Acidity variations along hydrological processes of snow deposit, snowmelt and runoff.

N. Ishikawa, H. Narita, Y. Ishii and Y. Kodama.
(Hokkaido University, Sapporo, 060, Japan)

Abstract

Assessment of the acidification and changes of the chemical contents of seasonal snow within the snowmelt process were carried out in northern Hokkaido, Japan. The range of pH in the dry snow was 4.7 to 5.3 and EC was 11 to 56 $\mu\text{S}/\text{cm}$. These values were similar to those of the snow accumulated on the forest floor and the canopy. Horizontal distributions of pH in snow cover were found to be homogenous. However, once melt water penetrated, the homogenous distributions were partly destroyed even in winter. During the snowmelt period pH of the snow increased and EC decreased to below 10 $\mu\text{S}/\text{cm}$. pH of the melt water that percolated through 10cm deep soil accounted for 6.4 to 5.8, and those of the stream 7.1 to 6.8. The values did not change much through the snowy season. The percolated water showed high concentrations of SO_4^{2-} and NO_3^- compared with those of snow, but the water contained higher Ca^{2+} concentrations, which neutralized the anion, and pH of the water increased.

Key words: acidity, snowmelt, runoff, anion, electric conductivity

1. Introduction

Pollutants emitted into the air from fossil combustion such as exhaust gas from automobiles and various industrial manufacturing processes are removed by rainfall (snowfall) or gravitational fallout. Cleansing of the air results in deposition of pollutants on the earth surface, soil and water reservoirs. There are many studies of acid rain and the influences on the ecosystem. In snowy regions chemical constituents in snow stay on the ground surface or forest canopy for a long time during cold periods and subsequently run off into rivers or lakes in a short time at snowmelt season, which sometimes induces a rapid depression of pH of river water (Ishii *et al.*, 1992, Suzuki, 1982, Johannessen and Henrikson, 1978). Therefore, acidity of snow has been recognized as an important factor in environmental problems. However, there is little information about the changes of pH and chemical contents within the snowmelt process (Suzuki, 1991), or the effects of the forest on the chemistry of snow (Jones, 1988). The objectives of this paper are to assess the change of acidification and chemical contents of seasonal snow within the processes of snow deposit, snowmelt and runoff.

2. Observation site and method

The measurements of acidity (pH), electric conductivity (EC) and chemical constituents of snow, melt water and river water were carried out from 1994 to 1996 and include two snow cover seasons at a small watershed located within the Moshiri Basin (142°17'E, 44°22'N) northern Hokkaido, Japan. The basin is one of the coldest areas in Japan, with an annual mean air temperature of 3.5°C. In winter, the basin is covered with 2-3m depth of snow, and a daily minimum air temperature below -20°C occurs

frequently. However, the temperature at the bottom of the snow cover stays at 0 °C and continuous runoff is maintained (Kojima and Motoyama, 1985). Vegetations at the watershed are mixed forests of evergreen needle-leaf trees and deciduous broad-leaved trees with bamboo bush undergrowth. The surface soil is composed primarily of silt and clay, and is underlain to a depth of 3m by tuffaceous silt stone and sandstone of the Neocene (Kobayashi *et al.*, 1995). Snow samples were taken from three fixed sites (open site, forest floor, forest canopy) near the outlet of the watershed 7 to 8 times during the snow season. Also, water samples were obtained from the bottom of the snow cover, from soil 10cm deep and from the stream. After the snow samples had been transferred to uncontaminated polyethylene bags and water samples were contained in polyethylene bottles, pH and EC were measured using a pH-potentiometer with a glass electrode and a portable conductometer. Anions and cations were determined by an ion chromatography (DIONEX-2000i/SP).

3. Results and Discussion

Table 1: pH and EC of snow cover at three sites

Monthly variations of pH and EC of snow at three sites are shown in Table 1.

