

Inorganic Constituents in Snow Accompanied by Winter Wind and their Origin in the Hokuriku Districts

Hideharu Honoki,^{*,a} Katsutoshi Tsushima,^b and Kazuichi Hayakawa^c

^aToyama Science Museum, 1–8–31 Nishinakano-machi, Toyama 939–8084, Japan, ^bThe Faculty of Science, Toyama University, 3190 Gofuku, Toyama 930–8555, Japan, and ^cFaculty of Pharmaceutical Sciences, Kanazawa University, 13–1 Takara-machi, Kanazawa 920–0934, Japan

(Received August 6, 2001; Accepted August 23, 2001)

The ion constituents contained in fresh snow immediately after snowfall were examined at 5–10 km intervals over 50 km from the coast of Hakui city in Ishikawa Prefecture leeward of the northwestern seasonal wind to the plain in Toyama city in Toyama Prefecture. The concentrations of sodium ions and sea-salt sulfate ions that originated from the Sea of Japan decreased exponentially from Hakui city in Ishikawa Prefecture to Toyama city. The concentration of non sea-salt sulfate ions, which probably originate from human activities, also decreased exponentially, but it was lower than the concentration of sea-salt sulfate ions until 25 km from Hakui city and higher in the farther regions. We considered that this was due to additive effects of non sea-salt sulfate ions transported from a distance and local sulfate ions. The concentration of non sea-salt sulfate ions transported from the Asian Continent was estimated in each sampling station. Its contribution was 0.98 of the total at the coast of Hakui city and 0.65 at Toyama city, respectively, and showed a pattern similar to those of sodium ions and sea-salt sulfate ions. The concentrations of ammonium ions and non sea-salt calcium ions were slightly higher in the plain in Toyama than on the coast of Hakui city, suggesting that they mostly originated from the sampling regions in this study. The concentration of nitrate ions was almost constant in the regions from the coast to the inland areas, suggesting also that they mostly originated from the sampling regions.

Key words — acid snow, sulfate ion, nitrate ion, ammonium ion, calcium ion, domestic origin

INTRODUCTION

Damage to the environment and the ecological system by acid rain includes destruction of forests and acidification of soils.^{1–4} Although acid rain was often observed in Europe, North America and East Asia, the damage has been reduced recently in Europe and North America by declining emission of sulfur oxides.^{5,6}

The nation-wide survey performed in Japan between 1983 and 1987 revealed that acid rain was observed in major cities.¹ It was later found that the deposition of non sea-salt sulfate ions in the districts along the Sea of Japan, mainly in the Hokuriku districts, was the highest in winter.^{7,8} Kitamura⁹ studied the deposit of non sea-salt sulfate ions using a sulfur isotope, and reported that the deposits in win-

ter in Kanazawa city in Ishikawa Prefecture were transported from regions of the north of the Chang Jiang River. Uno *et al.* reported the long-distance transportation and transformation of acidic compounds over the East Asia.¹⁰

Thus, most studies on acid rain in the districts along the Sea of Japan have focused on the transportation and deposition of substances from the Asian Continent. However, Ohizumi¹¹ suggested that only 20% of the deposition of sulfur in winter in Nagaoka city in Niigata Prefecture originated from coal combustion in the Asian Continent. Fujita^{8,12} tried to estimate the balance of sulfur oxides and nitrate ions in all regions of Japan including the Hokuriku districts. In the Hokuriku districts, the regions with heavy snowfall in winter extend up to 100 km from the coastline leeward of the seasonal wind to the mountainous regions, but it remains unknown how large the effects of substances from the Asian Continent are and how far they extend. Furthermore, the effects of substances originating in

*To whom correspondence should be addressed: Toyama Science Museum, 1–8–31 Nishinakano-machi, Toyama 939–8084, Japan. Tel.: +81-76-491-2123; Fax: +81-76-421-5950; E-mail: honoki@tsm.toyama.toyama.jp

local regions have not been evaluated. To evaluate the substances transported by the seasonal wind to the Hokuriku districts, it is necessary to examine the changes in their concentrations along the seasonal wind, as is often performed in studies of rivers, but such studies have not been made, except for sea-salt chloride ions.¹³⁾

In this study, we collected snow samples at several sampling stations from the northwest to the southeast in the Hokuriku districts along the direction of seasonal wind characteristic to these districts, and evaluated the origins of sea-salt constituents as well as acid and neutralizing substances by examining the relationship between their concentrations and the distance from the starting point on the coast in Hakui city.

