論文

ACID SNOW IN LAKE BIWA CATCHMENT AREA, JAPAN (1) —MICROSCOPIC DISTRIBUTION STRUCTURES OF ACIDIC MATERIALS—

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ABSTRACT

In order to predict acidification of meltwater from a snow cover, it is important to understand microscopic distribution structures of acidic materials within snow grains formed by the melt-refreeze process. For this purpose, the pH values were measured both at the first stage and at the last stage of the snowmelt process. In the first stage, the melting takes place mainly in the outer part of a snow grain and in the last stage, in the inner part. The characteristic distribution structures of acidic materials within snow grains in Lake Biwa catchment area were discussed by comparative studies carried out at Mt. Hakkouda and Mt. Tateyama which have colder climates, resulting in the different melt-refreeze processes.

In such a warm climatic region as the Lake Biwa catchment area, there are many possibilities to have the complicated concentric distribution structures of acidic materials within granular snow, since the melt-refreeze processes of snow cover layers take place repeatedly for a long period (even in the midwinter). Consequently, the pH value of the meltwater does not always increase as the snowmelt progresses, but it does decrease and the meltwater turns out to be more acidic in case that the acidic materials mainly concentrate in the central part of granular snow. In Lake Biwa catchment area, it should be noted that the acid shocks occur not only in the first stage but also in the last stage of the snowmelt.

I. Introduction

East Asia was identified as one of the world's acid rain regions in the late 1970's joining the northern part of Europe and the eastern part of North America (Wellburn, 1988). An average pH value of rainwater in Japan is around 4.7 (Tamaoki et al., 1991) and that in Lake Biwa catchment area is 4.4 (Yamanaka and Maehata, 1990). The pH value of winter precipitation along the coast of the Sea of Japan is lower in the western part of Japan than that in the northern part (Tamaoki et al., 1991). It is thought that the acidic materials originate from industrial activities in several countries in East Asia and have been transported to Japan by the westerlies of winter monsoon.

Lake Biwa, the largest lake and one of the most important freshwater resources in Japan, is located near Osaka in Honshu island (Fig. 1). During the winter season, the northern part of Lake Biwa catchment area is blanketed by a vast snow cover which is a very valuable water resource for the lake. Since the lowest pH value of meltwater was 3.8 in Lake Biwa catchment area (in this paper), the acidification is progressing due to the increasing emission of acidic materials from Japan, China, Korea and other countries in East Asia. Eriksson (1960) and Melack et al. (1985) reported that acidic materials deteriorate ecological systems in lakes, ground waters, forests and soils, particularly when the lake and its catchment area have a limited capacity to neutralize acids. It gives adverse impacts to fisheries, concrete structures

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Fig. 1 Locations of snow survey.

and even to human health. Since some 13 million people in Osaka, Kyoto and several other municipalities depend on Lake Biwa and its outflowing Yodo River for the water supply, it is necessary to preserve the water resource of the lake.

Snow crystals in the snow cover grow to be granular by the melt-refreeze process and the diameter of the granular snow may reach several millimeters. Along with a progress of the crystal growth caused by melt-refreeze process, the acidic materials tend to be concentrated in the outer part of the granular snow (Suzuki, 1982; Bale et al., 1989). Consequently, the pH value of the meltwater at the first stage of melting becomes low, with acidic chemical constituents 2 to 5 times more than the average value of the snow cover (Johannessen and Henriksen, 1978), and the so called "acid shock (acid flush)" results. This indicates that it is possible to estimate the characteristic distribution structures of acidic materials within granular snow by observing the relative difference between the pH value of the meltwater at the first stage and that at the last stage. These acid shocks have been reported in the northern part of Europe (Skartveit and Gjessing, 1979) and in the eastern part of North America (Cadle et al., 1984). It is thought that actual conditions of the acid shock depend on the melt-refreeze processes caused by the regional climate.