The intercepted snow on the canopy had fallen off completely by the end of March. pH of the snow at the open site was in the range of 4.7 to 5.3, and EC was 11 to 56 $\mu\text{S}/\text{cm}$ until March when

Date	Nov. 15		Dec. 20		Jan. 19		Feb. 21		Mar. 29		Apr. 25	
	pH	EC	pH	EC	pH	EC	pH	EC	pH	EC	pH	EC
R surf.	4.9	9	4.9	15	4.8	11	4.7	3	6.0	3	5.6	3
mean	4.8	55	5.1	24	4.8	22	4.8	18	5.5	8	5.2	12
F surf.	5.0	32	5.3	35	4.8	16	4.9	20	5.6	28	5.3	19
mean	4.9	28	5.0	26	5.0	34	5.1	25	5.3	18	5.4	16
L	5.1	43	5.1	31	4.7	26	4.7	28	x	x	x	x

R:open site, F:forest site, L:canopy

no snowmelt occurred. During the snowmelt period, pH increased significantly and EC decreased below 10 $\mu\text{S}/\text{cm}$. The values are similar to those of snow of the forest floor and canopy. Snow cover showed a layered structure, so it can be assumed that pH and EC of each layer indicates the values of snowfall when the layer formed. Figure 1 shows homogeneous distributions of pH in the lateral, and the pH of the respective layers kept the original values as long as snow was dry. The dominant pH of the whole snow is 5.0 to 5.5. Even in mid-winter, snowmelt occurred by temporary warm weather. Traces of melt water penetration were seen as layered ice or by the vertical structure of granular snow, which were different from the compacted snow nearby, and the laterally homogeneous distributions of pH were partly destroyed. After snowmelt began pH near the surface increased at first and then the pH of the whole snow rose to above 6.0. Some chemical

Fig.1 Distributions of pH

constituents were measured at the same time, whose distributions for the two periods showed the same pattern as pH, namely; a laterally homogeneous distribution when the snow was dry, but which was

destroyed by melt water percolation. Figure 2 shows ratios of SO_4^{2-} and Na^+ at three different times. The concentrations of both ions change drastically during the snowmelt period and the amounts in April decreased below 40% of mid-winter.

Comparisons of pH at different sites are seen in Fig.3. pH of snow at the forest has a similar value to the open site. pH of meltwater under 10cm deep soil was 6.4 to 5.8, and of the stream was 7.1 to 6.8, which means the soil had a moderating influence on the acidity of the meltwater. Variations of EC are also shown in the figure. The surface snow exhibited a smaller value (less than $10\mu\text{S}/\text{cm}$) during the season. EC of the whole snow was high in November and decreased during the snowmelt period, while the meltwater that percolated through 10cm of soil carried higher EC such as 40 to $50\mu\text{S}/\text{cm}$ and 70 to $80\mu\text{S}/\text{cm}$ to the stream.

Assuming the neutral condition of an ion, the ion balance of snowmelt water is expressed by the following equation (Ishii and Kobayashi, 1996),

$$[\text{H}^+] + [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] = [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}] + [\text{HCO}_3^-]$$

The main chemical constituents from human activity are NO_3^- , SO_4^{2-} , Ca^{2+} and NH_4^+ . However, SO_4^{2-} and Ca^{2+} include not only those artificially made but also those from sea salt origin. So we should evaluate only the non sea salt origin of SO_4^{2+} ($_{\text{nss}}\text{SO}_4^{2-}$) and Ca^{2+} ($_{\text{nss}}\text{Ca}^{2+}$) for considering the acidity of water. Monthly variations of pH and chemical constituents of snow at three sites and water from December to April in Fig.4, where all ions are expressed in $\mu\text{eq}/\text{l}$. Snow cover at three sites contained NO_3^- , SO_4^{2-} and NH_4^+ all the time but non Ca^{2+} , resulted low pH of snow. The water percolated

Fig.2 Changes of SO_4^{2-} and Na^+

Fig.3 Comparisons of pH and EC

through soil and stream water showed high concentrations of SO_4^{2-} and NO_3^- compared with snow, but they contained high Ca^{2+} , which neutralized the anions and the pH of the water increased. In this observation, carbonates in the water are not measured, but their importance is pointed out by Ishii (1996) and O'Brien *et al.* (1993). So it is necessary to consider the role of dissolved carbonate in the stream water.

4. Conclusion

Observations of the acidification and chemical constituents of seasonal snow within the snowmelt process were carried out at Moshiri Basin, Japan. pH of dry snow at the open site was in the range 4.7 to 5.3, which is similar to the snow accumulated on the forest floor and the canopy. Dry snow has laterally homogenous distributions of pH, EC and chemical constituents of each layered structure. However, the melt water percolation destroyed the homogeneous distribution. Meltwater showed higher pH such as 5.8 to 6.4 for the water percolated through only 10cm soil and 6.8 to 7.1 for the stream water. It contained high Ca^{2+} , which neutralized anions and increased the pH of the water.

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Fig.4. Variations of pH and ions