

Chemical characteristics of snow in the region along the Sea of Japan

KAZUHIDE SATOW

Nagaoka College of Technology, 888 Nishikataikai, Nagaoka, Niigata 940, Japan

ABSTRACT. The amount of acidity in precipitation has been measured in heavy-snowfall regions facing the Sea of Japan. The average pH value of precipitation measured throughout the year at Nagaoka was 4.80 during 4.5 years, 1987–92. During winter the pH value is lower and electric conductivity higher. The spatial distribution of chemical components in new-fallen snow was studied along a 55 km-long sampling route. Results from four surveys showed that acidic snows have average pH values of 4.63–4.90. From the distribution of anion and cation concentration in new-fallen snow, it is concluded that strong northwest monsoons during winter bring an abundance of snow with salt components and many non-salt components from the Sea of Japan and also, possibly, from the Asian continent.

INTRODUCTION

Acid precipitation is one of the serious social problems in China as well as in Europe, North America and Canada. The survey of acid precipitation has begun in neighboring Korea and China (Kim, 1991; Quan, 1991). The serious environmental damages suffered directly from acid precipitation have not yet been reported in Japan,

though acid rain has been observed also in Japan (Hara and others, 1990). It snows heavily, especially on the coast of the Sea of Japan in winter (December–March). However, the acid properties of snow in this area have not been investigated in detail; therefore the chemical features of snow have been analyzed.

At Nagaoka city in Niigata Prefecture, measurements of acid precipitation have been carried out throughout

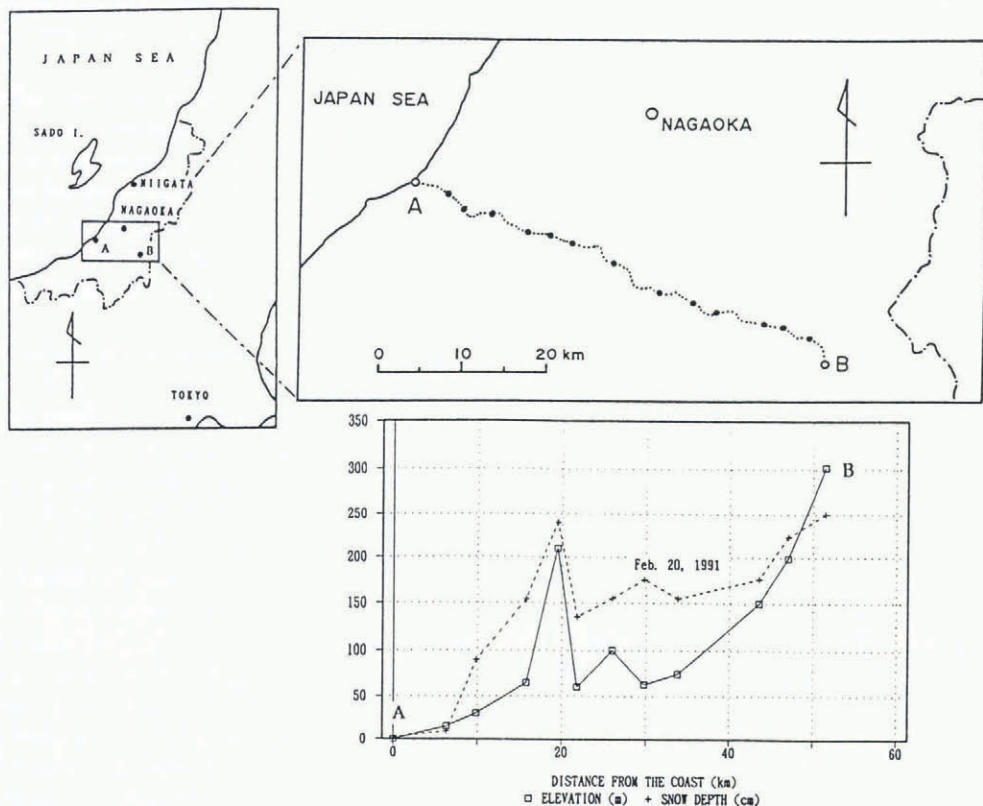


Fig. 1. Location map showing Nagaoka and the "investigation route" where snow was sampled. The lower part shows two profiles of elevation (m) and of snow depth (cm) along the route on 20 February 1991.

the year. A precipitation sampling bottle was regularly replaced every day. Nagaoka is located at 37°26' N, 138°54' E and 65.2 m a.s.l. In the average year, Nagaoka is covered with snow from December to March. The average maximum snow depth in winter has been about 140 cm for the past several decades.

