysis has been successfully used to assess source contributions from ground based particle measurements in the Arctic (Polissar et al., 1998; Siros and Barrie, 1999; Xie et al., 1999a; Yli-Tuomi et al., 2003b), and aerosol mass spectrometer (AMS) measurements made on ship cruises in the Arctic (Chang et al., 2011; Frossard et al., 2011). The goal of this paper is to apply PMF to weekly total suspended PM compositions measured from 1964–2010 at Kevo, Finland. The resolved
sources and their seasonal and long-term trends are discussed. Potential source contribution function (PSCF) analyses were performed on the sources to estimate the source locations.

METHODS

The Finnish Meteorological Institute (FMI) has been collecting weekly particle matter (PM) samples at Kevo, Finland (69°45′N, 27°02′N, height 98 m) since October 1964. Kevo is located 350 km north of the Arctic Circle (Fig. 1). The site is situated in the birch sub-zone of the boreal coniferous forest. The topography of the surrounding area is characterized by gently sloping fell highlands with river valleys. The elevation is mostly between 100 and 400 m above sea level. The area is sparsely populated (0.4 inhab/km²). The sun shines without setting from mid-May until the end of July, and remains below the horizon from late November to mid-January. The mean temperature of the coldest month (January) is –14.0°C and the warmest month (July) +13.1°C. The annual mean temperature is –1.3°C. The ground is already covered with snow in October, and on average, the snow cover remains until mid-May.

The Kevo Subarctic Research Station was originally established to monitor atmospheric radioactivity. From October 1964 to March 1978 rectangular 12 cm × 14 cm Whatman cellulous filters (Grade 42) were collected using a flow rate of approximately 7 m³/hr resulting in weekly sample volumes of about 1200 m³. Starting in January 1979, square 14 cm × 14 cm Whatman GF/A glass fiber filters were used with an average flow rate around 27 m³/hr and a weekly sample volume of approximately 4500 m³. The filters were analyzed for major ions and methane sulfonic acid (MSA) by ion chromatography (IC), near-total and soluble trace metals by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and black carbon (BC) by optical and thermal-optical methods (Dutkiewicz et al., 2014). The near-total trace metals were microwave acid digested and the soluble trace metals were water extracted. In this paper, the acid-digested elements will be designated “ad”, and the water-extracted elements “we”. Further details of the sample collection and chemical analysis are described in detail in Paatero et al. (1994), Laing et al. (2014a, b), Yli-Tuomi et al. (2003a), and Dutkiewicz et al. (2014).

Positive Matrix Factorization (PMF)

PMF was applied to the data using the EPA’s PMF V5 model. PMF is a multivariate receptor model that estimates the source profiles and their contributions based on a
Potential Source Contribution Function

Potential Source Contribution Function (PSCF) analysis was performed to determine source locations. Five-day back trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Hess, 1997, 1998). The archived metrolological data set REANALYSIS was used to compute back trajectories every day at 6 and 18 UTC with a starting height of 500 m above ground level. The choice of starting height is based on prior experience in a variety of PSCF applications (Cheng et al., 1993; Fan et al., 1994; Hopke et al., 1995; Polissar et al., 1999; Polissar et al., 2001; Lupu and Maenhaut, 2002). Additionally, this height is still below the 700 m maximum limit recommended by Westgate and Wania (2011). Fourteen trajectories were calculated per sample. PSCF analysis uses the chemical concentration and the back trajectories for each sample to determine source emission locations. The geographic area is divided into an array of 2.5° latitude × 2.5° longitude grid cells (Fan et al., 1994). If a trajectory passes through a cell it is assumed that what was emitted in that cell was transported to the receptor site. Using the mean concentration as the criteria value trajectories associated with samples above the criteria value are considered “high”. For each cell the ratio of high trajectories (nij) to total trajectories (nj) is calculated.

\[ PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \]  

(1)

If a cell has a small number of endpoints in it, it has a higher uncertainty associated with it. To account for this uncertainty the following weight function wij was multiplied to each cell:

\[ wij = \begin{cases} 1.0 & \text{if } np_{ij} > 2 \cdot \text{ave} \\ 0.75 & \text{if } np_{ij} < 2 \cdot \text{ave} \\ 0.5 & \text{if } 0.5 \cdot \text{ave} < np_{ij} \leq \text{ave} \\ 0.15 & \text{if } 0 < np_{ij} \leq 0.5 \cdot \text{ave} \end{cases} \]

(2)

where ave is the average number of end points in each cell, and npij is the number of the end points that fall in cell ij. This technique was employed by Cheng et al. (1993) and successfully used after (Hopke et al., 1995; Polissar et al., 1999; Xie et al., 1999b; Yli-Tuomi et al., 2003b).

