

## Sources of aerosol nitrate and non-sea-salt sulfate in the Iceland region

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### Abstract

Daily aerosol filter samples were collected on Heimaey, Iceland (63.40° N, 20.30° W), beginning in July 1991. Samples were analyzed for  $\text{NO}_3^-$ , non-sea-salt (nss)  $\text{SO}_4^{2-}$ , and methanesulfonate (MSA). Along with  $\text{SO}_2$  and nss- $\text{SO}_4^{2-}$ , MSA is a product of the atmospheric oxidation of dimethyl sulfide (DMS) that is produced by marine organisms. For much of the time, concentrations of aerosol nss- $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were relatively low. Occasionally, however, concentrations increased sharply, by an order of magnitude or more, often for periods of several days. These concentration peaks were usually associated with the presence of a high-pressure field over western Europe; the large-scale wind fields associated with the high pressure subsequently transported pollutants to the Iceland region. The 2-year mean  $\text{NO}_3^-$  aerosol concentration was  $0.239 \mu\text{g}/\text{m}^3$ , while that for nss- $\text{SO}_4^{2-}$  was  $0.642 \mu\text{g}/\text{m}^3$ ; the median values were, respectively,  $0.113 \mu\text{g}/\text{m}^3$  and  $0.367 \mu\text{g}/\text{m}^3$ . Excluding the high-aerosol events (i.e. about 10% of the samples), the  $\text{NO}_3^-$  average was  $0.131 \mu\text{g}/\text{m}^3$  and that for nss  $\text{SO}_4^{2-}$  was  $0.385 \mu\text{g}/\text{m}^3$ ; these values are similar to those measured in the pristine South Pacific. Thus, although pollution events were relatively infrequent, they had a substantial impact on atmospheric chemistry in this region, in effect doubling the annual mean concentrations. There was a very strong seasonal cycle in MSA concentrations, with a summer maximum of about  $500 \text{ ng}/\text{m}^3$ , which decreased to a few  $\text{ng}/\text{m}^3$  in December. The seasonal cycle of MSA matches that of *Phaeocystis pouchetii* and *Emiliania huxleyi*, both of which are strong DMS producers; intense and widespread blooms of these organisms are often found around Iceland in the late spring and summer. During the summer, the nss- $\text{SO}_4^{2-}$ /MSA ratio was very low much of the time, suggesting that biogenic DMS was the dominant source of aerosol nss- $\text{SO}_4^{2-}$  in this region in this season.

**Keywords:** Aerosols; Methanesulfonate; Sulfate; Nitrate; Dimethylsulfide

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## 1. Introduction

The North Atlantic Ocean is a relatively small ocean basin closely bordered by large continental land masses and many highly industrialized nations. About 50–60% of the global emissions inventory for  $\text{NO}_x$  and  $\text{SO}_2$  is located in North America and Europe (Hameed and Dignon, 1992). Because of the characteristics of large-scale atmospheric circulation, there is a high probability that gases and aerosols emitted on the continents will be transported by winds to the marine atmosphere and that a large fraction will most likely be deposited there.

There is great interest in long-range aerosol transport to the oceans because of the role that aerosols might play in climate. Recent modelling studies suggest that anthropogenic aerosols (most importantly,  $\text{SO}_4^{2-}$  aerosol) can exert a considerable cooling effect on climate through their direct interaction with solar radiation (Charlson et al., 1990, 1991, 1992). The magnitude of the estimated  $\text{SO}_4^{2-}$  aerosol cooling is such that it could substantially offset the estimated warming from increased  $\text{CO}_2$  and other greenhouse gases. The estimates of aerosol radiative effects are based on models that make many assumptions about the distribution, concentration, and physical properties of nss  $\text{SO}_4^{2-}$  aerosols, both natural and anthropogenic (Langner and Rodhe, 1991; Charlson et al., 1992). Because of the paucity of data, many of these assumptions are subject to debate. Indeed, a recent estimate of aerosol radiative effects (Kiehl and Briegleb, 1993) used somewhat different assumptions and obtained a global cooling average that was about half that predicted by Charlson et al. (1990, 1991, 1992).

Despite the apparent importance of pollution aerosols in some ocean regions, on a global scale, oceanic sources of reduced sulfur gases such as DMS still constitute a large fraction of the atmospheric sulfur budget. In the remote marine atmosphere (especially the southern hemisphere), oceanic DMS is by far the dominant source of submicron nss  $\text{SO}_4^{2-}$ . Indeed, the current interest in the anthropogenic effects of  $\text{SO}_4^{2-}$  aerosols derives from an initial focus on the role of oceanic DMS on climate (Shaw, 1983; Charlson et al., 1987).

