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winter/spring Arctic troposphere:

The roles as the sink of acidic species and the source of
reactive halogen species

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要 旨

大気中に存在するエアロゾル粒子は、大気中の化学反応や放射収支において、非常に重要な役割を担っている。大気エアロゾル粒子の主成分の一つは、海洋から放出される海塩粒子である。海塩粒子のソースは海洋であるため、海塩粒子に関する研究は、海洋・沿岸域の境界層内を中心に発展してきた。しかしながら、最近の航空機による観測結果では、上部対流圏においても海塩粒子が存在し、長距離輸送されていることが観測されていた。そのため、海塩粒子に関わる事象は境界層内や局地的な現象ではなく、より広い範囲に影響が及ぶ。さらに海塩粒子の多くは、粒子表面に液層を保持しうる環境に分布していることが多く、不均一反応の場として重要な機能も果たす。大気中の物質循環を考慮する上で海塩粒子に関わる諸過程と、その寄与を明らかにすることが重要となる。粒子上の不均一反応も含め、大気中の化学反応は光化学反応の有無で、その諸過程が大きく異なるため、昼夜を分けて議論することが好ましい。夜間の諸反応は、光化学過程で重要となる高反応性物質の生成・蓄積過程が重要と考えられているが、十分に理解はされていない。冬季の極域は極夜を含めて低日射の期間が長い。また、降水量も少ないため、大気中の物質の対流時間が中低緯度と比べると長いため、夜間の不均一反応を評価するには非常に有効かつ適切な環境である。冬季北極のような非常に極端な環境下での不均一反応に関する知見が得られれば、海塩粒子の介する不均一反応や物質循環を知る上で非常に有効となろう。

本研究を行うにあたり、北極域に位置する Ny-Ålesund で、大気エアロゾル粒子及び酸性ガス成分の観測を1994年～1998年の冬季(12月～3月初めのおよそ3ヶ月間)に行った。本研究は、冬季北極での大気観測より得られた各成分の濃度変化や各エアロゾル粒子成分の混合状態変化に基づいて、海塩粒子の大気中での役割とその諸過程に絞って議論を行う。

第一段階として、Ny-Ålesund での海塩成分の濃度変化と、その輸送過程についての検討を行った。海塩成分の主成分は、 Na^+ 、 Cl^- であるため、海洋性大気輸送・流入の指標とした。 Na^+ 、 Cl^- の濃度変化と気象要素(気温など)との比較から、海塩粒子を大量に含む海洋性大気は低気圧の活動に伴い、中緯度開水域から輸送されていたことが示された。また、海洋の生物活動から放出された前駆体の光化学反応生成物であるメタンスルホン酸イオンの存在から、かなり低緯度域からも海洋性大気が Ny-Ålesund に輸送されることが示唆された。 Na^+ 濃度の粒径分布変化から、長距離輸送を経た古(laged)海洋性大気の流入・混合も示された。古海洋性大気の判定のために、海洋性大気の年齢にあたる定性的な指標として、粗大粒子中の Na^+ 濃度と微小粒子での濃度の比(C/F比)を導入した。

次に、アルカリ物質を主成分(NaCl)とする海塩粒子の酸性成分のシンクとしての

機能について調べた。古海洋性大気では、海塩成分と粒子に取り込まれた酸性成分との不均一反応に起因すると考えられる脱ハロゲン化が見られた。個々の海塩粒子の組成をみると、変質した海塩粒子には、硫酸イオン、亜硫酸イオン、メタンスルホン酸イオン、硝酸イオン、亜硝酸イオンが内部混合状態で存在し、それらはナトリウム塩やカリウム塩として存在していた。各成分の粒径分布や海塩粒子との内部混合状態を比較すると、硫黄系酸性成分の海塩粒子への内部混合は硫黄系酸性成分のシンクの一部として機能するが、硫黄の物質循環から見ると、その寄与は非常に小さかった。海塩粒子の変質の観点から見ると、同時にハロゲン化合物の放出が起こるため、ハロゲンサイクルに与える影響は無視できない。一方、硝酸イオンの粒径分布は海塩粒子の粒径分布と類似し、主に粗大粒子域に分布していた。ニトロソ薄膜法による個々の粒子観察結果から、ほとんどの硝酸イオンは、濡れた海塩粒子と内部混合状態で存在していることが示された。硝酸イオンを含有する割合は、古海洋性大気中で増加し、比較的新鮮な海洋性大気では減少する傾向が見られた。この傾向から、海塩粒子が大気中を輸送されている間に、海塩粒子上で徐々に硝酸イオン取り込み・生成が起き、徐々に海塩粒子が変質を受けていたことが示唆される。海塩粒子上で起こる硝酸イオン生成過程を調べるために、簡単な取り込みモデルを用いて、各反応性窒素酸化物からの硝酸イオン生成の寄与を求めた。その結果、海塩粒子上の硝酸イオンは、主にガス状硝酸の海塩粒子への取り込みが寄与していたが、冬季北極のような極夜、あるいは低日射量の環境下では、夜間に濃度増加が見られる N_2O_5 や NO_3 からの硝酸生成の寄与も無視できなかった。海塩粒子が主に分布する粗大粒子の除去速度を考慮すると、海塩粒子が反応性窒素酸化物の収支においてシンクとして、非常に重要な役割を果たしていることが伺える。硫酸や硝酸による海塩粒子の変質だけでは、 HCl や HBr といった成分のみが大気に放出されるが、 N_2O_5 や NO_3 による硝酸イオン生成過程では ClNO_2 や BrNO_2 といった高反応性ハロゲン化合物が放出されるため、微量反応性窒素酸化物による海塩粒子の変質が大気中のハロゲンサイクルにおいて極めて重要な役割をしている可能性を示唆する。

海塩粒子は酸性成分のシンクとして機能しながら、同時に海塩粒子の変質により反応性無機ハロゲン化合物を大気へ放出していた。次に、反応性無機ハロゲン化合物のソースとしての海塩粒子について検討した。ガス状無機塩素化合物 (g_Cl) の濃度レベルは、海塩粒子の変質による脱 Cl^- (dep_Cl) 量とほぼ一致していた。特に、1996/1997 年の冬季での観測では、濃度レベルだけではなく、 g_Cl と dep_Cl の濃度変化も極めて類似していたため、冬季北極域における g_Cl は、海塩粒子の変質による脱 Cl^- を主なソースとしていることが考えられる。一方、ガス状無機臭素化合物 (g_Br) は、冬季から春先にかけて徐々に増加していく傾向が見られた。また、粒子状無機臭素化合物 (p_Br) は、海塩相当分の Br 濃度よりも過剰に存在しており、冬季北極大気中では、無機臭素化合物の蓄積が起こっている可能性が示唆される。このような傾向は、 g_Cl や粒子態 Cl^- の濃度変化には、全く見られなかった。 g_Br 濃度が増加する際には、硝酸イオン濃

度や硝酸イオンが海塩粒子に内部混合している割合が増加していた。海塩粒子上での硝酸イオン生成を見積もった時と同様に、簡単なモデル計算をしたところ、海塩粒子の変質から発生しうる g_Bg 量は、実際の g_Br 濃度レベルだった。海塩粒子上での硝酸イオン生成には、反応性ハロゲン化物の生成が伴うことを考慮すると、海塩粒子の変質が g_Br の主なソースの一つとしての役割を果たしていると考えられる。また、冬季北極のような長期の低日射量下では、 N_2O_5 などの微量反応性窒素酸化物による海塩粒子の変質の寄与が大きくなるため、 $BrNO_2$ などの高反応性ハロゲン化合物のソースとしての寄与が示唆された。

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Abstract

Atmospheric aerosol particles have important roles on atmospheric chemistry and radiation budget. One of major constituents of aerosols is sea-salts emitted from sea surface. Recent works showed the long-range transport of sea-salt particles, so that contribution of chemical and/or physical processes of sea-salt particles should be widespread. In addition, sea-salt particles are mostly distributed under the conditions with higher humidity than deliquescence point of sea-salts. Thus, wet or deliquescence condition of sea-salt particles should enhance the heterogeneous reactions on the particles. Although the heterogeneous reactions on sea-salt particles are believed to play roles of source of higher reactive species, and sink of acidic species, we have still less of a few information. In particular, the heterogeneous reaction in nighttime should play an important role in polar regions with longer night, *polar night*, and less solar radiation. In the present study, the heterogeneous processes on sea-salt particles in Arctic winter/early-spring were focused. Atmospheric aerosol particles and acidic gases were collected at Ny-Ålesund, Svalbard during the winter/early-spring.

Major sea-salt constituents were Na^+ and Cl^- at Ny-Ålesund. The concentrations of Na^+ and Cl^- increased in oceanic air mass with lower concentrations of pollutants. Since methanesulfonate was often observed in oceanic air mass, oceanic air mass should be transported from mid-latitude area with photo oxidation and bioactivity. Variations of size distribution of Na^+ concentration suggested transport of aged oceanic air mass. For identification of aged oceanic air mass, the molar ratio of Na^+ concentration in coarse mode to that in fine mode was used as index of aged-oceanic air mass.

In aged oceanic air mass, obvious halogen depletion from sea-salt particles was observed. Single particle analysis showed the internal mixing between sea-salts and acidic species such as sulfate, sulfite, methanesulfonate, nitrate and nitrite. Then, the heterogeneous reactions between sea-salts and acidic species may cause the halogen depletion from sea-salt particles. Size distributions of acidic sulfur species showed that most of sulfur species were externally mixed with sea-salt particles. Then, the contribution of sea-salt particles to sink of acidic sulfur species may be smaller, although some sea-salt particles were depleted by acidic sulfur species. On the other hand, single particle analysis showed that most of NO_3^- was internally mixed with wet sea-salt particles. Considering lower molar ratio of NO_3^- to Na^+ in seawater, NO_3^- in sea-salt particles should be formed through the heterogeneous processes during the transport. Uptake model estimation suggested that NO_3^- in sea-salt particles may be

mostly due to uptake of gaseous HNO_3 , and the heterogeneous formation from N_2O_5 and NO_3 may also have important contribution in winter/early-spring Arctic troposphere with no or less solar radiation. Hence, sea-salt particles should play important role in sink of reactive nitrogen oxides.

The release of reactive halogen species can occur simultaneously with the modification of sea-salt particles by acidic species. The concentrations of gaseous inorganic chlorine species (g_Cl) varied in the range of the level of depleted Cl^- amount estimated from seawater ratio. Furthermore the feature of g_Cl in 1996/1997 winter showed quite similar to that of depleted Cl^- amounts. Then the Cl^- depletion of sea-salt particles may be identified as dominant sources of g_Cl in the winter/early-spring Arctic troposphere. On the other hand, the variations of gaseous inorganic bromine species (g_Br) tended to increase gradually toward spring season. Moreover, particulate bromine species (p_Br : $\text{Br}^- + \text{BrO}_3^-$) exceeded to sea-salt Br^- concentration. Then, inorganic bromine species should be accumulated in the atmosphere during the winter. Similar tendency was not observed in the features of g_Cl and particulate Cl^- . Since higher g_Br concentration was found in higher reacted fraction on nitron-thin-film and/or higher NO_3^- concentration, g_Br may be also released through the modification of sea-salt particles. Considering the contribution of minor reactive nitrogen oxides such as N_2O_5 and NO_3 to heterogeneous formation of NO_3^- , higher reactive bromine species such as BrNO_2 might be released and accumulated in the atmosphere.

Chapter 1

General Introduction

1_1. Atmospheric aerosol

Atmospheric aerosol particles play a critical role in the atmospheric chemistry and radiation budget. Some recent works suggested the role of aerosol particles as chemical reaction sites in the atmosphere [*e.g.*, Iwasaka *et al.*, 1988; Okada *et al.*, 1990; Pósfai *et al.*, 1995; Roth and Okada, 1998; Hara *et al.*, 1999]. In addition, aerosol particles, emitted by human activities and biomass burning, are believed to be responsible for partially masking the expected increases in surface temperature associated with greenhouse gas radiative forcing (Turco *et al.*, 1990; Penner *et al.*, 1994; Pilinis *et al.*, 1995; IPCC, 1995). Of course, aerosol particles, derived from natural sources, should have an influence on radiation budgets [Winter and Chýlek, 1997; Murphy *et al.*, 1998]. Aerosols also have an important impact on precipitation cycles through the formation of cloud-condensation-nuclei [*e.g.*, Hegg *et al.*, 1990, 1996; Lin *et al.*, 1992; Zaizen *et al.*, 1996; Harrison *et al.*, 1996; Matsumoto *et al.*, 1998]. Thus the better understanding of chemical/physical processes by aerosol particles is required for revealing each process of atmospheric chemistry and climate change.

Unlike atmospheric gases, atmospheric aerosol particles have an infinite number of sizes (a few nm ~ > 100 μm) and a variable mixed composition. There are three principal types of aerosol sources: (1) dispersion materials at the Earth's surface (*e.g.*, sea-salt and dust particles), (2) high temperature processes including combustion and volcanic activity (*e.g.*, soot and organic species), and (3) chemical reaction or phase transformation in atmosphere such as gas-to-particle conversion (*e.g.*, H_2SO_4 and ammonium species). Table 1_1 shows the estimations of global source strength of atmospheric aerosol particles. Aerosol particles, emitted from the surface sources through the shattering and wind blowing, have the largest contribution to aerosol mass concentration, especially sea-salts and dusts which are mostly distributed in coarse mode (>2 μm in

Table 1_1. Global aerosol particle production rates from the sources (Tg yr⁻¹)

Surface sources	
Sea-salts	1000 - 2000
Mineral dusts	~2000
Volcanoes	15 - 90
Biogenic materials	~100
Sum	3100 - 4200
Gas-to-particle conversion ^b	
Sulfates from Biogenic gasses	60 - 110
Sulfate from volcanic SO ₂	4 - 45
Nitrates from NO _x	40 - 200
Organic matters	40 - 200
Sum	145 - 555
Anthropogenic sources ^b	
Industrial dusts	40 - 130
Soot	5 - 25
Biomass burning (except soot)	50 - 140
Sulfates from anthropogenic SO ₂	12 - 180
Nitrates from NO _x	20 - 50
Organic matters	5 - 25
Sum	240 - 550

a. Jaenicke, 1993; b. Jonas et al., 1995

diameter). On the other hand, aerosol particles in fine mode (sub- μm in diameter) are mostly composed of sulfates and organic species, which are formed mainly through gas-to-particle conversion. Precursors of aerosol particles are emitted from the natural sources such as marine bioactivity [*e.g.*, Berresheim, 1987; Pszenny *et al.*, 1989; Bates *et al.*, 1992; Matral *et al.*, 1993; Andreae *et al.*, 1995], and human activity such as combustion processes [*e.g.*, Hameed and Dignon, 1988; Barrie *et al.*, 1989; Spiro *et al.*, 1992]. Despite the recent increase of the contribution of anthropologic matters to global atmospheric environment, natural

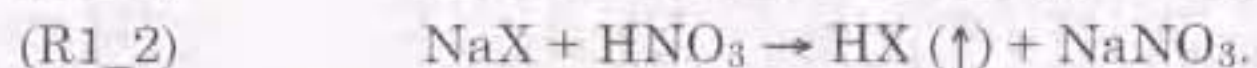
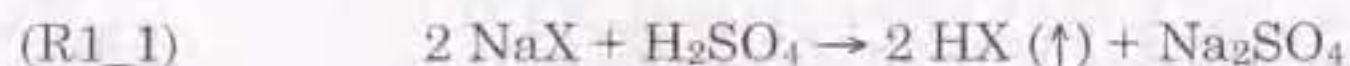
sources such as wave shattering and bio-activity in ocean cannot be neglected in the effect on atmospheric environment because of the largest source strength and larger surface area of ocean on Earth's surface. Therefore, the understanding each chemical/physical process of marine-origin species is essential to reveal atmospheric aerosol science in global scale.

Marine aerosol particles mostly consist of sea-salts and sulfates [Warneck, 1988; Fitzgerald, 1991; Murphy *et al.*, 1998]. Despite of the largest mass concentration of sea-salts in the atmosphere, however, most investigations about climate impact by aerosol particles were based on the estimation of influence of fine sulfate particles —mostly sulfate or sulfuric acid— (*e.g.*, Charlson *et al.*, 1987, 1992; IPCC, 1995). Indeed, Murphy *et al.* [1998] showed important radiative effects of sea-salt aerosols. Atmospheric chemistry associated with sea-salt particles has been built from the observations in marine boundary layer (PBL) [Mouri *et al.*, 1993; McInnen *et al.*, 1994; Gradel and Keene, 1995; Ayers *et al.*, 1999], coastal area [Wu and Ono, 1988], lower and upper free troposphere [Patterson *et al.*, 1980; Ikegami *et al.*, 1991, 1993 and 1994], laboratory measurements [*e.g.*, Fenter *et al.*, 1994; Seisel *et al.*, 1997; ten Brink, 1998] and model estimation [Clegg and Toumi, 1997; Keene *et al.*, 1998]. Although the concentrations of sea-salts such as Na^+ and Cl^- decreased with altitude [Blanchard, 1984; Warneck, 1988], some airborne measurements over tropical and mid-latitude area [Patterson, 1980; Ikegami *et al.*, 1991, 1993, 1994] and polar region [Yamazaki *et al.*, 1989] showed the presence of sea-salt particles in upper troposphere due to the long-range transport and/or the convection. According to Yamazaki *et al.* [1989], sea-salt particles in upper troposphere over Syowa station, Antarctica, may be transported from mid-latitudes and tropical region. This suggested that sea-salt chemistry should have a large influence not only in PBL but also in larger scale —global scale or not? —.

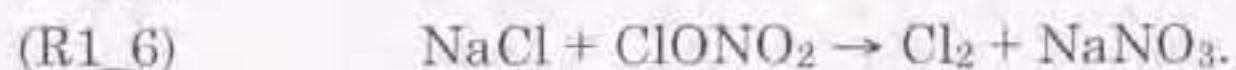
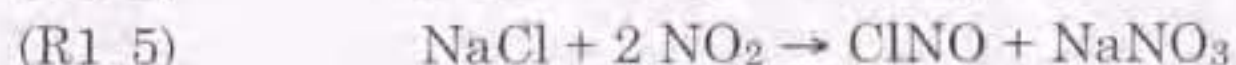
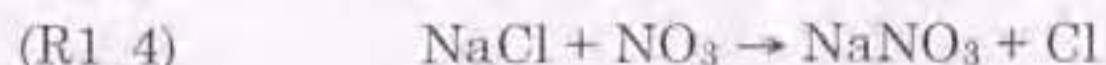
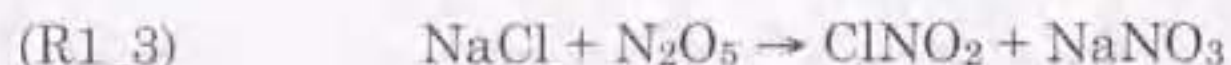
1_2. Heterogeneous chemistry on sea-salt particles

In general, heterogeneous reactions on aerosol particles mean chemical reactions resulting from interaction gaseous species with aerosol particles. The reactions can occur at the surface of dry particles; at the surface of deliquesced particles by the interaction with liquid water, or in the aqueous phase by the interaction with other solutes. For example, one of the best-known processes is the reaction involving sea-salt particles. The processes are believed to be a major

global source of volatile inorganic chlorine in the troposphere. Major constituent of sea-salt particles is sodium chloride (NaCl), which deliquescence point is about 70 %, and re-crystallization point is 45-48 % in droplet evaporation [Tang *et al.*, 1997]. Moreover, minor constituents such as MgCl₂ and CaCl₂ have lower deliquescence points (MgCl₂: 33%, CaCl₂, 24.5%) [Pruppacher and Klett, 1997]. Then, many sea-salt particles are probably present under the conditions with higher relative humidity than re-crystallization point, so that most sea-salt particles may be present as deliquescent particles or droplets except the condition with lower relative humidity such as upper troposphere and stratosphere. The wet and/or liquid surface on sea-salt particles is very important in atmospheric aerosol chemistry because the heterogeneous processes are enhanced on wet surface [van Doren *et al.*, 1990; Behnke *et al.*, 1996; Thomas *et al.*, 1998]. Early works about heterogeneous reactions on sea-salt particles had been investigated since 1950's [Junge, 1956; Junge and Ryan, 1958; Robbins *et al.*, 1959; Martens *et al.*, 1973; Hitchcock *et al.*, 1980]. Consequently, it is well-known that the heterogeneous reactions on sea-salt particles cause the modification of sea-salts—halogen depletion—, for examples, (X= Cl, Br, I)



The above reactions (R1_1 and R1_2) are based on the heterogeneous reactions between acidic species and sea-salts as alkaline halides. Indeed, some field measurements showed the internal mixing states between sea-salts and acidic species such as sulfates and nitrates in marine boundary layer [Wouters *et al.*, 1990; Sievering *et al.*, 1991, 1992, 1995; McInnes *et al.*, 1994; Pósfai *et al.*, 1995; Hara *et al.*, 1996, 1999]. Therefore the heterogeneous reactions on sea-salt particles have the possibility of an important role as the sink of acidic species in the atmosphere. Recent laboratory measurements also suggested other possible reactions between sea-salts and reactive nitrogen oxides [*e.g.*, Behnke *et al.*, 1996; Rossi *et al.*, 1996], for examples,



The products in the above reactions (R1_3 - R1_6) have a high reactivity and unstableness in daytime, and can release high reactive halogen radicals through the photochemical decomposition. In addition, previous works suggested a large influence of halogen radicals on the atmospheric chemical reactions with organic species [Jobson *et al.*, 1994; Kawamura, *private communication*] and ozone budgets [*e.g.*, Barrie *et al.*, 1988; Zellner, 1999; Georgii and Warneck, 1999]. In particular, surface ozone depletion during the polar sunrise has been observed as one of typical phenomena associated with atmospheric halogen chemistry for last decade. According to Barrie *et al.* [1988], this phenomenon might be due to the catalytic reactions by halogen radicals. Similar phenomenon is not still observed in mid-latitudes and tropical regions, but similar processes are likely to have somewhat contribution to ozone budget and other atmospheric chemical processes in mid-latitudes [Vogt *et al.*, 1996; Sander and Crutzen, 1996; Hebestreit *et al.*, 1999; Dickerson *et al.*, 1999, Nagao *et al.*, 1999]. The catalytic system of halogen radicals requires the sources of the precursors and the recycle processes of lower reactive halogen species to higher reactive halogen species in the atmosphere. Although some reactive halogen species are released from the modification of sea-salt particles as mentioned above (*e.g.*, R1_1 - R1_6), the details of the heterogeneous processes on sea-salt particles as the source of reactive halogen species in the troposphere, especially polar regions, are still unknown.

1_3. Previous study about heterogeneous processes on aerosol particles

The heterogeneous chemistry of aerosol has been developed on the discussion with bulk analysis of aerosol constituents [*e.g.*, Martens *et al.*, 1973; Hitchcock *et al.*, 1980; Luria *et al.*, 1991; Sievering *et al.*, 1991, 1992, 1995; Mizohata and Ito, 1995], the model calculations [*e.g.*, Zhang *et al.*, 1994; Dentener *et al.*, 1996] and the laboratory measurements [*e.g.*, Finlayson-Pitts *et al.*, 1986, 1989; Behnke *et al.*, 1996]. However, most of the field measurements rarely dealt with the interaction of gaseous matters, the heterogeneously mixing states and the various phases of individual aerosol particles—with wet or dry surface?—in the atmosphere, in spite of basic information for heterogeneous processes. Then this study attempt to discuss the aerosol heterogeneous chemistry based on not only bulk concentration of each specie but also the mixing

states of individual aerosol particles and the interaction of gaseous reactive species.

1_4. Previous works of individual particle analysis

Individual particle analysis has been made mostly by means of the electron microscopy (EM) equipped with energy-dispersive X-ray spectrometer (EDX), which provides only the information of major element ($Z \geq 5$) in each aerosol particle [e.g., Okada *et al.*, 1990; Mouri and Okada, 1993; McInnes *et al.*, 1994]. Chemical tests have been often applied to identification of some ion species using electron microscopy; SO_4^{2-} [Bigg *et al.*, 1974; Qian *et al.*, 1991; Yamato and Tanaka, 1994], NO_3^- [Isawa and Ono, 1979; Mamane and Pueschel, 1980; Wu and Ono, 1988; Mamane *et al.*, 1992; Qian *et al.*, 1991; Hara *et al.*, 1999], Cl^- [Ueno and Williams, 1983; Häufel and Weisweiler, 1998], and NH_4^+ [Weisweiler and Schwarz, 1988]. The recent review of thin-film-techniques was given by Qian and Ishizaka [1993], and Podzimek and Podzimek [1999]. In the present study, scanning electron microscopy (SEM) and nitron-thin-film technique were used for the observation of phase and morphology of individual aerosol particles, and the identification of NO_3^- . But chemical states such as NaNO_3 in individual particles cannot be obtained from by means of thin-film technique. Then laser microprobe mass spectrometry (LAMMS), which offers individual particle analysis with high sensitivity for all elements for elemental, fragmental, and molecular information with regulated laser power density, was utilized for the identification of chemical states in individual particles. Details of the LAMMS technique are described by Verbueken *et al.* [1988], Hara *et al.* [1996], and De Bock and Van Grieken [1999].

1_5. Atmospheric observations in Arctic region

The observation in remote and Polar Regions is suitable for the investigation of atmospheric aerosol chemistry because of less local anthropologic sources and unique meteorological condition. Polar region has especially unique conditions on the variation of solar radiation, so that polar region is very useful field from the viewpoint of atmospheric chemistry in nighttime and/or daytime. In winter/spring Arctic, a large amount of pollutants (e.g., acidic gasses, organic

matters, and heavy metals) are transported from mid-latitude area including Russian, Europe and north-America [Rahn *et al.*, 1980; Barrie and Hoff, 1984; Pacyna, 1993; Heintzenberg and Leck, 1994]. Thus the measurements in the winter Arctic region will provide a better understanding of nighttime chemistry under conditions with slightly anthropogenic influence.

Also winter Arctic region is very important from the viewpoint of global earth science and atmospheric chemistry. Last two-decade years, many investigators focused mostly Arctic haze phenomena due to transport of pollutants from mid-latitude area [e.g., Rahn, 1981; Schnell, 1984; Jaffrezo and Davidson, 1994; Sturges *et al.*, 1993; Franke *et al.*, 1997]. Transport of pollutants to Arctic region should cause the contamination in the Arctic region [Murozumi *et al.*, 1969; Headley, 1996; Hong *et al.*, 1996; Reimann *et al.*, 1996] and the large influence on eco-system in Arctic region [Norheim, 1967; Godzik, 1991; Grodzinska and Godzik, 1991; Headley, 1996]. Moreover, atmospheric chemistry during polar sunrise — associated with low ozone episodes on surface — has been observed for last decade year [e.g., Barrie *et al.*, 1994; Barrie and Platt, 1997]. Previous works [e.g., Barrie and Platt, 1997] showed that these phenomena were closely related to photochemical processes of higher reactive species and anthropogenic species, which should be gradually accumulated in winter season and/or nighttime with no- or less solar radiation. During outbreaks of Arctic air mass with a large amount of higher reactive species —such as PAN, HONO, N_2O_5 , and halogen species—, which are unstable under the conditions with solar radiation and warmer air, Arctic air mass can affect significantly the oxidant chemistry of northern hemispheric troposphere. However, better understanding of the sources of high reactive species is not obtained yet.

1_6. Purpose and focus in this study

This study mainly aimed to obtain the better understanding of chemical roles —sink of acidic species, and sources of reactive halogen species— of sea-salt particles in winter/spring Arctic from the viewpoint of heterogeneous chemistry on sea-salt particles. In Chapter 2, the details of observation at Ny-Ålesund and analysis are given. Chapter 3 describes and discusses the transport of oceanic air mass and aging/modification processes of sea salt particles. The role as the sink of sea-salt particles is discussed in Chapter 4 on the basis of the measured variations of the concentration of each specie in aerosol particles and acidic

gasses, mixing states of individual aerosol particles, and simple uptake model. Then Chapter 5 discusses the roles of sea-salt particles as the sources of reactive halogen species.

Chapter 2

Sample and experiments

2-1. Sampling location and the local environment

All atmospheric samples were collected at Ny-Ålesund (78°55'N, 11°56'E), Svalbard, during the winter/springs (December - early March) in 1994/1995, 1995/1996, 1996/1997 and 1997/1998. The location of Ny-Ålesund, Svalbard, is shown in Figure 2_1a and 2_1b. The observatory, *Rabben*, was built on the hill (about 40m a.s.l.), and located westerly about 1.5 km away from the village of Ny-Ålesund (a few m a.s.l.) where there is a power. Northern side of *Rabben* looks toward the inlet, *Kingsfjorden*, with the covered sea ice and snow during the winter/springs, and southern side toward mountains and glacier such as *Mt. Zeppelin* (474m a.s.l.) and *Bröggerbreane*. Although there is a small airport in southern front of *Rabben*, flights were usually once or twice a week in wintertime. Air sampling was stopped completely between a preparation of airplane arriving—mainly clearing snow—and the departure in order to prevent the local contamination.

The population of the village was 20 – 50 during the winters. About vehicles such as cars and snowmobiles were used in the village. Then local traffic should have insignificant contribution to contaminate local atmosphere. Since electric power is supplied to all buildings and systems such as heating and cooking, activities of a thermal power station may have the largest contribution to local atmospheric contamination.

2_1_1. Meteorological condition at Ny-Ålesund during the winter

Wind roses of hourly average resultant wind directions and speed are

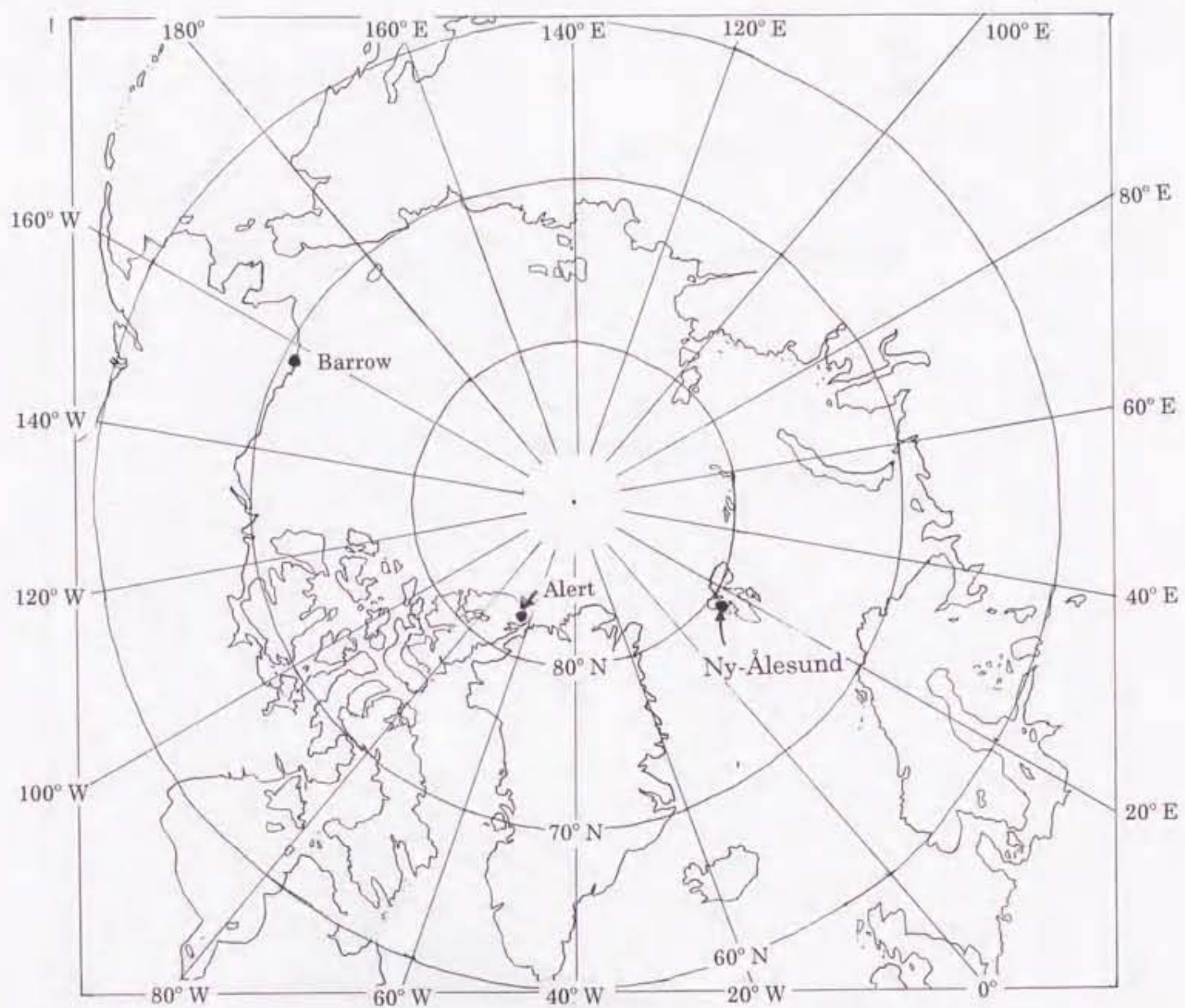


Figure 2_1a. Location of Ny-Ålesund and other observatory in Arctic region.

