Seasonal distributions of fine aerosol sulfate in the North American Arctic basin during TOPSE

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Seasonal distributions of fine aerosol sulfate in the North American Arctic basin during TOPSE

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[1] We used the mist chamber/ion chromatography technique to quantify fine aerosol SO$_4^{2-}$ (<2.7 μm) in the Arctic during the Tropospheric Ozone Production about the Spring Equinox Experiment (TOPSE) with about 2.5 min time resolution. Our effective sample area ranged from 50° to 86°N and 53° to 100°W. The seasonal evolution of fine aerosol sulfate in the Arctic troposphere during TOPSE was consistent with the phenomenon of Arctic haze. Arctic haze has been attributed to pollution from sources in the Arctic and pollution transported meridionally along stable isentropes into the Arctic in geographically broad but vertically narrow bands. These layers became more prevalent at higher altitudes as the season progressed toward summer, and the relevant isentropes are not held so close to the surface. Mean fine particle SO$_4^{2-}$ mixing ratios during TOPSE in February below 1000 m were elevated (112 pptv) and highly variable (between 28 and 290 pptv) but were significantly lower at higher altitudes (about 40 pptv). As the season progressed, elevated mixing ratios and higher variability were observed at higher altitudes, up to 7 km. In May, mixing ratios at the lowest altitudes declined but still remained higher than in February at all altitudes. The high variability in our measurements likely reflects the vertical heterogeneity of the wintertime Arctic atmosphere as the airborne sampling platform passed in and out of these layers. It is presumed that mixing ratios and variability will continue to decline at all altitudes into the summer as wet deposition processes become important in removing aerosol SO$_4^{2-}$ from the troposphere. INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 9315 Information Related to Geographic Region: Arctic region; KEYWORDS: TOPSE, fine sulfate, polar sunrise, mist chamber


1. Introduction

[2] Accumulation of aerosols and anthropogenic pollutant gases in the troposphere during the Arctic wintertime is well documented [Rahn and Heidman, 1981; Barrie, 1986]. The slow transformation and removal processes due to cold sub-zero temperatures, absence of wet precipitation, and low levels of solar radiation [Barrie, 1986] coupled with a slow, low- level, long-range meridional transport of Eurasian mid and high latitudinal pollutants into the Arctic lead to annual wintertime events which have become to be known as Arctic haze. This visual haze is largely due to the aerosol light scattering properties of accumulation mode particles [Brock et al., 1989], which exhibit a dominant presence around the 0.01–0.5 μm effective diameter range [Blanchet and List, 1983]. The hazes have been shown to be primarily of anthropogenic origin [Radke and Hobbs, 1984] with aerosol SO$_4^{2-}$ constituting more than half of the total aerosol mass [Shaw and Khalil, 1989]. Most of this SO$_4^{2-}$ mass is derived from anthropogenic emissions of SO$_2$ rather than primary particulate emissions [Barrie and Hoff, 1985]. Much of these emissions are believed to have originated from Europe and Russia [Rahn and Heidman, 1981] and been transported isentropically into the Arctic in multiday long pulses as low pressure systems run-up against the quasi-stationary Siberian high [Barrie, 1986].

[3] Arctic Haze is believed to influence radiative budgets, snowpack albedo, snowpack chemical composition, and microphysical properties of Arctic clouds [Brock et al., 1990]. Measurements of SO$_4^{2-}$ aerosols in the Arctic have often been limited to geographically fixed locations. These data tend to be lacking information on spatial variability, both horizontally and vertically. Intensive airborne measurement campaigns conducted in both the summer (ABLE 3A-3B, 1988, 1990) and winter (AGASP I-IV, 1983, 1986, 1989, and
In the early months of 2000, the heavily instrumented NSF/NCAR C-130 research aircraft conducted a series of trips into the Arctic beginning on February 4, 2000 and continuing until May 23, 2000. This campaign was called the Tropospheric Ozone Production about the Spring Equinox Experiment, or TOPSE. The primary objective of TOPSE was to study Arctic ozone production, loss and transport with a focus on the commonly observed springtime Arctic ozone maximum. It consisted of seven trips (42 total flights) from Boulder, Colorado (38°N) into the high Arctic environment (86°N). Atlas et al. [2003] provides an instrument payload description and detailed objectives of the flights conducted during TOPSE. A summary flight track plot including all flights conducted during TOPSE is shown as Figure 1.