To address the issue of aerosol sources and transport, a network of four atmospheric sampling stations was established in 1989 in the middle and low latitudes of the North Atlantic as a part of the Atmosphere/Ocean Chemistry Experiment (AEROCE): Mace Head, Ireland; Bermuda; Barbados, West Indies; Tenerife, Canary Islands (Fig. 1). A major objective of the AEROCE program is to characterize the chemical climatology of tropospheric  $\text{O}_3$  and  $\text{CO}$  and a number of important aerosol species, including  $\text{NO}_3^-$  and nss- $\text{SO}_4^{2-}$ , and to assess the relative importance of natural and anthropogenic sources. The data from this network show that all areas in the low and mid-latitudes are frequently and strongly impacted by the transport of  $\text{NO}_3^-$  and nss- $\text{SO}_4^{2-}$  and/or their precursors from continental, principally pollutant, sources (Savoie et al., 1989a, 1992, 1994a; Arimoto et al., 1992; Ellis et al., 1993). The annual mean concentrations of  $\text{NO}_3^-$  and nss- $\text{SO}_4^{2-}$  over most of the North Atlantic are much higher than values from remote oceanic regions in the South Pacific. For example, the annual mean aerosol  $\text{NO}_3^-$  concentrations at the AEROCE sites range from about 0.6 to 1.1  $\mu\text{g}/\text{m}^3$  compared to values of 0.1–0.2  $\mu\text{g}/\text{m}^3$  in

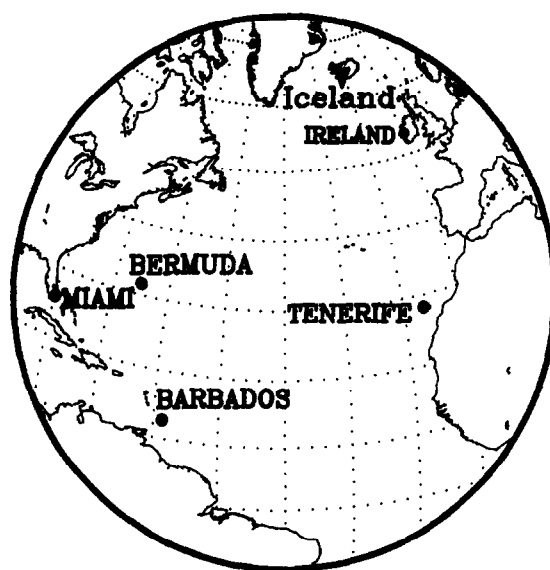


Fig. 1. Map showing the location of the Iceland station on Heimaey and of AEROCE stations in the North Atlantic.

the equatorial and central South Pacific. If these differences are due to pollutants, then pollutants account for the major fraction of the  $\text{NO}_3^-$  aerosol over most of the North Atlantic, from a minimum of 60% to a maximum of 90%.

In an effort to characterize the transport of natural and pollutant materials to the high latitudes, we established an aerosol sampling station at Stórhöfði on Heimaey in the Vestmannaeyjar Islands, Iceland, in July 1991 (Fig. 1). Heimaey is a small island located 12 km off the south coast of Iceland, about 110 km southeast of Reykjavik. In September 1992, instrumentation was installed at Stórhöfði for the measurement of ozone and carbon monoxide. These research activities are a part of the United States (Department of Commerce) National Oceanic and Atmospheric Administration's Climate and Global Change Program (US/NOAA/CGCP). The research program on Heimaey is designed to be complementary to activities carried out in the AEROCE program and it follows identical protocols. At this time we present only the aerosol data.

## 2. Sampling and analysis

The aerosol sampling apparatus is situated about 30 m south-southwest of the lighthouse at Stórhöfði on the southern end of Heimaey. Aerosol particles are collected as air is drawn through  $20 \times 25$ -cm Whatman-41 filters at a flow rate of about  $1 \text{ m}^3/\text{min}$ . The total mass collection efficiency of Whatman-41 filters is greater than 90% for  $\text{nss-SO}_4^{2-}$  and methanesulfonate (MSA) and 95% for  $\text{NO}_3^-$  and sea salt (Savoie et al., 1989a; Pszenny et al., 1993). Filters are changed every day. To minimize the possibility of sampling under wind conditions that could transport aerosols from sources on Iceland, the sampler is automatically controlled by a wind sensor system that activates the pump only when the winds come over the open ocean at speeds greater than  $1 \text{ m/s}$ . The over-ocean sampling sector extends from  $90^\circ$  through south to  $270^\circ$ . During the course of the program, the winds met the sampling conditions on average 51% of the time.

After exposure, the filters are returned to Miami for analysis. Quarter sections of each of the filter samples are extracted with 20 ml of 18

Mohm/cm Milli-Q water in three separate aliquots of 10, 5, and 5 ml.  $\text{Na}^+$  in the extracts is determined within  $\pm 2\%$  by flame atomic absorption and  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and MSA within  $\pm 5\%$  by suppressed ion chromatography (Savoie et al., 1989a). Non-sea-salt (nss)  $\text{SO}_4^{2-}$  is calculated as total  $\text{SO}_4^{2-}$  minus  $\text{Na}^+ \times 0.2517$ , the  $\text{SO}_4^{2-}/\text{Na}^+$  mass ratio in seawater.  $\text{NH}_4^+$  is analyzed by automated colorimetry of indophenol blue (Patton and Crouch, 1977). Procedural filter blanks are taken routinely; the filter is handled in the same way as a regular sample, except that no air is drawn through it. The concentrations of the ions in the ambient aerosol samples are typically at least 10 times higher than those in the blank filters. We present data only for filters that had passed more than about  $100 \text{ m}^3$  of air, which is roughly equivalent to a daily duty cycle of about 10%.