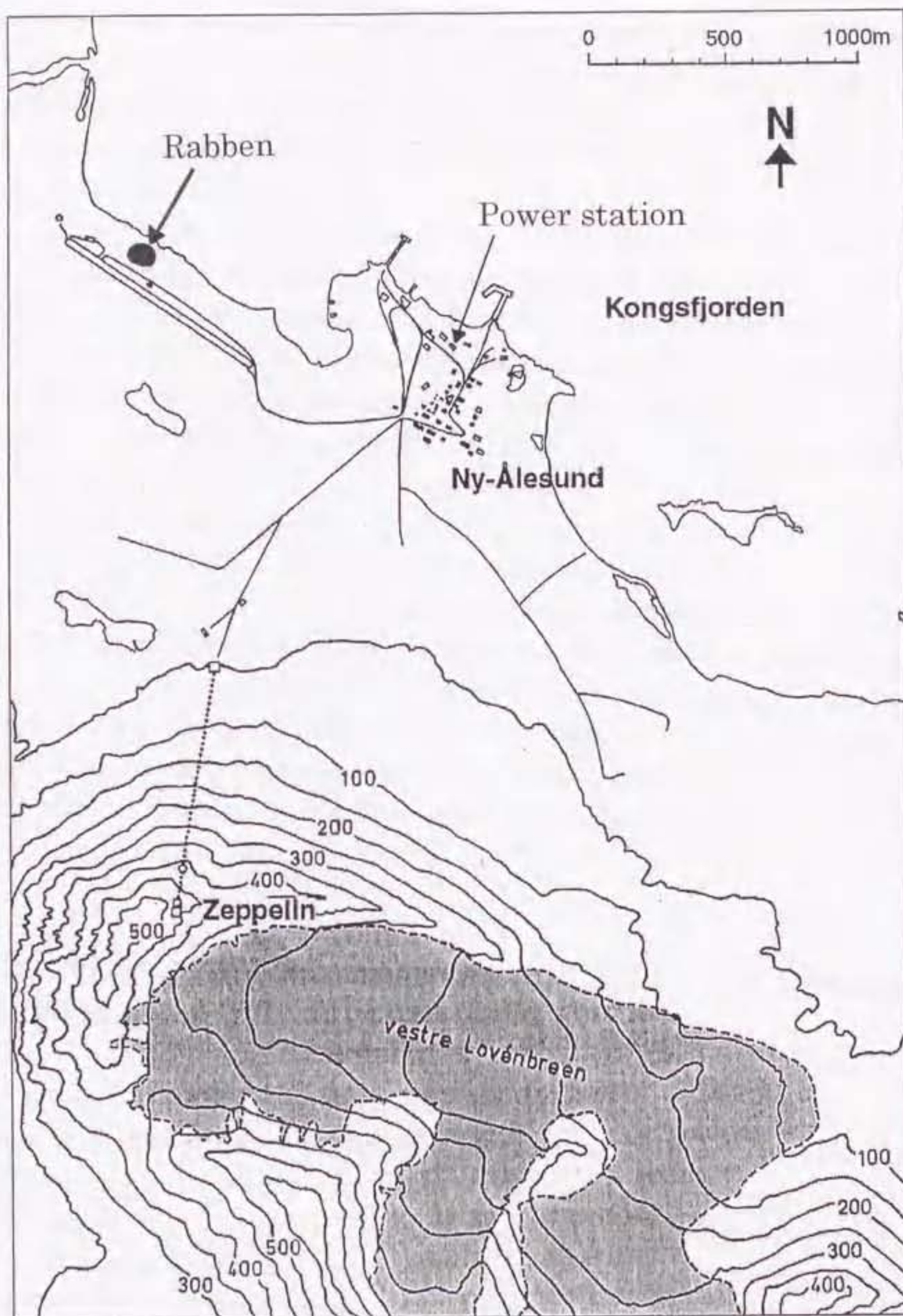


Figure 2_1b. Topographic map of Ny-Ålesund and surroundings. The shaded area shows a glacier.

presented in 16 direction classes and 3 speed classes (Figure 2_2). Prevailing wind was not observed during the winter times in each winter. When the wind was blowing from the village —eastern side of *Rabben*—, some samples might be contaminated slightly from the local human activities (*e.g.*, power station and a few traffic) in the village.

Figure 2_3 shows the variations of ambient temperature, relative humidity and wind speed in past 3 winters, 1995/1996, 1996/1997 and 1997/1998. In each winter, sudden increase of air temperature and relative humidity to 0 °C and >95% was found under the conditions with storm and precipitation. These events may be derived from storm access associated with the transport of oceanic air mass from mid-latitudes. Details of transport of oceanic air mass were described in Chapter 3.

As the warm current comes up to Greenland Sea, open sea area is distributed to southern side of Svalbard as shown in Figure 2_4a and b. In past 2 winters, 1996/1997 and 1997/1998, the sea ice grew from mid-January toward spring season. The farthest distance from the ice margin to Ny-Ålesund was above 100 km in both winters. Then, very local emission sea-salt particles from sea surface should have few contributions to atmospheric sea-salt particles at Ny-Ålesund. This distance was quite shorter than other Arctic observatory such as at Barrow and Alert where is >1000km away from open sea area in winter/spring season.

2-2. Samples of aerosol particles and acidic gas for bulk analysis

A two-stage low volume impactor (LVI) with a back-up filter was used to collection of aerosol particles for subsequent chemical analysis. The LVI, which is made from conductive plastic, separated aerosol particles into a coarse (>2.3 µm in diameter) and the fine (0.2 ~ 2.3 µm in diameter) fraction at a flow rate of 1.2 L min⁻¹. As sampling medium was used aluminum foil for 1994/1995 winter, pre-cleaned Cu plate for 1995/1996 winter and polyethylene sheet for 1996/1997 and 1997/1998 winters. Sampling of size-segregated aerosols was carried out continuously for 2-3 days at a flow rate of 1.2 L min⁻¹.

No-size-segregated aerosol particles and acidic gases were collected using a filter holder with a Teflon membrane filter (47 mm PTFE with pore size of 1.0 µm; Advantec) followed by two 47 mm filter papers (5A; Advantec) impregnated

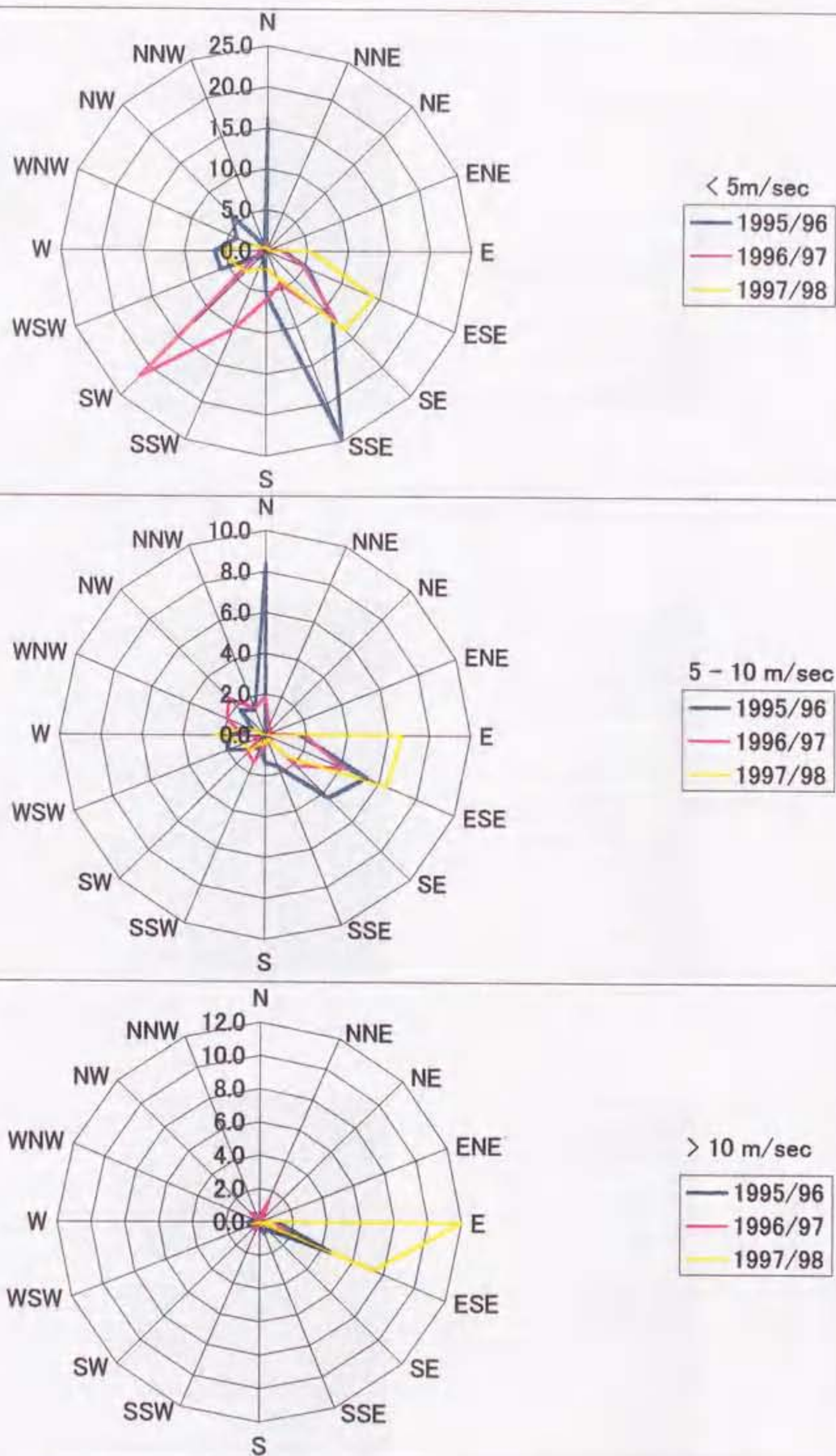


Figure 2_2. Wind rose of surface winds for Ny-Alesund for 1995-1998. The distribution of resultant wind direction and speed are given in units of percent occurrence for the past 3 winters. Wind speed is displayed as a function of direction in 3 speed classes.

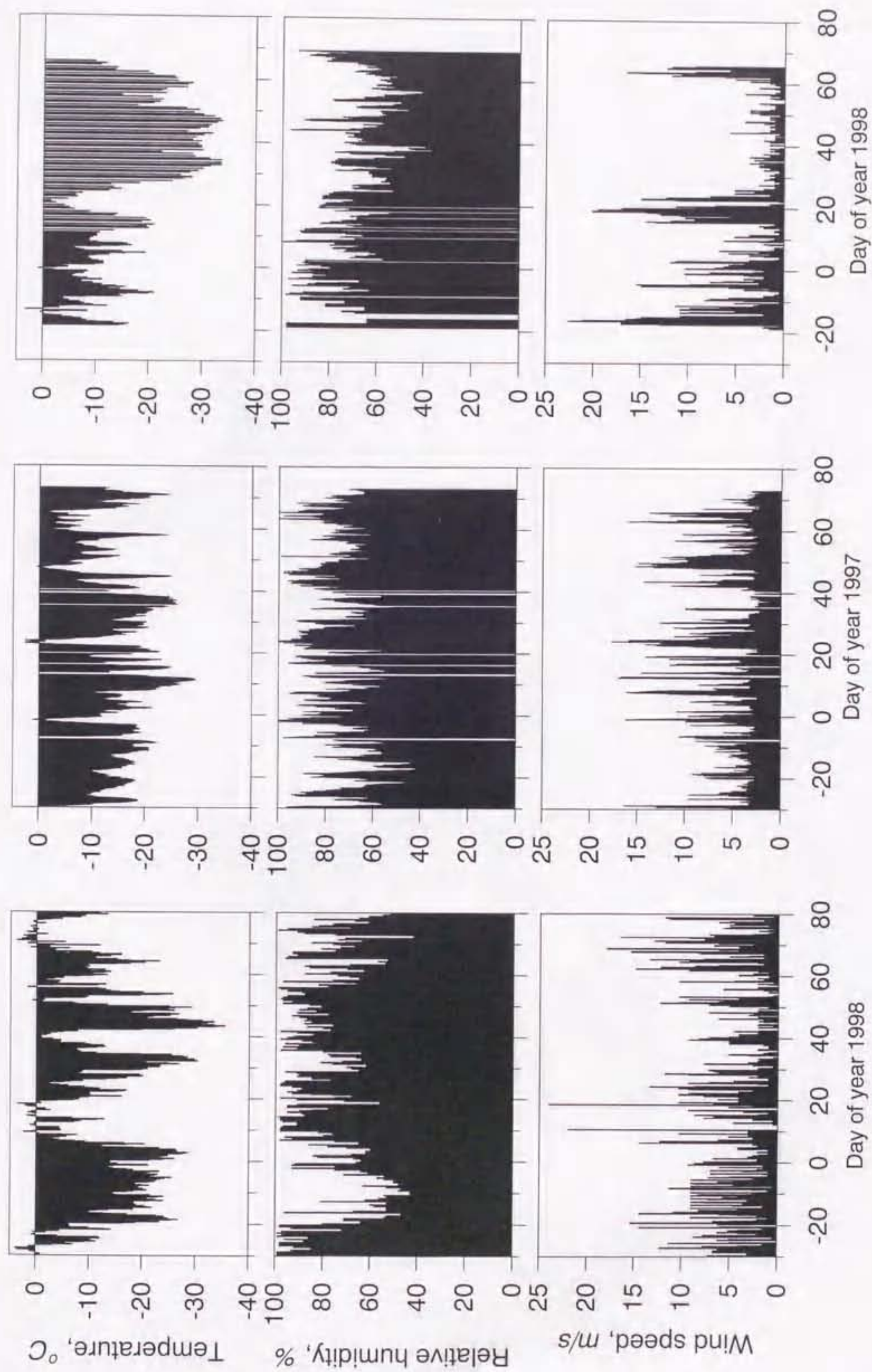


Figure 2_3. Variations of air temperature, relative humidity and wind speed in past 3 winters (1995/1996, 1996/1997 and 1997/1998)

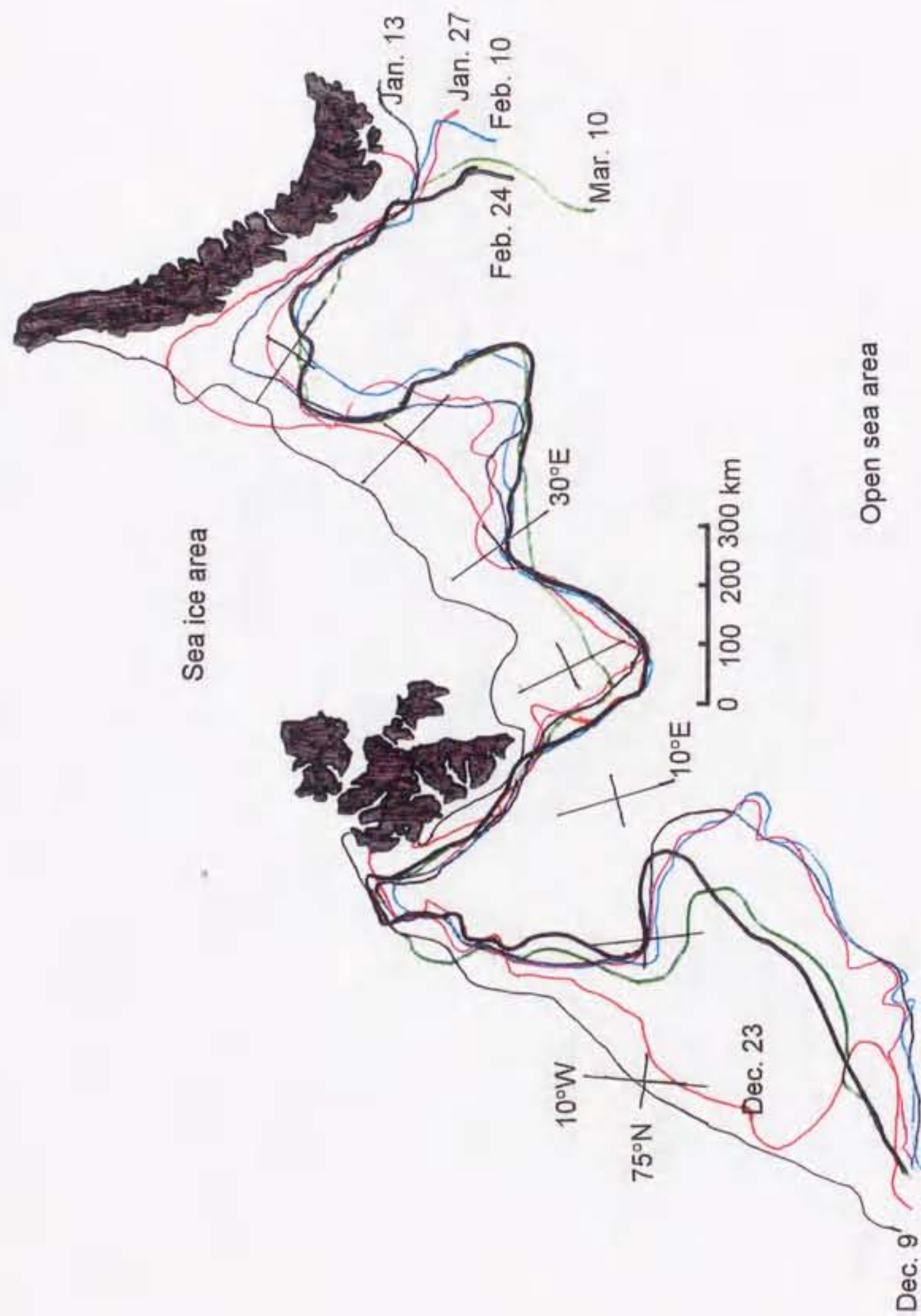


Figure 2_4a. Location of sea-ice margin near Svalbard in 1996/1997 winter.
This figure was made by data from Norwegian Meteorological
institute.

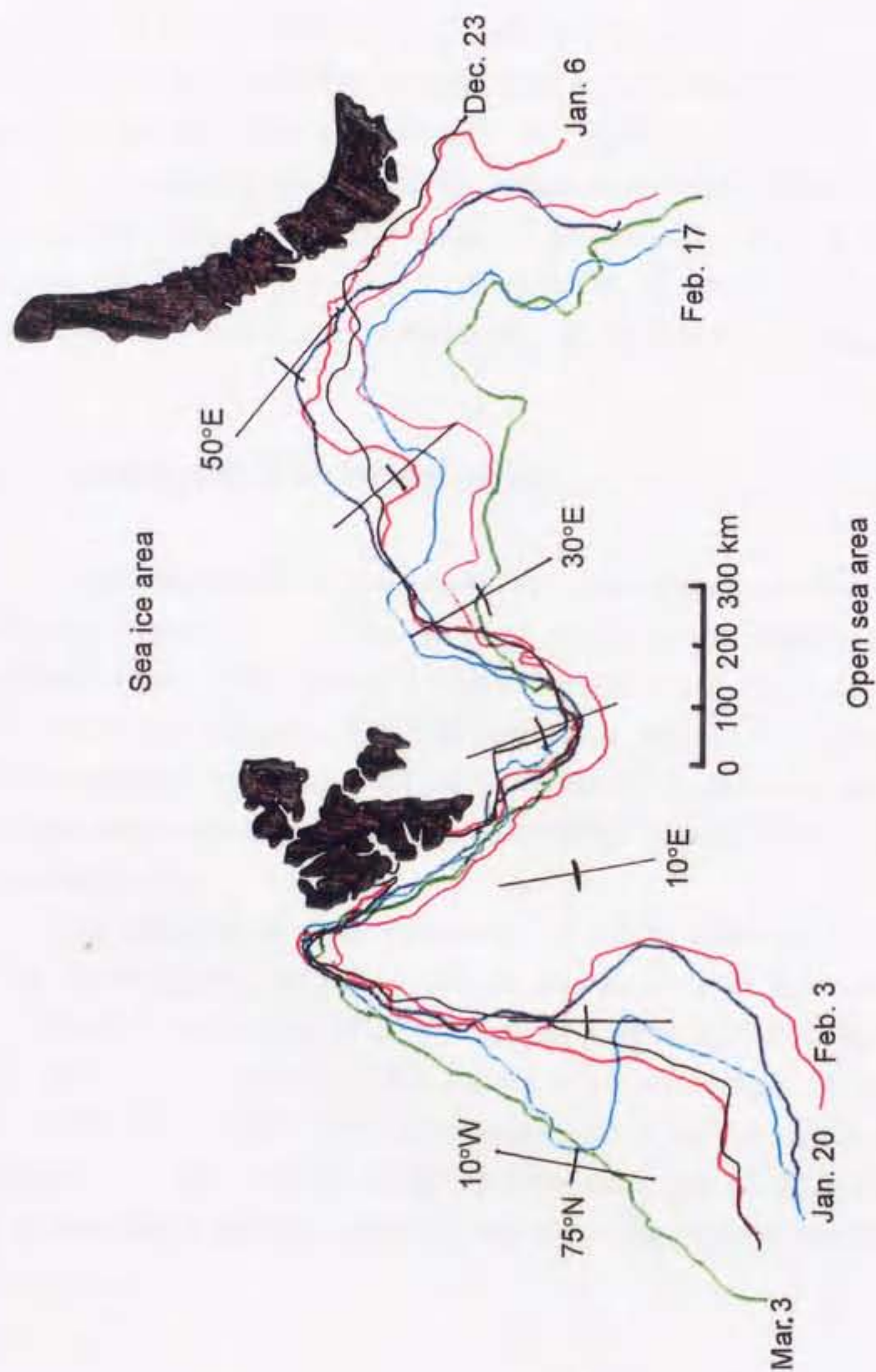


Figure 2_4b. Location of sea-ice margin near Svalbard in 1997/1998 winter.
This figure was made by data from Norwegian Meteorological institute.

with aqueous solution (300 μ l) of 1 % Na_2CO_3 and 1 % Glycerol. Sampling of non-size-segregated aerosols and acidic gases was continuous for half ~ one day at a flow rate of 5 L min^{-1} in 1995/1996 winter and 18 L min^{-1} in 1996/1997 and 1997/1998 winters. Sampling time depended on the weather conditions.

All air samplers were set outside and supported downward facing in weather shields at a height of 1.5 m from snow surface because of collection of the atmospheric samples under ambient temperature, and because of the reduction of volatilization of thermally unstable species such as ammonium nitrate. Each atmospheric sample was kept into polypropylene 15 ml centrifuge vials with an airtight cap (Iwaki Co.) immediately after sampling in order to prevent contamination during the sample storage. Sample vials were packed in polyethylene bags and were kept at about -20°C in a freezer until chemical analysis in Japan. For qualitative check of atmospheric samples, procedural blank samples were taken periodically. Details were given later section (2-2-2).

2-2-1. Analytical Procedures

For extraction of water-soluble constituents in aerosol particles, 14 ml of ultra-pure water (18.3 M Ω , Milli-Q water) was added to each sample vial. Concentrations of the water soluble constituents were determined with an ion chromatograph (Dionex, DX-300) using a 500 μ l 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.

For extraction and treatment of acidic gaseous components on alkaline impregnated filters, 10 ml of ultra-pure water and 0.3 ml of 3% H_2O_2 solution were added to samples of the alkaline impregnated filters. Concentrations of acidic gases were measured by an ion chromatograph (TOA, ICA-5000) using a 100 μ l injection loop in 1995/96 winter and a 200 μ l injection loop in 1996-1998 equipped with an AS12A analytical column, an AG12A guard column and an auto suppression system (ASRS-I, all columns and equipment are manufactured by Dionex).

2-2-2. Procedural blank level of each medium

Procedural blanks are determined for the background in the filter field blanks rather than the sensitivity of analytical technique. Field blanks were taken periodically for each sampling system: once per 2 weeks for LVI samples and once a week for alkaline impregnated filters and its prefilter. Blank samples were treated as air samples but without the passage of air. When the field blanks were above the analytical detection limit of ion chromatograph, atmospheric concentrations were corrected by the mean value of field blanks. The correction was done only if the sample amount was two standard deviations (2σ) above the mean field blank levels. Atmospheric concentrations of each constituent were calculated using total volume of air at 0 °C and 1 atm and the sample amount corrected by the mean procedural blank in the present study. Procedural blanks and sampling medium of each sampling system were listed in Tables 2_1a and 2_1b. Atmospheric concentrations of the procedural blank samples were estimated using a mean sampling air volume in each winter.

2-3. Aerosol sampling for individual particle analysis

Atmospheric aerosol particles for individual particle analysis were collected daily on electron microscopic grid with collodion film and some reagents for SEM observation, and on aluminum foil for LAMMS analysis using a 2-stage LVI (cut-off diameter, 2.3 μm and 0.2 μm at flow rate of 1.2 L min⁻¹) for 10 minutes in SEM samples and 15-20 minutes in LAMMS samples. The LVI was also set downward facing in weather shields at a height of about 1.5 m from snow surface as same as bulk sampling.

2-3-1. Aerosol samples for SEM observation

Sampling of aerosol particles for SEM observation was carried out only in 1996/1997 and 1997/1998 winters. Nitron (C₂₀H₁₆N₄) coated and/or carbon coated collodion films on copper electron microscopic grids were used as sampling medium. Samples were kept into polyethylene capsules immediately after sample collection. The polyethylene capsules with each sample except nitron-thin-films were packed in polyethylene bags with a zipper. Nitron-thin-films were packed into the bag after octanol vapor treatment as described below. All bags with samples were put into airtight box with silica gels until SEM observation in the

Table 2_1a. Blank concentration (nmol/m³) of each anion

<i>Sampling medium for LVI</i>										
	MSA	BrO3	Cl	NO2	Br	NO3	SO4	Oxalate	PO4	Volume(m3)
1995/96	n.d.	-	0.056	n.d.	n.d.	0.032	n.d.	n.d.	n.d.	3.4
1996/97	n.d.	-	0.01	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	3.7
1997/98	0.12	0.02	0.01	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	2.6
1995/96	0.01	-	0.31	n.d.	n.d.	0.11	0.01	n.d.	n.d.	3.4
1996/97	0.01	-	0.31	0.04	0.00	0.11	0.01	n.d.	n.d.	3.7
1997/98	0.11	n.d.	0.58	n.d.	n.d.	0.42	0.37	n.d.	n.d.	2.6
<i>Sampling medium for prefilter</i>										
	MSA	BrO3	Cl	NO2	Br	NO3	SO4	Oxalate	PO4	Volume(m3)
1995/96	n.d.	-	5.91	1.09	n.d.	1.68	0.21	n.d.	n.d.	2.6
1996/97	n.d.	-	0.49	0.04	n.d.	0.38	0.32	n.d.	n.d.	11.5
1997/98	0.05	n.d.	0.09	n.d.	0.01	0.11	0.10	n.d.	n.d.	10.9

-: not determined

n.d.: not detected

laboratory.

In the present study, SEM observation was mainly based on nitron-thin-film-technique because focused were the mixing states of nitrates, which react with nitron to form obvious needle-like crystals after exposing to octanol vapor. Details of the nitron-thin-film technique were described by Isawa and Ono [1979], Mamane and Pueshel [1980], and Wu and Ono [1988]. Nitron-thin-films were exposed to octanol vapor for about 24 hours immediately after sample collection in order to grow the needle-like crystals due to nitrates, and to prevent them from the contamination and the evaporation of $\text{HNO}_3/\text{NO}_3^-$ until SEM observation. All SEM samples were transported to Japan and then were observed with SEM (Akashi Beam Tech., ABT-55) in the laboratory at Nagoya University. For the reduction of sample damage (*e.g.*, vaporization) and charging of samples by radiation of electron beam, a accelerate voltage was regulated to 5 kV during the SEM observation. To estimate the number fraction for aerosol particles containing NO_3^- , the number of aerosol particles on nitron-thin-films and aerosol particles with positive reaction on nitron-thin-film were counted from SEM images. More than 85 particles (maximum 2104 particles) were counted for one sample stage fraction.

2-3-2. Aerosol samples for LAMMS analysis

SEM has been only used for the observation of aerosol morphology and the phase. The nitron-thin-film technique has been only used to identify effectively particles containing NO_3^- . Thus, the individual aerosol particles were analyzed with LAMMS for identification of chemical composition in individual aerosol particles containing NO_3^- . Commercial aluminum foils were chosen for sampling medium for LAMMS samples because of high purity, clean surface and no isotope. The LAMMS samples in winter Arctic were kept into polypropylene 15 ml centrifuge vials with an airtight cap (Iwaki co.) immediately after sampling in order to prevent contamination until analysis in laboratory. The sample vials were also packed in polyethylene bags as same as filter samples and were kept at about -20°C in a freezer until LAMMS analysis in Japan.

2-3-3 Instruments of LAMMS

A reflection-type laser microprobe mass spectrometer, LAMMA-1000 (Leybold-Heraeus GmbH), was used in this study. Aluminum foil with aerosol particles was fixed on sample holder using conductive double adhesive tape. Individual aerosol particles collected on an aluminum foil were ionized by a laser pulse beam ($\tau=6$ nsec of Q-switched 4th harmonic Nd-YAG laser, $\lambda=266$ nm) focused 1 – 2 μm in diameter, and the generated ions were perpendicularly introduced into a time-of-flight type mass spectrometer, where the ions were separated according to their m/z ratios. For measurements of the samples, the laser energy density was maintained at a slightly over the threshold of ionization in order to obtain fragmental and molecular information.

2-3-4. Reference spectra for identification of unknown samples

LAMMS is suitable for identification of chemical composition in individual aerosol particles because molecular and some fragment ions can be detected. However, it is difficult to identify unknown samples directly, because the ionization mechanism and fragmental patterns of each specie is still unknown. For interpretation of sample spectra, pure reagents were used as the reference materials. An aliquot of a saturated solution of a reference reagent prepared with ultra pure water (18.3 M Ω ; Milli-Q water) was placed on aluminum foil substrate and dried in vacuum set on a sample stage of the LAMMS. Soot samples were prepared by the combustion of candle and some organic species such as toluene and benzene. Soil samples were collected at Antarctic region (Midori pond and Lang Hovde). Spectra of pure silicate materials were also obtained by Tsugoshi *et al.* [1991]. Examples of typical spectra of reference reagents in negative ion mode were shown in Figure 2_5. The characteristic fragment ions of reference samples for identification of unknown species were given in Table 2-2.