This field campaign provided an excellent opportunity to use the University of New Hampshire's dual mist chamber/ion chromatograph technique to examine the seasonal and vertical distributions of fine aerosol SO$_4^{2-}$ in the Arctic. This technique was developed for the measurement of soluble gases such as HNO$_3$, CH$_3$COOH, HCOOH [Talbot et al., 1999], SO$_2$ [Klemm and Talbot, 1991], HCl [Keene et al., 1993], and HONO [Dibb, 2003]. Experiments during prior intensive aircraft campaigns have demonstrated that with only minor modifications, measurements of fine soluble aerosols is possible. This technique is well suited for Arctic haze related aerosol SO$_4^{2-}$ since the aerosols are present predominantly in the accumulation size mode [Rahn and McCaffrey, 1979; Radke et al., 1984]. Previously, soluble aerosol sampling has been restricted to Teflon filter exposure and subsequent solvent/water extraction. The Teflon filter technique, although yielding more potential...
2. Methods

Twelve bulk aerosol measurements were made during TOPSE using the NCAR-RAF Small Community Aerosol Inlet (SCAI) and Teflon filters. These measurements were made primarily to help speciate detectable, but unexpected, amounts of soluble Br⁻ detected by the mist chamber/ion chromatograph system in many low altitude samples. Aerosol SO₄ was also detected and quantified in these samples, providing some measure of comparison to the mist chamber samples.

3. Results
3.1. Filter Intercomparisons: Previous Missions

Chemical analysis of the samples collected by the mist chambers was conducted in near real-time using ion chromatography. The aqueous samples were removed from the mist chamber by computer controlled syringe pumps (Kloehn 50300) and injected into custom fabricated ion chromatographs employing sample preconcentration (Dionex TAC-LP1). Separation was achieved using a helium purified carbonate/bicarbonate eluent and Dionex AS4A analytical columns. Background conductivity was suppressed using Dionex ASRS-Ultra suppressors. Detection of Cl⁻, Br⁻, NO₃, SO₃ and SO₄ was accomplished using a Dionex CD-20 conductivity detector equipped with a DS-3 temperature controlled cell. Sulfur dioxide is quickly converted in the mist chamber to aqueous sulfite (SO₃⁻) which is easily detected by ion chromatography. Based on laboratory tests and sample stream filtering of SO₄, it has been determined that very little SO₃ is converted to SO₄ in the very short time between sample collection and analysis. Digitized data was then sent to a data acquisition computer using standard ethernet communications where post processing took place. An internal spike of known aqueous concentration of phosphate into the mist chamber and subsequent analysis was used to track any evaporative losses of water from the mist chamber during sampling. Two independent systems operated in tandem, which allowed for continuous sampling with an average 2.5-minute time resolution. It is important to note that, unlike conventional filter techniques, all sample and fluid handling was in a closed system and isolated from the aircraft cabin ambient air to prevent contamination.
South Pacific, we collected non-size selected aerosol $\text{SO}_4^{2-}$ data using the standard Teflon filter technique and the mist chamber/ion-chromatography technique simultaneously. Dibb et al. [2003] describes the sampling methodology and presents some data for the samples collected using the Teflon filter technique. Filter exposure times averaged 14.2 min ($\sigma = 7.2$) on the DC-8 and 14.8 min ($\sigma = 5.4$) on the P3-B. Since the standard Teflon filter technique was designed for bulk aerosol sampling rather than a size selected fraction, some correction to make the data comparable was necessary. Although most non-marine aerosol $\text{SO}_4^{2-}$ mass is in accumulation size mode [Warneck, 1988], there can be a significant fraction associated with sea-salt or crustal dust that is in the much larger coarse mode, especially in a marine environment. This makes a simple sea-salt correction to the total $\text{SO}_4^{2-}$ an acceptable method to approximate the fine aerosol $\text{SO}_4^{2-}$ (or non-sea salt) component. Magnesium was used as the sea-salt tracer element for the determination of sea-salt $\text{SO}_4^{2-}$ with Keene et al. [1986] presents a discussion of the use of sea-salt ratios for the determination of sea-salt $\text{SO}_4^{2-}$ and crustal dust.