Because Whatman-41 and other cellulose filters coated with NaCl are known to collect  $\text{HNO}_3$  vapor with high efficiency (Okita et al., 1976; Appel et al., 1980, 1981; Forrest et al., 1980), we consider our measured  $\text{NO}_3^-$  concentrations to be those of total inorganic  $\text{NO}_3^-$ , i.e. particulate  $\text{NO}_3^-$  plus gaseous  $\text{HNO}_3$  (Savoie et al., 1989a). However, the concentration of gaseous  $\text{HNO}_3$  in the near-surface marine boundary layer is typically around 20% or less of the total  $\text{NO}_3^-$  (Savoie and Prospero, 1982; Savoie, 1984).

## 3. Results and discussion

### 3.1. Aerosol nitrate and nss-sulfate

The daily aerosol concentration data for the period July 1991 through March 1993 are shown in Fig. 2. Monthly means are shown in Fig. 3. For the most part, concentrations of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  are relatively low. The mean concentration of  $\text{NO}_3^-$  (for the period July 1991–May 1993) is  $0.239 \mu\text{g}/\text{m}^3$ , while that for  $\text{nss-SO}_4^{2-}$  is  $0.642 \mu\text{g}/\text{m}^3$ . These values are considerably lower than those measured in the AEROCE network. These relationships are depicted in Fig. 4, which shows the means for the AEROCE stations and for selected remote stations in the Pacific and the coastal Antarctic (Savoie et al., 1989a,b).

The monthly means (Fig. 3) suggest that there

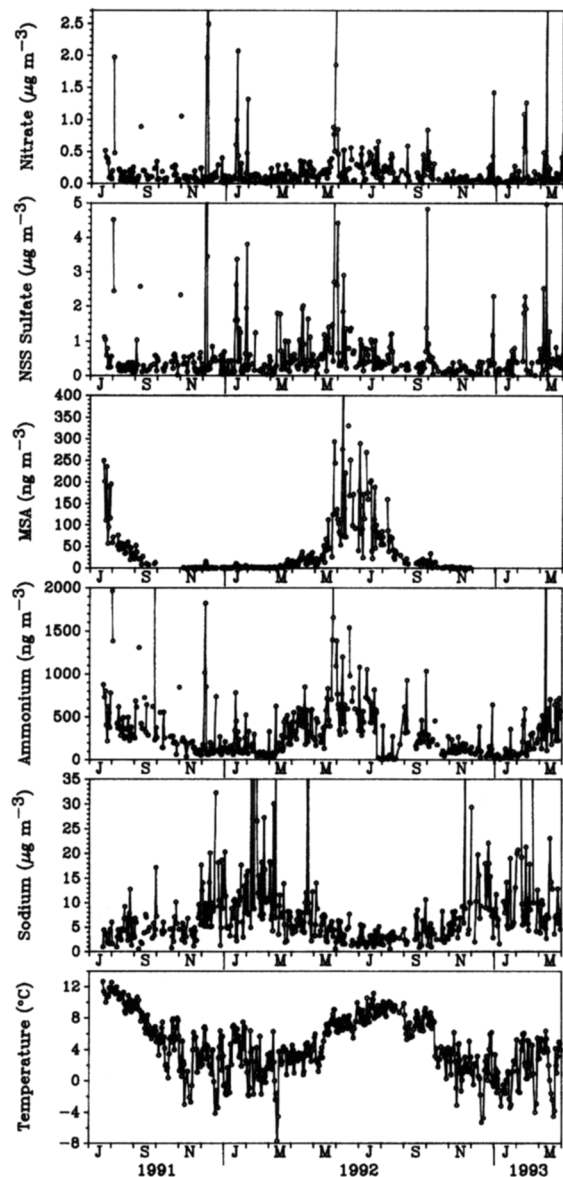


Fig. 2. Time series of daily sample data for aerosol  $\text{NO}_3^-$ ,  $\text{nss-SO}_4^{2-}$ , MSA,  $\text{NH}_4^+$ , and  $\text{Na}^+$ . Also shown is the daily mean temperature at Stórhöfði, Heimaey.

is a seasonal cycle in the  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  concentrations, with the maximum in the summer months. The concentrations in December 1991 and January 1992 stand out, but the December values are driven by one large aerosol event (the highest in the record) and the January values by two strong events.

