Identification of Source Nature and Seasonal Variations of Arctic Aerosol by Positive Matrix Factorization

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ABSTRACT

Week-long samples of airborne particulate matter were obtained at Alert, Northwest Territories, Canada, between 1980 and 1991. The concentrations of 24 particulate constituents have some strong, persistent seasonal variations that depend on the transport from their sources. In order to explore the nature of the cyclical variation of the different processes that give rise to the measured concentrations, the observations were arranged into both a two-way matrix and a three-way data array. For the latter, the three modes consist of chemical constituents, weeks within a year, and years. The two-way bilinear model and a three-way trilinear model were used to fit the data and a new data analysis technique, positive matrix factorization (PMF), has been used to obtain the solutions. PMF utilizes the error estimates of the observations to provide an optimal pointwise scaling data array for weighting, which enables it to handle missing data, a common occurrence in environmental measurements. It can also apply nonnegative constraints to the factors. Five factors have been obtained that reproduce the data quite well for both two-way and three-way analyses. Each factor represents a probable source with a compositional profile and distinctive seasonal variations. Specifically, there are (i) an acid photochemical factor typified by Br^-, H^+, and SO_4^{2-} and characterized by a concentration maximum around April, or shortly after polar sunrise; (ii) a soil factor representing by Si, Al, and Ca and having its main seasonal maximum in September and October; (iii) an anthropogenic factor dominated by SO_4^{2-} together with metallic species like Pb, Zn, V, As, Sb, Se, In, etc., peaking from December to April; (iv) a sea salt factor consisting mainly of Cl, Na, and K with maximum concentrations during the period from October to April; and (v) a biogenic factor characterized by methanesulfonate and having a primary maximum at May and a secondary maximum in August. The results obtained by both two-way and three-way PMF analyses are generally consistent with one another. However, there are differences because of additional constraints on the solution imposed by the three-way analysis. The results also help to confirm the hypotheses regarding the origins of the Arctic aerosol.

1. Introduction

The nature, origins, and transport of the Arctic aerosol have been the subjects of active research since 1970. Arctic haze was thought to consist mainly of windblown dust in the early studies. Based on routine ground-level observations of the chemical composition of suspended particulate matter that are available from the late 1970s on, considerable progress has been made in understanding the origin of the airborne particulate matter. It is now known that the Arctic atmosphere is not a pristine environment unaffected by air pollution and that Arctic haze originates from both man-made pollution and natural sources like windblown dust and sea salt (Barrie 1986). The concentration of pollution in the Arctic has a strong seasonal variation characterized by a summer minimum and a winter maximum. Furthermore, during winter, much of the particulate matter is mostly of man-made origin, while in summer, the lower concentrations are contributed mainly by natural origins (Barrie 1986; Barrie and Hoff 1985). In order to understand the real or potential effects of the Arctic air pollution to the polar ecosystem and global climate and to develop an appropriate strategy for controlling and reducing the extent of Arctic air pollution, a series of questions, such

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as the nature of the man-made pollutants, the origins of the chemical species, the mechanism of the long-range transportation, and the transformation of gaseous compounds in the atmosphere that occurs in the cold polar region, needs to be understood.

By collecting samples of airborne particles over time and characterizing those samples by analytical measurement of a variety of chemical species, a dataset can be developed such that the nature (underlying structure) of ambient air pollution data can be determined using multivariate receptor models (Hopke 1991). Techniques commonly used are principal component analysis (PCA) and target transformation factor analysis (Hopke 1988). However, the widely used PCA and related techniques suffer from several drawbacks. The factors of PCA are rarely physically explainable without rotation, and no fully satisfactory transformation (rotation) techniques have yet been found. In addition, PCA really represents a least squares minimization. This fit is weighted by implicitly assuming unrealistic standard deviations for the variables in the data matrix. Thus, the results of a principal components analysis do not represent a minimum variance solution since they are based on an incorrect weighting (Barrie and Barrie 1990). A different approach, called positive matrix factorization (PMF), was recently developed by Paatero and Tapper (1993, 1994) to address such problems. This new technique differs from the customary PCA because the error estimates for the individual data point values are utilized as point-by-point weights. In addition, constraints on the results such as nonnegativity of the factors is integrated in the computational process. These are very useful features for the receptor modeling of environmental data. In the analysis of airborne particle samples using nuclear analytical methods such as X-ray fluorescence or instrumental neutron activation analysis (INAA), error estimates of the observations are readily available. For the factor analysis of such data, both of the resulting matrices must be nonnegative. PMF has been successfully applied to the analysis of daily precipitation sample data from Finland (Juntto and Paatero 1994), for the source identification of bulk wet deposition in Finland (Anttila et al. 1995), and of aerosol in Alaska (Polissar et al. 1996).

Data collected in air pollution monitoring systems can logically be arranged into three-way data arrays in order to examine the spatial and temporal variations of the system as a whole. An obvious example is data from air-quality-monitoring networks that routinely collect a time sequence of samples from multiple sites and analyze those samples for a variety of species (Zeng and Hopke 1990) so that the three ways are location, time, and chemical species. In other cases, a typical two-way data block from a time sequence of measurements from a single monitoring site can be rearranged into a three-way or even higher data array if there are inherent periodic variations (daily, weekly, monthly, or yearly) that exist in the observations and the objective of the analysis is to reveal the nature of the assumed periodicity.

There have been some efforts to employ three-way data analysis techniques for receptor modeling (Zeng and Hopke 1990, 1992a,b) and relationship elucidation (Gemperline et al. 1992) of environmental data. By applying three-way analysis methods to both simulated and real ambient airborne particle data, Zeng and Hopke (1990, 1992a) tested three-mode factor analysis for receptor modeling. The same authors also tried to fit three-way environmental data into a trilinear model, and direct trilinear decomposition algorithm was used for solving the trilinear model (Zeng and Hopke 1992b). Positive matrix factorization can be extended to fit a trilinear model to three-way data arrays, but it has not been previously used in this manner (Paatero 1997a).

Inspection of the time series of aerosol species concentrations at Alert over the time interval from 1980 to 1991 shows recurring yearly cyclical variations. From the time series of the aerosol species (Barrie and Hoff 1985) and with the aid of a principal component analysis (Barrie and Barrie 1990), Barrie and coworkers have tried to identify the possible pollution sources of Arctic aerosol and their seasonal variations. Because of a substantial number of missing data and values below the detection limit existing in the aerosol measurements, especially for the summers, only winter data were used in the principal component analysis (Barrie and Barrie 1990). They identified four sources including soil, sea salt, anthropogenic aerosol, and a fourth factor associated either with photochemical reaction (Barrie and Barrie 1990) or a halogen factor (Barrie and Hoff 1985). Seasonal variations of the possible sources were revealed by the time series of four elements with each representing a different source (Barrie and Barrie 1990), or by the average seasonal variation of groups of species that were believed to come from the same sources (Barrie and Hoff 1985). However, considering the possibility of multiple sources of some species and the inherent randomness of the observations, it is difficult to identify the number of possible sources, their composition, and the seasonal variation of each source simply from the time series of the original measurements.

In this report, the complete set of aerosol measurements from Alert, Northwest Territories, Canada, between September of 1980 and August of 1991 was arranged into both two-way and three-way data arrays and PMF was used for both bilinear and trilinear modeling. Based on the chemical composition data and the factors from the PMF modeling, the possible sources of aerosol particulate and their seasonal variation were identified.