In winter, the spatial distribution of acid snow has also been studied. Figure 1 shows the location of the observation area. The surface-snow samples along an "investigation route" were gathered in rinsed bottles. The chemical characteristics of precipitation in heavy-snowfall areas have been examined from these snow samples in my home laboratory.

The value of pH was measured in the laboratory using a pH meter (COM-11, Denki-Kagaku-Keiki Limited). The measurement of electrical conductivity (EC) was made using an electrical conductivity meter (DS-15, Horiba Limited). Anions and cations were analysed using a Shimadzu Model HIC-6A ion chromatograph.

ACIDITY MEASUREMENTS IN PRECIPITATION AT NAGAOKA

Figures 2 and 3 show the change of pH and EC in precipitation at Nagaoka during the period December 1987–March 1992. The total number of samples over four years and five months was 705. A typical seasonal variation of pH can be seen, especially in 1989, showing lower pH values in winter and higher pH values in summer.

Winter values described here are for values gathered December–March, and summer values from April–November. At Nagaoka, it can be said that the mean winter value of pH was 4.59, the mean summer value was 4.98, and the average value over 4.5 years was 4.80. We can recognize that the acid precipitation falls year-round at Nagaoka. As for EC in close connection with ion concentration, the mean winter value was 88.9 $\mu\text{S cm}^{-1}$, the mean summer value 48.5 $\mu\text{S cm}^{-1}$, averaging at 58.1 $\mu\text{S cm}^{-1}$.

The ratios of Na^+ to Cl^- concentrations are almost the same values as for sea salt, and these concentrations become higher in winter. When the northwest seasonal

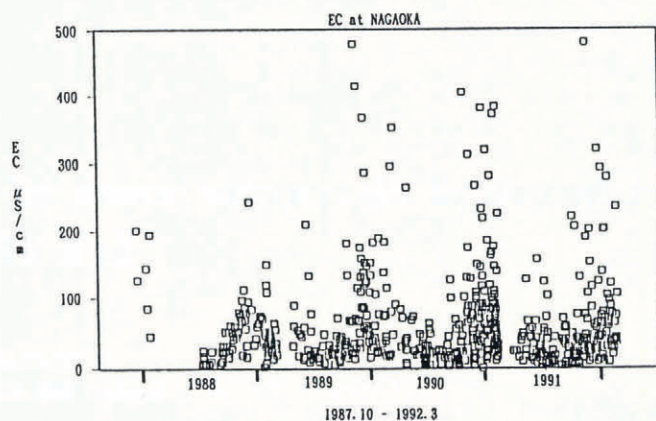


Fig. 3. Electric conductivity (EC) variation ($\mu\text{S cm}^{-1}$) during same period as Figure 2.

wind blows across the Sea of Japan where a warm current runs northward, a large amount of moisture is absorbed into the air during winter. As a result, this moisture precipitates as heavy snowfall in the regions facing the sea. Therefore, the high values of EC and ion concentration in snow during winter are caused by the containment of lots of sea-salt composition brought by the strong seasonal wind blowing toward Japan.

SPATIAL DISTRIBUTION OF ACID SNOW

To examine the spatial distribution of chemical features of snow, specimens of fresh snow were gathered along an investigation route extending for 55 km from the coast towards the inland, as shown in Figure 1. The elevation of this route rises from sea level at the coast to 300 m a.s.l. towards mountain ranges in the central part of Japan, with a hill along the route (Fig. 1). The depth of snow is closely related to the elevation, as shown in measurements for 20 February 1991 (Fig. 1).

The specimens of new snow were collected as follows. Following periods of uninterrupted snow, a freshly deposited snow layer was divided into an upper layer and a lower layer, which were sampled separately. Figure 4 shows examples of four analyses: A, 23 January 1990; B, 8 January 1991; C, 20 February 1991; and D, 22 February 1992. In each case the depth of new snow was 10–20 cm.

