

Chemical survey of the snowpack in central Japan

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Abstract

In order to elucidate the spatial variation of chemicals deposited with snowfall in central Japan and the chemical characteristics of the snowpack in the mountainous area, samples from new surface snow and from snow pits were collected during the 2000–2001 winter season. There is a clear relationship between rising electric conductivity (EC) and falling pH for the new surface snow samples. The Na^+ concentration correlates well with the Cl^- and Mg^{2+} concentrations for new surface snow, suggesting that the contributions of sources other than sea salt are negligible. Thus, sea water is the predominant source of Na^+ , Cl^- , and Mg^{2+} in new surface snow in central Japan. The ratio of Cl^- /anions in new surface snow correlates well with latitude; there is a higher ratio of Cl^- /anions at the sampling locations near the Sea of Japan. On the other hand, the ratio of NO_3^- / nssSO_4^{2-} is high in the southern locations. The pH value for the snow pit samples is determined by the acid index. The colored layers deposited during the Kosa event are characterized by high EC, high pH, and high ion concentrations. The EC and Cl^- concentration in new surface snow along roads are higher on the coastal plain than farther inland. On the other hand, the pH and ratio of NO_3^- / nssSO_4^{2-} are lower on the coast than farther inland.

Key words: new surface snow, sea salt, acid index, mountainous area

1. Introduction

Since the mid-20th century, a large amount of pollutants has been released into the atmosphere, and the amount of pollutants present in precipitation has increased. Urban and industrial areas are major sources of pollutants. Sea salt is another major source of the chemicals present in precipitation in Japan, which is surrounded by sea. Some portion of the chemicals present in precipitation is deposited near their source, but the overall deposition pattern of chemicals is affected by local as well as remote sources. Chemical substances accumulate with snowfall during winter and are preserved in the snowpack (Suzuki, 1982), and a chemical analysis of the snowpack can be useful for determining the spatial distribution of chemical deposition.

Suzuki (1983, 1984) sampled winter precipitation and the snowpack in winter in the Sapporo area, in the northern island of Japan. The origin of the chemical substances in the samples was investigated. The presence of SO_4^{2-} was attributed to the use of fossil fuels in Sapporo city, whereas Na^+ and Cl^- were attributed to sea salt from the Sea of Japan. Suzuki

and Endo (1995) sampled the winter precipitation in Tohkamachi, central Japan. The chemical characteristics of the samples and the corresponding weather conditions were investigated. Large amounts of sea salt were deposited by the north-west wind during the winter monsoon, and acid-containing materials were deposited when a low-pressure system passed the south coast of Honshu, the main island of Japan.

Considerable winter precipitation was observed on the Sea of Japan side of the country; two main patterns, the winter monsoon pattern and the low-pressure pattern, passed over the Sea of Japan. On the Pacific side, on the other hand, winter precipitation occurred due to the passage of a low-pressure system along the south coast of Japan. The Japan Alps is a mountainous area in Honshu, where precipitation occurs from all these systems throughout the winter. The different sources of water producing the different precipitations are thought to account for the different ion species included in the snowpack. Along the coast of the Sea of Japan, many ion species are present in the precipitation, and it has been reported that the pH of winter precipitation is low (Satow, 1993; Suzuki and Endo, 1995).

There was no outbreak source of artificial chemi-

cals near the mountainous regions. It is thought that if the snowpack does not melt, the chemicals originating from wet and dry deposition are accumulated and stored intermittently. The chemical components preserved in the snowpack during a cold period can result from various atmospheric conditions.

The purpose of this study is to clarify the spatial variation of chemicals deposited with snowfall in central Japan and the chemical characteristics of the snowpack in the mountainous area.

2. Methods

2.1 New surface snow

New surface snow was collected at 184 locations (indicated by triangles and circles in Fig. 1) after snowfall during the 2000–2001 winter season. New snow refers to snow that has not melted and that retains the concentration of chemical constituents in the fallen snow. Snow samples are collected from within 5 cm of the snow surface. Linked circles indicate the routes for same-day sampling of new surface snow along a road. Fig. 2 shows the relationship between northern latitude and altitude for the sampling sites. The highest site is 3690 m above mean sea level (amsl) on Mt. Fuji. The summit of Mt. Fuji is 3776 m amsl. The northern sites are on coastal plains and thus, these sites are at low altitudes.

A clean small stainless steel scoop was used for sample collection. Each sample was placed into a

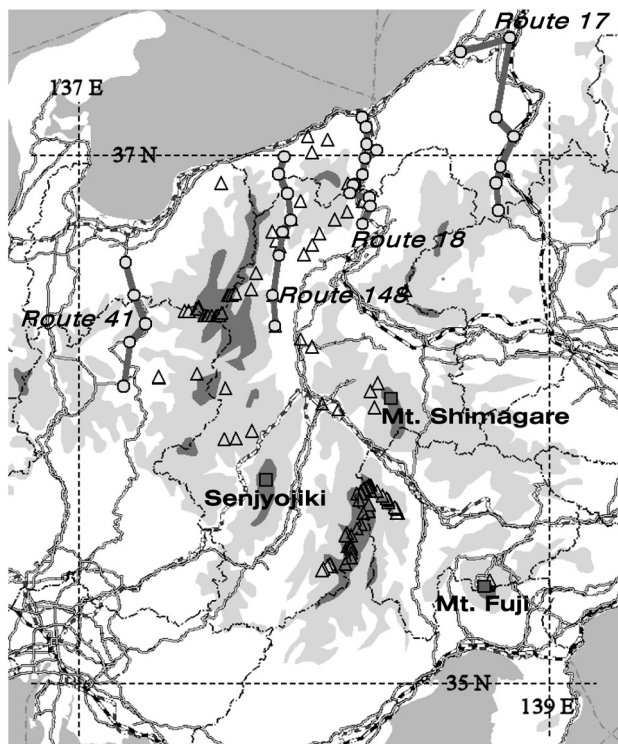


Fig. 1. Map of sampling sites.

