MULTIELEMENTAL ANALYSIS OF SOLUBLE AND INSOLUBLE COMPONENT IN FRESH SURFACE SNOW ON MOUNTAINS

Katsumi SAITOH[1], Yoshihiro IWATA[2], Katsuhiko KAWABATA[3],
Koichiro HIRANO[4] and Mamoru TAKAHASHI[5]

[1]*Akita Prefectural Institute of Environmental Science, 191-18 Yabase-Shimoyabase, Akita, 010 JAPAN*
[2]*College of Education, Akita University, 1-1 Gakuen-Machi, Tegata, Akita 010, JAPAN*
[3]*Yokogawa Analytical Systems Inc., 2-11-19 Naka-Cho, Musashino-Shi, Tokyo 180, JAPAN*
[4]*Yokohama City Research Institute of Environmental Science, 1-2-15 Takigashira, Isogo-Ku, Yokohama 235, JAPAN*
[5]*Akita Prefectural Industrial Waste Center, 45 Amaikezawa, kamiyodogawa, kyowa-Town, Akita 019-23, JAPAN*

Abstract: Chemical composition of soluble and insoluble were determined in fresh surface snow samples which were collected at the top or near the top (700-1500m altitude) of five mountains in Akita Pref. of Japan. The snow samples were thawed and separated to soluble and insoluble component by filtration. Various anions and cations were determined by Ion Chromatography, and 37 soluble elements were determined by Inductively Coupled Plasma Mass Spectrometer. 19 kinds of insoluble elements on the filter were determined by Particle Induced X-ray Emission. These results were represented as a back ground of elemental composition for fresh surface snow and several characteristics, *i.e.* effect of sea salt, for each mountains were observed.

Key words: Multielemental analysis, Fresh surface snow, Mountain snow, Ion Chromatography, ICP-MS, PIXE

INTRODUCTION

Various scientific fields are concerned with composition and chemical form of elements in rain and snow. Many reports have been described that a lot of ions and elements in precipitation by human activity such as industrial and traffic. It is very interesting in elemental and ionic composition for fresh surface snow on mountains far from human living area because they have similar composition to clouds and also arising native rain and snow. But there are few research project for determination of multielements in fresh surface snow on mountains.

Multielemental analysis and chemical characterization are necessary for environmental science because this field often needs many kinds and number of analytical data. Ion Chromatography (IC) has been often used for determination and characterization of soluble ions in rain and snow. Nowadays, many scientists recognize Inductively Coupled Plasma Mass Spectrometer (ICP-MS) as a powerful tool for simultaneous analysis for trace soluble elements in water sample. On the other hand, multielemental analysis for insoluble component in rainfall and snowfall is not so easy because mass of the component is limited and often complete dissolution is not able to do. A newcomer to simultaneous analysis for trace element, Particle Induced X-ray Emission (PIXE) is suitable for small amount of analytical sample on a thin film.

In this paper, we collected fresh snow samples from five mountains far from human living and separated soluble and insoluble component by filtration. We analyzed soluble component by IC and ICP-MS, insoluble component by PIXE.

EXPERIMENTAL

Sampling location of fresh surface snow shows in Fig.1, and sampling site and date give in Table 1. The samples were collected with deposit gauzes and transported into polyethylene bottles (2L). The gauzes and the plastic bottles were cleaned and kept in polyethylene bags prior to the sampling.

The snow samples were slowly thawed at room temperature in laboratory. The samples were filtered by a polycarbonate filter (Ncuclepore 25mmφ, 0.2μm) on a membrane filter (Millipore 25mmφ, 0.8μm). The analyses of anions of Cl^-, NO_2^-, Br^-, SO_4^{2-} and NO_3^-, and of cations of Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} were determined by IC (Dionex DX-100). Details of IC analysis are described elsewhere [1]. Soluble elements were analyzed by ICP-MS (Yokogawa HP 4500), and details of ICP-MS were demonstrated elsewhere [2,3]. In ICP-MS analysis, the semi-quantitative analysis of 71 elements (Li - U) was conducted using internal standards of Y, Se and Tl. And then 37 elements were analyzed quantitatively using standard solution for each elements. For the insoluble elements, Particle Induced X-ray Emission (PIXE) analysis [4,5] was carried out with insoluble component on the polycarbonate filter for 200 mL of the thawed snow samples, and used one of the Japan radioisotope association Nishina memorial cyclotron center.

