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VARIATION OF CONCENTRATIONS OF SULFATE, METHANESULFONATE AND SULFUR DIOXIDE AT NY-ÅLESUND IN 1995/96 WINTER

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Abstract: Atmospheric aerosol particles and sulfur dioxides were collected at Ny-Ålesund (78°55′N, 11°56′E) in the winter of 1995/96. The concentrations of water soluble constituents of aerosol particles and gaseous acidic compounds were determined with ion chromatography. High concentrations of sea salts and methanesulfonate were found under warm and humid storm conditions, whereas non sea salt (nss)-SO_4^{2-} and SO_2 showed high concentrations in cold and dry Arctic air masses. Variation of nss-SO_4^{2-} concentrations in mid-December coincided with the variation of SO_2 concentration, but the increase of nss-SO_4^{2-} concentration in early-February lagged behind increase of SO_2 concentration. We discuss this time-lag variation using a simple box model.

1. Introduction

In the Arctic in winter and spring, atmospheric pollutants (*e.g.* SO_2, nss-SO_4^{2-}, soot, heavy metals and organic matter) are transported from industrial regions at mid-latitudes (RAHN *et al.*, 1980; BARRIE and HOFF, 1984; HEITZENBERG and LECK, 1994; PACYNA, 1993). Due to less wet deposition in the Arctic winter, the residence time of the particulate pollutants is expected to be longer than that in mid-latitudes. A major water-soluble constituent of the particulate pollutants in the Arctic winter is non-sea-salt (nss)-SO_4^{2-}, which is mainly produced through the oxidation of SO_2 transported from industrial regions at mid-latitudes. Simultaneous measurements of nss-SO_4^{2-} and SO_2 in the Arctic winter have provided an insight into gas-to-particle conversion in the sulfur-polluted polar night (HEITZENBERG and LARSSEN, 1983; BARRIE and HOFF, 1984; BARRIE *et al.*, 1994). According to observations at Alert, Canadian high Arctic (BARRIE and HOFF, 1984), the SO_2 oxidation rate was lowest ($\approx$0.04%/h) in mid-winter due to low temperature and less solar radiation, and high in spring (during the polar sunrise period). SHAW (1984) suggested a possibility of new particle formation through SO_2 oxidation during long-range transport. Some previous work in the Arctic in winter and spring (HEITZENBERG *et al.*, 1981; BARRIE and BARRIE, 1990) suggested that nss-SO_4^{2-} exists in a partly acidic state. Due to the long residence time of aerosol particles in winter and spring Arctic, new and/or aged aerosol particles containing nss-SO_4^{2-} would be internally mixed with other types of aerosol particles such as sea salt particles and soot through chemical and physical processes. Thus particles containing acidic nss-SO_4^{2-} cause the modification of other aerosol particles (*e.g.* Cl-depletion of sea salt particles). However, simultaneous measurements of nss-SO_4^{2-} and SO_2 (HEITZENBERG and LARSSEN, 1983; BARRIE and HOFF, 1984; BARRIE *et al.*, 1994) have not had the time resolution needed to consider daily-scale time variation. Most studies on the conversion rate and processes from SO_2 to nss-SO_4^{2-} have been based on laboratory measurements (MARTIN and DAMSCHEN, 1981; MAAHS, 1983; DLUGI and GÜSTEN, 1983; IBUSUKI and TAKEUCHI, 1987). Hence, we do not have sufficient knowledge of about gas-to-particle conversion and modification of aerosol particles in the actual winter Arctic atmosphere. This study aims to obtain more knowledge about the conversion from SO_2 to nss-SO_4^{2-} and modification of aerosol particles in the winter Arctic in relation to weather conditions.

2. Sample and Analysis

Aerosol particles and acidic gases were collected from 15 December, 1995 until 20 February, 1996 at Ny-Ålesund (78°55′N, 11°56′E), Spitsbergen, Norway. Figure 1 shows the location of Ny-Ålesund. The sampling station was about 1.5 km away from the village of Ny-Ålesund. Aerosol particles were collected on pre-cleaned Cu-plates with a 2-stage impactor (cut-off diameter, 2.3 μm and 0.2 μm) and Teflon membrane back-up filter (Millipore, omnipore filter, pore size 0.2 μm ϕ) at flow rate of 1.1 L/min for 3 days.

