

Vertical variations of sea-salt modification in the boundary layer of spring Arctic during the ASTAR 2000 campaign

By K. HARA^{1*}, K. OSADA², C. NISHITA², S. YAMAGATA³, T. YAMANOCUHI¹, A. HERBER⁴,
K. MATSUNAGA², Y. IWASAKA², M. NAGATANI⁵ and H. NAKATA⁵, ¹National Institute of Polar
Research, Japan; ²Division of Earth and Environmental Sciences, Graduate School of Environmental Studies,
Nagoya University, Japan; ³Graduate School of Engineering, Hokkaido University, Japan; ⁴Alfred Wegener
Institute, Germany; ⁵Solar Terrestrial Environment Laboratory, Nagoya University, Japan

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ABSTRACT

Airborne and ground-based aerosol/gas measurements were carried out in Svalbard between mid-March and mid-April 2000. From the viewpoint of vertical features of sea-salt modification in the lower troposphere (≤ 1500 m) of the Arctic spring, more than 1000 individual sea-salt particles were analyzed with scanning electron microscopy energy dispersive X-ray spectrometry (SEM-EDX) in the present study. Individual particle analysis suggested a vertical gradient of sea-salt modification in fine sea-salt particles with an altitude of 59–1485 m above sea level (asl), e.g. chlorine liberation rates of 33.0% (212 m asl) and 81.0% (1266 m asl) on 15 March, and 72.7% (100 m asl), 83.8% (495 m asl) and 95.8% (1411 m asl) on 26 March. Sea salts may be dominantly modified with SO_2 and SO_4^{2-} under Arctic haze conditions with higher SO_2 concentration ($\geq 2 \text{ nmol m}^{-3}$), whereas they are dominantly modified with NO_3^- and reactive nitrogen oxides under Arctic background conditions, with $[\text{HNO}_3]$ of 0.15–1.3 nmol m^{-3} and $[\text{SO}_2]$ of 0.04–2 nmol m^{-3} . Vertical trends in sea-salt modification suggested that it makes a significant contribution to the formation of reactive halogen species in the upper boundary layer and the lower free troposphere of the spring Arctic.

1. Introduction

Sea-salt particles are a major aerosol constituent in the lower troposphere, and play an important role in the formation of cloud condensation nuclei (CCN) (e.g., Hegg et al., 1992), and the sources of gaseous reactive halogen species such as HX, X, X_2 , XO, and HOX (X = Cl and Br) through the heterogeneous reactions in the marine boundary layer (Chameides and Stelson, 1992; Ayers et al., 1999). In particular, the heterogeneous reactions in sea-salt particles in polar regions are believed to make a significant contribution

to the sources of gaseous reactive halogen species, which have a close relationship to surface ozone depletion during the polar sunrise (Fan and Jacob, 1992; Michalowski et al., 2000; Hara et al., 2002a).

Surface ozone depletion is often observed during the polar sunrise in both the Arctic and Antarctic (e.g., Barrie et al., 1988; Murayama et al., 1992; Wessel et al., 1998; Langendörfer et al., 1999). Currently, it is believed that surface ozone depletion occurs via the BrO_x catalytic system ($\text{Br} \rightleftharpoons \text{BrO}$). According to field measurements (McElroy et al., 1999; Fitzenberger et al., 2000; Hara et al., 2002a), a higher BrO concentration and enrichment of particulate bromate (BrO_3^-) were suggested in the upper boundary layer (UBL) and lower free troposphere (LFT) of the winter/spring Arctic in spite of the fewer BrO free-tropospheric sources.

*Corresponding author.
e-mail: harakei@pmg.nipr.ac.jp

Thus, the higher concentrations and enrichment of bromine species in the LFT and the UBL are likely to be an outstanding issue in atmospheric halogen cycles relating to surface ozone depletion.

A model estimation by von Glasow and Sander (2001) suggested a vertical gradient (increasing) of halogen activation from sea-salt particles due to vertical gradients of air temperature, relative humidity, and pH in sea-salt particles in the boundary layer. Also, other investigators (Chameides and Stelson, 1992; Keene et al., 1998; Fridlind and Jacobson, 2000) indicated that pH may be critical in sea-salt aerosol aqueous chemistry in the boundary layer. When this vertical gradient of halogen activation (sea-salt modification) occurs efficiently in the marine boundary, more highly modified sea-salt particles should be observed in the UBL and LFT. Furthermore, the vertical features of sea-salt modification can impact on CCN formation, since a gradual change of chemical composition of the particles will alter their hygroscopic properties.

However, few field observations (Miura et al., 2000) have been made on profiles of sea-salt particles and their modification in the UBL and LFT because of sampling difficulties in the upper atmosphere, partic-

ularly in the polar regions. Information on the vertical profiles of sea-salt modification is important, since it will probably lead to a better understanding of atmospheric halogen cycles closely coupled to surface ozone depletion during the polar sunrise. In the present study, we report on our efforts to obtain this knowledge during the Actic Study of Tropospheric Aerosol and Radiation (ASTAR) campaign, which was carried out in 2000 around the Svalbard. Details of the ASTAR 2000 campaign were described in an overview paper (Yamanouchi et al., submitted to *J. Geophys. Res.*).

2. Sample and experiments

2.1. Airborne aerosol sampling

Airborne aerosol measurements were carried out on board an aircraft (Polar 4; Dornier 228) during the ASTAR 2000 campaign around Spitsbergen Svalbard, as shown in Fig. 1. The area around Ny-Ålesund (as an airborne measuring site) was mainly chosen because of concurrent ground-based aerosol/gas measurements at Ny-Ålesund in the same region. In the observation

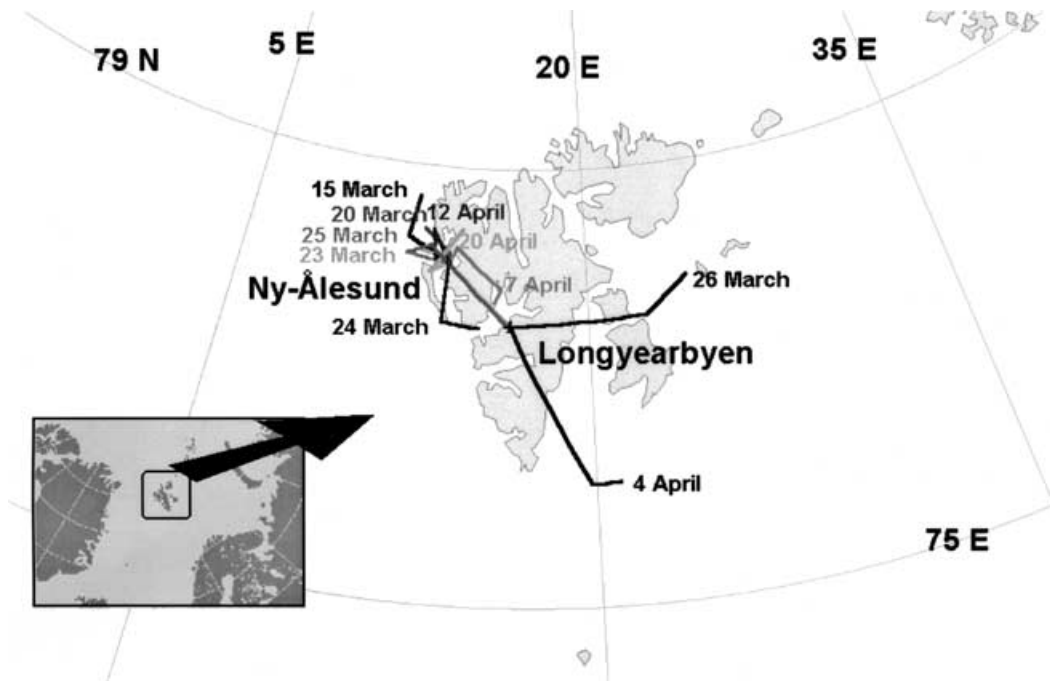


Fig. 1. The geographical locations of airborne aerosol measurements during the ASTAR 2000.

area, Polar 4 followed an ascending flight pattern with several level flights from <50 to >7000 m above sea level (asl).

