

Chemical property of snow meltwater in a snowy temperate area

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(Received August 22, 2002; Revised manuscript received November 5, 2002)

Abstract

We studied the chemical properties of snow meltwater in a snowy temperate area, where air temperature above the freezing point and rainfall are observed even in mid-winter. The amount of bottom-melt beneath the snow cover in the snowy temperate area we studied was below 1 mm day^{-1} , which is similar to the amount in a snowy cold area. However, in the case of winter melting, the pH of the meltwater decreased and its electric conductivity increased correspondingly. As the snowmelt progressed, the oxygen-18 ($\delta^{18}\text{O}$) of the snow cover increased gradually, and as a result, the $\delta^{18}\text{O}$ of the meltwater also increased accordingly. We conducted a multiple regression analysis with four species of acidifying ions (NO_3^- and nss-SO_4^{2-}) and neutralizing ions (NH_4^+ and nss-Ca^{2+}) in meltwater as independent variables and H^+ as a dependent variable. We could explain 86% of the H^+ concentration fluctuation in meltwater based on the concentrations of these four ion species. A clear diurnal variation is observed in anion concentrations in meltwater at the peak melt season. The anion enrichment factors in meltwater are higher in the order of NO_3^- , nss-SO_4^{2-} and Cl^- , with values of 7.7, 7.2 and 4.0, respectively.

1. Introduction

Macroscopic transportation of chemical substances in the snowpack is conducted by the downflow of meltwater. If there is no meltwater runoff in the snowpack resulting from surface melting, then chemical substances in the snowpack will be retained in each snow layer. In snowy cold areas where the air temperature seldom rises above the freezing point, chemical substances brought in by snowfall or dry deposition remain stored in the snow cover until the melting season, since surface melting hardly takes place in winter. On the other hand, in snowy temperate areas where the air temperature rises above the freezing point and rainfall is observed occasionally even in mid-winter, frequent melting prevents chemical substances from accumulating in the snowpack (Suzuki and Endo, 1991). The acidification of meltwater, which has been actualized in Scandinavia and on the North American continent, has occurred mainly because both regions are snowy cold areas. Many studies about the chemical properties of meltwater in snowy cold areas have been carried out (Suzuki, 1982, 1991; Jones, 1985; Jones and Sochanska, 1985; Bales *et al.*, 1993; Harrington and Bales, 1998), but few have been done on the meltwater properties in snowy temperate areas.

According to the investigation of mountainous stream water in a snowy temperate area, even in the

case of winter melting, the HCO_3^- concentration in stream water decreases while the concentrations of Cl^- , NO_3^- and SO_4^{2-} increase (Suzuki, 1995; 1996). Consequently, the pH of stream water decreased temporarily. Thus, we conclude that the concentrations of chemical substances (the meltwater does not contain HCO_3^-) increase and the pH value decreases in the meltwater resulting from winter melting in a snowy temperate area.

Suzuki (1993) used a tennis court as a snow lysimeter and reported the compositional fluctuation of oxygen isotopes in meltwater in a snowy temperate area. Suzuki (1993) also discussed the fluctuations of anion concentration in meltwater, although the observation was carried out only during a few days in the snowmelt season. While Suzuki (1995) also obtained the budgets of anions through a snow lysimeter, fluctuations of anion concentrations were not well described in that study. Therefore, in the present study, we collected meltwater samples continuously with a $2 \text{ m} \times 2 \text{ m}$ snow lysimeter throughout the snow coverage season. Using these samples, we investigated the variation of chemical properties of meltwater.

2. Methods

The samples of meltwater and snowpack were collected in the mountainous area in Aizu-Tajima, northeast Japan, at the 1992-93 winter season. In the

residential district (altitude of 570 m a.s.l), the mean monthly air temperature is -2.6°C in January, and the mean yearly maximum depth of snow is 93 cm. The study site at the mountainous area, at an altitude of 754 m, was about 8 km from the residential district to the southwest. In the mountainous area, the air temperature is lower and the snow is deeper than in the residential district.