The field observations were carried out at Mt. Kanakuso (1020m above sea level) and Tochinoki Pass (760m a. s. l.) in Lake Biwa catchment area, Mt. Hakkouda (910m a. s. l.) in the northern region and Mt. Tateyama (2450m a. s. l.) in the central region of Honshu island in Japan (Fig. 1). These observational points are several kilometers far from the nearby road and located at the mountain ridge. Figure 2 shows an estimated monthly mean air temperature during cold seasons at Tochinoki Pass, Mt. Kanakuso, Mt. Hakkouda and Mt. Tateyama. Monthly mean air temperatures are estimated from that of Hikone, Toyama and Aomori recorded from 1961 to 1990 (Suzuki, 1992) by using a temperature lapse rate, $0.67^{\circ}\text{C}/100\text{m}$, observed in Lake Biwa catchment area. Each region has its own characteristics in monthly mean air temperatures from October to May (Fig. 2), showing that Mt. Hakkouda and Mt. Tateyama have colder climate than Mt. Kanakuso and Tochinoki Pass in Lake Biwa catchment area. This paper compares the actual conditions of acid snow and the associated characteristic distribution structures of the acidic materials within granular snows observed at Mt. Kanakuso and Tochinoki Pass in Lake Biwa catchment area with those at Mt. Tateyama in Toyama Prefecture and at Mt. Hakkouda in Aomori Prefecture (Fig. 1) where the regional climate is different.

Fig. 2 Estimated monthly mean air temperature during cold seasons at Tochinoki Pass, Mt. Kanakuso, Mt. Hakkouda and Mt. Tateyama.

Fig. 3 Schematic diagram of pH measurements. Circle: snow grains, dots: meltwater, I: sampling stage, II: the first stage of melting and III: the last stage of melting.

2. Observational methods and results

Snow was directly sampled from each snow layer at a snow pit by using the sampling bottle with the volume of 100 ml and the weight of an about 50 g. The samples were melted under the room temperature of about 20 °C. The pH values of the meltwater were measured in the sampling bottle both at the first stage and at the last stage of the snowmelt process within a few hours after the sampling. The pH values were measured using pH meters of TOA-HM-11P and HACK ONE 44300 combination electrode.

At the sampling stage, there is scarcely meltwater inside a bottle (I in Fig. 3) and it is difficult to measure

the pH value of the meltwater by using the above mentioned pH meters. However, the snow grains and meltwater coexist in the first stage of melting when about 30% of snow grains melt up and the sensor of the above mentioned pH meter is filled up with the meltwater in the sampling bottle. Hence, the effect of the meltwater existed at the sampling stage becomes negligible (II in Fig. 3), and it is also thought that the effects of the meltwater from snow samples near the walls of the sampling bottle become small, when snow grains are soaked in the meltwater. In the last stage, the snow grains completely melt up (III in Fig. 3) and the meltwater of the last stage contains that of the first stage. The observational methods described here were designed in order to compare the pH value of the so-called acid shock, the snowmelt of the first stage, with that of the last stage, since it is thought that, in the first stage, the melting takes place mainly in the outer part of a snow grain and in the last stage, in the inner part of a snow grain.

Figure 4 shows a vertical profile of pH values of the meltwater, sampled from the snow cover with completely turned granular snow grains (Fig. 5) at Mt. kanakuso in the northern part of Lake Biwa catchment area on 3 April, 1991 and the snow depth was 190cm. The pH values range from 4.2 to 5.6 in the

Fig. 4 pH values of Mt. Kanakuso in the northern part of Lake Biwa catchment area.

first stage and from 4.4 to 6.0 in the last stage of the snowmelt. There are three different granular snow layers, each with its characteristic pH value changes. 1) The last stage samples exhibit lower pH values in the snow layer from 0 to 30cm. 2) The pH values of the meltwater at the first stage and the last stage samples were nearly identical in the snow layer from 70 to 100cm. 3) The pH values of the meltwater at the last stage samples exhibit higher pH values in the snow layer from 30 to 70cm and from 100 to 190cm. Figure 6 is the profile of the pH values of meltwater sampled from Tochinoki Pass in the northern part of Lake Biwa catchment area on 26 December, 1992 and the snow depth was 100cm. There were a new snow layer from 0 to 30cm and granular snow layers from 30 to 100cm. The pH values ranged from 4.0 to 4.7 in the first stage and from 3.8 to 4.3 in the last stage. The pH value, 3.8, was the lowest that had been observed

so far in Lake Biwa catchment area, and the actual pH value of the meltwater added in the latter stage had to be lower than 3.8 since the meltwater of the last stage contained that of the first stage whose pH value was higher than 4.0 (Fig. 6). The pH values of the meltwater at the last stage turned out to be more acidic both in the new snow layer from 0 to 30cm and in the lower part of the granular snow layers from 70 to 100cm, though no significant difference in pH values was found in the upper part of the granular snow layers from 40 to 60cm. This indicates that there are several snow layers with distinct characteristics in pH values changes and the pH value of the meltwater does not always increase according to the snowmelt process as it is reported at the time of the finding of the acid shock

Fig. 5 Granular snow grains observed at Mt. Kanakuso in Lake Biwa catchment area.