2. Sampling and chemical composition determination

Airborne particulate samples were collected at Alert, Northwest Territories, Canada (latitude 82.3°N, longitude 62.5°W) by the Atmospheric Environment Services

TABLE 1. The analytical method, geometric mean, and estimated detection limit of measured concentration for each aerosol constituent.

Aerosol	Analytical method	Geometric mean	Detection limit
Cl^-	IC	51.34	10
Br^-	IC	1.53	1
NO_3^-	IC	45.53	1.5
SO_4^{2-}	IC	500.8	4
H^+	IC	1.01	0.3
Na^+	IC	71.14	4
NH_4^+	IC	57.16	6
K^+	IC	7.35	3
MSA	IC	4.27	4
Zn	ICP	2.25	1
Pb	ICP	0.60	0.2
Mn	INAA	0.69	0.05
V	INAA	0.21	0.005
Al	INAA	58.43	1
Ca	INAA	70.57	5
Ti	INAA	5.23	0.5
I^-	INAA	0.24	0.03
In	INAA	0.00073	0.0005
Si	INAA	192.3	190
As	INAA	0.13	0.05
La	INAA	0.033	0.04
Sb	INAA	0.025	0.04
Sm	INAA	0.0086	0.005
Se	INAA	0.027	0.05

of Canada. Samples have been collected on a weekly basis since July 1980. Details of the sampling and procedures of chemical analyses were given by Barrie et al. (1989) and Barrie and Hoff (1985). Major ions were analyzed by ion chromatography (IC), and trace element data were obtained by instrumental neutron activation analysis (INAA) and by inductively coupled plasma emission spectroscopy (ICP). The range of average detection limits for the different analytical techniques were given by Barrie and Hoff (1985) and Barrie and Barrie (1990). A detailed summary of statistics of the chemical concentrations of aerosol species were reported and a comprehensive frequency distribution analysis suggested that most of the species are lognormally distributed (Cheng et al. 1991). Since some species have a large number of missing data and values below detection limits, data for only 24 chemical species measured in samples obtained between September 1980 and August 1991 were used in this analysis. After replacing the missing data with the corresponding geometric means, there are 532 weekly average concentrations. Thus, a 532 × 24 data matrix was available for the two-way data analysis. Table 1 lists the chemical constituents used in the data analysis, together with the analytical techniques used, the geometric mean, and the estimated detection limits for the measured species. In order to convert the data into a three-way array, an additional 40 entries were created in the appropriate time intervals for all species and their values were assigned as the corresponding geometric mean. The 572 data points of each chemical species were folded into a 52 × 11 matrix, signifying 11 separate years, each containing 52 weeks. Thus, a 52 × 11 × 24 three-way data array was constructed.

3. Data analysis

a. Brief description of PMF

Suppose $\mathbf{X}$ is an n by m matrix consisting of the measurements of n chemical species in m samples. The objective of receptor modeling is to determine the number of pollutant sources p, the chemical compositions of each source, and the amount that each of the p sources contribute to each sample. The corresponding two-way factor model can be written as

$$\mathbf{X} = \mathbf{GF} + \mathbf{E}, \tag{1}$$

where $\mathbf{G}$ is an n by p matrix of source compositions (source profiles) and $\mathbf{F}$ is a p by m matrix of source contributions to the samples. Each sample is an observation along the time axis, so $\mathbf{F}$ describes the temporal variation of the sources, and $\mathbf{E}$ represents the part of the data variance unmodeled by the p factor model.

In PMF, sources are constrained to have nonnegative species concentration, and no sample can have a negative source contribution. The error estimates for each observed data point were used as point-by-point weights. The essence of PMF can thus be presented as

$$\min_{G,F,} Q(\mathbf{X}, \sigma, G, F), \tag{2}$$

where

$$Q = \left\| \frac{(X - GF)}{\sigma} \right\|_F^2 = \sum_i \sum_j \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2, \tag{3}$$

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}, \tag{4}$$

with $g_{ik} \geq 0$ and $f_{kj} \geq 0$ for $k = 1, \cdots, p$, and $\boldsymbol{\sigma}$ is the known matrix of uncertainties of $\mathbf{X}$. Thus, this is a least squares problem with the values of G and F to be determined.

This form of factorization is quite different from PCA. Matrices $\mathbf{G}$ and $\mathbf{F}$ are determined so that the Frobenius norm of $\mathbf{E}$ divided by $\boldsymbol{\sigma}$ (elementwise) is minimized. As shown by Paatero and Tapper (1993, 1994), it is impossible to perform factorization by using singular value decomposition on such a point-by-point weighted matrix. PMF uses a unique algorithm in which both matrices are varied simultaneous in each interation step. The algorithm is described by Paatero (1997b). The process continues until convergence.

For a three-way data array, there are different methods to extend two-way factorization to three-way situations. In one approach to three-way analysis, the data are fit to a trilinear model, commonly called the PARAFAC model, which can be expressed as

$$x = ABC + E, \tag{5}$$

or

$$x_{ijk} = a_{ih}b_{jh}c_{kh} + e_{ijk} \quad \text{for } h = 1, \cdots, p, \qquad (6)$$

where **X** is an n by m by q three-way data array; **A**, **B**, **C** are the resulting two-way factor matrices for each of the three modes, and **E** is the unmodeled part of **X**. Based on the same nonnegativity constraints and minimization criterion, PMF can solve the trilinear model (Paatero 1997a).

b. Data arrangement

Application of PMF requires that error estimates for the data be chosen judiciously so that the estimates reflect the quality and reliability of each of the data points. Successful applications of two-way PMF to aerosol mass apportionment have been previously published (Juntto and Paatero 1994; Polissar et al. 1996). Based on the detection limits and uncertainties associated with the chemical measurements, an error matrix was computed and used in the PMF analyses. However, it may be that the variation inherent in the process being studied is larger than the measurement error. In this case, the experimental error estimates may not adequately reflect the variability for the measured values. Examples of this kind are likely for Poisson or lognormally distributed data where the latter is commonly encountered in environmental studies. Unknown expectation values are then needed in order to estimate the standard deviations of the distribution or "error estimates." PMF offers an option to solve such a problem (Paatero 1997b). By making rough a priori approximations of the geometric standard deviations, an initial factor solution of the problem is computed. The initial factorization gives approximate expectation values for these variables. The program is then able to compute better approximations for the standard deviations. Since the concentrations of most Alert particulate species were lognormally distributed (Cheng et al. 1991), this option was adopted in the analysis.

For solving the lognormal model, the logarithm of the geometric standard deviation [log(GSD)] for each measured value has to be specified. Often the same value is adequate to represent the variability of the measured points for each species, so a constant could be used as the estimate. A problem in this approach is that zeroes cannot occur in a lognormal distribution, but zero values do occur in practice. These values make the factorization unreliable if they are processed under the assumption of *pure* lognormality. Hence it is necessary to modify this assumption. The current version of PMF assumes that there is an additional normally distributed error superimposed onto the underlying lognormal distribution. The detection limits for the measured values were used as these additional errors. Based on the published detection limit range by Barrie and Hoff (1985) and Barrie and Barrie (1990) and by inspecting the data itself, detection limits were estimated and are listed in Table 1. From our experience, it appears that fully accurate estimates of detection limits are unnecessary to obtain useful factor analysis results.