Circles: new surface snow along a road
 Triangles: new surface snow at mountainous site
 Squares: snow pit

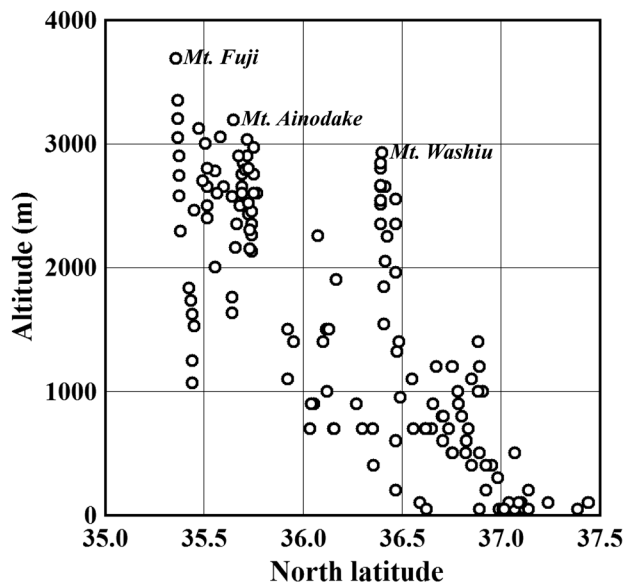


Fig. 2. Relationship between north latitude and altitude for sampling sites.

sample bag (NASCO: Whirl-PAK) and sealed for transportation to the laboratory. Samples were preserved without melting in a freezer until their analysis. They were allowed to melt at room temperature before analysis. The pH, electric conductivity (EC), and concentrations of major ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-}) were measured with a pH meter, conductivity meter, and ion chromatograph (DIONEZ: DX-500), respectively. All the analytical work was performed in a clean room.

2.2 Snow pit

Snow pit samples were collected from Mt. Shimagare (2255 m amsl) on March 16, 2001, from Senjyojiki (2600 m amsl) on March 21, 2001, and from Mt. Fuji (3690 m amsl) on April 08, 2001 (indicated by squares in Fig. 1). For sample collection, snow pits were dug to ground level. Samples were then collected from the snow surface layer down to the ground level, at intervals of 3 cm. A cubic stainless steel snow sampler with a height of 3 cm was used for sample collection. The methods of transportation and analysis were the same as for the surface snow samples.

3. Results and Discussion

3.1 Chemistry of new surface snow

Fig. 3 shows the relationship between EC and pH of the new surface snow samples. There is a clear relationship between rising EC and falling pH. The percentage of acidic snow (pH less than 5.62) in all samples is 68%, and the mean pH is 5.37. It is conceivable that acid precipitation is frequent in central Japan in winter. The minimum pH is 4.37 and the maximum pH is 7.06.

Fig. 4 shows the relationship between the Na^+ concentration and the concentrations of other ions

(Cl^- , SO_4^{2-} , Mg^{2+} and Ca^{2+}) in all the new surface snow samples collected in this study. In the figure, the Na^+ concentration correlates well with the Cl^-

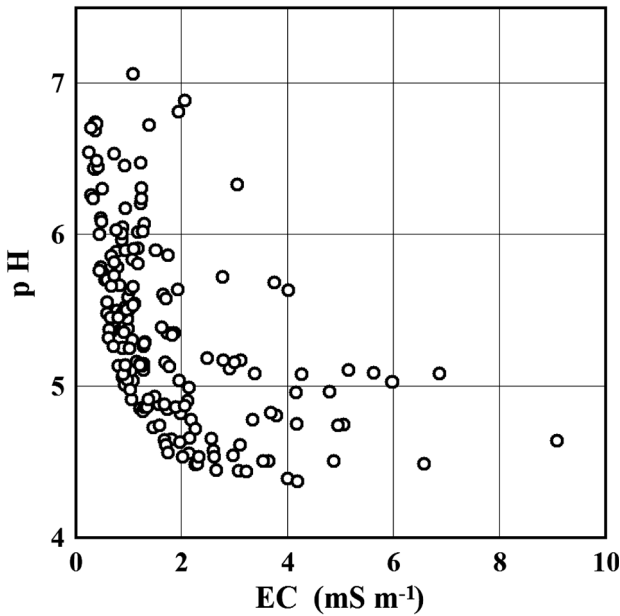


Fig. 3. Relationship between electric conductivity (EC) and pH of the new surface snow samples.

and Mg^{2+} concentrations, suggesting that the contributions of sources other than sea salt are negligible. Thus, it is concluded that sea water is the predominant source of Na^+ , Cl^- , and Mg^{2+} in new surface snow in central Japan. In contrast, there is no such relationship between Na^+ and SO_4^{2-} or Ca^{2+} , suggesting that SO_4^{2-} and Ca^{2+} are of both sea salt and non-sea salt origin. Non-sea salt SO_4^{2-} and Ca^{2+} originate mainly from anthropogenic dust, and organic sources (Suzuki, 1997). Most of the non-sea salt SO_4^{2-} in winter precipitation originates from the combustion of fossil fuels, and this non-sea salt SO_4^{2-} contribute to the acidic anion load (Suzuki, 1997).