There is some uncertainty in using a week-long sampling period. For each week long sample, two back-trajectories are taken per day, for a total of 14 back-trajectories per sample. Sivertsen et al. (1992) found polluted air from the Kola Peninsula to the Norwegian and Finish Arctic to be episodic, lasting 2–24 hours. Due to the long sampling period every “high” sample will include “polluted” and “clean” trajectories. Despite this artifact, major sources have been found using PSCF on week-long samples in the Arctic, at Kevo (Yli-Tuomi et al., 2003b) and Alert (Cheng et al., 1993; Hopke et al., 1995; Xie et al., 1999b). Another artifact arises from local sources. Sources close to the receptor site can cause high concentration samples regardless of air mass direction. Usually no clear local source areas can be found in PSCF analysis.

RESULTS

Detailed descriptions of the chemical compositions of the collected PM samples are provided in Laing et al. (2013; 2014a, b). The samples from 1964–1978 were collected using Whatman 42 cellulose filters, and the samples from 1979–2010 collected using Whatman GF/A glass-fiber filters. The glass-fiber filters had significantly higher blank values than the cellulose filters, which limited the availability of species in the dataset. Due to high blank concentration in the glass fiber filters, many species (Cl–, Al, Br, Cr, Li, Si, In, Zn) were rendered useless. The lack of certain species, specifically ones characteristic of soil related particles (Al, Si), markers of some industrial sources (Cr, Zn), and sea salt (Cl–) hindered identification of all of the possible sources. There are a number of species that have both an acid digested and water extracted value. The value with the
lower percentage of values below the detection limit and better determined uncertainties was chosen to include in the PMF analyses.

One of the assumptions of the PMF model is that the composition of the emission sources is constant over the period of sampling at the receptors. With a 47-year sampling period, it is unlikely that all of the sources affecting Kevo retained constant profiles. The entire dataset (1964–2010) and three subsets were analyzed separately using EPA PMF V5. The three subsets are 1964–1978, 1979–1990, and 1991–2010. The first split point was 1978, when the filter type changed from Whatman 42 cellulose to a glass fiber filter. The second split point was 1990, which was chosen based on sharp drops in concentrations of a number of species due to the economic collapse of the Soviet Union (Laing et al., 2013, 2014b). The change in the political-economic system in Europe around 1989–1991 was expected to change the nature of the sources and the related source profiles before and after 1990.

The choice of the number of factors was made based on producing physically realistic results with good fits to the data as evidenced by the scaled residuals. A 10-source model with an FPEAK of 0.5, a 9-source model with an FPEAK of 1.0, and a 10-source model with a FPEAK of 0.0 provided the most physically realistic solutions for the 1964–1978, 1979–1990, 1991–2010, and 1964–2010 time periods, respectively. There were no significant changes in the Q value after the rotations.

1964–1978

Ten factors were determined in the PMF analysis for the years 1964–1978 (Figs. 2 and S1 in the supplemental material). Se and Mo were down weighted by a factor of 3 because the signal-to-noise ratio was below 2. Re was poorly modeled and therefore, it was downweighted by a factor of 3. Seven data points were removed from that analysis for being anomalous. An extra modeling error of 14% was added. Yli-Tuomi et al. (2003b) used a mixed 2-way/3-way Multilinear Engine model on the same time period at Kevo but using INAA trace metal data instead of ICP-MS data employed in the present analysis.

