CONCENTRATION CHANGES OF MSA AND MAJOR IONS IN ARCTIC AEROSOLS DURING POLAR SUNRISE

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Abstract: Aerosol samples were collected at Alert, Canada during the polar sunrise period. Major soluble species and MSA were determined by an ion chromatograph. Correlation coefficients among the concentrations of Na^+, Mg^{2+}, K^+ and Cl^- are high. The ratios of Mg^{2+}/Na^+ in the winter samples are higher than that found in sea water. A part of K^+ and Mg^{2+} in winter aerosols consists of wind-blown dust. The predominant source of Na^+ and Cl^- in Arctic aerosols is considered to be sea salt, but quantity loss of Cl^- is observed around April. Reactions between sea salt and $nssSO_4^{2-}$ would produce particles and liberate HCl gas. The concentration of MSA has two peaks, in spring and summer. Chemical elements of Arctic aerosols are classified into three groups. The dissimilarity is larger from MSA to the others.

1. Introduction

The first report of Arctic air pollution and the coining of the term "Arctic haze" was published about 40 years ago. Arctic haze aerosols in the lower troposphere of the Arctic are found to undergo a very strong seasonal variation. They are 20–40 times more abundant in winter than in summer. Furthermore, in winter the Arctic aerosols are mostly of anthropogenic origin while in summer, what little there is consisted of wind-blown dust and sea salt (BARRIE, 1986). Anthropogenic acidic constituents are transported to the Arctic from mid-latitudes in winter, and photochemical reactions seem to occurs actively during the polar sunrise period. We have collected Arctic aerosols at Alert, Canada during the polar sunrise period using of Pallflex quartz fiber filter. The purpose of this paper is to describe concentration changes of methanesulfonic acid (MSA) and major ions in the Arctic aerosols during the polar sunrise period.

2. Experimental Methods

Aerosol samples were collected from February 19 to June 10, 1991 on a weekly basis, at Alert, Northwest Territories, Canada. For details of the sampling site, refer to BARRIE and HOFF (1984). Sixteen aerosol samples were analyzed in this study. The samples from approximately 16000 m³ of air were collected by a high-volume air sampler on a 20×25 cm² Pallflex quartz fiber filter. A part of the aerosol filter sample was cut into pieces and water soluble ionic species were extracted with ultra pure water.

Major soluble species (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and methanesulfonic acid (MSA) were determined by ion chromatograph (Dionex-2020i/ SP). Anions were measured by using Dionex-AG4A, AS4A columns, 1.8 mM Na_2CO_3/ 1.7 mM $NaHCO_3$ eluent and auto-suppressor ASRS-1/SRC-1. MSA was measured by the same columns and suppressor of anions with the exception of 0.3 mM $NaHCO_3$ eluent. Cations were measured by using Dionex-CG12, CS12 columns, 20 mM MSA eluent and auto-suppressor CSRS-1/SRC-1.

3. Results and Discussion

3.1. Ionic components in aerosol samples

Correlation matrices of the concentrations of MSA and major ions are given in Table 1. Correlation coefficients among the concentrations of Na^+, Mg^{2+}, K^+ and Cl^- are high, as shown in Table 1. There is a pronounced seasonal cycle of Na^+ and Cl^- concentrations with peak levels during the period November to March (STURGES and BARRIE, 1988). The high correlation coefficient between Na^+ and Cl^- confirms that they are almost exclusively of marine origin in Arctic aerosols (STURGES and BARRIE, 1988). The correlation coefficient between Na^+ and Mg^{2+} is higher than that between Na^+ and Cl^-; and the ratios of Mg^{2+}/Na^+ in the winter samples are higher than that found in sea water. A part of Mg^{2+} in winter aerosols consists of wind-blown dust. The predominant source of Na^+ and Cl^- in Arctic aerosols is considered to be sea salt, but quantity loss of Cl^- is observed around April as described later.

