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Behavior of Hydrogen Ion and Other Ions at Thaw Season in Sapporo

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Abstract

By the report in the last time, we had reported that H^+ volumes 4 to 5 times larger than the weekly mean H^+ deposition flux were loaded on the ground in mid- and late March at Sapporo Art Park in Sapporo[1]. This time, using the 3-year data for 6 weeks from mid-February to last March, which included the data in 1999, research was conducted about three points. First point was the volume of each ions which flowed out in one week, second point was comparisons of outflow pattern between H^+ outflow and other ion outflow, and third point was comparisons of H^+ in precipitation with the weekly mean deposition flux in 1999.

Consequently, outflow patterns between hydrogen ion (H^+) and other ions had the coefficient, but they were not too strong. However, there was some pair of ion outflow pattern indicated very strong correlation, for example, a pair of sulfate ion (SO_4^{2-}) and nitrate ion (NO_3^-). H^+ outflows in 1999 were observed from mid-February, since it was rather warmer in that month compared to the previous seasons. Only H^+ outflow 2.3 times larger than the weekly mean H^+ depositions flux could be observed in mid-and last March.

1. Introduction

H^+ derived from wet and dry deposition, along with various other ions, accumulates in snow in snowy regions. In the snowmelt season, H^+ and other ions flow out with the meltwater. It is said that H^+ in particular may cause an acid shock that is a temporary decline in the pH of soil, lakes and marshes.

By the report in the last time, a study was conducted on H^+ concentrations in accumulated snow during 6 weeks from mid-February to late March in 1997 and 1998 at Sapporo Art Park in Sapporo. As a result, we had reported that H^+ volumes 4 to 5 times larger than the weekly mean H^+ deposition flux were loaded on the ground in mid- and late March.

In this time, using the 3-year data collected at the same sampling site over the same month from 1997 to 1999, we report about three points. First point is volume of each ion that flowed out in one week. Second point is comparisons of outflow pattern between H^+ outflow and other ion outflows. And third point is comparisons of H^+ in precipitation with the weekly mean deposition flux in 1999.

2. Method

2-1 Research periods

Research was conducted for six weeks between February 19 and April 2, 1997; February 18 and March 31, 1998; and February 17 and March 31, 1999. Snow samples were collected almost every Wednesday.

2-2 Sampling site

The open air concert hall at Sapporo Art Park

2-3 Sample collection procedures

After the snow was vertically dug to the ground of sampling site and measured a depth, samples from all layers of snow were collected in polyethylene bags using a stainless steel sampler 5.5 cm in diameter, 100cm long and with a taper at the tip.

2-4 Analytical procedures

(1) Pretreatment

After each sample was melted at room temperature and filtered using a 0.45 um membrane filter, each ion in samples was measured using apparatuses and procedures in accordance with the Acid Rain Analysis Manual.

(2) Analytical method

pH : Glass Electrode Method

Metal ions such as Ca^{2+},Na^{+} : ICP Spectrometry

Anions such as SO_4^{2-},NO_3^{-},Cl^{-}: Ion Chromatography

NH_4^{+}: Indophenol Method

(3) Data

The product of the ion equivalent concentration (ueq/l) and the value (mm)[2], which was determined from the volume of melted snow samples and the area of the sampler, was regarded as the accumulation in snow (ueq/m^2). Also, ion volume that flowed out was regarded as the outflow (ueq/m^2).

To compare H^+ outflow with H^+ deposition flux (ueq/m^2) in one week, the value determined by dividing the total H^+ deposition flux in the annual precipitation by 52 had been regarded as the weekly mean H^+ deposition flux. The value in 1999 was approximately 420 ueq/m^2 in both 2 years.

3. Results and Discussions

Each ion outflow was calculated from the difference in each ion accumulation in snow sampled every week and from each ion deposition flux in the snowfall during one week[1]. Figure 1 to Figure 6 shows the changes in main ion outflow over time.

In figure 1, the H^+ outflow in 1999 was 462-963 ueq/m^2. Though H^+ outflow after the 5th week of research in mid-March 1997 and 1998 had been 60 and 80%[1] of total H^+ outflow in research periods, its