MATERIALS AND METHODS

Sampling — Hakui city in Ishikawa Prefecture is located upstream of Toyama city in Toyama Prefecture on the northwestern seasonal wind characteristic to the Hokuriku districts in winter. Sampling stations were determined in parks, parking areas and Toyama city branch offices at 5–10 km intervals on a 52 km northwest-southeast line from the coast of Hakui city to the plain in Toyama city. (Some sampling stations differed depending on the investigation year.) All sampling stations, except for a mountain summit (altitude, 180 m) were in the plain at altitudes lower than 100 m (Fig. 1).

Before the seasonal wind blows, there is generally a rainfall due to the passing of a depression or a front in the Hokuriku districts. Such precipitates were considered to contain a large amount of various domestic pollutants including those originating in the local regions because of the direction of air movement, and because the change in the weather often caused rain. To minimize the effects, only fresh snow samples were used in this investigation. Sampling was performed on 4 February 1995, 3, 8 and 10 February 1996, 30 January and 4 February 1997, 9 January 1999, and 21 January, 16 February, and 8 March 2000 (total, 10 times).

Fresh snow was collected from the superficial layer to the deepest layer using an acrylic pipe or a pallet, the volume was measured, and the samples put into polyethylene bags were taken to the laboratory of the Toyama Science Museum.

Analysis — After measuring the weight of samples, they were melted at room temperature and

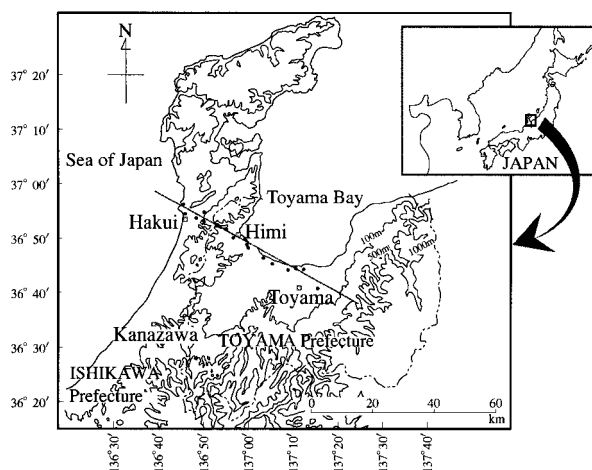


Fig. 1. Location of Sampling Station

filtered with a 0.45 μm membrane filter. pH of the filtrate was measured using a D-14 pH meter (Horiba, Tokyo, Japan), and the electrical conductivity was measured using an ES-14 conductivity meter (Horiba, Japan). The ion constituents were analyzed by ion chromatography (non-suppressor type, Shimadzu, Kyoto, Japan). The columns used were IC-C2 for analysis of cations and IC-C3 for anions, which were kept at 40°C. As the cation eluent, a mixture of 1.0 mM pyridine-2,6-dicarboxylic acid and 5.0 mM L-tartaric acid was used at a flow rate of 1.0 ml/min, and a mixture of 8.0 mM *p*-hydroxybenzoic acid, 3.2 mM tris(hydroxymethyl) aminomethane, and 50.0 mM boric acid was used at a flow rate of 1.2 ml/min for the anion eluent. To analyze the anions, 761 Compaq ion chromatographic apparatus (suppressor type, Metrome Inc., Herisau, Switzerland) was also used with an IC anion column (Star-Ion A300). As the eluent, a mixture of 2.4 mM sodium bicarbonate and 2.5 mM sodium carbonate was used at a flow rate of 0.8 ml/min.