2-3-5. Relative abundance for the quantitative estimation by LAMMS

Because of poor reproducibility of LAMMS spectra, the relative abundance was used as the denominator in this study. A fixed number of individual aerosol particles visually focused were shot, and the ratios of the

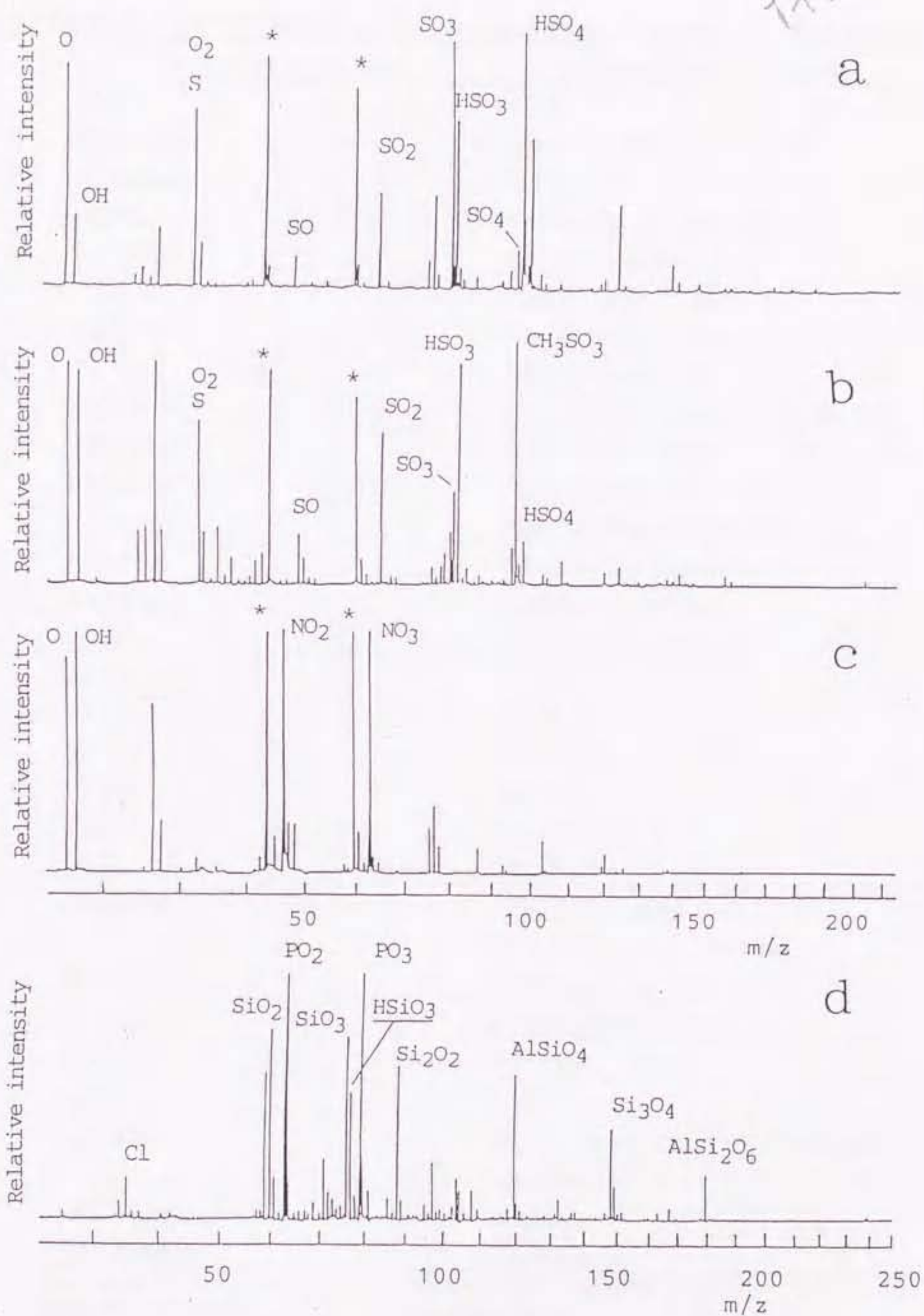


Figure 2_5. Examples of reference spectra
 (a) Sulfuric acid on Al foil
 (b) Ammonium methanesulfonate
 (c) Ammonium nitrate
 (d) Soil sample collected at Midori pond near Syowa station

Table 2_2 List of reference reagents and their characteristic fragment ions

Reference materials	Characteristic ion species
H ₂ SO ₄	HSO _n ⁻ (n= 3, 4; m/z= 81, 97)
(NH ₄) ₂ SO ₄	HSO _n ⁻ (n= 3, 4; m/z= 81, 97)
NH ₄ HSO ₄	HSO _n ⁻ (n= 3, 4; m/z= 81, 97)
Al ₂ SO ₄	HSO _n ⁻ (n= 3, 4; m/z= 81, 97)
Na ₂ SO ₄	Na ₃ SO ₄ ⁺ (m/z= 165)
	NaSO ₄ ⁻ (m/z=119)
Na ₂ SO ₃	Na ₃ SO ₃ ⁺ (m/z= 165)
	NaSO ₃ ⁻ (m/z=119)
CaSO ₄	SO _n ⁻ (n=1-4) (m/z= 48, 64, 80, 96)
CH ₃ SO ₃ H	CH ₃ SO ₃ ⁻ (m/z=95)
NaCH ₃ SO ₃	Na ₂ CH ₃ SO ₃ ⁺ (m/z=141)
	Na(CH ₃ SO ₃) ₂ ⁻ (m/z=213)
NH ₄ NO ₃	NO _n ⁻ (n=2,3; m/z=46, 62)
NaNO ₃	Na ₂ NO ₃ ⁺ (m/z=108)
NaNO ₂	Na(NO ₂) ₂ ⁻ (m/z=115)
NaCl	Na _m Cl _n [*]
KCl	K _m Cl _n [*]
MgCl ₂	Mg _m Cl _n [*]
CaCl ₂	Ca _m Cl _n [*]
CuCl ₂	Cu _m Cl _n [*]
NaBr	Na _m Br _n [*]
Na ₂ HPO ₄	Na ₃ HPO ₄ ⁺ (m/z=119)
	(Na ₂ PO ₄)NaO ⁻ (m/z=180)
K ₃ PO ₄	KHPO ₄ ⁻ (m/z=135)
(COOH) ₂	COOCOO ⁻ (m/z=88)
NaBrO ₃	Br ⁻ (m/z= 79, 81)
Soot ¹⁾	C _n [*]
Silicates	Si _m O _n [*] and XSi _m O _n [*] (X=metallic elements) ⁴⁾
Soil samples ²⁾	Al _x Si _y O _z ⁻
Soil samples ³⁾	Al _x Si _y O _z ⁻

1) Soot samples were prepared by combustion of toluene, benzene and candle.

2) Sand was collected at Midori pond, near Syowa station, Antarctica.

3) Rock was collected at Lang Hovde, Antarctica.

4) Tsugosi *et al.*, 1991

*: Fragment ions were obtained in both ion modes.

frequency of detected characteristic peaks for a specific component to the total analyzed particle number was defined as relative abundance of the species; hence, no matrix effect and poor reproductivity were encountered. Thus, relative abundance means the abundance of particles that contains the species of concern at more than their detection limit vs the total analyzed particles on the stage. However attention should be paid to the fact that relative abundance does not necessarily mean the absolute concentration of the species in the atmosphere because of total amount of particles collected was different for each sampling and the amount of particles on each stage were too small to be weighted. The discussion in Chapter 5 used the relative abundance as the denominator but not as their absolute concentration in the atmosphere. The relative error of the abundance in this study was less than 2 % against 200 shots. Interpretation of LAMMS spectra is manually done by comparison with reference spectra.

Chapter 3

Sea-salt particles in winter Arctic atmosphere —Transport of oceanic air mass and aging process—

3_1. Introduction

Sea-salt particles are one of the dominant species of atmospheric aerosol particles in troposphere, especially over oceanic and coastal regions. Sea-salt particles can play an important role in the atmospheric heterogeneous processes as mentioned in Chapter 1, so that the better understanding of chemical and physical properties such as phase, size distribution of sea-salt particles, and mixing states of each aerosol constituent is essential to reveal the roles of sea-salt particles, and the heterogeneous processes on the particles. This chapter summarizes the variations and the size distribution of sea-salts in aerosol particles, mainly Na^+ and Cl^- , and then attempts to estimate the aging index of oceanic air mass containing a large amount of sea-salt particles at Ny-Ålesund.

3_2. Results and discussion

3_2_1. Transport of oceanic air mass

The variations of non-size-segregated Na^+ concentration, air temperature, relative humidity, and wind speed in winters of the past 3 winters, 1995/1996, 1996/1997 and 1997/1998, were shown in Figure 3_1. The spiky peaks of Na^+ concentration were found under the windy condition and/or storm condition with higher relative humidity and higher temperature as marked by asterisks. Molar ratio of Na^+ concentration to Cl^- concentration in each winter was almost similar to molar ratio in seawater ($[\text{Cl}^-]/[\text{Na}^+] \approx 1.2$, Wilson [1975]) as shown in Figure 3_2. This correlation suggests that Na^+ and Cl^- in the atmosphere were mostly derived

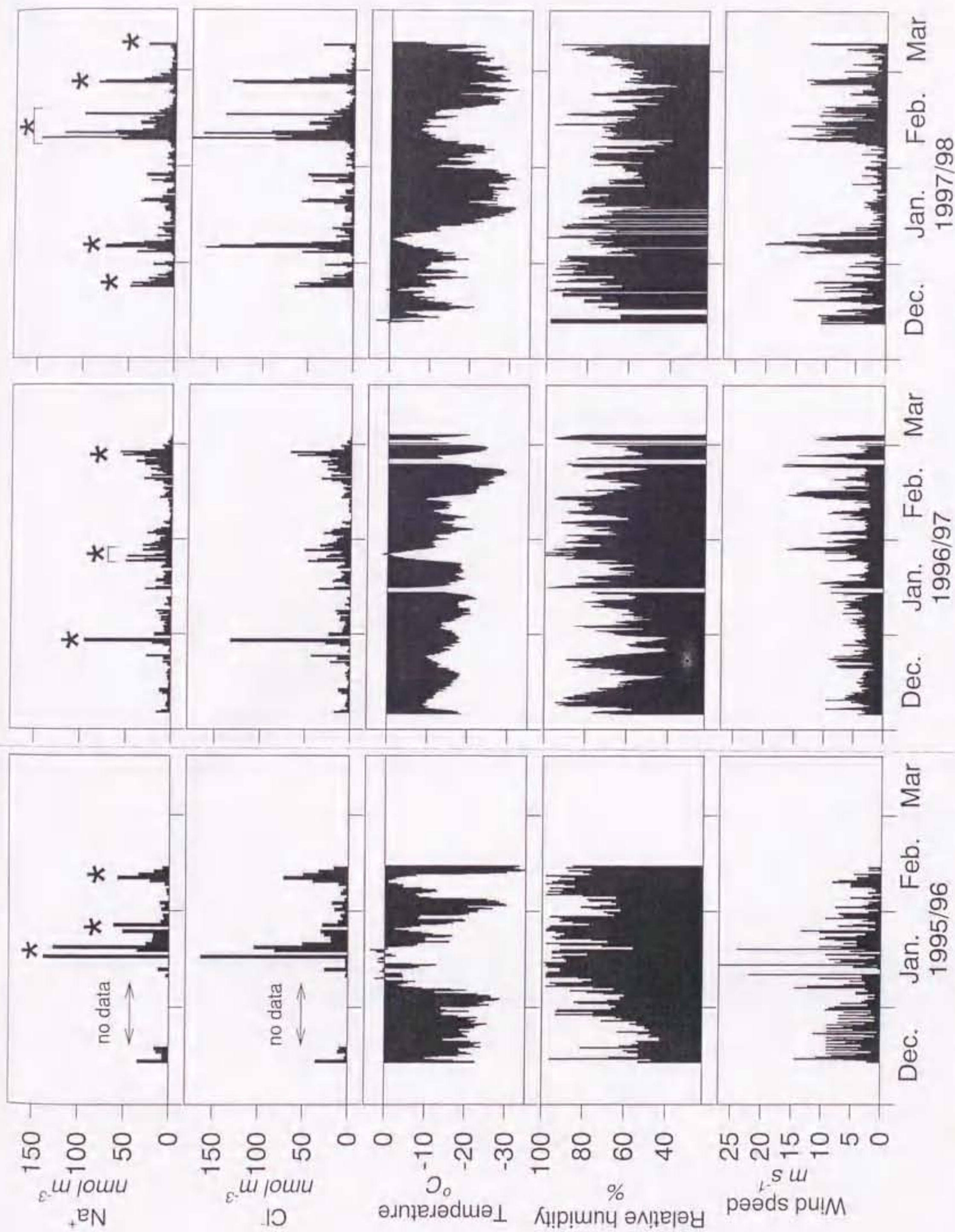


Figure 3_1. Variations of concentrations of Na⁺ and Cl⁻, temperature, relative humidity and wind speed. Asterisks indicate the storm conditions.

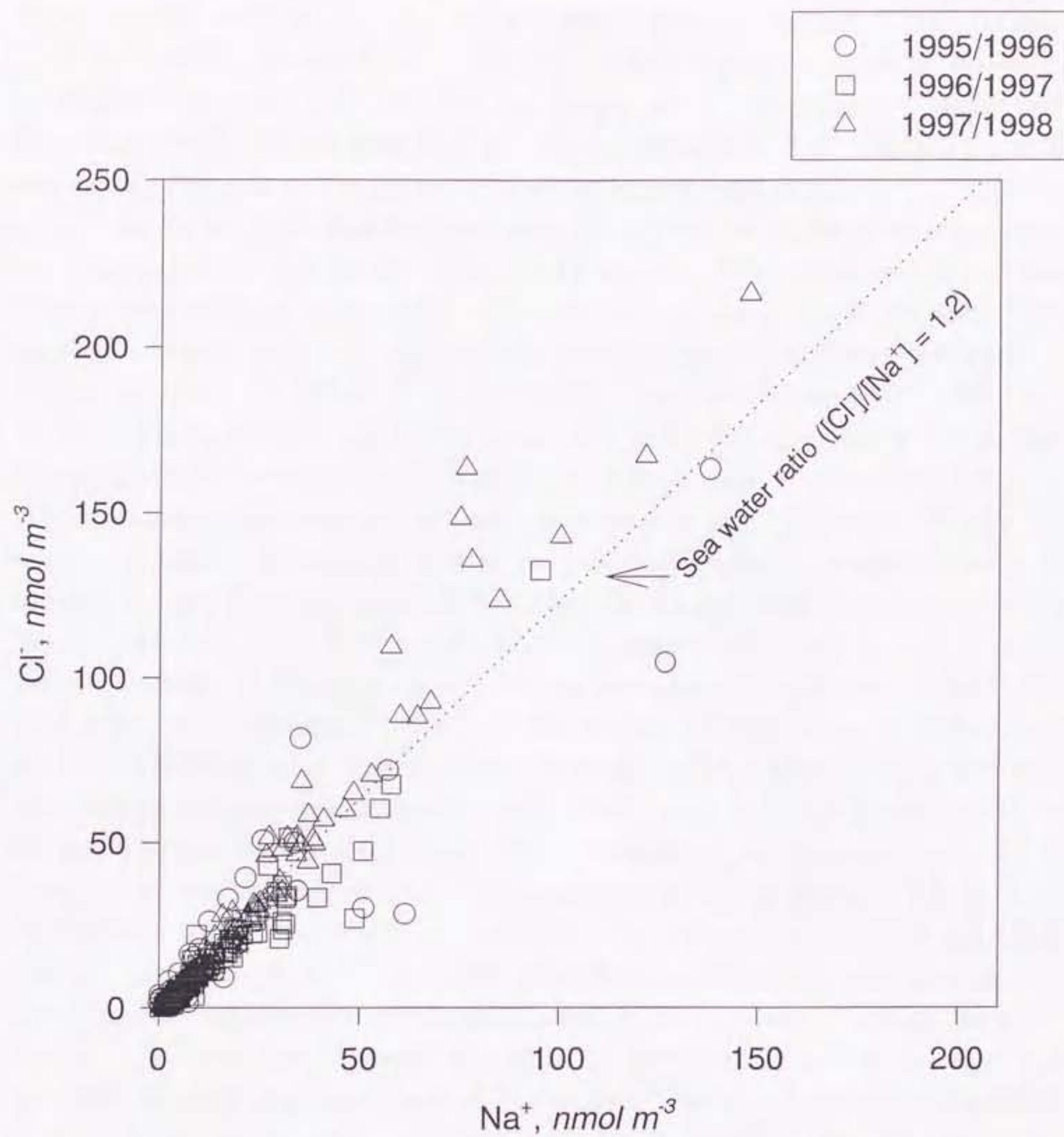


Figure 3_2. The correlation between Na^+ concentration and Cl^- concentration in past three winters, 1995/1996, 1996/1997 and 1997/1998.

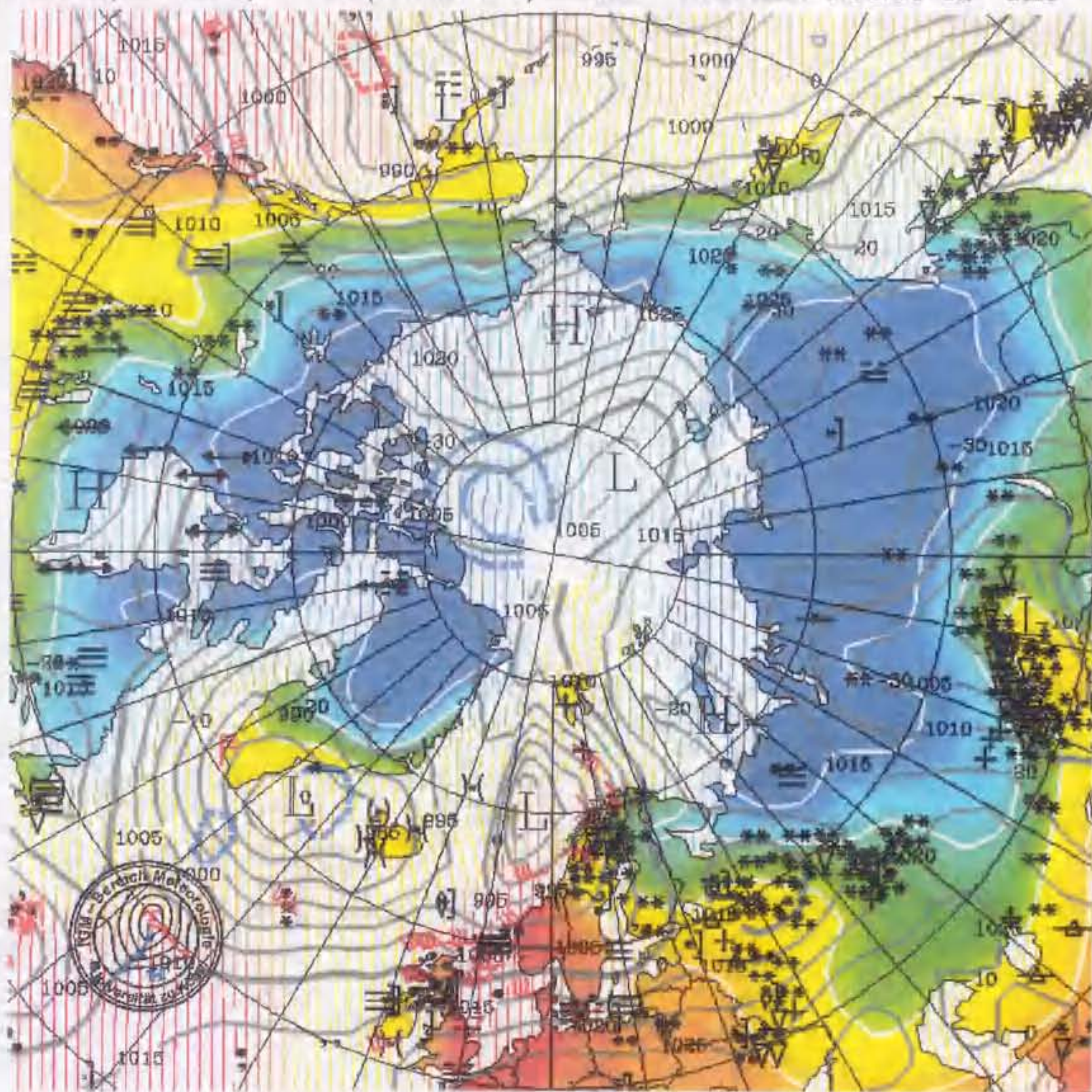
from sea-salt particles directly emitted from open sea surface. Then air mass with high concentration of Na^+ is likely identified as oceanic air mass. As shown in Figure 2_4a and 2_4b, the sea ice margin during December ~ March was located in south of Spitsbergen. Then very local emission of sea-salt particles around Ny-Ålesund can be ignored in spite of higher wind speed.

In Figure 3_3a and b shown were the typical examples of weather maps at surface level on 9 February 1998 and 16 January 1998, when higher Na^+ nss- SO_4^{2-} concentrations were found, respectively. Air parcel on 9 February 1998 should be transported from mid-latitude area through the access of low-pressure system as shown in Figure 3_3a. In addition, methanesulfonate (CH_3SO_3^-) was found in back-up mode and coarse mode (see in Figure 4_1) during the periods with high Na^+ concentration in 1995/1996 winter. Also Heitzenberg and Leck [1994] showed the presence of methanesulfonate at Ny-Ålesund during the winter seasons. Methanesulfonate is produced through photooxidation of dimethylsulfide (DMS) released from marine phytoplankton [Hatakeyama, 1985]. The concentrations of DMS and CH_3SO_3^- showed minimum in winter polar regions because of less bioactivity and less solar radiation [Turner *et al.*, 1989; Leck *et al.*, 1990; Bates *et al.*, 1992; Li and Barrie, 1993; Li *et al.*, 1993; Savoie *et al.*, 1993; Jaffrezo *et al.*, 1994]. Considering the lowest photooxidation ability in the dark Arctic winter [Barrie and Hoff, 1984], most of CH_3SO_3^- should be not produced in the dark winter Arctic. Then presence of methanesulfonate at Ny-Ålesund in winter season must be indirect evidence of transport from mid-latitude area with more bioactivity and active photochemical reactions. Although the air mass on 9 February 1998 was transported over Scandinavia, the concentrations of pollutants such as SO_2 and SO_4^{2-} were very lower as shown in Figure 3_4. Therefore, oceanic air mass at Ny-Ålesund should contain less pollutant despite transport from mid-latitudes. On the other hand, air parcel flowed from higher Arctic region on 16 January 1998, when higher concentrations of pollutants such as SO_2 and nss- SO_4^{2-} were found, as shown in Figure 3_3b. Therefore, Arctic air mass should be identified as polluted air mass.

3_2_2. Modification of sea-salt particles

Figure 3_5a shows the variations of Na^+ concentration and its mass size fraction in past 4 winters, 1994/1995, 1995/1996, 1996/1997 and 1997/1998, and Figure 3_5b those of Cl^- . Na^+ was mainly distributed in coarse

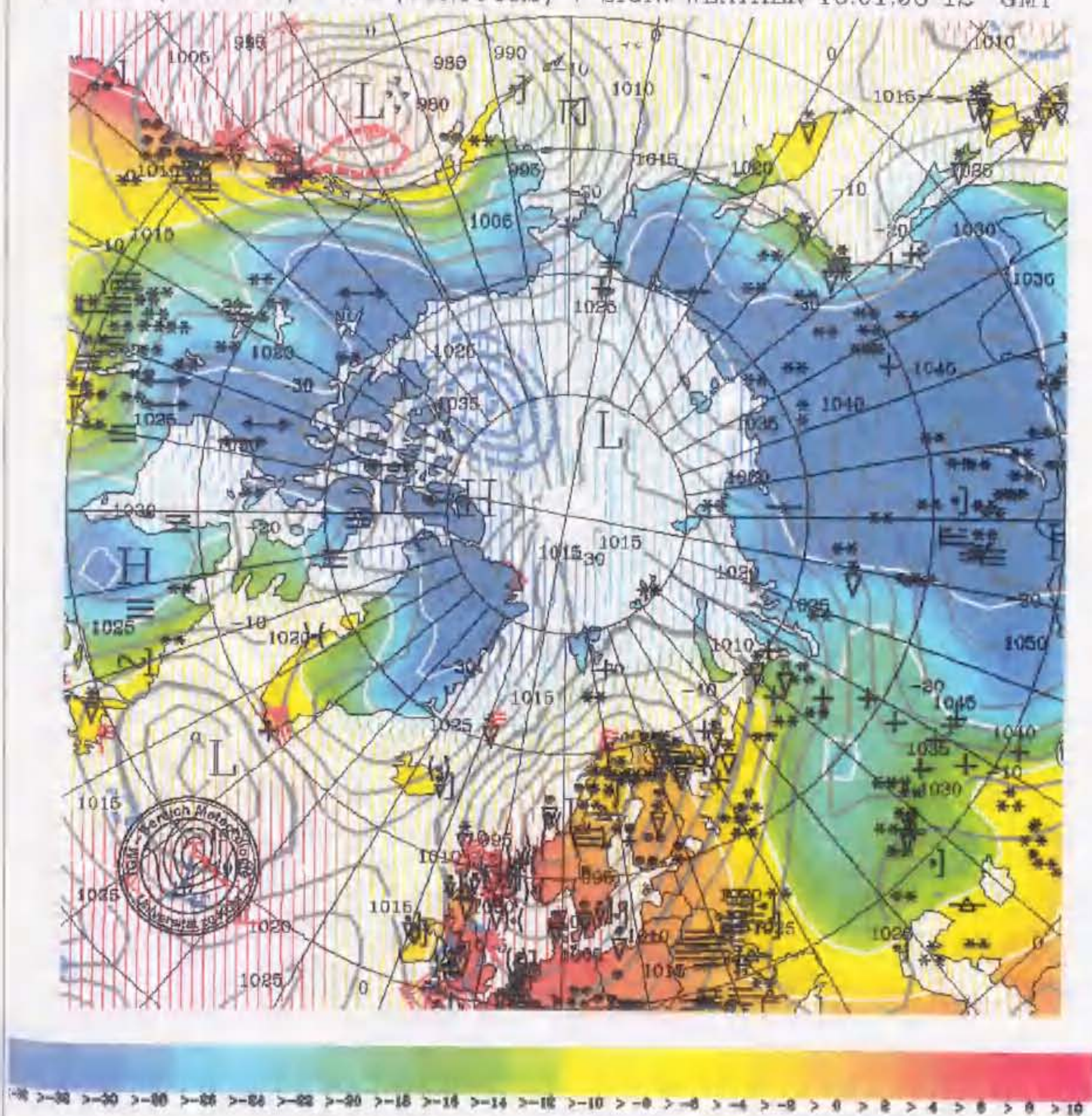
2M TEMP.(COLORED) + SLP(CONTOURS) + SIGN. WEATHER 9.02.98 12 GMT



Air temperature (°C)

Figure 3_3a. Weather map at surface level on 9 February 1998.

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Air temperature (°C)

Figure 3_3b. Weather map at surface level on 16 January 1998.