All instruments for aerosol observation were mounted in the interior of Polar 4. The sample air was taken in through an inlet pipe (inlet edge ≈ 15 mm) on the upper fuselage. Sampled air was introduced through the tube (internal diameter ≈ 25 mm) into a manifold in the cabin. Subsequently, sampled air was distributed into each individual instrument. Although the losses of aerosol particles of diameter $>2 \mu\text{m}$ will be significant in intake and inlet tubes, losses of fine aerosol particles ($<2\text{--}0.2 \mu\text{m}$ in diameter) can be neglected, as shown by Hermann et al. (2001). Thus, the modification of fine (0.2–2.0 μm) sea-salt particles will mainly be discussed in the present study.

Aerosol particles in airborne observations were collected using an Aerosol Impactor Sonde (AIS), developed in our laboratory for direct aerosol sampling during large-scale balloon-borne observations. It has a single-stage impactor with a 2.0 mm jet nozzle and a cut-off diameter of $\approx 0.2 \mu\text{m}$ at a flow rate of 22 L min^{-1} . During the airborne observation, AIS sampling was started manually just before achieving the lowest altitude (≈ 50 m asl). During the aerosol measurements, aerosol particles were collected on various chemical thin films (carbon-coated, BaCl_2 -coated, Ca-coated and nitron-coated collodion thin films) every 5 or 3 min during the observation. The sampling time (3–5 min) is probably too short to cause a significant sampling artifact such as reactions with gaseous species and volatilization in ambient air conditions. Collected aerosol samples were kept into polyethylene capsules after landing. The polyethylene capsules containing aerosol samples were packed into polyethylene bags with a zipper. All bags with aerosol samples put into an airtight box with silica gels until the observation by means of scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX) in order to prevent humidification that can lead to a morphology change and efficient chemical reactions. Aerosol samples taken on carbon-coated collodion thin films in the lower troposphere (≤ 1500 m) were used in the present study because of the low background from carbon-coated thin films in chemical analysis by EDX. In the high vacuum environment of SEM-EDX ($\sim 10^{-6}$ Torr), it is impossible to observe the ambient aerosol particles exactly in the atmosphere. Although the stain of the liquid phase in aerosol particles (e.g., sea-salt particles) in the winter/spring Arctic boundary layer were often observed by

SEM-EDX measurements (Hara et al., 1999), a significant fraction of the liquid phase must be lost owing to a high vacuum in the SEM chamber. Fortunately, however, Sheridan et al. (1993) pointed out that the detectable X-ray signature of aerosol constituents (e.g., S, O, N) was insignificantly affected by water volatilization under the vacuum conditions of SEM-EDX. Furthermore, Pardess et al. (1992) also indicated that evaporation of aerosol constituents was negligible during the exposure of the electron beam under the analytical conditions of 15–25 kV accelerating voltage and 100 s counting time. Considering our analytical conditions with 20 kV accelerating voltage and 30 s counting time, an analytical artifact for species of interest is probably negligible in the present study.

2.2. Analysis of aerosol particles taken from airborne sampling

Before SEM-EDX observations, post-carbon coating was treated on aerosol samples to reduce sample damage and discharge by the electron beam. Individual sea-salt particles were observed and analyzed with scanning electron microscopy (SEM-EDX; S-3000N, Hitachi) and EDX (EMAX-500, Horiba) equipped with an ultra-thin window detector (S-798, Horiba). EDX spectra were obtained at an acceleration voltage of 20 kV and a counting time of 30 s. Although the EDX used in the present study was able to detect light elements such as C, N, and O, high EDX background peaks from the collodion thin film used as sampling substrate rendered the analytical uncertain. We therefore exclude them from further discussion.

Although typically we attempted to analyze >50 particles per sample (total >1000 particles) with EDX, on the 4 April flight, only ca. 20 particles could be analyzed owing to the lower concentration of sea-salt particles. Sea-salt particles and modified sea-salt particles were identified by Na detection. However, some Na also originated from non-sea-salt (nss-) sources such as crustal and anthropogenic sources. In fact, a few (ca. 20% of the total; several percent on average) mineral/dust particles were observed in the LFT and UBL during the ASTAR 2000 campaign (Hara et al., submitted to *J. Geophys. Res.*). When mineral/dust particles are internally mixed with sea-salt particles, the presence of nss-Na can lead to an over-estimation of Cl^- depletion from sea-salt particles. Thus, internal mixtures of sea-salt and mineral/dust, which were identified by Na detection together with Al, Si, and/or

Fe, were excluded in our discussion on sea-salt modification. The internal mixing of sea salts and mineral/dusts (excluding sea-salt particles) was less than 1% of aerosol particles containing Na in the present study. Furthermore, to check analytical error and sensitivity, artificial particles of NaCl, Na₂SO₄ and mixtures of both were prepared and analyzed using EDX according to our standard procedure (a micro-grid with a collodion thin film).

2.3. Ground-based aerosol sampling in Ny-Ålesund

Ground-based sampling of aerosol particles and acidic gases was also carried out at Ny-Ålesund, Svalbard (78°55'N, 11°56'E) from early January until the end of April in 2000. Non-size-segregated aerosol particles and acidic gases were collected using a filter holder (NILU) with a 47 mm Teflon membrane filter with 1.0 μm pore size (PTFE, Advantec) in series with two-stage alkaline (1 wt% Na₂CO₃ + glycerol) impregnated filters for one day (March) and half a day (April) at a flow rate of 18 L min⁻¹. For aerosol sampling at ambient temperature the filter holders were mounted facing downward in weather shields to protect them from snow blowing at a height of 5 m from the snow surface because of the reduced volatility of thermal unstable species like ammonium nitrate. A plastic pipe (internal diameter ≈ 120 mm, length ≈ 600 mm) was used as a weather shield for protection from precipitation (mainly snow), so that the weather shield itself makes probably an insignificant sampling artifact (mainly particle loss) in our estimation. The inlet of the NILU filter holder (ca. 10 mm in diameter) can lead to a sampling artifact (a decreasing sampling efficiency of; >10–20% depending on wind velocity) in aerosol particles <5 μm in diameter under our sampling conditions. According to Barrie et al. (1994), the concentrations obtained by a filter-sampling system similar to the system and procedures (including measured gaseous and particulate species) in the present study were in good agreement with those obtained by the denuder system, which is generally believed to have a lower sampling artifact, in the winter/spring Arctic. Therefore, our system also did not have a significant sampling artifact in particulate and gaseous samples by the filter system. After sampling, each filter was immediately placed in an airtight centrifuge vial (15 mL) in order to prevent contamination during the sample storage. The vials were packed in polyethylene bags and were kept at about -20 °C in a freezer until chemical analysis in Japan. For a quantitative check

of the atmospheric samples, procedural blank samples were taken from each sampler periodically.