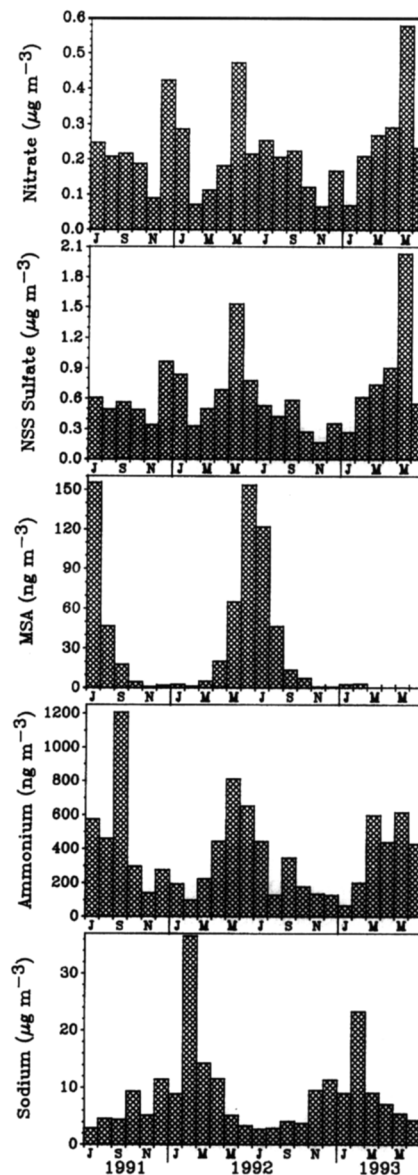


Fig. 3. Monthly mean aerosol concentrations for aerosol  $\text{NO}_3^-$ ,  $\text{nss-SO}_4^{2-}$ , MSA,  $\text{NH}_4^+$ , and  $\text{Na}^+$  at Heimaey.

The time series data (Fig. 2) show that while the concentrations of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  are generally quite low, there are brief periods when the concentrations rise very sharply. As discussed later, we can associate the largest of these high-concentration events with meteorological conditions that favor the transport of pollutants from distant sources. Although infrequent, these events

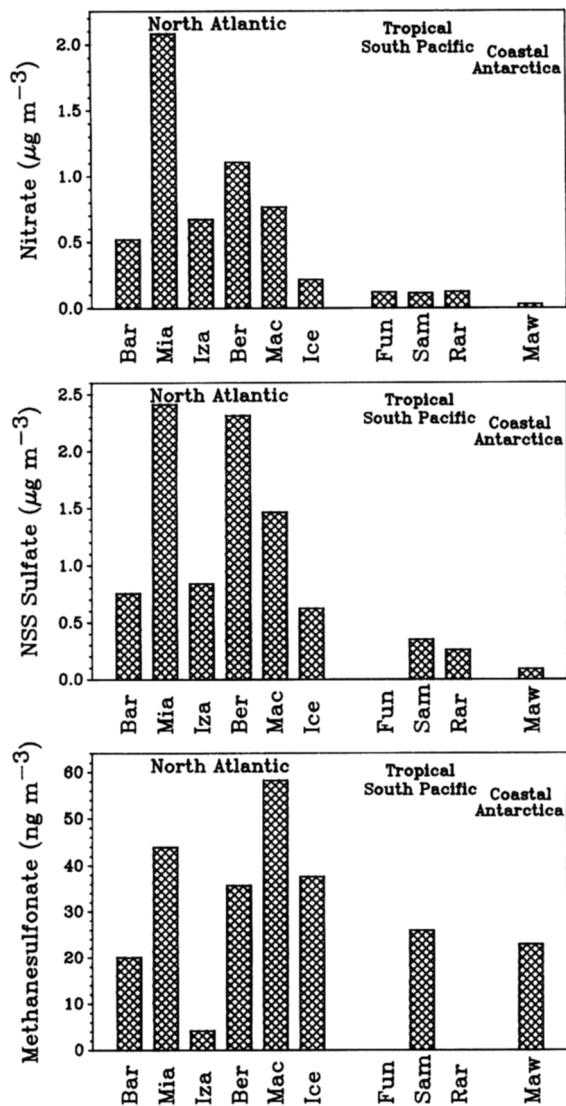


Fig. 4. Annual mean concentrations for aerosol  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  and MSA for various ocean regions. North Atlantic data are from Heimaey (Iceland) and from AEROCE stations: Ber, Bermuda; Bar, Barbados; Mac, Mace Head, Ireland; Iza, Izaña, Tenerife; Mia, Miami. The South Pacific data are: Fun, Funafuti, Tuvalu; Sam, American Samoa; Rar, Rarotonga, Cook Islands. Coastal Antarctic data are from Mawson (Maw) on the Indian Ocean coast.

have a great effect on the mean concentrations. The clearly identifiable high-concentration events account for roughly the highest 10% of the sample set; if these are eliminated, the mean (90%) is  $0.131 \mu\text{g/m}^3$ , which is 55% of the mean for the

entire data set ( $0.239 \mu\text{g/m}^3$ ). Similarly for  $\text{nss-SO}_4^{2-}$ , by eliminating the upper 10%, the mean (90%) is reduced to  $0.385 \mu\text{g/m}^3$ , which is 60% of the mean for the full data set ( $0.642 \mu\text{g/m}^3$ ). The 90% means are essentially identical to means for remote stations in the South Pacific (Savoie et al., 1989a,b, 1994b).