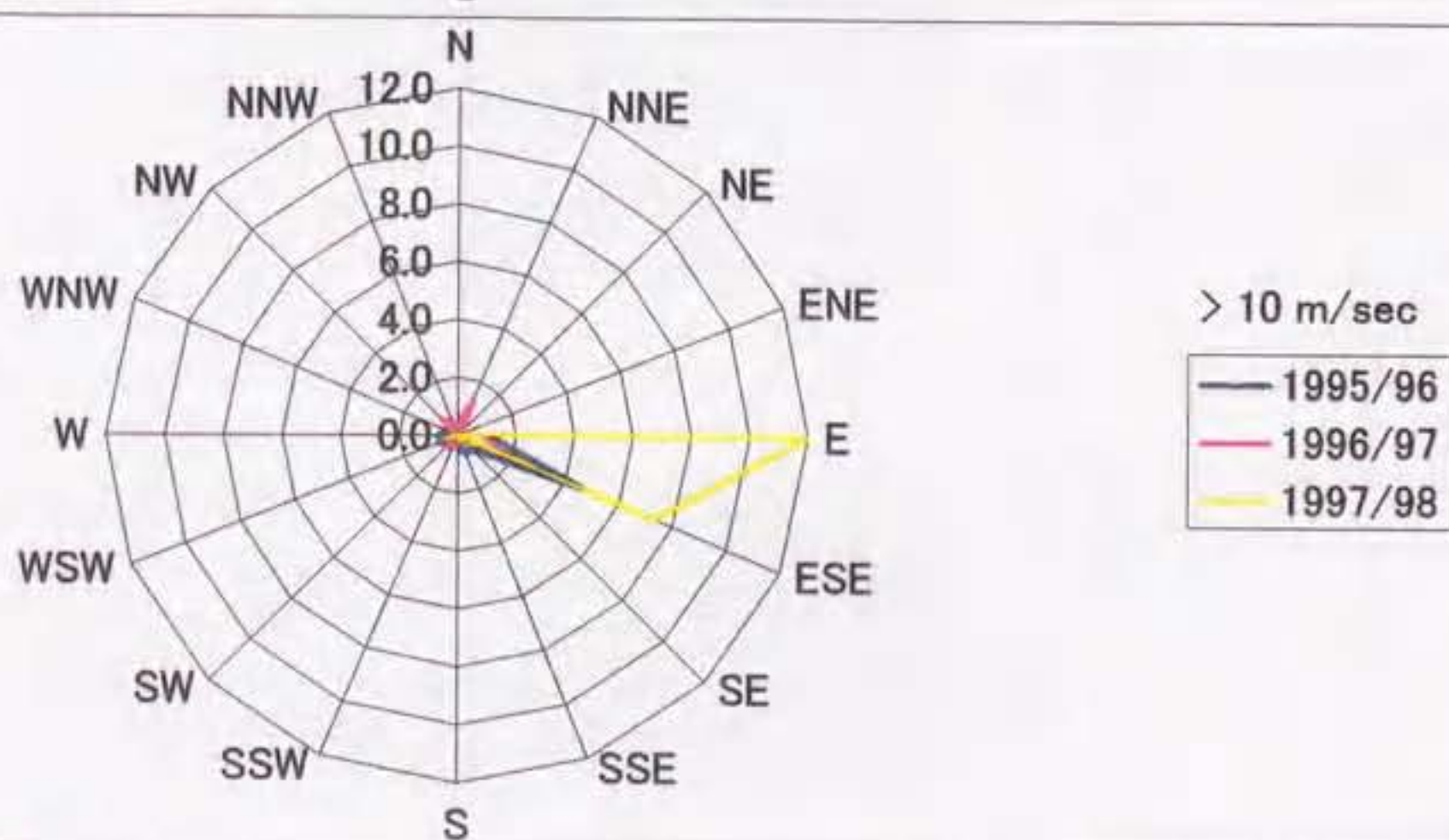
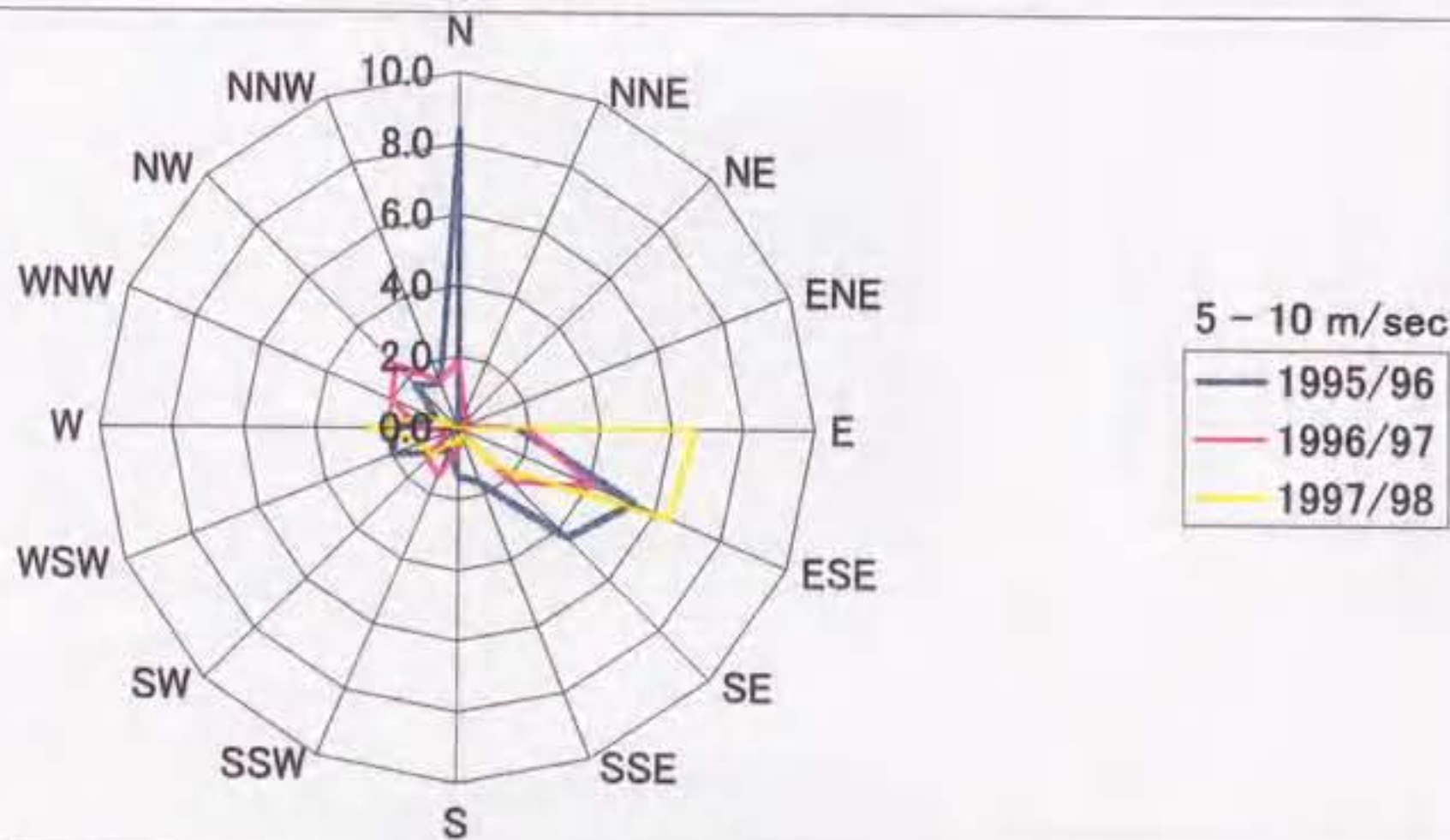
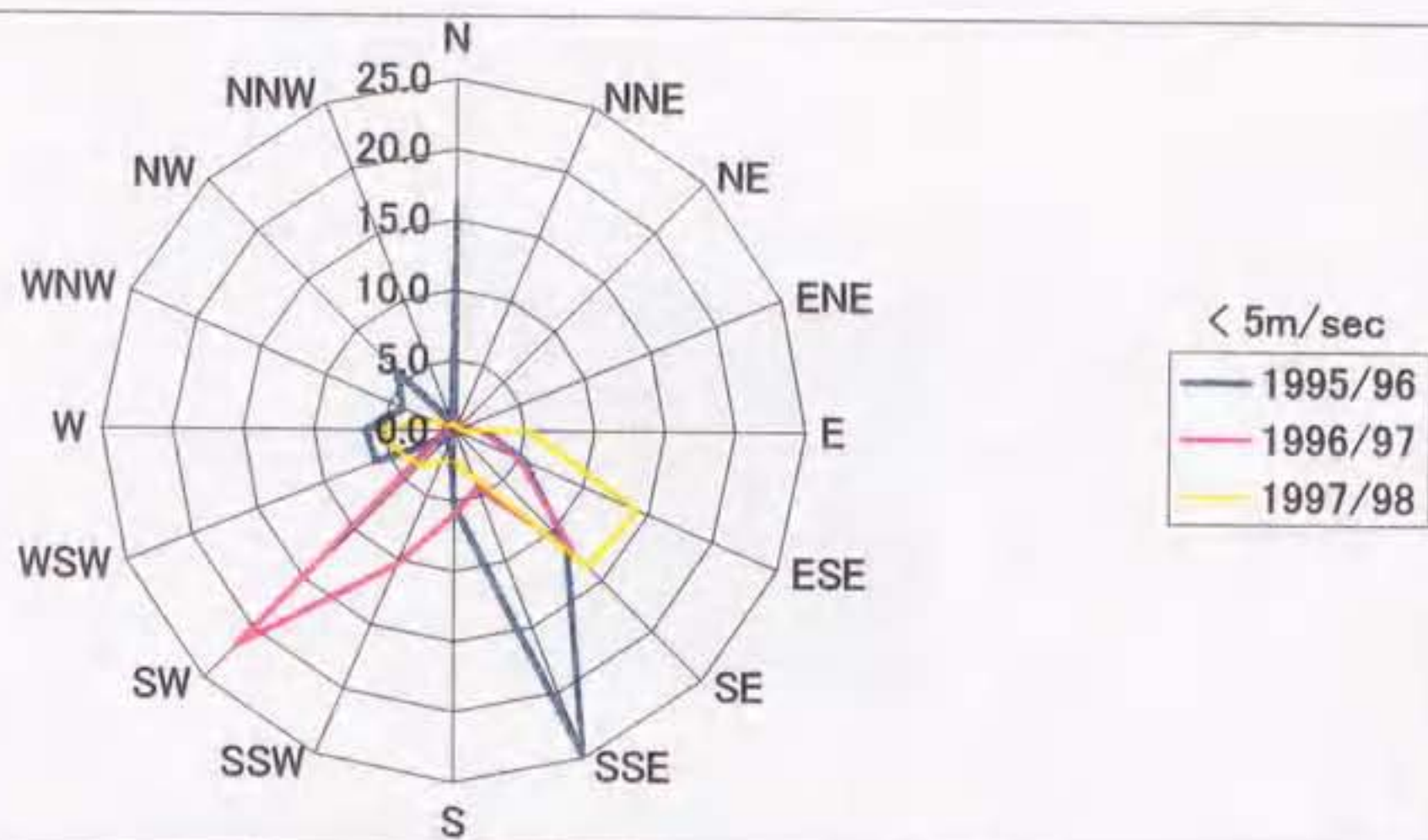


Figure 2_2. Wind rose of surface winds for Ny-Alesund for 1995-1998. The distribution of resultant wind direction and speed are given in units of percent occurrence for the past 3 winters. Wind speed is displayed as a function of direction in 3 speed classes.

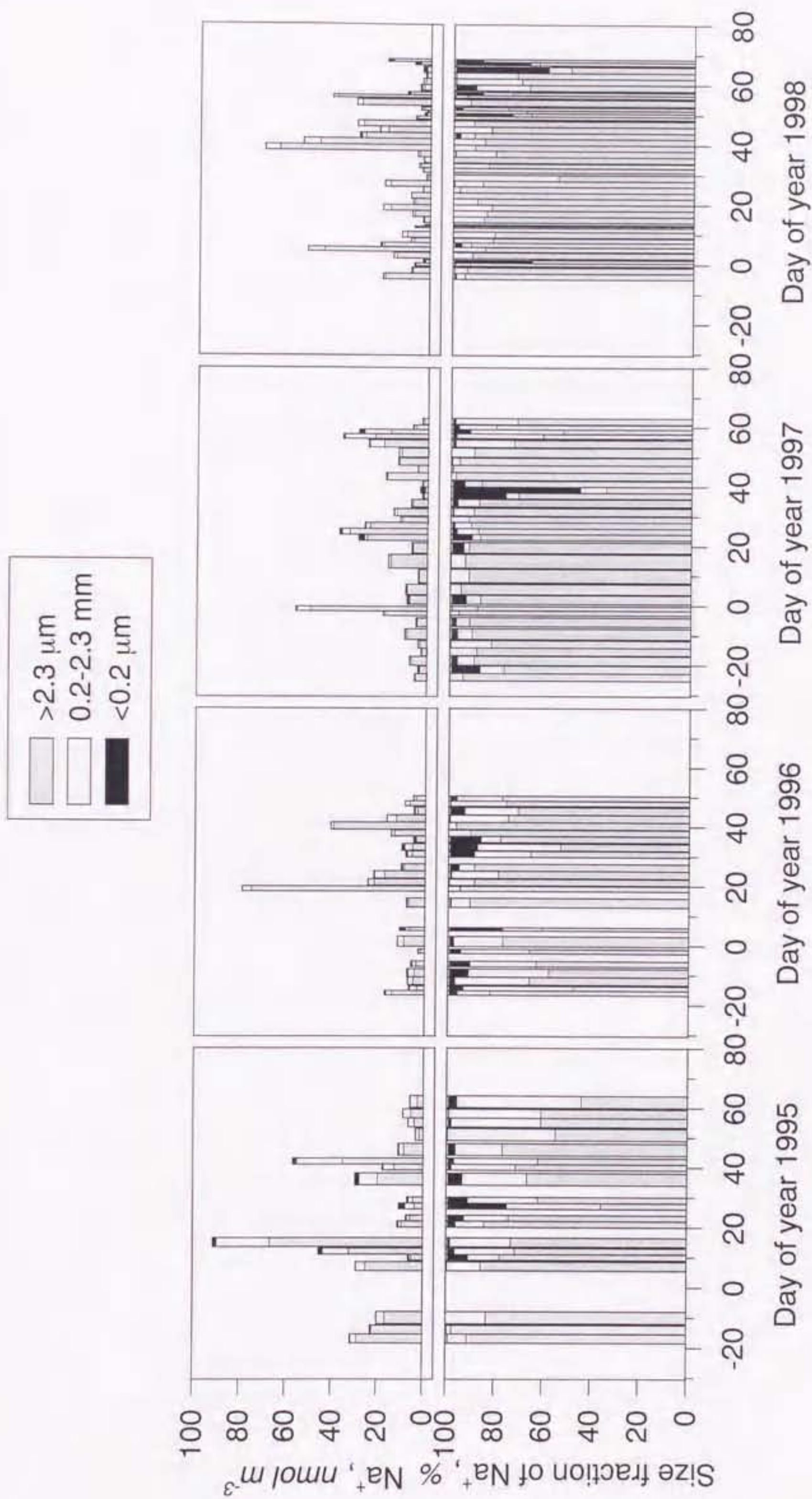


Figure 3_5a. The variations of size distribution of Na^+ , and mass size fraction of Na^+ in past four winters, 1994/1995, 1995/1996, 1996/1997 and 1997/1998.

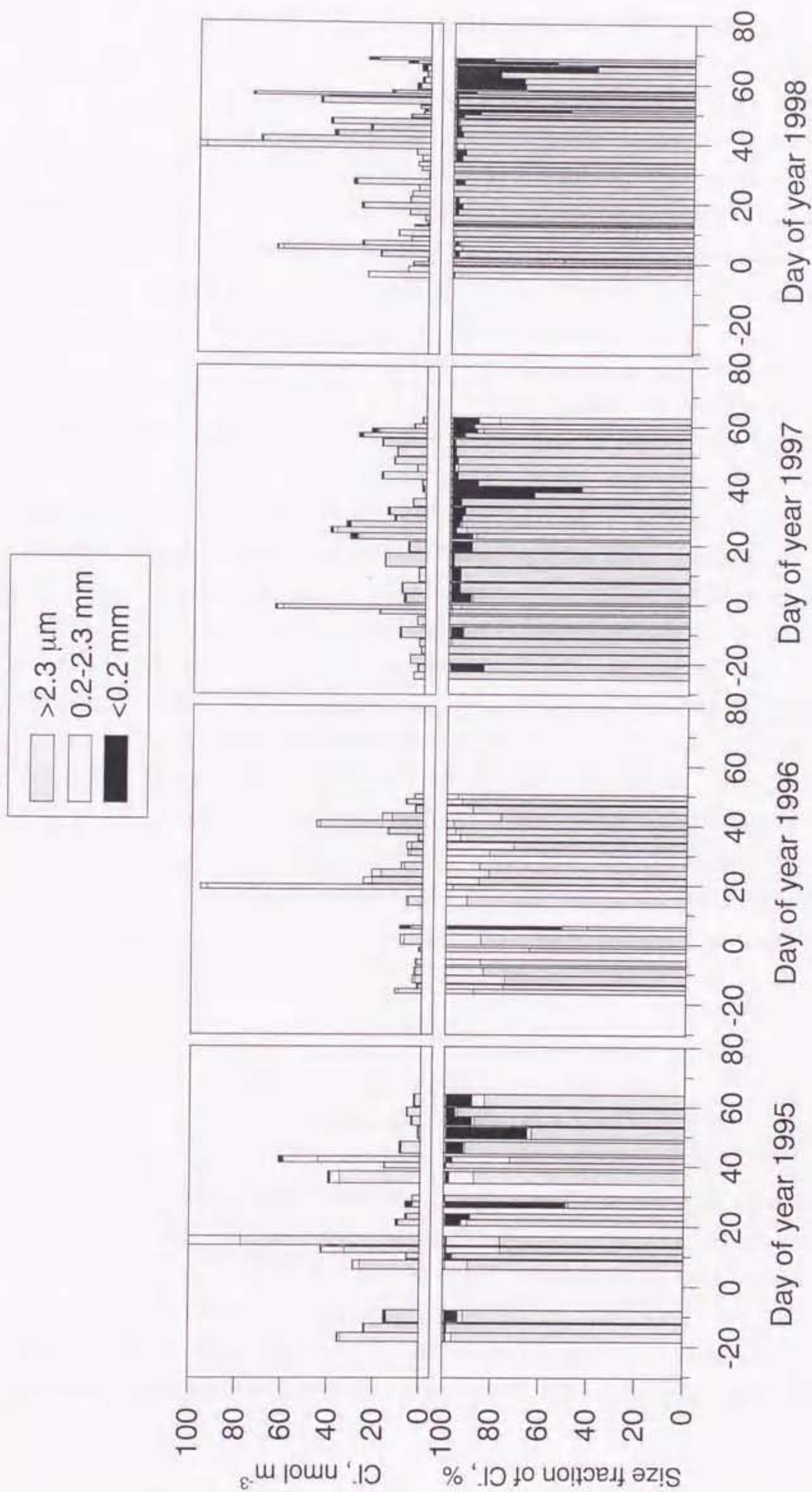
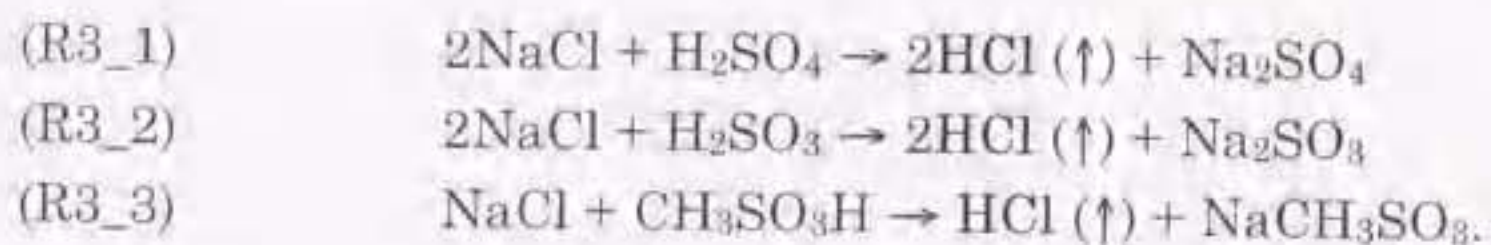


Figure 3_5b Variations of concentrations and size fraction of Cl^- in past 4 winters, 1994/1995, 1995/1996, 1996/1997 and 1997/1998.

mode ($> 2.3 \mu\text{m}$ in diameter) in every winters, and minor in fine and back-up mode ($0.2 - 2.3 \mu\text{m}$ in diameter). In contrast to size distribution of Na^+ , the concentrations of Cl^- in fine mode were quite lower than sea-salt (ss-) Cl^- concentration, estimated from Na^+ concentration using molar ratio ($[\text{Cl}^-]/[\text{Na}^+] \approx 1.20$ in seawater [Wilson, 1975]), in past 4 winters. This is likely due to chlorine depletion of sea-salt particles through the heterogeneous processes as described below and later Chapter. Indeed individual particle analysis by means of LAMMS showed the internal mixing states between sea-salts and acidic species such as SO_4^{2-} , SO_3^{2-} , CH_3SO_3^- , NO_3^- , and NO_2^- .

Individual particles analysis by means of LAMMS showed the internal mixing between sea-salts and some acidic species as shown in Figure 3_6. In Figure 3_6a, characteristic fragment ions due to NaCl (NaCl_2^+ , $m/z=93, 95$ and 97 ; Na_2Cl_3^+ , $m/z=151, 153$ and 155), KCl (KCl_2^+ , $m/z=109, 111$ and 113), MgCl_2 (MgCl_3^+ , $m/z=129, 131, 133$ and 135) CaCl_2 (CaCl_3^+ , $m/z= 145, 147$ and 149) were observed but fragment ions due to other species were not observed. The aerosol particle shown in Figure 3_6a should be identified as less modified sea-salt particle. On the other hand, characteristic fragment ions due to sea-salts (Na_2Cl^+ , $m/z= 81, 83$ and 85 ; NaKCl^+ , $m/z=97$ and 99) and mixture of $\text{CH}_3\text{SO}_3\text{Na}$ and $\text{CH}_3\text{SO}_3\text{K}$ ($\text{Na}_2\text{CH}_3\text{SO}_3^+$, $m/z= 141$; $\text{NaKCH}_3\text{SO}_3^+$, $m/z=157$) were observed in Figure 3_6b. In addition, the fragment ions due to mixture of Na_2SO_4 and K_2SO_4 (Na_3SO_4^+ , $m/z= 165$; $\text{Na}_2\text{KSO}_4^+$, $m/z= 181$; $\text{NaK}_2\text{SO}_4^+$, $m/z= 197$) were also obtained in Figure 3_6c. Considering that the lower molar ratio of sulfate to sea-salts in seawater as shown in Table 3_1 and that the characteristic fragment ions due to sulfate were hardly observed from sea-salt particles in freshly oceanic air mass, acidic species must be caused by heterogeneous processes on sea-salt particles during the transport, for examples,



Thus aerosol particles showing Figure 3_6b and 3_6c should be identified as modified sea-salt particles by sulfates and/or methanesulfonates. Internal mixing states of sulfates and methanesulfonates on sea-salt particles were often observed in marine atmosphere [Kolaitis *et al.*, 1989] and Antarctic region [Wouters *et al.*, 1990; Hara *et al.*, 1996]. In Figure 3_6d, the fragment ions due to sea-salts such as NaCl were not detected, whereas the fragment ions due to

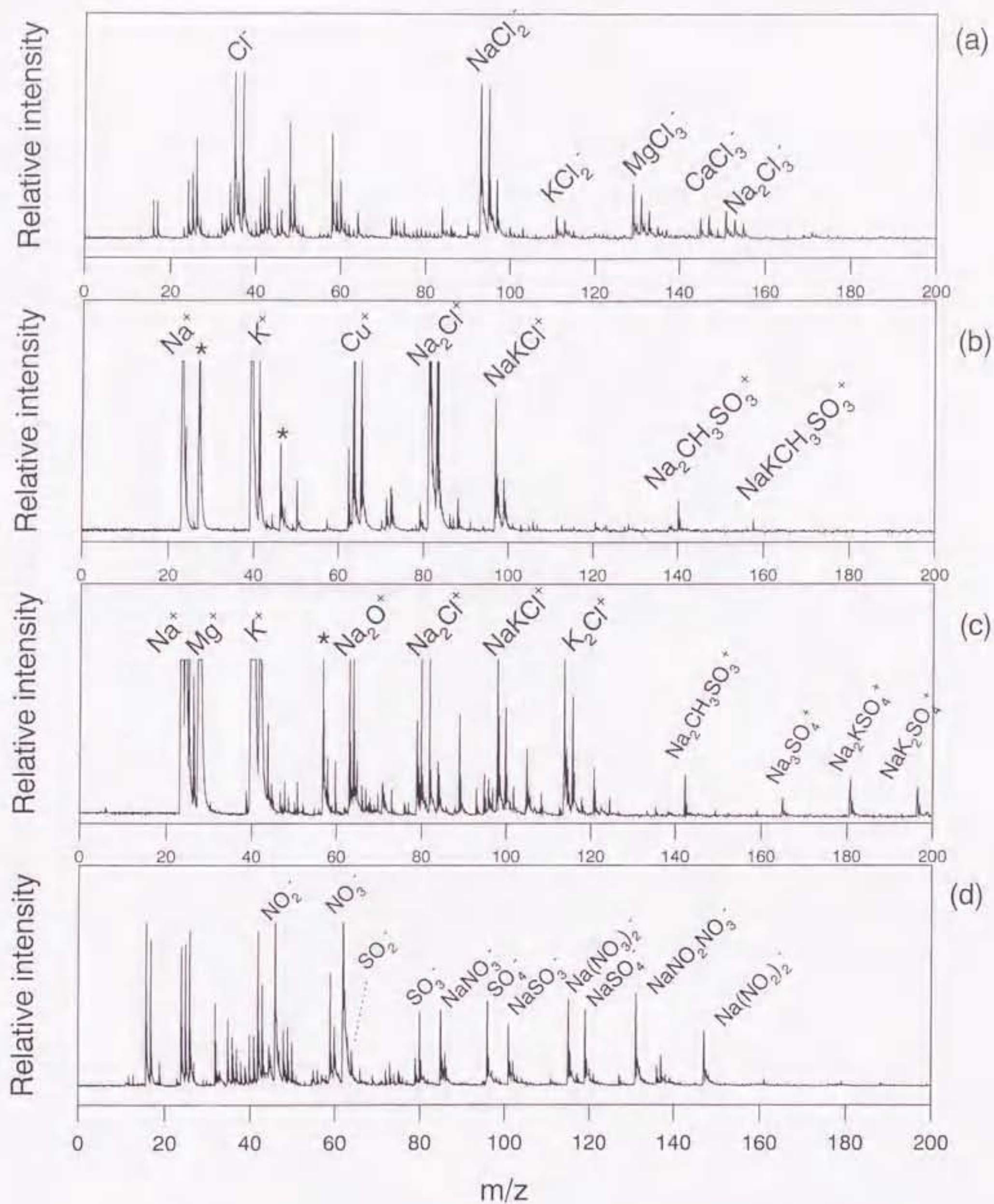


Figure 3_6. Examples of LAMMS spectra of coarse aerosol particles collected on 20 January 1996 (a, b), collected on 22 January 1996 (c), and collected on 25 January 1996 (d, e, f, g). Asterisks(*) indicate background peaks due to Al foil.

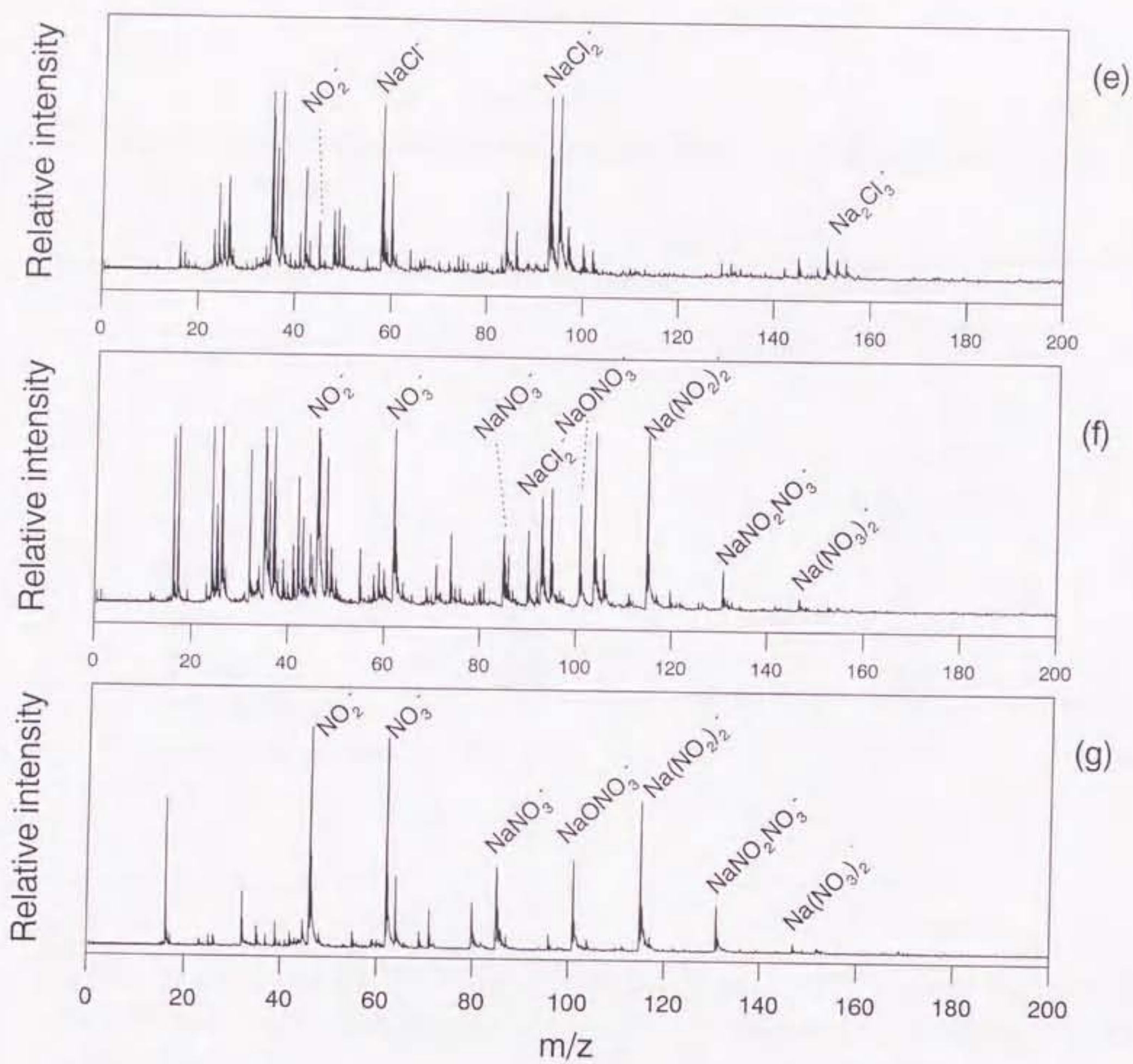


Figure 3_6. (continued)

Table 3_1. Concentrations and molar ratio of each specie in sea water

Species in sea water	Concentration $\mu\text{g/kg}$ (ppb)	Molar ratio to Na^+ concentration
Na^+	10.78×10^6	1
Cl^-	19.35×10^6	1.16
Br^-	67×10^3	1.79×10^{-3}
SO_4^{2-}	2.71×10^6	6.02×10^{-2}
SO_3^{2-}	n.d.	n.d.
CH_3SO_3^-	n.d.	n.d.
NO_3^-		$< 10^{-3*}$
NO_2^-	n.d.	n.d.

n.d.: not determined

*: Parungo *et al.*, 1987

Na_2SO_3 (NaSO_3^- , $m/z=103$), Na_2SO_4 (NaSO_4^- , $m/z=119$), NaNO_2 ($\text{Na}(\text{NO}_2)_2^-$, $m/z=115$) and NaNO_3 ($\text{Na}(\text{NO}_3)_2^-$, $m/z=147$) were observed. This particle should be identified as wholly Cl-depleted sea-salt particles. Sea-salt particles contained not only sulfur species but also inorganic nitrogen species such as nitrates and nitrites. In Figure 3_6e, fragment ions due to sea-salts (NaCl_2^- ; $m/z=93, 95$ and 97) were identified as dominant ions. Also NO_2^- ion ($m/z=46$) due to nitrate/nitrite and some nitrogen oxides was observed in Figure 3_6e but characteristic fragment ions due to NaNO_3 and NaNO_2 were not detected. The particle showing in Figure 3_6e might be identified as a slightly modified sea-salt particle by reactive nitrogen oxides. Since peak intensity of NO_2^- ion in Figure 3_6e was smaller than that in Figure 3_6f, a small amount of nitrate/nitrite or some nitrogen oxides may be present on the sea-salt particle. On the other hand, characteristic fragment ions due to sea-salts (NaCl_2^- ; $m/z=93, 95$ and 97), sodium nitrate ($\text{Na}(\text{NO}_3)_2^-$; $m/z=147$) and sodium nitrite ($\text{Na}(\text{NO}_2)_2^-$; $m/z=115$) were obtained in Figure 3_6f. This particle showing in Figure 3_6f might be identified as a sea-salt particle modified by reactive nitrogen oxides such as nitrates and

nitrites. Sea-salt particles containing nitrates have often been observed in the polluted marine atmosphere [references in Fitzgerald, 1991; Wu and Okada, 1994] and in winter Arctic [Hara *et al.*, 1999], with enrichment factors to seawater of nitrate relative to Na^+ of $>10^3$ [Parungo *et al.*, 1987] as shown in Table 3_1. Hence, NO_3^- in sea-salt particles also must be caused by heterogeneous processes in these cases. Nitrite on sea-salt particles could also be caused by heterogeneous processes on sea-salt particles as reported by Li [1994]. In Figure 3_6g, fragment ions due to NaCl were not detected, whereas $\text{Na}(\text{NO}_3)_2$ and $\text{Na}(\text{NO}_2)_2$ were obviously observed. Thus, the particle showing in Figure 3_6g might be identified as a wholly Cl-depleted sea-salt particle—more modified than that in Figure 3_6f—by reactive nitrogen oxides.

Individual particle analysis suggested that the less Cl⁻ concentration in fine mode may be due to the modification of sea-salt particles—Cl-depletion—by acidic species during the transport. Since fine particles have longer residence time in atmosphere [Warneck, 1988] and relatively larger surface area to their volume, prominent Cl-depletion of sea-salt particles could occur in fine mode. Other halogens such as Br⁻ and I⁻ in sea-salt particles can be depleted through the similar heterogeneous processes [Keene *et al.*, 1996; Ayers *et al.*, 1999]. As the modification of sea-salt particles, so called halogen depletion, should occur during the transport, aging processes of sea-salt particles and/or oceanic air mass must be important key to discuss the heterogeneous processes on sea-salt particles. Then the qualitative index of aging of oceanic air mass with many sea salt particles was estimated for identification of aged oceanic air mass in an attempt to understand to aging processes of sea-salt particles.