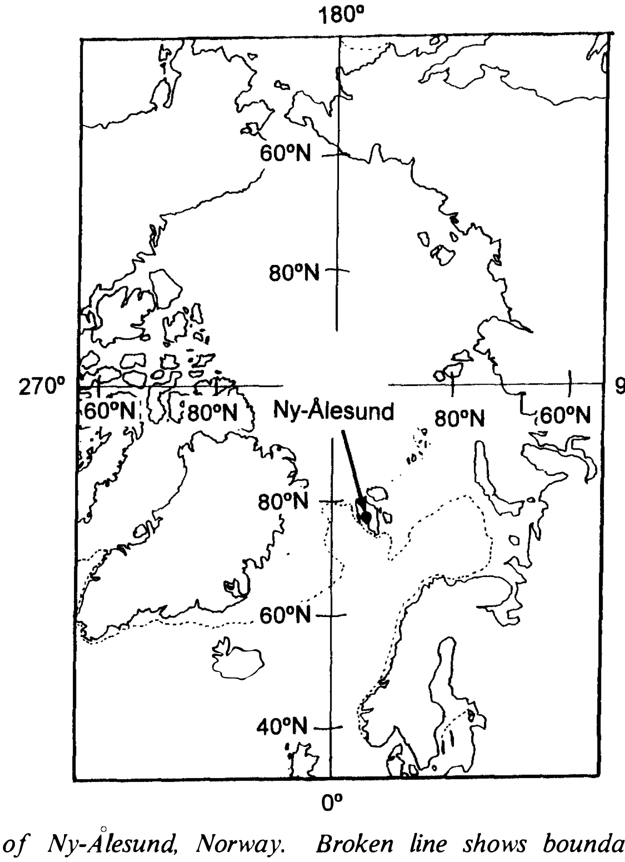

Fig. 1. Location of Ny-Ålesund, Norway. Broken line shows boundary of open water in March (PARKINSON and GLOERSEN, 1993).

Daily sampling of acidic gases was carried out at a flow rate of 5 L/min on alkaline impregnated filters (1% Na_2CO_3 and 1% Glycerol) with Teflon membrane prefilter (Pallflex products, TK-15,) for removing particulate matter. After sampling, the Cu-plates and filters were kept into polypropylene 15 m*l* centrifuge vials with an airtight cap in order to prevent contamination until analysis. Sample vials were packed in polyethylene bags and were kept at about −20°C in a freezer until chemical analysis.

For extraction of water soluble constituents in aerosol particles, 14 m*l* of ultra-pure water (18 MΩ, Milli-Q water) was added to each sample vial, then sample vials were treated about 5 min in an ultrasonic bath. Concentrations of water soluble constituents of aerosol particles were measured by an ion chromatograph (Dionex, DX-300) using a 500 μl injection loop for each flow system equipped with an AS11A analytical column and an AG11 guard column for anion separation, and a CS12 analytical column and CG12 guard column for cation separation. Samples for procedural blanks on the sampling site underwent the same procedure for actual samples but without the passage of air. Procedural blank levels of most ionic species extracted from the Cu-plate were below detection limits but some ion species were detectable for Cl^- 0.1 nmol/m^3 as converted to atmospheric concentrations using a typical sampling air volume (3.4 m^3). Also, procedural blank levels of some ionic species extracted from back-up filters were below detection limits, but some ion species were detectable for Na^+ 1.1 nmol/m^3, and Cl^- 1.4 nmol/m^3 as converted to atmospheric concentrations using a typical sampling air volume (3.4 m^3).

Ultra-pure water (10 m*l*) and 3% H_2O_2 solution (0.3 m*l*) was added to samples of alkaline impregnated filters for extraction of acidic gaseous components on the filter. Concentrations of acidic gaseous components were measured by an ion chromatograph (TOA, ICA-5000) using a 100 μl injection loop equipped with an AS12A analytical column, an AG12A guard column and an autosuppression system (ASRS-I, all columns are manufactured by Dionex). Procedural blank levels of each acidic gas were SO_2 0.2 nmol/m^3, HCl 5.9 nmol/m^3, HNO_2 1.1 nmol/m^3, and HNO_3 1.7 nmol/m^3 as converted to atmospheric concentrations using a typical sampling air volume (2.6 m^3).

