

CHARACTERIZATION OF ATMOSPHERIC AEROSOL PARTICLES IN A MOUNTAINOUS REGION IN NORTHERN JAPAN

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ABSTRACT

The purpose of this study is to clarify the chemical characterization of particulate matter (PM) in a mountainous region and examine the effect of atmospheric pollutants transported to Japan from Northeast Asian regions. Sampling of size-resolved airborne PM was carried out on the west side of Mt. Moriyoshi near the summit in northern Japan, from 1 – 16 February (winter period) and 7 – 19 July (summer period) in 2004. The concentrations of several elemental and ionic species in each size-resolved PM sample were determined by particle induced X-ray emission (PIXE) and ion chromatography analysis. From these results, in the winter period, it is suggested that soil and sea-salt particles of PM_{10} to $PM_{2.5}$ size and ammonium sulfate particles, *i.e.*, secondary-formed particles of $<PM_{1.0}$, have been transported to Japan from the continent. On the other hand, in the summer period, it is suggested that PM was formed from soil and sea-salt particles of $>PM_{10}$ to $PM_{2.5}$ size and secondary-formed particles of $<PM_{1.0}$.

Key Words: Atmospheric aerosol particles, Mountainous region, Long-range transport, PIXE, Ion chromatography

1. INTRODUCTION

The Japanese archipelago is located in the mid-latitudes off the east coast of Asia. In the winter, northwest winds (monsoons) from the Asian continent caused by an atmospheric pattern of western high and eastern low bring large amounts of snow to regions along the Sea of Japan side of Japan. These northwest winds transport various air contaminants of natural origin or man-made origin from the continent to Japan. This has been reported to affect the forest ecosystem of Japan (Nagafuchi, 2000). On the other hand, in the summer, the land and sea breeze, *i.e.*, southwestern wind and southeast wind, blows in daytime and at night, respectively. This land and sea breeze reflects local atmospheric conditions. The best way to gain insight into contaminants transported from the continent is to observe them in a mountainous region at 1200 m to 1500 m above sea level, which is in the vicinity of the top of the planetary boundary layer and is less directly affected by man-made pollution sources (Mizoguchi, 1991).

Consequently, in order to shed light on the long-range transport of atmospheric pollutants in the Northeast Asian regions, we studied a multi-probe chemical characterization and composition profile of airborne particulate matter (PM) on Mt. Moriyoshi (39° 58' N, 140° 32' E; altitude: 1454 m), located on the Sea of Japan side of northern Honshu, Japan, near Northwest China and Southwest Russia. PM samples were collected at the west side near the summit (altitude: 1167 m), from 1 – 16 February (winter period) and 7 – 19 July (summer period) in 2004, and chemical analysis of these samples was carried out. Elemental components of these samples were determined by means of particle induced X-ray emission (PIXE) analysis. Ionic species (anions: F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻; cations: Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) of these samples were analyzed by ion chromatography.

This present study focuses on the chemical characterization of PM in a mountainous region by elemental and ionic components and examines the effect of atmospheric pollutants transported to Japan from the Northeast Asian regions.

2. MATERIALS AND METHOD

PM sampling was carried out on the west side of Mt. Moriyoshi near the summit, from 1 – 16 February (winter period) and 7 – 19 July (summer period) in 2004. The PM sampling was actually performed approximately 2 m above the ground. The PM was collected using a 3-stage NLAS impactor (Tokyo Dylec Co., Ltd.; particle cut-size of stages was 10 µm, 2.5 µm and 1.0 µm for a flow rate of 3 L/min) with a two-day or three-day sampling interval on a polycarbonate filter (Nuclepore[®], diameter: 25 mmΦ, pore size: 0.2 µm) and a PTFE ultra-membrane filter (HORIBA Ltd., TFH-47, diameter: 47 mmΦ). Note that HORIBA TFH-47 was used as a backup filter and that approximately 0.15% of TiO₂ is present in HORIBA TFH-47. These filter samples of size-resolved PM were stored in Millipore PetriSlide[®] containers and kept in portable refrigerators during transport back to the laboratory, and they were stored in a freezer (-35°C) until they were analyzed.

Elemental compositions of each size-resolved PM filter sample were determined by PIXE at Nishina Memorial Cyclotron Center, Japan Radioisotope Association. For PIXE analysis, the filter samples were mounted on a Mylar[®] target frame and bombarded with 2.9 MeV protons from a small-size cyclotron (Sera et al., 1992). Beam currents, the accumulated charge and the typical measuring time were 20–45 nA, 23–60 µC, and 20–22 min, respectively for the Nuclepore filter samples. For the HORIBA filter samples, these were 5–16 nA, 3–13 µC, and 9–14 min, respectively. X-ray spectra were analyzed using the SAPIX program (Sera et al., 1992). Quantitative analysis of elemental values was performed based on the Nuclepore-Br method (Sera et al., 1997). Moreover, blank filters were analyzed with all the procedures. As for the accuracy of the PIXE analysis, it was confirmed by analysis using NIST standard reference materials (Saitoh et al., 2002; Saitoh et al., 2003).