3_2_3. Aging index of oceanic air mass

Figure 3_7 shows the typical size distributions of Na^+ and Cl⁻ concentrations in 1995/1996 winter. Although Na^+ concentration increased in each fraction under the storm condition as marked by asterisks, the increase of Na^+ concentration in fine mode in spite of no- or minor increase in the coarse was observed as marked by arrows in Figure 3_7. Preferential removal of coarse sea-salt particles through wet and dry deposition during transport would cause the relative increase of the concentration of Na^+ and Cl⁻ in the fine particle fraction. Then the air masses marked by arrows in Figure 3_7 should be identified as aged oceanic air mass. Transport of aged oceanic air mass to Ny-Ålesund was also

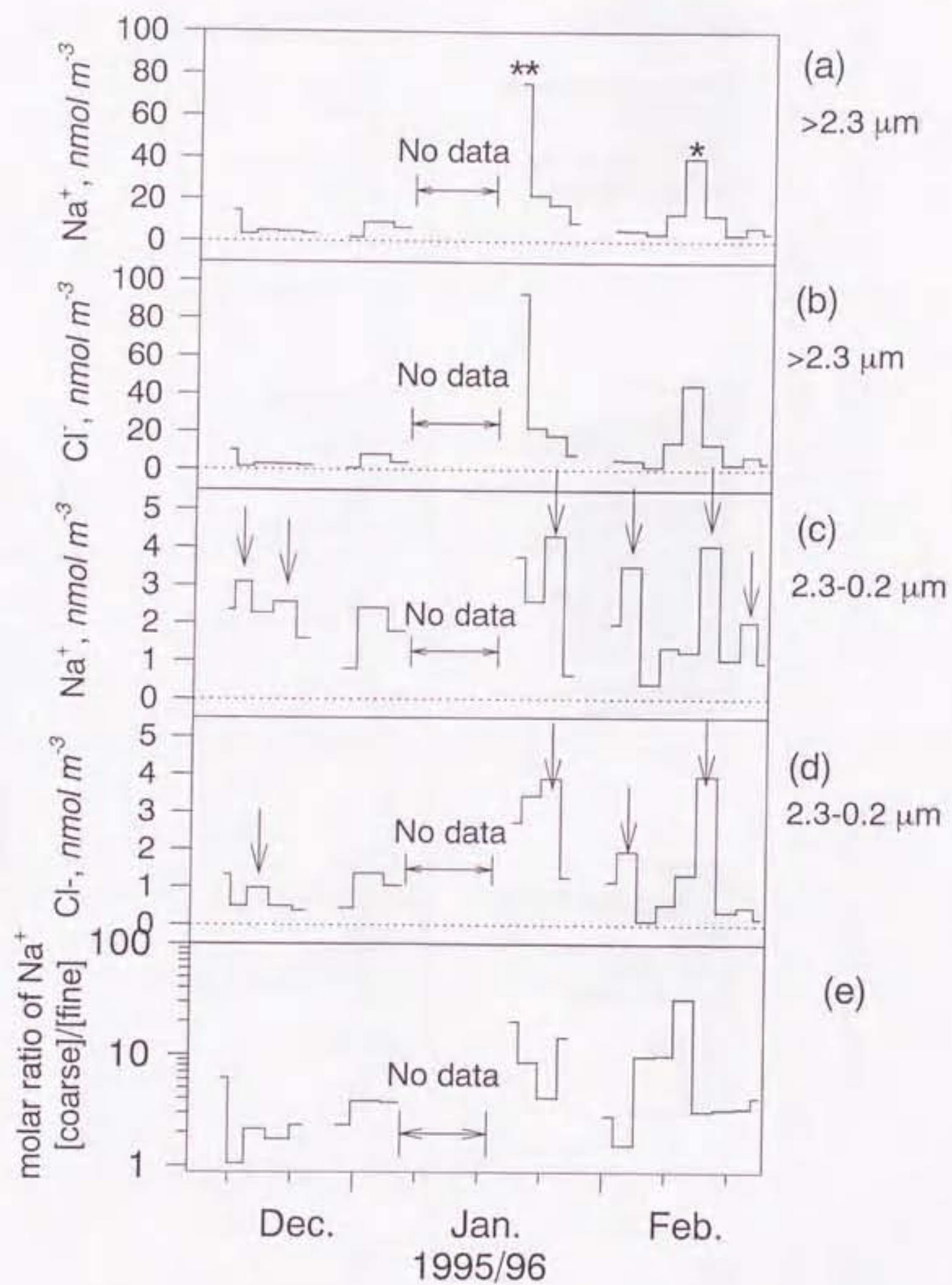


Figure 3_7. The variations of concentrations of Na^+ and Cl^- in coarse mode and fine mode, and molar ratio of Na^+ concentration in coarse mode to that in fine mode

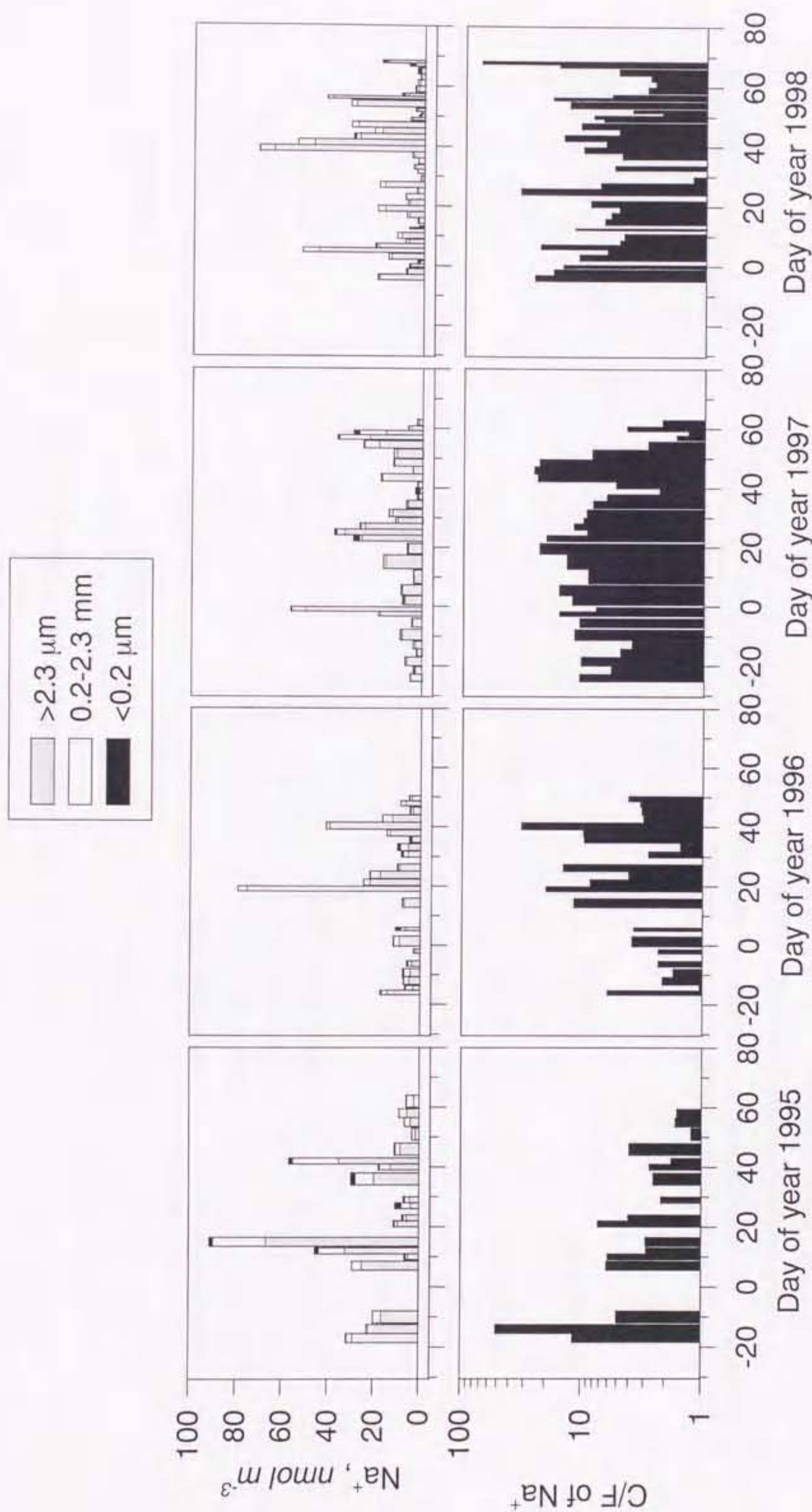


Figure 3_8. The variations of size distribution of Na^+ , and C/F ratio of Na^+ in past four winters, 1994/1995, 1995/1996, 1996/1997 and 1997/1998.

Table 3_2. C/F ratio of Na⁺ in Polar Regions

Location	Season/Month	C/F ratio of Na ⁺		References
		Range	mean	
Ny-Ålesund	1994/1995 winter	0.85 - 51.2	6.12	This study
Ny-Ålesund	1995/1996 winter	1.05 - 32.25	6.91	This study
Ny-Ålesund	1996/1997 winter	1.37 - 26.14	10.55	This study
Ny-Ålesund	1997/1998 winter	1.28 - 74.01	11.67	This study
Barrow	Winter			Li and Winchester [1990]
Barrow	1995 summer	3.7-12.3 ²⁾	0.87	Hara <i>et al.</i> [unpublished data]
Fair Banks	Winter	0.82 - 4.33	5.43	
Sevettijärvi ¹⁾	Summer		0.93	Virkkula <i>et al.</i> , [1995]
Antarctic sea	Nov. - Dec.	0.97-11.1 ³⁾		Osada <i>et al.</i>
				[private communication]

1): Sevettijärvi (69°35'N, 28°50'E) is located in Finnish Lapland, and >30 km away from Barents sea.

2): The C/F ratio in the directly wind flow from Arctic sea ranged from 8 to 12.3.

3): The C/F ratio under the condition covered with sea ice ranged from 0.97 to 2.00.

observed by Staebler *et al.* [1999]. This suggests that the molar ratio of Na^+ concentration in coarse particle fraction to that in fine particle fraction (C/F ratio) can be used as aging index of oceanic air mass. The variations of C/F ratio of Na^+ and size distribution of Na^+ in each winter were shown in Figure 3_8.

The C/F ratios of sea-salts in other region were given in Table 3_2. Lower C/F ratio of Na^+ at Ny-Ålesund was found in aged oceanic air masses, as mentioned above. Observations at Barrow and Antarctic Sea showed also the lower C/F ratio under the conditions isolated from open-sea area with the subsequent emission of sea-salt particles. Although mean C/F ratio of Na^+ was 0.867 [Li and Winchester, 1990] in winter seasons at Barrow where is >1000 km away from the opened sea area during the winter, C/F ratio ranged from 3.7 to 12.3 in summer season when open sea area is a few km away from the observation site. Also the C/F value during the cruise of 38th Japanese Antarctic Research Expedition in Antarctic sea ranged from 0.97 to 11.1, whereas lower C/F value, 0.97 - 2.00, was observed under the condition covered with sea ice. Then lower C/F ratio was found under the condition isolated from opened sea area. This tendency was likely due to preferential deposition of coarse sea-salt particles, and due to absence of subsequent forming of sea-salt particles from the sea surface. Hence C/F ratio of Na^+ can be used as an aging index of oceanic air mass in the observation site isolated from open sea area, for example polar and inland regions.

3_3. Chapter Summary

Sea-salt particles were one of the dominant aerosol species at Ny-Ålesund in every winter. Some sea-salt particles were internally mixed with sulfates, sulfites, methanesulfonates, nitrates and nitrites, which were likely due to heterogeneous reactions on sea-salt particles during the transport. The concentrations of sea-salts such as Na^+ and Cl^- increased in oceanic air mass transported from opened sea area through the storm accesses. Also the transport of aged oceanic air mass was often observed in Ny-Ålesund. For identification of aged oceanic air mass, molar ration of the concentration of Na^+ in coarse mode to that in fine mode (C/F ratio of Na^+) was used as the aging index of oceanic air masses.

Chapter 4

Sea-salt particles as scavenger for acidic species —Sulfur species and reactive nitrogen oxides—

4_1. Introduction

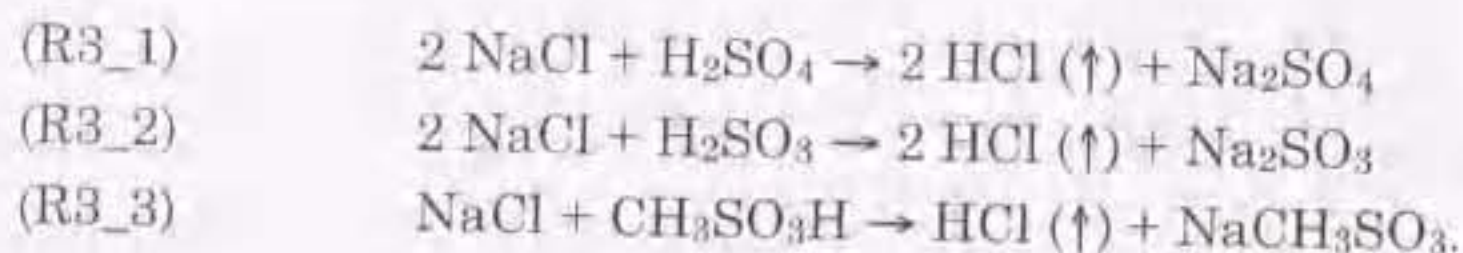
As described in Chapter 3, some sea-salt particles were internally mixed with SO_4^{2-} , SO_3^{2-} , CH_3SO_3^- , NO_3^- and NO_2^- , which are the most important acids in atmosphere, and are the end products of gaseous sulfur species [*e.g.*, Warneck, 1988] and reactive nitrogen oxides [*e.g.*, Ehhalt and Drummond, 1982; Roberts *et al.*, 1995] through gas phase reactions and heterogeneous processes on aerosol particles in the atmosphere. If the subsequent production and uptake of acidic species on sea-salt particles—internal mixing between acidic species and sea-salt particles—occur in winter Arctic atmosphere, sea-salt particles with higher deposition velocity through dry and wet processes [Warneck, 1988] can play an important role in sink of acidic species such as gaseous sulfur species and reactive nitrogen oxides.

The heterogeneous processes on sea-salts have been mainly discussed on the basis of laboratory measurements (*e.g.*, references in Table 4_1). However, it is important to know the ambient mixing states of particulate species in individual particles in order to understand the heterogeneous processes on sea-salt particles and its contribution in winter Arctic atmosphere. For better understanding of heterogeneous chemistry on sea-salt particles and sink processes of atmospheric acids, this chapter summarizes the measurement results, and then attempts to elucidate the chemical roles of sea-salt particles as the sink of atmospheric acids and its contribution.

4-2. Results and Discussion

4-2-1. The roles as the sink of sulfur species

Sulfate, sulfite and methanesulfonate in the modified sea-salt particles were in the forms of Na_2SO_4 , Na_2SO_3 and NaCH_3SO_3 (see Figure 3_5b, c and d), which should be formed through heterogeneous reactions on sea-salt particles, for example:



The formation of particulate sulfur species on sea-salt particles may be caused by (1) uptake of gaseous H_2SO_4 and $\text{CH}_3\text{SO}_3\text{H}$ on sea-salt particles, (2) oxidation of precursors on/in sea-salt particles, and (3) coagulation of acidic aerosol particles. As gaseous H_2SO_4 and $\text{CH}_3\text{SO}_3\text{H}$ are mainly formed through the reaction between precursors (*e.g.*, SO_2 and DMS: dimethylsulfide) and photochemical oxidant such as OH, the contribution of this process can be neglected in polar winter condition with less or no solar radiation. According to Luria *et al.* [1991] and Sievering *et al.* [1991, 1992, 1995], nss- SO_4^{2-} on sea-salt particles could be formed mainly through the heterogeneous oxidation of SO_2 with ozone rather than coagulation of fine sulfate particles. Recent work suggested that CH_3SO_3^- also could be formed through the heterogeneous oxidation of precursors on aerosol particles (Jafferson *et al.* [1998]). Thus nss- SO_4^{2-} and CH_3SO_3^- on sea-salt particles may be formed mainly through the heterogeneous processes during the transport.

Although nss- SO_4^{2-} was mostly found in fine mode in each winter (1994/1995, 1995/1996, 1996/1997 and 1997/1998) at Ny-Ålesund as shown in Figure 4_1, sulfates were also found in coarse mode (see in Figure 3_5a), which were mainly consisted of sea-salt particles. If sulfates in coarse mode were internally mixed with sea-salt particles, sea-salt particles have some contribution to sulfur cycles, especially sink processes. However, single particle analysis using LAMMS showed not only internal mixing states as shown in Figure 3_6c and 3_6d but also the presence of coarse sulfates as shown in Figure 4_2. The characteristic fragment ions such as HSO_n^- ($n=3$ and 4 ; $m/z=81$ and 97) due to H_2SO_4 , NH_4HSO_4 and/or $(\text{NH}_4)_2\text{SO}_4$ were observed. Then, this particle should be identified as not modified sea-salt particle, but sulfate particle, similar to fine sulfate particles. Coarse sulfate particles were observed in remote boundary layer [Mouri *et al.*, 1995]. In addition, coarse sulfate particles containing soot

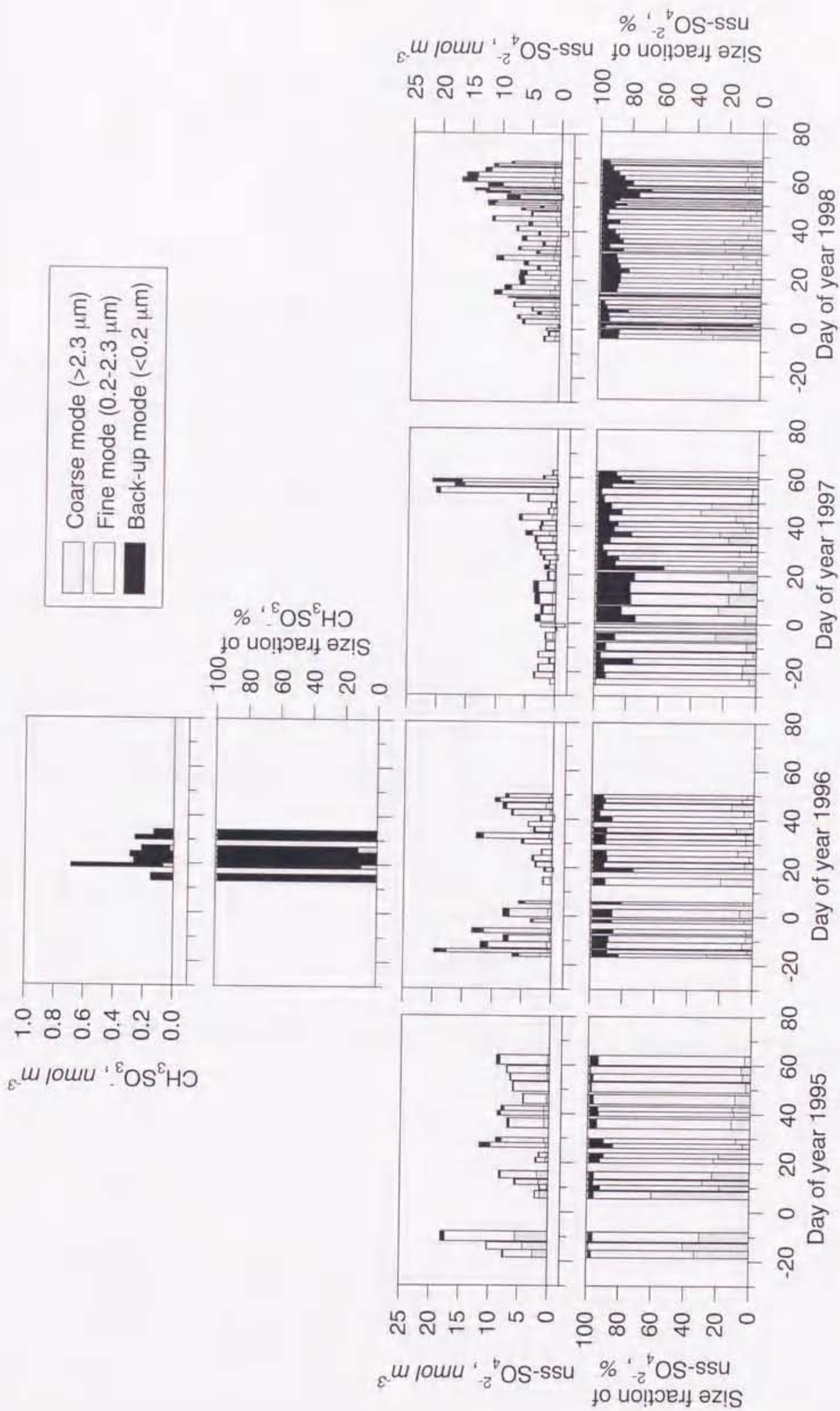


Figure 4_1. Variations of the concentrations and size fractions of nss-SO_4^{2-} and CH_3SO_3^- in past 4 winters (1994/1995, 1995/1996, 1996/1997 and 1997/1998) at Ny-Alesund.

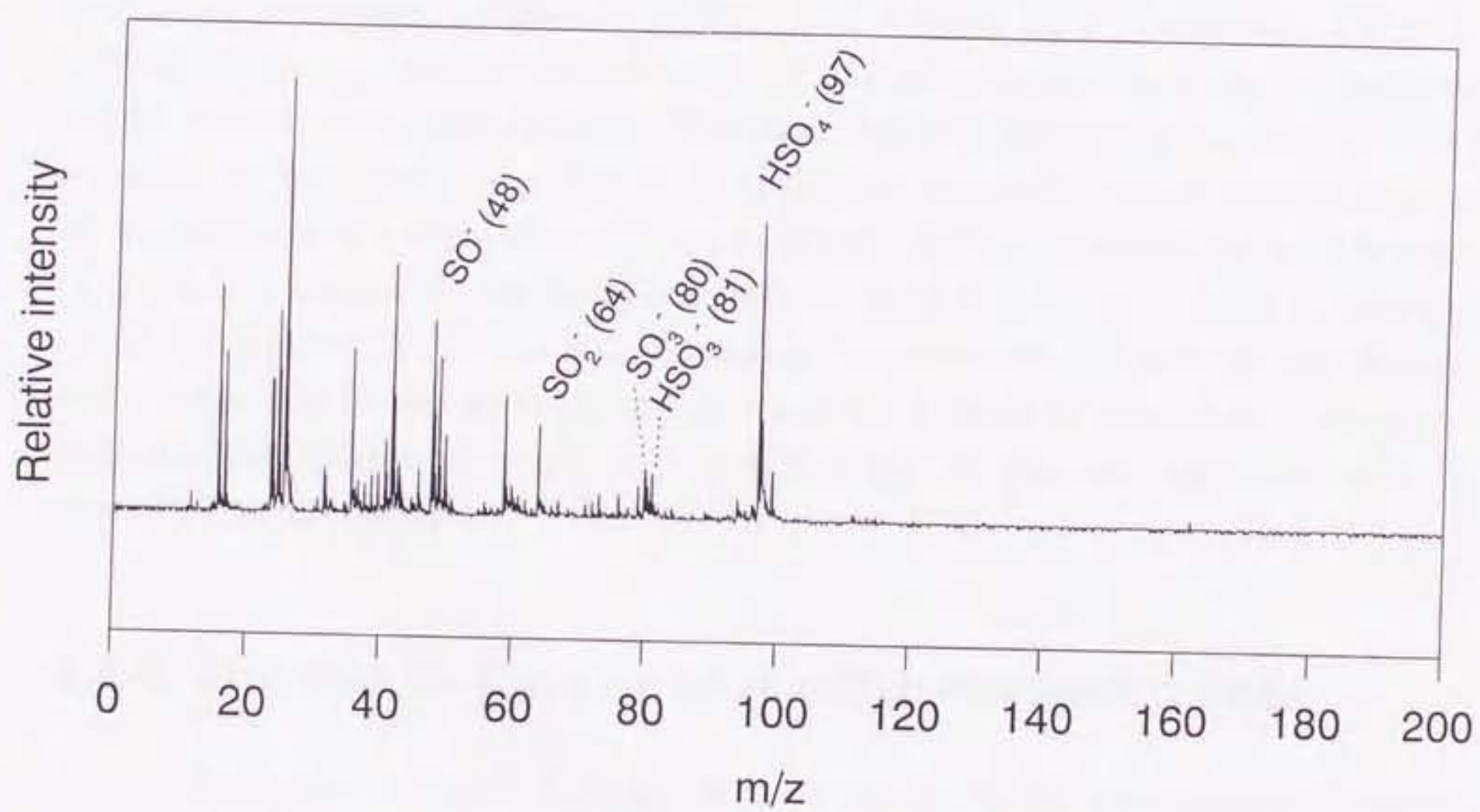


Figure 4_2. LAMMS spectrum of coarse sulfate particle collected on 3 February 1996

were also observed in 1995/1996, 1996/1997 and 1997/1998 winters. Sulfate particles contained soot even in remote marine boundary layer [Pósfai *et al.*, 1999]. According to Pósfai *et al.* [1999], internal mixing between sulfate and soot were perhaps derived from heterogeneous processes on soot particles. Because of higher concentration of soot in winter/spring Arctic [Heitzenberg and Leck, 1994], sulfate formation through the heterogeneous processes on soot particles maybe occurred. Indeed, many sulfate particles mixed internally with soot at Ny-Ålesund [Hara, unpublished data]. Considering low concentration of nss-SO_4^{2-} in coarse mode and mixing states of coarse sulfates, the heterogeneous formation of nss-SO_4^{2-} on sea-salt particles may have smaller contribution to removing processes of sulfur species in winter Arctic. In contrast, CH_3SO_3^- was distributed in coarse and back-up modes, and present as internal mixture with sea-salt particles in coarse modes as shown in Figure 3_5. However, CH_3SO_3^- concentration may be too low to have a significant influence on acidic sulfur cycle in the winter Arctic atmosphere. Therefore the modification of sea-salt particles by acidic sulfur species (*e.g.*, R3_1 - 3_3) may have smaller or less contribution to sink processes of acidic sulfur species in winter Arctic, whereas the modification of sea-salt particles by sulfur species might have some contribution to halogen cycles in winter Arctic because inorganic halogenated compounds are formed simultaneously in the modification of sea-salts. Details of emission of inorganic halogenated species through the modification of sea-salt particles will be described in next chapter.

4-2-2. The role as the sink of reactive nitrogen oxides

As shown in Figure 3_5e-g, some sea-salt particles were internally mixed with nitrates/nitrites, which were in the forms of NaNO_3 and NaNO_2 . How was the relation between sea-salt particles and inorganic nitrates? Figure 4_3 shows the size distribution of particulate NO_3^- concentration at Ny-Ålesund in the past 4 winters (1994-1997). Particulate NO_3^- in each winter was mostly distributed in the coarse particle fraction ($> 2.3 \mu\text{m}$ in diameter) and minor in fine mode. Above 90% of NO_3^- in average was distributed in coarse particle fraction especially in the 1996/1997 winter except for the end of February when the concentration of nss-Ca^{2+} and nss-Mg^{2+} , derived from mineral particles, suddenly increased. Gaseous HNO_3 concentration mostly ranged around or below the field blank level (0.6 nmol m^{-3}) in this study. According to Barrie [*personal communication*, 1997], the mean and maximum gaseous nitrate concentrations were 5 and 20 pptv ($0.2 -$

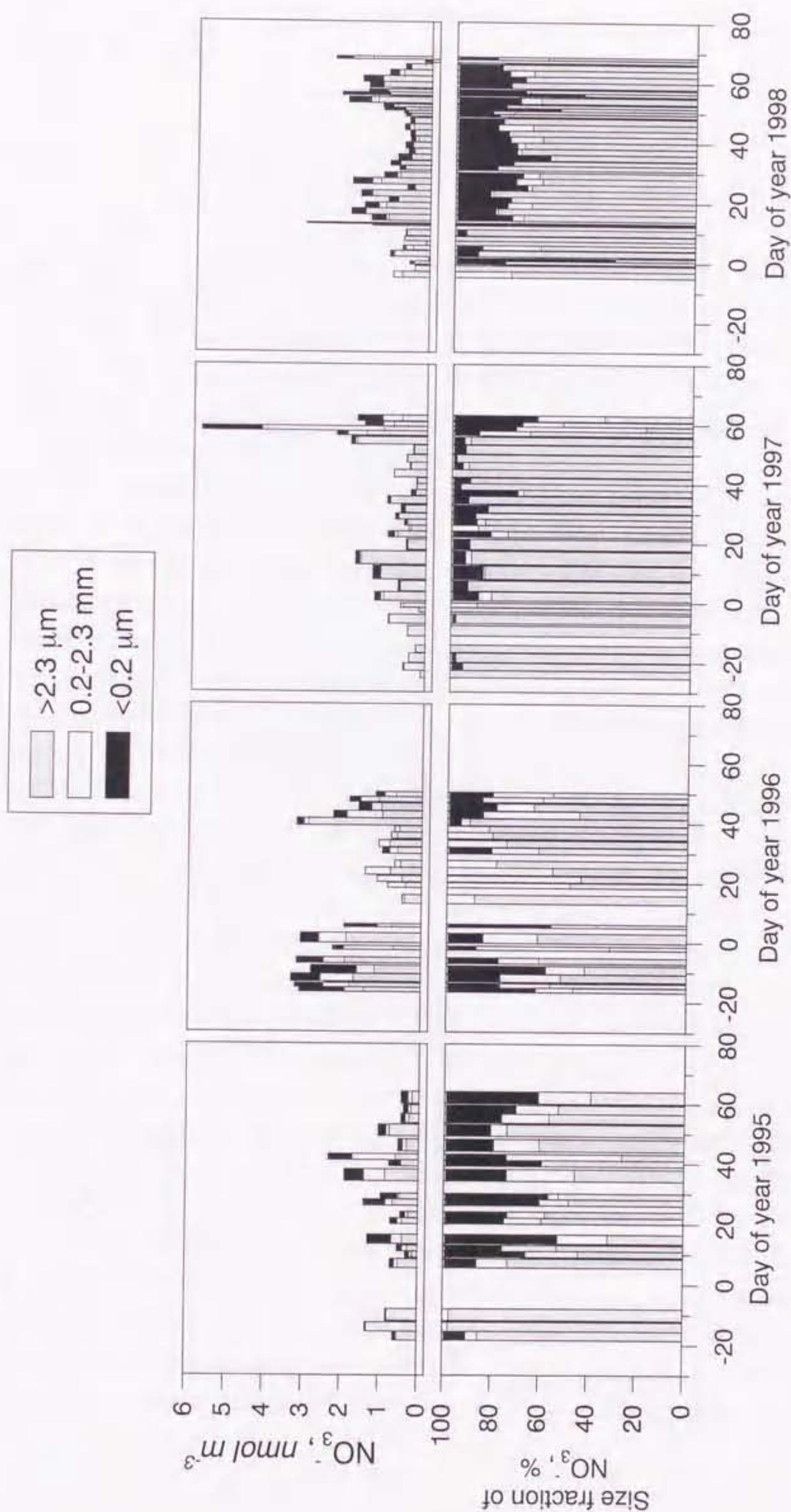


Figure 4_3. Variations of the concentrations and size fraction of NO_3^- in past 4 (1994/1995, 1995/1996, 1996/1997 1997/1998) winters at Ny-Alesund.