Fig. 5 shows the relationship between northern latitude of a sampling site and the ratios of Cl^- /anions, NO_3^- /anions, Ca^{2+} /cations, and $\text{NO}_3^-/\text{nssSO}_4^{2-}$ for all the new surface snow samples. It is shown in Fig. 1 that the sampling site on the northern side is near the Sea of Japan, while the southern sampling site is located inland. The ratio of Cl^- /anions correlates well ($r=0.82$; $p<0.01$) with northern latitude; there is a higher ratio of Cl^- /anions to the north. The same tendency was reported by Suzuki (1984) and Ueno (1993), who reported that the concentration of chemical constituents originating in sea water de-

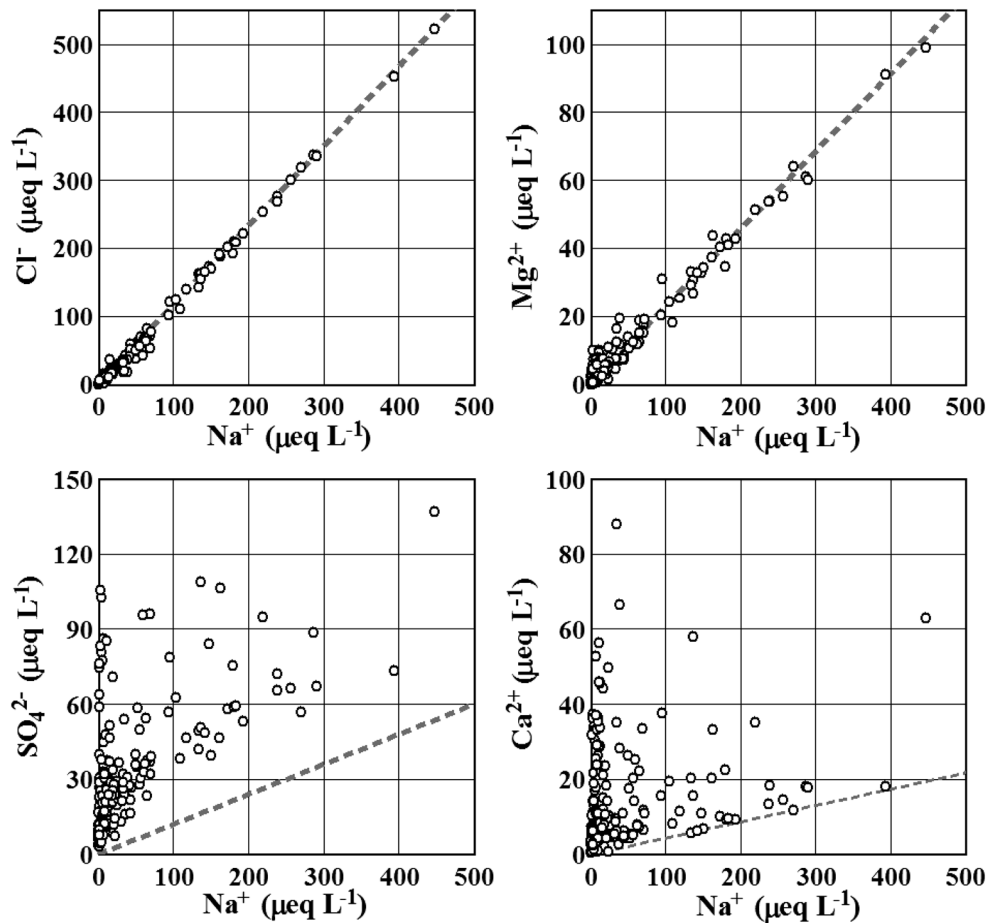


Fig. 4. Relationship between the Na^+ concentration and the concentrations of the other ions (Cl^- , SO_4^{2-} , Mg^{2+} , Ca^{2+}) in all the new surface snow samples. The broken lines represent the ratio for sea salt.