The snow lysimeter employed was $2\text{ m} \times 2\text{ m}$ square, with polyvinyl-chloride-coated surfaces. Collected meltwater was transported to a half-underground observation hut about 5 m away through plastic tubes. The meltwater was measured with a 500 ml tipping-bucket flow meter, and each snowmelt sample was collected with an automatic water sampler. After filtering the meltwater, we measured its pH and electric conductivity, and then we measured the major ion concentrations using an ion chromatograph (Dionex 2020i/SP). We determined the isotopic composition of oxygen-18 ($\delta^{18}\text{O}$) using a mass spectrometer (Finnigan MAT: delta S) on CO_2 equilibrated with samples. Snowpack sampling was performed in the same manner as that described by Suzuki (1982), except that an Adirondack-type corer was employed in this study for collecting the total snowpack sample. We calculated water equivalent and snow density from this sample. We then melted the snowpack sample and measured the meltwater pH, electric conductivity, major ion concentrations and $\delta^{18}\text{O}$.

We collected a precipitation sample at a several-day interval with a plastic funnel 30 cm diameter and a sample vial. Since we kept the funnel open during sampling, dry deposition was also included in the sample. This sample was subjected to chemical analyses in the same manner as the meltwater and snowpack.

We also observed weather conditions at the observation field where the snow lysimeter was located. Air temperature was automatically measured with a ventilated Pt resistance temperature sensor, precipitation was measured with a tipping-bucket rain/snow gauge and snow depth was measured with a surface-reflecting snow depth gauge.

3. Results and discussion

3.1. Weather conditions

Variations of precipitation, air temperature, snow depth and snowmelt runoff in the winter of 1992-93 are shown in Fig. 1. Snow cover was observed from December 12, 1992, until March 30, 1993, in this winter, so data from December 11 to March 31 are shown in this figure. Precipitation is classified as rainfall or snow, with 3°C of air temperature as a threshold. The snow depth, measured every 9:00 local standard time (LST), is indicated. It should be noted that snowmelt

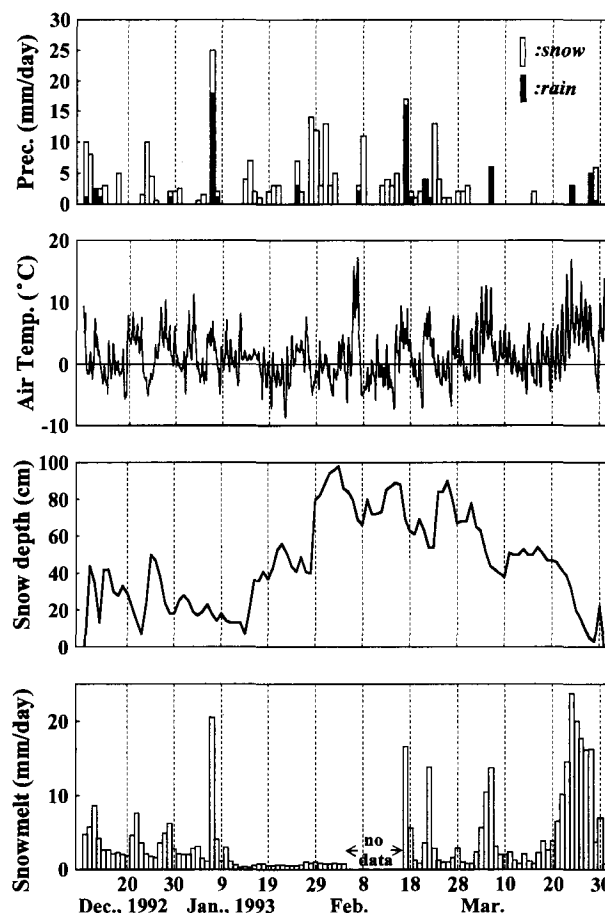


Fig. 1. The variations of precipitation, air temperature, snow depth and snowmelt runoff during the winter season in 1992-93.

runoff was not measured for February 5-16 by the mechanical failure.

A lot of snowmelt runoff was observed from the middle of December until the beginning of January. A cyclone passed through the southern coast at Honshu on January 7, and much rainfall was observed at the study site. Thus, snowmelt runoff also increased, so that 20.5 mm day^{-1} was recorded on that day. After this episode, the air temperature dropped, and a lot of snowfall was observed after the end of January. The maximum snow depth of 98 cm of this winter was recorded on February 3, and the snowmelt runoff in this period (January 11-February 4) was less than 1 mm day^{-1} .