The concentration (equivalent concentration) of sea-salt sulfate ions was determined by multiplying the concentration (equivalent concentration) of sodium ions by the equivalent concentration ratio of $\text{SO}_4^{2-}/\text{Na}^+$ in sea water (0.120). The concentration (equivalent concentration) of non sea-salt sulfate ions was determined by subtracting the concentration of sea-salt sulfate ions from that of total sulfate ions. The concentration of non sea-salt calcium ions was determined by the method similar to the determination of the concentration of non sea-salt sulfate ions ($\text{Ca}^{2+}/\text{Na}^+$ equivalent concentration ratio, 0.043). The mean concentration of each kind of ions at each sam-

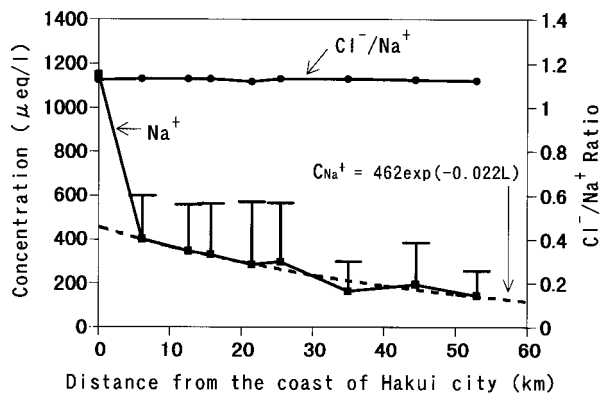


Fig. 2. Spatial Profiles of Sodium Ion Concentration and Cl^-/Na^+ Ratio in Snow

Each plot and vertical bar indicate the mean value and S.D., respectively of five to ten samples.

pling station was calculated by loading with the precipitation.

RESULTS AND DISCUSSION

Concentration Profile of Sodium Ions

Figure 2 shows the changes in the concentration of sodium ions with the distance from the coast of Hakui city. The concentration of sodium ions in fresh snow decreased with the increase in the distance from the coast of Hakui city as reported in the previous study,¹³⁾ and the following regression Eq. 1 was obtained from the measurements of the samples, except for the one collected at the coast of Hakui city.

$$C_{\text{Na}^+} = 462 \exp(-0.022L) (R = 0.96), \quad (1)$$

where C_{Na^+} denotes the concentration of sodium ions in snow at L km from the coast of Hakui city. According to the equation, the concentration of sodium ion in snow at the coast of Hakui city was $462 \mu\text{eq/l}$, and the decrease coefficient was -0.022 . The actual concentration of sodium ions in snow at the coast of Hakui city ($1153 \mu\text{eq/l}$) was much higher than the value obtained using Eq. 1 (Fig. 2), probably because sea-salt aerosol and a spray of sea water directly reached the sampling station. Therefore, the measurement at the coast of Hakui city was not used for the determination of Eq. 1.

Figure 2 also shows the changes in the concentration ratio of chloride ions to sodium ions in snow with the distance from the coast of Hakui city. The ratio (mean, 1.13) was almost the same as that in sea water (1.17) irrespective of the distance from the coast of Hakui city.

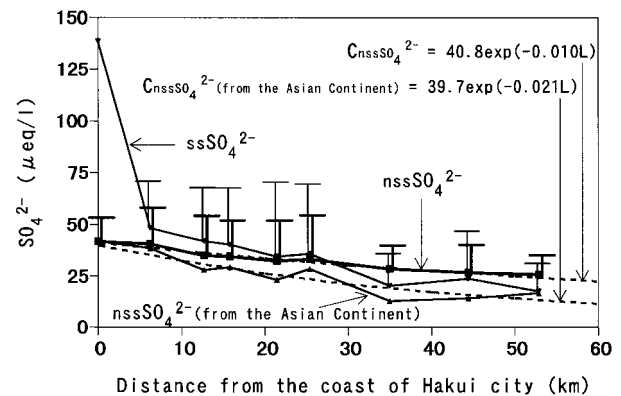


Fig. 3. Spatial Profiles of Sea-Salt and Non Sea-Salt Sulfate Ions

Each plot and vertical bar indicate the mean value and S.D., respectively of five to ten samples.

