

TEMPORAL VARIATIONS IN ACIDITY AND ION CONCENTRATIONS OF PRECIPITATION, SNOWPACK
AND OUTFLOW FROM SNOWPACK IN A TEMPERATE SNOW AREA OF JAPAN

By

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SYNOPSIS

This paper describes the temporal variations in acidity and main dissolved ion concentrations of precipitation, snowpack, and outflow from snowpack in a temperate snow area of Japan. In order to understand the characteristics of snow chemistry and the effect of rainfall and surface snowmelt on chemistry outflow from snowpack, snow sampling and water quality measurements (pH, electric conductivity, Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) were conducted from December 2008 to March 2009 at Tohkamachi experimental station, Japan. The mean pH of precipitation and outflow from snowpack were approximately 4.6 and 5.0, respectively. The acidified precipitation and outflow were high electric conductivity and mainly governed by sulfate. However, the chemical solutes derived from windblown mineral dust decreased acidification of snowfall in February with high electric conductivity. Temporary acidification of outflow occurred at the abrupt runoff after the stable and low outflow fed by largely bottom snowmelt due to ground heat. Ion fluxes at the snow surface and snow bottom suspect that percolation of surface snowmelt or rainfall to snow bottom flows the solutes eluted on the ice grain within snowpack and leads to temporary acidification and further ion-concentration enrichment of outflow.

INTRODUCTION

Chemical solutes in snowfall are stored in snowpack, and flow out of it with meltwater. Surface meltwater or rainfall repeats freezing and melting through the snowpack until it infiltrates to snow bottom. Relocation of chemical solutes within the snowpack during melt-refreeze cycles causes a preference elution on the surface of ice grains. These processes result in the release of chemical solutes from the snowpack in the early portion of melt (*melt*

fractionation) (1), (2). In areas where precipitation is acid, high acidic meltwater from snowpack may have an impact on forest ecosystems or soil microbes (3), (4). If snowmelt inflows directly from snowpack to a stream channel with little interaction with soil, abrupt ion enrichment may transfer to the stream channel. In regions where precipitation is acid and where the soil provides little buffering, there may be temporary acidification of streams or lakes (5), (6), resulting in stress conditions for aquatic biota or fish mortality (7), (8), (9). Kuramot et al. (10) measured water quality of snowpack, meltwater and stream water. Aga et al. (11) measured water quality of reservoirs and observed the increment of dissolved aluminum with slight and brief acidification in Hokkaido Island, Japan.

The Sea of Japan side of Japan's central mountain spine is one of the heaviest snow regions in the world, and the average annual maximum snow depth for this region is over 2 m in some lowlands (12). A large amount of chemical solutes are stored in the snowpack, and its storage capacity increases with high snowdepth. Since this area belongs to a temperate zone, frequent surface snowmelt or rainfall occurs even in mid-winter, and most of the snow layers are in wet. Moreover, chemical solutes contained in the snowfall are characterized by several chemical substances derived from soil, sea salt and human activities. In general, strong winter monsoon blows to Japanese Island from Eurasia continent, and absorbs a large amount of vapor over the Sea of Japan warmed by current. The winter precipitation in the Sea of Japan comprise Na^+ , Mg^{2+} and Cl^- derived from sea salt (13). It also contains Ca^{2+} derived from sea salt and terrestrial particles such as yellow sand (14). The major natural sources of SO_4^{2-} in precipitation are sea salt, marine phytoplankton, and volcanoes. The major natural sources of NO_3^- in precipitation are biomass burning and biological activities in soil. Sulfate oxides or nitrogen oxides are released due to the burning of fossil fuels. The contributions of anthropogenic sulfur or nitrogen are larger than these natural origins. There is some research on chemical properties of precipitation in this region (15), (16). Seto et al. (16) represented that the maximum concentrations of non-sea-salt SO_4^{2-} and non-sea-salt Ca^{2+} in precipitation occurred from winter to spring at most sites over Japan. Kuramoto et al. (10) investigated the chemical properties of winter snow in the Japan Alps and found that high concentrations of NO_3^- and SO_4^{2-} deposited in the snow layers formed due to low-pressure system and sea salts deposited in the snow layers formed due to winter monsoon. However, there are only a few studies of chemical properties of snowmelt water (17) and stream water (18) in temperate snow areas.

We conducted on-site sampling of precipitation, snowpack and outflow from snowpack, and measured their water quality in a temperate snow area of Japan. The purpose of this paper is to evaluate the impacts of rainfall or surface snowmelt on the temporal distribution of chemical solutes in the outflow from the snowpack.

STUDY AREA AND MESAUREMENT

Study area

Snow samplings and pit-wall observations of snow cover were conducted at Tohkamachi experimental station (37°08'N, 138°46'E; 200 m a.s.l.), Forestry and Forest Products Research Institute, Niigata prefecture, Japan (Fig. 1) from December 2008 to March 2009. Annual variations in winter meteorological conditions during past 6 years are shown in Fig. 2. In this paper, we defined the winter 2009 as the period from December 2008 to February 2009 for the convenience. The site of this study is located on the Sea of Japan side of Japan's central mountain spine, and belongs to temperate climates. The mean winter temperature during December to February is 1.4 °C for six years between 2004 and 2009. It is warmer than other domestic heavy snow areas such as Hokkaido and Tohoku, and heavy snow areas in the world such as Siberia and Scandinavia. The annual winter precipitation and snowdepth have larger variations than other regions where there is heavy snowfall. The mean annual maximum snowdepth was 193 cm, the highest maximum snowdepth was 314 cm in 2006 and the lowest maximum snowdepth was 84 cm in 2007 for

six years. There is a distinct negative correlation between mean winter temperature and winter precipitation (Takeuchi et al. (12)). This suggests that the total precipitation, including both snow and rain, decreases with increasing winter air temperature. As winter precipitation was the lowest and maximum snowdepth was the second lowest in 2009 between 2004 and 2009, the winter season in 2009, when we conducted snow samplings and pit-wall observations, was placed into the category of a “light snow year”.