The amount of midwinter bottom-melt from the snowpack in Moshiri, northern Hokkaido, which is a typical snowy cold area, averages $0.5\text{--}0.6\text{ mm day}^{-1}$ with a maximum of 1 mm day^{-1} (Kojima and Motoyama, 1985). The present result demonstrates that, even in a snowy temperate area, almost the same amount of bottom-melt from the snowpack is observed as in snowy cold areas (Fig. 1). Although snowmelt runoff was not measured on February 5-16, since a cyclone accompanied by a front passed through the Tohoku district on February 6-7, the temperature

rose temporarily, and presumably the amount of snowmelt runoff also increased in this period. There was a rainfall caused by the passage of a double cyclone on February 17, and snowmelt runoff increased as a result of that also. After this incident, snowmelt runoff repeatedly increased and decreased until the peak snowmelt season arrived in late March, ending when the snow cover disappeared on March 31.

3.2. Chemical properties of precipitation

Variations of pH, electric conductivity, anion concentrations and $\delta^{18}\text{O}$ of precipitation are shown in Fig. 2 with precipitation intensity. The collection period of each sample is indicated by the length of lines drawn in the figure. The electric conductivity and pH fluctuated between $11.7\text{--}57.5 \mu\text{S cm}^{-1}$ and between 4.29–5.07, respectively. Although we observed no time-based trend in the electric conductivity and pH, the mutual correlation coefficient between them is -0.69 , which is a relatively high correlation. Thus precipitation is more acidic when the net concentration of dissolved substances in precipitation is high.

In most cases, Cl^- has the highest concentration among anions in precipitation. However, in precipitation during March 3–10, and March 18 to April 1, concentrations of NO_3^- or SO_4^{2-} were larger than that of Cl^- , which affects the anion compositions of the snowmelt, as discussed later. We found no time-varying trend in the $\delta^{18}\text{O}$ of precipitation, its variation is relatively large, ranging between -8.27‰ and -13.90‰ . The $\delta^{18}\text{O}$ of precipitation mainly depends

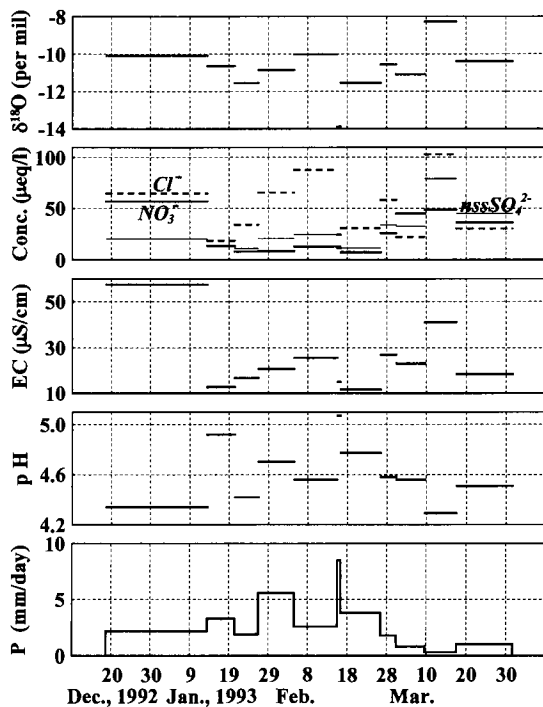


Fig. 2. The variations of precipitation intensity (P), pH, electric conductivity (EC), anion concentration and $\delta^{18}\text{O}$ in precipitation during the winter season in 1992 – 93.

on the condensation and freezing temperature (Dansgaard, 1964), as well as on synoptic conditions and the pathways of clouds bringing precipitation. On the other hand, precipitation collected in Tohkamachi, central Japan, revealed that the $\delta^{18}\text{O}$ of precipitation has no correlation (Suzuki and Endo, 1995).