These findings indicated that sea-salt constituents were transported from Hakui city in Ishikawa Prefecture leeward of the northwestern seasonal wind to Toyama city, and that although the concentrations decreased the ratio was maintained.

Some of the sampling stations in Toyama Prefecture were located near the coast of Toyama Bay (the nearest one was at 0.2 km up to the coast.) as shown in Fig. 1. However, no effects of sea salt originating from Toyama Bay were observed on the graph (Fig. 2). The direction of wind in winter on Toyama Plain is strongly affected by the landforms. Even though there is a sky-originating northwestern seasonal wind, the south wind from the land to Toyama Bay predominates.^{14,15)} The height of the boundary between the land-originating south wind and the sky-originating northwestern seasonal wind sometimes reaches several hundred meters.^{14,16)} Therefore, it was considered that sea salt in Toyama Bay was not transported to the plain with snow.

Concentration Profiles of Sea-Salt Sulfate Ions, Non Sea-Salt Sulfate Ions and Nitrate Ions

Figure 3 shows the changes in the concentrations of sea-salt sulfate ions originating from the Sea of Japan, non sea-salt sulfate ions, which probably originate from human activities, with the distance from the coast of Hakui city in Ishikawa Prefecture. Concentrations of sea-salt sulfate ions and non sea-salt sulfate ions at the coast of Hakui city were $55.4 \mu\text{eq/l}$ and $41.5 \mu\text{eq/l}$, respectively and these concentrations decreased to $17.3 \mu\text{eq/l}$ and $25.5 \mu\text{eq/l}$, respectively, at Toyama city. The changes in the concentration of sea-salt sulfate ions showed a pattern similar to those of sodium ions.

The concentration of non sea-salt sulfate ions, similar to that of sodium ions and sea-salt sulfate ions, decreased exponentially from the coast of Hakui city leeward of the northwestern seasonal wind, and the following regression Eq. 2 was obtained.

$$C_{\text{nssSO}_4^{2-}} = 40.8 \exp(-0.01L) (R = 0.98), \quad (2)$$

where $C_{\text{nssSO}_4^{2-}}$ denotes the concentration of non sea-salt sulfate ions in snow at L km from the coast of Hakui city. The decrease coefficient of non sea-salt sulfate ions was -0.01 , but it was $1/2$ that of sodium ions and sea-salt sulfate ions according to Eqs. 1 and 2.

Therefore, the concentration of non sea-salt sulfate ions was lower than that of sea-salt sulfate ions up to 25 km from the coast of Hakui city, but higher on the farther lee side (Fig. 3).

Unlike the concentrations of non sea-salt sulfate ions, sea-salt sulfate ions and sodium ions, the concentration of nitrate ions was almost constant in the regions from the coast of Hakui city leeward to the plain in Toyama city (the concentrations of nitrate ions at the coast of Hakui city and at Toyama city were $7.0 \mu\text{eq/l}$ and $6.9 \mu\text{eq/l}$, respectively), except for one sampling station near a manufacturing area at 35 km (Fig. 4).

Assessment of the Concentration of Acid Substances Originating from the Asian Continent

Acid substances contained in snow in winter in the Hokuriku districts are divided into 2 groups: one is transported from the Asian Continent by the northwestern seasonal wind, and the other originates from Japanese areas including the Hokuriku districts. The exponential decrease in the concentration of non sea-salt sulfate ions depending on the distance from the coast of Hakui city (Fig. 3) indicated that the non sea-salt sulfate ions were contained in the seasonal wind when it reached the coast of Hakui city, suggesting that a large quantity of sulfur oxides originated from the Asian Continent. On the other hand, the concentration of nitrate ions in snow was almost constant irrespective of the sampling station (Fig. 4), suggesting that a large quantity of nitrate ions originated from the local regions. The leeward elevation of the ratio $\text{NO}_3^-/(\text{NO}_3^- + \text{nssSO}_4^{2-})$ up to 35 km (Fig. 4) was considered to be caused by elevation of the relative contribution of domestic acid substances (nitrate ions and non sea-salt sulfate ions) captured by snow due to the leeward decrease in acid substances (mainly sulfate ions) originating from the