Ionic species in each size-resolved PM filter sample were determined by ion chromatography (Metrohm, Compact IC 761 for anions and Personal IC 790 for cations).

For ion chromatography analysis, half of the Nuclepore filter samples and a quarter of the HORIBA filter samples were directly treated with 10 mL of ultrapure water (made by Milli-Q Labo) for 20 min using an ultrasonic apparatus. Regarding the operating conditions during ion chromatography, the sample injection volume was 200 μL and the full-scale range of conductivity detection was 50 μS for anions. For cations, the full-scale range of conductivity detection was 1000 μS . Blank filters were analyzed with all the procedures, and the concentrations of ionic species that could be measured for the blank filters were always below the minimum determination limits. Ionic species concentrations were determined based on calibration curves generated from analysis of the continuing calibration standard solutions. Wako Pure Chemical Industries, Ltd.'s 1000 mg/L standard was used for standard solutions. The concentration of calibration standard solutions is zero (ultrapure water; made by Milli-Q Labo), 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 1 and 2 mg/L. For generation of calibration curves, determination of each concentration was repeated five times.

3. RESULTS AND DISCUSSION

In PIXE analysis of each size-resolved PM filter sample, 23 elements (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr and Pb) were determined in total. Errors for the analytical results are mainly from the spectrum fitting, the detection efficiency and the values of X-ray transmission through the absorber. For the Nuclepore filter samples, estimated relative error ($100 \times \text{error}/\text{count}$, in %) was smaller than 10% for eight elements (Na, Al, S, K, Ca, Fe, Zn and Br), 10 – 20% for five elements (Si, Cr, Mn, Cu and Pb) and 20 – 40% for four elements (Mg, Ti, Ga and Se). For the HORIBA filter samples, estimated relative error was smaller than 10% for two elements (Cl and Ca), 10 – 20% for five elements (Na, S, Fe, Ni and Zn) and 20 – 40% for four elements (Si, K, Br and Pb).

Tables 1 and 2 show the arithmetic mean concentration and the minimum and maximum values of elemental concentrations in each size-resolved PM for the winter and summer periods. Because approximately 0.15% of TiO_2 is contained in the backup filter, Ti, V and Cr concentrations in the PM on the backup filter is difficult to determine by PIXE analysis.

The major elemental components of each size-resolved PM sample, *i.e.*, $>\text{PM}_{10}$, $\text{PM}_{10} - \text{PM}_{2.5}$, $\text{PM}_{2.5} - \text{PM}_{1.0}$ and $<\text{PM}_{1.0}$, were Na, Mg, Al, Si, S, Cl, K, Ca and Fe for both the winter and summer periods. For the major components, in the size-resolved PM samples of the winter period, concentrations of Na, Al and Cl in $\text{PM}_{10} - \text{PM}_{2.5}$ particles are several times higher than those in other particle sizes, and these are not detected in particles $<\text{PM}_{1.0}$. However, S concentration in particles $<\text{PM}_{1.0}$ is several times higher than this in other particle sizes. Mg, Si, Ca and Fe reveal a high concentration in $\text{PM}_{10} - \text{PM}_{2.5}$ particles, and $\text{PM}_{2.5} - \text{PM}_{1.0}$ particles for K. On the other hand, in the summer period, as for $\text{PM}_{10} - \text{PM}_{2.5}$ particles, concentrations of Na, Cl, Si and Fe are several times higher than those in other particle sizes, and Na, Al and Cl are detected in particles $<\text{PM}_{1.0}$. S reveals a high concentration in particles $<\text{PM}_{1.0}$ and $\text{PM}_{2.5} - \text{PM}_{1.0}$ particles. Al shows a high concentration in $\text{PM}_{10} - \text{PM}_{2.5}$ and $\text{PM}_{2.5} - \text{PM}_{1.0}$ particles, $\text{PM}_{10} - \text{PM}_{2.5}$

particles for Mn and Ca, PM_{2.5} – PM_{1.0} particles for K. Comparing the arithmetic means of major elemental concentrations in the particles >PM_{1.0}, PM₁₀ – PM_{2.5}, PM_{2.5} – PM_{1.0} and <PM_{1.0} for the winter and summer periods, elemental concentrations in the summer period samples are a little higher than the elemental concentrations in the winter period samples.