3.2. Filter Intercomparisons During TOPSE

[10] The NCAR Small Community Aerosol Inlet (SCAI) with flow straightening shroud and a University of New Hampshire modified curved leading edge nozzle was employed during TOPSE to sample the aerosol associated radionuclide tracers $^7\text{Be}$ and $^{210}\text{Pb}$ [Dibb, 2003]. This inlet was also used to collect a limited number of bulk aerosol samples isokinetically on Teflon filters at low altitudes (<2 km asl). These samples were collected in order to facilitate speciation of soluble bromide observed in the mist chamber/ion chromatography analysis, however, aerosol $\text{SO}_4^{2-}$ was also quantified in these samples. This provided a basis for comparison of TOPSE mist chamber/ion chromatography samples to bulk aerosol filter samples. Figure 4 shows excellent agreement in the $\text{SO}_4^{2-}$ data when measured using the two techniques. The variability in the mist chamber data represents the standard deviation of the mean mixing ratio measured by the mist chamber during the approximately 15 minute time period that a bulk filter sample was being collected. It is not unexpected that the bulk aerosol data has a tendency to show slightly higher mixing ratios than the mist chamber data this close to the surface. Intercomparisons during the NASA PEM-Tropics B experiment suggest that agreement is even better at higher altitudes where $\text{SO}_4^{2-}$ is almost exclusively on fine aerosols and uninfluenced by sea-salt or crustal dust.

3.3. Fine Aerosol $\text{SO}_4^{2-}$ Measured During TOPSE

[11] A summary of the fine aerosol $\text{SO}_4^{2-}$ data collected during TOPSE is presented in Table 1. The Table is restricted to latitudes greater than 50°N, since data collected south of 50°N were generally collected during transit flights to the primary study region. In order to examine the seasonal evolution of fine aerosol $\text{SO}_4^{2-}$ in the Arctic, the data were summarized by trip and grouped into discrete 1000-m altitude bins in the latitude range of 50°N–86°N. Mixing ratios as high as 1766 pptv and as low as 4 pptv were observed during TOPSE (Table 1). The lowest values were generally observed during the first trip in early February. This trip also had the lowest variability in most altitude bins. The highest values were observed during the sixth trip in late April, which also exhibited the greatest variability.

[12] Our measured values are consistent with data presented by Lazrus and Ferek [1984] from the 1983 AGASP airborne sampling campaign. They report $\text{SO}_4^{2-}$ concentrations in the Arctic as low as 7.3 neq/m$^3$ (82 pptv) and as high as 110 neq/m$^3$ (1233 pptv). Their samples, however, represent much longer periods of integration, and are less likely to represent a completely homogenous sample. That is, each one of their samples is more prone to have passed in and out of haze layers. This explains the smaller range of mixing ratios reported. Their highest value presented is reported to have been collected while flying in a continuous haze layer and may reflect a more homogeneous sample. Indeed, their highest mixing ratio reported is very similar to what we observed.

[13] The frequency distribution of our raw aerosol $\text{SO}_4^{2-}$ data is highly skewed by less frequent but very high values. This can be explained by an abundance of cleaner air riddled with thin, highly polluted, layers. That is, since the polluted layers can be strongly delineated from the cleaner air, there appeared to be an absence of more moderate transition layers. Arithmetic means are only representative of data that has an approximately normal frequency distribution. This makes using arithmetic means for our $\text{SO}_4^{2-}$ data bins very misleading. Using medians can have the opposite effect since the median is not very sensitive to our less frequently occurring, but very large observations. To address this problem, we use geometric means. This statistic can be applied since the data are more nearly lognormally distributed. This statistical tool addresses more of the real variability within the data set without placing emphasis on unusually high or low values. It also allows us to visualize real variability in the form of lognormally transformed standard deviations; presented graphically as unequal length error bars in Figure 5.

[14] During the first trip in early February, fine aerosol $\text{SO}_4^{2-}$ mixing ratios were relatively low and not highly variable above 1000 m (Figure 5, top panel). Below 1000 m the range of mixing ratios was significantly higher and yielded a geometric mean of 110 pptv. This mean was more than two-fold higher than in any other altitude bin during this trip. Interestingly, Ridley et al. [2003] report a rarity of pollution events at very low altitude. $\text{SO}_4^{2-}$ mixing ratios were, however, noticeably enhanced all the way to the
lowest altitudes surveyed during TOPSE throughout the campaign. Barrie [1986] reported data summarized by Rahn and Heidman [1981] noting that winter/spring pollution aerosols measured from a ground based Arctic aerosol sampling network averaged 2 µg/m3 SO4 (466 pptv). This is consistent with our observations of near-surface SO4 enhancements.

[15] During the second trip (late February), mean mixing ratios in the two lowest bins were almost double what was observed during the first trip, but mean mixing ratios above 2000 m remained around 50 pptv and were not highly variable. This trend of increasing mean mixing ratios at increasingly higher altitudes as the season progressed continued into trip 3 in early March. Mean mixing ratios below...
5000 m all appeared to be enhanced and increasingly variable with respect to earlier trips. There was also a gradient of about 70 pptv in mean mixing ratios (100 to 170 pptv) between the 2000 to 3000 m bin and below 1000 m.