The measured K^+ concentration shows a high correlation coefficient with Na^+ concentration. Non sea salt K^+ (nssK^+) concentration is calculated after subtracting sea salt K^+, based on sea salt content relative to Na^+. About 61% of the measured K^+ in this study is in excess of that in sea salt. The amount of nssK^+ is large in the winter samples and the Na^+ concentration has a peak during winter. Therefore, the K^+ concentration shows a high correlation coefficient with Na^+ concentration. Non sea salt K^+ is linked to coal or biomass combustion (ANDREAE, 1983).

The correlation between SO_4^{2-} and NH_4^+ is high. This result suggests that the secondary aerosol is formed after gas phase oxidation of SO_2 and neutralization by NH_4^+. Nitrate concentration shows a high correlation with sea salt elements. However, the source of NO_3^- is not sea water. NO_3^- may be a product of gas phase reactions or

Table 1. Correlation matrices of the ions in aerosols.

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
MSA	−0.541	−0.386	−0.612	−0.573	−0.490	−0.462	−0.545	−0.408
SO_4^{2-}	0.447	0.959	0.464	0.395	0.709	0.090	0.033	
NO_3^-	0.725	0.122	0.764	0.797	0.469	0.812		
Cl^-	0.862	0.138	0.898	0.916	0.353			
Ca^{2+}	0.550	0.788	0.621	0.591				
Mg^{2+}	0.978	0.400	0.988					
K^+	0.962	0.476						
NH_4^+	0.411							

underline : significant level at 0.1%

may be involved in photochemical reactions leading to the formation of some of the ions (LI and WINCHESTER, 1989b). The same variation pattern is observed for NO_3^- and sea salt elements. This result suggests that they reflect transport from southerly latitudes.

The measured MSA concentration dose not have a high correlation with other ions, however, MSA concentration indicates negative correlation with other ions. The concentration of MSA has two peaks, in spring and summer. On the other hand, other ion concentrations have peaks in winter or spring (LI and BARRIE, 1993). MSA and H_2SO_4 are predominant end products of the oxidation of dimethyl sulfide (DMS), which is produced by marine phytoplankton (HATAKEYAMA et al., 1985).

3.2. Chlorine depletion in Arctic aerosols

The reaction between sea salt and acidic NO_3^- and SO_4^{2-} is expected to liberate HCl gas to the atmosphere, leaving the particles enriched in NO_3^- and non sea salt SO_4^{2-} (nssSO_4^{2-}) and depleted in Cl^- (ERIKSSON, 1959; McINNES et al., 1994):

$$HNO_3(g) + NaCl(p) \rightarrow HCl(g) + NaNO_3(p),$$
$$H_2SO_4(g) + 2NaCl(p) \rightarrow 2HCl(g) + Na_2SO_4(p).$$
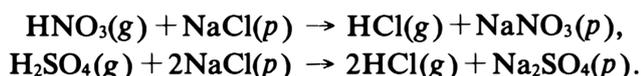
Nitrate concentration in the aerosol samples is very low; therefore, reactions between sea salt and nssSO_4^{2-} should produce particles and liberate HCl gas. Chlorine depletion in marine aerosols has been reported in several studies. STURGES and BARRIE (1988) reported the variations of enrichment factors of Cl^- relative to seawater for the Arctic aerosols. Distinct negative enrichments were evident around April and to a lesser extent during the autumn and winter months.