(Johannesen and Henriksen, 1978), and it may be related that there are different distribution structures of acidic materials within snow grains, which will be discussed later. Figure 7 shows the profile of the electric conductivities with the pH values in the first stage of the snowmelt at Tochinoki Pass. The electric

conductivities were more than $30 \mu\text{S}/\text{cm}$ in the upper part of the granular snow layers where the lower pH values were observed.

Figures 8 and 9 are profiles of the pH values and the electric conductivities of meltwater sampled from granular snow layers at Mt. Tateyama on 2 April, 1992 and the snow depth was 500cm. The pH values ranged from 3.6 to 5.0 in the first stage and from 4.2 to 5.6 in the last stage of the snowmelt. The pH values of the meltwater at the last stage were higher than that at the first stage except few snow layers in the middle part of the snow cover which showed no considerable changes. The electric conductivities rose to be more than $30 \mu\text{S}/\text{cm}$ in the middle part of the snow cover where the lower pH values were found. Hence, the higher the electric conductivities are, the lower the pH values are in the snow cover. Figure 10 indicates the profile of the pH values of the meltwater sampled from Mt. Hakkouda on 3 May, 1991 and the

Fig. 6 pH values of Tochinoki Pass in the northern part of Lake Biwa catchment area.

Fig. 7 Electric conductivities and pH values of Tochinoki Pass in the northern part of Lake Biwa catchment area.

snow depth was 65cm. There was a new snow layer from 0 to 10cm and granular snow layers were developed below 10cm. In the new snow layer, the pH value was 5.6 in the first stage and 5.3 in the last stage of the snowmelt. In the granular snow layers, the pH values ranged from 5.1 to 5.3 in the first stage and from 5.5 to 5.6 in the last stage. This shows that the pH value of the meltwater at the last stage was lower and the meltwater turned out to be more acidic in the new snow layer, but it became higher in the granular snow layers.

3. Discussion

A snow cover deposited in a single snowfall at a certain place is here called a unit snow cover layer. The distribution structures of chemical materials in the unit snow cover layer change macroscopically as well

Fig. 8 pH values of Mt. Tateyama in the central region of Honshu island in Japan.

Fig. 9 Electric conductivities of Mt. Tateyama in the central region of Honshu island in Japan.

Fig. 10 pH values of Mt. Hakkouda in the northern region of Honshu island in Japan.

as microscopically by melt-refreeze process under a temperate metamorphism. Since the eluted chemical materials flow down along water channels and redeposit in the unit snow cover layer underneath, the original distribution structures of chemical materials macroscopically change in the snow cover. Also, the distribution structures of chemical materials within snow grains in the unit snow cover layer change microscopically by the melt-refreeze process. Besides the above mentioned chemical materials within the unit snow cover layer and snow grains, dry fallouts, rainfall and riming formed during a hiatus (gap) of the snowfall are also able to change the distribution structures of acidic materials in the snow cover. In order to predict acidification of meltwater which results in acid shock, it is important to clarify how the macroscopic as well as microscopic distribution structures of acidic materials are formed not only in unit snow cover layers but also within snow grains.

From the observational results in Lake Biwa catchment area, Mt. Tateyama and Mt. Hakkouda, it is thought that there are characteristics in the distribution structures of acidic materials within snow grains since there are differences between the pH values of the meltwater at the first stage and those at the last stage, and that the microscopic characteristics control the macroscopic distribution structures of acidic materials in the unit snow cover layer. So, the author proposes the following models as one of speculations that there are characteristic distribution structures of acidic materials within snow grains as shown by Fig. 11 in which the shape of a hexagon represents a new snow crystal, that of an ellipse a granular snow grain, and the black dots acidic materials.

Fig. 11 Schematic distribution structures of acidic materials in snow grains.

