Tellus (2003), 55B, 23–34
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TELLUS
ISSN 0280–6509

The wet deposition of acid and some major ions over the Japanese Archipelago

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(Manuscript received 16 July 2001; in final form 20 September 2002)

ABSTRACT

The wet deposition of acid and some major ions over the Japanese Archipelago was presented. The country was divided into 15 climatic regions with 114 grid squares, and the annual and seasonal fluxes of non-sea salt sulfate, nitrate, ammonium and non-sea salt calcium were estimated. Wet deposition fluxes were determined from CRIEPI's regional monitoring data at 21 sites between October 1987 and September 1990. The concentration of these ions in precipitation increased during the cold season, and this tendency was noted on the northwestern region facing the continent across the Japan Sea. Estimated wet deposition of [nss-SO_4^{2-}] + [NO_3^-], here defined as the acidic component (AC), was approximately 75 meq m^{-2} yr^{-1}, and that for [NH_4^+] + [nss-Ca^{2+}], here defined as the basic component (BC), was approximately 52 meq m^{-2} yr^{-1}. If the concentration difference of AC − BC was converted to the wet deposition of H^+, it was approximately 23 meq m^{-2} yr^{-1}, or the total deposition over the Japanese Archipelago was approximately 17 Geq yr^{-1}. For Japan as a whole, wet deposition of inferred H^+ in the warm season and the cold season accounted for 45% and 55%, respectively. In the warm season, the major receptor of acid was the climate regions facing the Pacific Ocean, while in the cold season it was the climate regions facing the Japan Sea. The wet deposition over the Japanese Archipelago was influenced by two factors: meteorological conditions such as the wind system and rainfall pattern due to Asian monsoons, and the geographical distribution of emission sources of chemical substances through natural and anthropogenic activities in East Asia. It was suggested that in-flow of chemical substances from outside the region plays an important role in the wet deposition field over the Japanese Archipelago.

1. Introduction

Acid deposition began to attract attention as a regional-scale environmental problem during the 1970s in Europe and eastern North America. More recently, this problem has also arisen in East Asia because of the significant increase in atmospheric emissions resulting from high economic and high population growth (Galloway et al., 1987). Nationwide monitoring networks were therefore established in Japan in the mid-1980s (Okita, 1983; Hara, 1993; Fujita et al., 2000). As a result, an important conclusion was obtained that the concentrations of sulfate and nitrate in precipitation are relatively high on the Japan Sea side in the winter season. The sources of precursors have been actively discussed using long-range transport models (Ichikawa and Fujita, 1995; Ikeda and Higashino, 1997; Ichikawa et al., 1998).

To study the effects of acid deposition on the terrestrial ecosystem, it is essential to evaluate the concentration and wet deposition of hydrogen ion (H^+) over the Japanese Archipelago. Generally, concentration of H^+ in precipitation is a result of the acid–base balance in the atmosphere. Major acids in East Asia were thought to be sulfuric acid and nitric acid, and major bases, ammonia and calcium salts, respectively

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(Hara, 1993; Fujita et al., 2000). However, few data obtained by systematic observations were available, and no quantitative analysis on the wet deposition of nss-SO_4^{2-}, NO_3^-, NH_4^+, nss-Ca^{2+} and H^+ over the Japanese Archipelago has been performed.

The Central Research Institute of the Electric Power Industry (CRIEPI) established in October 1987 a cooperative monitoring network for precipitation chemistry to survey acid deposition (Fujita, 1996). Using the data obtained, we analyzed the precipitation chemistry in East Asia and the seasonal and long-term trends in the chemical composition of precipitation, made estimations for atmospheric sulfur budget and developed a long-range transport model to estimate acid deposition over the Japanese Archipelago (Ichikawa and Fujita, 1995; Fujita, 1996; Fujita et al., 2000; Takahashi and Fujita, 2000; Fujita et al., 2001).

In this study, on the basis of the data collected between October 1987 and September 1990, a period in which intense monitoring was conducted in Japan, the wet depositions of acid and some major ions during the cold season (October to March) and the warm season (April to September) were analyzed.