2.4. Analyses of aerosol and acidic gas samples taken in ground base sampling in Ny-Ålesund

For extraction of water-soluble constituents in aerosol particles, 14 mL of ultra-pure water (18.3 MΩ, Milli-Q water) were added to each sample vial. The concentrations of water-soluble constituents were determined with an ion chromatograph (Dionex, DX-300; injection loop 500 μL). Analytical and guard columns were as follows: anion separation AS11A, AG11; cation separation CS12, CG12. For the extraction of acidic gaseous species, ultra-pure water (10 mL; 18.3 MΩ, Milli-Q water) and H₂O₂ solution (3%; 300 μL) were added to each sample vial. Concentrations of acidic gases were measured with an ion chromatograph (TOA, ICA-5000) equipped with an AS12A analytical column and an AG12A guard column (Dionex). The injection loop (500 μL) was equipped with an autosuppression system (ASRS-I, all columns and equipment are manufactured by Dionex). Atmospheric concentrations of each species were corrected using procedural blank levels.

Backward and forward trajectory analysis was calculated using a vertical motion mode in the HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model, 1997 (Web address: <http://www.arl.noaa.gov/ready/hysplit4.html>, NOAA Air Resources Laboratory, Silver Spring, MD).

3. Results and discussion

3.1. Air quality in the boundary layer during the ASTAR 2000 campaign

In order to monitor air quality in the boundary layer during the ASTAR 2000 campaign, aerosol particles and acidic gases were simultaneously observed at the ground observatory (≈40 m asl) in Ny-Ålesund. Figure 2 shows the variations of major aerosol constituents (Na⁺, non-sea-salt SO₄²⁻, and NO₃⁻) and acidic gases (SO₂, HNO₃ and gaseous inorganic chlorine species, g Cl) from 15 March until 21 April 2000. Non-sea-salt (nss-) SO₄²⁻ concentration was estimated using the seawater ratio (Wilson, 1975) by the following equations;

$$\begin{aligned} [\text{nss-SO}_4^{2-}] &= [\text{SO}_4^{2-}] - [\text{sea salt (ss-) SO}_4^{2-}] \\ &= [\text{SO}_4^{2-}] - 0.18 \times [\text{Na}^+]. \end{aligned}$$

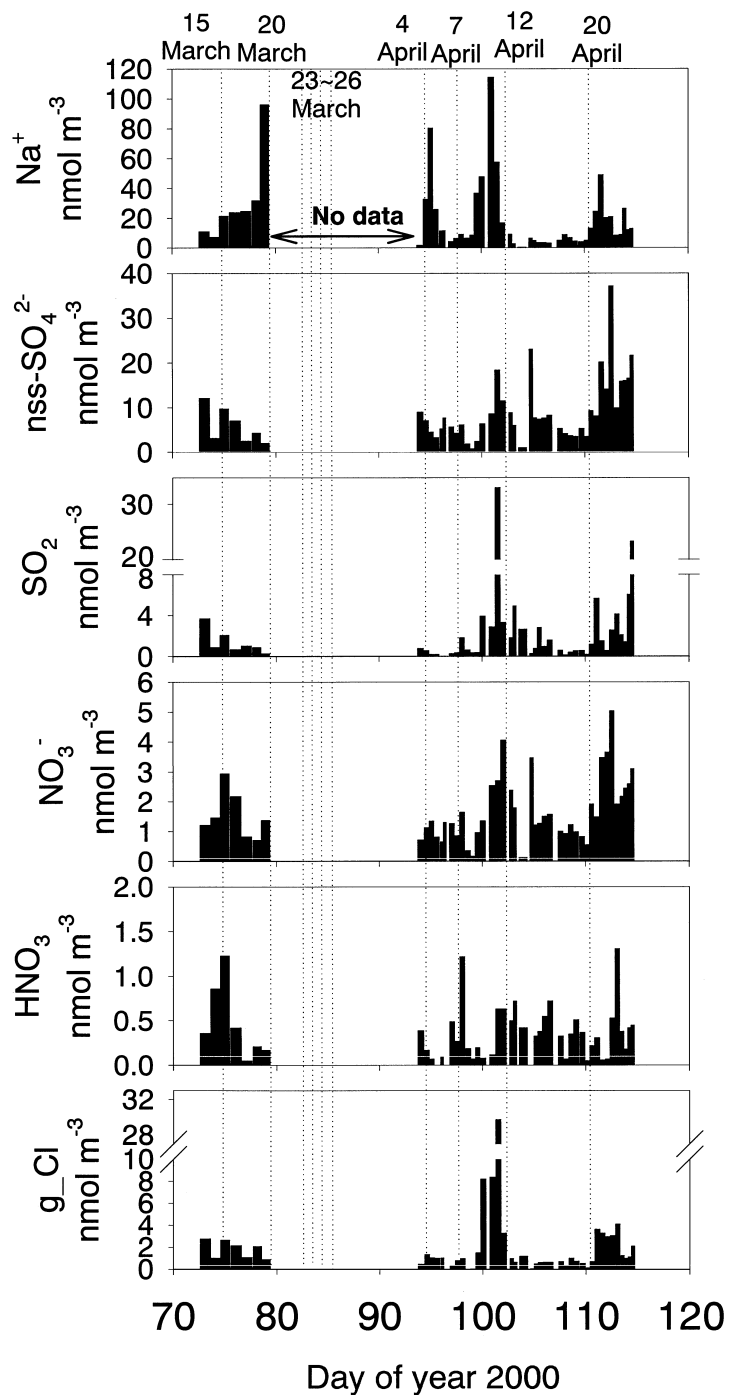


Fig. 2. Variations of major aerosol constituents (Na^+ , nss-SO_4^{2-} , and NO_3^-) and acidic gases (SO_2 and HNO_3 and inorganic gaseous chlorine (g_Cl)) on ground level in Ny-Ålesund during the ASTAR 2000 campaign. Broken and white lines indicated the periods of airborne measurements and blank levels, respectively.

Higher concentrations of Na^+ , nss-SO_4^{2-} and SO_2 due to transport of oceanic and polluted air masses were often observed during the ASTAR 2000 campaign. Also, mixing of both air masses (high Na^+ associated with high SO_2 and nss-SO_4^{2-}) was observed in $\text{DOY} \approx 102$. As shown in Fig. 2, however, airborne aerosol sampling was carried out both under the relative cleaner conditions with higher Na^+ and lower pollutant concentrations (nss-SO_4^{2-} and SO_2), and under the polluted conditions with higher nss-SO_4^{2-} and SO_2 concentrations. In addition, nss-SO_4^{2-} , SO_2 , NO_3^- and gaseous HNO_3 were identified as major atmospheric acidic species in the boundary layer of the spring Arctic. Although particulate oxalate, $(\text{COO}^-)_2$, was also observed, the oxalate concentration ranged by one or two orders lower than the major acidic species (mean oxalate concentration $\approx 0.11 \text{ nmol m}^{-3}$ during the campaign).