3. Results and Discussion

Figure 2 shows the variations of (a) air temperature and relative humidity (HANSSEN-BAUER, personal communication), (b) Na^+ concentration in the coarse particle fraction (> 2.3 μm), (c) Cl^- concentration in the coarse particle fraction, (d) Na^+ concentration in the fine particle fraction (2.3-0.2 μm), (e) Cl^- concentration in the fine particle fraction, and (f) molar ratio of Na^+ concentration in the coarse particle fraction to that in fine particle fraction. Na^+ and Cl^- were mostly found in the coarse particle fraction, less in the fine particle fraction. The concentrations of Na^+ and Cl^- were high in mid-January and early-February when concentrations of SO_2 and nss-SO_4^{2-} were low during precipitation events. The mean molar ratio of Cl^- to Na^+ in the coarse particle fraction was about 1.2, similar to the molar ratio ($\approx$1.2) in sea water (WILSON, 1975), so that Na^+ and Cl^- in the coarse particle fraction can be derived from sea salts. Increases of Na^+ and Cl^- concentrations in coarse particle fraction were coincident with cyclonic storm conditions of high temperature and high relative humidity. As shown in Fig. 1, the position of the sea ice margin in March was located just south of Spitsbergen (PARKINSON and GLOERSEN, 1993).

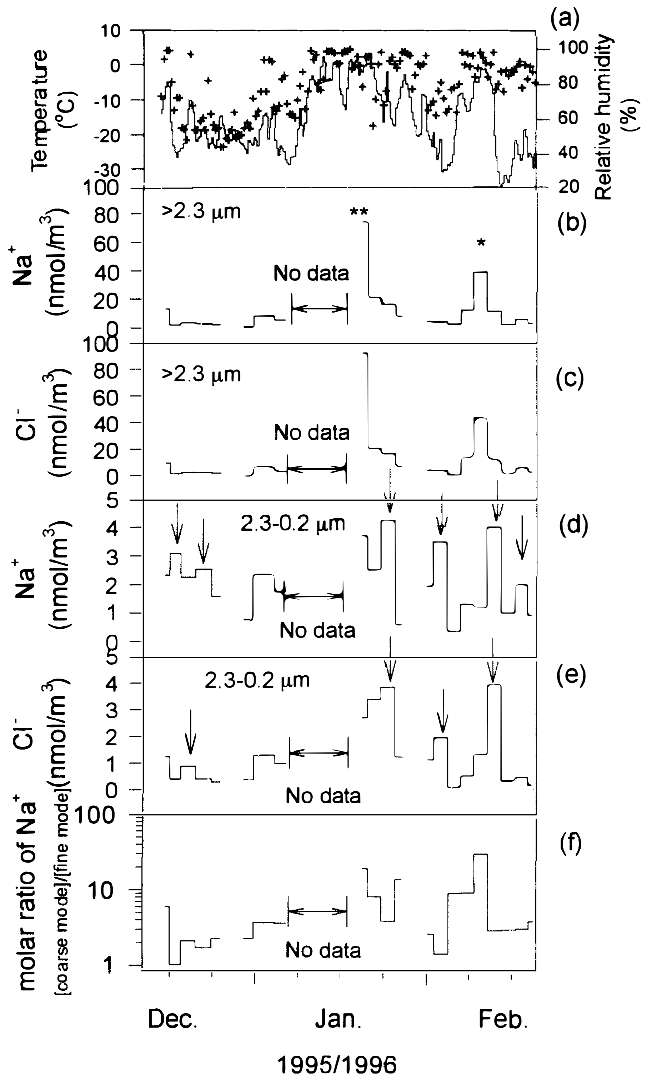

Fig. 2. Variations of (a) air temperature (—) and relative humidity (+), Na^+ and Cl^- concentrations in coarse particle (b and c), fine particle fractions (d and e) and (f) molar ratio of Na^+ in coarse particle fraction to fine particle fraction. Asterisks (∗) indicate storm conditions.

Hence, a fresh oceanic air mass containing a large amount of coarse sea salt particles would be transported from southern open oceanic region to Ny-Ålesund through storm access.

