

Decadal trends in aerosol chemical composition at Barrow, Alaska: 1976–2008

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Abstract. Aerosol measurements at Barrow, Alaska during the past 30 years have identified the long range transport of pollution associated with Arctic Haze as well as ocean-derived aerosols of more local origin. Here, we focus on measurements of aerosol chemical composition to assess (1) trends in Arctic Haze aerosol and implications for source regions, (2) the interaction between pollution-derived and ocean-derived aerosols and the resulting impacts on the chemistry of the Arctic boundary layer, and (3) the response of aerosols to a changing climate. Aerosol chemical composition measured at Barrow, AK during the Arctic haze season is compared for the years 1976–1977 and 1997–2008. Based on these two data sets, concentrations of non-sea salt (nss) sulfate (SO_4^-) and non-crustal (nc) vanadium (V) have decreased by about 60% over this 30 year period. Consistency in the ratios of nss SO_4^-/ncV and nc manganese (Mn)/ncV between the two data sets indicates that, although emissions have decreased in the source regions, the source regions have remained the same over this time period. The measurements from 1997–2008 indicate that, during the haze season, the nss SO_4^- aerosol at Barrow is becoming less neutralized by ammonium (NH_4^+) yielding an increasing sea salt aerosol chloride (Cl^-) deficit. The expected consequence is an increase in the release of Cl atoms to the atmosphere and a change in the lifetime of volatile organic compounds (VOCs) including methane. In addition, summertime concentrations of biogenically-derived methanesulfonate (MSA^-) and

nss SO_4^- are increasing at a rate of 12 and 8% per year, respectively. Further research is required to assess the environmental factors behind the increasing concentrations of biogenic aerosol.

1 Introduction

Arctic haze, defined here as the occurrence each winter and spring of increased aerosol concentrations and decreased visibility, was reported as early as the late 1800s (Nordenskiöld, 1883; Garrett and Verzella, 2008). It was not until the late 1970s, however, that it became possible to determine through chemical analyses that the haze was anthropogenic in origin and was a result of long range transport from the northern hemisphere mid-latitudes. These early studies used ratios of tracer species to identify likely source regions with the assumption that there are regional differences in pollution aerosol resulting from differences in combusted fuel, transportation, and industrial activities (e.g. Rahn and Shaw, 1980; Rahn and McCaffrey, 1980). The ratio of non-crustal (nc) manganese (Mn) to nc vanadium (V) was shown to be a useful tracer of regional sources.

NcV is a tracer of mid-latitude anthropogenic activity; its most significant pollution source is combustion of heavy residual oil (Zoller et al., 1973) which is too viscous to be used at cold temperatures. NcMn in the atmosphere results from a wider variety of anthropogenic activities including iron, steel, and ferro-alloy manufacturing; coal combustion; oil combustion; and mining (Pacyna et al., 1984). Rahn (1981) reported that the wintertime ncMn to ncV ratio



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was a factor of 5 higher in aerosol originating from Europe than from the northeast U.S. The higher ratios measured in Europe were attributed to the abundance of ferrous and non-ferrous industries and the lower ratios in the NE US were attributed to the residual oil burned for residential heating in the winter. Based on these regional values and taking into account the expected decrease in the ratio with transport due to the different size distributions of Mn and V, Rahn (1981) concluded that Europe was a more significant source region for Arctic aerosol than the NE US. Furthermore, compared to Norwegian Arctic aerosol, N. American Arctic aerosol was more influenced by a source in addition to Europe. It was suggested that the additional source was the central former Soviet Union. Raatz and Shaw (1984) confirmed that central Eurasian sources dominated the aerosol at Barrow during the winter in a follow up analysis that combined the 1976 to 1980 Barrow time series of ncMn and ncV concentrations with the synoptic conditions existing at the source regions and in the Arctic. Expanding the tracer analysis to seven elements, Lowenthal and Rahn (1985) determined that 70% of most tracer elements at Barrow came from the former Soviet Union during the winter of 1979–1980 and 25% came from Europe.