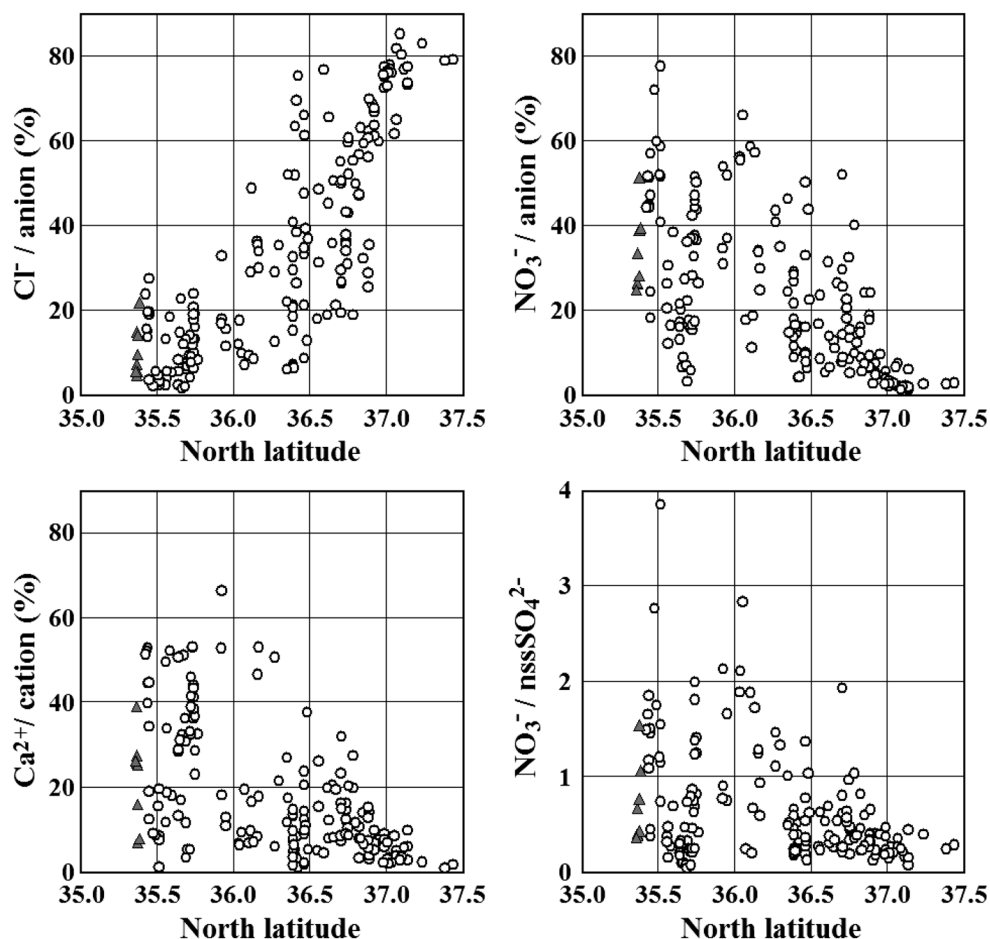


Fig. 5. Relationship between north latitude of sampling site and the ratios of $\text{Cl}^-/\text{anions}$, $\text{NO}_3^-/\text{anions}$, $\text{Ca}^{2+}/\text{cations}$, and $\text{NO}_3^-/\text{nssSO}_4^{2-}$ for all the new surface snow samples. Triangles indicate new surface snow samples from Mt. Fuji.

creased farther inland. Suzuki and Endo (1995) reported that the Na^+ concentration in snow increases in proportion to the height of the convective mixing layer. The ratio of chemicals originating from sea salt is high at coastal sampling locations in this study. At sampling locations on the northern slope of Mt. Fuji, there is a clear relationship between rising elevation and the falling ratio of chemicals of sea salt origin.

The ratios of $\text{NO}_3^-/\text{anions}$, $\text{Ca}^{2+}/\text{cations}$, and $\text{NO}_3^-/\text{nssSO}_4^{2-}$ are low at the sampling locations near the Sea of Japan. However, these ratios are high at the southern sampling locations. There is no snow cover in the southern part of central Japan; therefore, the ratio of $\text{Ca}^{2+}/\text{cations}$ is high at the southern sites. There are large cities and industrial areas along the Pacific coast; therefore, the ratio of $\text{NO}_3^-/\text{anions}$ is high in the south. Takahashi and Fujita (2000) reported the ratio of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ present in precipitation in Japan is higher than that in East Asia, which is explained by the rate of increase in NO_x emissions being higher than the rate of increase in SO_2 emissions in Japan. Precipitation in the southern locations is affected by artificial chemicals emitted in western Japan; therefore, the ratio of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ is high in

the south.

3.2 Chemistry of snow pit samples

Fig. 6 shows the relationship between EC and pH in the snow pit samples collected from Senjojiki, Mt. Shimagare and Mt. Fuji. There is a clear relationship between rising EC and falling pH, with a few exceptions. Samples for which a rise in pH corresponds to a rise in EC are considered to be snow deposited during Kosa event.

The relationship between the acid index (AI) and pH for the snow pit samples is shown in Fig. 7. The AI is calculated using the following formula.

$$\text{AI} = (\text{NO}_3^- + \text{nssSO}_4^{2-}) - (\text{nssCa}^{2+} + \text{NH}_4^+)$$

It is concluded that the pH value is determined by the AI. When the AI is higher, the pH is lower. In particular, the snow samples deposited during the Kosa event have a large negative AI value.

Fig. 8 shows the stratigraphy of the snowpit and vertical profiles of EC, pH, ion concentrations, and ratios of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ (N/S) at Mt. Shimagare on March 16, 2001. The symbol [y] in the stratigraphy denotes a colored layer deposited during the Kosa event. Such layers are characterized by high EC,

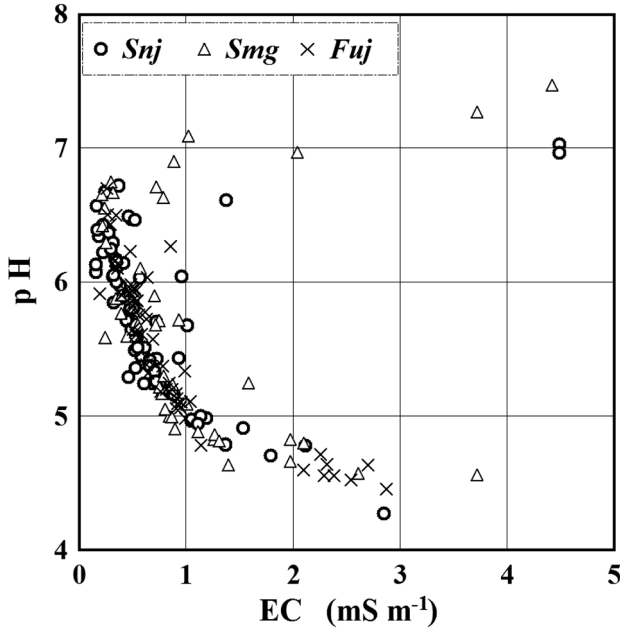


Fig. 6. Relationship between EC and pH in the snow pit samples collected from Senjojiki, Mt. Shimagare, and Mt. Fuji.