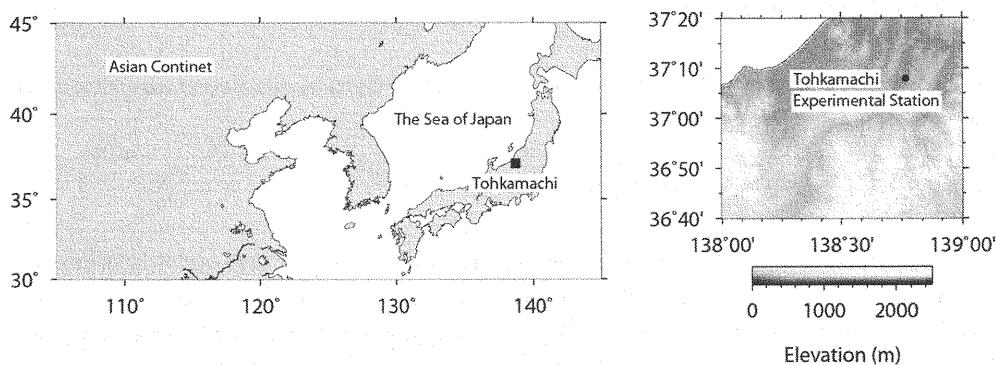


Fig. 1 Location of Tohkamachi experimental Station, Japan

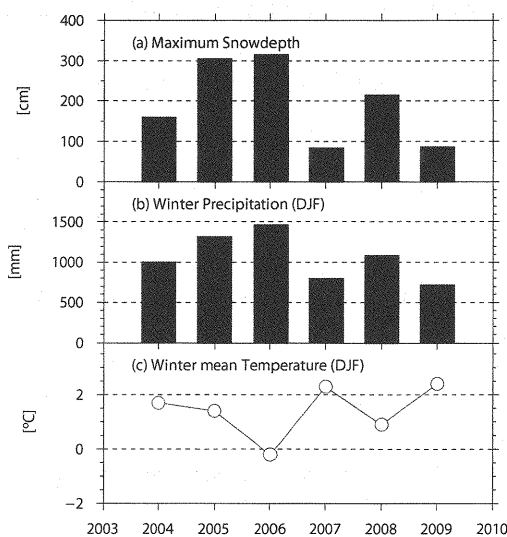


Fig. 2 Annual variations in (a) maximum snowdepth, (b) precipitation and (c) mean temperature during winter from December to February (DJF) at Tohkamachi experimental station

Hydrological observation

Air temperature, humidity, precipitation, wind velocity, snow depth and net radiation were measured automatically at Tohkamachi experimental station during the study period. Moreover, outflow from snowpack was measured with a snow-lysimeter, and the snow weight was measured with a metalwafer. We separated precipitation into rainfall or snowfall by using the following equations for snowfall occurrence ratio to total precipitation (19):

$$\begin{aligned} s &= 1 - 0.5\exp(-2.2(1.1 - T_w)^{1.3}) & (T_w > 1.1) \\ s &= 0.5\exp(-2.2(T_w - 1.1)^{1.3}) & (T_w \leq 1.1) \end{aligned} \quad (1)$$

where, s denotes snowfall occurrence probability and T_a denotes air temperature ($^{\circ}\text{C}$). Wet bulb temperature T_w ($^{\circ}\text{C}$) can be approximated near 1°C as follows:

$$T_w = 0.548T_a + 0.875e - 5.32 \quad (2)$$

where e is water vapor pressure (hPa). In present study, we categorized precipitation form as snowfall in case of $s > 0.5$, otherwise it is categorized as rainfall.

Snow samplings and water quality measurements

We collected daily snowfall accumulated over the past 24 hours on the plate at around 09:00 during the study period. In each time, the plate was put on the snow surface for the next sampling after removing the residue of the previous sampling. We also collected outflow from the snow-lysimeter at around 17:00 almost every day. In addition to these daily samplings, we collected outflow every 90-minutes on February 16 and 25 to investigate their diurnal variations. Pit-wall observations of snow cover and snow samplings were conducted seven times, approximately at 10-day intervals; January 5, 14 26, February 5, 16 25, and March 5. We measured snow temperature, density, moisture content, grain size and categorized the snow type at each snow layer. We also collected snow core samples, which were usually 10 to 20 cm in thickness of the snow core from snow surface to snow bottom with an acrylic sampler.

The pH, electric conductivity of collected precipitation, snowpack and outflow were measured by means of the glass electrode method (DKK-TOA, CM-30R and HM-30R) after the samples were melted and filtrated. Moreover, major dissolved ion concentrations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-}) were measured with an ion chromatography (DIONEX, ICS-1500).

We calculated non-sea-salt (nss) SO_4^{2-} was calculated with the ratio of SO_4^{2-} to Na^+ in the sea water (20) as below:

$$[\text{nssSO}_4^{2-}] = [\text{SO}_4^{2-}] - ([\text{SO}_4^{2-}]/[\text{Na}^+])_{\text{sea water}} [\text{Na}^+] \quad (3)$$

We also calculated nssCa^{2+} with the ratio of Ca^{2+} to Na^+ in the sea water as below:

$$[\text{nssCa}^{2+}] = [\text{Ca}^{2+}] - ([\text{Ca}^{2+}]/[\text{Na}^+])_{\text{sea water}} [\text{Na}^+] \quad (4)$$

These equations also assume that all Na^+ in the measured samples originate from sea water.

Table 1 Mean pH, electric conductivity (EC) and ion concentrations of snowfall and outflow during the study period

	pH	EC ($\mu\text{S}/\text{cm}$)	ion concentration ($\mu\text{eq}/\text{l}$)									
			Cl^-	NO_3^-	SO_4^{2-}	nssSO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	nssCa^{2+}
snowfall	4.6	53.0	224.2	24.5	74.5	51.9	188.1	32.4	5.3	46.1	26.8	18.5
outflow	5.0	44.0	223.5	18.2	61.9	39.7	185.1	23.8	5.1	45.0	24.6	16.5

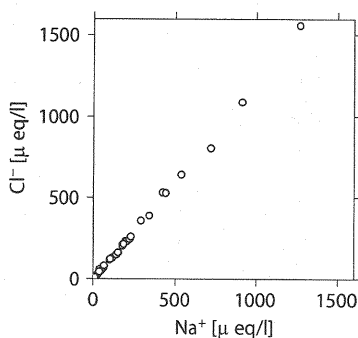


Fig. 3 Relationship between the measured concentrations of Na^+ and Cl^- in the precipitation samples