3.2. Meteorological conditions in the boundary layer during the airborne observations

Figure 3 shows typical examples of vertical profiles of air temperature and relative humidity in the lower troposphere. On 20 March and 7 April, temperature inversion and drastically decreasing relative humidity were found at 1200–1400 m asl, which should be the top of boundary layer. On 20 March and 7 April, the air temperature decreased with altitude. The temperature difference between the surface ($\approx 40 \text{ m asl}$) and the top of the boundary layer or LFT (1500 m asl) was $\Delta T \approx -8$ – -5 K . Although this temperature gradient (decreasing) was usual during the airborne measurements, lower temperature gradient profiles were also found in the lower troposphere (e.g., 4 April). A lower

relative humidity in the LFT ($\geq 1500 \text{ m asl}$) was identified as a common feature during the measurements. In addition, slightly increasing gradients of relative humidity were often observed in the lower boundary layer, for example on 4 and 7 April ($\leq 500 \text{ m asl}$, $\leq 1000 \text{ m asl}$, see Figs 3b and 3c, respectively), while a lower gradient profile was also observed on 20 March. If the increasing vertical gradient of relative humidity in the lower boundary layer ($\leq 700 \text{ m}$) induces a pH decrease in sea-salt particles, as suggested by von Glasow and Sander (2001), then the similar vertical features of the sea-salt modification should also be observed in the spring Arctic.

3.3. Vertical features of sea-salt modification with atmospheric acidic species in the boundary layer of spring Arctic

3.3.1. Sea-salt modification and its vertical gradient in lower troposphere.

Figure 4 shows the typical examples of EDX spectra of individual sea-salt particles showing modification. Major sea-salt constituents such as Na, Mg, Cl and S were obtained in EDX analysis. It is seen that the peak height of Cl relative to Na gradually decreased with increasing peak height of S relative to Na in each spectrum. Thus, it appears that acidic sulfur species such as H_2SO_4 and SO_2 may make a significant contribution to Cl liberation of sea-salt particles in the boundary layer of the spring Arctic.

For a more quantitative discussion, Fig. 5 illustrates the relative molar ratio of Na, S, and Cl for individual sea-salt particles. Modified sea-salt particles with a lower Cl ratio were often observed in the present study, although some sea-salt samples on 15 March (87–349 and 323–473 m) and 20 March showed an

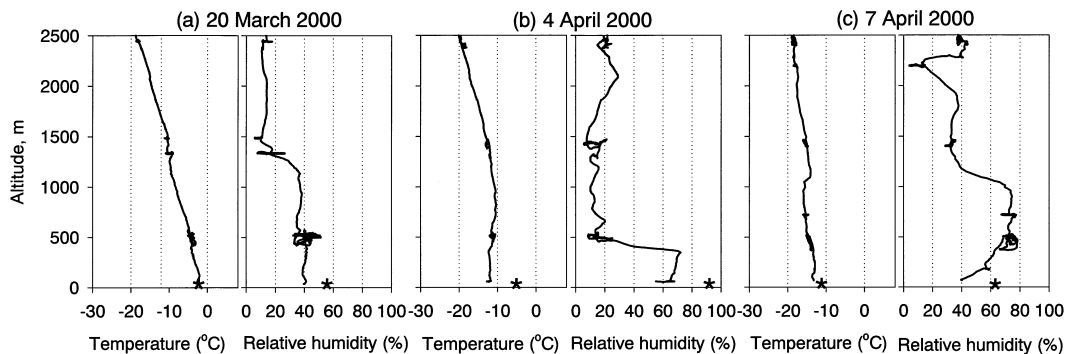


Fig. 3. Typical examples of vertical profiles of air temperature and relative humidity in lower troposphere during the campaign. Asterisks indicate the values observed at ground-base observatory in Ny-Ålesund.

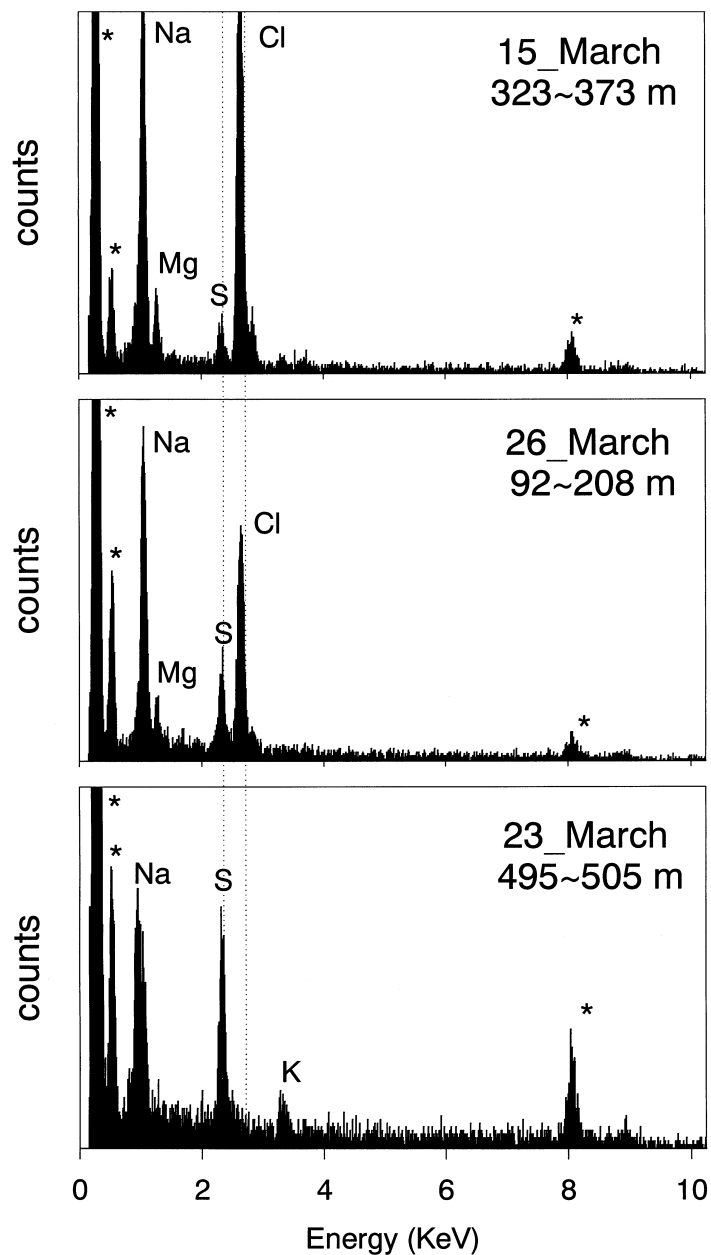


Fig. 4. Typical examples of EDX spectra of sea-salt particles: (a) sea-salt particles collected at 323–473 m asl on 15 March, (b) at 92–208 m asl on 26 March, and (c) 495–505 m asl on 23 March. Dotted lines indicate peak locations of S and Cl. Asterisks show background peaks of C, O, and Cu from a collodion thin film and a Cu micro-grid.