Factor 1 contains the majority of V and nss-SO4, and also contributions of Pb, BC, K, Ca, Mn, and Cd, that are representative of stationary fuel combustion. The Ni/ V ratio (0.27) is very close to the ratio from residual oil combustion (0.28; Pacyna et al., 1984). Significant amounts of Pb, BC, K, Ca, Mn, and Cd are not generally associated with residual oil combustion. The presence of these species suggests an inclusion of additional fossil fuel consumption and industrial sources in addition to oil combustion. Jalkanen et al. (2000) found shale oil power plants in Estonia to be a major source of Ca, Fe, K, and trace elements in the Gulf of Finland. The factor is highly seasonal with maxima in the winter and minima in the summer (Fig. 3). During the winter, long range transport from mid-latitude regions to the Arctic is greatly enhanced accounting for this seasonality. In addition there is an increase in residual oil consumption for building heating in the winter. The PSCF plots using winter/spring months (Jan–Apr) and all months point towards source areas in European Russia, Poland, the Baltic States, Belarus, and Ukraine (Figs. 4 and S2). These are regions of significant residual oil consumption (Pacyna et al., 1984; Pacyna and Pacyna, 2001; EIA, 2013).

The second and third factors account for almost all of the Ag (85%) and Au (90%), respectively. Ag has a unique time trend with very high concentrations in the late 1960s and then dropping off to very low concentrations from 1970–2010 (Laing et al., 2014b). The Ag factor time series reflects this decrease (Fig. S1). Because of the uniqueness of the time series, it is not surprising that Ag is in a factor with no other species significantly contributing to it. It has previously been hypothesized that the high concentrations from 1964–1970 were due to the occasional smelting of Norilsk ores at the Nikel smelter (Busunia et al., 2003). The Norilsk ores have a high Ag, Au, and Pt content compared to those from the Kola Peninsula (Reimann et al., 1997; Busunia et al., 2003). In 1971 the Norilsk ore shipped to the Kola Peninsula was exclusively smelted at the Severonickel plant in Monchegorsk. Neither factor 2 nor factor 3 has much seasonal variation indicating a local source (Fig. 3). A similar Ag factor was determined by Yli-Tuomi et al. (2003b).

The fourth factor is identified as the non-ferrous metal smelters on the Kola Peninsula. Co and Ni are highly correlated and have previously been suspected as coming from the Pechenganickel Ni-Cu-Co smelter in Nikel/Zapolyarny (Laing et al., 2014a, b). No obvious seasonal trend can be seen in this factor (Fig. 3), indicating that the contributions do not depend on long-range transport during the winter/spring. Some As is also included in this factor, although most is contributed by factor 6. Arsenic is mainly emitted from non-ferrous metal production (Pacyna et al., 1984; Pacyna and Pacyna, 2001; AMAP, 2005) and high concentrations of As in addition to Co, Ni, and Cu, have been found in moss near the Ni-Cu-Co smelters on the Kola Peninsula (Reimann et al., 1997). The PSCF plot (Fig. S3) suggests a large source area covering Finland, the Baltics, Belarus, Ukraine and European Russia including the Kola Peninsula.

A sea salt factor (factor 5) was determined having high levels of Na and Mg. The Na/Mg ratio is 12.8, which is close to but higher than the ratio in seawater (8.37) (Mason, 1966). The higher ratio and the fact that the seasonal trend has maxima in Mar-Apr and Aug-Sep minima may point towards an anthropogenic source of Na in addition to sea salt (Fig. 3). Transport from mid-latitude anthropogenic sources to the Arctic is enhanced during the winter and early spring. The PSCF plots using all month estimate source regions in the oceans to the north and west of Kevo (Fig. S4).

Factor 6 is a mixture of different industrial sources. There are high percentages of Sb, As, Se and Tl, as well as some Mo and Re. Many of these species have large sources on the Kola Peninsula from various industrial activities (Reimann et al., 1996, 1997; Reimann et al., 2001). The As/Sb ratio is similar to that found on Kola Peninsula and the Urals (Vinogradova and Polissar, 1995). A strong seasonality indicated an influence from distant sources as well (Fig. 3). An increase
Fig. 2. Source profiles for the Kevo 1964–1978 run with the contribution and % of species for each factor.
in source contribution is observed from 1966–1968 (Fig. S1). The species in this factor are emitted from stationary fuel combustion in addition to industrial activities on the Kola Peninsula. The PSCF plots using all of the months and winter/spring months (Figs. S5 and S6, respectively) suggest source regions in the Baltics, Poland, Belarus, western Kazakhstan, European Russia, which are known areas of large scale stationary fuel combustion (Pacyna et al., 1984; Pacyna and Pacyna, 2001; EIA, 2013). The Ural industrial area and possibly Noril’sk are also highlighted regions.