It is also useful to compare median values because these are less affected by extreme values in a data set. The medians for the full Iceland data set (that is, without eliminating any samples from the set) are  $0.113 \mu\text{g/m}^3$  for  $\text{NO}_3^-$  and  $0.368 \mu\text{g/m}^3$  for  $\text{nss-SO}_4^{2-}$ ; these medians are also quite similar to those obtained at the remote Pacific stations (Savoie et al., 1989a,b, 1994b). Thus, although pollution events are relatively infrequent, they appear to have a substantial impact on atmospheric chemistry in this region; if all of the high concentration spikes are due to pollution (about 10% of the samples), then pollution transport effectively doubles the concentrations of aerosol  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$ . This estimate is probably conservative; an additional pollution fraction may well be present in the other 90% of the sample set.

#### Meteorological setting

Using meteorological products available to the Icelandic Meteorological Office, we made a preliminary assessment of the synoptic meteorology conditions that were associated with the episodes of unusually high  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations. Transport trajectories were estimated in a general way based on the synoptic wind fields. We focus on the seven largest aerosol events in 1991 and early 1992 (i.e. the first 9 months of the data set).

**30 July–1 August 1991.** A relatively stagnant high-pressure field was centered over northern Europe and moved slowly north. Air movements were slow along paths that ran across the British Isles and the North Sea. These air parcels arrived in Iceland on 31 July.

**6–7 September 1991.** There was an extensive high over the British Isles and the ocean to the west. Wind fields were weak and diffuse. The air parcel arriving at Iceland on 6 September appears to have come from the center of the high, west of

Ireland. The most likely sources of pollution were in Britain and possibly parts of western Europe.

**29–30 October 1991.** During the previous week, a high-pressure field moved slowly from the southwest over the British Isles towards southern Scandinavia. On 27 October, wind fields suggested that transport took place slowly across Scotland; subsequently, there was rapid transport to southern Iceland through 30 October.

**5–6 December 1991.** This was one of the strongest pollution episodes measured in this program. A persistent and expanding high was located over the British Isles and it moved slowly northwest on 3–4 December. Air arriving at Iceland on 5 December can be traced close to the center of the high that was positioned northwest of Scotland on the 4th. The air arriving on 6 December at Iceland was traced across southern Ireland on the 5th and further back across the English Channel. Great Britain and central Europe were therefore the most likely sources. During this episode, there was a strong acidic precipitation event on Iceland, as reflected in the rainfall records at an air quality station located at Irafoss, 45 km east of Reykjavik. On the 6th and 7th, precipitation amounts were 40.4 mm and 28.3 mm with pH levels of 3.8 and 4.4, respectively. These pH values are among the lowest ever measured on Iceland.

**13–16 January 1992.** This major episode was traced to an almost stationary high over Great Britain and northcentral Europe on 10 January. On 10 and 11 January, transport occurred over southern England and northern France; transport paths subsequently turned to the north and arrived at Iceland on 13 January.

**28–29 January 1992.** During the previous week, an extensive and almost stationary high over the British Isles and northcentral Europe resulted in cold weather and poor visibility. The air arriving at Iceland on the 29th had moved from central Europe in the previous 2 or 3 days, passing south of the British Isles.

**11–13 March 1992.** This event was selected because the winds had a strong northerly component, mostly outside the sampling sector or marginally in the sector; consequently, the sampler operated only for brief periods. During this

time, a low over Iceland moved to the east, followed by strong northerly winds. None the less,  $\text{nss-SO}_4^{2-}$  concentrations were relatively high. Because winds were from the north, it might be possible to attribute the  $\text{nss-SO}_4^{2-}$  to sources on Iceland; local pollution is an unlikely source, however, because the  $\text{NO}_3^-$  concentrations were quite low. This event is discussed further in the following section.

#### *Comparisons with Irafoss data*

The synoptic interpretations for these events are supported by a comparison of the  $\text{nss-SO}_4^{2-}$  concentrations at Heimaey during these high-concentration episodes with those measured in an independent program at Irafoss as a part of the Icelandic air quality program (Fig. 5). Except for the first event at the end of July 1991, the concentrations at the two sites were remarkably similar. The agreement is particularly impressive when one considers that the sampling operations were completely independent and uncoordinated and the sampling and analytical protocols were different; also, the Irafoss sampler was not sectorized. In addition, the aerosol maxima at the two sites matched precisely in time. These factors suggest that the aerosols were carried in a large relatively well-mixed air mass; if the aerosol had been derived from local sources, we would expect to see larger differences between the two sites because of the location of Irafoss close to sources in the Reykjavik area.

