

Chemical dynamics of snowpack in the Northern Japan Alps during snowmelt season

Shailendra Kumar SHAH¹, Motoki TANAKA², Takayuki KURAMOTO¹ and Keisuke SUZUKI^{1,2}

¹ Correspondence to: Department of Environmental Science, Faculty of Science, Shinshu University, Asahi, Matsumoto, 390-8621, Japan

² Correspondence to: Institute of Mountain Science, Shinshu University, Asahi, Matsumoto, 390-8621, Japan

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Abstract

A snow pit study was conducted on Mt. Norikura in the Northern Japan Alps from January to April 2007 to clarify the chemical dynamics in the snowpack during the snowmelt season. Little snowmelt occurred before February 6, the first snowmelt occurred between February 6 and 21, and the peak of the snowmelt season occurred after March 7. Snow layers with remarkably high Cl^- , NO_3^- , and SO_4^{2-} concentrations in the snowpack were traced; furthermore, the snow layers with high SO_4^{2-} concentrations were found to disappear first. It was concluded that the ease with which the ions were flushed out from the snowpack was $\text{SO}_4^{2-} > \text{NO}_3^- = \text{Cl}^-$.

1. Introduction

In recent years, acid precipitation has been observed all over the world. The effects of acidic precipitation on inland water ecosystems across the many lakes of Scandinavia and eastern Canada have been reported (Gorham, 1961; Minns, 1981). And the pH of snowmelt water in particular has been reported to be extremely low. Therefore, it is important to understand the behaviors of anions in snowmelt water and the snowpack during the snowmelt season.

Before snowmelt, the concentration of dissolved ions in the snowpack is the same as that in the snow. However, these ions flow out with the snowmelt water during the snowmelt season. The concentration of these ions in the snowmelt water is high early in the snowmelt season, and it lowers as snowmelt progresses (Johannessen and Henriksen, 1978; Jones and Deblois, 1987). This is explained by the fact that the ions in a snow particle are released to the surface of the snow particle during the process by which it transforms into a granular snow particle in the snowpack; this phenomenon is due to the difference in freezing point between pure water and water containing dissolved ions. Thus, the snowmelt water that flows over the surface of the snow particle selectively dissolves the ions, leading to a higher concentration in snowmelt water than in the snowpack (Suzuki, 1982). Suzuki (1991) reported that the snow particles that constitute the snowpack release the ions to their surfaces during melting/refreezing cycles.

Since different ions will separate from snow particles at different rates, there must be a certain order in which the ions are flushed out of the snowpack; there have been some reports on this phenomenon (Brimblecombe *et al.*, 1985; Iizuka *et al.*, 2000). For example, Suzuki (1991) measured the daily variation of the anionic components in snowmelt water; he found that when refreeze occurred at the surface of the snowpack in the early morning, the ratios of SO_4^{2-} and NO_3^- were high, and by day the ratio of Cl^- was high. This results suggested that the order of the ease with which ions were flushed was $\text{SO}_4^{2-} = \text{NO}_3^- > \text{Cl}^-$. Brimblecombe *et al.* (1985) conducted snow pit work on two consecutive days in Scotland and compared the order in which different ions were flushed from the snowpack with the snowmelt. His results suggested that the order of the ease with which ions were flushed was $\text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{H}^+ > \text{Na}^+ > \text{Cl}^-$. Davies *et al.*, (1987) experimentally defined the order of the flush of each ion and reported it as $\text{Ca}^{2+} = \text{Mg}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Na}^+ > \text{Cl}^-$. Thus, each preceding report has indicated different orders and there is no unified opinion.

In most of the low-lying areas of Japan, snowmelts are frequent, even in the winter season. In contrast, in the high mountainous areas of Japan, snowmelts seldom occur. The chemical substances in a snowpack burst out intensively during the snowmelt season. In other words, the chemical dynamics in the snowpack in high mountainous areas during the snowmelt season are more conspicuous than those in the low-lying areas. The object of this study is to

clarify the chemical dynamics in the snowpack occurring in a mountainous area and the order in which different ions are flushed from the snowpack during the snowmelt season.