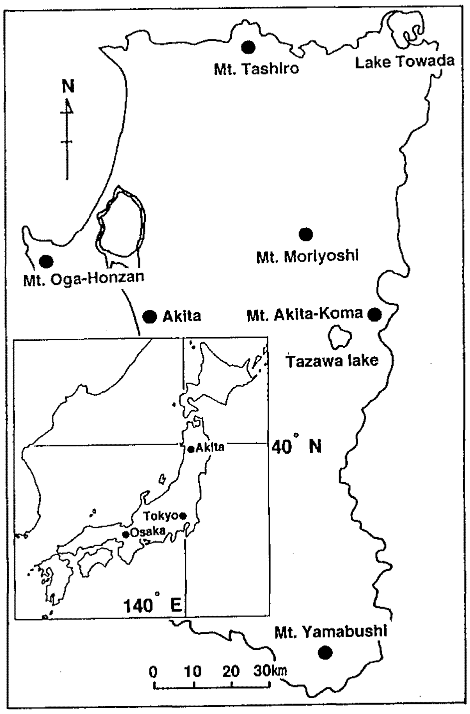

Fig. 1 Sampling location.

Table 1 Sampling site and date of fresh surface snow samples

Sampling Site	Point	Altitude (m)	Date
Mt. Yamabushi	The top	1315	19/Feb./'95
Mt. Akita-Koma	Near the top	1320	26/Feb./'95
Mt. Oga-Honzan	Near the top	650	28/Feb./'95
Mt. Tashiro	The top	1178	05/Mar./'95
Mt. Moriyoshi	The top	1454	12/Mar./'95

RESULTS AND DISCUSSION

pH and ion concentrations in fresh surface snow are shown in Table 2. pH was in the range of 4.80 to 4.47. The concentrations of ions were 92.0-12.2 μeq/L-range for SO_4^{2-}, 20.6-7.7 μeq/L-range for NO_3^-, 16.1-3.9 μeq/L-range for NH_4^+, 24.0-1.6 μeq/L-range for Ca_2^+. The ion concentrations in snow samples from the mountains, except Mt. Oga-Honzan, were the similar levels compared with several mountain samples in Japan [6-8]. Table 3 shows the contribution sea salt for ionic abundance. The ion concentrations in Mt. Oga-Honzan snow sample was influenced by sea salt.

The quantitative data of 37 soluble elements given in Table 4, resulted from the semi-quantitative analysis by which 44 elements were detected. The concentrations of soluble elements were several μg/L for nine major elements: Al, Mn, Fe, Ni, Cu, Zn, Sr, Ba, Pb, and 0.1-0.01 μg/L-range for 15 minor elements: Li, Sc, Ti, V, Cr, Co, Ga, Ge, As, Se, Rb, Mo, Cd, Sn, Sb, and 0.01-0.001 μg/L for 13 trace elements: Y, Zr, Cs, La, Ce, Pr, Nd, Hf, W, Tl, Bi, Th, U. The concentrations of soluble elements measured were higher in Mt.Akita-Koma than in other mountains. Although the differences in elemental compositions were not shown between the mountain snow samples.

Fig. 2 shows the elemental composition of insoluble constitute in snow samples. By the PIXE analysis, 19 elements were detected, and Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti and Fe were the major components in each mountain sample.

We hope these analytical methods and data for fresh surface snow on mountains will be useful for research for origin and transport of acid rain and snow.

Table 2 pH and ion concentrations in fresh surface snow

Sampling site	pH	EC (μS/cm)	Ion equivalent concentration (μeq / L)*1									
			Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Mt. Yamabushi	4.62	24.5	54.4	ND*2	ND	10.8	36.1	49.3	15.9	3.6	10.0	5.0
Mt. Akita-Koma	4.47	28.2	38.7	ND	ND	20.6	29.5	33.1	16.1	3.0	6.3	5.6
Mt. Oga-Honzan	4.55	89.7	539.1	ND	0.7	8.3	92.0	466.4	15.8	11.2	109.7	24.0
Mt. Tashiro	4.65	10.8	24.4	ND	ND	12.8	12.2	17.7	3.9	0.9	2.6	1.6
Mt. Moriyoshi	4.80	13.9	22.2	ND	ND	7.7	21.8	22.1	11.6	2.6	1.8	1.8

*1 Ion concentrations determined from three repeated measurements of each sample.
*2 Not detected.