0.8 nmol m⁻³) at Ny-Ålesund in 1996 winter, respectively. The particle fraction of inorganic nitrate (%),

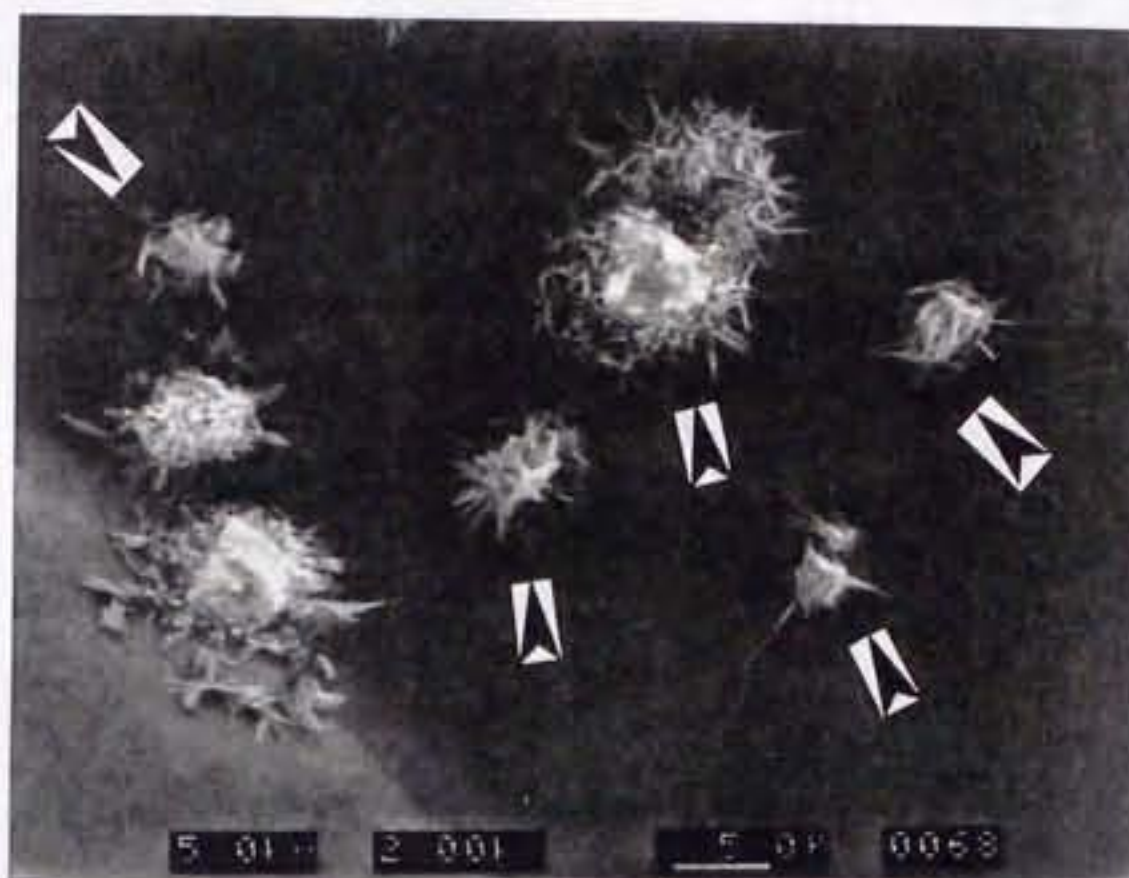
$$100 \times \frac{[NO_3^-]_{particle}}{[NO_3^- + HNO_3]_{total}}$$

may range from 85 to 98 % in 1996/97 winter using mean concentration measured by Barrie [*personal communication*, 1997] at Ny-Ålesund. Most of the inorganic nitrate was present as particulate NO₃⁻ in the coarse mode, which is dominated by sea-salt particles. A similar tendency of fractionation of inorganic nitrate to the particulate phase was also observed at Alert, Canadian high Arctic in winter-spring [Barrie *et al.*, 1994a].

Individual particle measurements were made with nitron-thin-film in order to understand the mixing state and phase of coarse particles. The typical SEM image of the coarse particles on nitron-thin-film are shown in Figure 4_4. Prominent needle-like crystals due to the reaction between NO₃⁻ and nitron were observed on the surface of the thin-film. Some particles with needle-like crystals had an angular-crystal nuclei similar to the shape of sea-salt particles shown in the papers by Miura *et al.* [1991], Ikegami *et al.* [1991 and 1994] and Pösfai *et al.* [1995]. As shown in Figure 3_5, nitrates were mostly in the forms of NaNO₃. Also LAMMS analysis showed particulate NO₃⁻ might be internally mixed with sea-salt particles and/or in the states of wholly Cl-depleted sea-salt particles. In Figure 4_4, some particles had the stains around the particle as marked by arrows. Because nitron-thin-film has a relatively high sensitivity to aqueous solution, impacting droplet on the film may form the stains. Actually, relative humidity at Ny-Ålesund in winter ranged from 42-98%, higher than the crystallization points (45-48%) of NaCl aerosols in droplet evaporation [Tang *et al.*, 1997]. Since NaCl particles have a large hysteresis effect in phase transformation [Tang *et al.*, 1997], liquid phase should remain on surface of most sea-salt particles in winter at Ny-Ålesund. The presence of liquid phase on sea-salt particles may enhance the uptake of gaseous HNO₃ and the formation of particulate NO₃⁻ through the heterogeneous reactions.

To estimate the number fraction of aerosol particles containing NO₃⁻, the number of coarse aerosol particles on nitron-thin-films and aerosol particles with positive reaction on nitron-thin-film were counted from SEM images. More than 85 particles (maximum 2104 particles) were counted for one sample stage fraction. Figure 4_5 shows the variations of (a) the total number concentration of

(a)



(b)

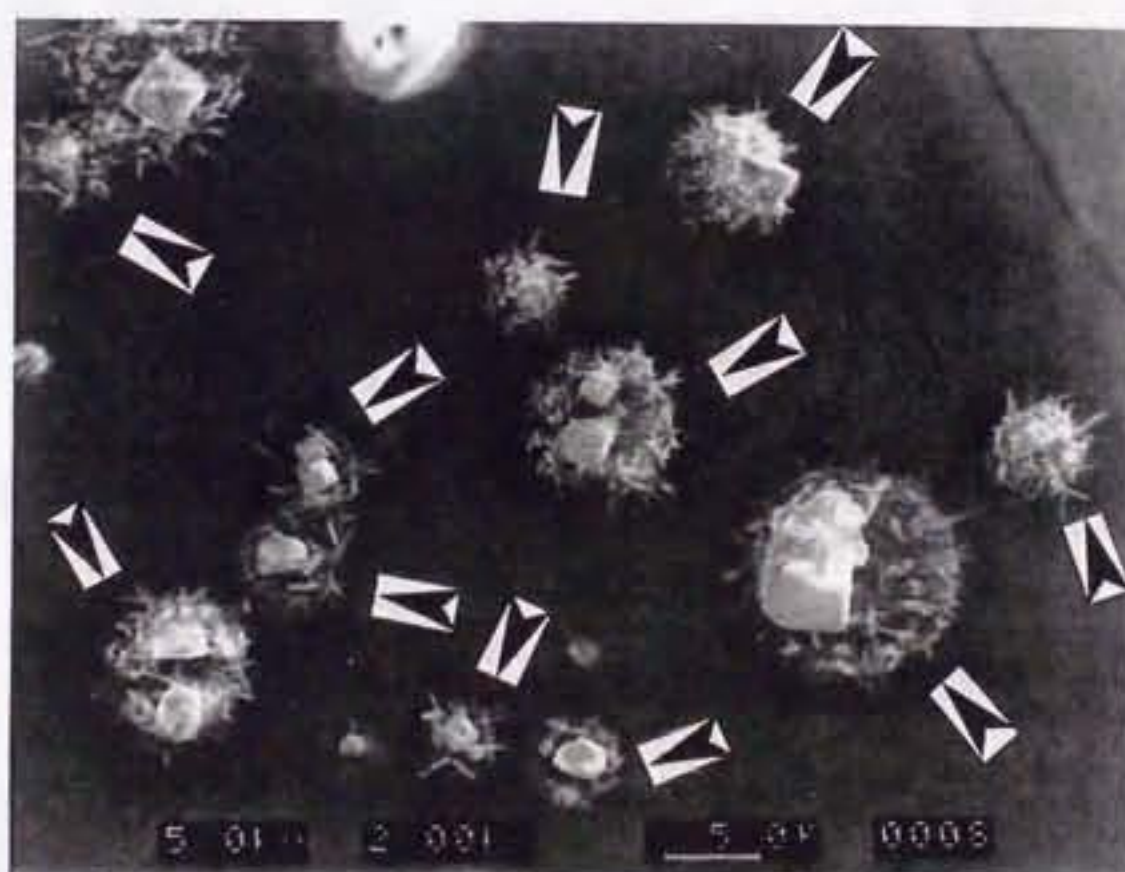


Figure 4_4 Typical SEM images of aerosol particles in coarse particle fraction on nitron-thin-film.

(a) aerosol particles collected at 17 December, 1996

(b) aerosol particles collected at 12 December, 1996

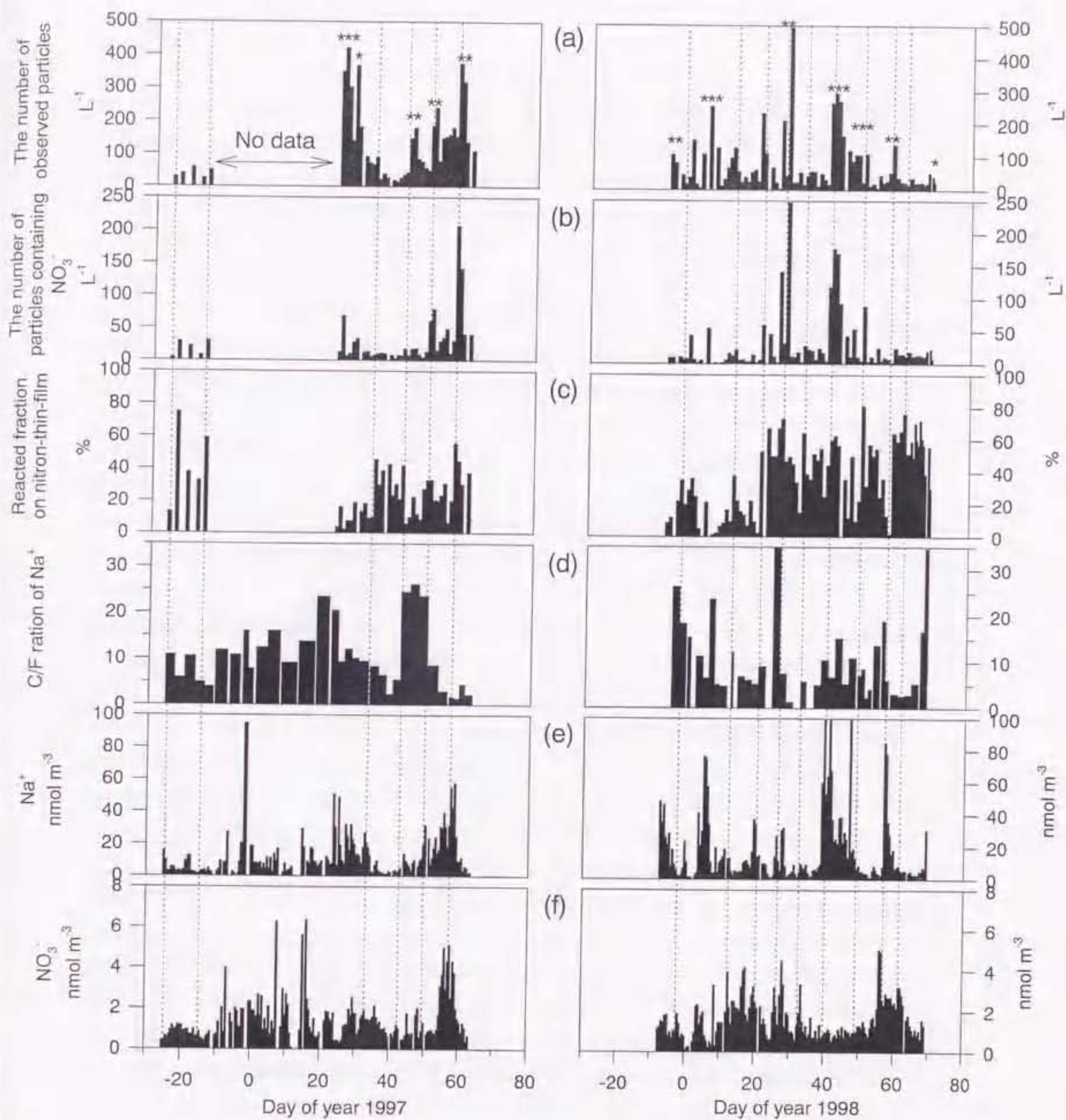


Figure 4_5. Variations of the number concentrations of coarse aerosol particles and particles containing NO_3^- , reacted fraction of coarse particles on nitron-thin-film, C/F ratio of Na^+ , the mass concentrations of Na^+ and NO_3^- in 1996/1997 and 1997/1998 winters. Asterisks indicated the storm conditions.

coarse particles, (b) the number concentration of coarse particles containing NO_3^- , (c) reacted fraction of coarse particles on nitron-thin-film, (d) molar ratio of Na^+ concentration in coarse mode to that in fine mode (C/F ratio), (e) Na^+ concentration on prefilter and (f) NO_3^- concentration in 1996/1997 and 1997/1998 winters. The value of C/F ratio of Na^+ concentration is used as an index of aging of oceanic air mass as described in Chapter 3. The total number concentration of coarse particles ranged from 14.4 to 420.0 L^{-1} in 1996/1997 winter, and from 4.3 to 2229.9 L^{-1} in 1997/1998 winter, and increased during the stormy conditions when Na^+ concentration sharply increased in both winters. On the other hand, the number concentration of aerosol particles containing NO_3^- ranged from 3.8 to 207.2 L^{-1} in 1996/1997 and from 0.3 to 1045.6 in 1997/1998 winter. Although the spiky peaks of the concentration of particles containing NO_3^- were found during the periods of higher concentration of coarse particles, poor correlation was observed between the number concentration of aerosol particles containing NO_3^- and that of coarse particles. The reacted fraction of coarse particles ranged from 2.6 to 74.7 % in 1996/1997 winter, from 1.4 to 80.7 % in 1997/1998 winter as shown in Figure 4_5c. Higher reacted fractions of coarse particles were observed in early December, early February and the end of February when the number concentration of coarse particles and C/F molar ratio of Na^+ concentration decreased below 10. High reacted fractions of coarse aerosol particles on nitron-thin-film were found in aged oceanic air with lower C/F ratio of Na^+ , so that the reacted fraction increases in aged oceanic air masses. Hence, particulate NO_3^- should be gradually formed on sea-salt particles during a long-range transport.

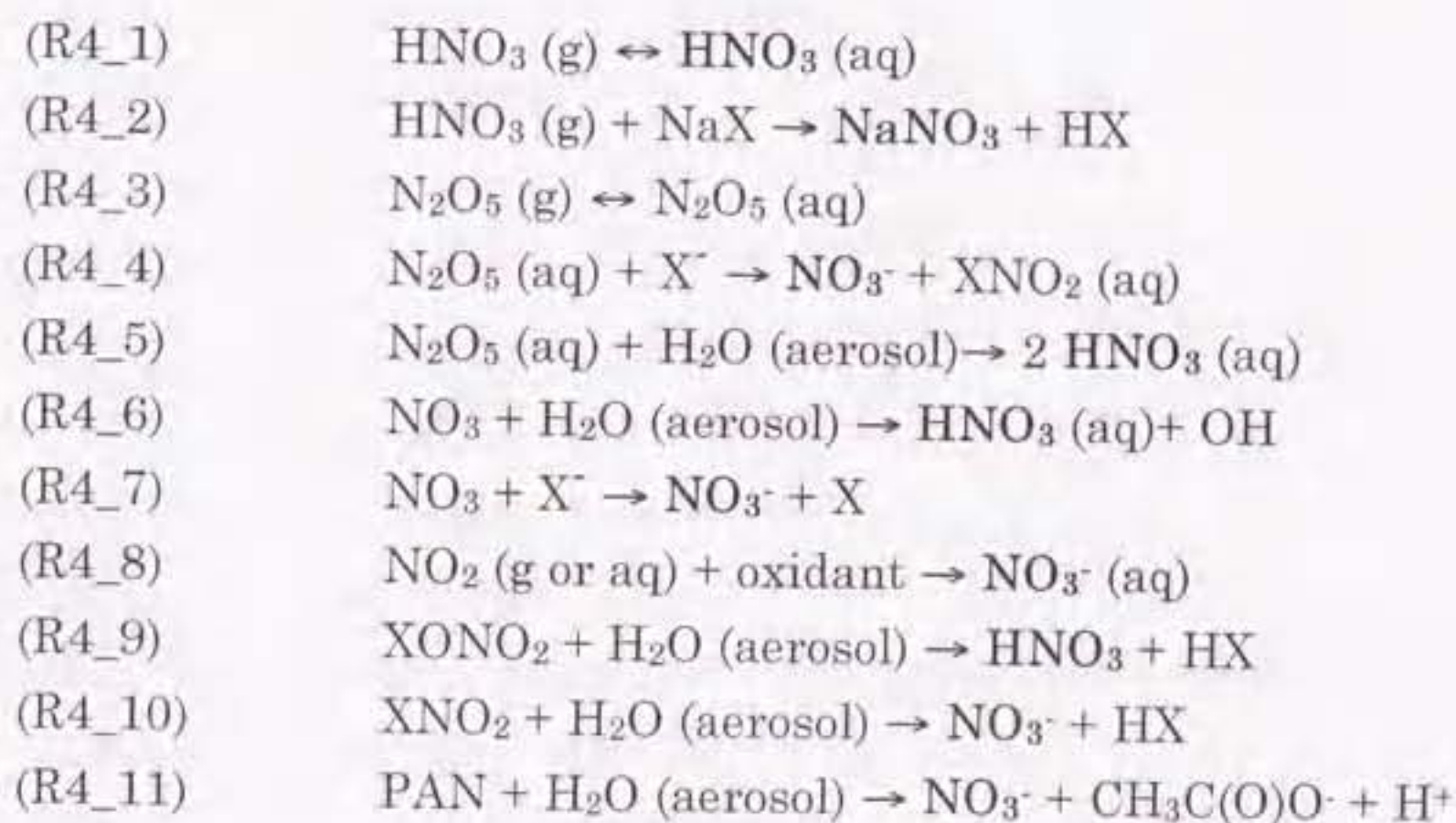
The nitron-reacted fraction of our samples was about 20 % on average. This value is much higher than the value (< 1 %) for upper marine boundary layer and free troposphere over Greenland Sea and near Svalbard [Parungo *et al.*, 1993]. As sea-salt -particle concentration decreased with increasing altitude [Blanchard, 1984], the nitron-reacted fraction may decrease significantly with altitude, assuming that reactive nitrogen oxides were internally mixed with sea-salt particles. On the other hand, without heterogeneous removal of HNO_3 with sea-salt s, much high HNO_3 concentration would be expected for upper troposphere due to lack of sea-salt particles. Indeed, high HNO_3 concentrations up to 367 pptv ($\approx 15 \text{ nmol m}^{-3}$) were reported in the free troposphere of spring Arctic [Jaeschke, 1997]. Thus, the high nitron-reacted fraction of coarse particles and the low concentration of gaseous HNO_3 suggest that sea-salt particles act as a large sink of inorganic nitrate within the marine boundary layer in winter Arctic. In turn, the presence of wholly Cl-depleted sea-salt particles might be used as an index of aging degree of sea-salt particles and oceanic air masses.

4_2_3. Estimation of the formation of particulate inorganic nitrates from reactive nitrogen oxides on sea-salt particles

For the estimation of contribution of each reactive nitrogen oxide to particulate NO_3^- formation, we carried out calculations using a simple uptake model. Time variation of particulate NO_3^- concentration, $[\text{NO}_3^-]$, in coarse particles was written by the following equation;

$$\frac{d[\text{NO}_3^-]}{dt} = \frac{d[\text{NO}_3^-]_{\text{hetero}}}{dt} - \frac{d[\text{HNO}_3]_{\text{evap}}}{dt} \quad \text{---(4_1).}$$

In equation (4_1), $d[\text{NO}_3^-]_{\text{hetero}}/dt$ and $d[\text{HNO}_3]_{\text{evap}}/dt$ mean the production rate of NO_3^- through the heterogeneous reaction, and HNO_3 loss rate through the evaporation from aerosol particles, respectively. The calculation was based on the heterogeneous formation of particulate NO_3^- in the liquid phase because of the presence of surface water, as mentioned above. The possible processes of heterogeneous formation of particulate NO_3^- on deliquescence sea-salt particles were as follows;



where X is Cl or Br [Finlayson-Pitts, 1983; Finlayson-Pitts and Pitts, 1986; Finlayson-Pitts *et al.*, 1989; van Doren *et al.*, 1990; Behnke *et al.*, 1991, 1992, 1994, 1996, 1997; Langer *et al.*, 1992; Fenter *et al.* 1994, 1996; George *et al.*,

Table 4_1. Uptake coefficients of reactive nitrogen oxides on salt in laboratory measurements

reagent	Uptake coefficient	T, K	Substrate condition	Reference
HNO ₃	0.193-0.158 ¹⁾	268-273	Water droplet	van Doren <i>et al.</i> [1990]
N ₂ O ₅	0.03	298	Wet salt aerosols	Behnke <i>et al.</i> [1991]
	0.039-0.014 ¹⁾	263-273	Droplets	George <i>et al.</i> [1994]
	0.032		Wet NaCl	Behnke [1997]
NO ₃	0.2×10^{-3} - 6.0×10^{-3}	273	NaCl solution	Rudich <i>et al.</i> [1996]
	2.0×10^{-3}	293	NaCl solution	Thomas <i>et al.</i> [1998]
NO ₂	6×10^{-5} - 5×10^{-8}	298	Dry NaCl	Vogt and Finlayson-Pitts [1994]
PAN	<10 ⁻⁴	199-226	H ₂ SO ₄ ²⁾	Zhang and Leu [1997]
ClNO ₂	3.41×10^{-6}	277.4	H ₂ O	Frenzel <i>et al.</i> [1998]
	2.7×10^{-7}	291	Wet salt aerosols	Behnke <i>et al.</i> [1997]
BrNO ₂	$>3.8 \times 10^{-6}$	291	NaCl solution	Frenzel <i>et al.</i> [1998]
	1.26×10^{-6}	275	H ₂ O	Frenzel <i>et al.</i> [1998]
BrONO ₂	>0.2	210-220	H ₂ SO ₄ ²⁾	Hanson and Ravishankara [1995]
ClONO ₂	6.7×10^{-3} - 4.6×10^{-3}	225-296	Dry NaCl	Timonen <i>et al.</i> [1994]

1): The values were used in model calculation.

2): The uptake coefficient on NaCl was still unknown as far as we knew.

1994; Timonen *et al.*, 1994; Vogt and Finlayson-Pitts, 1994; Hanson and Ravishankara, 1995; Karlson and Ljungström, 1995; Leu *et al.*, 1995 and 1997; Rossi *et al.*, 1996; Rudich *et al.*, 1996; Seisel *et al.*, 1997; Zhang *et al.*, 1997; Frenzel *et al.*, 1998; Thomas *et al.*, 1998].

The NO_3^- production rate through the heterogeneous reactions on sea-salt particles, $d[\text{NO}_3^-]_{\text{hetero}}/dt$, was only calculated for order-estimation of contribution of each reactive nitrogen oxide to particulate NO_3^- . The NO_3^- formation from ClONO_2 , ClNO_2 and BrNO_2 through reactions (R4_9) and (R4_10) was not included in the model calculation because of lower uptake coefficients (see in Table 4_1), and the absence of direct measurements of these species in the winter Arctic troposphere. On the other hand, BrONO_2 was included in the model calculation because of its higher uptake coefficient as given in Table 4_1 despite an absence of direct measurements. Sea-salt particles also contain NaBr that reacts with reactive nitrogen oxides to form particulate NO_3^- and reactive halogen species [Finlayson-Pitts *et al.*, 1989; Behnke *et al.*, 1994 and 1996; Frenzel *et al.*, 1998]. However, the molar ratio Br^- to Cl^- is about 1.54×10^{-3} in seawater [Wilson, 1975], as shown in Table 3_1. Moreover, the uptake coefficient of reactive nitrogen oxides on NaBr and KBr was of similar order to that on NaCl [Fenter *et al.*, 1994 and 1996; Leu *et al.*, 1995 and 1997; Rudich *et al.*, 1996; Rossi *et al.*, 1996; Seisel *et al.*, 1997]. Thus, the formation of particulate NO_3^- from the reaction between bromide and reactive nitrogen oxides was not included in the model calculation. Consequently, the heterogeneous production rate of particulate NO_3^- on sea-salt particles, $d[\text{NO}_3^-]_{\text{hetero}}/dt$ ($\text{nmol s}^{-1} \text{ m}^{-3}$), is here given by the following equation;

$$\frac{d[\text{NO}_3^-]_{\text{hetero}}}{dt} = k_1[\text{HNO}_3] + 2k_2[\text{N}_2\text{O}_3] + k_3[\text{NO}_3] + k_4[\text{NO}_2] + k_5[\text{BrONO}_2] + k_6[\text{PAN}] \quad \text{---(4_2)}.$$

In equation (4_2), k_i is the first-order rate constant for the removal of i species on the surface of sea-salt particles from the gas phase and is given by

$$k_i = \frac{1}{4} \bar{w}_i A \gamma_i \quad \text{---(4_3)},$$

where \bar{w}_i is the mean molecular speed of i species, A the surface area for reactions in cubic meter of air, and γ_i the reactive uptake coefficient of i species. The uptake

Table 4_2. Concentrations of each gaseous reactive nitrogen oxide in winter Arctic atmosphere

Specie	Concentration, <i>nmol m⁻³</i>	Location of measurements	Reference
HNO ₃	<0.6	Ny-Ålesund	This work
	0.2-0.9	Ny-Ålesund	Barrie *
NO _x	7.1-13.4	Ny-Ålesund	Beine <i>et al.</i> [1997] and Solberg <i>et al.</i> [1997]
HONO	0.2 – 3.1	Ny-Ålesund	Barrie *
	~3.1 ³⁾	Alert	Li [1994]
PAN	3.1 ~ 32.5	Ny-Ålesund	Beine <i>et al.</i> [1997]
Minor reactive nitrogen oxides ¹⁾	0.9 – 8.9	Ny-Ålesund	Solberg <i>et al.</i> [1997]
Ultra minor reactive nitrogen oxides ²⁾	~4.5 ⁴⁾		

*: Personal communication

1): NO₃ + N₂O₅ + HONO + HO₂NO₂ + HNO₃

2): NO₃ + N₂O₅ + HO₂NO₂

3): The values before polar sunrise

4): Concentration range was conjectured using the results of previous measurements in Table 2.

coefficient of each reactive nitrogen oxide is listed in Table 4_1. For the estimation of production rate of particulate NO₃, the following values were used; 2 µm for aerosol particle diameter and 263 and 273 K for air temperature. Moreover, we used 20 L⁻¹ as the number concentration of aerosol particles because the average number concentration of aerosol particles containing nitrate was ≈20 L⁻¹ except during storm conditions. Atmospheric concentration levels of each reactive nitrogen oxide in winter Arctic are listed in Table 4_2. As there

have never been direct measurements of N_2O_5 in the winter Arctic, the concentration of ultra minor reactive nitrogen oxides ($\text{NO}_3 + \text{N}_2\text{O}_5 + \text{HO}_2\text{NO}_2$) was assumed from the results of previous measurements as shown in Table 2. The concentration of BrONO_2 has not been measured in winter Arctic region. Therefore, the concentration of BrONO_2 was assumed to be 0.04 nmol m^{-3} on based on the concentration of BrO [Richiter *et al.*, 1998; Hebestreit *et al.*, 1999; McElroy *et al.*, 1999] as a precursor of BrONO_2 , the kinetic of following reaction: $\text{BrO} + \text{NO}_2 \rightarrow \text{BrONO}_2$, [De Moore, 1994] and the concentration of BrONO_2 calculated from model for bromine cycle in Arctic spring [Fan and Jacob, 1992]. The NO_3 production rate through the heterogeneous reactions was estimated for following three cases;

- case 1* assumed precursors; $\text{HNO}_3 + \text{N}_2\text{O}_5 + \text{NO}_3 + \text{BrONO}_2 + \text{NO}_2 + \text{PAN}$
- case 2* assumed precursors; $\text{HNO}_3 + \text{N}_2\text{O}_5 + \text{NO}_3 + \text{BrONO}_2$
- case 3* assumed precursors; $\text{HNO}_3 + \text{N}_2\text{O}_5 + \text{NO}_3$
- case 4* assumed precursor; HNO_3 .

The results of our model calculations suggests that heterogeneous production rate of particulate NO_3 was larger at 263 K (Figure 4_6a) than that at 273 K (Figure 4_6b). Consequently, production of particulate NO_3 in heterogeneous processes might be enhanced in the winter Arctic with lower temperature. The difference between *case 1* and *case 2* suggested that presence of NO_2 and peroxyacetyl nitrate (PAN) should have insignificant contribution to directly forming particulate NO_3 due to lower reaction probability in spite of the higher concentrations of NO_2 and PAN in winter Arctic (see in Table 4_1 and 4_2). As PAN is thermally decomposed in oceanic air mass with relatively high temperature ($> -10^\circ\text{C}$), PAN can play a role of the source of NO_2 , which can be precursors of ultra minor reactive nitrogen oxides such as N_2O_5 and NO_3 . The major process of forming particulate NO_3 should be the uptake of gaseous HNO_3 on wet surface of sea-salt particles. However, heterogeneous formation from ultra minor nitrogen oxides may have an important contribution to formation of particulate NO_3 under the condition of lower HNO_3 (g) concentration and/or higher concentrations of ultra minor reactive nitrogen oxides. Despite the high uptake coefficient of BrONO_2 , BrONO_2 may have a little contribution to forming NO_3 in the assumed concentration ($[\text{BrONO}_2] = 0.04 \text{ nmol m}^{-3}$). When BrONO_2 concentration is more than the assumed concentration, the contribution of BrONO_2 to NO_3 formation cannot be ignored. Using the mean number concentration of sea-salt particles containing nitrate, 20 L^{-1} , the observed average

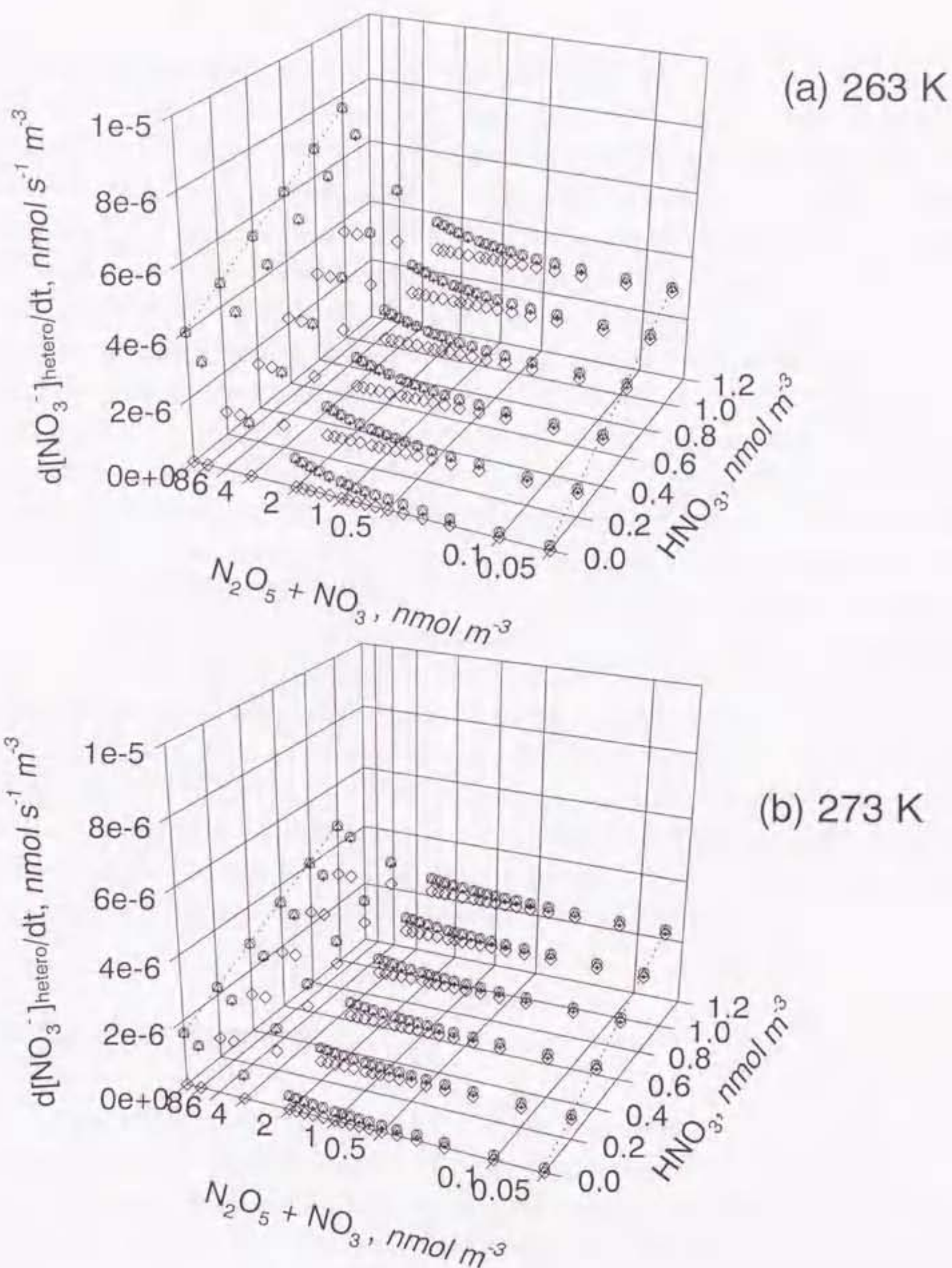


Figure 4_6. Production rate of particulate NO_3^- at 263 K (a) and 273 K (b)

Initial sea-salt-aerosol size: $2.0 \mu\text{m}$, $[\text{NO}_2] = 12 \text{ nmol m}^{-3}$, $[\text{PAN}] = 10 \text{ nmol m}^{-3}$,
 $[\text{BrONO}_2] = 0.04 \text{ nmol m}^{-3}$

Case 1 (circle): $\text{HNO}_3 + \text{N}_2\text{O}_5 + \text{NO}_3 + \text{BrONO}_2 + \text{NO}_2 + \text{PAN}$

Case 2 (triangle): $\text{HNO}_3 + \text{N}_2\text{O}_5 + \text{NO}_3 + \text{BrONO}_2$

Case 3 (cross): $\text{HNO}_3 + \text{N}_2\text{O}_5 + \text{NO}_3$

Case 4 (square): HNO_3

NO_3^- concentration in single aerosol particles containing NO_3^- was estimated to 5.0×10^{-5} nmol. Assuming that new sea-salt particles did not contain NO_3^- , it would take 10.3 days at 263 K and 13.9 days at 273 K in *case 1* to reach 5.0×10^{-5} nmol NO_3^- in a single sea-salt particle through the heterogeneous processes only in expected concentration levels, HNO_3 : 0.2 nmol m^{-3} and $\text{N}_2\text{O}_5 + \text{NO}_3$: 0.5 nmol m^{-3} . On the other hand, the time in *case 3* may be about 1.6 times at 263 K and about 1.4 times at 273 K as long as that in *case 1*. Considering the low HNO_3 (g) concentrations in the marine boundary of the winter Arctic and much shorter residence time (several days) for coarse sea-salt particles in lower marine boundary layer [Gong *et al.*, 1997], heterogeneous reaction between sea-salts and ultra minor reactive nitrogen oxides might be needed to sustain particulate NO_3^- concentration. Thus, the heterogeneous formation of particulate NO_3^- on sea-salt particles may have an important contribution to the rapid deposition from reactive nitrogen oxides in cold and dark atmosphere such as in the winter Arctic. These heterogeneous processes can occur not only in winter Arctic but also in any marine boundary layer in nighttime. In particular, the heterogeneous formation of particulate NO_3^- from ultra minor reactive nitrogen oxides may be more important in the polluted coastal areas with high concentrations of reactive nitrogen oxides. Moreover, the NO_3^- formation on sea-salt particles may have important contribution to halogen cycles in troposphere because higher reactive halogenated species can be emitted to atmosphere simultaneously through the heterogeneous reactions on sea-salt particles (R4_1 ~ R4_11).