2. Methods

The study site in this research is located at an altitude of 1590 m on the eastern side of Mt. Norikura (3026 m), which is in the southern part of the Northern Japan Alps in central Japan (Fig. 1). The timberline of Mt. Norikura is located at an altitude of approximately 2450 m. A major portion of Mt. Norikura below the timberline is covered with deciduous and coniferous forest. The mean air temperature recorded by the weather observation system that was set up at the study site was -1.7°C and the total precipitation at the study site was 519 mm during January–April 2007 (the snowy season).

Snow pit sampling was conducted during January–April 2007. The sampling was conducted a total of nine times at a frequency of two or three times per month from early in the formation of the snowpack until its disappearance.

The sampling was conducted in flat and open spaces selected by observation at the site: The snow pits were dug through the entire snowpack, the physical stratigraphy was observed, and the snow temperature was measured at 3-cm intervals of increasing depth; further, the density (100 cm^3) was recorded and snow samples were collected at each 3-cm interval. These measurements were conducted through the entire snowpack. A new snow pit was dug each snow pit work. The snow samples were placed in vinyl bags (NASCO: WHIRL-PAK) and melted in a clean room. The pH (DKK-TOA: GST-5420C) and electric conductivity (DKK-TOA: CT-84101B) were measured after filtration through a PTFE membrane filter with

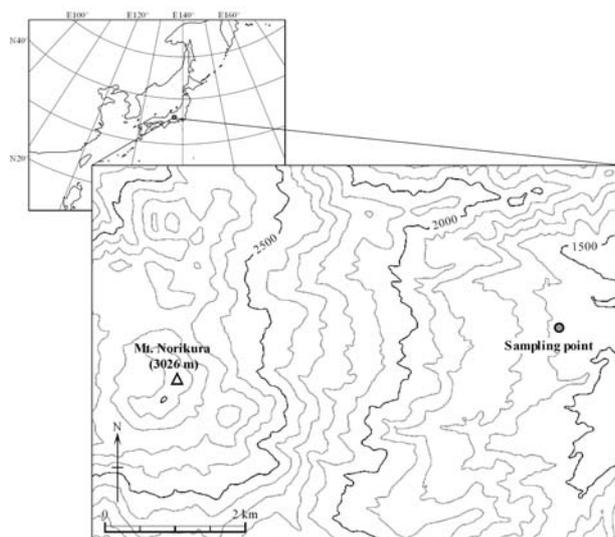


Fig. 1. Study site.

a pore size of $0.45\mu\text{m}$; the concentrations of the dissolved substances (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-}) were measured by the suppression method using an ion chromatograph (DIONEX: DX-500).

A weather observation station was set up near the snow pit sampling points for automatic measurements (KONA System: KADEC-Me-N). Air temperature was measured by a ventilated-type temperature sensor; snow depth, by a snow-depth gauge; and precipitation, by a tipping-bucket rain/snow gauge.

3. Results and Discussion

3.1 Source of chemical substances in snowpack

Figure 2 shows the relationship between the pH and the electrical conductivity (EC) in the snow layers. There is a clear relationship between falling pH and rising EC. The percentage of acid snow (less than 5.62) in all the samples was 96.6%, and the weighted mean pH was 5.0. Kurita and Ueda (2006) reported that the pH in the precipitation urban areas in Nagano Prefecture during 1972–2003 was approximately 5.0; the pH in the winter precipitation in the plateau areas in Nagano Prefecture was in the vicinity of 5.6 during 1993–1997. In other words, at the plateau area, there was little occurrence of acid precipitation. However, in this study, it is conceivable that acid precipitation was frequent in the mountainous area during January–April 2007, and the pH in the precipitation differed little from that in the urban areas of Nagano Prefecture.