The ratios of Cl^-/Na^+ in Arctic aerosols are shown in Fig. 1. Ratios of all samples are smaller than the ratio in sea water; however, until the beginning of March, ratios show relatively high values. Quantity loss of chlorine relative to sea water (LC) is calculated according to

$$LC = (Cl^-_{sea\ water}/Na^+_{sea\ water}) \cdot Na^+_{aerosol} - Cl^-_{aerosol}.$$
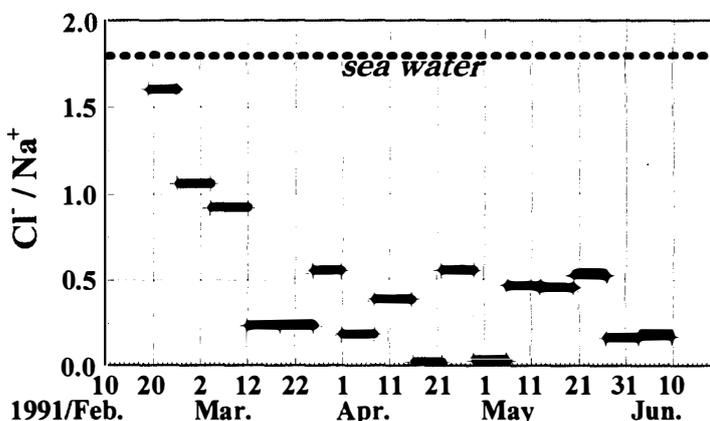
Fig. 1. The ratios of Cl^-/Na^+ in Arctic aerosols.
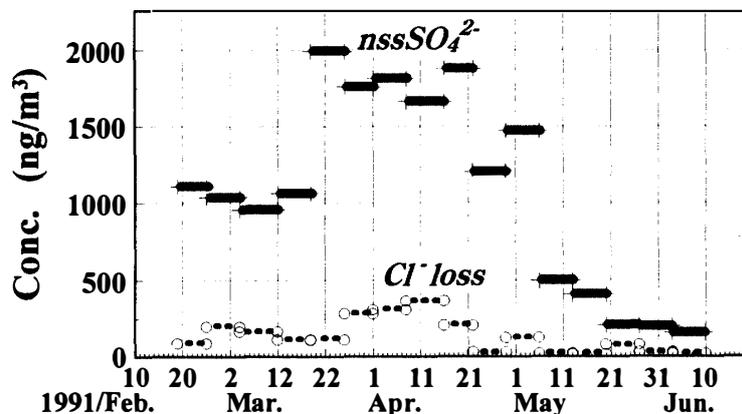
Fig. 2. Variations of Cl^- loss and $nssSO_4^{2-}$ concentration in Arctic aerosols.

Variations of Cl^- loss and $nssSO_4^{2-}$ in Arctic aerosols are shown in Fig. 2. Quantity loss of chlorine is evident around April, as in the results of STURGES and BARRIE. Mutual correlation between Cl^- loss and $nssSO_4^{2-}$ concentration is indicated in Fig. 2. Some mechanisms have been proposed, including photochemical reactions and reactions with pollutants such as sulfur oxide and nitrogen oxide. The occurrence of chloride depletion during the Arctic night rules out the possibility of photochemical effects as the only cause. On the other hand, reaction with acidic sulfates is quite plausible in view of the influx of pollution during the winter and spring. This mechanism is supported by the mutual correlation between Cl^- loss and $nssSO_4^{2-}$ concentration shown in Fig. 2.

3.3. Statistical analyses of Arctic aerosols

Principal component analysis has been used in previous studies based on aerosol elemental composition data; for example, in urban air pollution (HENRY and HIDY, 1979, 1982; ALPERT and HOPKE, 1981; THURSTON and SPENGLER, 1985) and Arctic aerosols (HEIDAM, 1981, 1982; LI and WINCHESTER, 1989a, b).

In this paper, principal component analysis is applied to the chemistry of Arctic aerosols collected during the polar sunrise period. The first step in the principal component analysis is to transform the original variables into a dimensionless normalized value. The normalized value of the element j for the aerosol sample i, N_{ij}, is obtained by the formula

$$N_{ij} = \frac{(C_{ij} - C_j)}{\sigma_j},$$

where C_{ij} is the original value of the jth element for sample i, C_j is the mean value for the jth element, and σ_j is the standard deviation of the jth element. The elements of Arctic aerosols are MSA, major ions (see Table 1) and calculated value of $nssSO_4^{2-}$ and Cl^- loss. The normalized values are used for the variables of varimax rotated principal component analysis.