In the new snow layer observed at Mt. Hakkouda and Tochinoki Pass, the acidic materials are thought to be concentrated in the central part of a new snow crystal as a crystal nucleus (structure I in Fig. 11), as the meltwater of the last stage turned out to be more acidic. So, it is considered that there are, in the crystal nucleus, acidic materials such as aerosols of sulfur etc. (Kumai, 1977, 1985). When the snowmelt comes to the last stage, the acidic materials of the central part begin

to melt and the pH value at the last stage decreases accordingly.

In the granular snow at Mt. Kanakuso in Lake Biwa catchment area, Mt. Hakkouda and Mt. Tateyama, the acidic materials are thought to be concentrated in the outer part of a snow grain (structure II in Fig. 11). Therefore, the meltwater of the first stage becomes more acidic, since the acidic outer part of a snow grain mostly melts up. This is a typical case of the acid shock that occurs in the first stage of the snowmelt, and the pH value of meltwater becomes higher in the last stage.

In the granular snow observed at Mt. Kanakuso and Tochinoki Pass in Lake Biwa catchment area, it is considered that there are two kinds of the distribution structures: 1) The acidic materials are distributed not only in the outer part but also in the inner part of a snow grain (structure III in Fig. 11). When the snowmelt proceeds in such unit snow cover layer, the pH value of the meltwater at the last stage will be as acidic as that at the first stage. 2) The acidic materials are mainly concentrated in the central part of a snow grain (structure IV in Fig. 11). The pH value of the meltwater at the last stage decreases and the melt-water turns out to be more acidic in such a unit snow cover layer as the acidic materials in the central part melt up in the last stage.

In such a warm climatic region as Lake Biwa catchment area, there are many possibilities to see granular snows with the distribution structures with grains of III and IV (Fig. 11) since the melt-refreeze processes of unit snow cover layers take place repeatedly for a long period (even in the midwinter). They form complicatedly concentric distribution structures of acidic materials in accordance with a growth of the granular snow. The pH value of the meltwater does not always increase as the snowmelt progresses, but it does occasionally decrease even in the last stage of the snowmelt and the meltwater turns out to be more acidic in the Lake Biwa catchment area according to the distribution characteristics of acidic materials that are mainly concentrate in the central part of a granular snow. Therefore, we have to keep in mind that acid shocks occur not only in the first stage but also even in the last stage of the snowmelt.

Since NO_3^- and SO_4^{2-} ions are preferentially removed from the snow cover while Na^+ and Cl^- ions tend to remain longer (Davies et al., 1982; Tsiouris et al., 1985; Brimblecomb et al. 1987), it can be explained that the ionic elution sequence has a close relation to the distribution structures of acidic materials within snow grains, and sulphuric and nitric acids are mainly concentrated in the outer part and sea salt constituents in the inner part of snow grains. When it will be possible to clarify microscopic distribution structures of the acidic materials within the granular snow by using a single crystal in order to avoid the analytical problems of the polycrystalline sample, or an x-ray fluorescence analyzer in future (Hondo, T., Pers. Commun.) as it has been done by an x-ray microanalyzer for thin-sections of rock samples, it will be possible to estimate precisely the future trend of the snowmelt acidification as well as the history of melt-refreeze processes in relation to characteristics of the regional climate.

It is observed that the higher the electric conductivities are, the lower the pH values are both at Tochinoki Pass and Mt. Tateyama. Since the electric conductivities became higher in the upper part of the granular snow layer at Tochinoki Pass that was once a surface of the snow cover with the longer hiatus of the snowfall before the formation of the new snow layer, the upper part of the granular snow layer with higher electric conductivities is probably caused by a deposition of dry fallouts of acidic materials. Therefore, it is thought that the snow layers with higher electric conductivities found at Mt. Tateyama were also caused by the dry fallouts during a gap of the snowfall.

The pH value of a river water was also measured at the same time when the snow survey was carried out in Lake Biwa catchment area, and it was 6.4, slightly acidic, in the upper stream of River Takatoki in the northern part of Lake Biwa catchment area. However it became around 7.1, or neutral, as it went downstream. The pH value of Lake Biwa was also neutral. So, it is thought that there is a high capacity of neutralization against acidification in the river and lake water due to the distributed development of soil

layers and carbonate rocks, etc. How long will the high capacity of neutralization against acidification last in Lake Biwa catchment area? The continuing monitoring of acidification of the snowmelt and river water is important to preserve water resources of Lake Biwa as the level of acidic material emission is possibly going to increase in Japan, China, Korea and other countries in East Asia.