Handling data with high uncertainties such as missing data, values below the detection limit, and outliers is another feature of PMF. By specifying large error estimates for these uncertain values, PMF can include such data in the analysis and the final fit will not be greatly affected. This feature is essential for the analysis of environmental data where below the detection limit and missing data are common occurrences. There were still some negative values because of blank correction, which were considered to be values below the detection limits. They were replaced by the corresponding detection limits. Missing data were replaced by the corresponding geometric means. Large error estimates were used for the missing data. In the three-way PMF analysis, missing data also included the extra 40 entries for every species, which were inserted at appropriate time positions in order to provide a consistent 52 week per year dataset for all 11 years. Also, a few abnormal data points for Ti and Se were detected by inspecting the species-pair scatterplots. They were replaced by the corresponding geometric means and large errors were assigned to the corresponding elements in the error matrix.

There is a difference between PCA and PMF in the determination of the dimension (number of factors) of the model. In PCA, the solution forms a hierarchy, that is, a higher dimension solution contains all the factors of the lower dimensions. In PMF, however, the factors are not orthogonal and thus there is no hierarchy. All of the factors may change when the dimension is varied. Therefore, PMF modeling was initially performed with a different number of factors. For the determination of the number of factors, it was useful to inspect the fit of the model to the data and the interpretability of the resulting factors.

In contrast to conventional PCA, PMF reduces the rotational ambiguity by applying nonnegativity constraints on the factors. In some cases, the results are fully unique with no rotational freedom at all (Juntto and Paatero 1994). The rotational ambiguity, however, is basically inherent in PMF as well. As indicated by Henry (1987), the commonly used natural physical constraints are generally insufficient to guarantee a unique, physically valid solution for factor analysis techniques. In this application, rotational freedom exists. The acceptable rotations were determined by trial and error. Although human intervention brings some degree of subjectivity to the results, there is a good reason for using the rotation to bring experience and other results into the analysis.

4. Results

Five factor solutions after rotation are presented. These five factors fit the data well and are the easiest to physically interpret for both the two- and three-way analyses. Accompanying the factors, individual error

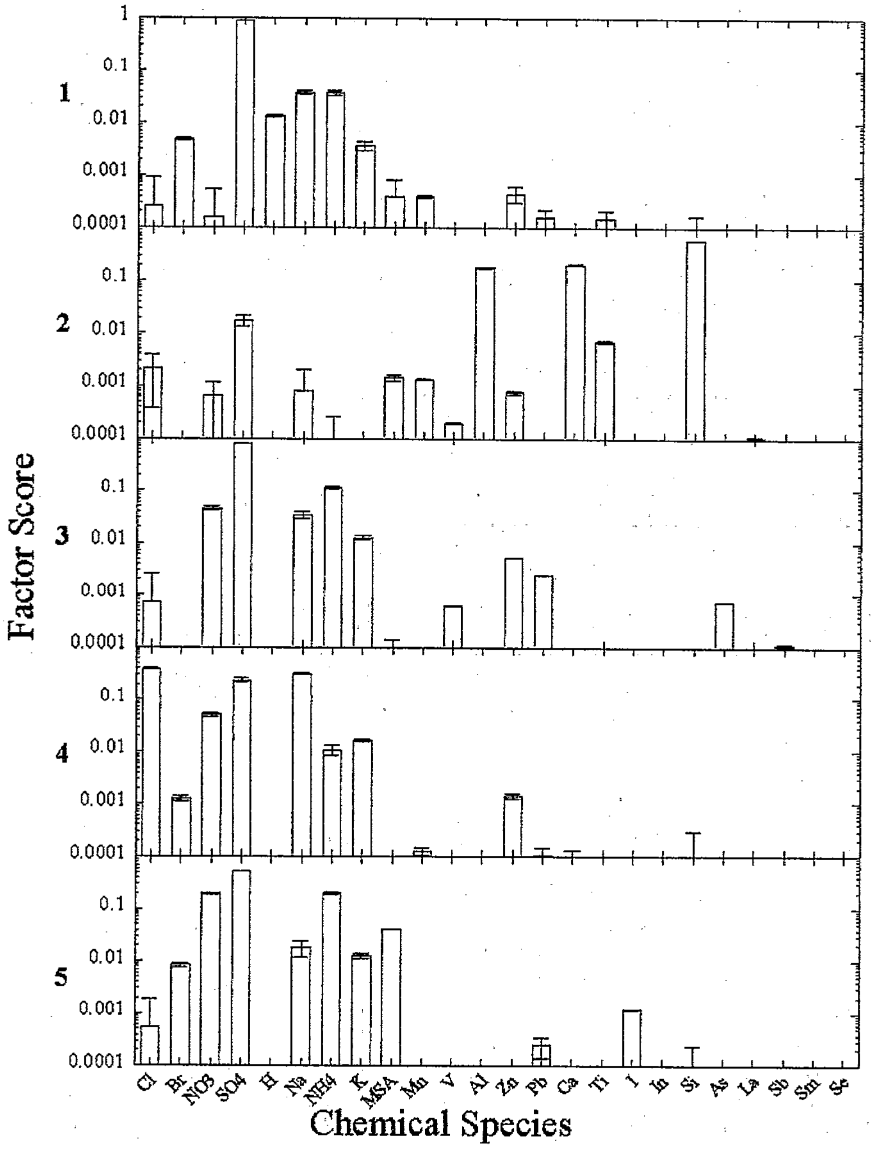

FIG. 1. **G** factors (source profiles) derived from the *N*-way PMF.

estimates were also computed for all the factor elements. The error estimates are calculated in a manner similar to that described by Roscoe and Hopke (1981) in which the errors in one factor matrix are estimated based on the errors in the ambient concentration values and assuming that the other matrix or matrices are error free. Each matrix is treated similarly in turn such that each matrix element has an uncertainty associated with it.

Figures 1 and 2 present the two-way PMF results. In Fig. 1, the five factors related to chemical compositions, that is, possible source profiles are shown. The left side of Fig. 2 shows the associated temporal variations of the five possible sources. In order to facilitate the investigation of the assumed yearly cyclical seasonal variation of each possible source and the comparison with the counterpart from the three-way analysis, the 11-year temporal variations from the two-way analysis were folded into 11, separate, year-long sections and displayed as overlapping curves on the right side of Fig. 2.

Figures 3–5 show the results from three-way PMF analysis. Specifically, displayed from top to bottom, the factors in Fig. 3 are regarded as sources profiles of the five possible origins, Fig. 4 shows factors associated with temporal variations, and Fig. 5 presents factors reflecting year-to-year time trends of the possible pollutant sources in the investigated period of 11 years.