Non-seasalt (nss) sulfate (SO_4^-) makes up a large but variable fraction of Arctic Haze aerosol (Quinn et al., 2007). During the winter and early spring, fossil fuel combustion in distant source regions is the primary source of nss SO_4^- since biological activity is at a minimum (e.g. Ferek et al., 1995). Rahn and McCaffrey (1980) compared wintertime nss SO_4^- to ncV ratios at Arctic and non-Arctic sites and found that ratios within the Arctic were over an order of magnitude larger than those measured in mid-latitude source regions. They attributed the higher Arctic ratios to oxidation of mid-latitude SO_2 while *enroute* to Barrow resulting in an aged version of mid-latitude aerosol.

During the summer, the oxidation of biogenically-produced dimethylsulfide yields aerosol nss SO_4^- and methanesulfonate (MSA^-). Concentrations of MSA^- due to local production peak from May to September as the ice recedes and phytoplankton productivity in surface waters begins (e.g. Li et al., 1993; Quinn et al., 2002). In addition, there is a rapid release of DMS from the ice into surface waters and from under the ice into the atmosphere following the ice break up (Levasseur et al., 1994; Ferek et al., 1995).

In this paper we compare concentrations of ncMn, ncV, nss SO_4^- , and ratios of tracer species measured at Barrow over the past decade to those measured during the late 1970s to assess changes in the concentrations and sources of Arctic Haze aerosol over the past 30 years. In addition, we present trends in summertime nss SO_4^- and MSA^- and changes in the composition of the inorganic fraction of the aerosol that have occurred at Barrow over the past decade and the implications associated with this changing aerosol composition.

2 Measurements

The 1976–1977 measurements were based on High-Volume samples collected over 3 to 7 days with subsequent analysis by instrumental neutron activation (Rahn and McCaffrey, 1980). Sample collection during the 1997–2008 period was done with a Berner-type multijet cascade impactor with an aerodynamic D_{50} cutoff diameter of $1\ \mu\text{m}$. Samples collected between 1997 and 2008 were analyzed for inorganic ions (Na^+ , NH_4^+ , Cl^- , SO_4^- , and MSA^-) by ion chromatography (Quinn et al., 1998). Samples collected between 2003 and 2008 were analyzed for trace elements (including Al, V, and Mn) by thin-film X-ray primary and secondary emission spectrometry (Bates et al., 2004). Sampling during the 1997–2008 period was sector controlled such that real-time wind speed and direction were used to exclude data from the locally polluted sector (130 to 360°). More details of the sample inlet, sampling procedures, and chemical analyses can be found in Delene and Ogren (2002) and Quinn et al. (2002). Given that the species considered here occur primarily in the submicrometer size range, the sampling methods used for the two different data sets should not affect the results.

Sea salt SO_4^- concentrations were calculated from measured Na^+ concentrations and the mass ratio of sulfate to sodium in seawater of 0.252 (Holland, 1978). Nss SO_4^- was calculated from the difference between the total and sea salt components. Crustal V and Mn concentrations were calculated from the mass ratio of the element to Al in crustal material using the values of Mason (1966) (0.00166 for V and 0.0117 for Mn). ncV and ncMn were calculated from the difference of the total and crustal V and Mn concentrations.

The existence of a monotonic increasing or decreasing trend in the time series was tested with the nonparametric Mann-Kendall test (Gilbert, 1987). The estimate for the slope of a linear trend was calculated with the nonparametric Sen's method (Sen, 1968). Trends are reported for significance levels, α , of 0.01, 0.05, and 0.1 where a significance level of <0.1 indicates that the probability of no trend is 10% or less. No α is reported if the significance level is >0.1 . The reported significance levels do not take into account uncertainties associated with measured concentrations or inter-annual variability. Hence, significance levels may be higher than those reported for the trends derived from the combined 1976–1977 and 1997–2008 data sets.

The haze season is defined throughout as January to April and is based on the months during which Arctic haze is most pronounced. Summer is defined here as July to September as these are the months with relatively high biogenic activity (based on MSA concentrations) and low anthropogenic impact (based on nss SO_4^- concentrations).