The meteorological assessments are supported by the temperature record at Heimaey (Fig. 5). Except for the event in March 1992, all pollution episodes were associated with a marked increase in air temperature. This is consistent with the synoptic interpretations presented in the previous section; we would expect that air masses advected from Europe over the mid-latitude North Atlantic would be relatively warm. On the other hand, the event in March 1992 is associated with a very sharp temperature drop, suggesting that the pollutants were transported from the polar regions, which is consistent with the strong northerly flow experienced at that time. Thus, the pollutants in this episode most likely were transported across the Arctic from sources in Europe, Asia, or North

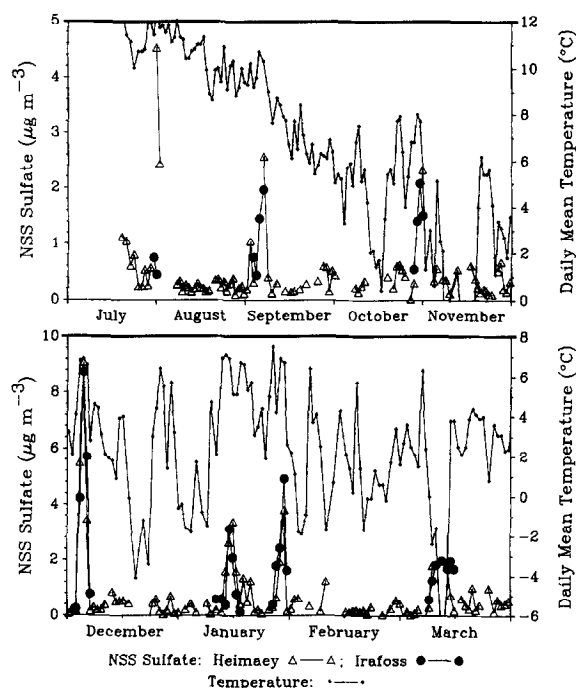


Fig. 5. Time series of daily aerosol  $\text{nss-SO}_4^{2-}$  concentrations for Stórhöfði (Heimaey) and for Irafoss, along with air temperatures at Stórhöfði; July 1991–March 1992.

America. The Arctic is known to be heavily impacted by pollutants from mid-latitude sources during the winter and spring (Barrie, 1986; Barrie and Barrie, 1990). Indeed the concentrations of  $\text{nss-SO}_4^{2-}$  at both Heimaey and Irafoss during this event (about  $2 \mu\text{g}/\text{m}^3$ ) were in the range of values from various sites in the Arctic for this season, typically  $1\text{--}4 \mu\text{g}/\text{m}^3$  (Barrie, 1986; Barrie and Barrie, 1990; Li and Barrie, 1993).

These meteorological studies are only preliminary attempts to understand the factors associated with long-range transport to Iceland. None the less, it is significant that six of the seven events were associated with the presence of a relatively stagnant high-pressure system over Europe and the seventh was associated with strong flow from the Arctic.

### 3.2. Methanesulfonate and oceanic sources of $\text{nss-sulfate}$

There is an extremely strong seasonal cycle in MSA concentrations (Figs. 2 and 3), with typical

values on the order of  $100 \text{ ng}/\text{m}^3$  or more in June and July. The summer concentrations that we measured on Heimaey are among the highest measured anywhere in the world. Concentrations decrease sharply in the fall, and in the winter they are about a factor of 100 lower than summer values.

The timing of the seasonal cycle of MSA at Iceland coincides with that of oceanic primary productivity in the region. On a global scale, the concentration of DMS in surface seawater is roughly proportional to primary productivity. Higher DMS concentrations are typically found in coastal and upwelling regions, while oligotrophic waters generally exhibit low levels (Andreae and Raemdonck, 1983; Cline and Bates, 1983; Andreae, 1990). In the North Pacific, the seasonal cycle in biological activity is reflected in surface water DMS, with higher concentrations during warmer months (Bates et al., 1987). As expected, the seasonal variability in DMS concentrations is most extreme in high-latitude waters because of the extreme seasonal variability in primary productivity (which varies strongly with light levels among other factors). High concentrations of DMS have been measured in association with spring blooms in the Bering Sea (Barnard et al., 1984) and in the North Sea (Turner et al., 1988).

Only certain groups of phytoplankton, mainly dinoflagellates, prymnesiophytes (including coccolithophores), and chrysophytes, are strong producers of DMS (Andreae et al., 1983; Keller et al., 1989). Two species in particular, *Phaeocystis pouchetii* and *Emiliania huxleyi*, are known to be very strong producers of DMS (Barnard et al., 1984; Turner et al., 1988; Gibson et al., 1990; Matrai and Keller, 1993). The waters around Iceland should be an excellent source of DMS because of the extremely large blooms of *Phaeocystis pouchetii* and *Emiliania huxleyi* that occur in the spring and summer in this region (Stefánsson and Jakobsson, 1989; Balch and Holligan, personal communication). The distribution of these species in Icelandic waters and the relationship to hydrographic features have been well documented because of the very intensive oceanographic studies carried out in support of fisheries activities. In this context, the distribution of inor-

ganic nutrients has been extensively monitored for over 25 years (Stefánsson and Olafsson, 1991).