All plots in Figs. 1–5 are in arbitrary units. Total mass values were not available and thus a renormalization could not be performed. The computed error estimates for all the factor elements have been presented in the corresponding factor plots as error bars except for the factors presented in Fig. 2. In Fig. 2, there are too many

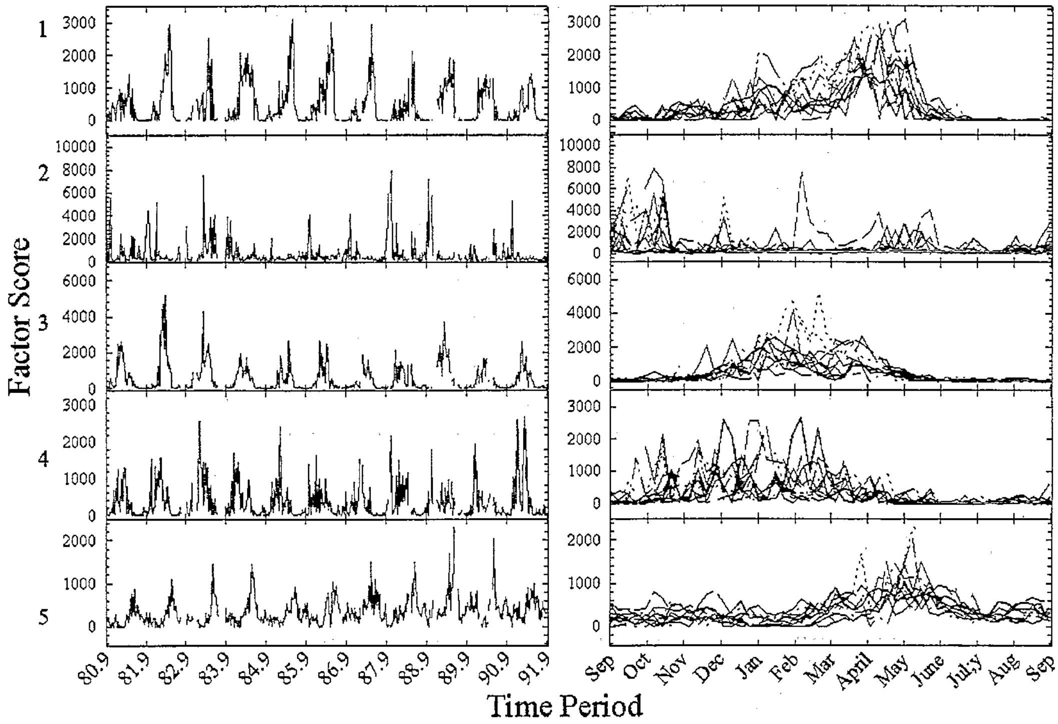

FIG. 2. **F** factors (time series) of two-way PMF (left); overlapping representation of **F** (time series) factors (right).

factors overlapping and the inclusion of error bars makes the plots indistinguishable.

Based on the source profiles shown in Figs. 1 and 3, the primary constituents and the attributions for each of the possible sources are given in Table 2. In order to check the fitness of the modeling, the weighted residuals of the model, that is, the residuals divided by the standard deviations of the data elements, were calculated for each species. The frequency distribution of the weighted residuals was plotted. Figure 6 shows the frequency distribution plots of the weighted fitted residual of representative species, one for each possible source and for SO_4^{2-}. The left part of Fig. 6 presents results from two-way analysis, while the right part comes from the three-way modeling.

The weighted residuals of most species are within the range of three units, thus one can conclude that quite good fits to the data have been achieved for both two- and three-way modeling. Generally, the two-way fit is better than three-way modeling. The Q value for the two-way fit was 14 004, while for the three-way fit the Q had increased to 48 826. If we have fit the data well, it could be expected that the Q value should be approximately equal to the number of data values, which in this case is 12 768 for the two-way dataset and 13 728 for the three-way set. Thus, the two-way Q values are only slightly above the value that would be achieved if all points were fit to their values within one unit of uncertainty for each point. The most notable decrease in the quality of fit is among the crustal and sea salt elements. Some typical r^2 are given in Table 3. One exception to the general trend in decreasing fits going from the two-way to the three-way solution was methanesulfonate (MSA), where the r^2 value increased from 0.166 to 0.356.

There are several reasons for these differences in the quality of the fits. First, the three-way data array contains 40 more uncertain data points than the two-way data matrix. The missing values may explain why there are more large residuals for three-way modeling than for the two-way fit. Second, the assumption of the underlying bilinear and trilinear structure in the data may not be well established. The repetitive behavior of the Arctic aerosol is caused by the influence of external periodic circumstances such as the emission of original sources and meteorological conditions on a global, or at least semiglobal, scale. Such periodicity cannot precisely recur from year to year. The randomness together with occasional nonperiodic source emissions or weather variations may obscure the underlying structure of the data being expressed by the bilinear or trilinear model. This effect would be particularly so for wind driven sources such as soil and sea salt. Hence a purely bilinear or trilinear model is only an approximation of the real structure of the data.

From Figs. 1 and 3, the first source is related to the species Br^-, H^+, and SO_4^{2-}. The seasonal variation of this factor has a maximum around April, just after polar sunrise. In the Arctic atmosphere, the air is at subzero temperatures in the dark during the winter. At polar

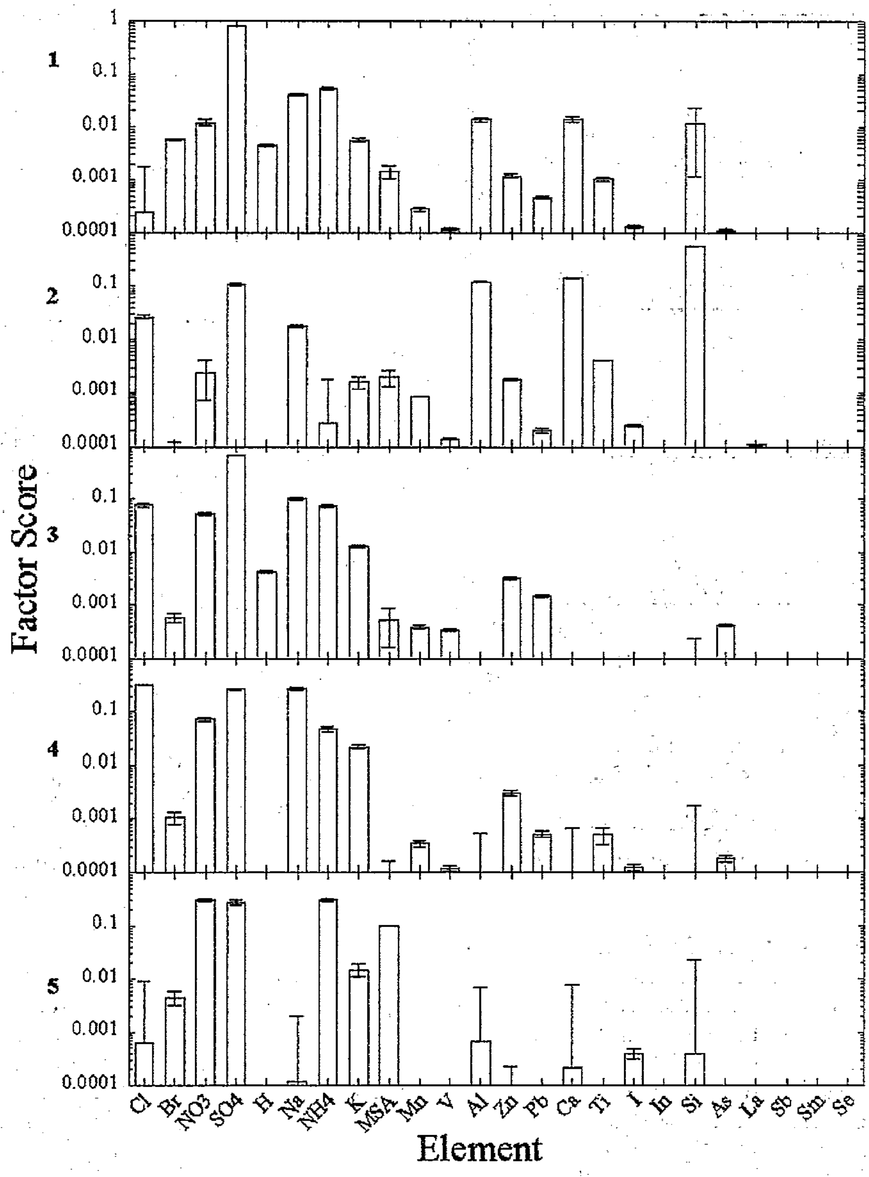

FIG. 3. A factors (source profiles) derived from the three-way PMF.

sunrise in the early spring, it is suddenly exposed to sunlight. When the sun rises after the winter darkness, photochemical reactions release Br, leading to troposphere O_3 depletion (Barrie et al. 1988, 1989). Thus this factor represents photochemical conversion of SO_2 to acidic sulfate as well as the production of particulate bromine. Based on PCA, Barrie and Barrie (1990) also obtained such a factor. The chemical mechanism involving the production of Br and the depletion of ozone in the lower Arctic troposphere at polar sunrise has been investigated by Barrie et al. (1988).