The majority of Fe (82%) is accounted for in factor 7, with considerable amounts of Mn and Cd as well. Fe, Mn, and Cd in this study were determined by water extraction so mainly represent the anthropogenic fraction and are not likely to be associated with soil. The acid-digested samples for these species were not able to be determined due to excessive blank concentrations. Iron in fuel oil fly ash is very soluble (36%) compared to urban particles (3%) and coal ash (0.2%) (Desboeufs et al., 2005), but since there is not any V or Ni in the factor, it is unlikely that stationary fuel combustion accounts for much of the Fe. In addition the seasonal trend has slight maxima in the winter but is muted compared to the stationary fuel combustion factor (Fig. 3), suggesting a relatively local source. There are several possible sources surrounding Kevo including the Kirkens iron mine and mill in northern Norway, the iron ore mines and mills at Kovdor and Olenegorsk on the Kola
Peninsula, and iron ore mine and mills in Gällivare and Kiruna, Sweden (Luzin et al., 1994; Basunia et al., 2003). Reimann et al. (1996) found enhanced Fe concentrations in moss around these areas.

The eighth factor contains the majority of Mo and W. Mo and W are chemically similar and have been found together in minerals on the Kola Peninsula (Barkov et al., 2000). Reimann et al. (1997) attributed large areas of high Mo concentrations in moss to mining, processing, and transportation of alkaline rocks around Monchegorsk, Apatity, Kandalaksha, and Olenegorsk on the Kola Peninsula. The seasonal trend has slight maxima in February but is not very pronounced (Fig. 3), possibly from long range transport from continental European anthropogenic sources. Mo is also emitted from coal and oil combustion (Pacyna et al., 1984), which may explain the BC in the factor. The PSCF plots estimates source regions to be European Russia, Eastern Europe, and possibly Western Kazakhstan (Figs. S7 and S8).

Factor 9 contributes 93% of the MSA and represents biogenic sulfate emitted during the summer months in the oceans surrounding northern Finland. The factor has highest contributions in May–July (Fig. 3). The MSA/sss-SO$_4$$_2$$_2$ ratio for the factor is 0.23, which is similar to a previous study at Kevo from 1964–1978 (Yli-Tuomi et al., 2003b). Estimated source areas include the Barents, Norwegian, and Greenland Seas (Fig. S9). More extensive discussion of the MSA values as Kevo can be found in Laing et al. (2013).

The tenth factor includes the majority of Cu and Sn. Cu and Sn both have a sample of high concentrations ending on 3/14/1977 (176 ng/m$^3$ and 177 ng/m$^3$ for Sn and Cu, respectively) and relatively high concentrations until 7/25/1977, but are not very well correlated otherwise. Back-trajectories for this sample do not show any specific direction, although there are some trajectories that travel over the Kola Peninsula. Pollution events to the Scandinavian Arctic from the Kola Peninsula, defined by high SO$_2$ concentrations typically last only a few hours (Sivertsen et al., 1992; Ahonen et al., 1997; Virkkula et al., 1999). Given that the sampling period is a week, and the polluted air mass could last only a couple hours, it is hard to specifically pinpoint a specific source area. Cu concentrations at Kevo were determined to be most likely from the Severonickel Cu-Ni-Co facilities in Monchegorsk, ~250 km south-east of Kevo (Laing et al., 2014a, b). Given the lack of seasonal variation (Fig. 3) and ambiguous PSCF results (Fig. S10) for this factor, it is assumed that the factor characterizes the Cu-Ni-Co industry on the Kola Peninsula.

Yli-Tuomi et al. (2003b) determined a soil factor not seen in our analysis due to the lack of “soil” species. The ICP-MS analysis results did not include Al and Si due to excessive filter blank levels. The acid digestion for ICP-MS did not include hydrofluoric acid, and the major cations (Na, Mg, K, Ca) and soluble trace metals were determined by water extraction. Therefore most of the soil component of the species is locked in silicate and aluminosilicate minerals.

**Fig. 4.** PSCF plot using winter/spring months (January–April) for factor 1 in the Kevo 1964–1978 run.
that were not digested or extracted. In addition a wood smoke factor, defined by high BC and K concentrations was not found in this study but was reported by Yli-Tuomi et al. (2003b).