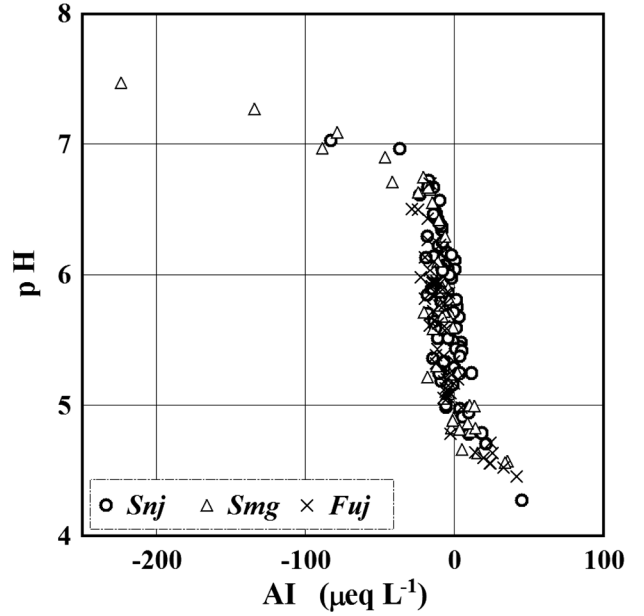


Fig. 7. Relationship between the acid index (AI) and pH for the snow pit samples.

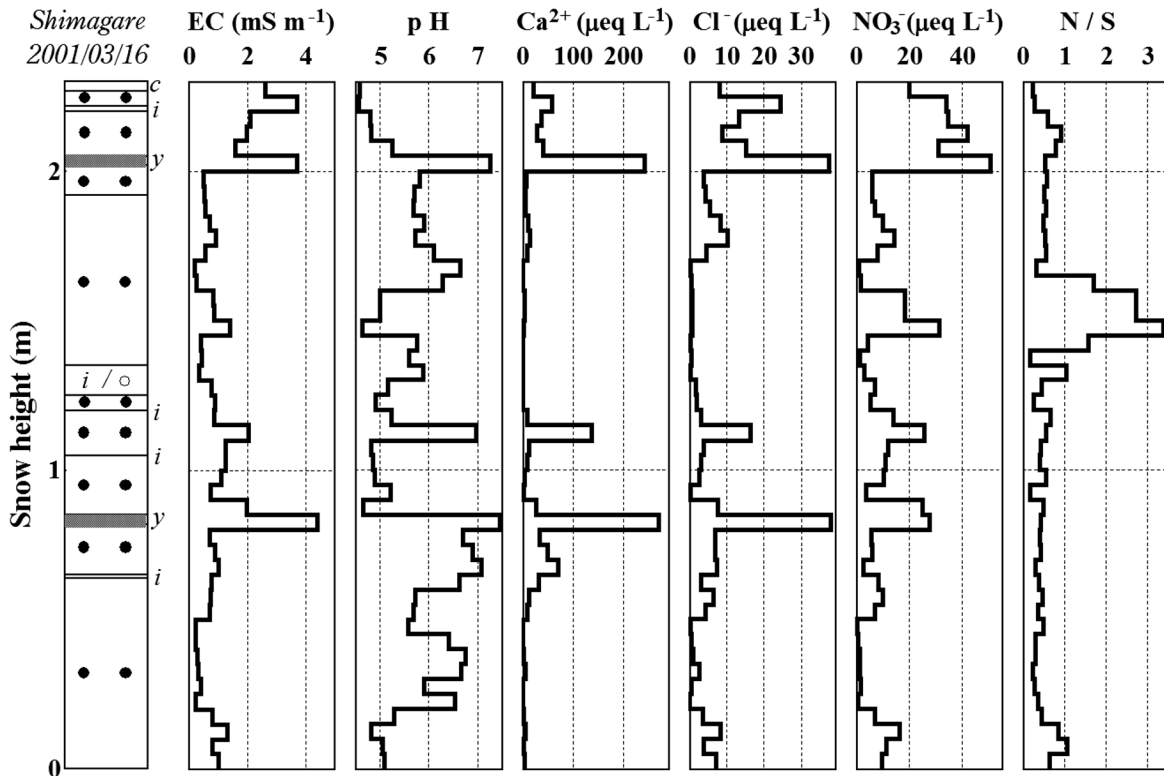


Fig. 8. The stratigraphy of the snowpit and vertical profiles of EC, pH, ion concentrations, and ratios of NO₃⁻/nssSO₄²⁻ (N/S) at Mt. Shimagare on March 16, 2001.

high pH, and high ion concentrations. It is believed that the upper colored layer was deposited on March 6 and 7, 2001, during the Kosa event.

Fig. 9 shows the stratigraphy and vertical profiles at Senjojiki on March 21, 2001, with the same notation as for Mt. Shimagare. There is one colored layer

indicating high EC, high pH, and high ion concentrations, similar to the figure for Mt. Shimagare. The colored layer is considered to be the Kosa layer deposited on March 6 and 7, 2001, similar to the case of Mt. Shimagare.