RESULTS AND DISCUSSION

Precipitation

The mean pH, electric conductivity and ion concentrations of collected precipitation are shown in Table 1. In general, Na^+ comes mainly from sea salt aerosol. Measured Cl^- had a high correlation with measured Na^+ ($r = 0.99$, see Fig. 3) and the ratios of Cl^- to Na^+ of the all precipitation samples nearly equal to standard ratio of the sea water. These results suggest that most of Cl^- in precipitation in Tohkamachi also comes from sea. We extracted nss Ca^{2+} from Ca^{2+} and nss SO_4^{2-} from SO_4^{2-} with equation (3) and (4) (see Table 1). These results showed that approximately 70% of Ca^{2+} and SO_4^{2-} were sea salt origin. The mean and minimum pH of collected precipitation were 4.6 and 3.9, respectively. Temporal variations in pH, electric conductivity, ion concentrations and daily precipitation are shown in Fig. 4. Most of the collected precipitation was below pH of 5.6, which is the level of equilibrium state with atmospheric CO_2 . There was a negative correlation between electric conductivity and pH of collected precipitation. Moreover, variation in SO_4^{2-} was most correlated with the variation in pH among measured ion parameters. Therefore, we inferred that sulfate is a major substance to acidify the precipitation. However, the pH and electric conductivity of precipitation on February 21 were distinctly different from chemical trends in whole winter, higher pH (=6.7) in spite of high electric conductivity and SO_4^{2-} concentration. Since most of ion parameters in the precipitation were the highest on February 21 among precipitation samples, ion enrichment led to high electric conductivity. The Ca^{2+} concentration (= 298.2 $\mu\text{eq/l}$) during this event was much higher than the mean ($\text{Ca}^{2+} = 26.8$ $\mu\text{eq/l}$) during the study period. Similarly, nss Ca^{2+} (= 242.5 $\mu\text{eq/l}$), which was calculated with equation (4), accounted for 81% of Ca^{2+} during this event and was much higher than the mean (nss $\text{Ca}^{2+} = 18.5$ $\mu\text{eq/l}$) during the study period. This Ca^{2+} is probably derived from terrestrial particles raised by wind such as yellow sand (21). Rainfall was observed from 15:00 on February 20 to 16:00 on February 21. An image processing with a CCD video camera, a method for automated identification of types of solid precipitation based on diameter and terminal velocity of snow particles (22), estimated that the precipitation form shifted from rainfall to snowfall at 19:00 on February 21 and that the total snowfall was 19.6mm at Tohkamachi experimental station. As depicted in Photo 1, the 5.2 mm thick snowfall layer between 8.9 mm and 14.1 mm in water equivalent from snow surface was yellowish with visual confirmation at Tohkamachi. Calcium carbonate, which is one of the major components of terrestrial particles, is weak base and has a neutralizing effect on acid water (23), (24), (25). Hence, these results suggest that yellow sand contained in snowfall on February 21 neutralizes the precipitation, and results in relatively high pH with high electric conductivity and sulfate concentration.

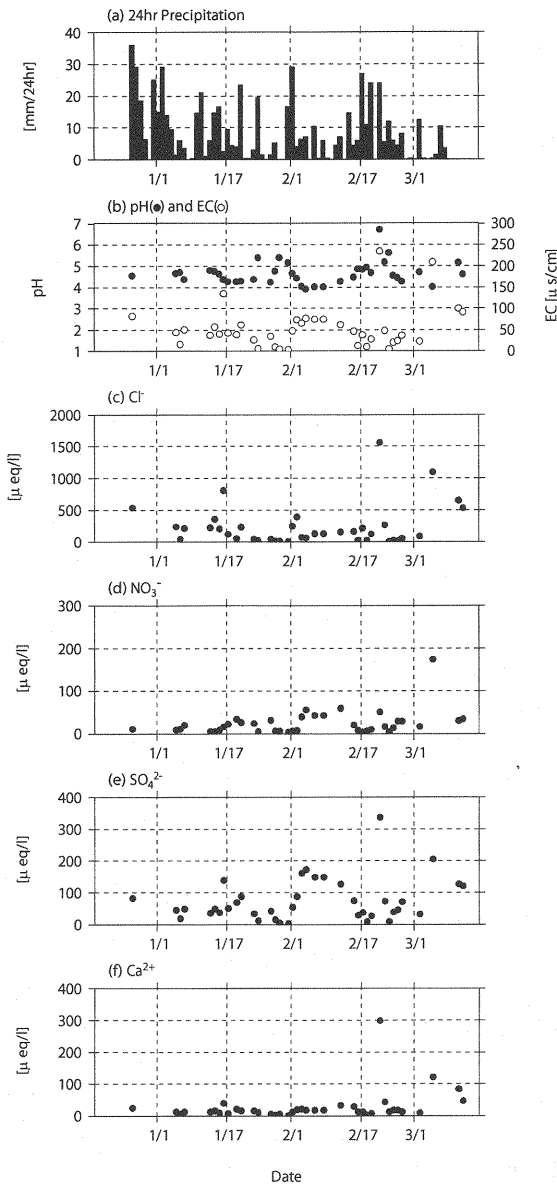


Fig. 4 Temporal variations in (a) precipitation and (b) pH and electric conductivity (EC), and ion concentrations ((c) Cl^- , (d) NO_3^- , (e) SO_4^{2-} , and (f) Ca^{2+})

Snowpack

We calculated the amount of solutes stored in the snowpack based on ion concentrations and sampled snow densities of each snow layer by pit-wall observations of snow cover (see Fig. 5). Snow water equivalent increased from mid-December to early January and began to decrease from early February, while the amounts of all solutes reached a peak on January 5 and declined after that. Fig. 6 shows the vertical profiles of the solutes (Cl^- , SO_4^{2-} , and Ca^{2+}) in the snowpack on January 5, 14, 26, February 16, and 25. All ion concentrations were relatively high at the