4_3. Chapter Summary

This chapter discussed the role of sea-salt particles as sink of acidic species. Most sulfur species (nss-SO_4^{2-}) were distributed in fine particle fraction. Moreover, coarse aerosol particles containing sulfates were not only internal mixture with sea-salt particles but also coarse sulfate particles internally mixed with soot. Although methanesulfonate in coarse mode were internal mixture of sea-salt particles, its concentration was too low to have a significant influence on sulfur cycles in winter Arctic. Then, sea-salt particles might have a small contribution to removing processes in acidic sulfur species.

In contrast, most inorganic nitrates (>85%) were present as particulate nitrates in coarse particle fraction. SEM observation using nitron-thin-film technique showed that most coarse particles had a liquid phase on the particle

surface and that some coarse particles contained inorganic nitrates. LAMMS analysis showed that inorganic nitrates/nitrites were mostly in the forms of $\text{NaNO}_3/\text{NaNO}_2$ on the modified and wholly Cl-depleted sea-salt particles. The number fraction of coarse aerosol particles containing nitrates increased in aged oceanic air masses. Considering lower molar ratio of NO_3^- to sea-salt Na^+ in seawater, NO_3^- on sea-salt particles must be formed during the transport.

The model estimation showed the dominant forming processes of particulate NO_3^- should be uptake of gaseous HNO_3 on sea-salt particles in winter Arctic troposphere. However, ultra minor reactive nitrogen oxides such as N_2O_5 , NO_3 and BrONO_2 may have a large contribution to particulate NO_3^- formation in winter Arctic with longer nighttime and/or dusk condition, since their concentrations are expected to increase in nighttime. Therefore, particulate NO_3^- formation in coarse sea-salt particles may play an important role as a sink of reactive nitrogen oxides in winter Arctic troposphere.

Chapter 5

Sea-salt particles as the sources of reactive halogen species

5_1. Introduction

The modification of sea-salt particles by acidic species causes the formation and emission of reactive halogen species to the atmosphere as described in the previous Chapter. Reactive halogen species are converted to halogen radicals, which play an important role in atmospheric chemistry, through photochemical processes. For example, there are strong indications that surface ozone depletion and other atmospheric photochemistry in the Arctic troposphere during polar sunrise is due to halogen-catalyzed cycles such as $\text{Br} \leftrightarrow \text{BrO}$ [e.g., Barrie *et al.*, 1988; Le Bras and Platt, 1995; Sander *et al.*, 1997; Barrie and Platt, 1997; Ramacher *et al.*, 1997 and 1999; Tuckermann *et al.*, 1997; Ariya *et al.*, 1998 and 1999; Summer and Shepson, 1999]. A key outstanding issue in atmospheric chemistry associated with halogen cycles in polar region is the source of reactive halogen species. As mentioned in Chapter 4, the modification of sea-salt particles by acidic species can be one of the important primary sources of gaseous reactive inorganic halogen species. According to Barrie and Platt [1997], the possible sources of reactive halogen species during Arctic spring are halogen liberation in sea-salts either in the aerosol particles or on the ice/snow surface, and decomposition of organohalogen species. This chapter discussed halogen liberation from sea-salt particles as one of the primary sources of reactive inorganic halogens.

5_2. Results and Discussion

5_2_1. Variations and mixing states of atmospheric halogen species

Figure 5_1 shows the variations of the concentrations of gaseous inorganic chlorine species (g_Cl) and gaseous inorganic bromine species (g_Br), and the variations of molar ratio of g_Cl concentration to g_Br concentration in 1996/1997 and 1997/1998 winters at Ny-Ålesund. Our analytical method cannot identify each gaseous halogen specie (HX , HOX , XNO_2 , XY , X_2 , $XONO_2$ and XNO ; X or $Y = Cl$ or Br) because of the release of Cl^- and Br^- from each specie upon pure water extraction. The g_Cl concentration ranged from BDL (0.5 nmol m^{-3}) to 11.9 nmol m^{-3} in 1996/1997 winter and from BDL to 6.4 nmol m^{-3} in 1997/1998 winter. On the other hand, the g_Br concentration ranged from BDL ($<0.01 \text{ nmol m}^{-3}$) to 0.71 nmol m^{-3} in 1996/97 winter and from BDL to 1.9 nmol m^{-3} in 1997/1998 winter. These ranges were almost similar to the ranges observed at Alert, Canadian high Arctic (Barrie *et al.* [1994]). The molar ratio of g_Cl concentration to g_Br concentration showed the quite lower value than the molar ratio in seawater ($[Cl^-]/[Br^-] \approx 648$). According to Keene *et al.* [1998] and Ayers *et al.* [1999], more efficient bromine deficit should take place on sea-salt particles than chlorine deficit in marine boundary layer. Thus, the lower molar ratio of g_Cl to g_Br than seawater ratio may be caused by halogen fractionation in the halogen liberation either on sea-salt particles or sea-salts on the surface of snow and sea ice.

The concentration of g_Br gradually increased toward spring in both winters as shown in Figure 5_1. The increasing rates, estimated from the variation of running mean (5 points; 2.5 days), were given to

$[g_Br] = 0.0018 [\text{day of year 1997}] + 0.051$ ($R^2 = 0.69$) in 1996/1997 winter,
and

$[g_Br] = 0.0046 [\text{day of year 1998}] + 0.052$ ($R^2 = 0.43$) in 1997/1998 winter.

However, the increasing tendency in the concentrations of particulate bromine species (p_Br ; Br^- and BrO_3^-) was not observed as shown in Figure 5_2. Also the increasing tendencies of g_Cl and particulate chlorine species (p_Cl) were not observed in both winters. As shown in Figure 5_2, mass fraction of g_Br had a minimum around the winter solstice in both winters, and gradually increased toward to spring season. The mass fraction of g_Br reached up to about 60% in early March, whereas mean mass fractions of $nss\text{-}Br$ were 16% in 1996/1997 winter and 19% in 1997/1998 winter. Therefore, inorganic bromine species ($inorg_Br = g_Br + p_Br$) should be gradually accumulated in winter Arctic troposphere, and may be distributed mostly in gaseous phase and partly in

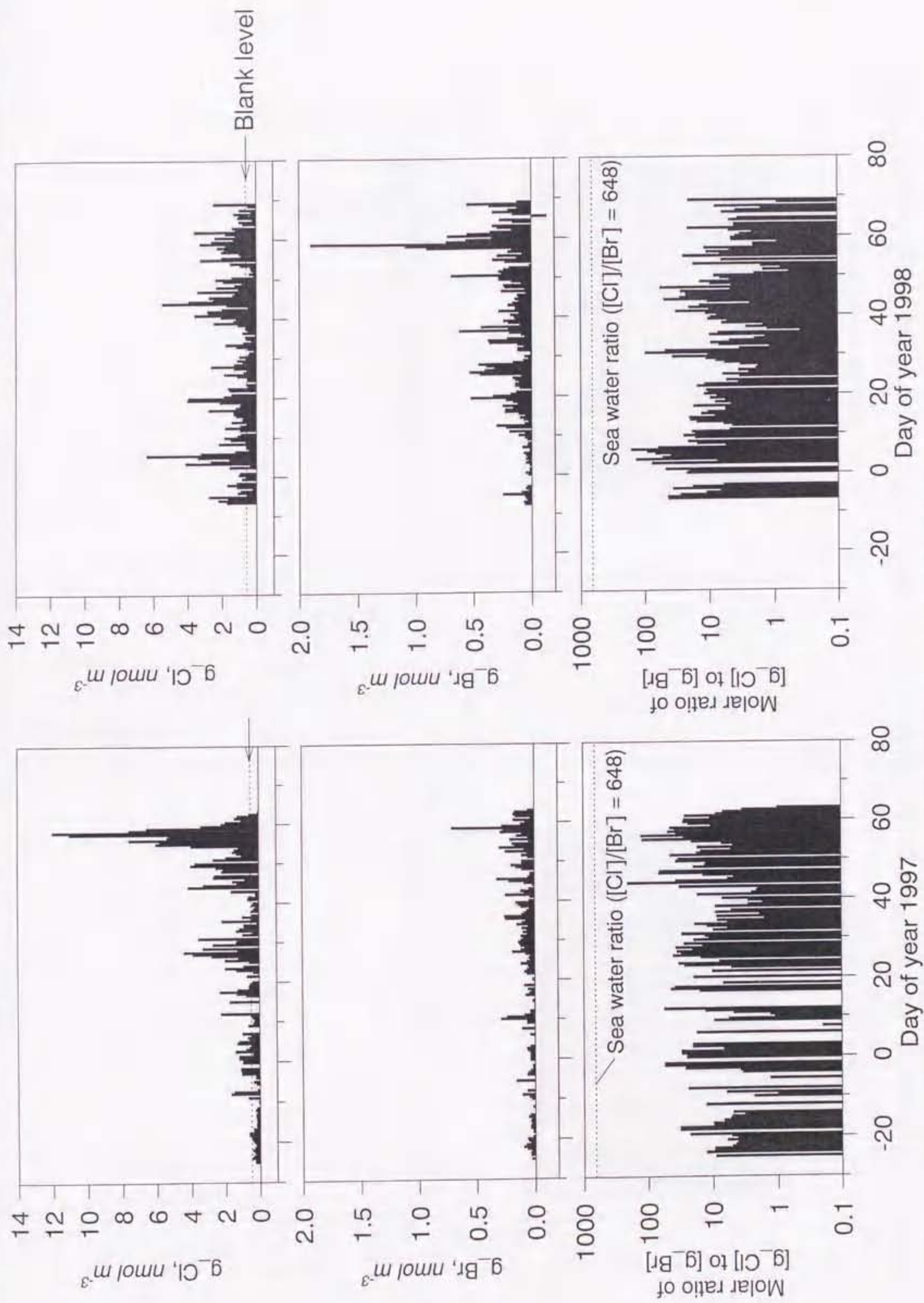


Figure 5_1. Variations of the concentrations of g_{Cl} and g_{Br} , and molar ratio of g_{Cl} concentration to g_{Br} concentration in 1996/1997 and 1997/1998 winters.

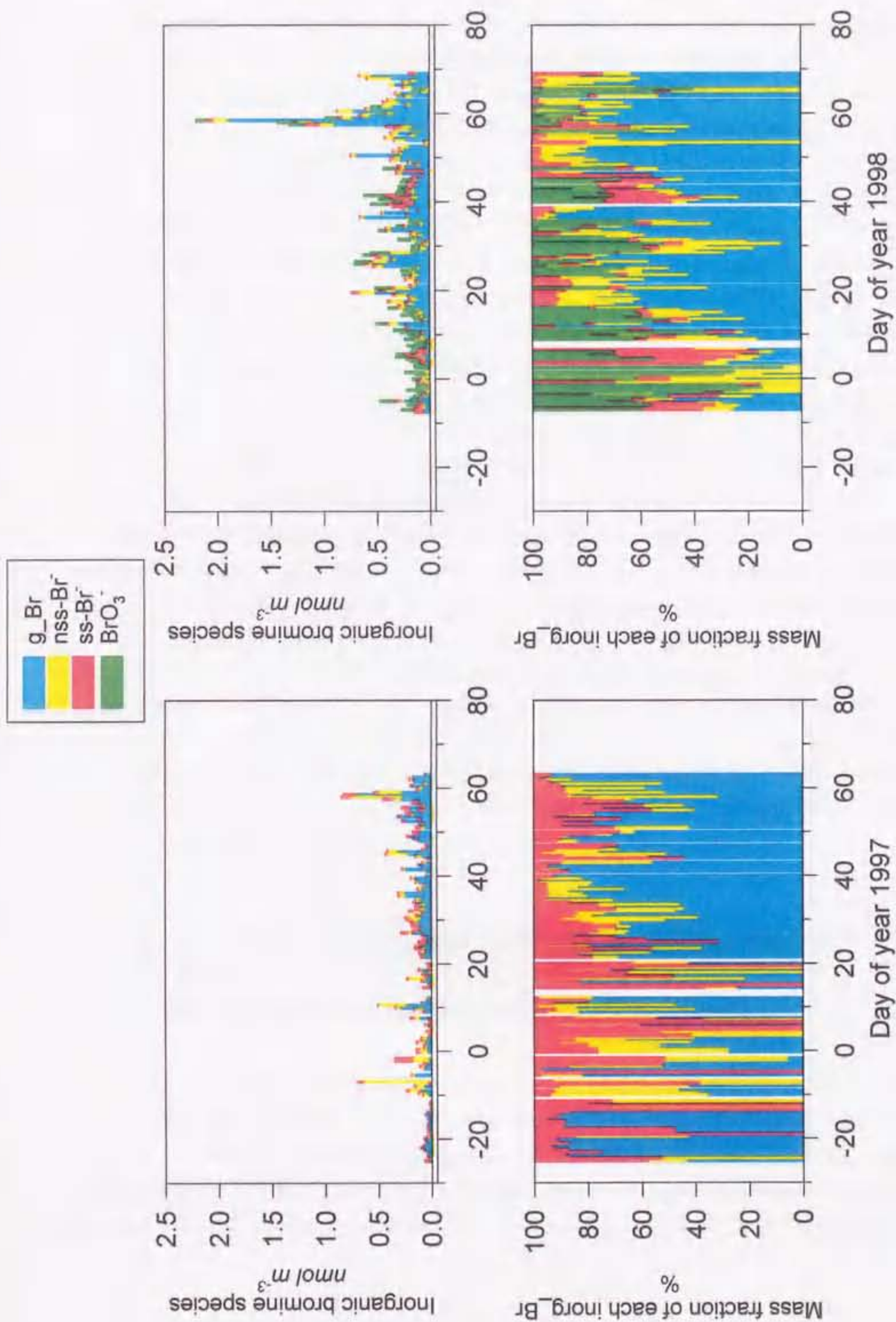


Figure 5_2. Variations of concentrations of gaseous inorganic bromine species (g_Br) and particulate bromine species (p_Br), and their mass fraction in 1996/97 and 1997/98 winters. Bromate was not determined in 1996/1997.

particulate phase in the winter Arctic troposphere. Exceeded bromine species to ss-Br were often observed in other Arctic regions (Barrow and Alert) during the winter/spring [Berg *et al.*, 1983; Sturges and Barrie, 1988; Sturges *et al.*, 1990; Sturges and Shaw, 1993; Barrie *et al.*, 1994a, 1994b; Li *et al.*, 1994]. In order to obtain the mixing states of aerosol particles containing exceeded bromine species, individual particles analysis was carried out using LAMMS in the present study.

LAMMS analysis showed that brominated species were often detected with sulfates and/or soot in fine mode, although the chemical state of particulate bromine species such as bromides and bromate was not identified in this study because of only detection of Br⁻ ($m/z=79$ and 81). In addition, ss-Br may be too low concentration in sea-salt particles to detect Br⁻, considering the seawater ratio ($[Br^-]/[Na^+]=1.79\times 10^{-3}$). Thus, obtained Br⁻ should be derived from the exceeded bromine species in aerosol particles. Figure 5_3 indicates the variations of relative abundance of bromine, and sulfate detected together with bromine in fine mode in 1995/1996 and 1996/1997 winters. The features and ranges of relative abundance of bromine species (Figure 5_3a and b) were similar to those of bromine species detected with sulfates. The exceeded bromine species in particulate phase may be internally mixed in fine sulfate particles in winter Arctic troposphere. Because of higher concentration of g_Br, the exceeded bromine species were likely due to uptake of g_Br on fine sulfate particles during the transport. Higher relative abundance of sulfates particles containing bromine species was found in oceanic air masses with higher Na⁺ concentration, whereas less found in polluted or Arctic air masses with higher SO₂ or nss-SO₄²⁻ concentrations. This variation suggested the possibility that the exceeded bromine species in fine sulfate particles and g_Br was derived from marine origins. Details of sources of g_Br were discussed in later section.

5_2_2. Sources of inorganic halogen species in winter Arctic

a. Source of gaseous inorganic chlorine species

In contrast to the variation of inorg_Br, the increasing tendency of g_Cl and p_Cl concentrations was not obtained in both 1996/1997 and 1997/1998 winters, so that an insufficient or less accumulation of inorganic chlorine species ($\text{inorg_Cl} = \text{g_Cl} + \text{p_Cl}$) occurred in winter Arctic troposphere. Most of p_Cl was in the form of Cl₂, which concentration is almost equivalent to ss-Cl⁻ except the

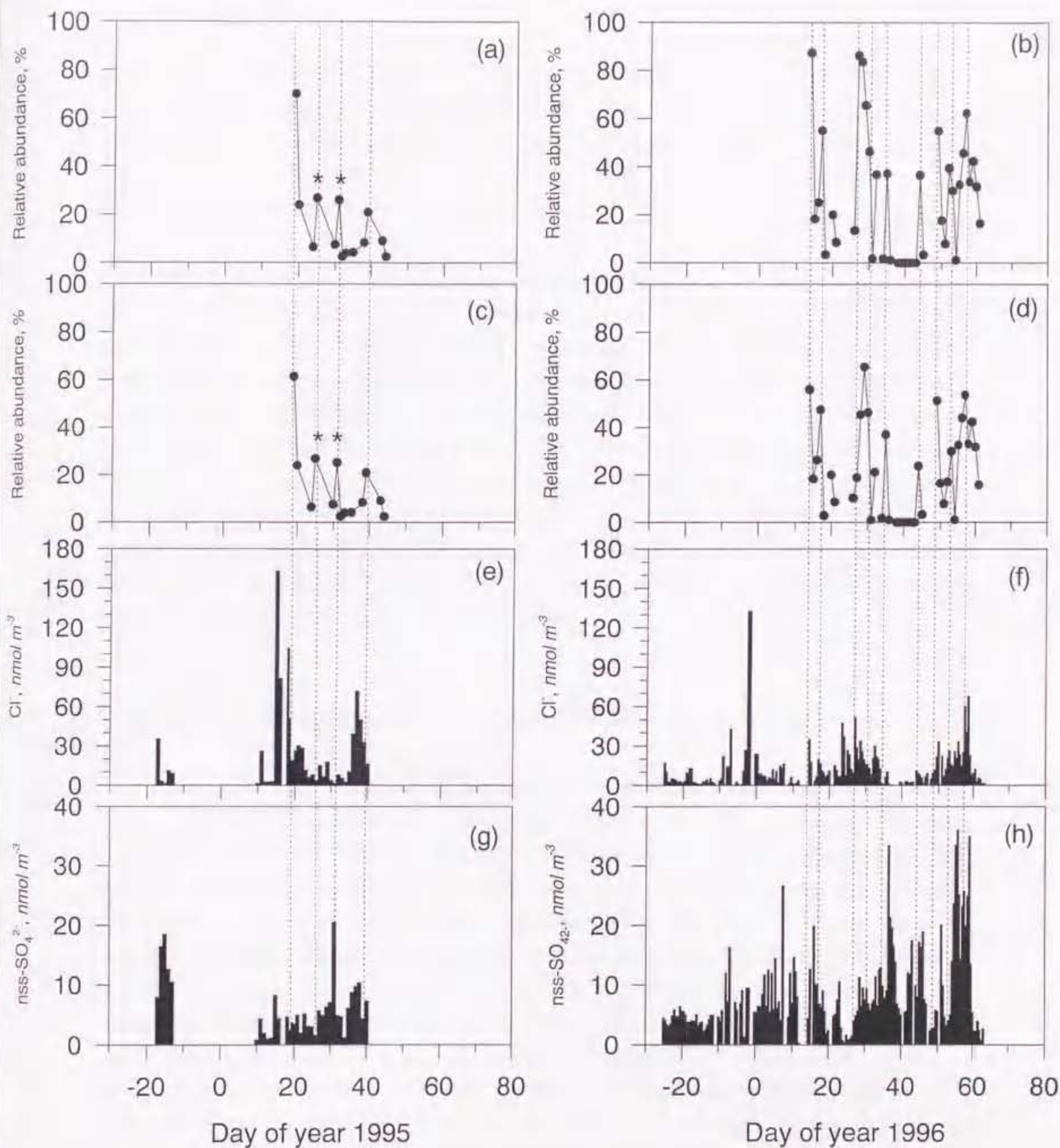


Figure 5_3. Variations of (a, b) relative abundance of bromine species, (c, d) relative abundance of bromine species detected with sulfates, and the concentrations of (e, f) Na^+ and (g, h) nss-SO_4^{2-} in 1995/1996 and 1996/1997 winters. Asterisks indicated the transport of aged oceanic air mass.

periods with large Cl⁻ depletion on sea-salt particles by acidic species. Since Cl⁻ depletion was often observed, depleted Cl⁻ (dep_Cl⁻) amount was estimated arithmetically from the following equation using seawater ratio;

$$[\text{Dep_Cl}] = [\text{ss_Cl}] - [\text{Cl}] = 1.2 \times [\text{Na}^+] - [\text{Cl}] \quad \text{---(5.1).}$$

Figure 5_4 shows the variations of the concentrations of g_Cl, dep_Cl⁻ and Cl⁻ in 1996/1997 and 1997/1998 winters. Lower dep_Cl⁻ concentration was found in the periods with higher concentrations of sea-salts, whereas higher dep_Cl⁻ was observed in the periods with lower Na⁺ concentration. Then less Cl⁻ depletion on sea-salt particles probably occurs in relatively fresh oceanic air mass, and obvious Cl⁻ depletion was observed in aged oceanic air mass. In both winters, dep_Cl⁻ concentration showed almost similar range to g_Cl concentrations. Moreover the variations of dep_Cl⁻ concentrations had a good correspondence to that of g_Cl in 1996/1997 winter. Hence g_Cl in winter/spring Arctic troposphere might result from volatilization from sea-salt particles by acid displacement reactions involving HNO₃, H₂SO₄, and others.

b. Sources of gaseous inorganic bromine species

In contrast to inorg_Cl, the inorg_Br concentration exceeded atmospheric ss-Br⁻ concentration, and an increasing tendency of g_Br concentration was observed, as mentioned above. The accumulation of inorg_Br must depend on the balance between the source strength and sink strength. Here, the source processes of inorg_Br were only discussed for the first step of better-understanding in atmospheric bromine cycles in winter/spring Arctic troposphere because of large uncertainty in deposition and removing processes of each inorg_Br under the winter/spring Arctic condition. Some investigators suggested the following sources of g_Br; (1) halogen depletion of atmospheric sea-salt particles through the heterogeneous processes [Mozurkewich, 1995; Vogt *et al.*, 1996; Oum *et al.*, 1998a], (2) halogen liberation from sea-salts on the surface of sea ice and/or snow through the heterogeneous processes [McConnell and Henderson, 1993; Tang and McConnell, 1996; Oum *et al.*, 1998b], (3) the decomposition of organic bromine species (org_Br) and organic chlorine species (org_Cl) such as CH₃Br and CHBr₃ [Oltmans *et al.*, 1989; Li *et al.*, 1994; Elliott and Rowland, 1995; Yokouchi *et al.*, 1996] and (4) human activities [Thomas *et*

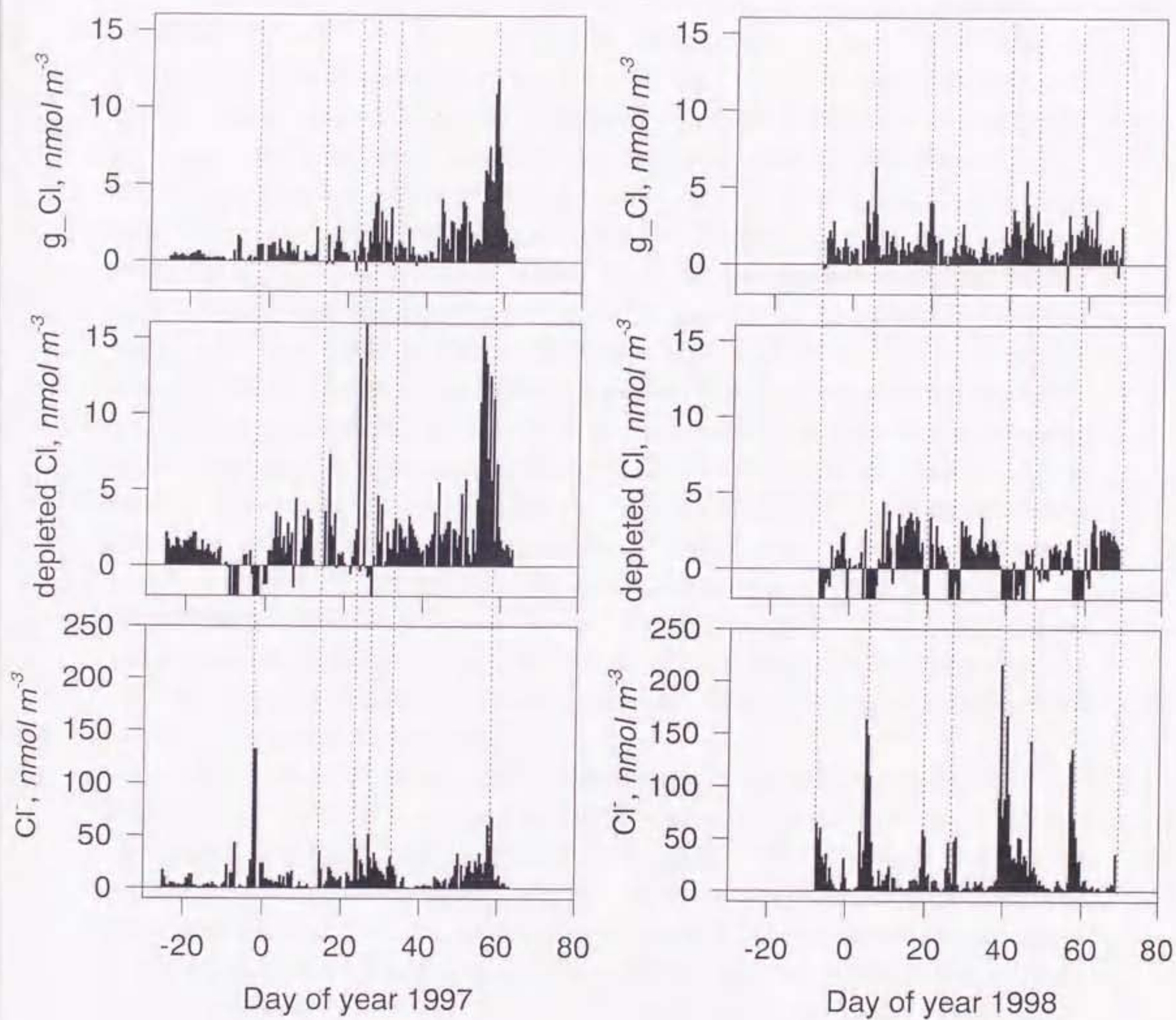


Figure 5_4. Variations of the concentrations of g_{Cl} , depleted Cl^- , and Cl^- in 1996/1997 and 1997/1998 winters.

et al., 1997].

As the decomposition of org_Br occurs mainly through photochemical processes [Li *et al.*, 1994; Yokouchi *et al.*, 1996], the contribution of photochemical decomposition of org_Br and org_Cl can be neglected or less in winter Arctic during the periods (December - January) with no solar radiation. Although org_Br and org_Cl can also decompose through the reaction with NO_3 , which concentration increase in nighttime, reaction rate is too slow to have sufficient contribution to sustain inorg_Br concentration in winter Arctic troposphere [Singh and Fabian, 1999]. Thus the decomposition of org_Br may have insignificant contribution to inorg_Br formation in winter/early-spring Arctic with less solar radiation. However, transport of air mass from mid-latitudes, where org_Br should be decomposed through photochemical processes, maybe have a possibility the sources of reactive halogen species in winter/spring Arctic. Although some org_Br such as CH_3Br can be hydrated slightly, org_Br have too slow hydrolysis rate [Elliot and Rowland, 1995] and low concentration [Yokouchi *et al.*, 1996] to have a significant contribution to inorg_Br in winter Arctic troposphere. Therefore, the decomposition of org_Br may have an insignificant or small contribution to the release of inorg_Br in dark/dusk winter Arctic. Indeed, Li *et al.* [1994] and Barrie *et al.* [1994a, 1994b] suggested the lower contribution of organic bromine species to inorg_Br at Alert, Canadian high Arctic, in winter/spring seasons.