Figure 3 shows the relationship between the Na^+ concentration and the concentrations of the other ions (Cl^- , SO_4^{2-} , and Ca^{2+}) in all the snow samples collected in this study. In the figure, the relationship between Na^+ and Cl^- is nearly equal to that in sea salt, suggest-

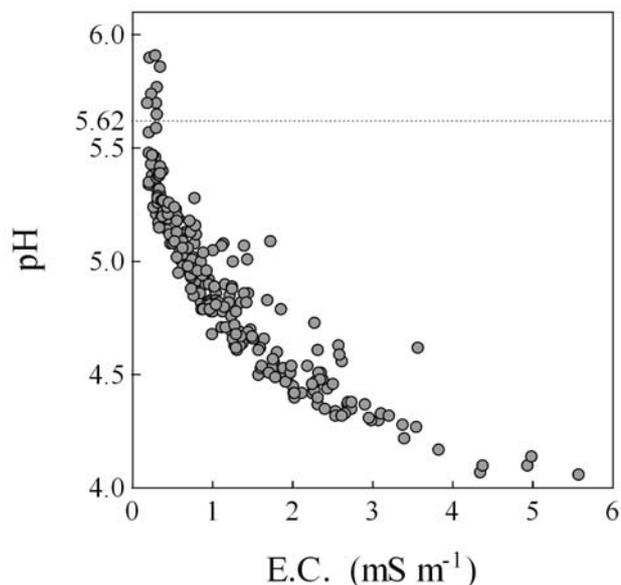


Fig. 2. Relationship between pH and electrical conductivity (EC) in snow layers.