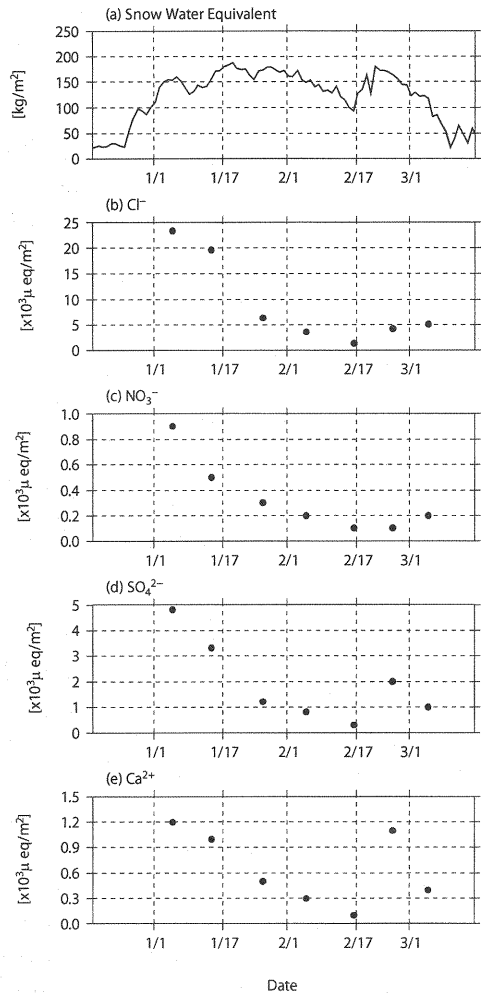


Fig. 5 Temporal variations in (a) snow water equivalent and amounts of solutes ((b) Cl^- , (c) NO_3^- , (d) SO_4^{2-} , and (e) Ca^{2+}) in snowpack

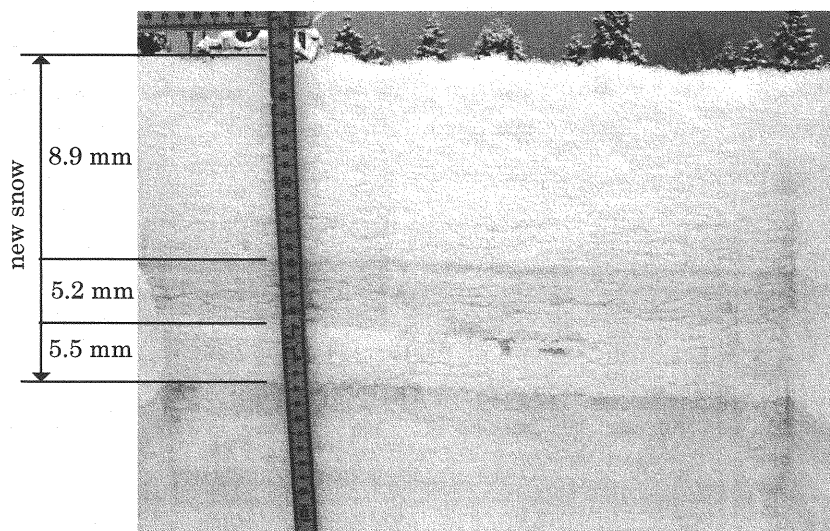


Photo 1 Stratigraphy of a snow pit wall including the layers accumulated from 19:00 on February 20 to 16:00 on February 21. The layer thickness represents in snow water equivalent.

the same snow layers between 10 and 30 cm and between 40 and 44 cm on January 5; between 30 and 40 cm and between 50 and 63 cm on January 14; and between 17 and 24 cm on February 25 in height from snow bottom at the pit-wall observation. The high concentrations at the snow layer between 10 and 30 cm in height from the snow bottom on January 5, declined by an insignificant amount at the same height on January 14. Similarly, the high concentrations at the snow layer between 30 and 40 cm from the snow bottom on January 14 also declined by an insignificant amount in the snowpack at the same height on January 26. These results suggest that the solutes within the snow layers, in which concentration of solutes is high, flow out of snowpack due to percolation of surface snowmelt or rainfall to the snow bottom.

Hourly precipitation, air temperature and outflow from the snowpack are shown in Fig. 7. Since air temperature repeated below-above freezing during the month of January, surface meltwater or rainfall is likely to repeat freezing and melting in the snowpack. As a result, chemical substances may elute on the surface of ice grain in the snowpack. Colbeck (1) demonstrated that melt-freeze cycles concentrate the impurities in the snowpack by means of laboratory experiments. Precipitation separating method categorized the precipitation on January 19 as rainfall. Rainfall probably reached the snow bottom since the peak of outflow responded to that of precipitation. The Cl^- mass flux from precipitation to snowpack ($F_{\text{in_Cl}}$) and SO_4^{2-} mass flux from precipitation to snowpack ($F_{\text{in_SO}_4}$) were 2925.5 and 1065.6 $\mu\text{eq}/\text{m}^2$ on January 19. On the other hand, The Cl^- mass flux from snowpack to the ground ($F_{\text{out_Cl}}$) and SO_4^{2-} mass flux from snowpack to the ground ($F_{\text{out_SO}_4}$) were 7569.3 and 3059.7 $\mu\text{eq}/\text{m}^2$ on January 19. These differences of Cl^- and SO_4^{2-} fluxes between precipitation and outflow ($F_{\text{out_Cl}} - F_{\text{in_Cl}}$ and $F_{\text{out_SO}_4} - F_{\text{in_SO}_4}$) suggest that the chemical solutes eluted on the surface of ice grains flowed out due to the passage of liquid water (surface melt or rainfall) through the snowpack. The amounts of SO_4^{2-} and Ca^{2+} increased February 17 and 25 in Fig. 5. They also increased at the snow layer between 17 and 24 cm from the snow bottom on February 25 in Fig. 6. These increases are probably due to terrestrial particles contained in precipitation on February 21.