3.3. Chemical properties of meltwater

Variations in the pH, electric conductivity and $\delta^{18}\text{O}$ of meltwater over the study period are shown in Fig. 3 along with the daily snowmelt runoff. In addition, variations of the water equivalent, pH, electric conductivity and $\delta^{18}\text{O}$ of the total snowpack are shown in Fig. 3. Although snowmelt runoff was observed beginning on December 11, as mentioned above, we began collecting meltwater on December 19. Meltwater sampling was continued even when runoff was not measured (February 5–16). After December 22, the pH of the meltwater fell to less than 5.0, and its minimum of 4.16 was recorded on February 6. In the case of winter melting, meltwater becomes increasingly acidic, and its electric conductivity increases correspondingly. It had been generally presumed that che-

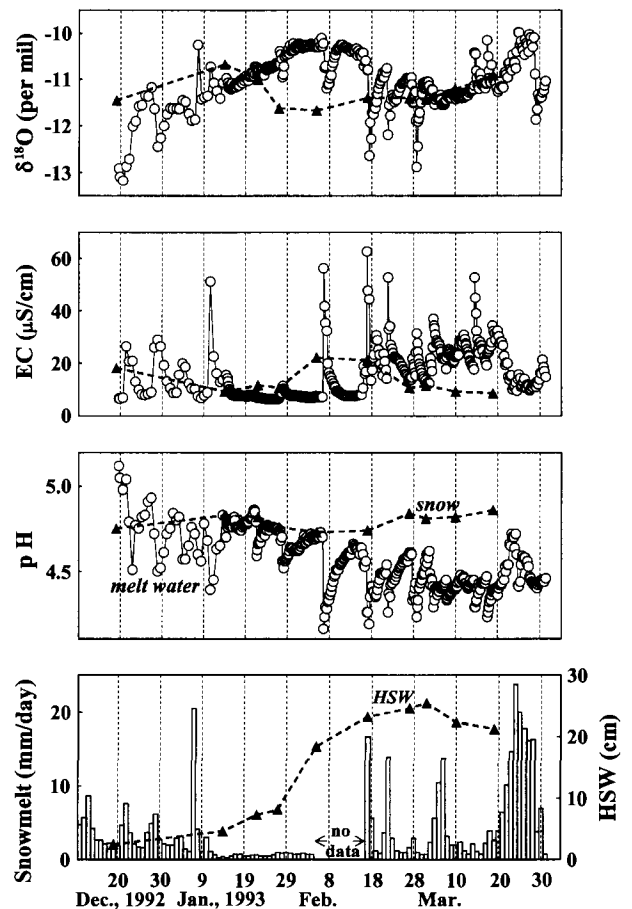


Fig. 3. The variations of snowmelt runoff and water equivalent of the snowpack (HSW), pH, electric conductivity (EC) and $\delta^{18}\text{O}$ in the meltwater and snowpack during the winter season in 1992 – 93.

mical substances were hardly accumulated in snow cover and that meltwater acidification seldom took place in snowy temperate areas, since winter melting occurred frequently. However, in reality, even when melting occurs frequently at an interval of less than 10 days, the electric conductivity of meltwater increases and the pH decreases. In the case of winter melting, the pH of meltwater is lower, while the electric conductivity inversely is higher, compared with the pH and electric conductivity of the total snowpack. However, these relations do not necessarily hold for bottom-melt. We assume that this is so because bottom-melt takes place only in the bottom layer of the snowpack.