SO_2 , nss- SO_4^{2-} were used as the tracer of polluted air masses in the present study, because major pollutants in winter Arctic are SO_2 , nss- SO_4^{2-} and soot [Barrie and Hoff, 1984; Barrie and Bottenheim, 1993]. Figure 5_5 shows the variations of the concentrations of g_Br, SO_2 and nss- SO_4^{2-} in 1996/1997 and 1997/1998 winters. Poor correspondence between g_Br concentrations and those of SO_2 and nss- SO_4^{2-} was found in both 1996/1997 and 1997/1998 winters. Then, most of inorg_Br in winter and spring Arctic may be released from other processes rather than anthropologic sources. According to Sturges and Barrie [1988], atmospheric bromine species might be derived from biological activity in a sea. Also Sturges and Shaw [1993] suggested that particulate bromine species was derived from the marine-origins.

As mentioned above, halogen depletion of atmospheric sea-salts either in sea-salt particles or on sea-ice/snow through the heterogeneous processes is expected as the g_Br sources in winter Arctic troposphere. Gaseous reactive bromine species can be released through following heterogeneous reactions;

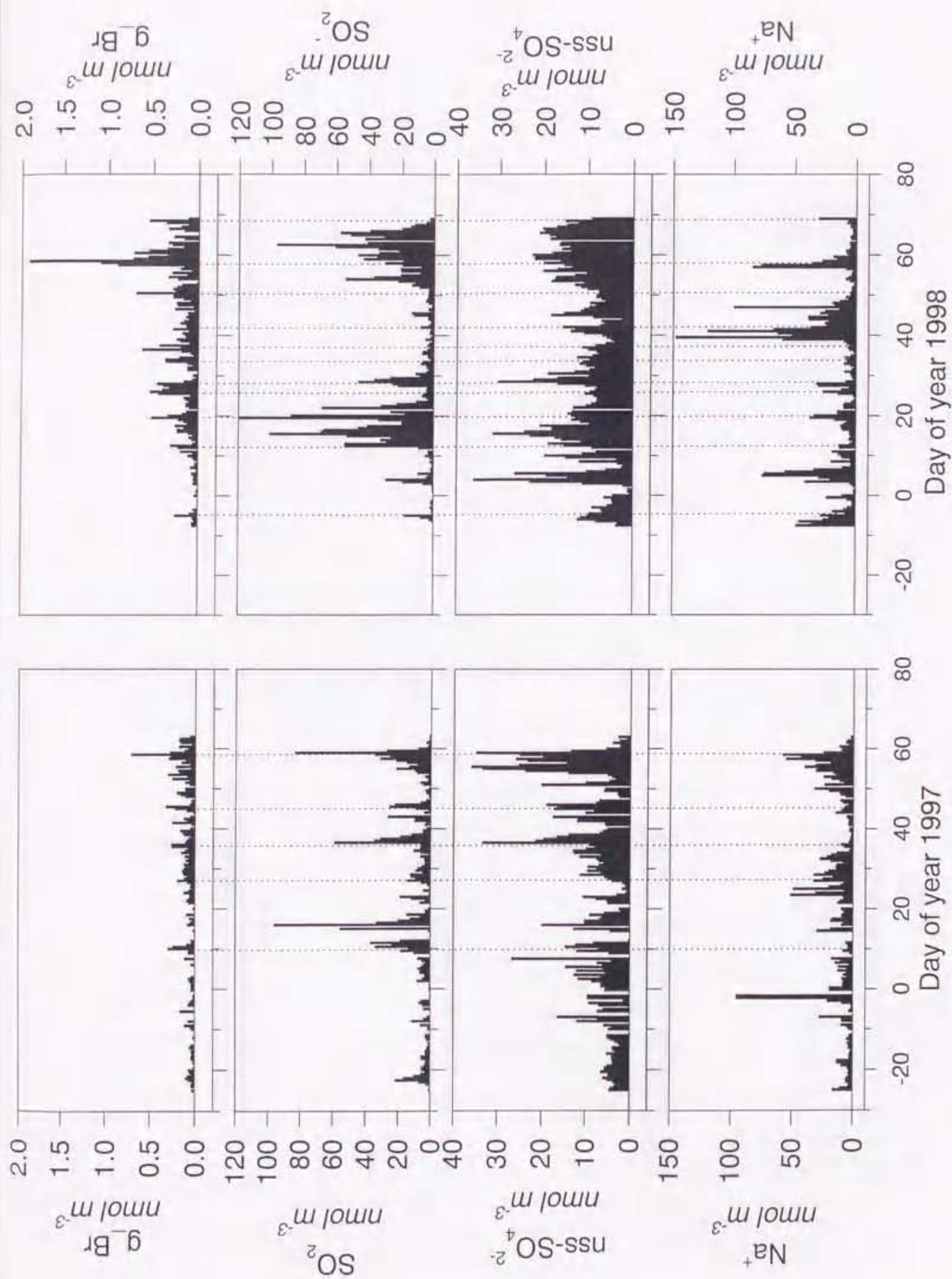


Figure 5_5. Variations of the concentrations of g_Br , SO_2 , nss-SO_4^{2-} , and Na^+ in 1996/1997 and 1997/1998 winters.

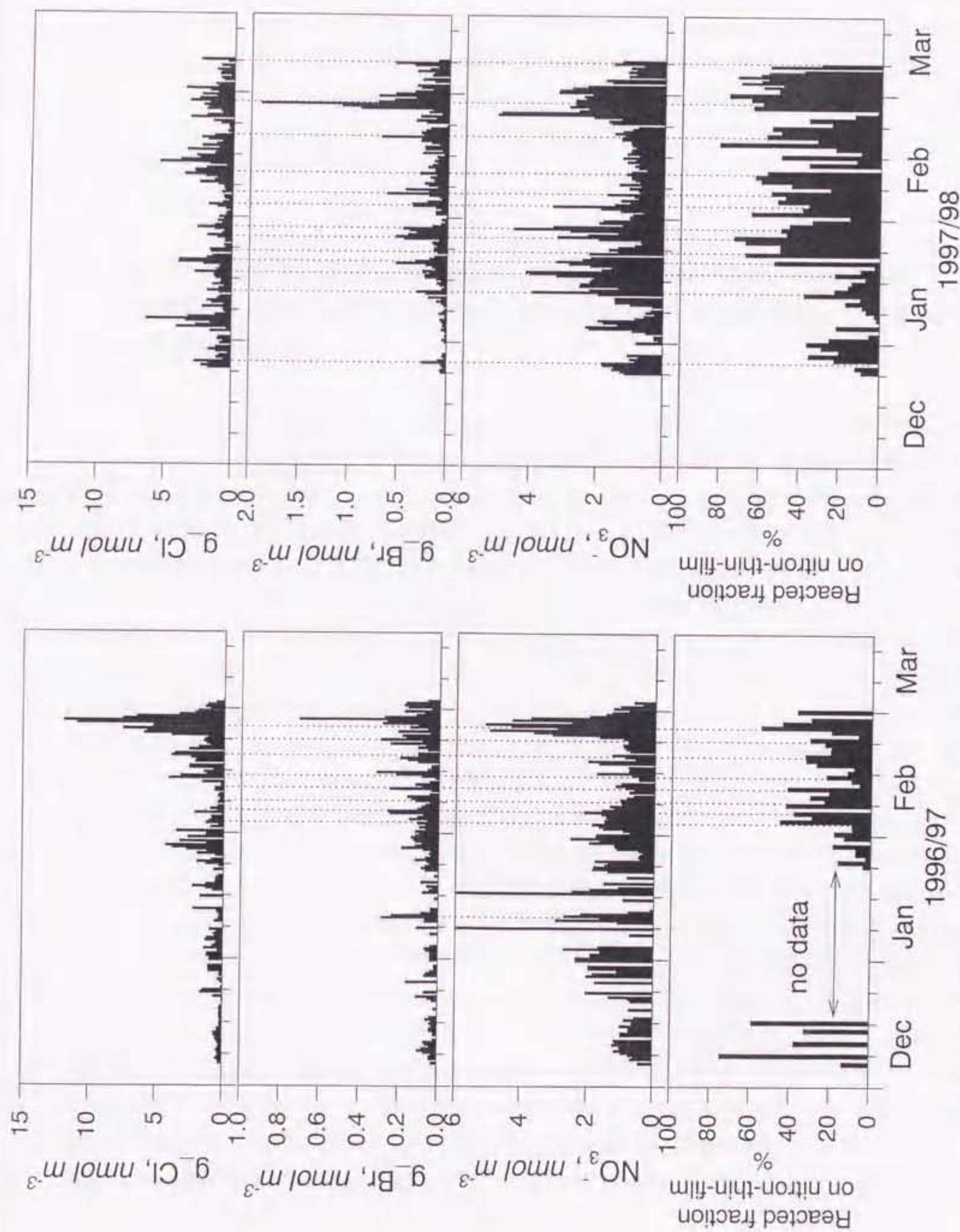


Figure 5_6. The variations of the concentrations of gaseous inorganic chlorines, gaseous inorganic bromines, and particulate NO_3^- , and reacted fraction on nitron thin films in 1996/1997 and 1997/1998 winters.

modification of coarse sea-salt particles by reactive nitrogen oxides was also observed in coastal region of mid-latitude [Pio and Lopes, 1998]. In addition, Ayers *et al.* [1999] suggested that preferential bromine liberation might occur on coarse sea-salt particles in marine boundary layer. Thus, a correspondence between g_Br , NO_3^- , and higher reacted fraction on nitron-thin-film suggested that the modification of coarse sea-salt particles by reactive nitrogen oxides is likely one of important sources of g_Br in winter Arctic troposphere, since the release of g_Br occurred together with particulate NO_3^- formation on sea-salt particles through the above reactions (R 5_4 ~ R5_9).

c. Estimation of the emission rate of gaseous inorganic bromine species from heterogeneous reactions on sea-salt particles

For the estimation of the release-amount of g_Br through the heterogeneous processes on sea-salt particles, simple uptake model as same as that in Chapter 4 was used. In this Chapter, ss_Br^- concentration was added. Other initial parameters such as surface area of aerosol particles and the concentration of reactive nitrogen oxides were as same as the model estimates in Chapter 4. The release rate of g_Br in the forming of particulate inorganic nitrates was only estimated in this model because of large uncertainty of deposition/decomposition velocity of each gaseous halogen specie in winter Arctic troposphere. Moreover, the fractionation of halogen species in the deficits on sea-salt particles, as mentioned above, was neglected in the model estimation because of large uncertainty in the fractionation processes, so that releasing rate of g_Cl and g_Br from sea-salt particles was assumed to depend on sea water ratio in sea-salt particles. Figure 5_7 shows the results of the estimation of releasing rate of g_Br and g_Cl through the heterogeneous reactions between sea-salts and reactive nitrogen oxides. The increasing rate of g_Br concentration, $-0.0018 \text{ nmol m}^{-3} \text{ day}^{-1}$ in 1996/1997 winter and $0.0046 \text{ nmol m}^{-3} \text{ day}^{-1}$ in 1997/1998 winter as describe above— was ranged in the estimated releasing rate of g_Br . Then, heterogeneous reactions between reactive nitrogen oxides and sea-salt particles might be one of important sources of g_Br in winter/spring Arctic troposphere. During the higher concentrations of ultra minor reactive nitrogen oxides such as N_2O_5 and NO_3 under the dark/dusk condition in winter/spring Arctic, significant amounts of higher reactive brominated species such as $BrNO_2$

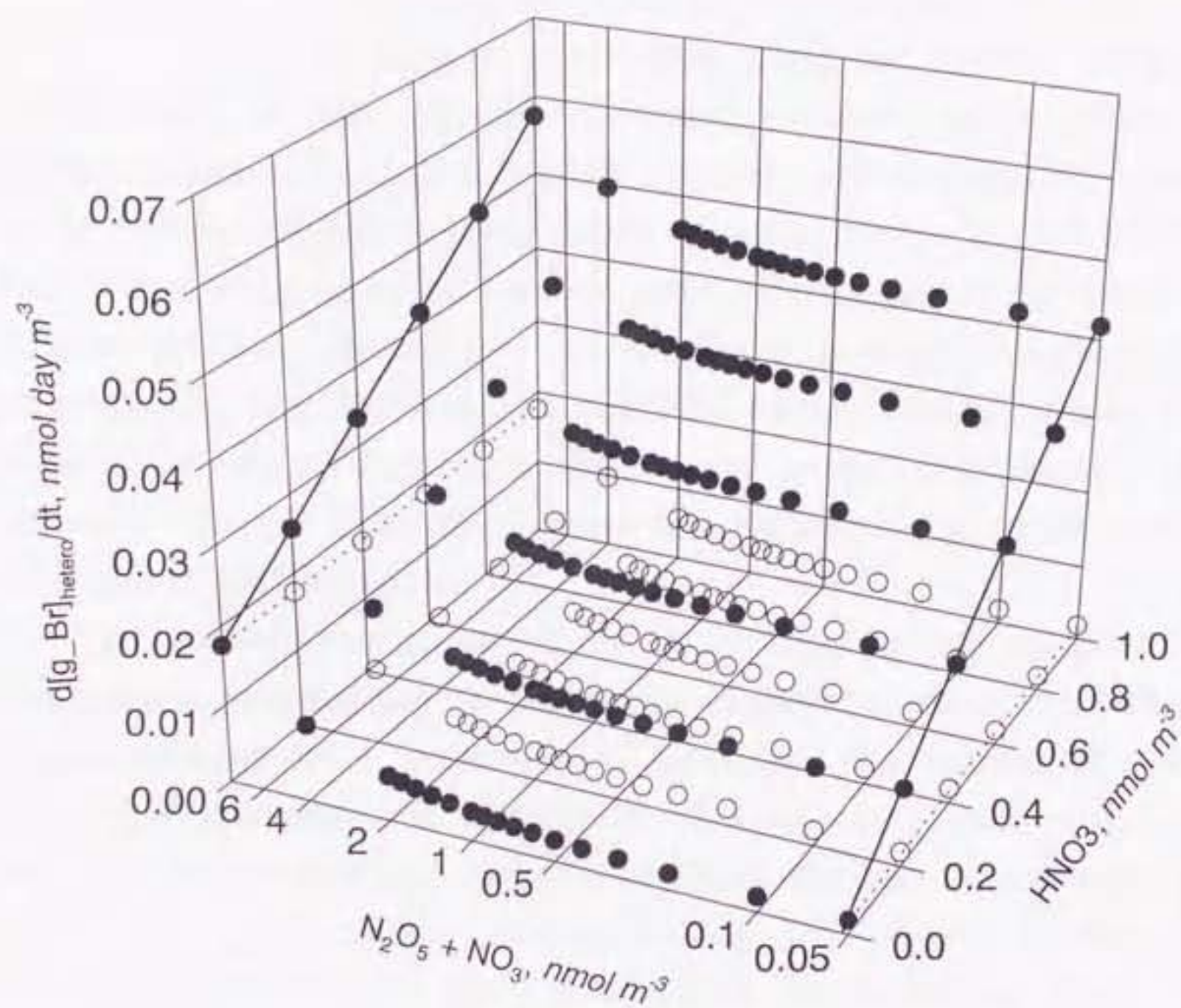


Figure 5_7. Estimated releasing rate of g_{Br} at 263 K; Filled circle indicates total releasing rate of g_{Br} ; Open circle indicates releasing rate of g_{Br} through the reaction between bromide and ultra minor reactive nitrogen oxides.

and Br can be released through the heterogeneous reactions on sea-salt particles (*e.g.*, R5_5 and R5_6). Indeed, presence of BrO_3^- in the winter Arctic troposphere should suggest indirect evidence of significant amount of higher reactive brominated species in the atmosphere, because precursor of BrO_3^- is BrO^- that might result from the ozone oxidation of Br in sea-salt particles and/or uptake of BrO/HOBr . Li *et al.* [1994] also suggested the contribution of higher reactive bromine species such as Br_2 in the dark period and HOBr in light to inorg_Br. If air masses containing significant amounts of higher reactive brominated species including inorg_Br are exposed to enough intensity solar radiation to release halogen radicals, the catalytic system related surface ozone depletion could start in polar sunrise. Furthermore, Arctic air mass with higher concentrations of unstable and high reactive species may affect the atmospheric chemistry — especially oxidant chemistry — of northern hemispheric troposphere, when reactive species are decomposed through photochemical processes during the outbreaks of Arctic air mass to mid-latitudes. Indeed the meteorological condition as shown in Figure 3_3b may cause the outbreaks of Arctic air mass around Spitsbergen to mid-latitudes.

The heterogeneous reactions on sea-salt particles may have a large contribution to sustain the concentration of gaseous inorganic halogen species in the winter/spring Arctic atmosphere. Although the release of gaseous halogen species from the snow/ice surface is also expected, we cannot estimate the contribution because of less knowledge about the kinetics on snow/ice surface in winter Arctic. For better understanding of halogen cycles during polar winter/spring, we will need more information, for examples, ① size distribution of particulate brominated species, ② kinetics of each reaction related with halogen species under low temperature, and ③ deposition/decomposition velocity of gaseous halogen species under the condition during polar winter/spring.

5_3. Chapter summary

In Chapter 5, the variations and sources of inorganic halogen species were discussed from the viewpoint of the modification of sea-salt particles as the sources.

Obvious Cl⁻ depletion was found in aged oceanic air mass, but less in fresh oceanic air mass. By comparison between variation of g_Cl and dep_Cl amounts, the dominant source of g_Cl was probably the Cl⁻ liberation of sea-salt

particles through the heterogeneous reactions in winter/spring Arctic troposphere. Although g_Br can be release from the modification of sea-salt particles, molar ratio of g_Cl concentration to g_Br concentration showed quite lower value than molar ratio of Cl⁻ to Br⁻ in seawater. This tendency may result from fractionation of g_Br in the modification of sea-salt particles. Then, g_Br was likely enriched to seawater ratio in winter Arctic troposphere.

Inorg_Br was gradually accumulated in the atmosphere from winter season toward to spring season, although this tendency was not observed in the feature of inorg_Cl. Exceeded inorg_Br to ss-Br concentrations was distributed in gaseous phase ($\approx 60\%$ in average), and slightly in particulate phase ($\approx 16\%$ in average). Single particle analysis using LAMMS showed that the exceeded bromine species in particulate phase were internally mixed in fine sulfate particles. The variation of relative abundance of sulfates internally mixed with bromine species suggested that inorg_Br was derived from the marine-origin. In addition, the variations of g_Br had a good correspondence to the variations of NO₃⁻ concentration and/or reacted fraction of coarse particles —occurrence of aerosol particles containing NO₃⁻— on nitron-thin-films. According to simple uptake model estimation, g_Br releasing rate from the modification of sea-salt particles also showed similar range to g_Br concentration and increasing rate of g_Br concentration in winter/spring Arctic troposphere. Therefore, the modification of sea-salt particles was one of significant sources of g_Br in winter/spring Arctic troposphere.

Chapter 6

Conclusions

The present study investigated the heterogeneous chemistry on sea-salt particles in winter/spring Arctic troposphere, and its chemical roles as sink of acidic species and source of reactive halogen species.

Oceanic air mass containing large amount of wet sea-salt particles was transported from mid-latitudes to Ny-Ålesund through storm access. Also aged oceanic air mass, which was identified using aging index (C/F ratio of Na^+), was also often observed. Although the modification of sea-salt particles—halogen liberation—rarely occurred in fresh oceanic air mass, large halogen liberation on sea-salt particles was observed in aged oceanic air mass. Single particle analysis by means of LAMMS and thin-film technique showed some modified sea-salt particles contained acidic species such as sulfates, sulfites, methanesulfonates, nitrates, and nitrites. Then, sea-salt particles should be gradually modified—halogen liberation—by acidic species during the transport. As sea-salt particles was mostly distributed in coarse mode ($> 2\mu\text{m}$ in diameter) with shorter residence time in the atmosphere, sea-salt particles as alkaline reagent can play a role in deposition or removal processes of atmospheric acidic species.

Major particulate sulfur specie was sulfate, and minor was methanesulfonate in winter/spring Arctic troposphere. Sulfates were mostly distributed in fine mode ($0.2 - 2\mu\text{m}$ in diameter). Coarse aerosol particles containing sulfates were present as the internally mixtures of sulfate/sea-salt particles and soot/sulfate particles, whereas most fine sulfates were externally mixing with sea-salt particles. Then, sea-salt particles may have a small or less contribution to removing acidic sulfur species from atmosphere. On the other hand, inorganic nitrates were mostly ($>85\%$) present as internal mixture of coarse sea-salt particles. Then, coarse sea-salt particles with short residence time may enhance to significant removing of atmospheric reactive nitrogen oxides,

which were converted to particulate nitrates on sea-salt particles through heterogeneous reactions. Simple uptake model estimation showed that dominant precursor of particulate NO_3^- on sea-salt particles is probably gaseous HNO_3 , and minor source of NO_3^- formation may be the heterogeneous reactions between ultra minor reactive nitrogen oxides such as N_2O_5 and NO_3 and sea-salts. Since the concentrations of N_2O_5 and NO_3 increase in nighttime, winter Arctic condition with polar night and low solar radiation likely enhance the particulate NO_3^- formation on sea-salt particles, and the release of higher reactive halogen species such as BrNO_2 .

Finally, the sources of gaseous inorganic halogen species were discussed from the viewpoint of heterogeneous reactions on sea-salt particles. The dominant source of gaseous chlorine species (g_Cl) might be the modification of sea-salt particles in winter/spring winter Arctic troposphere. In contrast, inorganic bromine species (inorg_Br) was enriched to seawater ratio ($[\text{Cl}^-]/[\text{Br}^-]$) in winter Arctic atmosphere. Exceeded inorg_Br (gaseous Bromine species and nss-Br) was mostly distributed in gaseous phase (>60% in mid-February – early March), and slightly in particulate phase. Although gaseous bromine species (g_Br) can be release from the modification of sea-salt particles as well as in the case of g_Cl , molar ratio of g_Cl concentration to g_Br concentration showed quite lower range than molar ratio of Cl^- to Br^- in seawater. This might be caused by fractionation of g_Br in the modification of sea-salt particles. Single particle analysis using LAMMS showed that the exceeded bromine species in particulate phase were internally mixed in fine sulfate particles and suggested that inorg_Br was derived from the marine-origin. The variations of g_Br had a good correspondence to the variations of NO_3^- concentration and/or reacted fraction of coarse particles —occurrence of aerosol particles containing NO_3^- — on nitron-thin-films. Then, the cycles of reactive nitrogen oxides were likely linked to the processes of g_Br emission. According to simple uptake model estimation, g_Br releasing rate from the modification of sea-salt particles by reactive nitrogen oxides also showed the similar range to g_Br concentration and the increasing rate of g_Br concentration in winter/spring Arctic troposphere. Therefore, the modification of sea salt particles was probably identified as one of significant sources of g_Br in winter/spring Arctic troposphere.

Sea-salt particles play important roles of the sink of acidic species, and the sources of reactive halogen species in winter/spring Arctic troposphere. When arctic air masses with higher concentrations of higher reactive halogen species are flowed to mid-latitude atmosphere, Arctic air mass may affect the

atmospheric chemistry, especially oxidant chemistry. Figure 6_1a and b schematize the chemical roles of sea-salt particles in winter/spring Arctic region and north hemispheric troposphere.

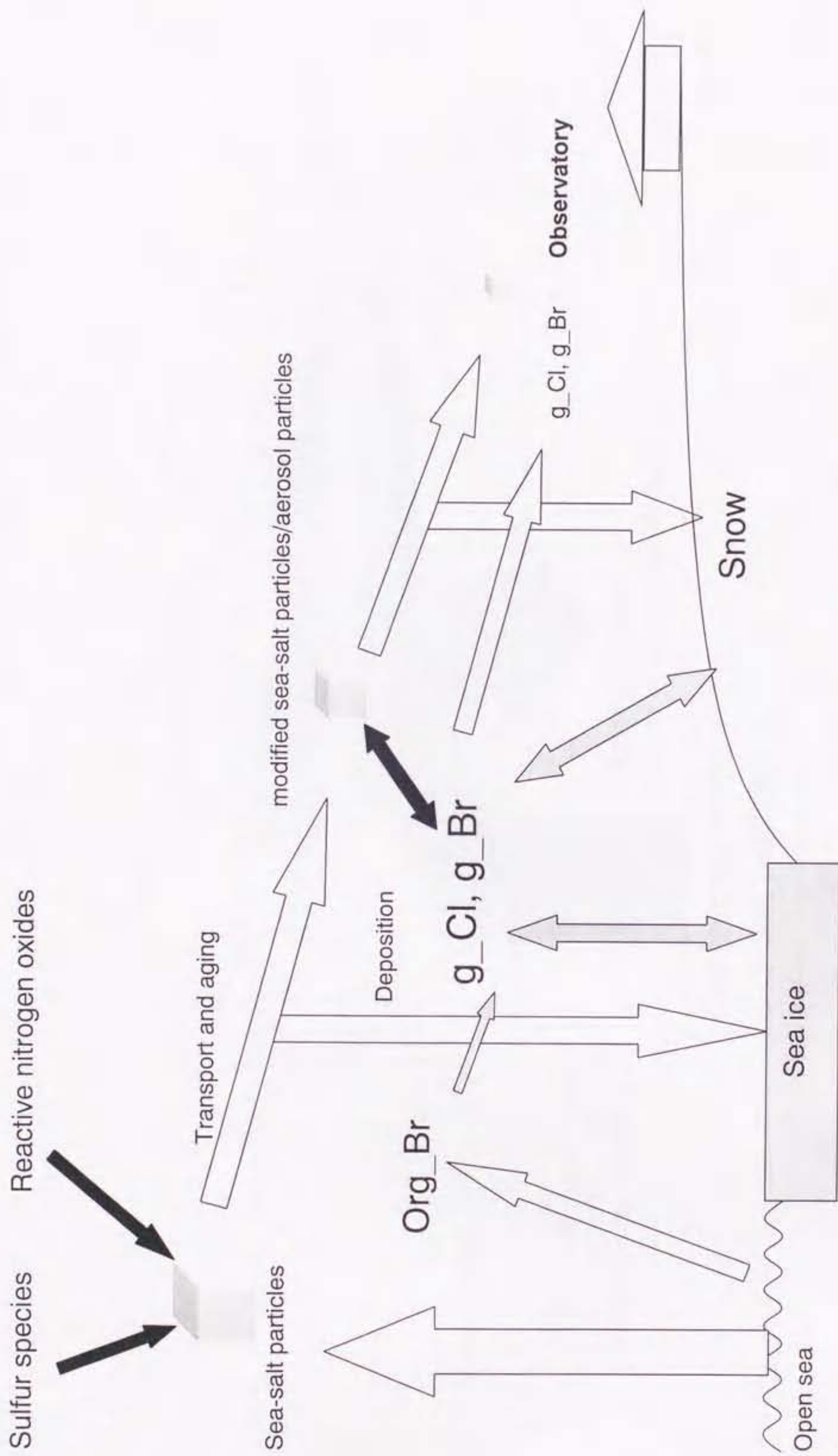


Figure 6_1a. Diagram of the chemical processes of sea-salt particles in winter/spring Arctic troposphere: White arrows show physical processes; Black arrows show chemical processes; Gray arrows mean the processes with some uncertainty.

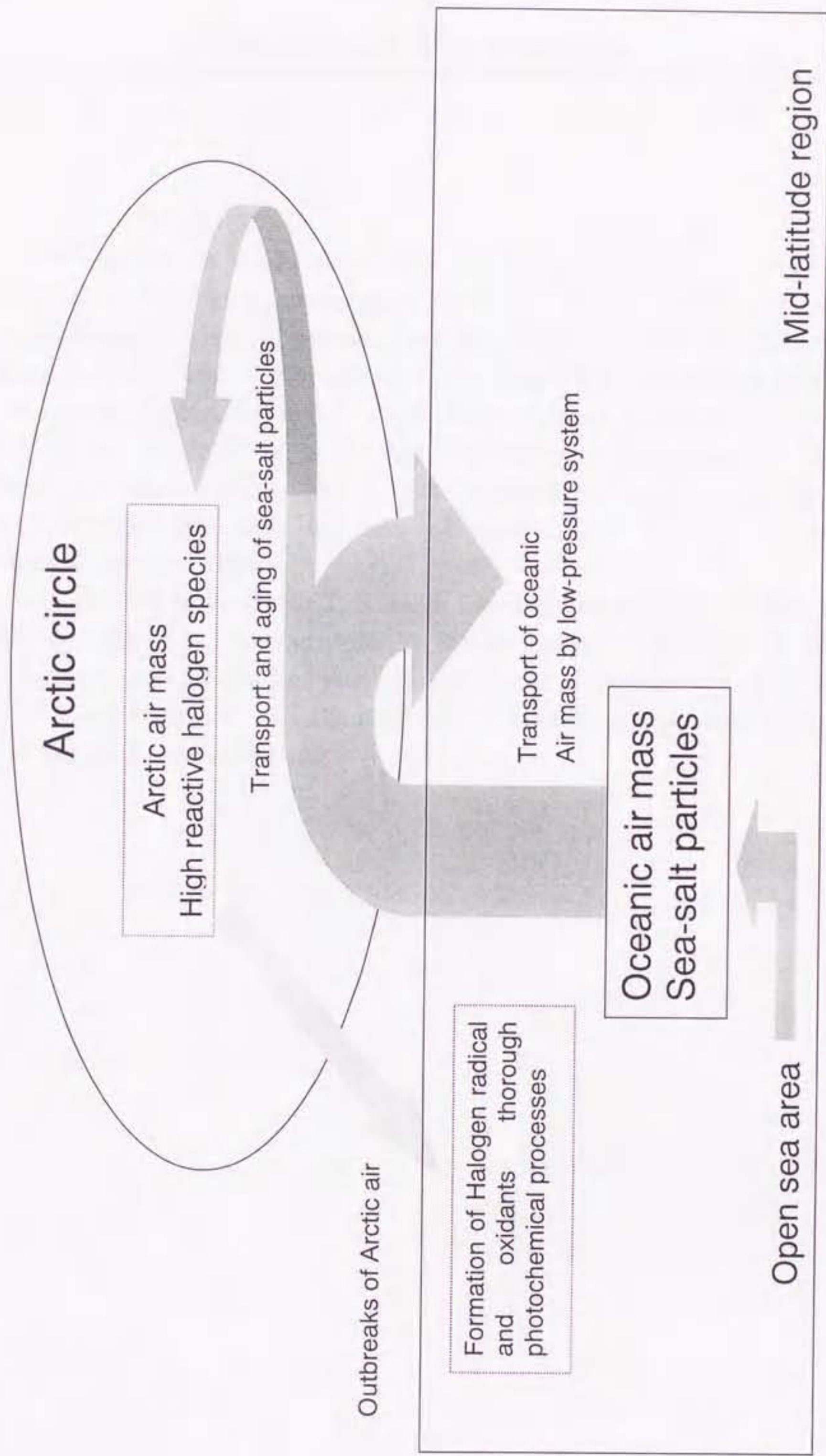


Figure 6_1b. Diagram of the roles of sea-salt particles in north hemispheric troposphere

Acknowledgements

I am grateful to Professor Y. Iwasaka for providing me to study the aerosols at Solar Terrestrial Environment laboratory, Nagoya University and for valuable guidance and helpful advice. I am also grateful to Drs. T. Shibata, K. Matsunaga, K. Osada and M. Hayashi for many discussions and suggestions, and help of sampling at Ny-Ålesund. I would like to thank Professor Furuya for providing me to use LAMMS at Science University of Tokyo and for useful suggestions. I wish to thank Dr. S. Matoba, Messrs. M. Watanabe and K. Shiraishi, and Ms. M. Kido for help of sampling at Ny-Ålesund and/or preparation of sample analysis.

I am grateful to Professor T. Kikuchi for useful suggestions in very early stage of this study. I am also grateful to the members of observations at Ny-Ålesund for help of sampling and staying, and to the staff members of National Institute of Polar Research, and the staff members of Kings Bay Kull Company for help of sampling at Ny-Ålesund.

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A

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