The second factor is dominated by Si, Al, and Ca, the major constituents of soil, and this factor can be regarded as a windblown dust factor. From Figs. 1 and 3, it seems that windblown dust is the major origin of Ti, La, Sm, and Mn in the Arctic aerosol. The seasonal variation of soil factor features two peaks (see Figs. 2 and 4), one around April/May and another in the late summer–early fall period from September to October. According to previous studies (Barrie and Barrier 1990), soil dust in the Arctic is not only of local origin, but also from remote areas. The peak in April/May may probably be associated with long-range transported desert dust from Asia raised by storms occurring particularly in April and May, while the peak in September/October is probably caused by the onset of transport farther south reaching areas of suspendable soil.

There is a sharp peak around February 1983 appearing in the seasonal variation of soil factor obtained by

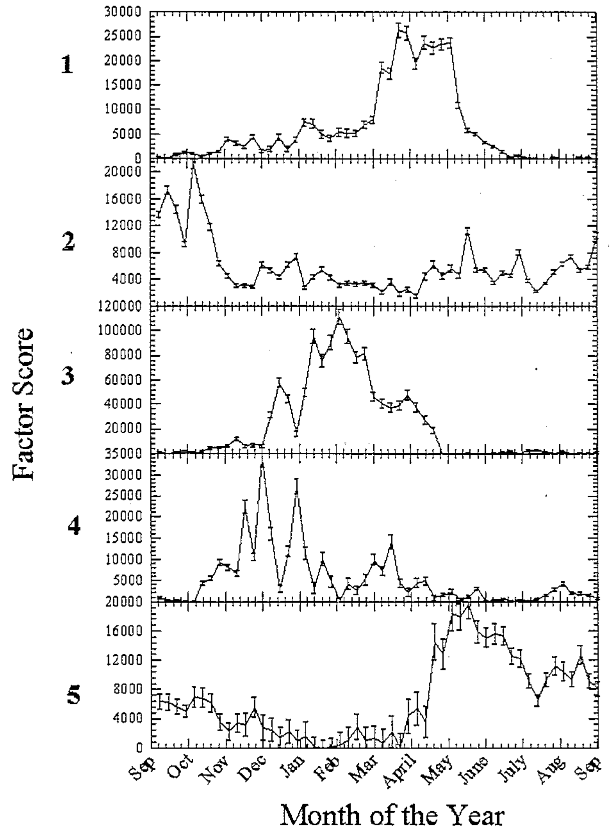

FIG. 4. B factors (weekly variations) of the three-way PMF.

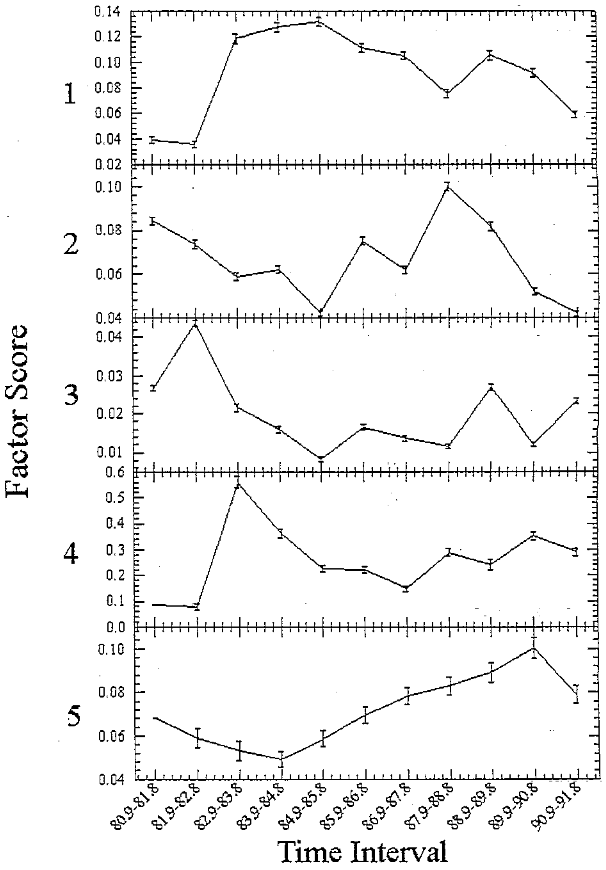

FIG. 5. C factors (yearly trends) of the three-way PMF.

the two-way analysis (see Fig. 2). By inspecting the time series of the original observations of Al, Ca, La, Sm, and Mn (no Si data are available for 1983), it was found that there is exactly the same sharp peak as that in the seasonal variation of this factor. Such unusual peaks must have been caused by an unusual event in that time period. Examination of the wind data for this week indicates that there were high winds with a maximum reaching 119 km h^{-1}. Under such blizzard conditions, the snow can be blown from the ground, resulting in the aerosolization of the local soil. Compared to the three-way result (Fig. 4), the influence of such unusual observations on the three-way PMF is much less since these peaks appear in only 1 of the 11 years of data. Thus, these values are not strongly reflected in the results.

The third factor contains species like SO_4^{2-}, NO_3^-, and NH_4^+, etc., which are considered to be of anthropogenic origin. Sulfates constitute approximately 30% of the total mass of suspended particulate matter in the Arctic atmosphere (Barrie 1986; Barrie and Barrie 1990). They are thought to consist of two parts: (i) primary sulfates, which originate from particulate pollution released during fossil fuel combustion and processing of sulfide ores, and (ii) secondary sulfates, which are produced in the atmosphere from the oxidation of sulfur dioxide. The oxidation rate and residence time of sulfur dioxide in the Arctic atmosphere has been studied (Barrie and Hoff 1984). Investigation also apportioned sulfate into a variety of sources, which showed that about 62%–74% of sulfates in the summer and 78%–85% of sulfates in the winter are of anthropogenic origin (Li and Barrie 1993; Li et al. 1993). Results of an analysis of the isotopic

TABLE 2. The composition of each of the factors identified in the five-factor PMF analysis.