Table 1. Elemental concentrations (ng/m³) of the size-resolved PM during winter period at Mt. Moriyoshi*

Element	>PM ₁₀		PM ₁₀ -PM _{2.5}		PM _{2.5} -PM _{1.0}		<PM _{1.0}	
	Mean	Min - Max	Mean	Min - Max	Mean	Min - Max	Mean	Min - Max
Na	27.9	ND** - 72.1	190	71.3 - 285	25.9	19.8 - 31.8	–	ND
Mg	9.9	ND - 20.5	47.7	19.4 - 61.0	34.4	ND - 56.7	–	ND
Al	8.0	ND - 14.4	102	23.8 - 208	47.6	29.1 - 94.1	–	ND
Si	24.8	9.7 - 61.2	243	74.3 - 560	98.6	70.4 - 148	102	ND - 254
S	17.0	8.5 - 36.5	83.0	44.2 - 116	200	130 - 301	660	473 - 762
Cl	18.1	ND - 59.7	154	37.8 - 283	12.7	ND - 28.2	–	ND
K	3.1	ND - 6.6	21.3	8.0 - 41.8	34.9	18.2 - 57.1	10.4	ND - 51.8
Ca	8.4	1.3 - 22.0	56.3	11.0 - 94.2	17.8	8.9 - 27.2	44.5	16.3 - 122
Ti	0.2	ND - 0.6	3.5	1.2 - 7.5	2.0	1.5 - 3.3	Non-determination	
V	–	ND	0.3	ND - 0.7	0.2	ND - 0.7	Non-determination	
Cr	0.1	ND - 0.2	0.2	ND - 0.7	0.2	ND - 0.6	Non-determination	
Mn	0.1	ND - 0.2	1.6	0.5 - 3.0	3.6	1.4 - 7.8	–	ND
Fe	2.4	0.1 - 6.3	39.2	9.0 - 85.9	21.8	15.1 - 27.6	14.6	9.2 - 28.9
Ni	–	ND	0.1	ND - 0.3	0.1	ND - 0.3	0.5	ND - 1.3
Cu	–	ND	0.2	ND - 0.5	0.1	ND - 0.2	0.2	ND - 1.2
Zn	0.8	ND - 3.8	1.4	0.6 - 2.2	5.3	3.4 - 8.3	4.7	3.0 - 9.2
Ga	–	ND	–	ND	–	ND	2.0	ND - 5.5
As	–	ND	0.2	ND - 0.4	0.4	0.2 - 0.6	1.5	ND - 3.6
Se	–	ND	0.1	ND - 0.3	0.1	ND - 0.2	0.3	ND - 1.7
Br	0.4	0.2 - 0.7	1.3	0.8 - 1.9	0.9	0.5 - 1.4	3.7	ND - 10.6
Rb	–	ND	0.1	ND - 0.3	–	ND	1.3	ND - 6.5
Sr	0.1	ND - 0.4	0.3	ND - 0.5	–	ND	2.9	ND - 14.4
Pb	0.1	ND - 0.2	0.5	ND - 1.2	2.8	1.6 - 4.0	2.4	ND - 7.4

*: Mean, minimum and maximum of five samples. **: Not detectable. Not detectable cases were assumed to be zero for calculation of mean.

Table 2. Elemental concentrations (ng/m³) of the size-resolved PM during summer period at Mt. Moriyoshi*