2. Methods

Geographical factors and meteorological conditions over East Asia, in which the Japanese Archipelago is located, are extremely complex. The two important factors that affect the climates in this region are the wind system and the rainfall amount. The left-hand side of Fig. 1 shows the distribution of annual rainfall amount and the climate regions for Japan. There are two areas of heavy rainfall, the area facing the Japan Sea, and the area facing the Pacific Ocean. The origins of precipitation in these two areas, however, are different. In the coastal area facing the Japan Sea, snowfall in winter is important, while in the area facing the Pacific Ocean, low pressures with fronts passing over the southern coast bring heavy rainfall in spring and autumn.

In this study, as shown in the right-hand side of Fig. 1, the Japanese Archipelago was divided into 114 grid squares, and 15 climate regions (Saito, 1957) were superimposed. The wet depositions of ions were estimated for each of these grid squares and climate blocks, and all over the region. The horizontal scale

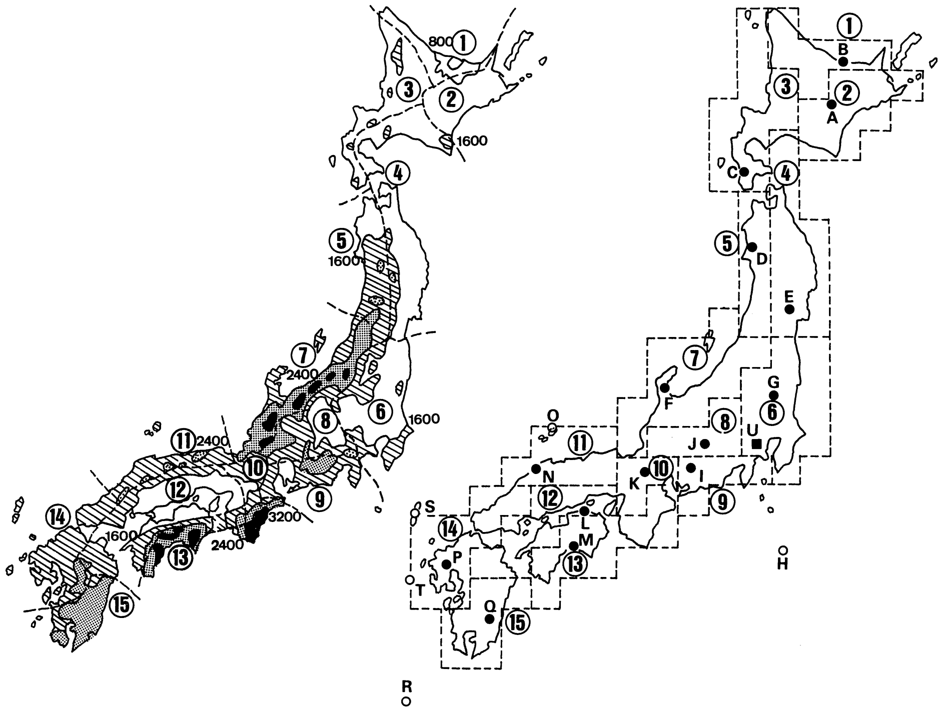

Fig. 1. Annual rainfall amount and climate regions for Japan (left) and climate blocks and mesh system used in the estimate of wet deposition of acid. Filled circles indicate climatological representative sites and clear circles indicate background sites of the CRIEPIs' monitoring network.

of each mesh grid is approximately 80 km × 80 km. This mesh system, a part of the region for the long-range transport model to estimate sulfur deposition in Japan (Ichikawa et al., 1998), includes the four major islands, Hokkaido, Honshu, Shikoku and Kyushu, but excludes the Kurile Islands and the southwestern islands. The total area of the mesh system is approximately 722 000 km^2, half of which is inland sea and coastal sea, and the other half land. Approximately 70% of the land area is covered with forest.

Precipitation chemistry monitoring was conducted at 21 sites during the period from October 1987 and September 1990 (Fujita, 1996). There were two types of sites in this monitoring network: climatological representative sites and background sites. For the former, one site was selected for each of the 15 climate regions based on certain criteria such as the topography, rainfall amount and distance from the major emission sources. For the latter, sites on five islands were selected from among those with manned land stations of the Japan Meteorological Agency near the major islands. An additional urban site (Komae/Tokyo) was sited in the climate region no. 6 (Kanto) to clarify the differences between chemical compositions of precipitation within the region.