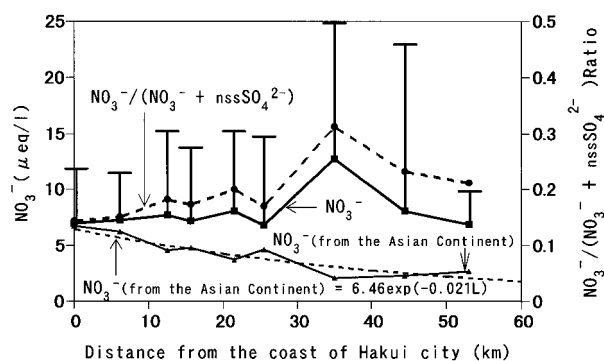


Fig. 4. Spatial Profiles of Nitrate Ion and $\text{NO}_3^-/(\text{NO}_3^- + \text{nssSO}_4^{2-})$ Ratio Value

Each plot and vertical bar indicate the mean value and S.D., respectively of five to ten samples.

Asian Continent.

The concentrations of non sea-salt sulfate ions and nitrate ions originating from the Asian Continent were estimated from the ratio $\text{NO}_3^-/(\text{NO}_3^- + \text{nssSO}_4^{2-})$ at each sampling station (Fig. 4) using the following methods, respectively (Figs. 3 and 4, respectively).

If the concentration of non sea-salt sulfate ions in snow is T_s ($\mu\text{eq/l}$) of which the fraction originating from the Asian Continent is x , the concentration of domestic non sea-salt sulfate ions is $T_s - x$. If the concentration of nitrate ions in snow is T_n ($\mu\text{eq/l}$) of which the fraction originating from the Asian Continent is y , the concentration of domestic nitrate ions is $T_n - y$. If the ratio $\text{NO}_3^-/(\text{NO}_3^- + \text{nssSO}_4^{2-})$ of acid substances originating from the Asian Continent is $Rc1$ and that of domestic acid substances is $Rc2$, $Rc1 = y/(y + x)$ and $Rc2 = (T_n - y)/[(T_s - x) + (T_n - y)]$. Using these equations, x and y were determined.

$$x = \frac{Rc2(1 - Rc1)(T_s + T_n) - (1 - Rc1)T_n}{(Rc2 - Rc1)},$$

$$y = \frac{Rc1}{(1 - Rc1)}x \quad (3)$$

Here, the $Rc1$ value of acid substances originating from the Asian Continent was regarded as 0.14, which was determined using the samples collected on the coast of Hakui city. As the $Rc2$ value, the mean value (0.32) at the Toyama Science Museum in the Toyama city center in summer (April–September) for five years (1995–1999)^{17–19} was used, according to the previous study.¹¹ However, as the $Rc2$ value for a sampling station (35 km from the coast of Hakui city) where the ratio was very high, the mean value (0.41) obtained by measurement during the same summer period at an acid rain moni-

toring station in Toyama city²⁰⁾ was used, because the environmental conditions around the two stations were similar.

According to Eq. 3, the concentrations of non sea-salt sulfate ions originated from the Asian Continent at the coast of Hakui city and Toyama city were $40.6 \mu\text{eq/l}$ and $16.6 \mu\text{eq/l}$, respectively. The contribution of domestic sources increased from 0.02 (at the coast of Hakui city) to 0.35 (at Toyama city). On the other hand, the concentrations of nitrate ions originated from the Asian Continent at the coast of Hakui city and Toyama city were $6.6 \mu\text{eq/l}$ and $2.7 \mu\text{eq/l}$, respectively. The domestic sources increased from 0.06 (at the coast of Hakui city) to 0.61 (at Toyama city). The following regression Eqs. 4 and 5 were obtained.

$$C_{\text{nssSO}_4^{2-}} \text{ (originated from the Asian Continent)} \\ = 39.7 \exp(-0.021L) (R = 0.89) \quad (4)$$

$$C_{\text{NO}_3^-} \text{ (originated from the Asian Continent)} \\ = 6.46 \exp(-0.021L) (R = 0.89) \quad (5)$$

These curves were lower than the concentrations of sea-salt sulfate ions in all sampling stations (Fig. 3). The decrease coefficient of the regression equation in non sea-salt sulfate ions was 0.021, which was similar to that of sodium ions and sea-salt sulfate ions (0.022). The decrease coefficient of nitrate ions originating from the Asian Continent was also 0.021 (Fig. 4).