4. Conclusion

From the observational results in Lake Biwa catchment area, Mt. Tateyama and Mt. Hakkouda, it is shown that the pH value of the meltwater does not always increase according to the snowmelt process as it is reported at the time of the finding of the acid shock (Johannesen and Henriksen, 1978), and it is estimated that there is a certain characteristic in the distribution structures of acidic materials within snow grains since there are differences between the pH values of the meltwater at the first stage and that at the last stage.

In the new snow layer observed at Mt. Hakkouda and Tochinoki Pass, the acidic materials are estimated to be concentrated in the central part of a new snow crystal as a crystal nucleus, as the meltwater of the last stage turned out to be more acidic. In the granular snow at Mt. Kanakuso in Lake Biwa catchment area, Mt. Hakkouda and Mt. Tateyama, the first stage of meltwater became more acidic and the acidic materials are thought to be concentrated in the outer part of a snow grain, since the acidic outer part of a snow grain mainly melts up in the first stage. This is a typical case of the so called acid shock. In the granular snow observed at Mt. Kanakuso and Tochinoki Pass in Lake Biwa catchment area, there are two kinds of the distribution structures. 1) The acidic materials are distributed not only in the outer part but also in the inner part of a snow grain. When the snowmelt proceeds in these snow layers, the pH value of the meltwater at the last stage will be as acidic as that at the first stage. 2) The acidic materials are mainly concentrated in the central part of a snow grain. The pH value of the meltwater at the last stage decreases since the acidic materials in the central part melt up in the last stage.

In such a warm climate region as Lake Biwa catchment area, there are many possibilities to see the granular snow with complicatedly concentric distribution structures of acidic materials within granular snow grains since the melt-refreeze processes of unit snow cover layers take place repeatedly for a long period (even in the midwinter). The pH value of the melt water does not always increase as the snowmelt progresses, but it does occasionally decrease in the last stage of the snowmelt and the meltwater turns out to be more acidic in the Lake Biwa catchment area in case that acidic materials mainly concentrate in the central part of a granular snow. Therefore, it is important to note that the acid shocks occur not only in the first stage but also even in the last stage of the snowmelt in Lake Biwa catchment area.

Acknowledgements

The author expresses heartfelt thanks to Drs. Okitsugu Watanabe, Takeo Hondoh, Hitoshi Shoji, Toshiyuki Kawamura and Tomomi Yamada for their important informations on observing the crystal structures by an x-ray fluorescence analyzer, and to Dr. Tetsuo Ohata, Messrs. Katsumoto Seko, Hajime Iida, Hironori Yabuki, Kazuki Nakamura for their kind assistance in field works at Mt. Tateyama.

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琵琶湖集水域の酸性雪(1)

—酸性物質の微視的分布構造—

伏見 碩二

要 旨

積雪層からの融雪水の酸性化を予測するには、融解再凍結作用によって形成される雪結晶内部の微視的な酸性物質の分布構造を明らかにする必要がある。そのため、雪結晶の外側部分が主に解け出すと考えられる融解初期と、雪結晶の内側部分までも解け出した融解後期の pH 値を測定し、両時期の融雪水の pH 値の変化から、暖候地の琵琶湖集水域における雪結晶内部の酸性物質の分布構造の特徴を、寒候地のため融解再凍結作用が異なる八甲田山と立山での比較観測によって考察した。

琵琶湖集水域のような暖候地では、寒候地に比べて、融解再凍結過程が長期間にわたくりかえし(真冬にさえも)起こるので、ザラメ雪内部の酸性物質の分布は複雑な同心円構造を示す、と考えられる。従って、融雪水の pH 値は融雪につれて高くなるとは限らずに、ザラメ雪の外側よりも内側のほうに酸性物質が分布する場合には、融雪の進行とともに融雪水はさらに酸性化するので、琵琶湖集水域のような暖候地では、アシッド・ショック (acid shock) は融雪初期のみならず、後期にも発生する可能性のある点に留意する必要がある。

キーワード：酸性雪、微視的分布構造、琵琶湖

Key words: acid snow, microscopic distribution structure, Lake Biwa

(1993年3月19日受付, 1993年10月13日改稿受付, 1994年1月21日受理; 討論期限1994年9月30日)