1979–1990

For the 1979–1990 interval, nine factors were resolved (Figs. 5 and S11). Compared to the 1964–1978 analysis, Au was not included due to a high percentage of below detection limit values. Sb-we was used instead of Sb-ad, and Re-ad used instead of Re-we because more values were above the detection limit. Pb was downweighted by a factor of 3 because the signal to noise ratio was below 2. Ag, Re, Se, and Tl were poorly modeled so were down weighted by a factor of 3. Because of the increased uncertainty due to high blank concentrations of the glass fiber filters, all of the cations (Na, K, Mg, Ca) were downweighted by a factor of 3. An additional 3% modeling error was added.

The first factor is characteristic of stationary fossil fuel combustion, mostly residual fuel oil, and is marked by high percentages of V, BC, K, Ca, and nss-SO₄. The Ni/V ratio (0.20) is similar to that found in the residual oil combustion factor for 1964–1978. Similar to 1964–1978 the seasonal trend has very pronounced winter maxima (Fig. 6), and there are amounts of Ag, Re, Pb, Se, Mo, and Sb in the factor not typically associated with oil combustion. The PSCF plot using winter and spring months suggest the same potential source areas, European Russia, Poland, the Baltic States, Belarus, and Ukraine, as the 1964–1978 stationary fossil fuel combustion factor (Fig. S12). For comparison, the 1980 global SO₂ emission rates (Dignon, 1993) are presented in Fig. S13. As these polluted air parcels travel from their source locations in Central and Eastern Europe, there is likely to be mixing with other sources such as coal combustion in the same regions and shale oil combustion in Estonia (Aunela-Tapola, 1997; Jalkanen et al., 2000). Mixing of sources on the same pathways may explain the addition of species such as Ca, Se, Mo, and Sb in the factor.

Factor 2 explains 82% of Sn, and there are also significant contributions of Pb, Na, and Mg. The seasonal trend is different than what is typical for Arctic Haze (Fig. 6). Instead of a winter/spring maximum, there is a minimum in May and a steady increase until October, where the contribution plateaus until March. The PSCF plot using winter and spring months (Fig. S14) suggest a possible source in the Ural industrial area. The plots also suggest sources in the Kara and Barents Sea, which could be due to the large winter maxima. It was speculated that the Mo and W factor in 1964–1978 was primarily from mining, processing, and transportation of alkaline rocks on the Kola Peninsula. The seasonal trend and addition of species from other industrial sources seem to point towards this factor being a mix of different industrial sources (Fig. 6). Mo, Mn, Se, and Tl are primarily emitted by coal combustion and the Sb/Mo ratio in this factor (0.72) is very similar to the ratio for coal combustion in Europe (0.75; Pacyna et al., 1984). The PSCF plot using the winter/spring months estimates source regions to be European Russia and Eastern Europe (Fig. S16), which is similar to the Mo, W factor (factor 8) determined for 1964–1978.

Factor 5 accounts for 85% of As, with a substantial amount of Se, Re, and Cd. The Cu-Ni-Co smelter facilities on the Kola Peninsula are a known source of As (Siivertsen et al., 1992; Reimann et al., 1997; Reimann et al., 2001; Barcan et al., 2002). As has a higher vapor pressure than other elements emitted from non-ferrous metal smelting and occur mainly in fine particles, which affects the residence time in the atmosphere (Kelley et al., 1995; Yli-Tuomi et al., 2003b). Suggested source regions include in European Russian, Belarus, Poland, Ukraine (Figs. S17 and S18). The plots also show smaller suggested source areas in the Ural industrial area and Pechora Basin, known areas of non-ferrous metal smelting and significant As emissions (Boyd et al., 2009). These source areas are very similar to the mixed industrial source (factor 6) in the 1964–1978 results.