Precipitation samples were collected at 10-day intervals using a wet-only sampler with 155 mm aperture. The samplers were set 1.5–2.0 m from the ground surface. The samples were stored in a 5 L polyethylene bottle in the sampler without preservatives. For measurement of the rainfall amount, tipping bucket rain gauges were used. Immediately after sampling, the samples were shipped to CRIEPI Tokyo laboratory for chemical analysis. The analytical parameters included pH, conductivity, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^- and Cl^-. For conductivity and pH measurements, samples were analyzed without pretreatment. For other parameters, samples were filtered through a Milipore filter with a pore size of 0.45 μm before analysis.

The accuracy of the data obtained for each parameter was confirmed using two indices, the ratio of total anion (TA) to total cation (TC) and the ratio of measured conductivity (ECobs) to calculated conductivity (ECcal), based on the method proposed by Miles and Yost (1982). Screening was performed using a graph on which the values of TA/TC and ECobs/ECcal were plotted; the data satisfying the condition that the deviations of both index values were ±20% within unity were identified. In addition, samples for dry or light rain periods, contamination with insects and foreign objects, and sampler failure were rejected. As a result, the percentage of valid samples for all sites (where the total number of 10-day samples collected at 21 sites during the 3-yr period was 2268) was 89.9%

To obtain estimates of wet depositions of ions over the terrestrial regions of Japan with available monitoring data, average concentrations for the climatological representative sites were multiplied by the average rainfall for each 80 km × 80 km grid square. The 3-yr average concentrations of each ion were weighted for precipitation according to the formula:

$$C_i = \Sigma C_{ij} P_{ij} / \Sigma P_{ij} \qquad (1)$$

where C_i is the weighted concentration of ions for site i, C_{ij} the concentration for site i and sampling period j, and P_{ij} the corresponding rainwater volume measured with the rain gauge at the site.

The 3-yr average rainfall for each grid square was calculated using the weather records at the 151 weather stations in Japan. The 30-yr period average rainfall was determined using the climatic table for 1961–1990. Rainfall amounts of each grid square were weighted by multiplying the inverse square of the distances from the center point of the grid to the three nearest weather stations.

3. Meteorological conditions

Figure 2 shows the ratio of annual rainfall amount of each year to that of the climate value (30-yr average) for each grid square. The rainfall amount changed year by year. When data for various regions were accumulated, little rain on the Japan Sea side and much rain on the Pacific Ocean side were canceled out, and the 3-yr average rainfall amount (1691 mm yr^{-1}) was similar to the climate value (1683 mm yr^{-1}). However, the total precipitation over the four climate regions of nos. 3, 5, 7 and 14 on the Japan Sea side was approximately 9% less than that of the climate value. In contrast, the total precipitation over the four climate regions of nos. 6, 9, 13 and 15 on the Pacific Ocean side was approximately 7% greater than that of the climate value. There was no substantial yearly difference between the annual rainfall amount in each climate region.

During the monitoring period, eruptions occurred at 10 active volcanoes in Japan. Sakurajima volcano, which lies in climate region no. 15 (S. Kyushu), may have emitted approximately 11 Gmol yr^{-1} SO_2, an amount almost equal to the total emissions of SO_2

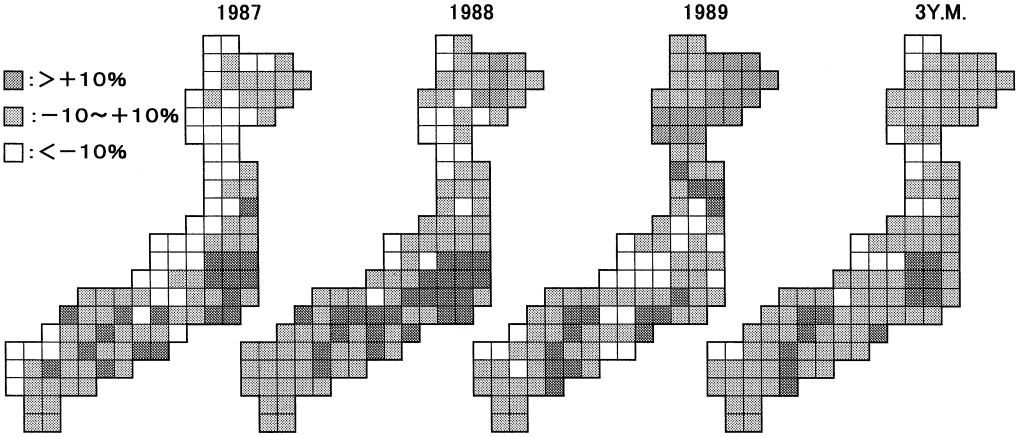

Fig. 2. The ratio of amount of annual rainfall each year to that of the climate value (30-yr average) for each grid square.

from all stationary sources in Japan (Fujita et al., 1992).