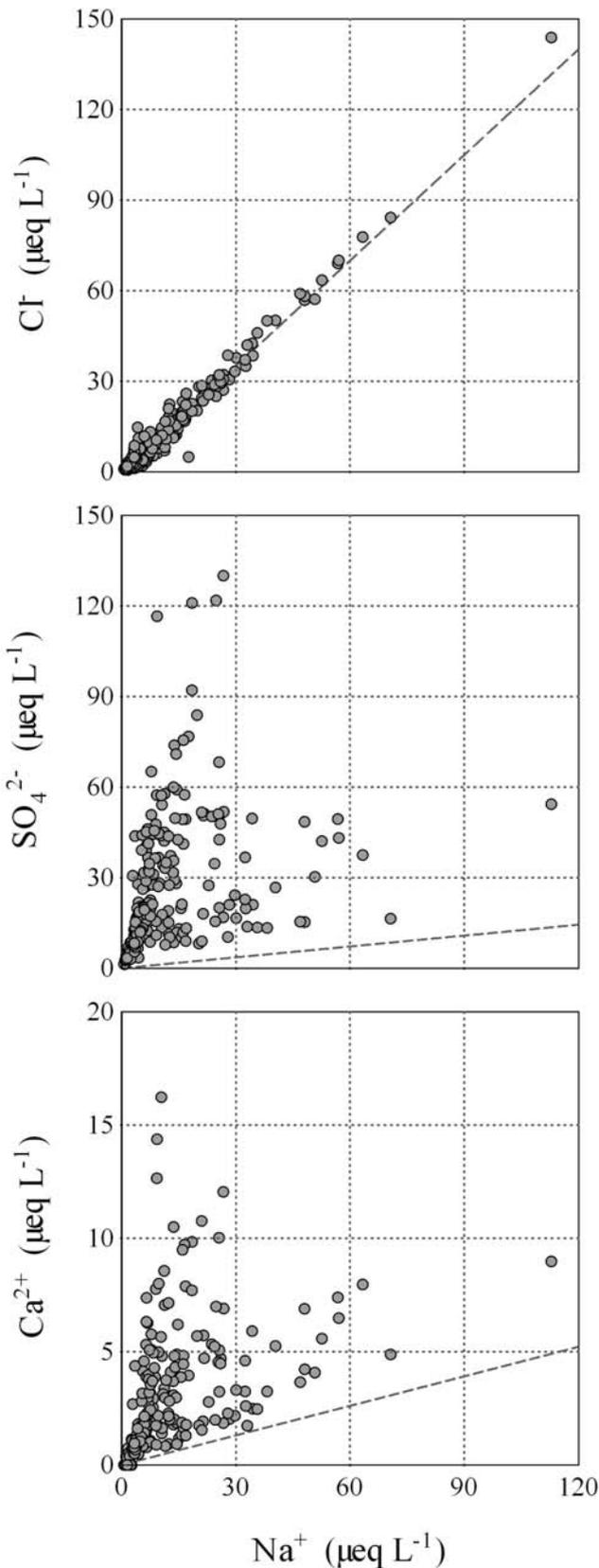


Fig. 3. Relationship between the concentrations of Cl^- , SO_4^{2-} , Ca^{2+} , and Na^+ in all of the snow samples collected in this study. The broken lines represent the ratio for sea water (Hanya *et al.*, 1999).

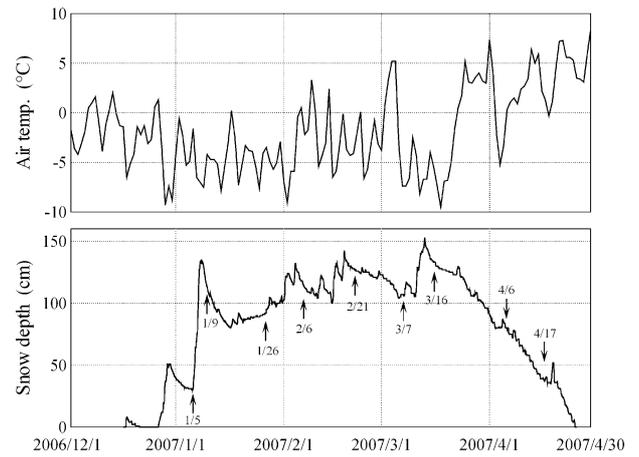


Fig. 4. Variations in daily mean air temperature and snow depth from December 1, 2006, to April 30, 2007. The arrows represent the days when the snow pit studies were conducted.

ing that the contributions of sources other than sea salt can be considered to be negligible. Thus, it was concluded that sea water was the predominant source of Na^+ and Cl^- in the snow. In contrast, no such relationship was observed between Na^+ and SO_4^{2-} or Ca^{2+} , suggesting that SO_4^{2-} and Ca^{2+} were 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 non-sea salt SO_4^{2-} contributes to the acidic anion load (Suzuki, 1997).

3.2 Variation in ionic concentration in snow layers

Figure 4 shows the variation in the daily mean air temperature and the snow depth from December 1, 2006, to April 30, 2007. The day that the snowpack began to be formed was December 17. The maximum snow depth was 153 cm, on March 15. After March 23, the snow depth decreased monotonically, and the snowpack had disappeared by April 25. The daily mean air temperature from December 17, the date that the snowpack was formed, to February 6, 2007, was below 0°C on the majority of days. The percentage of days on which the daily mean air temperature exceeded 0°C increased after February 7, and the daily mean air temperature was above 0°C on most days after March 23. It is conceivable that the rise in the air temperature after March 23 was the major cause of the monotonic decrease in the snow depth.

Figure 5 shows the vertical profile of the EC in the snow layers. Since the snow pit study site is approximately 300 m away from the weather observation station, the variation of the snow depth that was measured by the snow pit study does not always accord with that of the snow depth monitored by a snow-depth gauge. The ECs of all the snow layers decreased throughout the season, but in such a manner