The sixth factor is characterized by high percentage of Cu. One of the main sources of Cu for the entire dataset was speculated to be the Severonickel plant in Monchegorsk (Laing et al., 2014b). The seasonal variation is different from the general Arctic haze trend with maxima from October–January (Fig. 6). Trends typical of Arctic haze are seen most clearly in factors 1 and 4. The peculiar trend of this factor also differs from the other time periods’ factors dominated by Cu. Factor 10 and factor 4 from the 1964–1978 and 1991–2010 time periods, respectively, do not show any seasonality. The PSCF plot for all months suggests that the Ural area and Noril’sk non-ferrous metal facilities (Fig. 7). The Noril’sk smelter is a significant point source and is estimated to emit twice as much Cu to the atmosphere annually compared to the Kola Peninsula smelters (Boyd et al., 2009). The PSCF plot also suggests some source areas in the Barents and Kara Seas, which could be due to the substantial amount of Mg in the factor.

Factor 7 contains the majority of Mn and Cd. It is not certain why these two species are together in the factor. Mn is a siderophile predominantly emitted from ferrous metal production; Cd a chalcophile from non-ferrous metal production (Pacyna et al., 1984; Pacyna and Pacyna, 2001). A seasonal trend with maxima in February–April is observed in the monthly box plots (Fig. 6). Areas of high PSCF ratios include Central Russia near Moscow, the Urals, and Western Kazakhstan (Figs. S19 and S20). The ferrous metal factor (factor 8) explains 86% of Fe and is very similar to the ferrous metal factor from 1964–1978 (factor 7). Suggested source areas include Poland, the Baltics, Belarus, Ukraine, European Russia, and the Urals (Figs. S21 and S22).

The last factor is dominated by Co and Ni and represents non-ferrous metal smelting. It is very similar to factor 4 in 1964–1978. The seasonal plot shows a slight seasonal trend
Fig. 5. Source profiles for the Kevo 1979–1990 run with the contribution and % of species for each factor.
(Fig. 6), most likely due to the presence of V in the factor. The PSCF plots for all months and winter spring months are very similar to factor 3 in 1964–1978 with suggested source regions in European Russia, the Kola Peninsula, the Pechora Basin and the Ural industrial area (Figs. S23 and S24).

1991–2010

Nine factors were resolved for the 1991–2010 period (Figs. 8 and S25). The same species were used as in the 1979–1990 period. Ag, Re, Se, Pb, Tl, Na, K, Mg, and Ca were down weighted by a factor of 3. An additional 8% modeling error was added.

The first factor contains the majority of As and Re, with some Se and Cd, a result that is very similar to factor 5 in 1979–1990. The seasonal variation allude to heavy influence from relatively local sources (Fig. 9) and the PSCF plot for winter and spring months suggest source regions on the Kola Peninsula, the Urals (Fig. 10).

The second factor contains 83% of Sn. Sn has a unique time series with a sharp increase in contribution in 1992 (Fig. S25). The monthly box plots show no seasonal effects (Fig. 9) and the PSCF plot has no areas with a ratio higher than 0.2. The increase in the Sn factor matches a sudden decrease in the Cu factor. It was hypothesized in Laing et al. (2014b) that the increase may be related to a sudden change in the industrial process at the non-ferrous metal smelters on the Kola Peninsula in response to the collapse of the Soviet Union.
Factor 3 is stationary fossil fuel combustion with high contributions of V, BC, Na, K, nss-SO$_4$, Mo, and Sb. Similar to residual oil factors (1964–1978 factor 1; 1978–1990 factor 1), there are winter maxima and summer minima (Fig. 9), and PSCF plots estimate source locations in Eastern Europe and European Russia (Figs. S26 and S27).

The fourth factor is indicative of non-ferrous metal smelting, consisting of 84% of Cu. There is a lack of seasonal variation in this factor (Fig. 9), which differs from the Cu factor in 1979–1990 (factor 6). Furthermore, whereas the Cu factor from 1979–1990 has potential source regions in the Urals and possibly Noril’sk, the PSCF plots for this factor are inconclusive, they do not show any regions with a ratio higher than 0.4 (Fig. S28). Cu concentrations decreased dramatically after 1990 (Laing et al., 2014a, b). From 1991–2010 the average concentration was 4.55 µg/m$^3$, much lower than 1964–1978 (15.6 µg/m$^3$) and 1979–1990 (29.3 µg/m$^3$).

The biogenic sulfate (factor 5) is similar as the previous time periods with maxima in the summer and suggested source regions in the Barents, Norwegian, and Greenland Seas (Fig. S29).