The yellow sand phenomenon, namely transport of basic dust particles from the Asian continent, was observed in Japan on 23 and 29 January, 6 February, and 14 and 21 April 1988; 15–16 March and 2 and 4 April 1989; and 12–14 February, 5–6, 10 and 15 March and 9 May 1990. In particular, the phenomenon observed on 14 April 1988 and 15–16 March 1989 extended over most of western Japan.

4. Results

Table 1 lists the average concentration of ions in precipitation, weighted with the rainfall amount in the respective period for 21 sites. Annual average concentrations and coefficient of variations (standard deviation/average concentration) for all sites are also listed in the lower column. As shown in Table 1, the variations for sites were large for Cl^-, Na^+ and Mg^{2+} (>0.80), intermediate for Ca^{2+}, K^+ and H^+ (0.40–0.56), and low for NH_4^+, NO_3^- and SO_4^{2-} (<0.36) almost similar to that of rainfall amount (0.33).

When the origin of ions in precipitation was estimated using sodium as an index of sea salts, the ratio of sea salts to non-sea salts (ss/nss) differed significantly between monitoring sites. At sites on the inland area such as Otofuke, Inabu and Ohmi-Hachiman, less than 30% of ions originated from sea salts. In contrast, at sites on the small island such as Hachijo and Amami, more than 85% of ions originated from sea salts. For all over the terrestrial regions of Japan, approximately 65% of ions originated from sea salt and approximately 35% of ions originated from non-sea salts. The percentage of each ion for non-sea salt ions were nss-SO_4^{2-}, 33.5%; NO_3^-, 14.1%; nss-Ca^{2+}, 11.6%; NH_4^+, 20.1%; nss-K^+, 1.8%; and nss-Mg^{2+}, 2.5%, respectively. Contributions of nss-K^+ and nss-Mg^{2+} were relatively small compared with the other four ions, nss-SO_4^{2-}, NO_3^-, nss-Ca^{2+} and NH_4^+. The annual average ratio for NO_3^-/NH_4^+ (No/Nr) was approximately 0.78, and that for NO_3^-/nss-SO_4^{2-} (N/nssS) approximately 0.41, respectively.

If the four major ions cited above determined the hydrogen ion concentration, the acid–base concentration difference $([\text{nss-}SO_4^{2-}] + [NO_3^-]) - ([\text{nss-}Ca^{2+}] + [NH_4^+])$ is expected to be virtually equal to the hydrogen concentration $[H^+]$. Tsuruta (1989) defined the value of $[\text{nss-}SO_4^{2-}] + [NO_3^-]$ as "acidifying potential" and the value of $[\text{nss-}Ca^{2+}] + [NH_4^+]$ as "neutralizing potential," and discussed the qualitative differences in precipitation between Japan, China and eastern North America. Here, the value of $[\text{nss-}SO_4^{2-}] + [NO_3^-]$ is identical to the "input acidity" defined by Morgan (1982). In this paper, we defined the value of $[\text{nss-}SO_4^{2-}] + [NO_3^-]$ as the "acidic component" (AC), and the value of $[\text{nss-}Ca^{2+}] + [NH_4^+]$ as the "basic component" (BC).

Figure 3 shows the relationship between concentrations of observed H^+ and inferred H^+ defined by $AC - BC$, at 21 sites during the observation period (total number of samples $= 2039$). Both quantities were therefore interpreted as indicating a good agreement and it follows that the acidity of precipitation might be determined from major four ions.

Table 1. *Average concentration of major ions in precipitation at each monitoring site during the period from October 1987 and September 1990*