insignificant sea-salt modification. In addition, the Cl were ratio tends to decrease with an increasing S ratio (distributed on the stoichiometrical line of NaCl–Na₂SO₄) or slightly with an increase in the S ratio. This

suggests a contribution of some kind of acid, such as H₂SO₄/SO₂ and HNO₃, to sea-salt modification (details will be described in a later section). In addition, more sea-salt particles tend to be modified in the upper

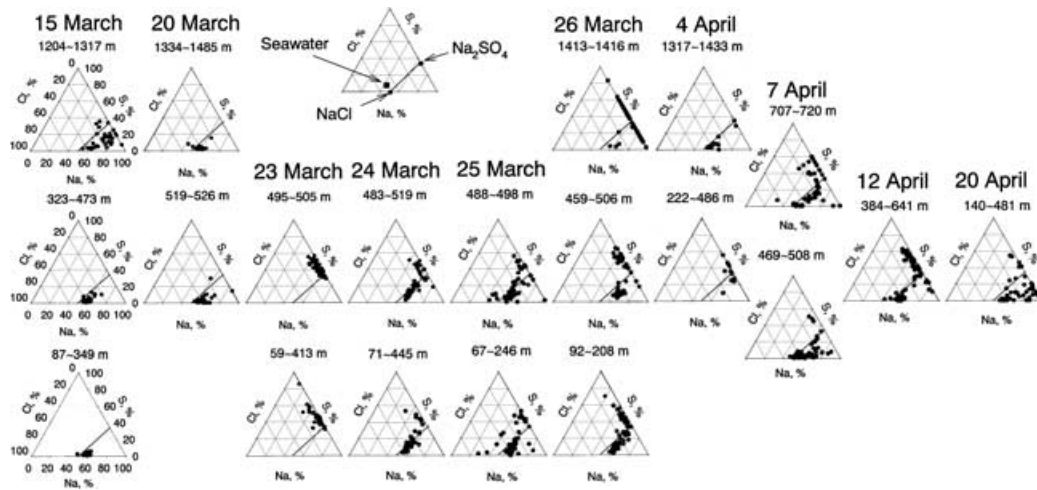


Fig. 5. The relative molar ratio of Na, S, and Cl in individual sea-salt particles during the ASTAR 2000 campaign. The thick line traces the stoichiometrical change of chemical composition from NaCl to Na₂SO₄. When NaCl (major sea-salt component) is gradually modified with H₂SO₄ and SO₂, each weight ratio should be distributed along with this thick line.

atmosphere on 15, 24 and 26 March. A similar tendency was also observed in the marine boundary layer of mid-latitudes (Miura et al., 2000). As mentioned above, the vertical features noted in the present study are observed largely in fine sea-salt particles owing to large losses of coarse sea-salt particles during the sampling. Other field measurements in the marine boundary layer (Miura et al., 1991; McInnes et al., 1994; Mouri et al., 1997) also revealed higher Cl⁻ liberation from sea-salt particles (lower Cl/Na) in finer sea-salt particles. Some investigators (Miura et al., 1991; McInnes et al., 1994; Mouri et al., 1997) described the contribution of longer residence time and larger surface area relative to particle volume to fine sea-salt modification. Recent laboratory measurements by Caffrey et al. (2001) suggested an important contribution of cloud processes to halogen depletion in sea-salt particles. Consequently, we should also discuss the following possibilities: (1) local sea-salt emission from the sea surface, (2) vertical gradient of sea-salt aerosol pH, relative humidity and air temperature, as described by von Glasow and Sander (2001), (3) history of cloud processes, and (4) vertical gradient of the concentrations of acidic species.

Sea-salt particles are emitted from the open sea surface through bubbles bursting at the sea surface (e.g., Blanchard, 1983). However, in our case, the sea surface of the observed area was often covered with sea ice as shown in Table 1. Since a covering of sea-ice

reduces sea-salt emission from the sea surface, the sea-salt emission will make an insignificant contribution in the observed area with sea-ice covering, especially on 15 March, 26 March, 4 April and 7 April. Thus, most sea-salt particles may be transported from the open-sea region (a few or several hundred kilometres away from the observation area), although some sea-salt particles can be released from frozen sea ice if a strong wind blows. Transport from the open sea surface to the Arctic region (the observed area) will cause a relative aging of sea-salt particles. Also, Hara et al. (1999) showed that aged sea-salt particles were often observed at ground level at Ny-Ålesund in the winter/spring Arctic. Hence, local sea-salt emission probably makes only an insignificant contribution to the vertical gradient of sea-salt modification.

As shown in Fig. 3, vertical gradients of temperature and relative humidity were observed in the lower troposphere (<1500 m). Under such conditions the vertical gradient of sea-salt modification was often obtained. However, less modification of sea-salt particles occurred in the upper boundary layer (or lower free troposphere) on 20 March and 4 April, when aerosol particles were also collected at higher altitude with lower relative humidity ($\leq 20\%$, as shown in Fig. 2). The lower level of modification under drier air conditions strongly suggests a large influence of relative humidity on sea-salt modification. Sea-salt particles should have a lower liquid water content (LWC) or an almost

Table 1. List of analyzed aerosol samples

Date	Altitude (m)			Mean temp. (°C)	Mean humidity (%)	Sea surface conditions
	Lowest	Mean	Highest			
15 March	87	212	349	-1.3	66.1	Covered
	323	462	473	-3.4	68.2	
	1204	1266	1317	-8.9	41.4	
20 March	519	520	526	-4.9	39.6	Partly covered
	1334	1412	1485	-10.0	17.9	
23 March	59	172	413	-5.6	48.6	Partly covered
	495	498	505	-10.3	54.8	
24 March	71	357	445	-9.0	37.6	Partly covered
	483	494	519	-10.3	54.8	
25 March	67	104	246	-11.0	47.8	Partly covered
	448	481	498	-14.7	65.5	
26 March	92	100	208	-18.2	51.5	Almost covered
	459	495	506	-18.0	45.9	
	1398	1411	1416	-19.5	47.3	
4 April	222	463	486	-11.6	42.3	Covered
	1317	1411	1433	-12.0	14.5	
7 April	385	415	508	-14.5	72.7	Covered
	707	719	720	-15.3	69.9	
12 April	384	473	641	-13.2	49.0	Partly covered
20 April	140	376	481	-13.1	59.3	Open

Covered, $\geq 95\%$; almost covered, 65–95%; partly covered, 30–65%; open, $\leq 30\%$. Ice density was manually observed from the pictures taken during the measuring flights.

Table 2. Relative humidity in deliquescence and recrystallization points of each salt

Salt	Deliquescence points (%)	Re-crystallization point (%)
NaCl	75.5–80 ^{a,b}	43 ^b
Na ₂ SO ₄	83.5 ^a	
NaNO ₃	76.0 ^a	
NaCl ⁻ NaNO ₃ ⁻ Na ₂ SO ₄	72 ^c	45 ^c
NaCl ⁻ NaNO ₃	68.0 ^{c,d}	
NaCl ⁻ KCl	72.7 ^d	
MgCl ₂ · 6H ₂ O	35–40 ^a	44 ^a

^aPruppacher and Klett (1978).