These results indicated that the concentrations of non sea-salt sulfate ions and nitrate ions originating from the Asian Continent decreased exponentially from the coast of Hakui city to Toyama city, and their decrease coefficients were considered to be similar to those of sea-salt constituents such as sodium ions and sea-salt sulfate ions.

Mean Concentration Profiles of Neutralizing Constituents

Figure 5 shows the changes in the concentrations of ammonium ions and non sea-salt calcium ions with the distance from the coast of Hakui city. The concentration of both constituents was slightly lower at the coast of Hakui city than that in the inland, although the deviation (standard deviation) of both constituents between the sampling stations was large. These results suggested that ammonium ions and non sea-salt calcium ions, like nitrate ions, in snow were not originated from the Asian Continent but mainly in Japan.

In conclusions, we sampled fresh snow imme-

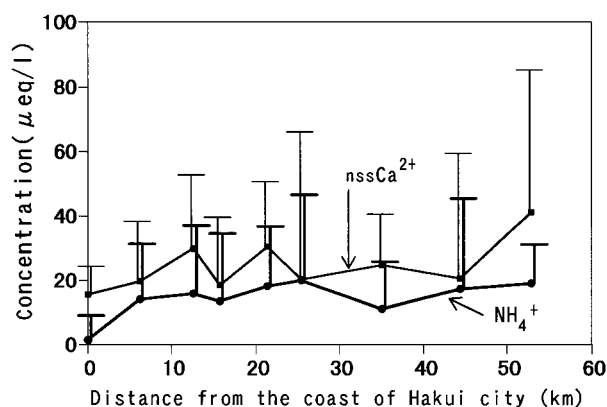


Fig. 5. Spatial Profiles of Ammonium Ion and Non Sea-Salt Calcium Ion

Each plot and vertical bar indicate the mean value and S.D., respectively of five to ten samples.

diately after it had fallen at 5–10 km intervals over 50 km from the coast of Hakui city in Ishikawa Prefecture leeward of the northwestern seasonal wind to the plain in Toyama city in Toyama Prefecture 10 times between 1995 and 2000, and examined non sea-salt sulfate ions, nitrate ions, ammonium ions and non sea-salt calcium ions in the snow samples. We considered that their origins were as follows.

- (1) The concentration of non sea-salt sulfate ions exponentially decreased. Of the non sea-salt sulfate ions, the concentration of non sea-salt sulfate ions originating from the Asian Continent decreased with a decrease coefficient similar to that of sea-salt sulfate ions and sodium ions.
- (2) With the exponential decrease in the concentration of non sea-salt sulfate ions originating from the Asian Continent, the concentration decreased from $41.6 \mu\text{eq/l}$ (at the coast of Hakui city) to $16.6 \mu\text{eq/l}$ (at Toyama city). Conversely, the contribution of domestic non sea-salt sulfate ions to the total concentration of non sea-salt sulfate ions gradually increased from 0.02 (at the coast of Hakui city) to 0.35 (at Toyama city).
- (3) There were no changes in the concentration of nitrate ions, suggesting that they originated in Japan.
- (4) The concentrations of ammonium ions and non sea-salt calcium ions were slightly high inland with a large deviation, suggesting that they mainly originated from Japan.

Acknowledgements A part of this research was financially supported by the Ministry of Education, Japan and Toyama Museum Association. The authors would like to thank Dr. Kentaro Murano, National

Institute for Environmental Studies for many helpful discussions, "Toyama's society for Snow" for their assistance in collecting snow samples and Ms. Sayoko Takahara for her assistance in drawing the figures.