Factor 6 is dominated by Mo and W. Similar to the 1964–1978 Mo and W factor (factor 8) there is a substantial contribution of BC and not much of anything else. Typical Arctic haze seasonality was observed with maxima in the late winter/spring and summer minima (Fig. 9). PSCF plots indicate potential source areas European Russia and Eastern Europe (Figs. S30 and S31), comparable to the Mo, W factors in 1964–1978 (factor 8) and 1979–1990 (factor 4).

The source profile for the ferrous metal factor (factor 7) is dominated by Fe and also some Mn. Similar factors are observed in 1964–1978 (factor 7) and 1979–1990 (factor 8). There is a lack of seasonal trend which seems to indicate the local iron mine and mills as the potential source. Source locations point towards these local sources on the Kola Peninsula as well as Central and Northern Russia (Figs. S32 and S33).

Factor eight is representative of a mix of industrial sources. There are high percentages of Ca, Mn, Cd, Sb, and Tl. Notably the highest percentages are Mn and Cd, which have their own factor in 1979–1990 (factor 7). There is greater seasonality in the 1991–2010 factor compared to the pure Mn and Cd factor in 1979–1990, most likely because of the addition of other species with source regions in mid-latitude Europe and Eurasia. Source regions are estimated to be predominantly in European Russia and Eastern Europe (Figs. S34 and S35).

Non-ferrous metal smelting, characterized by Ni and Co, was identified in factor 9. V contributes heavily to this factor as well, a result seen in 1979–1990. The addition of V has an effect on the seasonal variation, which is typical of Arctic Haze (Fig. 9). The PSCF plots do not show any areas with a PSCF ratio above 0.4. The areas shown are European Russia and northern Russia near the Kola Peninsula, White Sea, the Pechora Basin and the Urals (Figs. S36 and S37).
Fig. 8. Source profiles for the Kevo 1991–2010 run with the contribution and % of species for each factor.
Sea salt was not determined for the two time periods after 1978. Na and Mg were correlated ($r^2 = 0.459$) for the 1964–1979 time period but not for the 1979–1990 and 1991–2010 time periods. The increased uncertainty due to the high blanks in the glass fiber filters may account for the inability to resolve sea salt. Similar to 1964–1978, sources characterizing soil and wood smoke were not determined.

**1964–2010**

PMF analysis was performed on the entire dataset (1964–2010) as well as the selected time periods. The factor profiles are in Fig. 11, source contribution time series in Fig. 12, and yearly averaged time series in Fig. 13.

The first factor for 1964–2010 is the fossil fuel combustion defined by V, BC, K, Ca, and nss-SO$_4$ with some Se, Mo, and Sb. With the strong seasonality (Fig. S38), PSCF sources indicating areas of heavy fossil fuel consumption (Figs. S39 and S40), and a majority of vanadium, and a Ni/V ratio of 0.20, it can be assumed that this source mostly represents residual fuel combustion. The additional species in the factor (Ca, Se, Mo, Sb) indicate a mix of other industrial sources, coal consumption, and shale oil consumption in the source (Payna et al., 1984; Jalkanen et al., 2000; Pacyna and Pacyna, 2001).

Mo, W, and Se dominate the second factor. Mo and W have known sources on the Kola Peninsula from mining activities. The seasonality is pronounced with winter maxima possibly due to influence of coal and stationary fuel.
combustion in the mid-latitudes. In Europe Se and Mo are primarily emitted from coal and oil combustion (Pacyna et al., 1984; Pacyna and Pacyna, 2001). The PSCF maps vaguely suggest European Russia, the Baltics, Poland, Germany, Belarus and Ukraine as sources (Figs. S41 and S42).

Factor three characterizes Ag and Au. The contribution for this factor has a peak in the late 1960s and early 1970s, then decreases sharply after 1978 (Fig. 13). Because of this decrease it is best to analyze these factors in 1964–1978.

The fourth factor contains 85% of Cu and is representative of non-ferrous metal smelting. The time series shows the increase in contribution from ~1977 to ~1990 previously discussed (Fig. 13). The 1964–2010 PSCF results are very similar to 1978–1990 only not as defined (Fig. S43). As the 1978–1990 time period is when the Cu contribution was at its peak, this result is expected.

Fe dominates the fifth factor with no significant percentage of any other species. The yearly averaged time series shows a steadily decreasing contribution over the 47-year time period (Fig. 13). The 1964–2010 PSCF results are very similar to 1978–1990 only not as defined (Fig. S43). As the 1978–1990 time period is when the Cu contribution was at its peak, this result is expected.