The spatial distribution of pH shows that both A and B have a similar tendency, with only a small difference between the upper and the lower layer of new snow. The pH value decreases from the coast and then increases gradually towards inland, and again drops at the farthest area from the coast. The measurements of EC give the value below 50 $\mu\text{S cm}^{-1}$, showing that the EC value decreases from the coast towards inland. In example C, the pH value of the lower layer of new snow was lower than that of the upper layer, and the EC value of the lower layer had higher values than that of the upper layer. This means that new snow at the beginning of snowfall has lower pH values and higher EC values than that towards the end of snowfall. The EC values of the lower layers were above 150 $\mu\text{S cm}^{-1}$. In the case of D, EC distribution shows that the EC values of the lower layer were lower than that of the upper layer, in contrast to

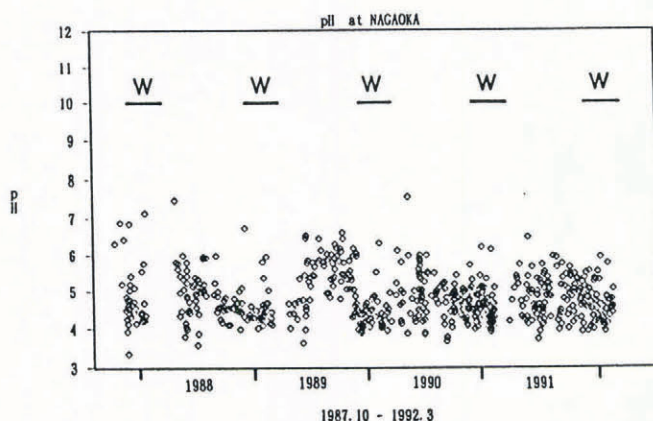


Fig. 2. pH variation in precipitation at Nagaoka during a period from October 1987–March 1992. "W" indicates a winter period, December–March.