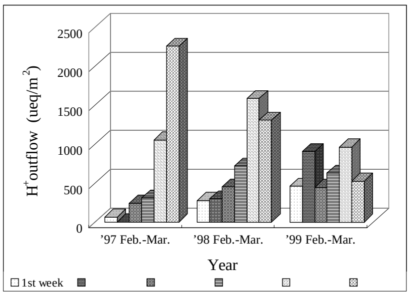


Figure 1 H^+ outflow in each year

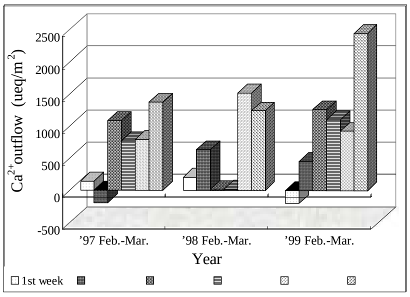


Figure 2 Ca^{2+} outflow in each year

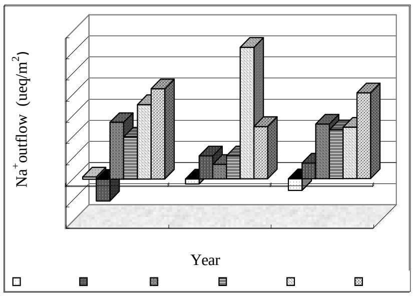
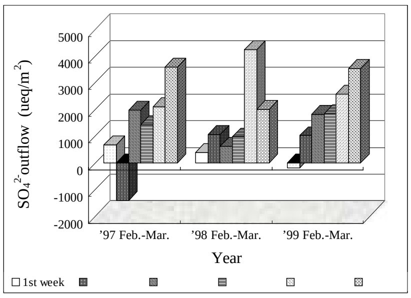
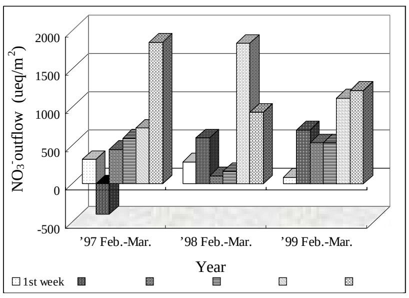


Figure 3 Na^+ outflow in each year





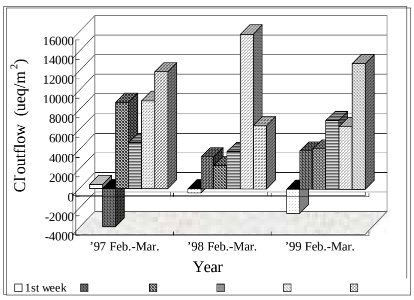


Figure 4 SO_4^{2-} outflow in each year Figure 5 NO_3^- outflow in each year Figure 6 Cl^- outflow in each year outflow during the same period in 1999 was only about 40% and there was no significant increase in H^+ outflow. It will be a reason that even in the first week of research, the outflow in 1999 was greater than in the previous years during the same period.

Table 1 shows percentage of ion outflows after the 5th week of research in mid-March to total ion outflow of research periods. Other ion outflows in 1997 were 60 to 65% except for Ca^{2+} and NH_4^+, were 67 to 76% except for NH_4^+ in 1998, and were 53 to 57% except for NH_4^+ in 1999. It seems that H^+ outflow may be doing different behavior to other ion outflows.

Therefore, we compared the relationship between H^+ outflow and other ion outflows. Table 2 shows correlation coefficients. H^+ outflow indicated good correlation except for Ca^{2+} and NH_4^+, and these correlation coefficients were 0.67 to 0.82. On then other hand, because coefficients of Ca^{2+} and NH_4^+ were 0.45 and 0.23, these correlation showed hardly. Especially, NH_4^+ outflow did not show correlation with other ions. However, there were pair of ions indicated very strong correlation, for example, a pair of SO_4^{2-} and another ions as NO_3^-, Cl^- and Na^+. These coefficients were 0.94 to 0.97, and a pair of Cl^- and Na^+ had a very strong too. It was found that outflow patterns between H^+ and other ions had coefficients, but they were not very strong.

Table 3 shows the ratio of H^+ outflow to the weekly mean H^+ deposition flux. In 1999, the maximum H^+ outflow was only 2.3 times higher than the weekly mean deposition flux, even though the outflow exceeded the mean deposition flux in the 1st week already. On the other hand, the outflow exceeded the mean deposition flux at last in the 5th week in 1997, and approximately 1.1 times higher in the 3rd week in 1998.

Figure 7 shows correlation between H^+ outflow and value of temperature(°C) multiplied by time(hour). A correlation coefficient was obtained, indicating a strong

Table 1 Percentage of ion outflows after the 5th week of research in mid-March to total ion outflow of research periods in each year (%)

	H^+	SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	Na^+	NH_4^+
1997	84	58	65	60	52	62	39
1998	62	67	71	70	76	75	58
1999	38	57	56	56	54	53	23

Table 2 correlation coefficients each ion outflow

	H^+	SO_4^{2-}	NO_3^-	Cl^-	Ca^{2+}	Na^+	NH_4^+
H^+	1.000						
SO_4^{2-}	0.703	1.000					
NO_3^-	0.823	0.936	1.000				
Cl^-	0.676	0.967	0.876	1.000			
Ca^{2+}	0.449	0.877	0.777	0.858	1.000		
Na^+	0.690	0.961	0.878	0.974	0.849	1.000	
NH_4^+	0.228	0.357	0.281	0.427	0.461	0.310	1.000

Coefficient in gray color is significant. (N=18,1%)

Table 3 Raito of H^+ outflow to the weekly mean H^+ deposition flux in the precipitation.