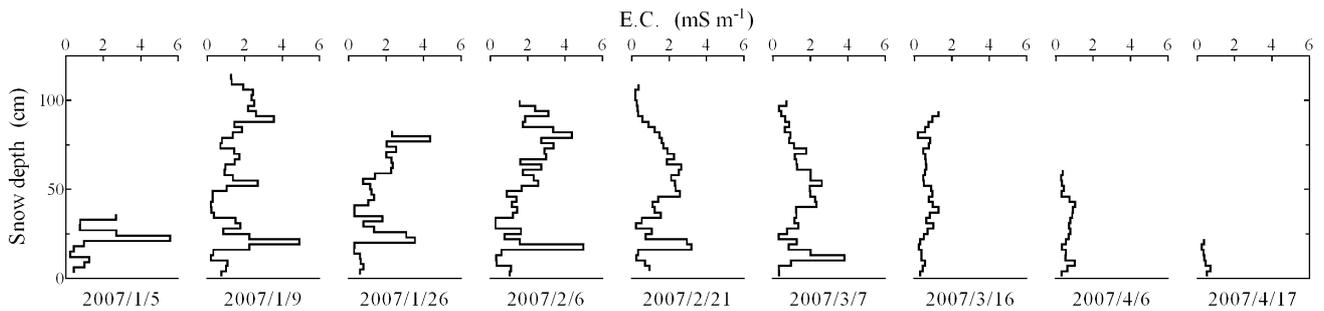


Fig. 5. Vertical profile of the EC of the snow layers.