Factor	Constituents	Possible source origin
1	Br^-· SO_4^{2-}, H^+· NH_4^+,	Acidic photochemical
2	Si, Al, Ca, Mn, Ti, La, Sm, SO_4^{2-}	Soil
3	SO_4^{2-}, Zn, Pb, As, Sb, Se, V, In	Anthropogenic
4	Cl^-· Na^+, SO_4^{2-}, K^+	Sea salt
5	MSA, SO_4^{2-}, NO_3^-, NH_4^+, Br^-, I^-	Biogenic

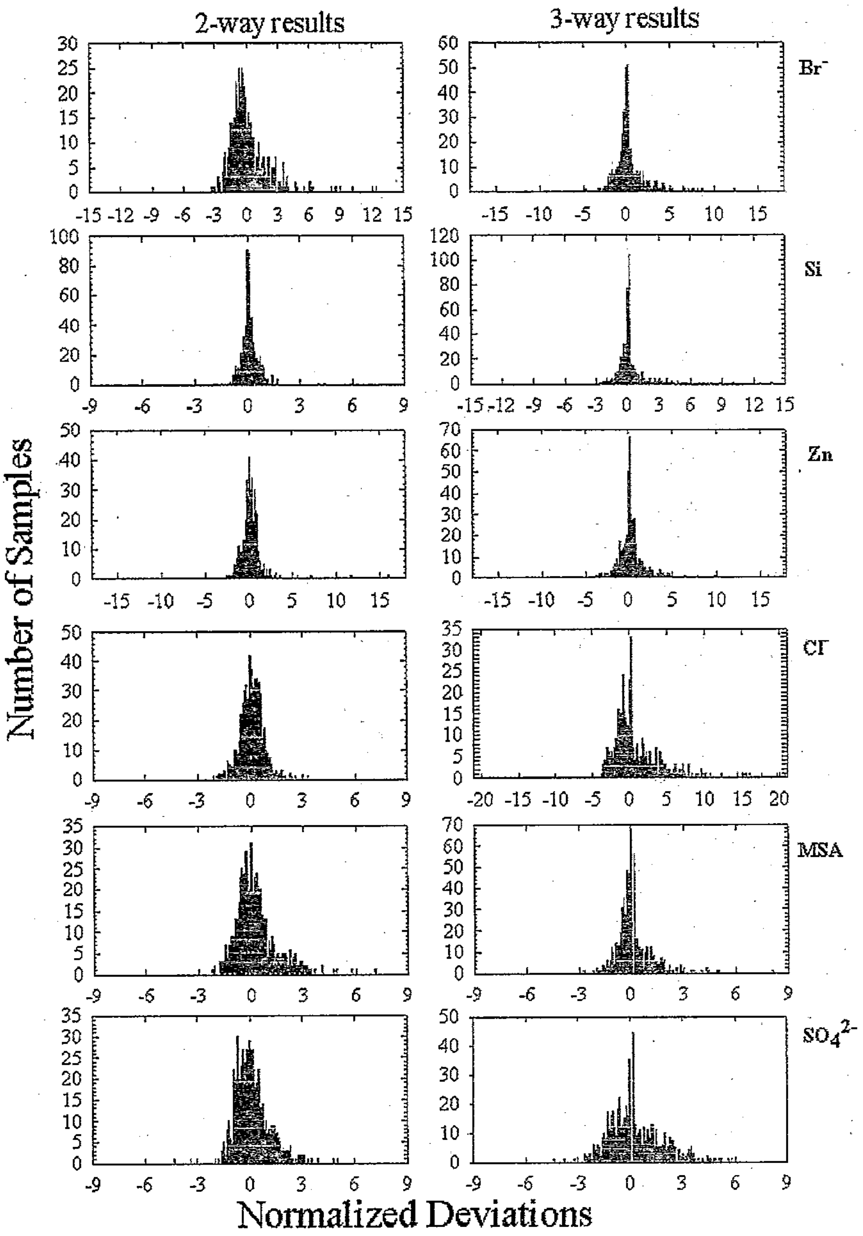

FIG. 6. Standardized residuals of some representative species from the two-way (left) and three-way (right) PMF modeling.

composition of sulfur in the Arctic haze suggested that most of the sulfur comes from Europe rather than more local areas (Nriagu et al. 1991).

With the aid of meteorological information, Cheng et al. (1993) and Hopke et al. (1995) investigated the source origin and preferred pathways for sulfur transport to Alert by using potential source contribution function (PSCF). In winter and spring, anthropogenic SO_4^{2-} has high PSCF areas in Europe that coincide with known emissions there. Also, those regions with high PSCF patterns in eastern Canada or off the east coast of North America are close to emissions in eastern North America, and the high PSCF areas in central Canada and near the Ural Mountains in Russian coincide with the known smelting activities in these areas. In summer, no high PSCF areas were observed, which reflects the poor transport of material into the Arctic region and the strong removal of particulate SO_4^{2-} by precipitation in the summer (Cheng et al. 1993; Hopke et al. 1995).

Besides the major constituent sulfate, Figs. 1 and 3 show that Zn, Pb, As, Sb, Se, V, and In are mostly contributed by this factor. These elements are generally considered to be associated with anthropogenic activities. The element Pb usually comes mainly from anti-

TABLE 3. Values of the squared correlation coefficients r^2 for the relationships between the reproduced values from two- and three-way PMF and the original data values calculated using weighted values and omitting missing and below detection limit values*.

Species	Two-way	Three-way	Species	Two-way	Three-way
Cl	0.992	0.750	Zn	0.467	0.410
Br	0.716	0.731	Pb	0.891	0.778
NO_3	0.948	0.863	Ca	0.981	0.459
SO_4	0.996	0.987	Ti	0.961	0.396
H	0.997	0.929	I	0.620	0.411
Na	0.996	0.934	In	0.890	0.616
NH_4	0.974	0.921	Si	0.838	0.212
K	0.903	0.773	As	0.972	0.852
MSA	0.166	0.356	La	0.908	0.185
Mn	0.965	0.605	Sb	0.888	0.661
V	0.997	0.906	Sm	0.432	0.149
Al	0.996	0.561	Se	0.731	0.638

knock agents in gasoline and from nonferrous metal smelting. The PSCF analysis suggested that high values in most parts of eastern Europe, Russia, and the Baltic states, also high potential source areas, were identified in the northeastern United States and Quebec, (Cheng et al. 1993). Zinc can be emitted from nonferrous metal production process such as copper–nickel production or incineration. Four high PSCF areas were identified by Cheng et al. (1993) as in Siberia, close to the Bering Sea; in the Alaska area; in northeastern Canada; and in the Moscow area. The elements Sb and As are most probably released from fossil fuel combustion and V from fuel oil combustion. High PSCF patterns were found for As in central and eastern Russia and central Canada and for V in the western Iberian Peninsula, the area of western Europe, the Kuznetsk area in the central former Soviet Union, and two areas around Alaska (Cheng et al. 1993). Indium is an indicator of smelting and Se probably results from both smelting and coal-fired power plants.

The species in the anthropogenic factor come from different source origins. This fact suggests that pollutants entering the Arctic from individual sources in source regions are mixed in the atmosphere before reaching the Arctic. From Figs. 1 and 3, it can be seen that some species are attributed to multiple factors. This may either reflect the multiple source nature of the species or may just be because of the insufficient resolution of the data analyses themselves. However, the whole pattern of the contribution of the species does coincide with current knowledge of the source attribution of aerosol particles. As shown in Figs. 2 and 4, the anthropogenic factor peaks in January/February.

Sea salt is another possible source of part of the Arctic aerosol (see Figs. 1 and 3) and contributes Cl^-, Na^+, K^+, and SO_4^{2-}. It has a broader peak over the whole winter period from October to April. According to Barrie and Barrie (1990), this seasonal feature probably reflects a combination of longer aerosol residence times and a stronger sea spray source in the winter than in the summer.