Mean mixing ratios were above 100 pptv in all altitude bins and above about 225 pptv below 2000 m by trip 4 in late March. The steepest gradient in SO4 = mean mixing ratio was no longer below 1000 m, but rather between 1000 and 3000 m. The trend of increasing mean mixing ratios in all altitude bins from trip to trip but decreasing mean mixing ratios with altitude began to show marked change during trip 5 in early April. Mean mixing ratios below 2000 m were lower than on the previous trip while mean mixing ratios above 2000 m continued to increase, albeit less dramatically. During the last two trips, fine aerosol sulfate mean mixing ratios generally continued to decrease below 3000 m and increase above 4000 m. By the end of the data collection phase of TOPSE, SO4 = mean mixing ratios showed no obvious altitude gradient and were greater than threefold higher at all altitudes above 1000 m than they were in early February (about 30 percent higher below 1000 m).

Talbot et al. [1992] reported aerosol sulfate mixing ratios averaging 29 pptv in the boundary layer and 65 pptv

Figure 4. Intercomparison of the mist chamber/ion chromatograph technique to Teflon filter bulk aerosol SO4 = samples from TOPSE during periods of collection of the bulk aerosol samples. There were an average of 6 mist chamber samples collected for each of the approximately 15 minute bulk filter sample.
Table 1. Summary of Fine Aerosol Sulfate, North of 50-Degree Latitude, Binned by Trip and Altitude

<table>
<thead>
<tr>
<th>Trip</th>
<th>&lt;1000 m</th>
<th>1000–2000 m</th>
<th>2000–3000 m</th>
<th>3000–4000 m</th>
<th>4000–5000 m</th>
<th>5000–6000 m</th>
<th>6000–7000 m</th>
<th>&gt;7000 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trip 1</td>
<td>31</td>
<td>124</td>
<td>112</td>
<td>28</td>
<td>290</td>
<td>69</td>
<td>23</td>
<td>15</td>
</tr>
<tr>
<td>Trip 2</td>
<td>59</td>
<td>165</td>
<td>155</td>
<td>48</td>
<td>406</td>
<td>28</td>
<td>39</td>
<td>12</td>
</tr>
<tr>
<td>Trip 3</td>
<td>34</td>
<td>171</td>
<td>168</td>
<td>98</td>
<td>313</td>
<td>28</td>
<td>39</td>
<td>12</td>
</tr>
<tr>
<td>Trip 4</td>
<td>85</td>
<td>206</td>
<td>212</td>
<td>118</td>
<td>530</td>
<td>28</td>
<td>39</td>
<td>12</td>
</tr>
<tr>
<td>Trip 5</td>
<td>100–2000 m</td>
<td>58</td>
<td>242</td>
<td>219</td>
<td>19</td>
<td>540</td>
<td>28</td>
<td>39</td>
</tr>
<tr>
<td>Trip 6</td>
<td>2000–3000 m</td>
<td>49</td>
<td>211</td>
<td>158</td>
<td>40</td>
<td>597</td>
<td>28</td>
<td>39</td>
</tr>
<tr>
<td>Trip 7</td>
<td>3000–4000 m</td>
<td>40</td>
<td>133</td>
<td>129</td>
<td>34</td>
<td>446</td>
<td>28</td>
<td>39</td>
</tr>
<tr>
<td>Trip 8</td>
<td>4000–5000 m</td>
<td>13</td>
<td>117</td>
<td>83</td>
<td>8</td>
<td>543</td>
<td>28</td>
<td>39</td>
</tr>
<tr>
<td>Trip 9</td>
<td>5000–6000 m</td>
<td>21</td>
<td>86</td>
<td>101</td>
<td>23</td>
<td>337</td>
<td>28</td>
<td>39</td>
</tr>
<tr>
<td>Trip 10</td>
<td>6000–7000 m</td>
<td>35</td>
<td>50</td>
<td>46</td>
<td>8</td>
<td>189</td>
<td>28</td>
<td>39</td>
</tr>
<tr>
<td>Trip 11</td>
<td>&gt;7000 m</td>
<td>67</td>
<td>23</td>
<td>19</td>
<td>12</td>
<td>25</td>
<td>28</td>
<td>39</td>
</tr>
</tbody>
</table>