Two principal components account for 84.3% of the total variance of the chemical variables of Arctic aerosols. Figure 3 shows the relation between the component loadings of the first principal component and the component loadings of the second
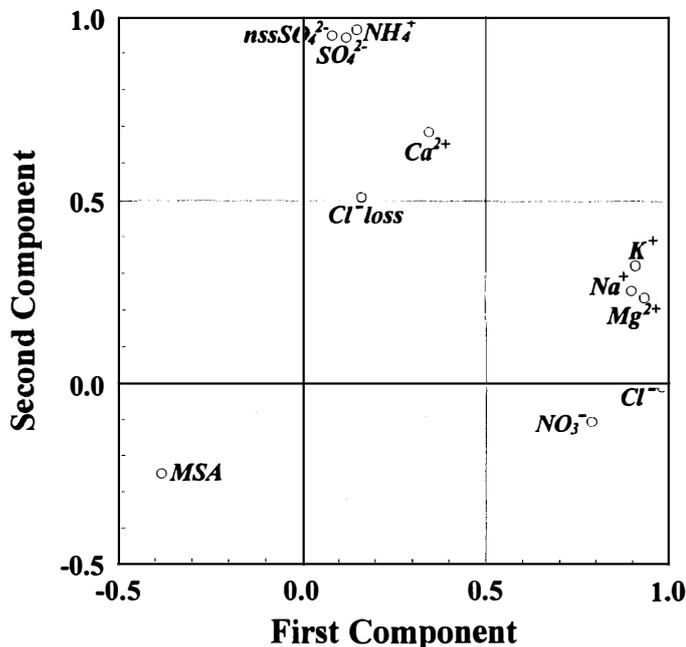
Fig. 3. The relationship between the component loadings of the
first and second principal components.
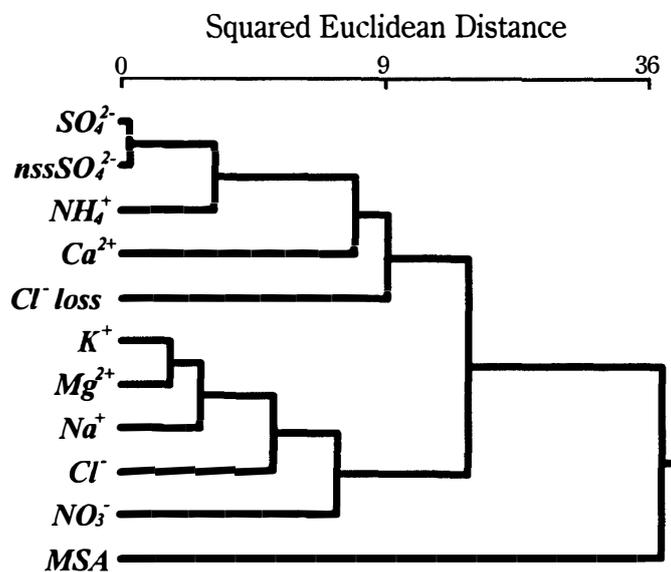
Fig. 4. Dendrogram of the cluster analysis.

principal component. The first principal component explains 58.7% of the total vari-
ance. The first component correlates well with Cl^-, Mg^{2+}, K^+ and Na^+, all of which
have component loadings 0.90 or above. Thus, the first component seems to show a sea
salt component. The second component accounts for 25.6% of the total variance. The
second component correlates well with NH_4^+, $nssSO_4^{2-}$ and SO_4^{2-}, all of which have
component loadings of 0.95 or above. Thus, the second component indicates anthropo-
genic source or the secondary aerosol formed after gas phase oxidation of SO_2 and

neutralization by NH_4^+.