Table 3 Contribution of sea salt

Sampling site	Contribution percentage					
	Cl^-	Br^-	SO_4^{2-}	K^+	Mg^{2+}	Ca^{2+}
Mt. Yamabushi	100	- *	16.2	28.6	0	40.0
Mt. Akita-Koma	100	-	13.4	25.0	0	27.3
Mt. Oga-Honzan	100	100	60.9	88.6	97.0	85.4
Mt. Tashiro	85.1	-	16.9	50.0	0	33.3
Mt. Moriyoshi	100	-	12.4	20.0	0	50.0

* Not detected.

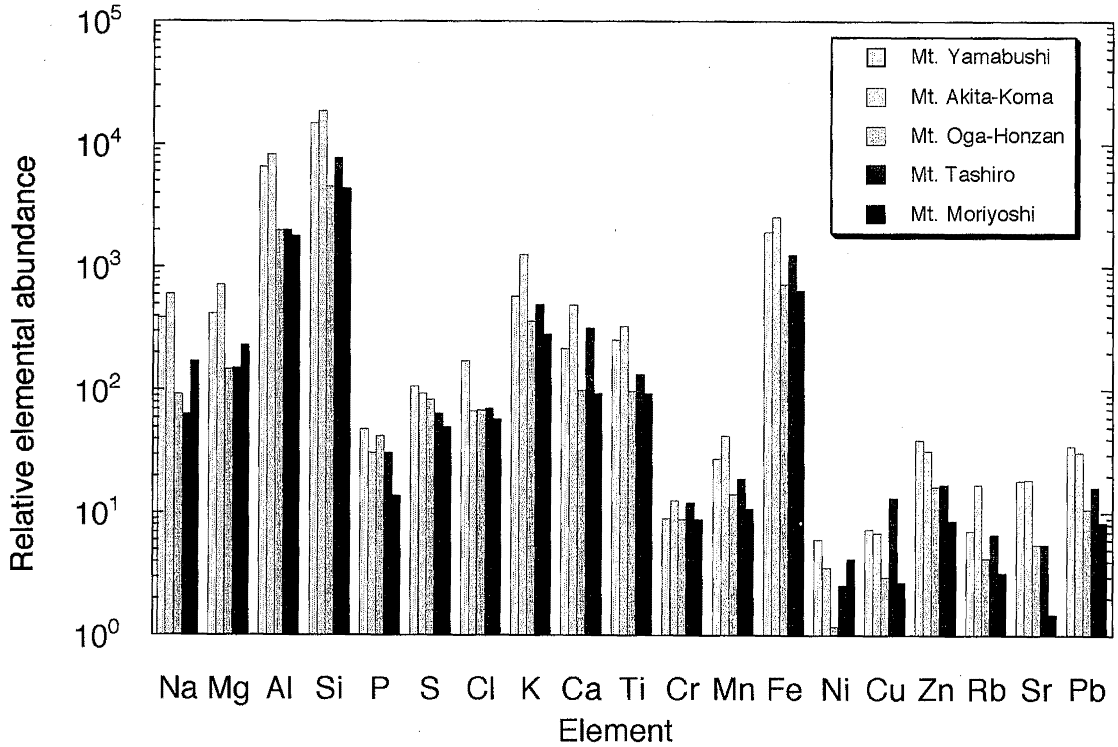

Fig. 2 Elemental composition of insoluble constitute in fresh surface snow.