As marked by arrows in Figs. 2d and e, concentrations of Na^+ and Cl^- in the fine particle fraction (2.3-0.2 μm), however, increased in spite of no- or minor increase in the coarse-fraction (>2.3 μm) and no storm conditions. In Fig. 2f, relatively high molar ratios of Na^+ concentration in the coarse fraction to that in the fine fraction were found in mid-January and early February under storm conditions, but relatively low molar ratios were found during the periods marked by arrows in Figs. 2d and e. Preferential removal of coarse sea salt particles through wet deposition and/or dry deposition during transport would cause the relative increase of concentration of Na^+ and Cl^- in the fine particle fraction (2.3-0.2 μm) with no- or minor increase in the coarse-fraction (>2.3 μm), because the dry and wet deposition coefficients in the coarse particle fraction were much larger than those in the fine particle fraction (Warneck, 1988). Hence, aged oceanic air masses containing a smaller amount of coarse sea salt particles would be transported during the non-storm periods marked by arrows in Figs. 2d and e.

Figure 3 shows the variations of concentrations of $CH_3SO_3^-$ in coarse particles and the back up fraction. Methanesulfonate was mainly found in the back-up fraction (<0.2 μm). Small amounts of $CH_3SO_3^-$ were found in the coarse particle fraction (>2.3 μm) only between mid-January and early February with high concentrations of Na^+ and Cl^-. No $CH_3SO_3^-$ was detected from the fine particle fraction (2.3-0.2 μm) for all samples. This unique short-term variation of $CH_3SO_3^-$ concentration suggests that $CH_3SO_3^-$ exists only in oceanic air. This is probably related to the origin and formation of $CH_3SO_3^-$ in air. Methanesulfonate is produced through photooxidation of dimethylsulfide (DMS) released from marine phytoplankton (Hatakeyama *et al.*, 1985). Concentrations of DMS and $CH_3SO_3^-$ in the marine atmosphere showed minimum in the polar winter (Bates *et al.*, 1992; Leck *et al.*, 1990; Turner *et al.*, 1989; Li and Barrie, 1993; Li *et al.*, 1993; Savoie *et al.*, 1993; Jaffrezo *et al.*, 1994). Moreover, the photooxidation ability was very low in the dark Arctic winter (Barrie and Hoff, 1984). Thus, most $CH_3SO_3^-$ may not be produced in the dark Arctic winter. It is likely that $CH_3SO_3^-$ is transported from the middle latitudes where there are emission sources of DMS and higher photooxidation abilities than in the dark winter Arctic.

Methanesulfonate in the coarse particle fraction was found twice during this study period. Similar results were often observed in samples from the marine boundary layer (Pszenny *et al.*, 1989; Quinn *et al.*, 1993; Putaud *et al.*, 1993; Huebert *et al.*, 1996). Since the concentration of $CH_3SO_3^-$ was highest in the back-up fraction, $CH_3SO_3^-$ in the coarse particle fraction would be caused by coagulation of fine-Aitken particles containing $CH_3SO_3^-$ and condensation of CH_3SO_3H vapor to coarse particles such as sea salt particles.

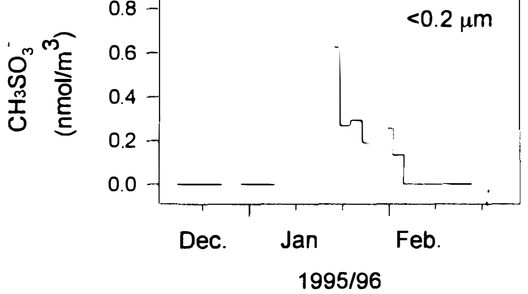

Fig. 3. Variations of $CH_3SO_3^-$ concentration in (a) coarse particle fraction and (b) back-up fraction. Asterisks (*) indicate storm conditions.

Previous studies of compositions in individual marine aerosol particles, collected in Antarctica (Wouters *et al.*, 1990; Hara *et al.*, 1996) and the south Bahamas (Kolaitis *et al.*, 1989) suggest that sodium methanesulfonate ($NaCH_3SO_3$) would be a product of the