Climate region		Site	Rainfall	H^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	AC	BC			
			mm yr^{-1}	μeq L^{-1}											ss/nss	No/Nr	N/nssS
① NE. Hokkaido	B	Tokoro	1029	7.6	188.2	7.2	41.8	25.9	17.6	272.3	8.9	53.9	40.2	35.2	6.39	0.51	0.28
② SE. Hokkaido	A	Otofuke	1146	8.2	11.5	2.1	3.8	12.3	14.2	12.3	12.1	23.8	34.6	26.1	0.40	0.85	0.54
③ W. Hokkaido	C	Otobe	1265	10.2	178.9	8.0	46.6	35.7	16.9	245.8	14.4	63.8	56.7	44.8	4.12	0.86	0.34
④ E. Tohoku	E	Takashimizu	1287	11.6	24.1	2.3	7.0	8.5	20.6	28.9	14.0	28.3	39.5	28.1	0.77	0.68	0.55
⑤ W. Tohoku	D	Noshiro	1632	13.2	162.6	6.9	41.8	27.4	18.3	226.0	15.0	62.7	58.1	38.5	3.89	0.82	0.35
⑥ Kanto	G	Shiobara	1627	12.7	14.0	2.2	4.5	6.9	27.3	17.3	18.1	28.8	45.3	33.6	0.39	0.66	0.67
⑦ Hokuriku	F	Kashima	2158	19.7	107.4	4.5	28.3	16.0	16.6	138.6	14.5	50.8	52.4	27.9	2.75	0.88	0.38
⑧ Tosan	J	Komagane	1653	8.5	7.1	2.0	3.4	10.4	15.7	7.6	11.3	21.5	32.0	25.8	0.25	0.72	0.55
⑨ Tokai	I	Inabu	1872	32.3	20.8	2.4	6.7	11.8	27.9	35.1	24.7	42.0	64.2	38.8	0.46	0.89	0.62
⑩ Kinki	K	Ohmi-Hachimann	1635	20.4	22.1	2.7	6.0	8.0	16.8	25.8	15.5	32.6	45.4	23.9	0.62	0.92	0.52
⑪ San-in	N	Izumo	1821	16.5	74.0	4.0	20.2	14.1	24.6	98.3	13.6	47.7	52.5	35.4	1.85	0.55	0.35
⑫ Setouchi	L	Takamatsu	1551	25.0	35.1	2.8	9.8	10.0	20.8	42.3	16.6	40.1	52.4	29.3	0.83	0.80	0.46
⑬ Nankai	M	Nangoku	2583	16.2	26.4	2.8	7.1	5.5	7.4	33.1	7.6	25.5	29.9	11.8	1.16	1.03	0.34
⑭ N. Kyushu	P	Taku	1900	21.6	28.1	3.0	8.5	9.4	25.5	38.2	10.9	45.3	52.8	33.7	0.69	0.43	0.26
⑮ S. Kyushu	Q	Takaoka	2430	14.5	26.8	2.5	7.4	7.1	19.1	39.8	6.6	30.3	33.7	25.0	1.02	0.35	0.24
	H	Hachijo	3262	11.8	161.7	5.8	42.2	14.3	5.3	226.8	7.5	38.7	26.7	12.6	7.83	1.42	0.39
	O	Oki	1890	18.3	111.4	5.3	30.2	14.6	13.7	145.6	13.0	47.8	47.3	23.5	3.15	0.94	0.38
	R	Amami	3051	11.5	124.1	7.0	32.0	10.0	7.3	166.7	6.5	34.0	25.6	12.0	6.05	0.88	0.34
	S	Tsushima	2178	11.9	51.8	4.0	15.6	22.1	16.3	63.5	11.6	40.4	45.8	36.2	1.36	0.71	0.34
	T	Fukue	2362	17.2	60.8	3.7	16.4	11.1	14.0	78.2	9.4	37.7	39.9	22.5	1.95	0.67	0.31
	U	Komae/Tokyo	1460	32.3	20.8	2.4	6.7	11.8	27.9	35.1	24.7	42.0	64.2	38.8	0.46	0.89	0.62
		Average	1691	15.4	71.8	4.1	19.0	14.1	17.3	97.1	12.6	39.8	43.7	28.2	2.21	0.78	0.41
		Variation	0.33	0.40	0.86	0.48	0.80	0.56	0.36	0.90	0.35	0.31	0.25	0.32			

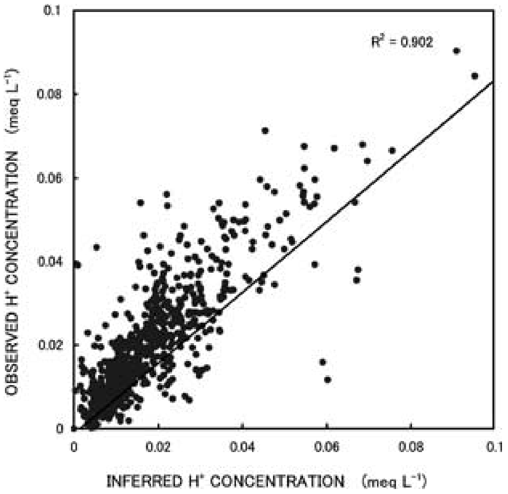

Fig. 3. Relationship between concentrations of observed and inferred H^+ in precipitation at 21 sites in Japan.