Fig. 10 shows the stratigraphy and vertical pro-

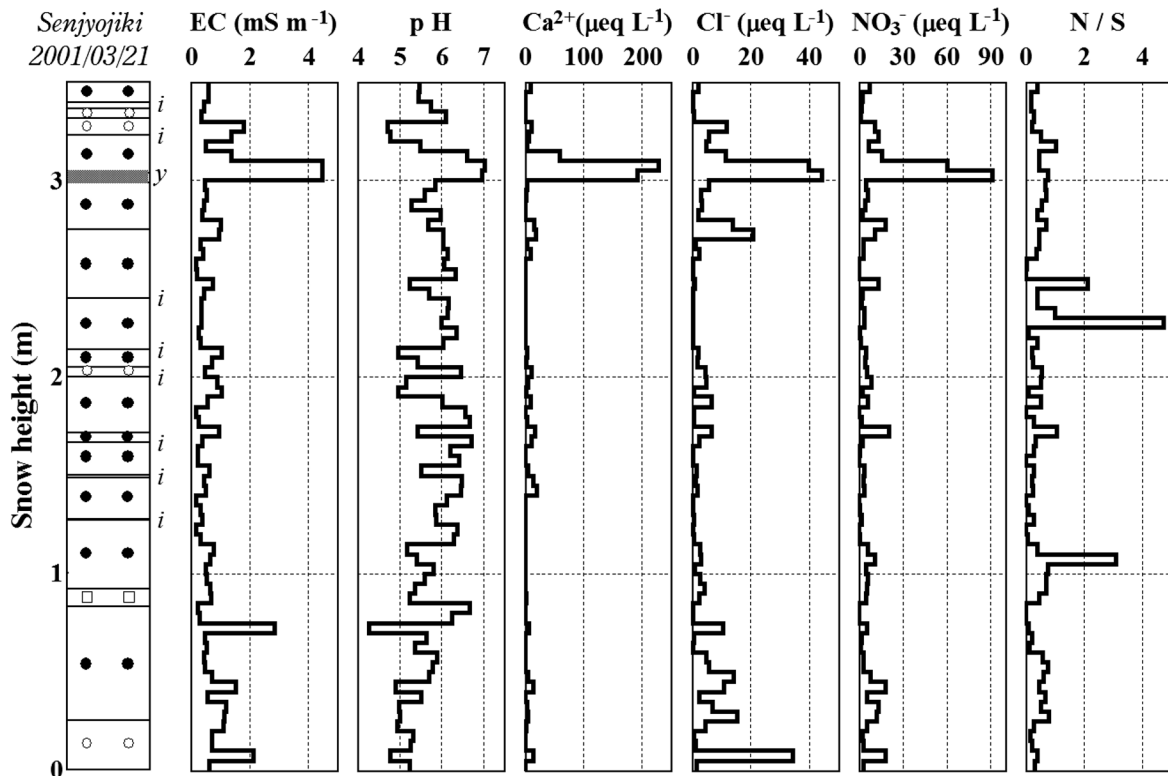


Fig. 9. The stratigraphy and vertical profiles at Senjojiki on March 21, 2001, with the same notation as for Mt. Shimagare.

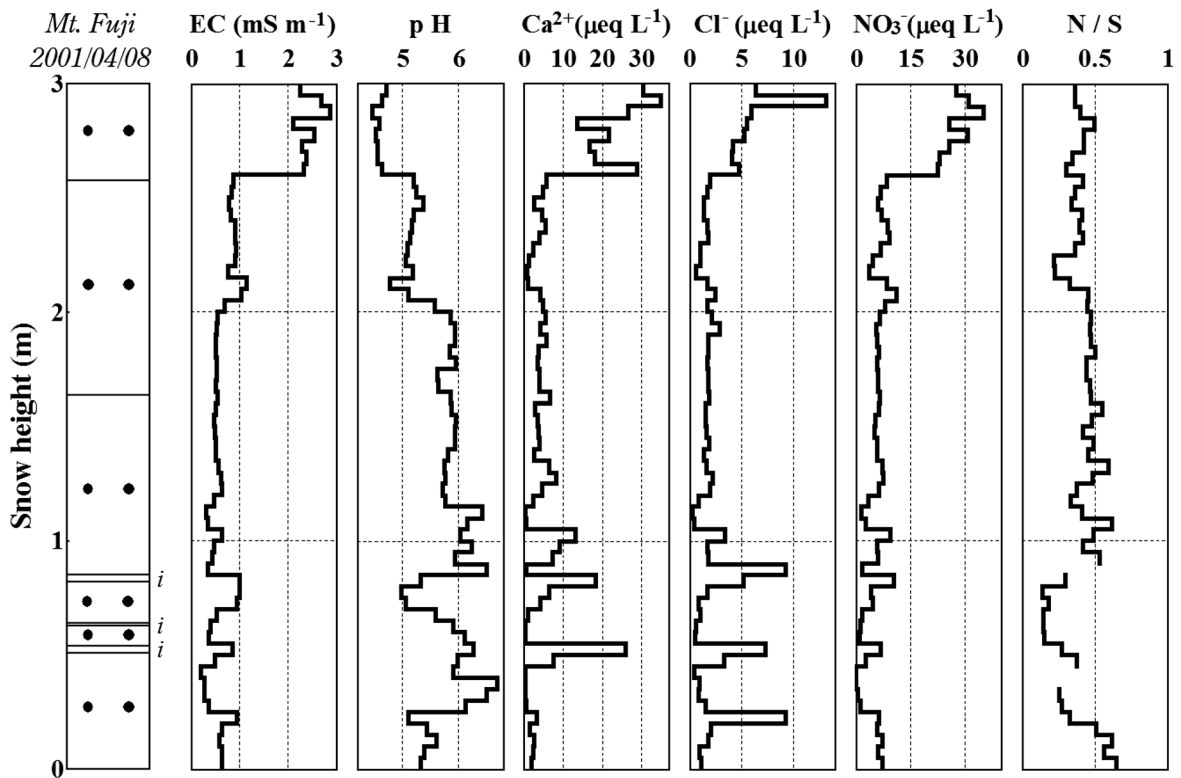


Fig. 10. The stratigraphy and vertical profiles at Mt. Fuji on April 8, 2001, with the same notation as for Mt. Shimagare.

files at Mt. Fuji on April 8, 2001, similar to the figure for Mt. Shimagare. No colored layer was found.