The annual mean MSA concentrations at some of the other stations in the North Atlantic are equal to, or somewhat greater than, those at Iceland (Fig. 4). Although MSA concentrations are extremely high at Heimaey during the summer, the season of high productivity around Iceland is relatively short and winter productivity is extremely low compared to other locations. In contrast, the low-latitude stations show substantial concentrations of MSA all year long. Note, in particular, the very high mean concentration at Mace Head. Productivity is extremely high in the region west and north of the British Isles during the late spring and summer; also, during the remainder of the year, there is a substantial transport of aerosol MSA from the mid- and low-latitudes of the North Atlantic to the Mace Head region. The net effect of these processes is to produce a relatively uniform mean annual concentration of MSA across the entire North Atlantic. The one exception is Izaña, which is located at an altitude of 2400 m and, hence, lies above the top of the marine boundary layer much of the time.

The only comparable long-term record of MSA at high latitudes is that at Alert, Canada (71.3° N, 156.8° W) (Li and Barrie, 1993; Li et al., 1993). The seasonal cycle of MSA at Alert is similar to that at Heimaey, except that the summer monthly means at Alert are about an order of magnitude lower, typically a few 10's of ng/m<sup>3</sup>.

There is a considerable body of literature that discusses the use of the ratio of nss-SO<sub>4</sub><sup>2-</sup> to MSA to estimate the relative contributions of anthropogenic and natural precursors to nss-SO<sub>4</sub><sup>2-</sup> (see for example the discussions in Savoie et al., 1989b, 1992, 1993, 1994a,b; Andreae, 1990; Barrie and Barrie, 1990; Prospero et al., 1991; Li and Barrie, 1993; Li et al., 1993). It is generally assumed that, in the absence of anthropogenic influences, the atmospheric chemistry reaction pathways will lead to a relatively constant ratio and that deviations from this ratio can be attributed to the admixing of anthropogenic nss-SO<sub>4</sub><sup>2-</sup>. However, the ratio nss-SO<sub>4</sub><sup>2-</sup>/MSA appears to be latitude-dependent for reasons that

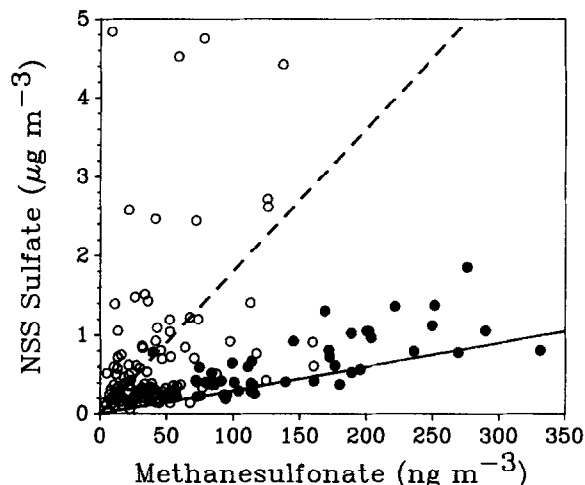


Fig. 6. Scatter plot of nss-SO<sub>4</sub><sup>2-</sup> versus MSA for the months of May–September during the period of record (July 1991–May 1993). The samples collected during June and July (i.e. when oceanic productivity is particularly high) are indicated by filled circles. The slope of the solid line indicates an nss-SO<sub>4</sub><sup>2-</sup>/MSA mass ratio of 3, which appears to be representative of the ‘clean air’ end-member ratio of nss-SO<sub>4</sub><sup>2-</sup>/MSA for DMS oxidation in this region. The dashed line indicates a ratio of 18, which is typical for the ‘clean air’ end-member ratio at the middle- and low-latitude stations in the North Atlantic.

are not understood. The ratio in the high latitudes tends to be relatively low (typically 2–6), whereas in the middle and low latitudes it is considerably higher, typically in the range 16–20. Fig. 6 shows a scatter plot of nss-SO<sub>4</sub><sup>2-</sup> concentration versus MSA for each sample collected from May through September of each of the years for which we have data (July 1991–May 1993); samples taken during the months June and July 1992 (i.e. when oceanic productivity was particularly high) are coded. During June and July, most of the sample ratios fall into the range 2–6; these low ratios, coupled with the high productivity, suggest that nss-SO<sub>4</sub><sup>2-</sup> is derived largely from biogenic sources in the Icelandic region during the summer months.