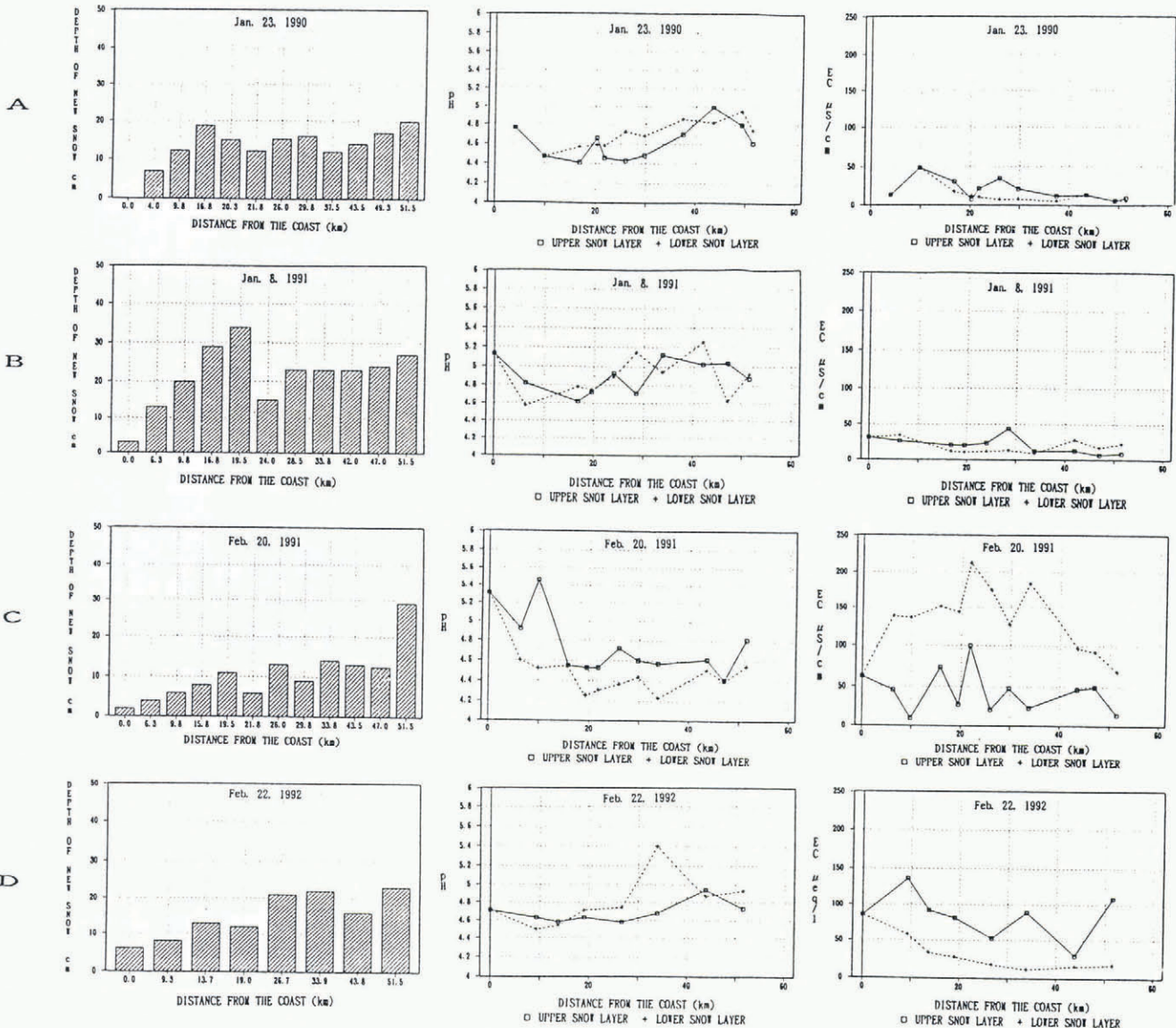


Fig. 4. Distribution of snow depth (cm), pH and EC ($\mu\text{S cm}^{-1}$) of new snowfall along the "investigation route". A, B, C and D show measurements from 23 January 1990, 8 January 1991, 20 February 1991 and 22 February 1992, respectively. The left end of each graph is the coast (A in Fig. 1) and right end is furthest inland from the coast (B in Fig. 2). Solid lines in pH and EC variations indicate upper-layer values, and chain lines are lower-layer values in a new-snow layer.

example C. The EC values of the lower layer were smaller, with almost the same order as in A and B, and those of the upper layers were 50–150 $\mu\text{S cm}^{-1}$.

The average pH values were 4.66 for A, 4.90 for B, 4.63 for C and 4.74 for D. Average EC values were 16.7 $\mu\text{S cm}^{-1}$ (A), 19.3 $\mu\text{S cm}^{-1}$ (B), 89.4 $\mu\text{S cm}^{-1}$ (C) and 58.6 $\mu\text{S cm}^{-1}$ (D). As mentioned above, new snow of the same snow depth has differences in chemical characteristics. Next the ion compositions of new snow were analyzed in examples B and C.

Ion composition in example B, 8 January 1991

Samples for upper snow layers and lower snow layers were analysed to determine major ion concentrations (anions: Cl^- , NO_3^- , SO_4^{2-} ; and cations: Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) as shown in Figure 5. In the upper layers (Fig. 5A1 and B1), both anions and cations decrease from the coast towards inland except at one

point, but Ca^{2+} becomes higher at the point furthest inland from the coast. With regard to lower layers, both anions and cations decrease from the coast towards inland and again increase (Fig. 5A2 and B2). To remove the influence of sea-salt components, non-sea-salt sulfate (nss-SO_4^{2-}) concentration has been calculated according to the relationship

$$\text{nss-SO}_4^{2-} = \text{SO}_4^{2-} - a\text{Na}^+$$

where a is 0.119, expressed in equivalents per litre. In the same manner, nss-K^+ , nss-Mg^{2+} and nss-Ca^{2+} were also calculated, using a to be 0.021, 0.226 and 0.043, respectively. The distribution of non-sea-salt ions was almost uniform (Fig. 5C1, D1, C2 and D2). Only nss-Ca^{2+} had a higher value in the upper snow at the farthest point inland from the coast (Fig. 5D1). It is interesting that first-fallen snow has a higher concentration of sea-salt components both at the coastal area and at the area furthest inland from the coast, although the reason is not