3.3 Same day sampling along the road

Linked circles in Fig. 1 indicate the routes for same day sampling of the new surface snow along a road. Starting from the west, the sampling routes are

along Routes 41, 148, 18, and 17.

Fig. 11 shows the altitude of sampling sites, EC, pH, ion concentrations, and ratios of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ in new surface snow along Route 41 on February 11, 2001. It snowed on the night of February 10, 2001. The EC and Cl^- concentration are higher on the coastal plain than farther inland. Chemicals of sea salt origin are transported from sea water; therefore, these chemicals are highly concentrated on the coastal plain. On the other hand, pH, concentrations of NO_3^- and nssSO_4^{2-} , and the ratio of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ are lower on the coast than farther inland.

Fig. 12 shows the altitude of sampling sites, EC, pH, ion concentrations, and the ratios of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ in new surface snow along Route 148 on January 31, 2001. It snowed on the night of January 30. The EC and Cl^- concentration were higher on the coastal plain than farther inland. Chemicals of sea salt origin are transported from sea water; therefore, these chemicals are more concentrated on the coastal plains. Inland points more than several kilometers from the coast are situated in mountainous areas, where the Cl^- concentration decreases rapidly. The concentrations of NO_3^- and nssSO_4^{2-} are higher on the coastal plain than farther inland. The ratio of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ in new surface snow is lower on the coastal plain than farther inland.

Fig. 13 shows the altitude of sampling sites, EC, pH, ion concentrations, and the ratio of $\text{NO}_3^-/\text{nssSO}_4^{2-}$

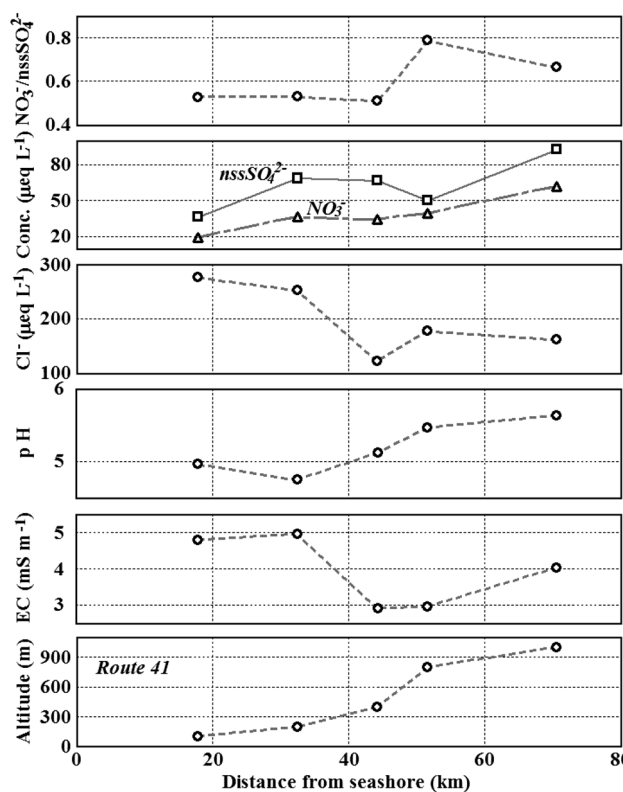


Fig. 11. Altitude of sampling site, EC, pH, ion concentrations, and ratios of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ in new surface snow along Route 41 on February 11, 2001.

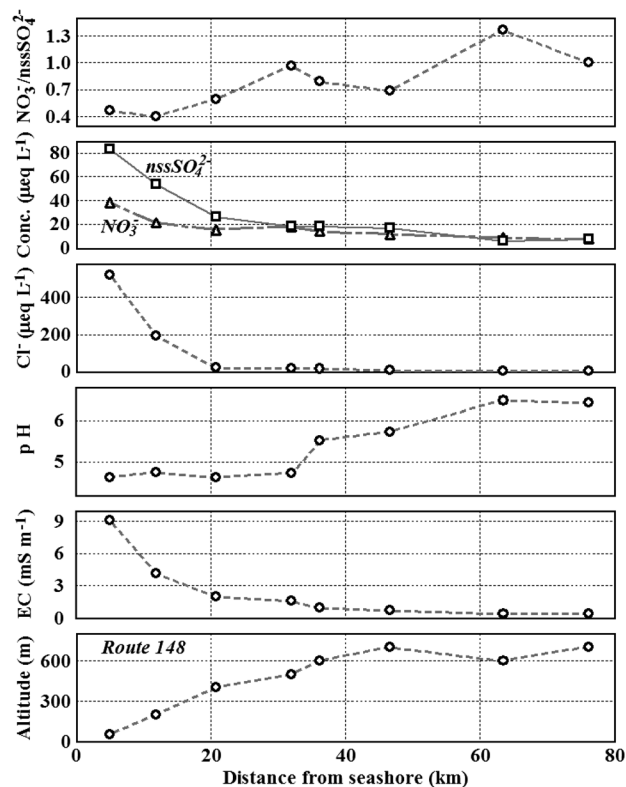


Fig. 12. Altitude of sampling site, EC, pH, ion concentrations, and ratios of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ in new surface snow along Route 148 on January 31, 2001.