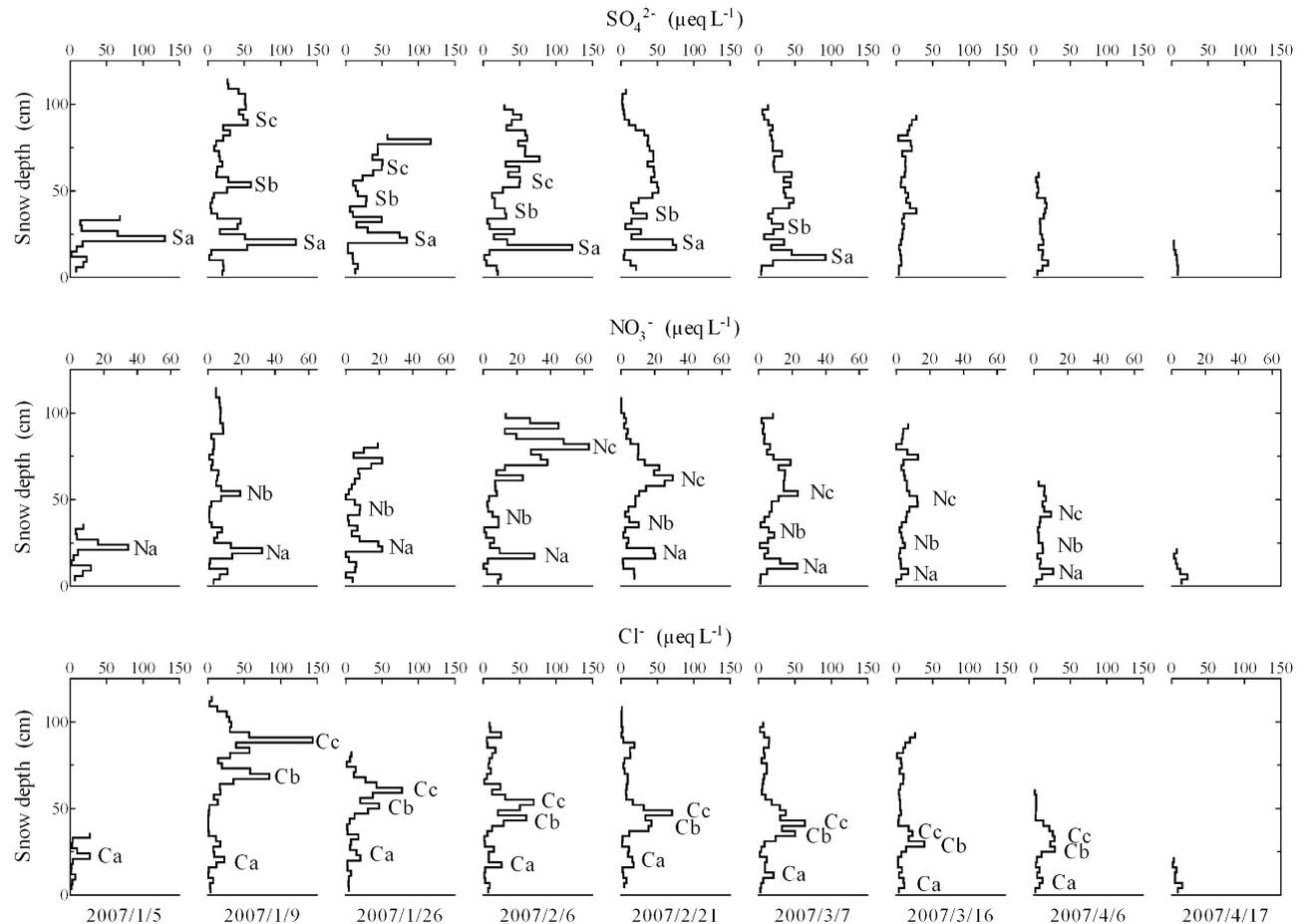


Fig. 6. Vertical profiles of the anionic concentrations in the snow layers. The snow layers with remarkably high Cl^- , NO_3^- and SO_4^{2-} concentrations are labeled Ca-Cc, Na-Nc, and Sa-Sc, respectively. These labeled snow layers are monitored until their disappearance.

that the relative order of the ECs remained constant, that is, the layer with the highest EC at the start of the season continued to be the layer with the highest value throughout the remainder of the season until the disappearance of the layer. The ECs of the snow layers measured on January 5, January 9, January 26, and February 6 were $0.24\text{--}5.57\text{ mS m}^{-1}$, $0.20\text{--}4.93\text{ mS m}^{-1}$, $0.28\text{--}4.34\text{ mS m}^{-1}$, and $0.28\text{--}4.98\text{ mS m}^{-1}$, respectively, and the vertical profile of the EC in the snow layers exhibited spikes. The ECs of the snow layers measured on February 21 and March 7 had little difference ($0.20\text{--}3.20\text{ mS m}^{-1}$ and $0.30\text{--}3.82\text{ mS m}^{-1}$, respec-

tively). These ranges are lower than those observed on February 6, and the shape of the vertical profile of the ECs in the upper snowpack was smooth. On and after March 16, the range of the EC values continued to decrease as the season progressed, and the shape of the vertical profile of the EC in the snow layers became smoother. The remarkable decrease in the EC between March 7 and March 16 suggests that ions were significantly flushed out from the snowpack. On March 16, most of the snow layers were granular snow. Moreover, on and after March 16, the snow temperature of the entire snowpack was approx-

imately 0°C. These facts indicate that significant snowmelt occurred between March 7 and March 16.

In other words, it is conceivable that little snowmelt occurred before February 6, the first snowmelt occurred between February 6 and 21, and the significant snowmelt season set in between March 7 and 16. Though the air temperature was comparatively low during 7–16 March, it was at 0.4–6.3°C from 9:00–18:00 on March 10. It is presumed that the major reason for the significant snowmelt was the rise in the air temperature during this period.

The vertical profiles of the anionic concentrations in the snow layers are shown in Fig. 6. The snow layers with remarkably high Cl^- , NO_3^- , and SO_4^{2-} concentrations were labeled Ca through Cc, Na through Nc, and Sa through Sc, respectively. These labeled snow layers were monitored up until the time they disappeared. Sa, Na and Ca were observed on January 5, and Sb, Sc, Nb, Cb, and Cc were formed by the snowfall associated with the passing low-pressure system and the snow clouds formed during the Asian winter monsoon; Nc was observed on February 6. All of the labeled snow layers could be observed on February 6. However, it was difficult to identify the snow layer that corresponded to Sc on February 21. The disappearance of Sc corresponded to the smoothing of the vertical profile of the EC in the upper snowpack (Fig. 5). Sa and Sb disappeared on March 16. However, Na–Nc and Ca–Cc could be traced until April 6. The date of disappearance of the SO_4^{2-} layer differed from those of the NO_3^- and Cl^- layers. This implies that the selective flushing of SO_4^{2-} from the snowpack occurred early in the snowmelt season.