As previously stated, the incursion of pollutant nss-SO<sub>4</sub><sup>2-</sup> is reflected in very sharp concentration increases. The anomalous nature of these nss-SO<sub>4</sub><sup>2-</sup> episodes is reflected in a sharp increase in the nss-SO<sub>4</sub><sup>2-</sup>/MSA ratio and coupled with the concurrent increase of both aerosol nss-SO<sub>4</sub><sup>2-</sup>

and  $\text{NO}_3^-$ . The effects of the incursion of polluted air masses on the  $\text{nss-SO}_4^{2-}/\text{MSA}$  ratio can be seen in Fig. 6 where many of the samples have  $\text{nss-SO}_4^{2-}/\text{MSA}$  ratios that are much higher than either the high-latitude summer ratio (2–6) or the mid-low-latitude ratio (16–20).

### 3.3. Ammonium

There is considerable interest in the sources of ammonia in the marine atmosphere because it is the major acid neutralizing gaseous species in the atmosphere and, as such, it is tightly linked to the sulfate aerosol. At Heimaey, the  $\text{NH}_4^+$  concentration shows a very strong seasonal cycle (Fig. 2) similar to that for MSA. It differs, however, in a number of respects. First, the ratio of summer-to-winter  $\text{NH}_4^+$  concentrations is not nearly so great as that for MSA. Second, the strong increase in  $\text{NH}_4^+$  concentrations begins in early spring, much earlier than for MSA. There are clear signs in the MSA data, however, that concentrations do begin to increase significantly in the spring at about the same time as they do for  $\text{NH}_4^+$ ; the MSA levels, though, remain relatively low until summer. None the less, the similarities between the seasonal concentration patterns for these two species suggest that  $\text{NH}_4^+$  may have a substantial oceanic source. Similarly strong correlations among the seasonal patterns of  $\text{nss-SO}_4^{2-}$ , MSA, and  $\text{NH}_4^+$  are observed in aerosol data from sampling stations on the coast of Antarctica (Prospero et al., 1991; Savoie et al. 1992, 1993).

The  $\text{NH}_4^+$  data must be viewed with caution, however. Heimaey is the nesting ground for huge colonies of sea birds. Thus, we are concerned that the local soils might serve as a source of  $\text{NH}_3$  that could subsequently be captured on our filters through reaction with acid species (primarily  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$ ). However, if the soils were to serve as a source, we would expect to see some relation to temperature. The temperature record (Figs. 2 and 5) does not show any obvious relationship. Note, for example, that the  $\text{NH}_4^+$  concentration increases sharply in mid-March 1992. In contrast, the temperature during March 1992 remains relatively low for the entire month and into April.

### 3.4. Sodium

The  $\text{Na}^+$  concentrations (Fig. 2) show a distinct seasonal pattern with maximum concentrations in the winter and minimum concentrations in the summer. This pattern is clearly related to the seasonal variation in wind speed and to the strong winds associated with storms.

## 4. Conclusions

About 90% of the aerosol samples at Heimaey yielded concentrations of  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$  that were comparable to values obtained in relatively remote ocean regions such as the South Pacific. However, about 10% of the sample set yielded much higher concentrations; the synoptic meteorological conditions in effect prior to and during the largest of these aerosol events suggest that these aerosols (or their precursors) were derived from sources in Europe. If the  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$  in these events are indeed attributable to pollution sources, then about half the  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$  aerosol mass in the Iceland region has an anthropogenic origin. Moreover, there may be a substantial anthropogenic fraction in the other 90% of the sample set as well. The fact that we observe such high concentrations of pollution-derived  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$  suggests that significant concentrations of other pollutants (e.g. trace metals and organic materials) might also be present in these air parcels.

The natural  $\text{nss-SO}_4^{2-}$  aerosol component is also of great interest because of the possible linkage to the prolific biological DMS sources in the waters surrounding Iceland. Over the longer term it will be interesting to see if the temporal variability of MSA and  $\text{nss-SO}_4^{2-}$  on Iceland can be related to variations in regional productivity and especially the relationship to *Phaeocystis pouchetii* and *Emiliania huxleyi*. Because of its location near the oceanic polar front, the hydrographic environment of the Iceland region is determined by the relative contributions of three water types: relatively warm, nutrient-rich North Atlantic waters, cold, low-salinity polar waters, and arctic waters. Consequently, the hydrography is very sensitive to meteorological forcing. Ad-

vected Atlantic waters provide an important source of nutrients, both directly (due to high loadings) and indirectly (because of the much more efficient renewal of surface waters by vertical mixing in the Atlantic waters compared to the highly stratified polar or arctic waters). The extensive data record for these waters shows that the distributions of  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$  and  $\text{SiO}_4^{3-}$  are closely linked to these factors (Stefánsson and Olafsson, 1991). Over the 25 years of record, variations in nutrient concentrations could be associated with intense blooms of *Phaeocystis pouchetii*. Thus, with a few more years of data, it might be possible to link  $\text{nss-SO}_4^{2-}$  aerosol concentrations in the Icelandic region to *Phaeocystis* distributions and to the hydrological factors that control them. In this way, we might be able to establish a more direct quantitative linkage between oceanic sources of DMS and aerosol composition and physical properties and, hence, the biological link to climate.

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