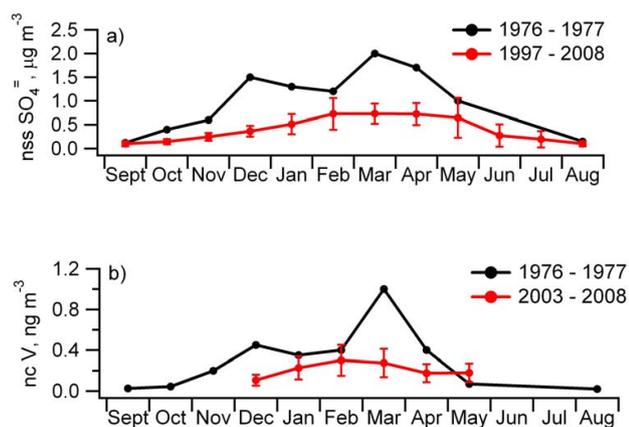


Fig. 1. Monthly averaged values from 1976–1977 and 1997–2008 for (a) nss SO_4^- and (b) ncV . The 1976–1977 data are from Rahn and McCaffrey (1980). Vertical bars for the 1997–2008 data here and throughout are the 1σ standard deviation of the monthly average.

3 Results and discussion

3.1 Non-seasalt SO_4^- and non-crustal V at Barrow

Rahn and McCaffrey (1980) published the first year-round measurements of nss SO_4^- and ncV at Barrow, AK covering the period of September 1976 to September 1977. These measurements revealed the seasonality of Arctic Haze with an increase in the concentration of both species in the fall, a maximum in the winter and early spring, and a decrease in late spring. More recent measurements of nss SO_4^- (October 1997 to April 2008) and ncV (January 2005 to April 2008) reveal a similar seasonal cycle but overall lower concentrations (Fig. 1). The broad winter to early spring maximum in nss SO_4^- has been attributed to an initial transport of anthropogenic nss SO_4^- produced in mid-latitude source regions and the transport and subsequent oxidation of SO_2 to SO_4^- as light levels increase *enroute* to and within the Arctic itself (Barrie and Hoff, 1984). The nss SO_4^- December maximum apparent in the earlier data set but not in the latter may be due to inter-annual variability or to a change in emissions and/or the SO_2 oxidation efficiency in the source regions.

Combining the 1976–1977 and 1997–2008 data sets and performing a linear regression of concentrations averaged over the haze season versus year reveals a decrease of about 60% over the past 30 years for both nss SO_4^- and ncV (Fig. 2a and b). This change corresponds to a 2% decrease per year. The similarity in the haze season $\text{nss SO}_4^-/\text{ncV}$ ratio for the two data sets is shown in Fig. 2c. The reported value for 1976–1977 was 3 while haze season values between 2003 and 2008 ranged from 2.9 to 4.2. For comparison, wintertime values reported for the NE US and Europe are much lower at 0.28 and 0.26, respectively (Rahn and McCaffrey, 1980).

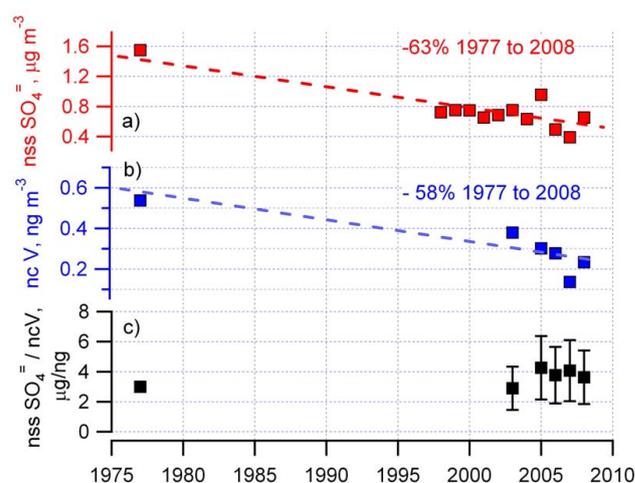


Fig. 2. Concentrations of (a) nss SO_4^- and (b) ncV averaged over the haze season (January–April) and (c) the $\text{nss SO}_4^-/\text{ncV}$ ratio. The 1976–1977 data are from Rahn and McCaffrey (1980).