Table 4 Element concentrations in fresh surface snow (μg/L)*1

Element	Mt. Yamabushi	Mt. Akita-Koma	Mt. Oga-Honzan	Mt. Tashiro	Mt. Moriyoshi
Major elements					
Al (27)*2	4.18	21.4	4.62	4.51	2.17
Mn (55)	1.18	4.28	1.17	0.819	0.484
Fe (57)	16.3	35.4	12.3	4.30	16.0
Ni (60)	ND*3	0.806	ND	1.37	ND
Cu (63)	0.493	1.38	0.746	1.64	0.528
Zn (66)	8.94	10.5	2.66	7.05	1.25
Sr (88)	0.442	2.39	7.89	0.541	0.371
Ba (138)	0.343	1.73	0.488	0.372	0.364
Pb (208)	3.62	3.96	1.51	2.64	0.873
Minor elements					
Li (7)	ND	0.073	0.164	0.014	0.011
Sc (45)	0.050	0.053	0.044	0.012	0.077
Ti (47)	0.049	0.374	0.050	0.061	0.053
V (51)	0.119	0.394	0.307	0.082	0.150
Cr (53)	0.557	0.221	0.233	0.154	0.151
Co (59)	0.036	0.053	0.007	0.076	0.006
Ga (69)	0.044	0.157	0.044	0.025	0.033
Ge (72)	0.012	0.072	0.037	0.008	0.024
As (75)	0.247	0.988	0.316	0.196	0.170
Se (82)	0.085	0.308	0.299	0.084	0.343
Rb (85)	0.080	0.322	0.212	0.578	0.118
Mo (95)	0.032	0.121	0.049	0.035	0.030
Cd (111)	0.142	0.201	0.053	0.104	0.056
Sn (120)	0.027	0.108	0.021	0.084	0.023
Sb (121)	0.066	0.192	0.044	0.072	0.049
Trace elements					
Y (89)	ND	0.019	0.003	0.002	ND
Zr (90)	0.002	0.021	0.004	0.006	0.005
Cs (133)	0.007	0.008	0.007	0.005	0.003
La (139)	0.010	0.024	0.006	0.011	0.003
Ce (140)	0.004	0.033	0.002	0.009	ND
Pr (141)	0.001	0.005	0.001	0.002	0.001
Nd (146)	0.004	0.018	0.005	0.006	0.004
Hf (178)	0.002	0.001	0.002	0.001	0.002
W (182)	0.002	0.028	0.006	0.004	0.005
Tl (205)	0.001	0.017	0.005	0.001	0.003
Bi(209)	0.001	0.011	0.007	0.006	0.004
Th (232)	0.001	0.007	0.001	0.001	0.001
U (238)	0.001	0.013	0.004	0.001	0.001

*1 Element concentrations determined from three repeated measurement of each sample. *2 Mass number. *3 Not detected. The underlines are maximum value for each element.

REFERENCES

1. K. Saitoh, Journal of Environmental. Laboratories Association, 21, 96-99 (1996).
2. K. Kwabata, Y. Kishi, O. Kawaguchi, Y. Watanabe, Y. Inoue, Anal. Chem., 63, 2137-2140 (1991).
3. K. Saitoh, H. Sugiyama, C.A. Strussmann, F. Takashima, K. Kawabata, Bulletin of the Society of Sea Water Science, Japan, 48, 248-256 (1994).
4. K. Sera, T. Yanagisawa, H. Tsunoda, S. Hutatukawa, Y. Saitoh, S. Suzuki, H. Orihara, International Journal of PIXE, 2, 325-330 (1992).

5. Particle Induced X-ray Emission Spectrometry (PIXE), S.A.E. Johansson, J.L. Campbell and K.G. Malmqvist, John Wiley & Sons, Inc., (1995).
6. N. Fukuzaki, K. Mori, T. Mori, Proceedings of the 33rd Annual Meeting of the Japan Society of Air Pollution, Osaka, 521 (1992).
7. N. Fukuzaki, T. Ohizumi, Y. Ito, Proceedings of the 33rd Annual Meeting of the Japan Society of Air Pollution, Chiba City, 221 (1993).
8. E. Maruta, Y. Dokiya, K. Tsuboi, Environ. Sci., 6, 311-320 (1993).

山岳における新雪中の溶存および不溶成分の多元素分析

斉藤　勝美[1]・岩田　吉弘[2]・川端　克彦[3]・平野　耕一郎[4]・高橋　守[5]

1995年2月から3月に，秋田県内の標高700～1500mの独立峰（山伏山，秋田駒ヶ岳，男鹿本山，田代岳および森吉山）の頂上あるいは頂上付近での降雪直後の表面雪を採取し，溶存および不溶成分の分析をした。溶存成分は，イオンクロマトグラフィーにより数種の陰イオンと陽イオン，ICP-MSにより37元素を定量した。不溶成分は，PIXEにより分析し，17元素の存在を確認した。これらの結果は，降雪に含まれる溶存および不溶成分のベースになると考えられた。また，海塩粒子の影響はいずれの山岳でも観測された。

[1]秋田県環境技術センター，[2]秋田大学教育学部，[3]横河アナリティカルシステムズ㈱，[4]横浜市環境科学研究所，[5]秋田県環境保全センター（元秋田県環境技術センター）

本稿は，1997 International Congress of ACID SNOW AND RAIN (Oct. 6-8, 1997, Niigata, JAPAN)においてのプロシィーデング原稿である。