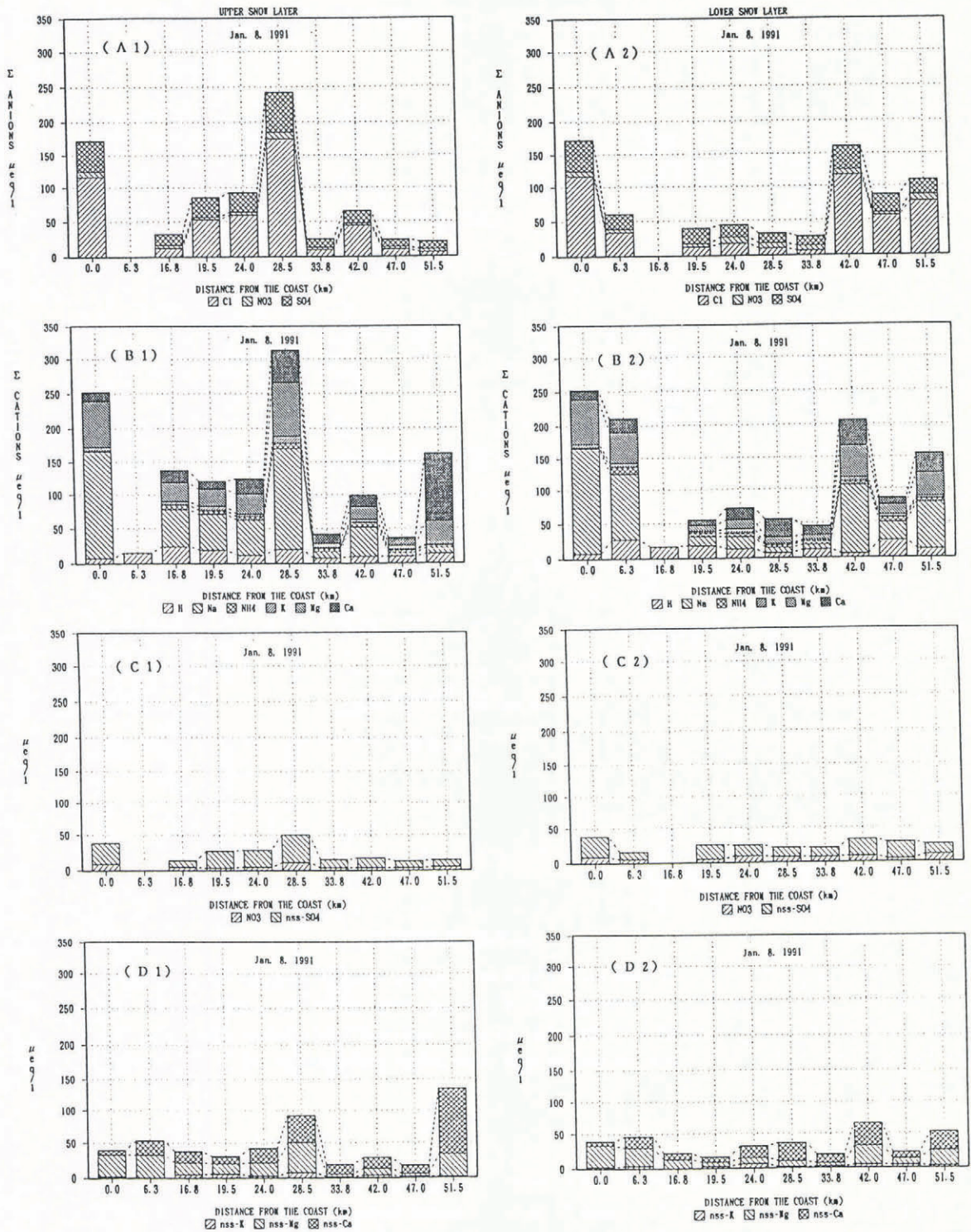


Fig. 5. Anions Cl^- , NO_3^- and SO_4^{2-} concentrations (A1 and A2), cations H^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} concentrations (B1 and B2), non-sea-salt cations concentrations ($nss-K^+$, $nss-Mg^{2+}$ and $nss-Ca^{2+}$: D1 and D2) of new snow sampled on 8 January 1991 along the observation route. Left graphs show the upper-layer values and right graphs the lower layer values in a new-snow layer. Unit: $\mu eq/l$.

evident (Fig. 5A2 and B2). No close relation between pH and $(NO_3^- + nss-SO_4^{2-})$ is apparent.