Element	>PM ₁₀		PM ₁₀ -PM _{2.5}		PM _{2.5} -PM _{1.0}		<PM _{1.0}	
	Mean	Min - Max	Mean	Min - Max	Mean	Min - Max	Mean	Min - Max
Na	42.3	ND** - 145	210	155 - 340	86.7	28.1 - 133	114	ND - 434
Mg	21.4	ND - 70.5	68.6	25.3 - 138	43.8	21.3 - 78.4	14.5	ND - 72.5
Al	65.0	ND - 248	219	41.4 - 609	228	24.6 - 496	15.0	ND - 74.9
Si	34.5	22.0 - 53.2	304	101 - 629	146	29.8 - 294	71.2	27.7 - 97.0
S	31.1	9.0 - 71.1	201	77.6 - 530	1470	47.2 - 3320	1070	150 - 2650
Cl	49.5	ND - 237	136	ND - 274	5.6	ND - 27.9	69.4	ND - 347
K	2.9	2.3 - 3.5	56.7	5.7 - 109	71.0	8.0 - 195	33.4	17.8 - 48.2
Ca	10.5	1.2 - 42.4	71.3	35.3 - 165	20.2	11.0 - 35.6	49.5	17.2 - 129
Ti	0.2	ND - 0.4	5.6	1.7 - 14.2	2.4	0.7 - 6.1	Non-determination	
V	–	ND	–	ND	0.3	ND - 1.0	Non-determination	
Cr	0.9	ND - 4.6	0.2	ND - 0.8	0.2	ND - 0.7	Non-determination	
Mn	0.2	ND - 0.5	1.8	0.4 - 4.6	1.8	0.2 - 4.5	–	ND
Fe	7.6	0.7 - 31.2	64.0	6.0 - 185	29.1	2.1 - 76.9	10.3	3.4 - 25.0
Ni	0.4	ND - 1.8	0.3	ND - 0.8	0.3	ND - 0.7	0.9	ND - 4.3
Cu	0.1	ND - 0.5	1.6	0.3 - 2.6	0.7	ND - 1.5	0.2	ND - 1.0
Zn	0.5	ND - 2.1	5.4	0.5 - 18.0	12.9	0.3 - 39.7	4.8	ND - 13.4
Ga	–	ND	–	ND	0.1	ND - 0.5	0.7	ND - 1.2
As	–	ND	–	ND	0.1	ND - 0.3	–	ND
Se	–	ND	–	ND	0.1	ND - 0.4	–	ND
Br	0.6	0.4 - 0.8	2.2	1.6 - 3.0	2.0	0.8 - 3.1	2.4	ND - 5.5
Rb	–	ND	–	ND	0.1	ND - 0.6	–	ND
Sr	0.1	ND - 0.3	2.6	ND - 0.5	0.1	ND - 0.4	–	ND
Pb	0.1	ND - 0.5	2.0	0.9 - 5.2	6.2	ND - 20.2	3.7	ND - 12.9

*: Mean, minimum and maximum of five samples. **: Not detectable. Not detectable cases were assumed to be zero for calculation of mean.

As for ionic species, F⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ were determined. The major ion components in the winter period samples were Cl⁻, NO₃⁻, SO₄²⁻, Na⁺ and NH₄⁺, and these plus NO₂⁻ in the summer period samples. The determination limit of anions is 0.005 mg/L (0.005 – 0.012 µg/m³), except for Cl⁻, NO₂⁻ and SO₄²⁻. The determination limit of Cl⁻, NO₂⁻ and SO₄²⁻ is 0.01 mg/L (0.009 – 0.025 µg/m³). For cations, the determination limit is 0.01 mg/L (0.009 – 0.025 µg/m³). The detection limit is 0.001 mg/L (0.001 – 0.002 µg/m³) for all the ionic species, and concentrations of Br⁻ and PO₄³⁻ were smaller than 0.002 µg/m³ for all the samples.

Tables 3 and 4 show the arithmetic mean concentration and minimum and maximum values of ionic species concentrations in each size-resolved PM for the winter and summer periods. In the winter period, concentrations of Cl⁻, NO₃⁻ and Na⁺ in PM₁₀ –

PM_{2.5} particles are several times higher than those in the other particle sizes. However, SO₄²⁻ and NH₄⁺ reveal a high concentration in particles <PM_{1.0}. On the other hand, in the summer period, Na⁺ reveals a high concentration in PM₁₀ – PM_{2.5} particles, but NO₃⁻

Table 3. Ionic species (μg/m³) of the size-resolved PM during winter period at Mt. Moriyoshi*

Element	>PM ₁₀		PM ₁₀ -PM _{2.5}		PM _{2.5} -PM _{1.0}		<PM _{1.0}	
	Mean	Min - Max	Mean	Min - Max	Mean	Min - Max	Mean	Min - Max
F ⁻	0.002	ND** - <u>0.005</u>	0.005	ND - 0.012	0.001	ND - <u>0.006</u>	0.005	ND - 0.024
Cl ⁻	0.056	0.024 - 0.087	0.089	0.035 - 0.152	0.037	0.008 - 0.082	-	ND
NO ₂ ⁻	0.004	ND - <u>0.012</u>	0.002	ND - <u>0.005</u>	0.004	ND - 0.010	0.055	ND - 0.118
Br ⁻	-	ND	-	ND	-	ND	-	ND
NO ₃ ⁻	0.041	ND - 0.077	0.119	0.035 - 0.231	0.096	0.041 - 0.177	0.107	0.077 - 0.141
PO ₄ ³⁻	-	ND	-	ND	-	ND	-	ND
SO ₄ ²⁻	0.075	0.046 - 0.135	0.326	0.060 - 1.200	0.395	0.251 - 0.558	1.679	1.398 - 2.179
Na ⁺	0.035	0.011 - 0.066	0.067	0.033 - 0.100	0.022	0.002 - 0.056	0.023	ND - 0.073
NH ₄ ⁺	0.056	0.046 - 0.074	0.063	0.051 - 0.084	0.152	0.098 - 0.213	0.519	0.294 - 0.909
K ⁺	0.046	0.014 - 0.080	0.054	0.008 - 0.121	0.033	ND - 0.072	0.081	0.019 - 0.109
Mg ²⁺	-	ND	-	ND	0.004	ND - 0.022	0.026	ND - 0.077
Ca ²⁺	0.013	ND - 0.025	0.015	<u>0.006</u> - 0.026	0.034	0.025 - 0.040	-	ND