The observation that the electric conductivity of meltwater increases and the pH decreases upon melting is attributed to segregation of the chemical substances to the exterior of the snow particles (Suzuki, 1982). On the other hand, the change of $\delta^{18}\text{O}$ of meltwater is thought to occur as follows: When snow particles melt into liquid water, the $\delta^{18}\text{O}$ of meltwater decreases. Therefore, the $\delta^{18}\text{O}$ of snowpack increases gradually, and, as a result, the $\delta^{18}\text{O}$ of meltwater increases accordingly (Stichler *et al.*, 1986; Suzuki, 1993). However, since there might be new precipitation while the snowmelt progresses, the $\delta^{18}\text{O}$ of the snowpack would continue to change. The $\delta^{18}\text{O}$ of precipitation collected during January 21–27 was as low as -11.56 , and the $\delta^{18}\text{O}$ of the total snowpack also fell as a result. However, since snowmelt took place only at the bottom of the snowpack during this period, the $\delta^{18}\text{O}$ of meltwater increased gradually. As melting on the surface of the snowpack took place on February 6, the $\delta^{18}\text{O}$ of the meltwater decreased temporarily. The $\delta^{18}\text{O}$ of precipitation dropped to -13.90 during February 16–17, and the $\delta^{18}\text{O}$ of the meltwater in this period decreased temporarily and abruptly. On the other hand, the $\delta^{18}\text{O}$ of the meltwater increased conversely on March 14 or 17. This is because the $\delta^{18}\text{O}$ of precipitation during the March 10–18 period was as high as -8.27 . A similar episode was also observed on January 7. Thus we concluded that increases or decreases in the $\delta^{18}\text{O}$ of meltwater depend upon whether the precipitation supply on the surface of the snowpack has high $\delta^{18}\text{O}$ or low $\delta^{18}\text{O}$.

3.4. Acidification of meltwater

The pH of precipitation is determined by the balance of acidifying ions (NO_3^- , nss-SO_4^{2-}) and neutralizing ions (NH_4^+ , nss-Ca^{2+}) (Suzuki and Endo, 1994). In other words, the pH of precipitation is defined by the acidification index (AI) expressed as Eq. 1.

$$\text{AI}(\mu\text{eq l}^{-1}) = (\text{NO}_3^- + \text{nss-SO}_4^{2-}) - (\text{NH}_4^+ + \text{nss-Ca}^{2+}). \quad (1)$$

The relationship between the AI and pH of meltwater for 418 samples collected in the studied winter is illustrated in Fig. 4. As is apparent in the

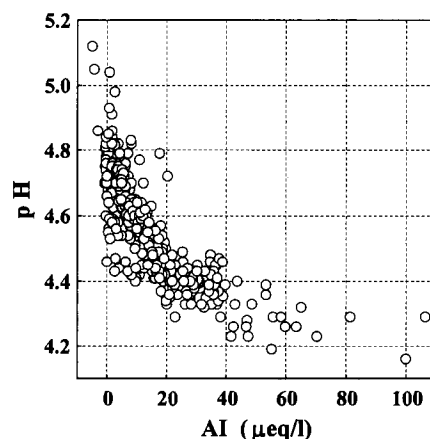


Fig. 4. The relationship between the acidification index and pH in meltwater.

figure, the pH is high when the AI of meltwater is low, and the pH decreases as the AI increases. As is the case with precipitation, the pH of meltwater is clearly determined by four ion species constituting the AI. A multiple regression analysis, with concentrations of four acidifying and neutralizing ion species as independent variables and H^+ as a dependent variable, yields Eq. 2,

$$\text{H}^+ = 1.08 \cdot \text{NO}_3^- + 0.621 \cdot \text{nss-SO}_4^{2-} - 0.164 \cdot \text{NH}_4^+ - 1.86 \cdot \text{nss-Ca}^{2+} + 27.4, \quad (2)$$

where the determination coefficient is 0.860. Thus 86% of H^+ concentration fluctuation can be explained by concentrations of these four ion species.

3.5. Variation of anion concentration in meltwater at the snowmelt season

Fluctuations of snowmelt runoff, anion concentrations, H^+ concentration and anion composition in March 1993 are shown in Fig. 5. A clear diurnal variation is observed in the snowmelt runoff. Although not so much in this month, precipitation was observed on March 7, 16, 24, 28 and 29. It was mainly snowfall on March 16 and 29 and otherwise was rainfall. The effect of rainfall is indicated in the hydrograph of snowmelt runoff on these days. Furthermore, we observed clear variations in anion composition when rainfall caused melting. The proportion of Cl^- in the total anions decreased rapidly on March 7, 24 and 28, while those of NO_3^- and nss-SO_4^{2-} increased. As mentioned previously, this result is attributed to the fact that Cl^- is less concentrated than NO_3^- and nss-SO_4^{2-} in rainfall. Thus, in the case of melting caused by rainfall, the ion composition of precipitation may directly affect that of meltwater. A large variation of anion composition was observed on March 14 and 17. Although the proportion of Cl^- dropped and the proportions of NO_3^- and nss-SO_4^{2-} increased on both days, there is a difference in the manner of concentration variation. Anion concentrations of all species increased, while the proportion of