Ion composition in example C, 20 February 1991

The spatial distribution of ion concentration in example C is shown in Figure 6. C has 3–12 times higher ion concentrations than B. It is remarkable that the concentrations of both anions and cations of first-fallen

snow were about three times higher than those of last-fallen snow (Fig. 6A1–A2 and 6B1–B2). The lower layer contained many graupels (soft hailstones). This fact may be due to the result of the formation process of graupels in the atmosphere.

$(NO_3^- + nss-SO_4^{2-})$ concentrations of non-sea-salt components at the coastal area were higher in first-fallen snow (Fig. 6C2). As shown in Figure 6D1 and D2, non-sea-salt components of cations were much higher (4

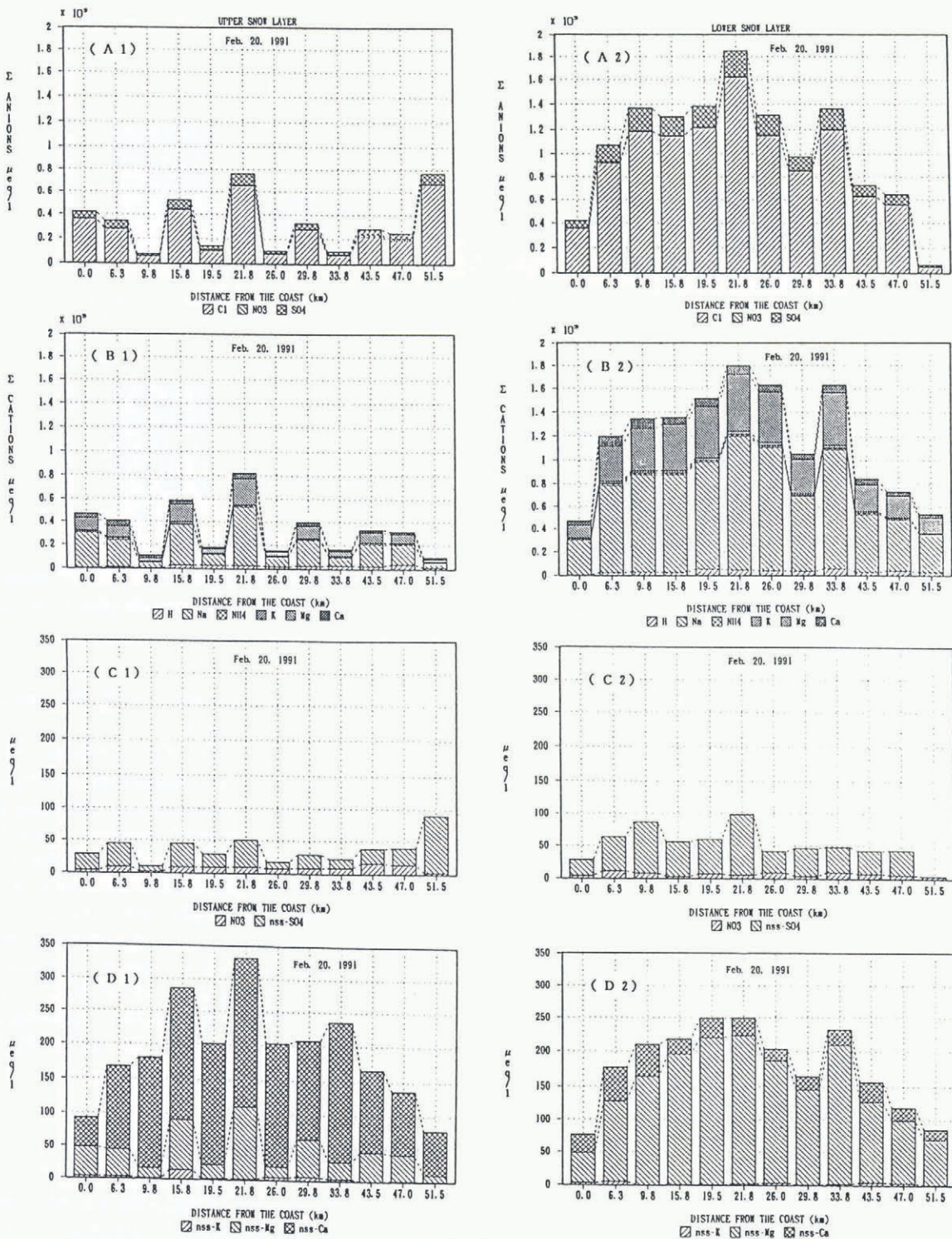


Fig. 6. Same as Figure 5 except for new snow sampled on 20 February 1991.