Indication of italic and under bar is value of under the determination limit. *: Mean, minimum and maximum of five samples. **: Not detectable. Not detectable cases were assumed to be zero for calculation of mean.

Table 4. Ionic species (μg/m³) of the size-resolved PM during summer period at Mt. Moriyoshi*

Element	>PM ₁₀		PM ₁₀ -PM _{2.5}		PM _{2.5} -PM _{1.0}		<PM _{1.0}	
	Mean	Min - Max	Mean	Min - Max	Mean	Min - Max	Mean	Min - Max
F ⁻	0.007	<u>0.003</u> - 0.012	0.010	<u>0.005</u> - 0.020	0.015	0.008 - 0.028	0.049	ND - 0.129
Cl ⁻	0.101	<u>0.007</u> - 0.399	0.093	ND - 0.216	0.026	0.003 - 0.051	0.078	ND - 0.277
NO ₂ ⁻	0.072	0.020 - 0.122	0.117	0.033 - 0.341	0.118	0.044 - 0.161	0.117	0.084 - 0.181
Br ⁻	-	ND**	-	ND	-	ND	-	ND
NO ₃ ⁻	0.077	0.002 - 0.139	0.172	0.062 - 0.241	0.067	0.021 - 0.136	0.883	0.005 - 4.365
PO ₄ ³⁻	-	ND	-	ND	-	ND	-	ND
SO ₄ ²⁻	0.097	0.022 - 0.223	0.376	0.111 - 1.192	2.016	0.028 - 6.370	2.786	0.362 - 6.233
Na ⁺	0.063	ND - 0.188	0.103	0.030 - 0.167	0.043	0.021 - 0.062	0.002	ND - 0.012
NH ₄ ⁺	0.020	<u>0.009</u> - 0.037	0.084	<u>0.009</u> - 0.364	0.555	<u>0.012</u> - 1.897	1.027	0.162 - 2.341
K ⁺	0.018	ND - 0.065	0.019	ND - 0.034	0.010	ND - 0.042	-	ND
Mg ²⁺	-	ND	0.004	ND - 0.019	0.015	ND - 0.062	-	ND
Ca ²⁺	0.013	ND - 0.039	0.021	ND - 0.032	0.018	<u>0.011</u> - 0.030	-	ND

Indication of italic and under bar is value of under the determination limit. *: Mean, minimum and maximum of five samples. **: Not detectable. Not detectable cases were assumed to be zero for calculation of mean.

shows a high concentration in particles $<PM_{1.0}$. Cl^- exhibits a low concentration in $PM_{2.5} - PM_{1.0}$ particles. NO_2^- concentration do not differ with particle size. SO_4^{2-} and NH_4^+ are similar in the winter period samples. Comparing the arithmetic means of ionic species concentrations in the $>PM_{1.0}$, $PM_{10} - PM_{2.5}$, $PM_{2.5} - PM_{1.0}$ and $<PM_{1.0}$ particles for the winter and summer periods, like the elements, the ionic species concentrations in the summer period samples are a little higher than the ionic species concentrations in the winter period samples.

From elemental ionic species analysis results of the size-resolved PM samples, in the winter period, it is suggested that soil and sea-salt particles from PM_{10} to $PM_{2.5}$ in size and ammonium sulfate particles, *i.e.*, secondary-formed particles $<PM_{1.0}$, have been transported to Japan from the continent. On the other hand, in the summer period, it is suggested that PM was formed from soil and sea-salt particles $>PM_{10}$ to $PM_{2.5}$ in size and secondary-formed particles $<PM_{1.0}$. The existent forms of chemical components in aerosol particles in a mountainous region will be an important factor when we consider the origin of air pollutants transported over long distances in Northeast Asian regions. Moreover, the chemical data in aerosol particles in a mountainous region will be important when judging aerosol particles in large cities or their environs.

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