The chemical variables of Arctic aerosols are classified by using the cluster analysis. The normalized values which were described before are used as the variables of cluster analysis. Squared Euclidean distance is used, and each element is analyzed by the centroid method. The dendrogram obtained from cluster analysis is shown in Fig. 4. Three major groups are classified as shown in Fig. 4 by the criterion of value 10 of squared Euclidean distance. The dissimilarity is larger from MSA to the other ions. MSA is an end product of the oxidation of DMS, which is produced by marine phytoplankton, and MSA has a different source with other ions. Referring to Fig. 4, there seem to be two major groups, one of which is anthropogenic origin or reacted elements. The other group shows sea salt elements or elements transported from southerly latitudes.

3.4. Concentration changes during the polar sunrise period

One chemical variable of each major group classified by the cluster analysis is illustrated in this section. The concentration change of MSA is shown in Fig. 5. Two peaks are recognized in Fig. 5. One occurs at the beginning of May, the second peak is
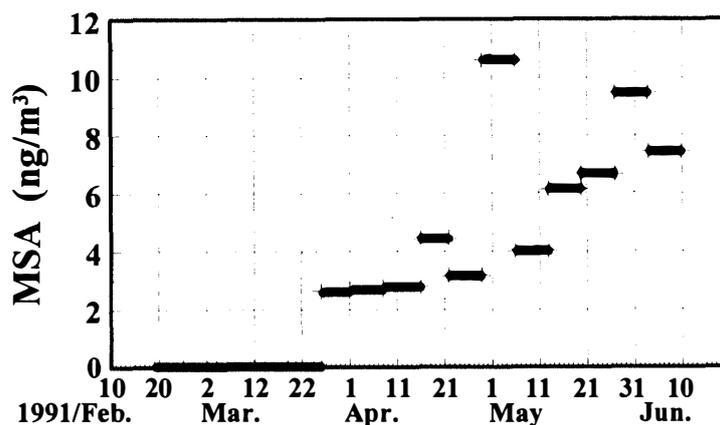
Fig. 5.   Concentration change of MSA in Arctic aerosols.
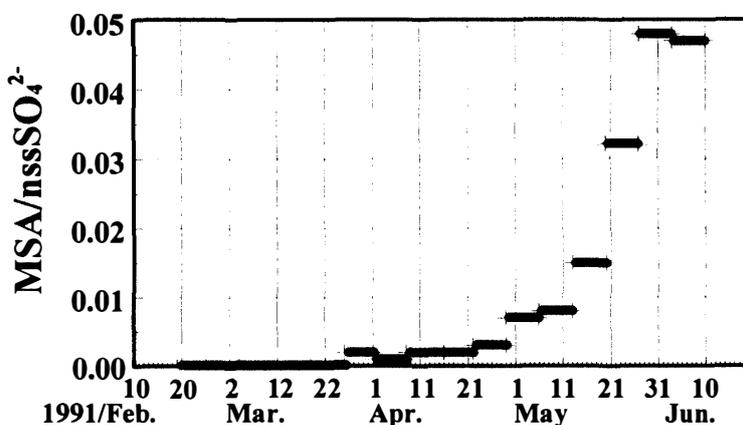
Fig. 6.   The ratios of $MSA/nssSO_4^{2-}$ in Arctic aerosols.

observed during May–June. After the end of May, MSA concentration appears to increase to a summer broad peak. This dual peak (spring and summer) feature in the MSA seasonal cycle at Alert is persistent from year to year (LI *et al.*, 1993).

The ratio MSA/nssSO$_4{}^{2-}$ in aerosols is used as a tracer of transport pathways (LI *et al.*, 1993). The MSA/nssSO$_4{}^{2-}$ ratios in this study are plotted in Fig. 6. In the Arctic aerosols, the highest ratio occurs in summer (July to August) when advection of pollution from mid-latitudes is at a minimum, as shown by the low nssSO$_4{}^{2-}$ (LI *et al.*, 1993). The MSA/nssSO$_4{}^{2-}$ ratio appears to increase to a summer peak.