3.3 Variation in anion load in snowpack

Figure 7 shows the variations in the snow water equivalent (SWE) and anion load. Although the snow had already melted on February 21, the SWE tended to increase until March 7 and ever afterward. Although SO_4^{2-} , NO_3^- , and Cl^- loads decreased slightly on February 21, the variations in them were similar to those in the SWE. It is conceivable that snowmelt did not occur actively from January 6 to March 7; the deposited snowfall was more than the volume of melt runoff until March 7. It is conceivable that the snowmelt observed on February 21 was a temporary snowmelt event due to a temporary air temperature rise (Fig. 4), and that regular snowmelt only began after March 7.

The SWE values on March 7 and 16 were 420 mm and 314 mm, respectively; thus, the SWE of 106 mm was lost from the snowpack, presumably during the same period. During this period, reductions in the SO_4^{2-} , NO_3^- , and Cl^- loads from the snowpack were observed to be 362 mg m⁻², 115 mg m⁻², and 115 mg m⁻², respectively. The ratio of the loss of each anionic load to the loss of SWE during each period (March 7 to 16,

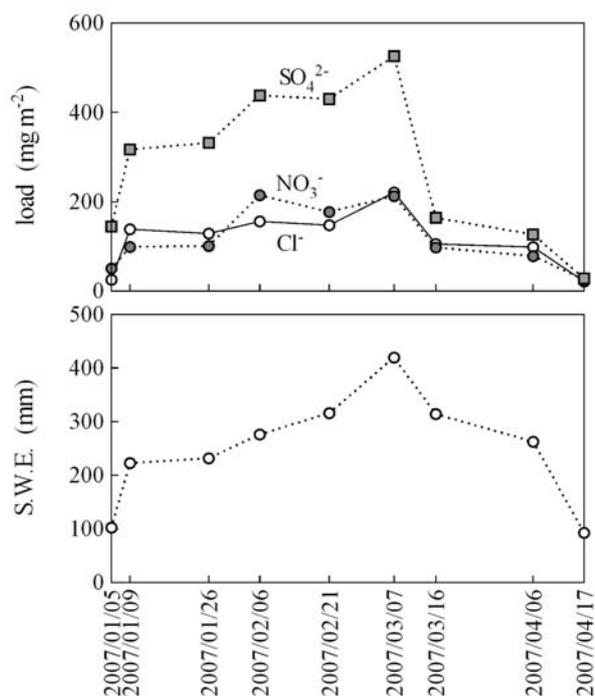


Fig. 7. Variations in the snow water equivalent (SWE) and anion loads from January 5 to April 17, 2007.

Table 1. Ratio of loss of each anion to loss of SWE during each period (March 7 to 16, March 16 to April 6, and April 6 to 17).

Period	Ratio of lost chemical load to lost SWE		
	Cl ⁻ /SWE	NO ₃ ⁻ /SWE	SO ₄ ²⁻ /SWE
2007/03/07–03/16	1.10	1.09	3.44
2007/03/16–04/06	0.13	0.37	0.73
2007/04/06–04/17	0.45	0.31	0.58

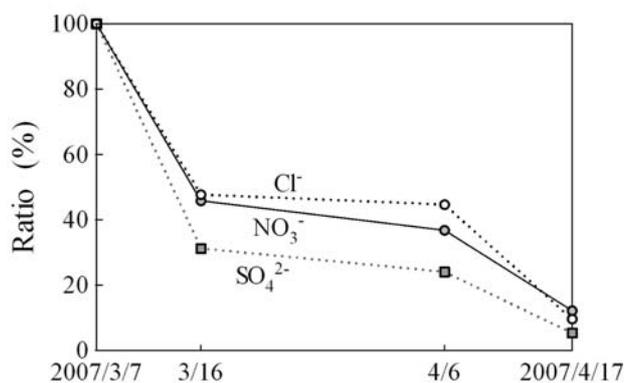


Fig. 8. Ratio of decrease in the anion loads in the snowpack from March 7 to April 17, 2007.