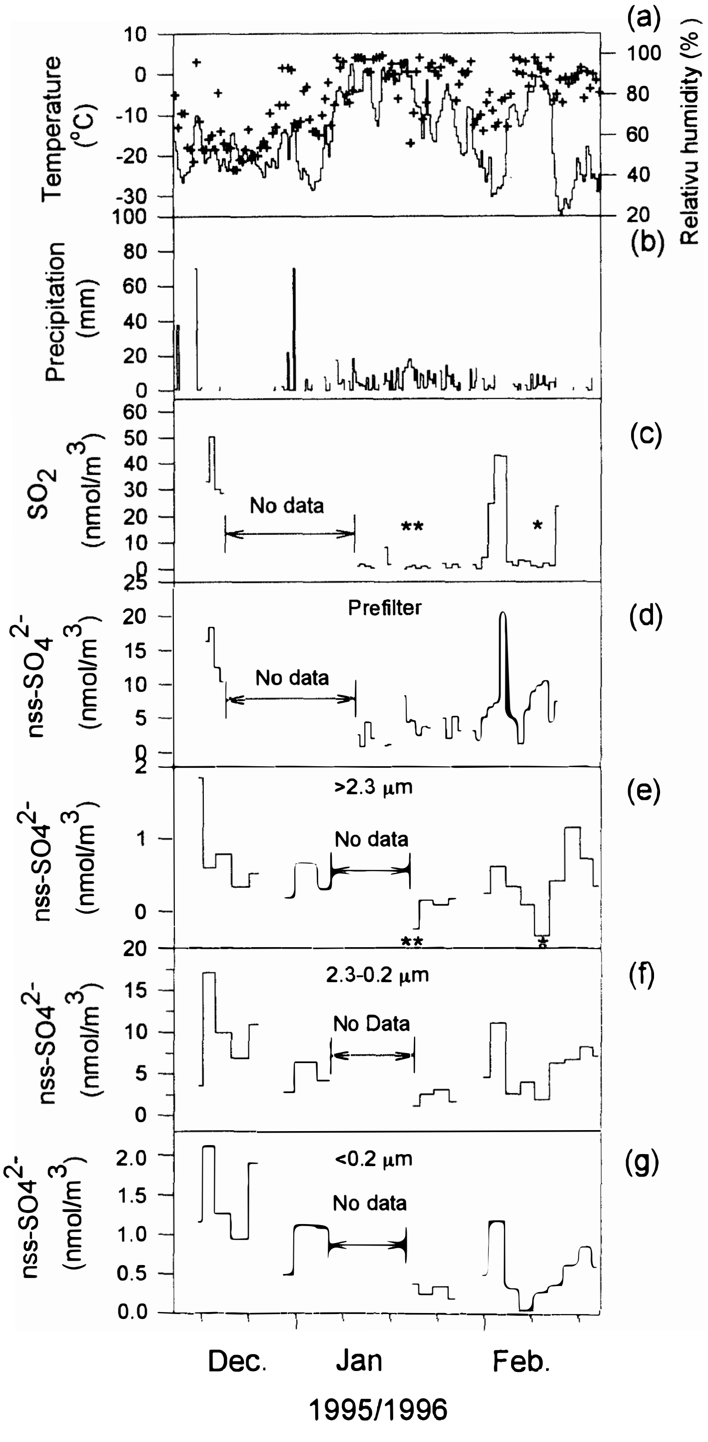

Fig. 4. *Variations of temperature (—) and relative humidity (+), (b) precipitation, (c)* SO_2 *concentration,* nss-SO_4^{2-} *concentration in (d) prefilter, (e) coarse particles, (f) fine particle and (g) back-up filter. Asterisks (*) indicate storm conditions.*

following reaction

$$NaCl + CH_3SO_3H \rightarrow NaCH_3SO_3 + HCl(\uparrow).$$

Therefore, part of the $CH_3SO_3^-$ in the coarse particle fraction may be identified as sodium $NaCH_3SO_3$ formed by modification of sea salt particles.

Figure 4 shows the variations of (a) air temperature and relative humidity (HANSSEN-BAUER, personal communication), (b) precipitation events, (c) SO_2 concentration, concentration of nss-SO_4^{2-} (d) in the prefilter, (e) in the coarse fraction ($>2.3\ \mu$m), (f) in the fine fraction (2.3–0.2 μm) and (g) in the back-up fraction ($<0.2\ \mu$m). Measurable acidic gas in this study period was solely SO_2. The concentration of nss-SO_4^{2-} was calculated from the concentration of Na^+ in the sample and equivalent ratio of SO_4^{2-}/Na^+ (0.12) in sea water (WILSON, 1975). The concentrations of SO_2 and nss-SO_4^{2-} were lower under rain and snow conditions in mid-January. This variation would be caused by efficient removal of aerosol particles and acidic gases by precipitation and transport of oceanic air with low pollutant concentrations. The concentrations of nss-SO_4^{2-} and SO_2 showed maxima during clear, dry and colder days in mid-December and early February. The variation of SO_2 concentration was similar to that of nss-SO_4^{2-} concentrations in all size fractions.