The concentration change of Na$^+$ is shown in Fig. 7. LI and BARRIE (1993) reported that the seasonal cycle of Na$^+$ exhibits a broad peak for winter to spring (October to April). This peak is caused by the combination of two factors: a longer residence time and a greater sea salt source strength than in other seasons. The peak in Fig. 7 is considered to be the tail of this broad peak.

The maximum concentration of SO$_4{}^{2-}$ in Arctic aerosols occurs during winter–spring (January to April) when transport of air pollution from mid-latitude sources to the Arctic is strongest and precipitation scavenging is lowest (BARRIE, 1986). Figure 8 shows the concentration change of SO$_4{}^{2-}$ in this study. Non sea salt SO$_4{}^{2-}$ occupies 97%
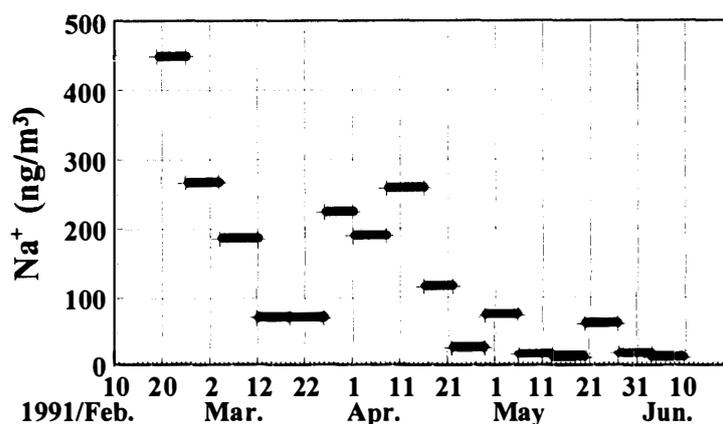
Fig. 7. Concentration change of Na$^+$ in Arctic aerosols.
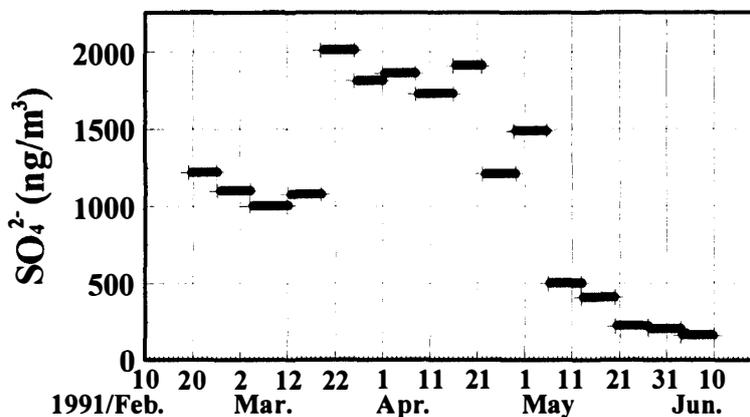
Fig. 8. Concentration change of SO$_4{}^{2-}$ in Arctic aerosols.

of total SO_4^{2-} in the aerosol samples. The concentration of SO_4^{2-} of aerosol samples collected in mid-February is the tail of the winter peak. In April, the second peak of SO_4^{2-} is noticed in Fig. 8.