	1st week	2nd week	3rd week	4th week	5th week	6th week
1997	0.15	0.01	0.56	0.72	2.45	5.23
1998	0.67	0.72	1.09	1.74	3.83	3.16
1999	1.08	2.12	1.04	1.47	2.25	1.24

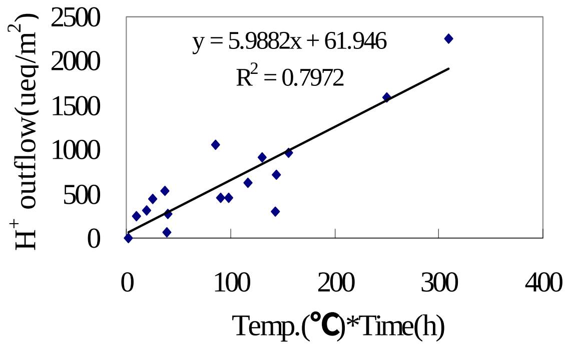


Figure 7 Correlation between H^+ outflow and the value of temperature(°C) multiplied by time(hour).

correlation.

In Figure 1, the pattern of H^+ outflow in 1999 was different from those in the previous years. Compared with the previous years, the average temperature above 0 °C was higher and the total duration of such temperatures was also longer in the first two weeks, and both of these values also tended to decrease in the 5th and 6th weeks. Therefore the product of the temperature above 0℃ multiplied by its duration was thought to be a cause for the different patterns of H^+ outflow.

It was found that H^+ volumes 2.3 times larger than the mean volume of H^+ from precipitation were loaded on the ground surface in the 5th and 6th weeks in mid- and late March, 1999, which is the snowmelt season in Sapporo. It was also confirmed that the H^+ outflow increased and its outflow became equivalent to the weekly mean H^+ deposition flux in the first week of research in mid-February, because the temperature rose and remained above 0℃.

4. Conclusion

(1) There was a good correlation between H^+ outflow and other ions except for Ca^{2+} and NH_4^+. These correlation coefficients were 0.67 to 0.82 and those were not too strong. However there were a pair of ions indicated very strong correlation, for example, a pair of SO_4^{2-} with NO_3^-, Cl^- and Na^+. These coefficients were 0.94 to 0.97, and a pair of Cl^- and Na^+ had a very strong too.

(2) It was found that H^+ volumes 2.3 times larger than the mean volume of H^+ from precipitation were loaded on the ground surface in the 5th and 6th weeks in mid- and late March 1999. Also it was confirmed that the H^+ outflow increased and its outflow became equivalent to the weekly mean H^+ deposition flux in the first week of research in mid-February because the temperature rose and remained above 0℃ in 1999.

5. Reference

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(2) Norio Fukuzaki Tsuyosi Ohizumi: Movement and elution of chemical constit-uents in snowcover, Journal of Japan Society for Airpollution, **30,** 94-103, 1995

札幌市における融雪期の水素イオンと他のイオンの挙動について

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要　旨

積雪中には，水素イオン(H^+)をはじめとする各種イオンが蓄積されている。融雪期になるとH^+などのイオン類は流出し，特に，H^+によって土壌，湖沼などのｐＨが一時的に低下するアシッドショック現象が生じることがあると言われている。

すでに，札幌の融雪時における積雪中のH^+の挙動について検討を加えるため，1997年，1998年の2月中旬から3月末まで芸術の森公園で調査を行い，H^+の流出量は３月中旬の第5週目以降の２週間で，湿性降下物の週平均H^+沈着量の約4倍から5倍の流出量があることを報告している。

今回は，1999年のデータも含めた3年間のデータを基にH^+の他，硫酸イオンなどの陰イオン類とカルシウムイオンなどの陽イオン類について1週間の流出量，H^+と各イオンの流出パターンの比較，1999年におけるのH^+と素湿性降下物の週平均H^+沈着量の比較を行った。

その結果，水素イオンと幾つかのイオンは流出量に相関があったが，硫酸イオンと硝酸イオンの流出量ほど強い相関ではなかった。また，カルシウムイオンとアンモニウムイオンの流出量とは相関がみられなかった。1999年の調査期間における水素イオンの流出は，前年度と前々年度に比べ２月に暖かい日が多かったので，２月最初の調査の週から認められた。週平均H^+沈着量も３月の中旬以降で最大2.3倍程度と低めであった。