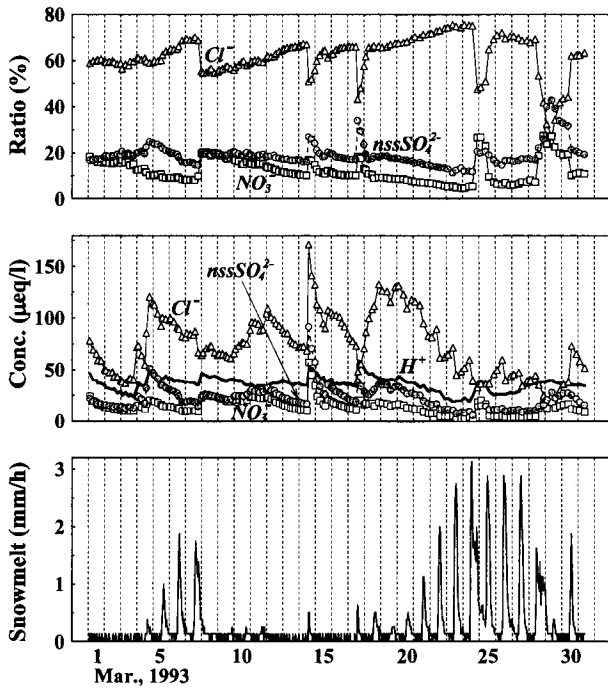


Fig. 5. The variations of snowmelt runoff, H^+ and anion concentrations and anion composition in meltwater in March 1993.

Cl^- in total anion decreased on March 14. Cl^- concentration decreased while NO_3^- , $nss-SO_4^{2-}$ and H^+ concentrations increased on March 17. For 16 days during March 8-23, no rainfall was observed. Melting was increased on March 14 and 17 due to high air temperatures and solar radiation. The melting on March 14 was surface-melting after the one-week interval following the rainfall on March 7, so we suppose that concentrations of all anions and H^+ increased. After the melting on March 17, we observed a clear diurnal variation in anion concentrations for March 18-24. Thus the mode of fluctuation of snowmelt runoff and anion concentrations during the snowmelt season is clarified.

3.6. Runoff of anions from snowpack

During March 19-31, during the snowmelt season, meltwater samples were collected at intervals of 6 hours. Then, assuming that anion concentration was constant for 6 hours before and after the sampling time, we calculated the hourly anion runoff from the snowpack by multiplying this anion concentration by the hourly snowmelt runoff. Moreover, the hourly anion runoff was integrated into the daily anion runoff, where a day starts at 9:00 LST. The results are shown in Fig. 6. Although there was a little snowmelt runoff at the early snowmelt season, anion concentrations were relatively high, and, as a result, anion runoff reached about 40 percent of the maximum. The ionic runoff of Cl^- was the highest, followed by $nss-SO_4^{2-}$ and NO_3^- . However, when the influence of rainfall must be considered, like on March 24 or 28, NO_3^-

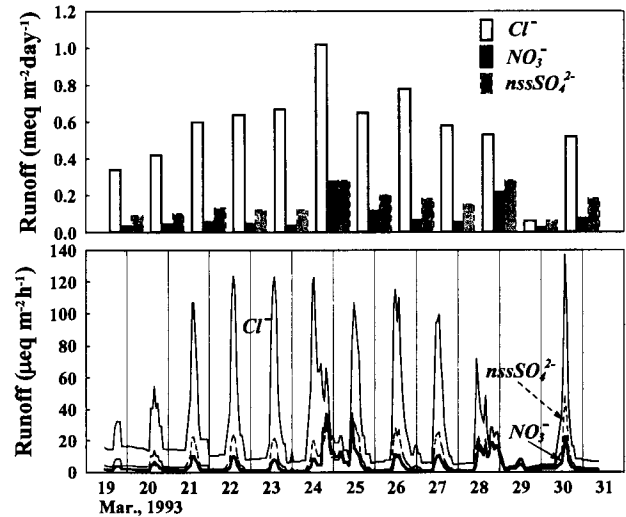


Fig. 6. The variations of hourly and daily anion runoff from the snowpack during March 19 - 31, 1993.