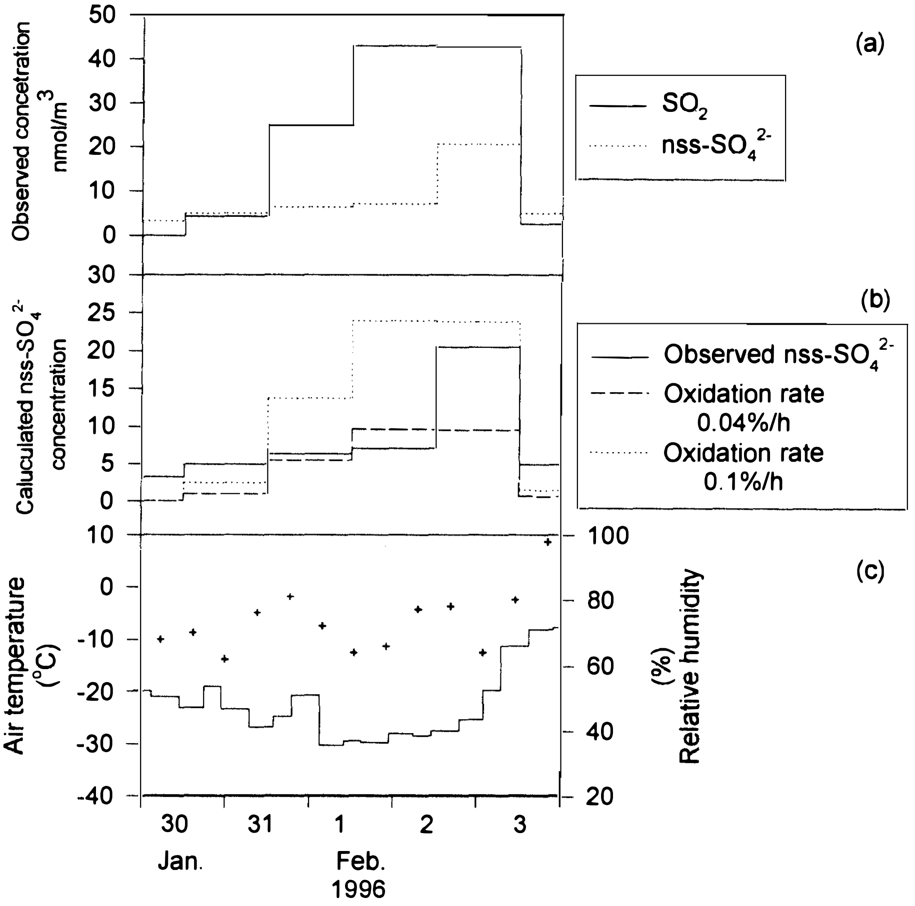

Fig. 5. Short-term variations of (a) SO_2 and nss-SO_4^{2-} concentrations, (b) calculated nss-SO_4^{2-} concentrations and (c) air temperature (—) and relative humidity (+).

The concentrations of nss-SO_4^{2-} showed a remarkable increase of about 8–13 nmol/m^3 in fine particle mode (2.3–0.2 μm) and several nmol/m^3 in back up-mode (<0.2 μm) in mid-December and early February. Although the variation of nss-SO_4^{2-} concentration in mid-December coincided with the variation of SO_2 concentration, the increase of nss-SO_4^{2-} concentration in early February lagged behind the increase of SO_2 concentration, as shown in Fig. 5a. This time lag of 2 days was not observed for other elevated events in mid-December. This time lag would be caused by mixing of air masses or variation of SO_2 oxidation rate to particulate nss-SO_4^{2-}.

Figure 5 shows short term variations of (a) the observed concentrations of SO_2 and nss-SO_4^{2-}, (b) the nss-SO_4^{2-} concentrations calculated by the same simple box model as described in BARRIE and HOFF (1984), and (c) air temperature and relative humidity (HANSSEN-BAUER, personal communication) between 30 January and 3 February. Parameters in this model were the dry deposition velocities of particulate and gaseous sulfur, oxidation rate of SO_2 and the height of the mixing layer. Concentrations of nss-SO_4^{2-} were estimated using the following equation:

$$\frac{d[\text{nss-SO}_4^{2-}]}{dt} = k[\text{SO}_2] - \frac{V_p}{H}[\text{nss-SO}_4^{2-}],$$

k: oxidation rate,
V_p: dry deposition velocity of particulate sulfur,
H: height of mixing layer.