times), compared with example B. A striking feature is that nss-Mg^{2+} concentration was higher in the first snowfall (Fig. 6D2) and nss-Ca^{2+} was higher in the last snowfall (Fig. 6D1). The reason is not evident, but it must be supposed that there are some influences of long-range transport of Asian desert dust (KOSA) particles (Iwasaka, 1990) and pollutant materials from the Asian continent, judging from weather conditions such as strong northwest winds during winter. There is not such a close relationship between pH and $(\text{NO}_3^- + \text{nss-SO}_4^{2-})$ in this case.

Figure 7 shows mean anion and cation components for

B and C. In the case of example B, mean anion components hardly differed in both first snowfall and last snowfall (Fig. 7A), but the total mean cation components, mainly Ca^{2+} concentration, increased during snowfall (Fig. 7B). On the other hand, mean anion and cation components in example C decreased very quickly during snowfall (Fig. 7C and D).

A strong correlation between Na^+ and Cl^- is observed in Figure 8A in the case of C, showing a sea-water ratio. This figure also led to the conclusion that snowfall in this region is strongly influenced by northwest monsoon in winter. Both nss-SO_4^- and nss-Mg^{2+} were closely related

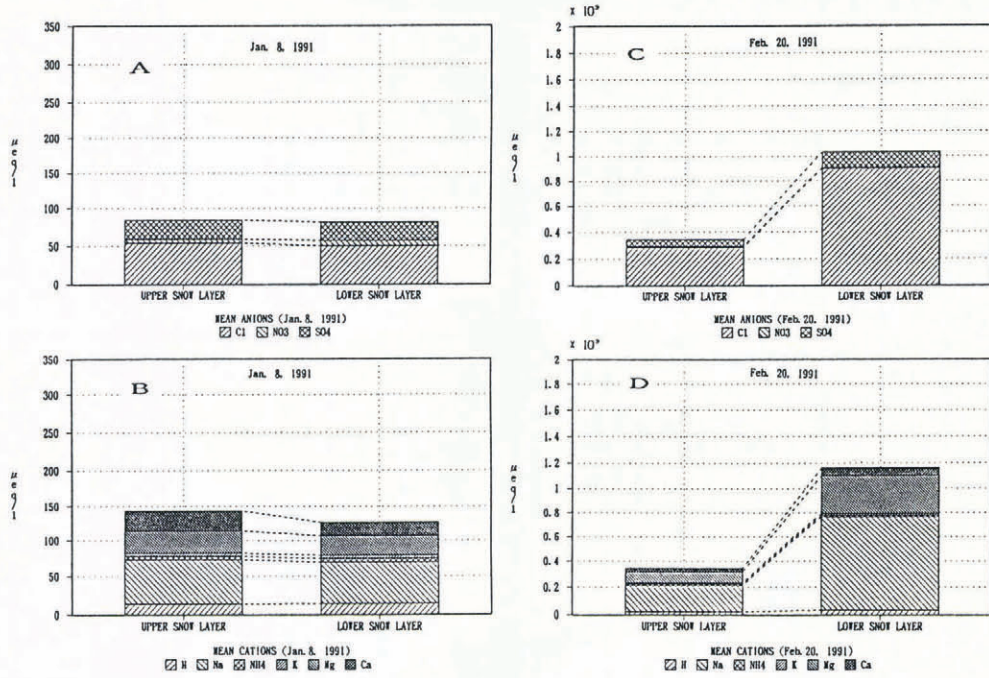
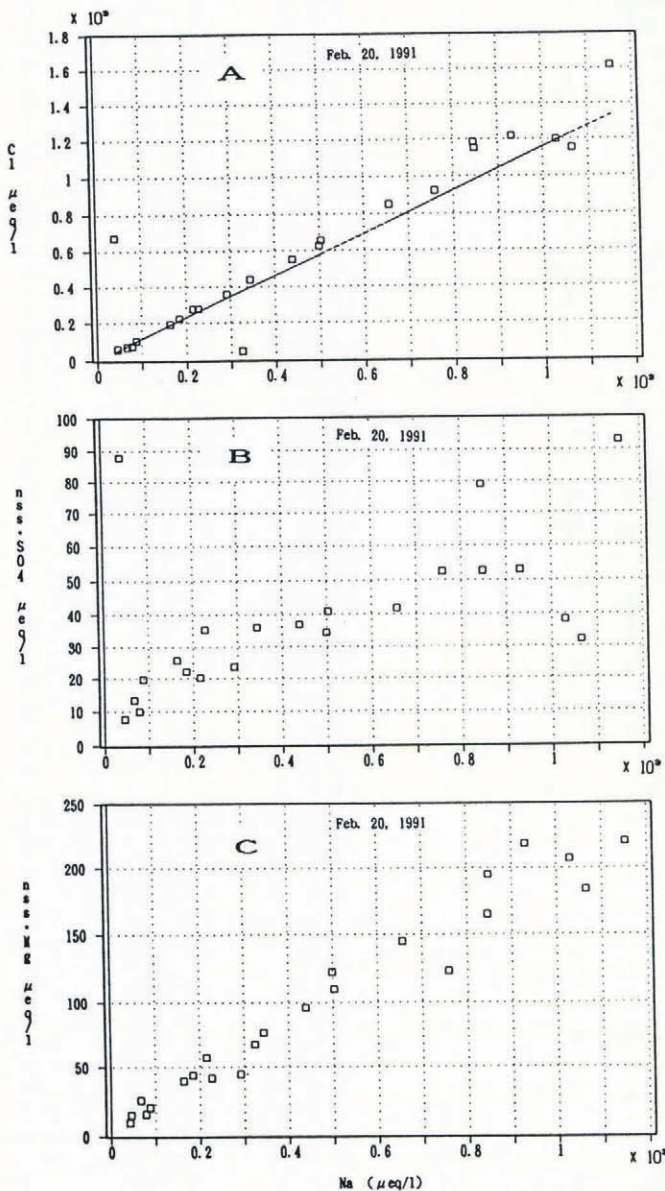