runoff from the snowpack may reach as high a level as that of $nss-SO_4^{2-}$. We found the ratio of the ionic runoff from the snowpack to the total ions accumulated in the snowpack on March 19 and added by following precipitation (wet deposition) to be 89, 93 and 94% for NO_3^- , $nss-SO_4^{2-}$ and Cl^- , respectively. This result supports the validity of the ionic runoff estimation described above.

3.7. Enrichment of anions in meltwater

As no precipitation was observed between the snow survey time on March 19 and 18:00 LST, March 24, it is assumed that anion enrichment occurred because of the snowmelt in this period. The ion enrichment factor is defined as the ratio of the ion concentration in meltwater to that of the total snowpack. The variations of anion enrichment factors in this period are shown in Fig. 7. All anions have higher concentration, thus are enriched, in meltwater than in snowpack. The enrichment factors decreased as snowmelt proceeded, finally reaching approximate unity on March 24. The primary anion enrichment factors in snowmelt are higher in the order of NO_3^- , $nss-SO_4^{2-}$ and

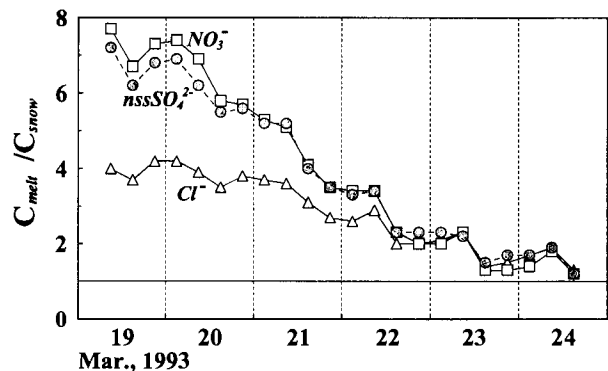


Fig. 7. The variations of anion enrichment factors during March 19 - 24, 1993.

Cl⁻, and are 7.7, 7.2 and 4.0, respectively. Brimblecombe *et al.* (1985) and Davies *et al.* (1987) have also reported that the enrichment factors of SO₄²⁻ and NO₃⁻ are large compared with that of Cl⁻.

4. Concluding remarks

We investigated the chemical properties of meltwater in a snowy temperate area. Although surface melting occurs frequently throughout the snow coverage season, only bottom melting takes place if the air temperature stays low for days. The amount of snowpack bottom melting is below 1 mm day⁻¹, which is almost as much as that in snowy cold areas. In the case of winter melting, the pH of meltwater drops and its electric conductivity increases correspondingly. In this case, the pH of meltwater is lower, while its electric conductivity is higher, compared with the pH and electric conductivity levels of the total snowpack. When snowmelt advances, the δ¹⁸O of snowpack increases gradually, and, as a result, the δ¹⁸O of meltwater also increases as the melting proceeds. This suggests that whether the δ¹⁸O of meltwater increases or decreases depends upon whether the precipitation supply on the surface of the snowpack has a high or low level of δ¹⁸O. A multiple regression analysis, with concentrations of acidifying ions (NO₃⁻ and nss-SO₄²⁻) and neutralizing ions (NH₄⁺ and nss-Ca²⁺) as independent variables and H⁺ as a dependent variable, demonstrates that 86% of H⁺ concentration fluctuation can be explained by the concentrations of these four ion species. We observed a clear diurnal variation in anion concentrations during the snowmelt season. Moreover, anion concentrations in the meltwater are higher than those in the snowpack, and the enrichment factor decreases gradually as melting proceeds. The anion enrichment factors in meltwater are higher in the order of NO₃⁻, nss-SO₄²⁻ and Cl⁻, and are 7.7, 7.2 and 4.0, respectively.

Acknowledgments

This research was supported by a Grant-in-aid for Scientific Research of the Japanese Ministry of Education, Science, Sports and Culture.

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