Outflow from snowpack

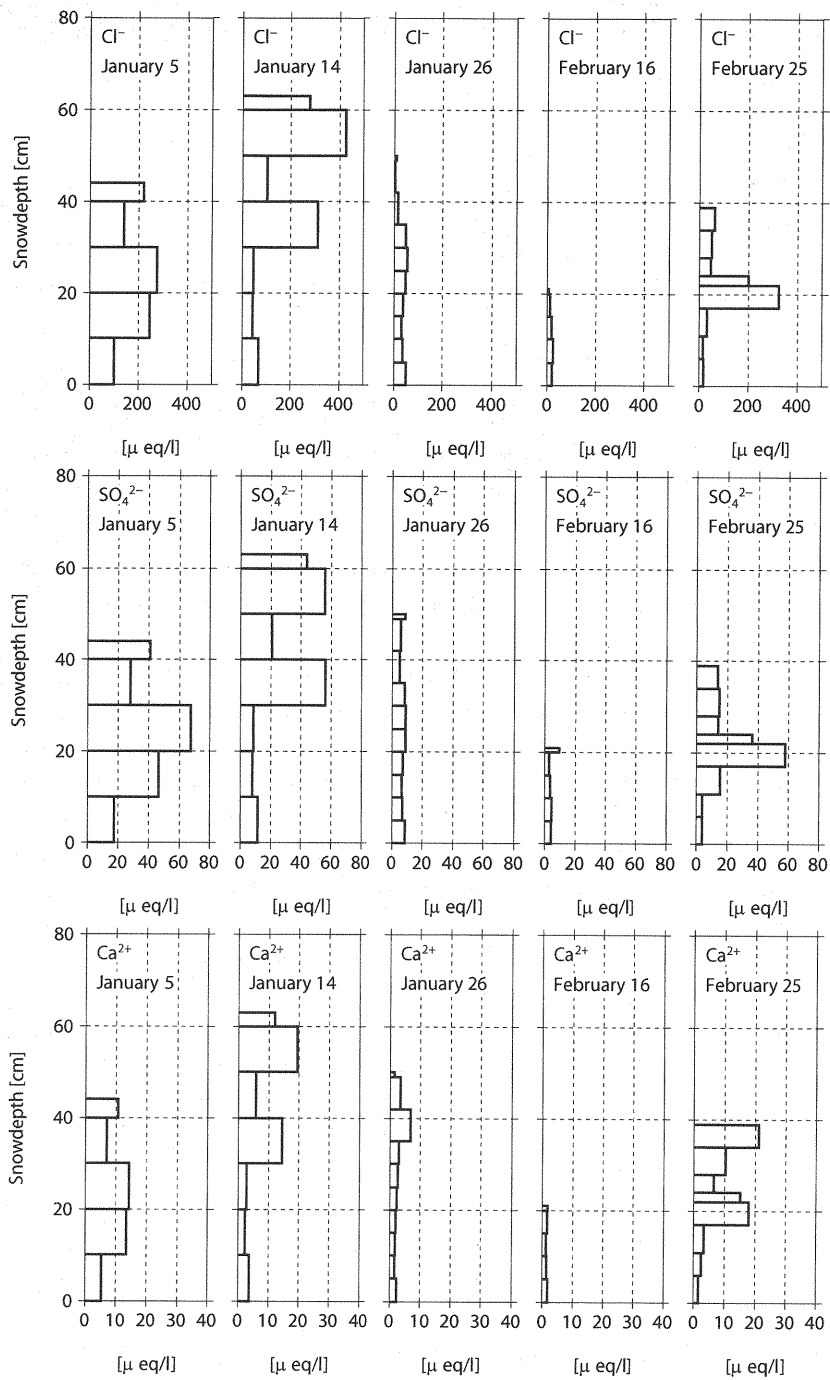


Fig. 6 Vertical profiles of Cl^- , SO_4^{2-} and Ca^{2+} in snowpack on January 5, 14, 26, February 16 and 25

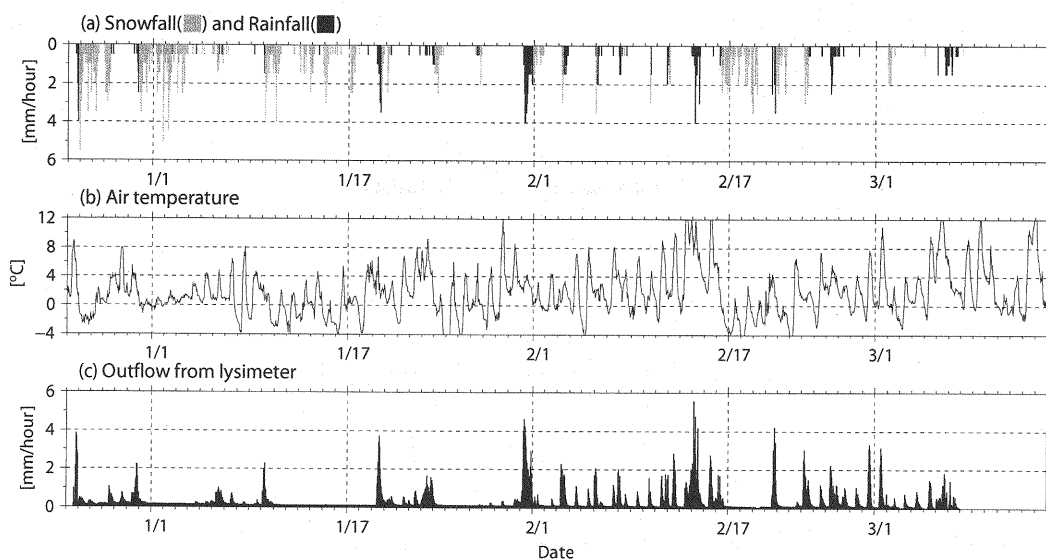


Fig. 7 Diurnal variations in (a) fractions of snow and rain in the precipitation, (b) air temperature and (c) outflow during the study period