The stability in the $\text{nss SO}_4^-/\text{ncV}$ ratio indicates that the same source regions are being measured today as 30 years ago and that the decrease in the concentrations of nss SO_4^- and ncV is, in large part, a result of a decrease in emissions in the source regions. Hence, this result supports time series estimates of sulfur emissions that report a decline globally and, in particular, for countries that are known source regions to the Arctic, from the 1970s through 2000 (e.g. Berge et al., 1999; Erismann et al., 2003; Stern, 2005).

Changes in the frequency of transport of pollution to the Arctic and removal during transport may also have influenced measured concentrations at Barrow. Strong transport into the Arctic from Eurasia during winter is due, in part, to the persistence of the Siberian high (Barrie, 1986; Christensen, 1997). Weakening of the Siberian High over the past quarter century (Gong and Ho, 2002) may be contributing to less pollution reaching the Arctic from Eurasia. Determining the relative importance of transport frequency and removal processes will require further studies that combine modeled transport and removal with measured concentrations and known changes in emissions.

3.2 Non-crustal Mn and V at Barrow

Rahn (1981) reported ncMn/ncV ratios greater than 1 for the N. American Arctic based on measurements made during the winter and spring of 1976–1978. Values reported for Barrow and Mould Bay, NWT averaged around 2 and 1.5, respectively. The ncMn/ncV ratio averaged over the haze season at Barrow between 2003 and 2008 ranged from 1.3 to 2.3. Recreating the ncV vs. ncMn scatter plot of Rahn (1981) and adding the 2003–2008 data show that the recent Barrow measurements agree with the unique N. American Arctic data from 30 years ago (Fig. 3). The ncMn/ncV ratio measured

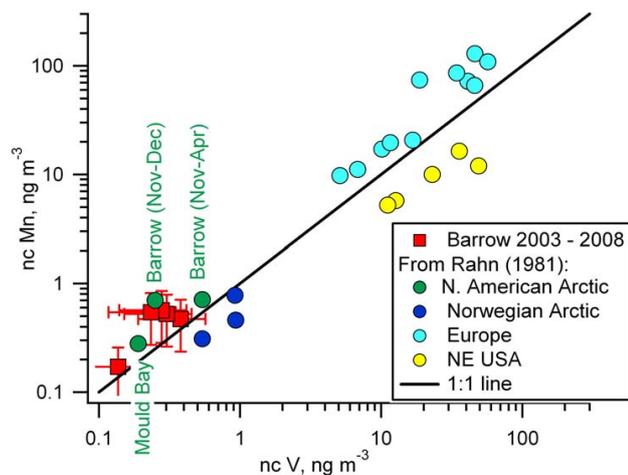


Fig. 3. A comparison of ncV versus ncMn from Barrow (2003–2008) with values previously reported by Rahn (1981) for the North American Arctic (Barrow and Mould Bay), the Norwegian Arctic (Bear Island and Spitsbergen), Europe, and the N. E. US.

at Barrow has remained in the same range and distinct from the Norwegian Arctic and the NE US. Again, these results indicate that emissions in the source regions to the Arctic have decreased over the past 3 decades but the source regions themselves have not changed.