^bTang et al. (1997).

^cTang and Munkelwitz (1994).

^dFinlayson-Pitts and Pitts Jr. (2000).

dry surface at lower relative humidity (<30%) because of the slightly higher recrystallization points of NaCl and MgCl₂ (44% and 25%, respectively) as given in Table 2. Sea-salt particles in the upper atmosphere on days with lower relative humidity (e.g., 20 March and

7 April) are likely to have an almost dry surface or lower LWCs. Such dry conditions in the particles may reduce their modification through heterogeneous reactions with atmospheric acidic species. Indeed, on other days or other samples, the relative humidity ranged by more than 40%, as shown in Fig. 2 and Table 1. Thus, this tendency strongly suggests that relative humidity makes a significant contribution to sea-salt modification in the spring Arctic. According to the model estimation by von Glasow and Sander (2001), vertical gradients of relative humidity and air temperature should enhance the LWC, causing a highly efficient uptake of acidic gases, and a consequent decrease in aerosol pH. Also, model studies (Katoshevski et al., 1999; Fridlind and Jacobson, 2000) suggested sufficient Cl⁻ liberation from sea-salt particles with acidic conditions. Moreover, they showed that the pH of sea-salt particles may change from 7–9 (fresh sea-salt particles) to <2 (aged sea-salt particle) at high relative humidity and high acidic concentrations. Therefore, vertical features of air temperature, relative humidity and pH of sea-salt particles may make a significant

contribution to the vertical gradient of sea-salt modification in the lower troposphere of the spring Arctic.

As suggested by Caffrey et al. (2001), cloud processes can also cause an important Cl^- liberation from cloud-processed sea-salt particles. Cloud often appears in the UBL and LFT, so that similar processes are expected to occur in the Arctic region. However, the airborne measurements during the ASTAR 2000 campaign were carried out under clear sky conditions because aerosol optical measurements required cloudless conditions. In addition, it is difficult to calculate a backward trajectory in cloud conditions. Consequently, clear evidence of the contribution of cloud processes was not obtained in the present study. When cloud droplets (cloud-processed sea-salt particles) are evaporated, some modified sea-salt particles might remain in the atmosphere. Since this process can occur not only in the polar regions but also in the marine boundary layer of mid-latitudes, a detailed discussion about the contribution of cloud process will be needed for a better understanding of sea-salt modification and cycles of reactive halogen species in UBL and LFT of the polar regions and mid-latitudes.

The vertical profile of acidic gases must also critically control the vertical gradient of sea-salt modification, since the latter is based on the uptake of acidic gases by sea-salt particles followed by heterogeneous reactions. However, vertical profiles of acidic gases in the lower troposphere (<2000 m) were not measured in the present study because of insufficient sampling time. In fact, they have rarely been observed (Radke et al., 1984; Thornton et al., 1989; Jaeschke et al., 1997). Although these investigations showed that higher SO_2 concentrations in the lower troposphere were associated with Arctic haze conditions, vertical resolution of measurements was too low to discuss the gradient of acidic gases in the boundary layer (<1500 m). According to Jaeschke et al. (1997), gaseous HNO_3 concentrations were often higher in the LFT, with fewer sea-salt particles, than in the boundary layer in the spring Arctic regions. Under conditions with less vertical advection, a high aerosol (e.g., sea-salt) concentration in the boundary layer relative to LFT can result in a lower vertical gradient of acidic gas concentrations (e.g., SO_2 and HNO_3) through deposition and heterogeneous processes in the boundary layer. However, the vertical gradient of acidic gases can make a contribution to the vertical gradient of sea-salt modification when vertical advection from LFT to UBL occurs, as suggested by Hara et al. (submitted to *J. Geophys. Res.*). For more detailed discussion on

the vertical gradient of sea-salt modification and acidic gases, a high vertical resolution observation of acidic gases should be needed.

3.3.2. Atmospheric acidic species related to sea-salt modification in the lower troposphere of the spring Arctic. The distribution of relative molar ratio (Na, Cl, and S) of individual modified sea-salt particles (Fig. 5) can be classified into (a) distribution along with the stoichiometrical $\text{NaCl-Na}_2\text{SO}_4$ line (e.g., 24–26 March), (b) distribution slightly less with increasing S ratio (e.g., 15 March, 7 April and 20 April), and (c) highly Cl depleted sea-salt particles (23 March). Both types (a) and (b) appear to be mixed on 15 March (1204–1317 m), 7 April and 20 April. In particular, mixing of relatively fresh sea-salt particles (similar to sea-water ratio) occurred on 12 April when surface O_3 depletion was observed in Ny-Ålesund (Hara et al., submitted to *J. Geophys. Res.*). The modified sea-salt particles of type (a) are probably due to Cl^- liberation by H_2SO_4 and SO_2 , by the well known reaction:



H_2SO_4 and acidic SO_4^{2-} in sea-salt particles may be formed/supplied by way of heterogeneous processes relating to gaseous SO_2 and H_2SO_4 , and coagulation of fine acidic sulfate particles (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts Jr., 2000). Indeed, the modified sea-salt particles with acidic sulfur [types (a) and (c)] were mainly observed under the Arctic haze conditions with higher SO_2 and nss- SO_4^{2-} concentrations as described below. On the other hand, the modified sea-salt particles of type (b) may be due to the dominant heterogeneous reactions with acidic species other than H_2SO_4 and SO_2 in sea-salt particles. Type (b) modified sea-salt particles were found in the higher concentrations of NO_3^- and/or HNO_3 as shown in Fig. 2. Although the SO_2 concentration was similar to the HNO_3 concentration during the type (b) periods, the Henry's law coefficient of HNO_3 (ca. 10^5 – 10^6 M atm^{-1}) is considerably larger than that of SO_2 (ca. 1 M atm^{-1}) (references in Sander, 1999). This suggests the dominant contribution of HNO_3 to sea-salt modification in type (b), while the Henry's law coefficient often shows pseudo-values owing to non-equilibrium conditions (diffusion limitation of gases) when rapid oxidation and reactions occur in the heterogeneous processes. The uptake coefficient, γ , of HNO_3 ($\gamma_{\text{HNO}_3} = 0.07$ – 0.193 , van Doren et al., 1990) and its precursors ($\gamma_{\text{N}_2\text{O}_5} = 0.013$ – 0.06 , van Doren et al., 1990, George et al., 1994) is approximately two orders larger than

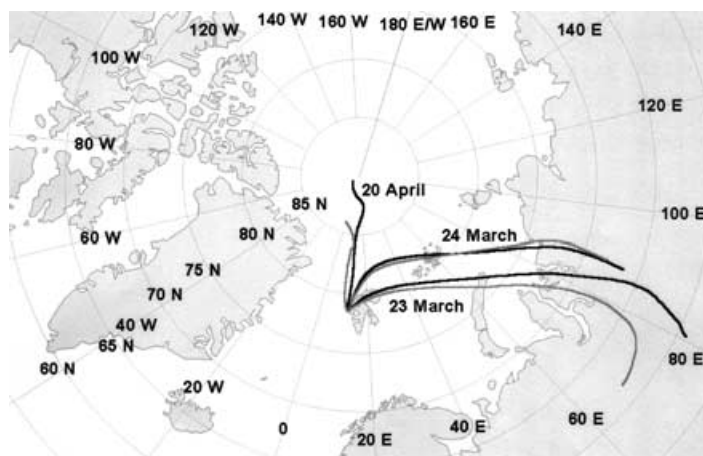
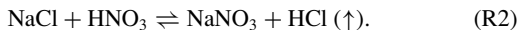


Fig. 6. Typical examples of backward trajectories on 23 March, 24 March, and 20 April. The black line indicates the trajectory from 500 m asl, and the grey line that from 1000 m asl.