Temporal variations in amounts of outflow from the snowpack, observed with a snow-lysimeter, and its ion concentrations (Cl^- , NO_3^- , SO_4^{2-} , and Ca^{2+}) are shown in Fig. 8. Similar to the collected precipitation, most of the collected outflow was below the pH of 5.6, equilibrium with atmospheric CO_2 . The mean pH (= 5.0) and the lowest pH (= 4.1) of outflow were slightly higher than those of the precipitation. Similar to chemical properties of precipitation, pH of outflow had a negative correlation with electric conductivity. Moreover, variations in SO_4^{2-} and NO_3^- had negative correlations with pH ($r = -0.48$, SO_4^{2-} ; $r = -0.45$, NO_3^-). Fig. 8 shows that pH of outflow decreased (pH = 4.1) steeply and EC increased when abrupt runoff occurred after outflow had been stable and low, from December 31 to 5, from January 12 to 18, and from January 25 to 30, in spite of temperate snow area. Most of the hourly outflow was 0.12 mm below the air temperature of 0 °C from January 12 to 18 according to Fig. 7 (b) and (c). Hence, we defined hourly bottom snowmelt caused by ground heat as 0.12 mm at the study site by assuming that surface snowmelt did not occur and that precipitation form was solid below the freezing point. The ratios of bottom snowmelt to outflow were 63, 99, and 81% during the three periods from December 31 to January 5, from January 12 to 18, and from January 25 to 30, respectively. Thus, low and stable outflow is largely fed by bottom snowmelt by ground heat. Vertical profiles of solutes in the snowpack (see Fig. 6) show that the amounts of solutes at the bottom layer were lower than the average in snowdepth. Hence, electric conductivity of outflow was low when outflow was largely fed by bottom snowmelt. Moreover, pH of outflow became lower with high electric conductivity when abrupt runoff occurred after stable and low outflow on January 6 and 19 (see Fig. 8). All ion concentrations including SO_4^{2-} and NO_3^- in outflow were high during these events. The solutes eluted in middle or upper snow layer were likely to flow out due to percolation of surface snowmelt or rainfall, and solutes flow out of the snowpack may lead to further ion-concentration enrichment and acidification of outflow.

Fig. 9 shows diurnal variations in outflow from snowpack, fractions of snowfall and rainfall, pH and electric conductivity of outflow, SO_4^{2-} concentrations in outflow, and SO_4^{2-} flux from snowpack to the ground on February 16. Rainfall shifted to snowfall at 07:00 after two hours rain. Outflow from snowpack reached the peak at 08:00 after the shift of rainfall to snowfall. Outflow declined gradually after the peak and remained low and stable (0.12 mm per hour) after 20:00. Electric conductivity and SO_4^{2-} reached the peak during the rain and declined with decrease in outflow. The SO_4^{2-} flux from rainfall to snowpack ($F_{\text{in}, \text{SO}_4}$) was $39.6 \mu\text{eq}/\text{m}^2$ from 05:00 to 07:00. The SO_4^{2-} flux

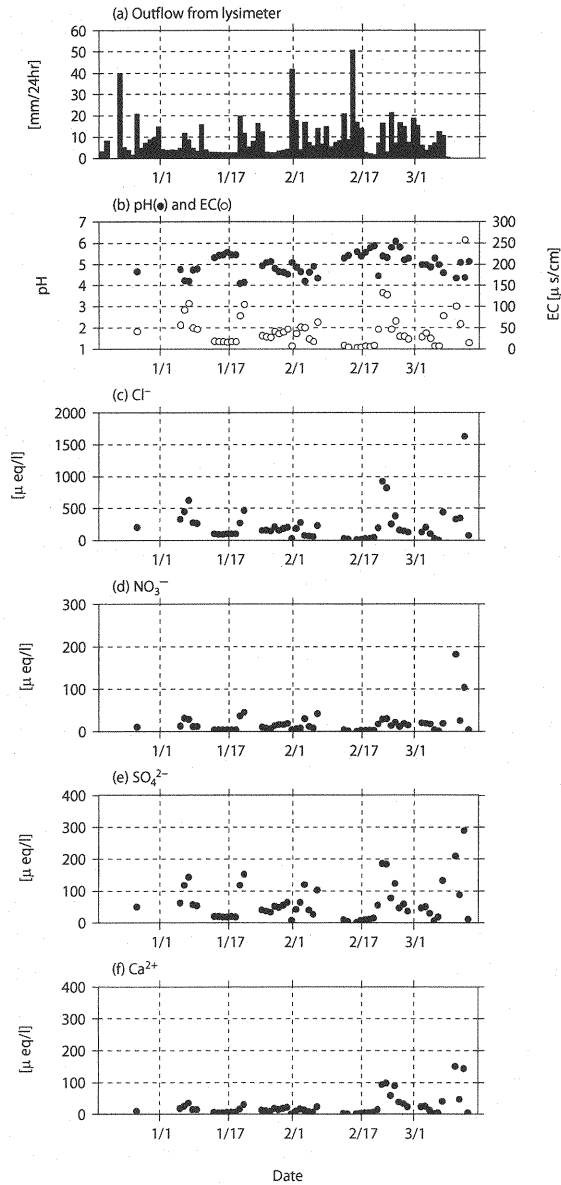


Fig. 8 Temporal variations in (a) outflow from the snow-lysimeter, (b) pH and electric conductivity (EC), and ion concentrations ((c) Cl^- , (d) NO_3^- , and (e) SO_4^{2-}) in outflow

from snowpack to the ground ($F_{\text{out_SO}_4}$) was $130.3 \mu\text{eq/m}^2$ from 05:00 to 20:00. Moreover, the SO_4^{2-} flux fed by bottom snowmelt ($F_{\text{out_bsm_SO}_4}$) was estimated to be $15.1 \mu\text{eq/m}^2$ from 05:00 to 20:00 with the assumptions that the SO_4^{2-} concentration in bottom snowmelt was constant and equaled that of outflow at 21:00. Mass balance of SO_4^{2-} in the snowpack ($F_{\text{out_SO}_4} - F_{\text{out_bsm_SO}_4} - F_{\text{in_SO}_4} = 75.6 \mu\text{eq/m}^2$) suggests that the rainfall or surface snowmelt flowed the solutes eluted on the surface of ice grain within snowpack passing through snowpack and that solutes flow out led to ion enrichment in the outflow.