The dry deposition velocity (V_p) of nss-SO_4^{2-} is less than 0.05 cm/s in the winter Arctic (IBRAHIM, 1983). The value of V_p is fixed at 0.05 cm/s in this study. Because there were no precipitation events between 30 January and 3 February, precipitation scavenging is not included in this model as a first approximation. Also, the contribution of biogenic sulfur species is neglected in this model, since previous works (LI and BARRIE, 1993; HEITZENBERG and LECK, 1994) suggest little contribution of biogenic sulfur species toward total nss-SO_4^{2-} in winter/spring Arctic. In fact, total $CH_3SO_3^-$ concentrations, 0.9 nmol/m^3 were far lower than the nss-SO_4^{2-} concentration, ~21.5 nmol/m^3, for this study.

The oxidation rate of SO_2 between 1 and 2 February ranged from 0.030%/h to 0.046%/h, whereas the oxidation rate on 3 February increased to 0.086%/h. The value of SO_2 oxidation rate on 3 February, 0.086%/h, was larger than the value estimated by BARRIE and HOFF (1984), ≈0.04%/h, in mid-winter of the Canadian high Arctic. Air temperature rose from -30°C to -10°C on 3 February, when concentrations of Na^+ and Cl^- in the fine particle fraction increased as shown in Figs. 2b and d. This suggests that aged oceanic air was transported to Ny-Ålesund in early February. Because fresh oceanic air masses containing high concentrations of Na^+ and Cl^- in coarse particle fractions show low SO_2 and nss-SO_4^{2-} concentrations, the high SO_2 and nss-SO_4^{2-} concentrations on February 3 would not be derived from fresh oceanic air masses. Also, the contribution of biogenic sulfur species to variation of nss-SO_4^{2-} concentration was low in the Arctic winter, as stated above. Thus, the mixing of oceanic air masses and the presence of biogenic sulfur compounds should make minor contributions to the time lag of increase of nss-SO_4^{2-} concentration.

As SO_2 is not photochemically oxidized in the dark Arctic winter, plausible oxidation reactions include liquid phase oxidation in cloud droplets with H_2O_2 (MARTIN and

DAMSCHEN, 1981) and oxidation by O_3 (MAAHS, 1983), heterogeneous oxidation in sea salt particles with O_3 (SIEVERING *et al.*, 1992), catalyzed oxidation by metallic ions (IBUSUKI and TAKEUCHI, 1987) and oxidation on fly ash (DLUGI and GÜSTEN, 1983). As the SO_2 oxidation rate through each process depends on reaction rate and solubility of SO_2, the overall oxidation rate of SO_2 would strongly depend on air temperature. According to observations at Alert, Canadian Arctic (BARRIE and HOFF, 1984), the oxidation rate of SO_2 in mid-winter (February) was about 0.04%/h. Although a sudden increase of air temperature occurred in early February, temperature dependence of the oxidation rate was not assumed in this model calculation. Hence, the difference on 3 February might have been caused by the temperature-dependence of the oxidation rate of SO_2.

After 3 February, air temperature increased to -5°C, then observed nss-SO_4^{2-} and SO_2 concentrations suddenly decreased to be less than 5 nmol/m^3. As relative humidity suddenly increased to 100% on 4 February during a precipitation event (see Figs. 4b and 5c), this decrease of nss-SO_4^{2-} and SO_2 concentrations is probably due to exchange of air masses and/or deposition by precipitation events (see Fig. 4b).

4. Conclusions

We have shown the concentration variation of water soluble constituents in atmospheric aerosol particles and SO_2 collected at Ny-Ålesund, Spitsbergen, Norway. A large amount of sea salt particles and a small amount of methanesulfonate were transported from the oceanic region to Ny-Ålesund through cyclonic storm activity. The variation of nss-SO_4^{2-} concentration coincided with that of SO_2 concentration in December. But a time lag of sudden increase of nss-SO_4^{2-} concentration behind gradual increase of SO_2 concentration was found in early February. This tendency could not be explained by only a simple box model of SO_2 oxidation.

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