$\gamma_{\text{SO}_2} = <8 \times 10^{-5} - <5 \times 10^{-4}$ on sea-salts (Gebel et al., 2000). Although laboratory measurements (van Doren et al., 1990, 1991) indicated that γ_{HNO_3} slightly depended on pH (acidity in aerosol water), γ_{HNO_3} on acidic surface (H_2SO_4) is approximately two orders larger than γ_{SO_2} . In addition, $\gamma_{\text{N}_2\text{O}_5}$ showed less pH dependence relative to γ_{HNO_3} (van Doren et al., 1990, 1991). Hence, sea-salt modification via reactions with reactive nitrogen oxides may be enhanced rather than with SO_2 and H_2SO_4 when HNO_3 concentration was similar to SO_2 concentration. Also, Hara et al. (1999) indicated dominant internal mixing states of NO_3^- on sea-salt particles, and a significant contribution of reactive nitrogen oxides such as HNO_3 , N_2O_5 and NO_3 to NO_3^- formation on sea-salt particles in the boundary layer of the winter/spring Arctic, for example, by way of the reaction:



In addition, Hara et al. (2002b) and Kerminen et al. (1999) suggested internal mixing between sea-salts and oxalate in the Arctic boundary layer. However, mean oxalate concentration during the ASTAR 2000 campaign was 0.11 nmol m^{-3} , 1–2 orders lower than NO_3^- (mean, 1.62 nmol m^{-3}) and nss-SO_4^{2-} (mean, 8.42 nmol m^{-3}). Therefore, sea-salt modification in type (b) might be attributed to the heterogeneous reactions mainly with reactive nitrogen oxides (NO_3^-), slightly with nss-SO_4^{2-} , and less with oxalate.

The dominance of sea-salt modification with H_2SO_4 and SO_2 was observed clearly between 23 and

26 March. As shown in Fig. 6, the backward trajectory between 23 and 26 March suggested a larger anthropogenic influence from an industrial region in Russia. Indeed, almost complete liberation of Cl^- ($\text{Cl}/\text{Na} \approx 0$) occurred on 23 March, as shown in Fig. 5, when the heaviest Arctic haze was observed (Yamanouchi et al., submitted to *J. Geophys. Res.*). Thus, sea-salt modification with SO_2 and nss-SO_4^{2-} may be enhanced under Arctic haze conditions with higher concentrations of SO_2 and nss-SO_4^{2-} . On the other hand, direct anthropogenic impact over 80 h was not observed in dominant sea-salt modification with NO_3^- , as shown in Fig. 6 (20 April). This trajectory analysis supported lower concentrations of SO_2 and nss-SO_4^{2-} in sea-salt modification dominated by NO_3^- (e.g., 15 and 20 March and 7 and 20 April). Therefore, sea-salt modification with reactive nitrogen oxides may represent the main factor in the background Arctic boundary layer (not Arctic haze conditions).

3.4. Atmospheric impact of the vertical features of sea-salt modification

Sea-salt modification with acidic species such as SO_4^{2-} and NO_3^- leads to the release of gaseous reactive halogen species due to the gradual change of chemical compositions of sea-salt particles, for example, from NaCl to Na_2SO_4 , NaNO_3 , and their mixtures. Thus, the vertical gradient of sea-salt modification should exhibit the following characteristics: (1) higher concentrations of gaseous reactive halogen species and

Table 3. Estimation of plausible amount of liberated Cl^- and other parameters under conditions with sea-ice covering

Date	Mean altitude (m)	R_{Cl} (%)	Mean aerosol concentration of $>0.2 \mu\text{m}$ (L^{-1})	Mean aerosol concentration of $>1 \mu\text{m}$ (L^{-1})	Mean estimated amount of Cl^- liberated (mol m^{-3})
15 March	212	33.0	2×10^4 – 3×10^4	60–120	0.66
	462	34.8	2×10^4 – 4×10^4	20–100	0.67
	1266	81.0	0.9×10^5 – 1.3×10^5	–10	1.62
20 March	520	43.0	No data	No data	0.86
	1412	31.0	No data	No data	0.62
23 March	172	91.3	2.6×10^4	10–20	1.83
	498	93.6	2.3×10^4	10–20	1.87
24 March	357	51.3	$(2-3) \times 10^5$	70–100	1.03
	494	70.6	$(2-3) \times 10^5$	70–100	1.41
25 March	104	51.8	No data	No data	1.04
	481	57.3	No data	No data	1.15
26 March	100	72.7	$(2-2.4) \times 10^4$	20–30	1.45
	495	83.8	$(1.7-2) \times 10^4$	15–30	1.68
	1411	95.8	$(1.7-2.4) \times 10^4$	15–20	1.92
4 April	463	93.5	$(1-2) \times 10^4$	7–12	1.87
	1411	41.4	0.9×10^4 – 1×10^4	10–40	0.83
7 April	415	46.3	$(1-1.5) \times 10^4$	9–20	0.93
	719	67.5	$(1-2) \times 10^4$	4–12	1.35
12 April	473	60.7	$(1.5-2.5) \times 10^4$	16–30	1.21
20 April	376	70.8	No data	No data	1.42

(2) a change of susceptibility to CCN formation in the UBL and LFT of the spring Arctic.

In order to discuss the above possibilities, we first consider the amount of Cl^- liberation and the number concentration of sea-salt particles. For estimation of the amount of Cl^- liberation in both the upper and lower boundary layer, we attempt to calculate the depleted Cl^- amount as follows:

$$\left(\frac{\text{Cl}}{\text{Na}}\right)_{\text{liberation}} = \left(\frac{\text{Cl}}{\text{Na}}\right)_{\text{fresh sea-salt}} - \left(\frac{\text{Cl}}{\text{Na}}\right)_{\text{ambient sea-salt}}$$

where $(\text{Cl}/\text{Na})_{\text{liberation}}$, $(\text{Cl}/\text{Na})_{\text{fresh sea-salt}}$, and $(\text{Cl}/\text{Na})_{\text{ambient sea-salt}}$ are the molar ratio of liberated Cl^- , fresh sea-salt particles, and ambient sea-salt particles in individual sea-salt particles, respectively. Here, the molar ratio ($\text{Cl}/\text{Na} \approx 1.2$) in seawater was used as that of fresh sea-salt particles. The weight ratio of liberated Cl^- to total Cl^- (R_{Cl}) in fresh sea-salt particles can be estimated using following equation:

$$(R_{\text{Cl}^-}, \text{Cl}^- \text{ liberated ratio, \%}) = \frac{\sum \left(\frac{\text{Cl}}{\text{Na}}\right)_{\text{liberation}}}{\sum \left(\frac{\text{Cl}}{\text{Na}}\right)_{\text{fresh sea-salt}}} \times 100.$$