REFERENCES

- 1) Murano, K. (1993) *Acid rain and acid fog*, Shokabo, Japan, pp. 1–6 (in Japanese).
- 2) Sato, K. (1999) Effect of acidic deposition on the soil and freshwater environments. *Jpn. Soc. Water Environ.*, **22**, 177–180 (in Japanese).
- 3) Izuta, T. (2001) Nitrogen saturation and its effect on trees of the ecological system of forests. *Jpn. Soc. Atmos. Environ.*, **36**, A1–A13 (in Japanese).
- 4) Aber, J. D., Nadelhoffer, K. J., Steudler, P. and Mellilo, J. M. (1989) Nitrogen saturation in northern forest ecosystems. *BioScience*, **39**, 378–386.
- 5) Stoddard, J. L., Jeffries, D. S., Liikewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., Forsius, M., Johannessen, M., Kahl, J. S., Kellogg, J. H., Kemp, A., Mannio, J., Monteith, D. T., Murdoch, P. S., Patrick, S., Rebsdorf, A., Skjelkvale, B. L., Stainton, M. P., Traaen, T., van Dam, H., Webster, K. E., Wieting, J. and Wilander, A. (1999) Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* (London), **401**, 575–578.
- 6) Lynch, J. A., Bowersox, van C. and Grimm, J. W. (2000) Acid rain reduced in eastern United States. *Environ. Sci. Technol.*, **34**, 940–949.
- 7) Zenkoken Working Group (1994) Report of the nation-wide survey of acid rain in 1992. *Zenkoku Kougaiken Kaishi*, **19**, 58–122 (in Japanese).
- 8) Fujita, S. (1996) An estimation for atmospheric sulfur budget over the Japanese archipelago. *Environ. Sci.*, **9**, 185–199 (in Japanese).
- 9) Kitamura, M., Sugiyama, M., Ohhashi, T. and Nakai, N. (1993) An estimation of origin of sulfate ion in rain water in view of sulfur isotopic variations. *Geochemistry*, **27**, 109–118 (in Japanese).
- 10) Uno, I., Ohara, T., Mori, A., Utsunomiya, A., Wakamatu, S. and Murano, K. (1997) Numerical analysis of long-range transport and transformation over the East Asia. *Jpn. Soc. Atmos. Environ.*, **32**, 267–285 (in Japanese).
- 11) Ohizumi, T., Fukuzaki, N. and Kusakabe, M. (1994) Contribution of various sulfur sources to atmospheric sulfate deposition in Niigata Prefecture, Japan. *Chem. Soc. Jpn., Chem. Ind. Chem.*, **1994**, 822–827 (in Japanese).
- 12) Fujita, S., Takahashi, A., Hayami, H. and Sakurai, T. (2000) Wet deposition of nitrate ion and ammonium ion over the Japanese Archipelago. *Environ. Sci.*, **13**, 491–501 (in Japanese).
- 13) Tsunogai, S. and Shinagawa, T. (1977) Chemical components transported by winter monsoon. *Geochemistry*, **11**, 1–8 (in Japanese).
- 14) Toyama local meteorological observatory (1967) Report of winds in Toyama Prefecture. *Technical report of the Japan Meteorological Agency*, **58**, 62–73 (in Japanese).
- 15) Ishimori, S. (1984) Maritime Meteorology in Toyama Bay. *Research Studies of Toyama Mercantile Marine College*, **1984**, 135–148 (in Japanese).
- 16) Okubo, A. and Kurokawa, Y. (2000) Three-dimensional structure of shearlines with heavy snowfall and less visibility formed in the winter-type pressure-pattern in Toyama Prefecture. *Tenki*, **47**, 255–265 (in Japanese).
- 17) Honoki, H. (1996) Observation report of acid rain at Toyama Science Museum. 1991–1995. *Bulletin of the Toyama Science Museum*, **19**, 67–74 (in Japanese).
- 18) Honoki, H. (1999) Acid rain observation data at Toyama Science Museum (Jan. 1996–Mar. 1998). *Bulletin of the Toyama Science Museum*, **22**, 177–181 (in Japanese).
- 19) Honoki, H. (2000) Acid rain observation data (Apr. 1998–Mar. 2000). *Bulletin of the Toyama Science Museum*, **24**, 103–106 (in Japanese).
- 20) Toyama city report. 1996–2000. *Environmental data* (in Japanese).