The fifth factor is characterized by the presence of MSA and iodine. Methanesulfonate is the product of the oxidation of sulfur-containing compounds like dimethylsulfide or dimethyldisulfide emitted by biogenic activity in the surface layer of the ocean. Iodine is produced by the photolysis of methyliodine, also produced by biological activity in the ocean. It, therefore, represents a biogenic component of the Arctic aerosol. From Figs. 2 and 4, it can be seen that there are two peaks in the seasonal variation of the factor, one around April/May and another about August. Li et al. (1993) attributed the spring peak to the sea surface temperature anomalies (SSTA) in the North Atlantic Ocean west of the coast of continental Europe, and the summer peak to the SSTA in ocean regions farther north in the Atlantic ocean off the coast of Norway and in the northwestern North Pacific Ocean. Hopke et al. (1995) identified locations of the sources of the MSA to samples collected at Alert and they found that different regions contribute to the observed concentrations during different time periods of the year. Also the preferred pathways for transport of MSA to the Arctic were suggested (Hopke et al. 1995).

Figure 5 shows the third mode factors of three-way PMF. These factors are assumed to reflect the year-to-year time trend of each source's contribution. These factors would involve changes in emission strength and year-to-year differences in the transport of material from midlatitudes to Alert.

5. Discussion

It can be seen that there are similarities between the factors derived by the two-way and three-way analyses. The three-way analysis imposes the condition that the week-to-week pattern of the source contributions should be the same from year to year. As can be seen in the right side of Fig. 2, the year-to-year variations are similar but not precisely identical. To examine the quality of the factors, the ratios of elements can be examined in the various factors. For example, Mn/Al in the soil factors (factor 2) was 0.0075 ± 0.0004 for the two-way analysis and 0.0073 ± 0.0002 for the three-way results. Similarly, the V/Al ratios are 0.0011 ± 0.0001 and 0.0012 ± 0.0001 for the two- and three-way results, respectively.

For sea salt (factor 4), the Cl/Na ratios are 1.26 ± 0.04 and 1.18 ± 0.05 in the two- and three-way results, respectively. Both are lower than their ratio in seawater, and there is higher $SO_4^=$ in both factors. The displacement of Cl by $SO_4^=$ in transport to Alert is quite reasonable and thus this factor also appears to be reasonable in both sets of results.

The anthropogenic factors are also quite similar in both results. Since this factor is dominated by the December to February time interval with reasonable regularity, it might be anticipated that the resulting source profiles should be similar. The two-way factor has much lower acidity (H^+) than the three-way factor. However, since there is some acidity during the dark winter period, some acidity in this factor seems reasonable, although there is probably an overestimate in the three-way factor because of the overlap with the start of the photochemical period.

In the photochemical factor (factor 1), it can be seen that there is some addition of crustal elements in the three-way results. Because of the imposition of the time coincidence constraints in the three-way analysis, part of the soil that is observed in the latter part of the mid-March–April time interval is forced into this factor.

The biogenic factors are similar, but there are some important differences. In the two-way factor, the MSA/$SO_4^=$ ratio is 0.079 ± 0.001 while in the three-way results, this ratio is 0.35 ± 0.04. Li et al. (1993) found from isotope ratio analysis that this ratio is typically 0.31 for biogenic sulfur in the Arctic region. Thus, the three-way results are much closer to the measured results.

In examining the periodicity of the factors during the year [Fig. 2 (right) and Fig. 4], the factors show strength during the year as anticipated. The anthropogenic factor is the Arctic haze that is transported to Alert during the winter months, while the photochemical factor shows a peak in the period from mid-March to early May. This pattern is fully consistent with the prior results of sampling at Alert.

The time sequence of soil shows a small peak in the spring (May–June) and larger peaks in September and October. Previous studies have suggested that the spring soil is transported from long distances while the fall peak is from a local source since the snow may be blown from areas around the sampling site.

The biogenic factor shows a late spring peak and a secondary peak in August and September. MSA shows a similar pattern, although it peaks more in August, while iodine tends to show a strong peak in September. Thus, it is the combination of elements in the factor that gives rise to the observed time pattern.

In general, the year-to-year variations in the three-way analysis are difficult to interpret. The variation of the biogenic factor (factor 5) shows a strong rise during the late 1980s and a sharp drop from 1990 to 1991. The decline, rise, and decline were suggestive of the inverse of volcanic activity affecting the level of particles in the stratosphere. There were several explosive eruptions in the early 1980s (Nyamuragira, Alaid, El Chichón) as well as the eruption of Mount Pinatubo in 1991. The input of SO_2 into the stratosphere resulted in an increase in the earth's optical depth as seen at Barrow, Alaska (Polissar et al. 1998), and some cooling of the atmosphere of the Northern Hemisphere has been attributed to this aerosol.

Because the level of biological activity should be related to average temperature, the scores for this factor were plotted against the Northern Hemisphere temperature anomaly (Fig. 7) as obtained from Jones et al. (1997). These results were compiled by Jones et al. (1986a,b,c), Jones (1988), Jones and Briffa (1992), and Briffa and Jones (1993). There is relatively good correlation between these quantities with a squared correlation coefficient of 0.780. We have been able to identify this factor because of the availability of methane sulfonic acid and iodine data. These results suggest that further examination of the concentration of MSA in remote locations may provide a good indicator for large-scale climate changes.

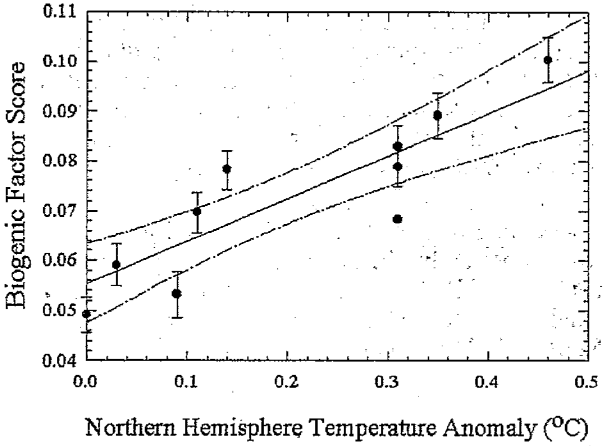

FIG. 7. Biogenic factor score against the Northern Hemisphere temperature anomalies for the time period from 1981 to 1991, relative to a reference period from 1950 to 1979.

Shaw (1983) suggested the potential importance of particles produced from biogenic sources of reduced sulfur compounds. Charlson et al. (1987) pointed to ocean sources of dimethyl sulfide leading to the formation of methane sulfonate and non–sea salt sulfate particles in the air. There are also terrestrial sources of reduced sulfur compounds. These biogenic sulfur sources should respond to changing temperature by producing additional reduced sulfur emissions. Bates and Quinn (1997) have very recently reported a possible increase in dimethyl sulfide in seawater from latitudes around the equator. Thus, these results may be the first indication of the interaction of climate with biogenic sulfur aerosol.

Even though quite good source profiles and reasonable seasonal variations have been obtained from three-way modeling, the other factors of the third mode from three-way PMF are not easily interpreted.

6. Conclusions

PMF has been used for the analysis of Arctic particle composition data from samples collected at Alert, Canada, between 1980 and 1991. The nature of the aerosol sources has been well explained. Five possible sources with distinctive seasonal variations have been retrieved. The Arctic airborne particulate matter includes particles derived from acidic photochemical reactions after polar sunrise, particles of long-range transported soil dust, long-range transported anthropogenic pollutants, sea salt aerosol, and aerosols originated from biogenic activity at the ocean surface. The resolved seasonal variations of the possible sources coincide with the hypotheses from previous investigations.