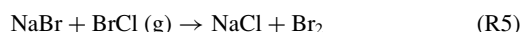
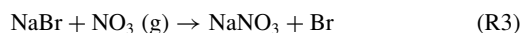
In the present study, an attempt to calculate the mean amount of Cl^- liberated was made. The number concentration of aerosol particles (>1.0 and $>0.2 \mu\text{m}$) by airborne measurements (Yamanouchi et al., submitted to *J. Geophys. Res.*) and by tethered-balloon-borne aerosol measurements in Ny-Ålesund (Hirasawa, personal communication) indicated lower or less vertical gradients in the boundary layer (<1500 m asl.). As shown in Table 3, vertical gradients of the number concentration of aerosol particles were not identified in the boundary layer during the ASTAR 2000 campaign. A similar distribution of sea-salt particles was also observed under steady-state conditions of the mid-latitude coastal region (Reide et al., 2001). Moreover, Hara et al. (submitted to *J. Geophys. Res.*) showed a similar relative abundance ($\approx 20\%$) of sea-salt particles in the boundary layer in each flight during the campaign. Assuming the lower vertical gradient

of the number concentration of sea-salt particles in the boundary layer, the ss-Cl⁻ concentration in the boundary layer can be estimated using the ambient Na⁺ at the surface and seawater ratio (molar ratio, Cl/Na ≈ 1.2; Wilson, 1975). The estimated ss-Cl⁻ concentration was 18.25 nmol m⁻³ on average (0.23 nmol m⁻³ minimum and 114.60 nmol m⁻³ maximum) during the measurements. According to previous studies (Hara et al., 1997; Hara, 2000), the mass size fraction of fine sea-salt particles was approximately 10% (≈2 nmol m⁻³). Here, mass size fraction means percentage of mass (concentration) in each size fraction such as coarse (>2.0 μm), fine (0.2–2.0 μm) and back-up (<0.2 μm) modes. Using sea-salt concentration in fine mode (≈2 nmol m⁻³) and R_{Cl}, the plausible amount of liberated Cl⁻ might be estimated as listed in Table 3. The estimated amount of liberated Cl⁻ in the lower boundary layer (<500 m asl) ranged in ambient g.Cl concentration at the surface as shown in Fig. 2. In addition, the estimated amount of liberated Cl⁻ in UBL was mostly 1.2–2 times larger depending on high R_{Cl} (efficient sea-salt modification), except 20 March and 4 April when the relative humidity in UBL was lower than the recrystallization point of sea salts (Tang and Munkelwitz, 1994). Thus, the lower vertical gradient of sea-salt modification on 20 March and 4 April strongly suggests that the aerosol surface water (liquid or deliquescence states) is critical for sea-salt modification in the atmosphere. Therefore, the vertical gradient of sea-salt modification is likely to play a significant role as a source of reactive chlorine species such as HCl in the boundary layer.

The subsequent Cl⁻ liberation in the UBL can lead to HCl release via the heterogeneous reactions like (R1). As suggested by Beichert and Finlayson-Pitts (1996), HCl phase partitioning requires pH decreasing in aerosol surface water. Indeed, a high sulfur ratio (probably strong acidic states) in modified sea-salt particles was only observed only in wholly Cl-depleted sea-salt particles or those with quite a lower Cl ratio (e.g., 23 March, 24 March, 26 March, 7 April and 12 April in Fig. 5), which probably have strong acidic states through the heterogeneous formation of H₂SO₄ and acidic SO₄²⁻. According to Fridlind and Jacobson (2000), uptake of gaseous HCl from sea-salt modification can strongly effect pH in coarse sea-salt particles, which are less modified and Cl-depleted (Miura et al., 1991; McInnes et al., 1994; Mouri et al., 1997; Katoshevski et al., 1999). Therefore, a vertical gradient of sea-salt

modification might also enhance sea-salt modification in less modified sea-salt particles in coarse mode through pH decreasing by HCl uptake.

As well as Cl liberation, Br liberation also can occur in sea-salt particles in the atmosphere, for example:



According to Hara et al. (2002a), NO₃⁻ formation on sea-salt particles from gaseous reactive nitrogen oxides (e.g., HNO₃, NO₃, N₂O₅, and BrONO₂) may make a significant contribution to efficient Br⁻ liberation in the winter/spring Arctic boundary layer. In particular, Sander et al. (1999) pointed out bromine deficits from sea-salt particles without aerosol acidity in (R6). Although these reactions [(R3)–(R6)] can occur in both non-acidic (pH ≥ 5.5) and acidic (pH ≤ 5.5) conditions in aerosol surface water, acidic conditions enhance bromine liberation from sea-salt particles, as suggested by Keene et al. (1998). Furthermore, von Glasow and Sander suggested that a vertical pH gradient in sea-salt particles due to the air temperature and relative humidity gradient enhances bromine activation in the upper boundary layer. Consequently, a vertical trend of Br⁻ liberation may also occur in the spring Arctic boundary layer. As a result, this vertical feature of sea-salt modification may enhance the higher concentration of gaseous reactive bromine species in the lower troposphere. Indeed, the tropospheric profile of BrO, which a key species in surface ozone depletion during the polar sunrise, showed a maximum between UBL and LFT (Fitzenberger et al., 2000). Also Hara et al. (submitted to J. Geophys. Res.) suggested the influence of air mass in the UBL and LFT on atmospheric bromine species and surface ozone depletion. Therefore, a higher sea-salt modification in the UBL and LFT may be an important source of gaseous reactive halogen species in the Arctic region.

With the change of chemical compositions in sea-salt particles during the transport their deliquescence and re-crystallization points should gradually change, as listed in Table 2. These changes may influence the

LWC in modified sea-salt particles and their hygroscopicity. Thus, sea-salt modification and its vertical variation are likely to change their affinity for CCN formation in the UBL and LFT of the Arctic region. If the vertical aspect of sea-salt modification occurs not only in the Arctic spring but also at mid-latitudes, as suggested by Miura et al. (2000), this vertical gradient may lead to a change in ability to form CCN and a significant release of gaseous reactive halogen species.

4. Summary

The significant vertical features of sea-salt modification were observed in aerosol samples taken in airborne measurements in the spring Arctic during the ASTAR 2000 campaign. More sea-salt particles tend to be modified with SO_4^{2-} and NO_3^- in the UBL and LFT. In addition, relative humidity played an important role in the sea-salt modification. As suggested by ground-based aerosol measurements and backward trajectory analysis, sea salts may be modified dominantly with SO_2 and SO_4^{2-} in Arctic haze conditions, whereas they are modified dominantly with NO_3^- and reactive nitrogen oxides in Arctic background conditions. Since sea-salt modification leads to emission of gaseous reactive halogen species and acidic species to

the atmosphere, the vertical variation of sea-salt modification in the LFT will probably make a significant contribution to atmospheric halogen cycles including surface ozone depletion during the polar sunrise.

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