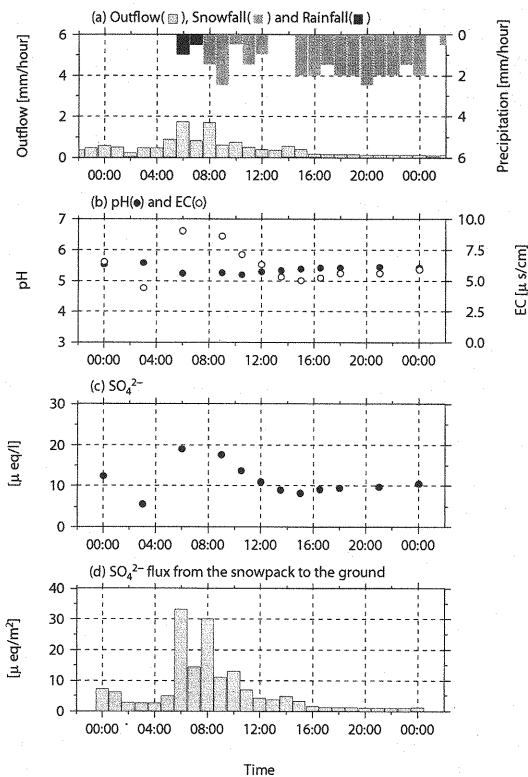


Fig. 9 Diurnal variations in (a) outflow and fractions of snow and rain, (b) pH and electric conductivity (EC) of outflow water, (c) SO_4^{2-} concentration in outflow, and (d) SO_4^{2-} flux from the snowpack to the ground on February 16

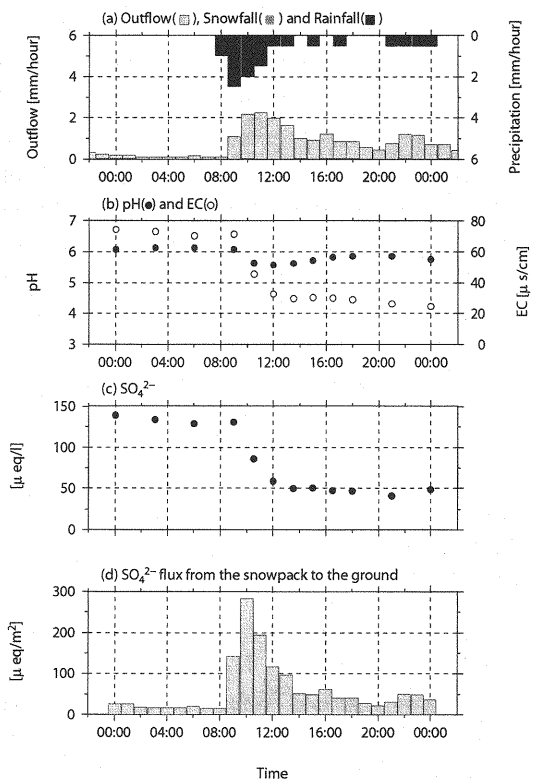


Fig. 10 Diurnal variations in (a) outflow and fractions of snow and rain, (b) pH and electric conductivity (EC) of outflow water, (c) SO_4^{2-} concentration in outflow, and (d) SO_4^{2-} flux from the snowpack to the ground on February 25

Fig. 10 shows diurnal variations in the fractions of snowfall and precipitation, pH and electric conductivity of outflow, SO_4^{2-} concentration in outflow and SO_4^{2-} flux from snowpack to the ground on February 25. Temporal variation in electric conductivity corresponded to that in SO_4^{2-} concentration. They remained high during low and stable outflow, declined during the period of six-hour continuous rain, and remained low and stable. However, SO_4^{2-} flux from snowpack to the ground was high during continuous rainfall. The SO_4^{2-} flux from precipitation to snowpack ($F_{\text{in_SO}_4}$) was $483.4 \mu\text{eq/m}^2$ from 07:00 to 13:00 and that from snowpack to the ground ($F_{\text{out_SO}_4}$) was $843.9 \mu\text{eq/m}^2$. Rainfall probably reached the snow bottom since outflow reached the peak two hours after the peak of rainfall. Therefore, Mass balance of SO_4^{2-} ($F_{\text{out_SO}_4} - F_{\text{in_SO}_4} = 360.5 \mu\text{eq/m}^2$) suggests the solutes flow out of the snowpack.

CONCLUSIONS

We conducted snow samplings of precipitation, snowpack and outflow from snowpack, and their water quality measurements (pH, electric conductivity, Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) from December 2008 to March 2009 at Tohkamachi experimental station in a temperate heavy snow area of Japan. We evaluated the relationship of temporal variations in acidity, electric conductivity and ion concentrations among winter precipitation, snowpack and outflow from snowpack. We draw the following conclusions from this study:

(1) The mean pH of precipitation and meltwater were 4.6 and 5.0 during the study period, respectively. Most sampled precipitation was below 5.6. Acidification of water is likely to be mainly governed by SO_4^{2-} among measured ion concentrations. However, when precipitation contained chemical solutes derived from terrestrial particles, pH of precipitation was high in spite of high electric conductivity and high SO_4^{2-} concentration. This was probably due to neutralization effect of calcium carbonate, which is one of the major components of terrestrial particles.

(2) Temporary acidification of outflow occurred and its electric conductivity increased correspondingly when surface snowmelt or rainfall occurred. We suspected that percolation of surface snowmelt or rainfall reaching the snow bottom caused solutes flow out of the surface of ice grain within the snowpack and led to ion enrichment and acidification of outflow from the snowpack.

In present study, bottom snowmelt by ground heat was extracted from outflow from snowpack. Further research is needed to divide rainfall, surface snowmelt, and bottom snowmelt from outflow. Moreover, our investigations were conducted for only one winter season, which was a light snow year. However, annual snow condition varies considerably in temperate snow areas of Japan. Hence, further measurement and analysis for several snow conditions are necessary to understand the storage effect of snowpack on water environment in river catchment.