3.3 Cl^- deficit at Barrow

Measurements of the concentration of inorganic ions in sub-micrometer aerosol particles have been made continuously at Barrow since the fall of 1997 allowing for the observation of changes in aerosol composition during both the haze season and during summer. Over the past decade, haze season concentrations of nss SO_4^- have decreased by about 2% per year (Fig. 4a) and NH_4^+ concentrations have decreased at a rate of 6% per year. As a result, the $\text{NH}_4^+/\text{nss SO}_4^-$ molar ratio has decreased by 6.4% per year ($\alpha=0.01$) (Fig. 4c). Reasons for the different rates of decrease in the observed concentrations for the two species are not clear. There is observational evidence that emissions of NH_3 and SO_2 are decreasing in source regions to the Arctic (e.g. Erismann et al., 1999; Berge et al., 1999). However, emissions for the Russian Federation and European Communities as used in EMEP Models indicate that SO_x emissions decreased at a higher rate between 1997 and 2008 than NH_3 emissions (Gauss et al., 2008a, b). Assessing the concentration decreases observed at Barrow will require not only accurate emission data for NH_3 and SO_x but also quantification of the reaction rate of gas phase NH_3 with acidic sulfate aerosol and removal of NH_4^+ and SO_4^- near the source region and *enroute* to Barrow.

The decreasing $\text{NH}_4^+/\text{nss SO}_4^-$ molar ratio results in an increasingly acidic anthropogenic aerosol that is available to react with sea salt aerosol in the Barrow boundary layer.

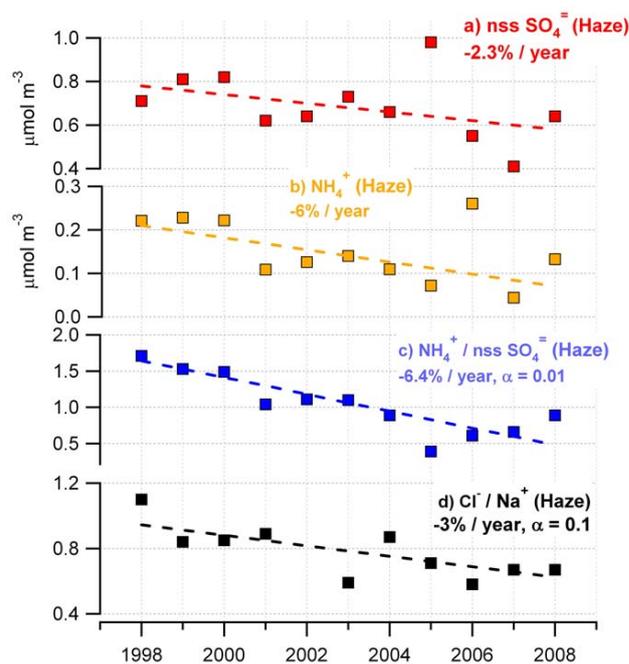


Fig. 4. Values of (a) nss SO_4^- , (b) NH_4^+ , (c), $\text{NH}_4^+/\text{nss SO}_4^-$ molar ratio and (d) Cl^-/Na^+ molar ratio averaged over the haze season (January–April) at Barrow. Lines indicate the Sen's slope estimates. α indicates the significance level of the trend.

Figure 4d shows a decrease in the Cl^- to Na^+ ratio, or an increase in Cl^- depletion from the sea salt aerosol, of 3% per year ($\alpha=0.1$). The correspondence of these two trends suggests that the less neutralized nss SO_4^- aerosol yields an increase in the HCl displacement from the sea salt aerosol. The consequent increase in concentration of Cl atoms, even at low concentrations, can reduce the lifetime of volatile organic compounds (VOCs) including CH_4 (Platt et al., 2004), a potent greenhouse gas, and impact reactions that destroy or produce O_3 (Knipping et al., 2003). In addition to HCl, there is evidence that highly reactive gases such as Cl_2 , HOCl, and ClNO_2 may also volatilize from sea salt aerosol (e.g. Pszenny et al., 1993). Hence, this result has potentially important implications for the Cl photochemistry occurring in the near-surface Arctic atmosphere (Keene et al., 1998).