4. Conclusions

Arctic aerosol samples were collected and analyzed during the polar sunrise period, at Alert, Canada. The major soluble species and MSA were determined by an ion chromatograph. Correlation coefficients among the concentrations of Na^+, Mg^{2+}, K^+ and Cl^- are high. The ratios of Mg^{2+}/Na^+ in the winter samples are higher than that found in sea water. Part of the K^+ and Mg^{2+} in winter aerosols consists of wind-blown dust. The predominant source of Na^+ and Cl^- in Arctic aerosols is considered to be sea salt, but quantity loss of Cl^- is observed around April. Mutual correlation between Cl^- loss and $nssSO_4^{2-}$ is noticed. This result suggests that a reaction between sea salt and acidic SO_4^{2-} occurs. The correlation between SO_4^{2-} concentration and NH_4^+ concentration is high. Secondary aerosols are formed after gas phase oxidation of SO_2 and neutralization by NH_4^+. The MSA concentration dose not have a high correlation with other ions; MSA concentration is negatively correlated with other ions. Two peaks of MSA concentration are noticed in spring and summer. Chemical elements of Arctic aerosols are classified into three groups by cluster analysis. The dissimilarity is larger from MSA to the others. One of the two major groups is anthropogenic elements or reacted elements. The other group is sea salt elements or elements transported from southerly latitudes.

Acknowledgments

References

ALPERT, D. J. and HOPKE, P. K. (1981): A determination of the sources of airborne particles collected during the Regional Air Pollution Study. Atmos. Environ., **15**, 675–687.

ANDREAE, M. O. (1983): Soot carbon and excess fine potassium: Long-range transport of combustion-derived aerosols. Science, **220**, 1148–1151.

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

BARRIE, L. A. and HOFF, R. M. (1984): The oxidation rate and residence time of sulphur dioxide in the Arctic atmosphere. Atmos. Environ., **18**, 2711–2722.

ERIKSSON, E. (1959): The yearly circulation of chlorine and sulfur in nature: Meteorological, geochemical and pedological implications. Tellus, **11**, 375–403.

HATAKEYAMA, S., IZUMI, K. and AKIMOTO, H. (1985): Yield of SO_2 and formation of aerosol in the photo-oxidation of DMS under atmospheric conditions. Atmos. Environ., **19**, 135–141.

HEIDAM, N. Z. (1981): On the origin of the Arctic aerosol- a statistical approach. Atmos. Environ., **15**, 1421 –1427.

HEIDAM, N. Z. (1982): Atmospheric aerosol factor models, mass and missing data. Atmos. Environ., **16**, 1923–1931.

Henry, R. C. and Hidy, G. M. (1979): Multivariate analysis of particulate sulfate and other air quality variables by principal components - I . Annual data from Los Angeles and New York. Atmos. Environ., **13**, 1581–1596.

Henry, R. C. and Hidy, G. M. (1982): Multivariate analysis of particulate sulfate and other air quality variables by principal components - II. Salt Lake City, Utah and St. Louis, Missouri. Atmos. Environ., **16**, 929–943.

Li, S.-M. and Barrie, L. A. (1993): Biogenic sulfur aerosol in the Arctic troposphere: 1. Contributions to total sulfate. J. Geophys. Res., **98**, 20613–20622.

Li, S.-M. and Winchester, J. W. (1989a): Resolution of ionic components of late winter Arctic aerosols. Atmos. Environ., **23**, 2387–2399.

Li, S.-M. and Winchester, J. W. (1989b): Geochemistry of organic and inorganic ions of late winter Arctic aerosols. Atmos. Environ., **23**, 2401–2415.

Li, S.-M., Barrie, L. A., Talbot, R. W., Harriss, R. C., Davidson, C. I. and Jaffrezo, J.-L. (1993): Seasonal and geographic variations of methanesulfonic acid in the Arctic troposphere. Atmos. Environ., **27A**, 3011–3024.

McInnes, L. M., Covert, D. S., Quinn, P. K. and Germani, M. S. (1994): Measurements of chloride depletion and sulfur enrichment in individual sea-salt particles collected from the remote marine boundary layer. J. Geophys. Res., **99**, 8257–8268.

Sturges, W. T. and Barrie, L. A. (1988): Chlorine, bromine and iodine in Arctic aerosols. Atmos. Environ., **22**, 1179–1194.

Thurston, G. D. and Spengler, J. D. (1985): A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. Atmos. Environ., **19**, 9–25.