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Non-ferrous metal smelting factor 1 is assigned to factor 7. In addition to Ni and Co, there is some contribution from V. A decreasing trend (Sen’s slope of ~2.01 %/yr) is observed in the yearly averaged time series (Fig. 13). Ni and Co have very similar decreasing trends over the 47-year time period (Laing et al., 2014b).

The eighth factor represents a mix of industrial sources and is characterized by high percentages of Mn, Cd, Pb, Sb, Ca, and Tl. The highest contributions of this factor are in the 1960s and early 1970s, after which the source undergoes decreases significantly until 2011 (Fig. 13). An overall trend of ~3.96 %/yr was determined using the seasonal Mann-Kendall trend test associated with Sen’s slope. All of the species in this factor have undergone dramatically decreasing trends from 1964–2010 (Laing et al., 2014b).

Factor 9 contains 87% of Sn in the analysis. Sn has a very unique time series with a dramatic increase in contribution in 1992 (Fig. 12). The sudden increase in 1992 is discussed in greater detail in analysis of the 1991–2010 run. The majority of As and Re are described in factor 10 and there is little contribution from any other species. There is a slight seasonal trend with maxima in February and March. The yearly average time series shows a decreasing trend (~2.36 %/yr; Fig. 13). In the other runs of shorter time period there are other species present in the source profile. The differences between the runs of similar sources will be discussed in more detail in the next section.

DISCUSSION AND CONCLUSION

Two factors representing non-ferrous metal smelters, one dominated by Co and Ni, the other by Cu, were observed.

Fig. 10. PSCF plot using winter/spring months (January–April) for factor 1 in the Kevo 1991–2010 run.
Fig. 11. Source profiles for the Kevo 1964–2010 run with the contribution and % of species for each factor.
Fig. 12. Contribution time series for the Kevo 1964–2010 run. The units are arbitrary so comparison between factors is not possible.

for all of the time periods. The Ni/Co ratios for the three runs in the Ni-Co factor are 16, 20, 26, and 21 for the 1964–1978, 1979–1990, 1991–2010, and 1964–2010 time periods, respectively, which are close to the ratios from the major Cu-Ni-Co smelters on the Kola Peninsula and Noril’sk. The Ni/Co ratio from emissions estimates from Nikel, Zapolyarny, Monchegorsk, and Noril’sk are 26, 30, 20, and 19, respectively (Boyd et al., 2009). The 1964–
1978 data subset has the lowest percentage of Co and Ni in the non-ferrous metal smelting factor (52% and 40% for Co and Ni, respectively) compared to the other runs which Co and Ni contribute between 62% and 71%. A lack of seasonality in 1964–1978 is not seen in the other time periods Ni-Co factors possibly because 1964–1978 does not contain a significant contribution of V as the others do. Arsenic contributes to the 1964–1978 data, which is not seen in the others. The Cu factor in 1964–1978 contains the majority of Sn, which splits to its own source factor in the other runs. Contributions of Cu peak from 1978–1990 (Fig. 13). The Cu factor for the middle time period (1979–1990) differs from the others in that a clear seasonality is observed and the estimated source areas suggest a possible
influence from the Urals and possibly Noril’sk.

Excluding the 1964–1978 interval in which Cu and Sn were together in a factor, the factors describing Fe and Sn changed very little between all of the runs. In the biogenic factor, the MSA/nss-\(\text{SO}_4\) ratio varied for the different time periods. The ratios for the 1964–1978, 1991–2010, and 1964–2010 time periods were relatively high (0.23, 0.22, and 0.13) compared to the 1979–1990 period (0.05). These ratios are lower than the MSA/nss-\(\text{SO}_4\) ratio for clean air parcels during summer at Svalbard (0.28; Heintzenberg and Leck, 1994), but Kevo is more heavily influenced by anthropogenic \(\text{SO}_2\) emissions than at Svalbard. In previous

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation under grants no. AGS-1007329 (Clarkson University) and AGS-1007261 (SUNY-Albany). The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYPLIT transport model used in this publication.

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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Received for review, April 24, 2014
Revised, September 16, 2014
Accepted, September 16, 2014