Notes to Table 1

*The geometric mean (M) commonly used for lognormally distributed data. It is the nth root of the product of the values in a given bin. [M(x) = (x1x2 ... xn) ^ (1/n)].
are confined to near the surface disappears as dramatically enhanced mixing ratios are observed at higher altitudes. We believe that, even in the late winter, vertical mixing is a small or non-existent component of the observed enhancement at higher elevations. Mixing of low-level air with the overlying free troposphere is inhibited by a persistent low-level inversion [Kahl, 1990]. Stable inversions can last for several weeks essentially decoupling the lower troposphere from higher altitudes [Bradley et al., 1992]. Elevated mixing ratios at higher and higher altitudes as the season progresses must be explained by transport into the Arctic along vertically higher isentropes tracing back to warmer and warmer source regions in northern Eurasia. A discussion of isentropic transport pathways coupled with source region potential temperatures during TOPSE is presented by Klonecki et al. [2003].

[21] During early April, below 3000 m, levels of SO$_4$$_2^-$ enhancement began to decline. An increase in inversion base depths and decrease in inversion persistence probabilities [Kahl et al., 1992] hint that solar surface heating may be beginning to stir up the lowest layers of the atmosphere while more stable isentropic transport can continue at higher altitudes. Removal processes, dominated by wet deposition [Barrie, 1985], become increasingly important and decrease mixing ratios at lower altitudes. By the end of May, surface mixing ratios of fine aerosol SO$_4$$_2^-$ are almost half of the maximum observed in March. Mixing ratios also appear to be beginning to decrease at higher altitudes. This is consistent with the much lower values observed at all altitudes during summer months by Talbot et al. [1992].

[22] The high variability observed in Figure 5 demonstrate that SO$_4$$_2^-$ aerosol mixing ratios in the Arctic winter are far from homogeneous. Mixing ratios during the late February trip (trip 2) in the 1000–2000 m altitude bin were observed to be as low as 23 pptv and as high as 1766. This is consistent with prior observations of multiple narrow haze bands covering between 20–200 km [Radke et al., 1984] which are often between tens of meters to 1 km thick, [Brock et al., 1989] and streaming slowly into the Arctic environment. Individual altitude bins of data presented here probably incorporate both cleaner and more polluted layers, leading to high variability within the bins. The observations of increasing SO$_4$$_2^-$ mean mixing ratios in an altitude bin during the winter can be attributed to more frequent

Figure 5. (opposite) Vertical distributions of geometric mean mixing ratios between 50 and 85 north latitude. Error bars represent 1 standard deviation about the geometric mean and are therefore asymmetric. They represent a measure of variability of mixing ratios observed (about 68%) and not error.

Figure 6. Seasonal progression of geometric mean mixing ratios of fine aerosol SO$_4$$_2^-$ in three altitude bins.
Figure 7. Latitudinal distributions of fine aerosol $\text{SO}_4^{2-}$ during winter and spring in 3 altitude bins. Raw data shown (circles) are discrete measurements made north of 50°N. Triangles represent geometric means of $\text{SO}_4^{2-}$ mixing ratios plotted at the mean latitude of the 5° bins.
occurrences of these narrow polluted layers within the bin region.

5. Conclusion

The mist chamber/ion chromatograph is shown to be an effective tool for the measurement of fine aerosol $SO_4^{2-}$ aboard an aircraft platform. During TOPSE, we collected an extensive fine aerosol $SO_4^{2-}$ data set. These measurements paint a four monthlong picture of the vertical distributions in the Arctic. Small-scale variability and poorly understood frequencies of haze layers, however, makes estimation of total aerosol burdens difficult [Brock et al., 1990]. The slow transport, and lack of major chemical transformations, however, does allow us to treat the approximately weeklong measurement campaigns as synoptic snapshots of the Arctic environment. It is shown that $SO_4^{2-}$ aerosols begin to build up at very low altitudes during the winter. The altitude at which the build up is most pronounced tended to migrate to higher altitudes as the season progressed toward spring. In spring, $SO_4^{2-}$ aerosols began to clean up at lower altitudes first, progressing upward. It is possible that much of the fine detail of the Arctic air is lost in the averaging and temporal gaps in the data. Follow-up investigations into the frequency, distribution, and spatial variability of Arctic pollution layers could help provide better information into the extent and magnitude of these layer as well as help better explain the extreme heterogeneity observed.

[24] Acknowledgments. We would like to express our sincere appreciation to the National Science Foundation (NSF) Office of Polar Programs (OPP) for supporting our research program through the National Center for Atmospheric Research (NCAR). We would also like to acknowledge Eliot Atlas with support from the Research Aviation Facility (RAF) for level-headdledly and successfully leading us through what proved to be a very challenging environment.

References


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