Fig. 7. The mean ionic balances (unit: $\mu\text{eq/l}$) in new snowfalls sampled along the "investigation route" on 8 January 1991 (A, anions; B, cations) and on 20 February 1991 (C, anions; D, cations). Graphs on left show the upper layer and graphs on right the lower layer.



to Na^+ concentration (Fig. 8B and C). We can also find the same tendency in the case of B.

This indicates that when the northwest wind blows strongly, many sea-salt components from the Sea of Japan are transported toward Japan, along with many non-sea-salt components from the Asian continent. Ueki and Iida (1989) reported that the SO_4^{2-} and Cl^- concentrations were higher in the snowfall than in the rainfall in summer season in Yamagata Prefecture, north of Niigata Prefecture. In Shimane, also facing the Sea of Japan, the average pH values in winter were 4.4–4.6 owing to the increase of concentration rates of nss-SO_4^{2-} and NO_3^- higher than that of NH_4^+ and nss-Ca^{2+} (Yamaguchi and others, 1989). These facts do not contradict the result of this study.

CONCLUDING REMARKS

Acidity in precipitation at Nagaoka has been examined throughout the year for the past 4.5 years. The average pH value is 4.80 and the average value in winter is lower. Electric conductivities in precipitation are higher in winter, and a lot of ionic compounds have been transported to the districts on the coast of the Sea of Japan.

Chemical characteristics of new-fallen snow in winter were analyzed along a line extending 55 km from the coast inland. The results of analyses for four new-fallen snows showed acidic snows in all cases with average pH

Fig. 8. Cl^- , nss-SO_4^{2-} and nss-Mg^{2+} concentration (A, B and C) plotted against Na^+ concentrations of new-snow samples along the "investigation route" on 20 February 1991 (unit: $\mu\text{eq/l}$). The straight line in A shows a sea-water ratio.

values of 4.63–4.90. The strong northwest wind during winter has transported snow to Japan with many components of sea salt from the Sea of Japan along with many components of non-sea-salt, possibly from the Asian continent.

New-fallen snow, including many graupels, was lower in pH value and showed higher concentrations of both anions and cations. In this case, nss-Mg concentration was particularly higher, showing the effect of the mechanism of the graupel formation process.

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