March 16 to April 6, and April 6 to 17) is shown in Table 1. As compared to other periods, the ratio of the reduction in concentration of each anion to the loss of SWE from March 7 to 16 is significantly higher. This indicates that the melt runoff during the early snowmelt season had a high ionic concentration.

Figure 8 shows the ratio of decrease in the anion

load in the snowpack from March 7 to April 17. The ratio of the decrease of SO_4^{2-} load is quite different from that of NO_3^- or Cl^- . The orders of the ratios of decrease during March 7 to 16 were $\text{SO}_4^{2-} > \text{NO}_3^- = \text{Cl}^-$. During March 16 to April 6 and April 6 to 17, the orders of the ratios of decrease were similar for all anions. In other words, the difference of flush degree of anion appears conspicuously in early snowmelt season, and the order of the ease with which the ions were flushed out from the snowpack was $\text{SO}_4^{2-} > \text{NO}_3^- = \text{Cl}^-$. As mentioned above, Brimblecombe *et al.* (1985), Davies *et al.*, (1987) and Suzuki (1991) reported that the ease with which each ion was flushed was $\text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{H}^+ > \text{Na}^+ > \text{Cl}^-$, $\text{Ca}^{2+} = \text{Mg}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Na}^+ > \text{Cl}^-$ and $\text{SO}_4^{2-} = \text{NO}_3^- > \text{Cl}^-$, respectively. SO_4^{2-} was easy to flush out from the snowpack than Cl^- . This fact is consistent with that of Brimblecombe *et al.* (1985), Davies *et al.*, (1987) and Suzuki (1991). However, the flush degree of NO_3^- is different every report.

Though it has been conceivable that the major reason for the order of the flush of each ion is that the degree of deposition of the chemical substance differs during the process in which it transforms into a granular snow particle (Suzuki, 2000), this mechanism has not appeared yet. Due to confirm this mechanism, a microscopic study at the snow particle level is necessary. However, a microscopic study at the snow particle level has not been performed so far, and this is a subject that has to be looked into.

4. Conclusion

The snow pit study was conducted on Mt. Norikura in the Northern Japan Alps from January to April, 2007 to clarify the chemical dynamics in the snowpack during the snowmelt season. The variation of the EC in snowpack indicates that little snowmelt occurred before February 6, the first snowmelt occurred between February 6 and 21, and the peak of snowmelt season occurred after March 7. Snow layers with remarkably high Cl^- , NO_3^- , and SO_4^{2-} concentrations were traced; furthermore, the snow layers with high SO_4^{2-} concentrations were found to disappear first. The percentage decrease in the anion loads in the snowpack during the snowmelt season differed. The orders of the ratio of decrease as the snowmelt proceeded were $\text{SO}_4^{2-} > \text{NO}_3^- = \text{Cl}^-$. SO_4^{2-} was easy to flush out from the snowpack than Cl^- . This fact is consistent with that of previous studies (Brimblecombe *et al.*, 1985; Davies *et al.*, 1987; Suzuki 1991). However, the flush degree of NO_3^- is different every study. It is conceivable that the order of the flush of each ion is influenced by the degree of deposi-

tion of the chemical substance during the process in which it transforms into a granular snow particle (Suzuki, 2000). However, this mechanism is as yet obscure. More data and a microscopic study at the snow particle level are required to confirm the order in which the ions are flushed out from the snowpack.

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