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REFERENCES

1. Colbeck, S. C. : A simulation of the enrichment of atmospheric pollutants in snow cover runoff, *Water Resources Research*, Vol.17, pp.1383-1388, 1981.
2. Johannessen, K. and Henriksen, A. : Chemistry of snowmelt water :changes in concentration during melting, *Water Resources Research*, Vol.14, pp.615-619, 1978.
3. Jones, H. G. : The ecology of snow-covered systems: a brief overview of nutrient cycling and life in the cold, *Hydrological Processes*, Vol.13, pp.2135-2147, 1999.
4. Lipson, D. A., Schadt, C. A. and Schmidt, S. K. : Changes in Soil Microbial Community Structure and Function in an Alpine Dry Meadow Following Spring Snow Melt, *Microbial Ecology*, Vol.42, pp.307-314, 2002.
5. Tartner, M., Abrahams, P. W., Blackwood, I. L., Bimblecombe, P. and Davies, T. D. : The impact of a single black snowfall on stream chemistry in the Scottish Highlands, *Nature*, Vol.332, pp.826-819, 1988.
6. Marsh, P. and Pomeroy, J. W. : Spatial and temporal variations in snowmelt runoff chemistry, Northwest Territories, Canada, *Water Resources Research*, Vol.35, pp.1559-1567, 1999.
7. Jeffries, D.S., Cox, C. M. and Dillon, P. J. : Depression of pH in lakes and streams in central Ontario during snowmelt, *Journal of the Fishers Research Board of Canada*, Vol.36, pp.640-646, 1979.
8. Driscoll, C. T., Backer, J. P., Bisosni, J. J. and Schofield, C. L. : Effect of aluminum speciation on fish in dilute acidified waters, *Nature*, Vol.284, pp.161-164, 1980.
9. Gunn, J. M. and Keller, W. : Spawning site water chemistry and lake trout (*Salvelinus namaycush*) sac fry survival during spring snowmelt, *Canadian Journal of Fishers and Aquatic Sciences*, Vol.41, pp.319-329, 1984.

10. Kuramoto, T., Saha, S. K., Tanaka, M. and Suzuki, K. : Chemical Characteristics of Snowpack due to Differences in Snowfall Type in Japan Alps, *Bulletin of Glaciological Research*, Vol.26, pp.15-21, 2008.
11. Aga, H., Noguchi, I. and Sakata, K. : Aquatic chemistry of a reservoir during the thaw season, *Water, Air, and Soil Pollution*, Vol.130, pp.811-816, 2001.
12. Takeuchi, Y., Endo, Y. and Murakami, S. : High correlation between winter precipitation and air temperature in heavy snow-snowfall areas in Japan, *Annals of Glaciology*, Vol.49, pp.7-10, 2008.
13. Suzuki, K. and Endo, Y. : Relation of Na^+ concentration and $\delta^{18}\text{O}$ in winter precipitation with weather conditions, *Geophysical Research Letters*, Vol.22, pp.591-594., 1995.
14. Iwasaka, Y., Yamamoto, M., Imasu, R. and Ono, A. : Transport of Asian dust (KOSA) particles: importance of weak Kosa events on the geochemical cycle of soil particles, *Tellus*, Vol.40B, pp.494-503, 1988.
15. Hara, H., Kitamura, M., Mori, A., Noguchi, I., Ohizumi, T., Seto, S., Takeuchi, T. and Deguchi, T. : Precipitation chemistry in Japan 1989-1993, *Water, Air and Soil pollution*, Vol.85, pp.2307-2312, 1995.
16. Seto, S., Nakamura, A., Noguchi, I., Ohizumi, T., Fukuzaki, N., Toyama, S., Maeda, M., Hayashi, K. and Hara, H. : Annual and seasonal trends in chemical composition of precipitation in Japan during 1989-1998, *Atmospheric Environment*, Vol.36, pp.3505-3517, 2002.
17. Suzuki, K. : Chemical property of snow meltwater in a snowy temperate area, *Bulletin of Glaciological Research*, Vol.20, pp.15-20, 2003.
18. Suzuki, K. : Chemistry of stream water in a snowy temperate catchment, *Hydrological Processes*, Vol.17, pp.2795-2810, 2003.
19. Yamazaki, T. : A one dimensional land surface model adaptable to intensely cold regions and its application in eastern Siberia, *Journal of the Meteorological Society of Japan*, Vol.79, pp.1107-1118, 2001.
20. Keene, W. C., Pszeny, A. A. P., Galloway, J. N. and Hawley, M. E. : Sea-salt correlations and interpretation of constituent ratios in marine precipitation, *Journal of Geophysical Research*, Vol.91, pp.6647-6658, 1986.
21. Zhang, D., Iwasaka, Y., Matsuki, A., Ueno, K. and Matsuzaki, T. : Coarse and accumulation mode particles associated with Asian dust in southern Japan, *Atmospheric Environment*, Vol.40, pp.1205-1215, 2006.
22. Shiina, T., Ishizaka, M., Muramoto, K., Nakai, S., Sato, A. and Iwamoto, K. : A method for automated identification of types of solid precipitation by image processing Part I A measurement method of diameter and fall speed by image processing, *Seppyo*, Vol.66, pp.637-646, 2004.
23. Terada, H., Ueda, H. and Wang, Z. : Trend of acid and neutralization by yellow sand in east Asia-a numerical study, *Atmospheric environment*, Vol.36, pp.503-509, 2002.
24. Wang, Z., Akimoto, H. and Uno, I. Neutralization of soil aerosol and its impact on the distribution of acid rain over east Asia: Observation and model results, *Journal of Geophysical Research*, Vol.17, No.D19, doi:10.1029/2001JD001040, 2002.
25. Yabuki, S., Makami, M., Nakamura, Y., Kanayama, S., FU, F., Liu, M. and Zhou, H. : The characteristics of atmospheric at Aksu, an Asian Dust-source region of North-West China: A summary of Observations over the three years from March 2001 to April 2004, *Journal of the Meteorological Society of Japan*, Vol.83, pp.45-72, 2005.

APPENDIX – NOTATION

The following symbols are used in this paper:

$[Ca^{2+}]$	= calcium ion concentration;
e	= water vapor pressure;
F_{in_Cl}	= flux of chloride ion from precipitation to snowpack;
F_{in_SO4}	= flux of sulfate ion from precipitation to snowpack;
F_{out_Cl}	= flux of chloride ion from snowpack to ground;
$F_{out_bsm_SO4}$	= flux of sulfate ion from snowpack to ground due to bottom snowmelt;
F_{out_SO4}	= flux of sulfate ion from snowpack to ground
$[Na^+]$	= sodium ion concentration;
$[nssCa^{2+}]$	= non-sea-salt calcium ion concentration;
$[nssSO_4^{2-}]$	= non-sea-salt sulfate ion concentration;
s	= snowfall occurrence probability;
$[SO_4^{2-}]$	= sulfate ion concentration;
T_a	= air Temperature; and
T_w	= wet bulb temperature.

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