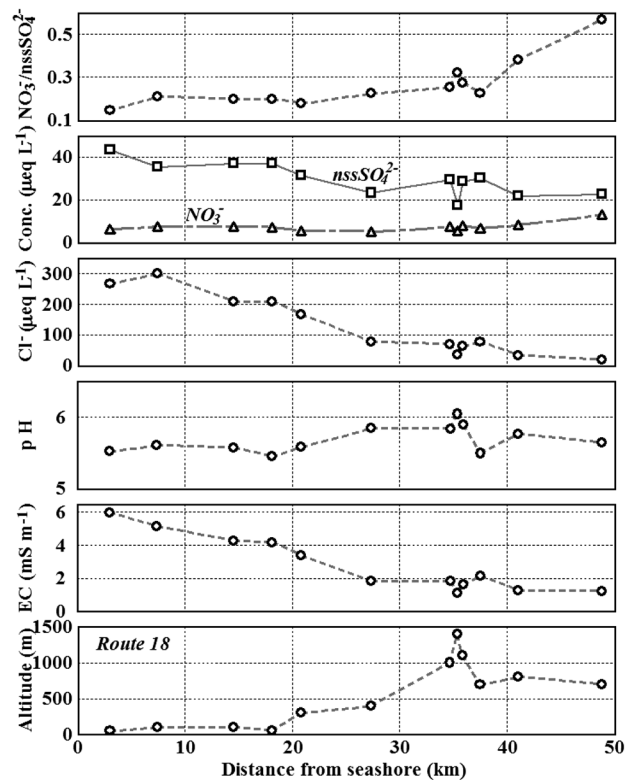


Fig. 13. Altitude of sampling site, EC, pH, ion concentrations, and ratios of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ in new surface snow along Route 18 on March 5, 2001.

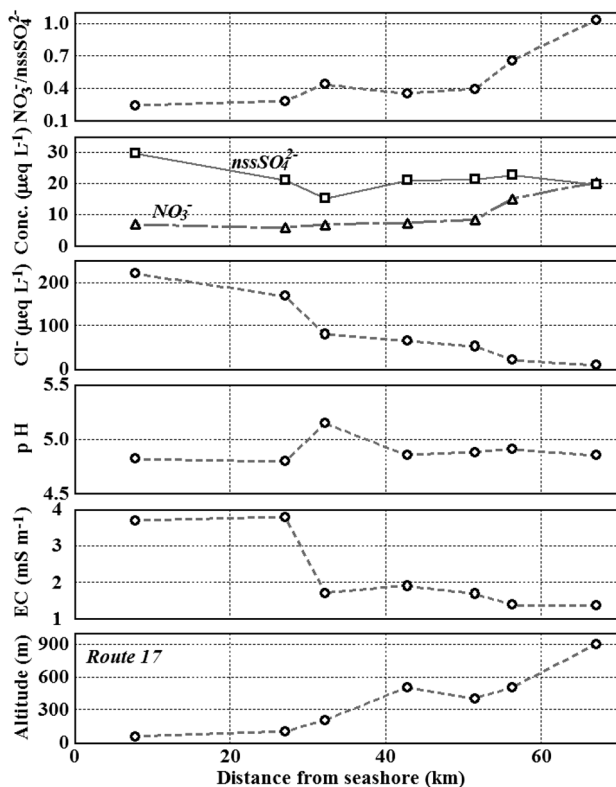


Fig. 14. Altitude of sampling site, EC, pH, ion concentrations, and ratios of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ in new surface snow along Route 17 on February 9, 2001.

nssSO_4^{2-} in new surface snow along Route 18 on March 5, 2001. It snowed the previous day. The same tendency as for Route 148 is recognized. The coastal plain along Route 18 is wider than along the other-route, and thus, there is a high concentration of chemicals of sea salt origin farther inland.

Fig. 14 shows the altitude of sampling sites, EC, pH, ion concentrations, and the ratios of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ in new surface snow along Route 17 on February 9, 2001. It snowed the previous day. The same tendency as for Route 18 is recognized.

4. Conclusions

New surface snow was collected at 184 locations after snowfall in central Japan, and snow pit samples were collected from Mt. Shimagare, Senjojiki, and Mt. Fuji.

There is a clear relationship between rising EC and falling pH for the new surface snow samples. The Na^+ concentration correlates well with the Cl^- and Mg^{2+} concentrations of new surface snow, suggesting that the contributions of sources other than sea salt are negligible. Thus, sea water is the predominant source of Na^+ , Cl^- , and Mg^{2+} in new surface snow in central Japan. The ratio of $\text{Cl}^-/\text{anions}$ for new surface snow correlates well with northern latitude. There is a higher ratio of $\text{Cl}^-/\text{anions}$ at the sampling location near the Sea of Japan. On the other hand, the ratio of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ is high in the southern location.

The pH value for the snow pit samples is determined by the AI. The colored layers deposited during the Kosa event are characterized by high EC, high pH, and high ion concentrations.

The EC and Cl^- concentration in new surface snow along roads are higher on the coastal plain than farther inland. However, the pH and ratio of $\text{NO}_3^-/\text{nssSO}_4^{2-}$ are lower on the coast than farther inland.

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