In contrast to the haze season, the summertime aerosol at Barrow is much less impacted by industrial pollutants from long range transport and more influenced by biogenic sources (e.g. Quinn et al., 2002). Concentrations of MSA^- , which is derived solely from the oxidation of biogenically produced DMS, begin to increase in April, peak in May through September, and decrease dramatically in October. The elevated concentrations of MSA^- in late spring may be due to long range transport from source regions in the North Pacific (Li et al., 1993). By late June, local biogenic production of MSA^- and nss SO_4^- becomes important as the ice melt begins and phytoplankton productivity in surface waters

increases. O'Dwyer et al. (2000) compared MSA^- preserved in a Svalbard ice core with sea surface temperature (SST) and sea-ice extent over the period between 1920 and 1996. They found high MSA^- concentrations were associated with warm SST and reduced sea-ice extent and suggested that MSA^- concentrations in ice cores may be useful as a proxy for past climate.

The correspondence between MSA^- and past climate may also be relevant for current and future changes in the Arctic. Over the past decade, there has been an increase in summertime concentrations of MSA^- of 12% per year ($\alpha=0.1$) and of nss SO_4^- of 8% per year ($\alpha=0.05$) (Fig. 5a and b). Although it is beyond the scope of this paper to attribute these increasing trends to particular factors, the ice core results suggest that they may be due to recent decreases in sea-ice cover and increases in mean sea surface temperature (SST). Further work is required to link the observed trends at Barrow to changing environmental factors. Particle number concentrations are highest at Barrow and other surface Arctic sites during the summer (Quinn et al., 2002; Engvall et al., 2008) suggesting a link between biogenic activity and enhanced particle production. The climatic importance of the biogenically produced particles at Barrow, in terms of their ability to act as cloud condensation nuclei, is yet to be determined.

4 Conclusions

A comparison of the aerosol chemical composition at Barrow, AK measured during the winter and spring of 1976–1977 and 1997–2008 indicates that the mass concentrations of species contributing to Arctic haze have decreased markedly over the past 30 years. In addition, it appears that while emissions have decreased, the source regions of Arctic haze are the same now as 3 decades ago. Further work is required to assess additional factors that may be contributing to decreasing aerosol concentrations observed at Barrow during the Arctic haze season including changes in the frequency of transport of pollution to the Arctic and removal during transport. In addition, accurate emission data for all species that undergo long range transport to the Arctic during the haze season would improve the understanding of the observed trends.

Measurements of concentrations of aerosol inorganic ions at Barrow over the past decade reveal an increase in the Cl^- deficit associated with sea salt aerosol. This increased release of HCl and perhaps other additional reactive Cl-containing gases has implications for halogen chemistry in near surface air at Barrow including changes in the lifetimes of ozone, methane, DMS, and other species. In addition, summertime concentrations of MSA^- and nss SO_4^- at Barrow have increased over the past decade. These increasing trends may be a result of a changing climate in the Arctic (e.g. warmer SST and reduced sea ice extent) and, if maintained, may affect the radiative balance within the Arctic through enhanced

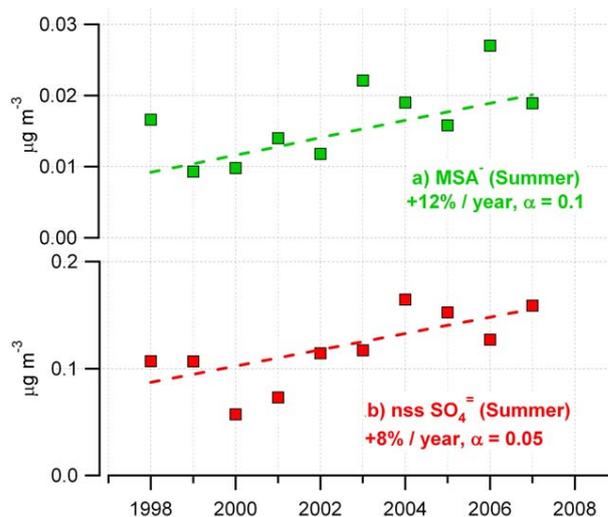


Fig. 5. Values of (a) MSA^- and (b) nss SO_4^- averaged over the summertime (July–September) at Barrow. Lines indicate the Sen's slope estimates. α indicates the significance level of the trend.

particle production. Further work is required to link the observed trends in summertime aerosol at Barrow to changing environmental factors.

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