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REFERENCES

Anttila, P., P. Paatero, U. Tapper, and O. Jarvinen, 1995: Source identification of bulk wet deposition in Finland by Positive Matrix Factorization. *Atmos. Environ.,* **29,** 1705–1718.

Barrie, L. A., 1986: Arctic air pollution: An overview of current knowledge. *Atmos. Environ.,* **20,** 643–663.

——, and R. M. Hoff, 1984: The oxidation rate and residence time of sulphur dioxide in the Arctic atmosphere. *Atmos. Environ.,* **18,** 2711–2722.

——, and ——, 1985: Five years of air chemistry observations in the Canadian Arctic. *Atmos. Environ.,* **19,** 1995–2010.

——, and M. J. Barrie, 1990: Chemical components of lower tropospheric aerosols in the high Arctic: Six years of observations. *J. Atmos. Chem.,* **11,** 211–226.

——, J. W. Bottenheim, R. C. Schnell, P. J. Crutzen, and R. J. Rasmussen, 1988: Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic troposphere. *Nature,* **334,** 138–141.

——, G. Den Hartog, J. W. Bottenheim, and S. Landsberger, 1989: Anthropogenic aerosols and gases in the lower troposphere at Alert Canada in April 1986. *J. Atmos. Chem.,* **9,** 101–127.

Bates, T. S., and P. K. Quinn, 1997: Dimethylsulfide (DMS) in the equatorial Pacific Ocean (1982 to 1996): Evidence of a climate feedback? *Geophys. Res. Lett.,* **24,** 861–864.

Briffa, K. R., and P. D. Jones, 1993: Global surface air temperate variations over the twentieth century: Part 2, Implications for large-scale high-frequency paleoclimatic studies. *Holocene,* **3,** 82–93.

Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren, 1987: Oceanic phytoplankton, atmospheric sulphur, cloud albedo, and climate. *Nature,* **326,** 655–661.

Cheng, M. D., P. K. Hopke, S. Landsberger, and L. A. Barrie, 1991: Distribution characteristics of trace elements and ionic species of aerosol collected at Canadian high Arctic. *Atmos. Environ.,* **25A,** 2903–2909.

——, ——, L. A. Barrie, A. Rippe, M. Olson, and S. Landsberger, 1993: Qualitative determination of source regions of aerosol in Canadian high Arctic. *Environ. Sci. Technol.,* **27,** 2063–2071.

Gemperline, P. J., K. H. Miller, T. L. West, J. E. Weinstein, J. C. Hamilton, and J. T. Bray, 1992: Principal component analysis, trace elements and blue crab shell disease. *Anal. Chem.,* **64,** 523A–532A.

Henry, R. C., 1987: Current factor analysis receptor models are ill-posed. *Atmos. Environ.,* **21,** 1815–1820.

Hopke, P. K., 1988: Target transformation factor analysis for aerosol source apportionment: A review and sensitivity study. *Atmos. Environ.,* **22,** 1777–1792.

——, 1991: *Receptor Modeling for Air Quality Management,* Elsevier, 303 pp.

——, L. A. Barrie, S. M. Li, M. D. Cheng, C. Li, and Y. Xie, 1995: Possible sources and preferred pathways for biogenic and non-seasalt sulfur for the high Arctic. *J. Geophys. Res.,* **100,** 16 595–16 603.

Jones, P. D., 1988: The influence of ENSO on global temperatures. *Climate Monit.,* **17,** 80–89.

——, and K. R. Briffa, 1992: Global surface air temperature variations over the twentieth century: Part 1, Spatial, temporal and seasonal details. *Holocene,* **2,** 105–179.

——, T. M. L. Wigley, and P. B. Wright, 1986a: Global temperature variations between 1861 and 1984. *Nature,* **322,** 430–434.

——, S. C. B. Raper, R. S. Bradley, H. F. Diaz, P. M. Kelly, and T. M. L. Wigley, 1986b: Northern Hemisphere surface air temperature variations: 1851–1984. *J. Climate Appl. Meteor.,* **25,** 161–179.

——, ——, and T. M. L. Wigley, 1986c: Southern Hemisphere surface air temperature variations: 1851–1984. *J. Climate Appl. Meteor.,* **25,** 1213–1230.

——, T. M. L. Wigley, and P. B. Wright, cited 1997: Global and hemispheric annual temperature variations between 1854 and 1991. ORNL Data Set NDP022R2. [Available online from http://www.ORNL.gov/~rgj/ESD_CDIAC.html.]

Juntto, S., and P. Paatero, 1994: Analysis of daily precipitation data by positive matrix factorization. *Environmetrics,* **5,** 127–144.

Li, S. M., and L. A. Barrie, 1993: Biogenic sulphur aerosol in the Arctic troposphere: 1. Contributions to total sulfate. *J. Geophys. Res.,* **98,** 20 613–20 622.

——, ——, and A. Sirois, 1993: Biogenic sulphur aerosol in the Arctic troposphere: 2. Trends and seasonal variations. *J. Geophys. Res.,* **98,** 20 623–20 631.

Nriagu, J. O., R. D. Coker, and L. A. Barrie, 1991: Origin of sulphur in Canadian Arctic haze from isotopic measurements. *Nature,* **349,** 142–145.

Paatero, P., 1997a: A weighted non-negative least-squares algorithm for three-way 'PARAFAC' factor analysis. *Chemom. Intell. Lab. Syst.,* **38,** 223–242.

——, 1997b: Least squares formulation of robust non-negative factor analysis. *Chemom. Intell. Lab. Syst.,* **37,** 23–35.

——, and U. Tapper, 1993: Analysis of different modes of factor analysis as least squares fit problems. *Chemom. Intell. Lab. Syst.,* **18,** 183–194.

——, and ——, 1994: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics,* **5,** 111–126.

Polissar, A. V., P. K. Hopke, W. C. Malm, and J. F. Sisler, 1996: The ratio of aerosol optical absorption coefficients to sulfur concentrations, as an indicator of smoke from forest fires when sampling in polar regions. *Atmos. Environ.,* **30,** 1147–1157.

——, ——, P. Paatero, Y. J. Kaufman, D. K. Hall, B. A. Bodhaine, and E. G. Dutton, 1998: The aerosol at Barrow, Alaska: Long-term trends and source locations. *Atmos. Environ.,* in press.

Roscoe, B. A., and P. K. Hopke, 1981: Error estimation of factor loadings and scores obtained with target transformation factor analysis. *Anal. Chim. Acta,* **132,** 89–97.

Shaw, G. E., 1983: Bio-controlled thermostasis involving the sulfur cycle. *Climate Change,* **5,** 297–303.

Zeng, Y., and P. K. Hopke, 1990: Methodological study applying three-mode factor analysis to three-way chemical data sets. *Chemom. Intell. Lab. Syst.,* **7,** 237–250.

——, and ——, 1992a: The application of three-mode factor analysis (TMFA) to receptor modeling of scenes particle data. *Atmos. Environ.,* **26A,** 1701–1711.

——, and ——, 1992b: A new receptor model: A direct trilinear decomposition followed by a matrix reconstruction. *J. Chemom.,* **6,** 65–83.