Figure 4 shows the 3-yr average wet depositions of nss-SO_4^{2-}, NO_3^-, NH_4^+, nss-Ca^{2+} and inferred H^+ for the annual average (upper chart), for the cold season (middle chart) and for the warm season (lower chart), respectively. The wet deposition of nss-SO_4^{2-} was high on the Japan Sea side centering on climate region no. 7 (Hokuriku) during the cold season and in western Japan centering on climate region no. 14 (N. E. Kyushu) during the warm season. For Japan as a whole, the wet deposition of nss-SO_4^{2-} in the warm season accounted for 50% of the total, and in the cold season, for 50%.

The wet deposition of NO_3^- was high on the Japan Sea side centering on climate region no. 7 (Hokuriku) during the cold season and on climate region no. 6 (Kanto) during the warm season. For Japan as a whole, the wet deposition of NO_3^- in the warm season accounted for 47% of the total, and in the cold season, for 53%. The increase in the wet deposition of NO_3^-, which was on the Japan Sea side during the cold season, had the same tendency as that of nss-SO_4^{2-}.

The wet deposition of NH_4^+ was high in climate regions nos. 7 (Hokuriku) and 11 (San-in) on the Japan Sea side during the cold season and in western Japan centering on climate regions nos. 14 (NW. Kyushu) and 6 (Kanto) during the warm season. For Japan as a whole, the wet deposition of NH_4^+ in the warm season accounted for 60% of the total, and in the cold season, for 40%. The percentage of deposition during the warm season was relatively high compared with that of other ions.

The wet deposition of nss-Ca^{2+} was high on the Japan Sea side centering on climate region no. 1 (W. Hokkaido) during the cold season, and was low on the Pacific Ocean side throughout the year. For Japan as a whole, the wet deposition of nss-Ca^{2+} in the warm season accounts for 43% of the total, and in the cold season, for 57%. The percentage of deposition during the cold season was relatively high compared with that of other ions. The center of the wet deposition was distributed to the north compared to those of nss-SO_4^{2-} and NO_3^-, which suggested that the origin and history of nss-Ca^{2+} and of nss-SO_4^{2-} and NO_3^- may not necessarily be the same.

From the above results, the wet deposition of inferred H^+ showed two distribution peaks, one on the Japan Sea side centering on climate region no. 7 (Hokuriku) in the cold season and the other on the Pacific Ocean side centering on climate regions nos. 9 (Tokai) and 13 (Nankai) in the warm season. For Japan as a whole, the wet deposition of H^+ in the cold season accounted for 55% of the total, and in the warm season, for 41%.

On the basis of the above analytical results, wet depositions of major ions over the terrestrial area of the Japanese Archipelago were calculated. As shown in Table 2, the estimated wet depositions for the 3-yr average rainfall amount were: nss-SO_4^{2-}, 54 meq m^{-2} yr^{-1}; NO_3^-, 21 meq m^{-2} yr^{-1}; NH_4^+, 34 meq m^{-2} yr^{-1}; and nss-Ca^{2+}, 19 meq m^{-2} yr^{-1}, respectively. Accordingly, the wet deposition of AC was approximately 75 meq m^{-2} yr^{-1} and that for BC, 52 meq m^{-2} yr^{-1}; if the difference was converted into the wet deposition of H^+, it was inferred as approximately 23 meq m^{-2} yr^{-1}. For the land area, maximum deposition of H^+ was revealed at climate region no. 7 (Hokuriku) and that of the second, at climate region no. 13 (Nankai). For the ocean area, maximum deposition of inferred H^+ was observed at Hachijo and that of the second, at Amami in the Pacific Ocean. Although the values of AC on these islands were low, values of BC were lower. These islands receive more than 3000 mm of rainfall per year. Therefore, for Hachijo and Amami, located more than 1000 km from the major SO_2 and NO_x emission sources in East Asia, relatively high wet deposition of H^+ was observed throughout the year.

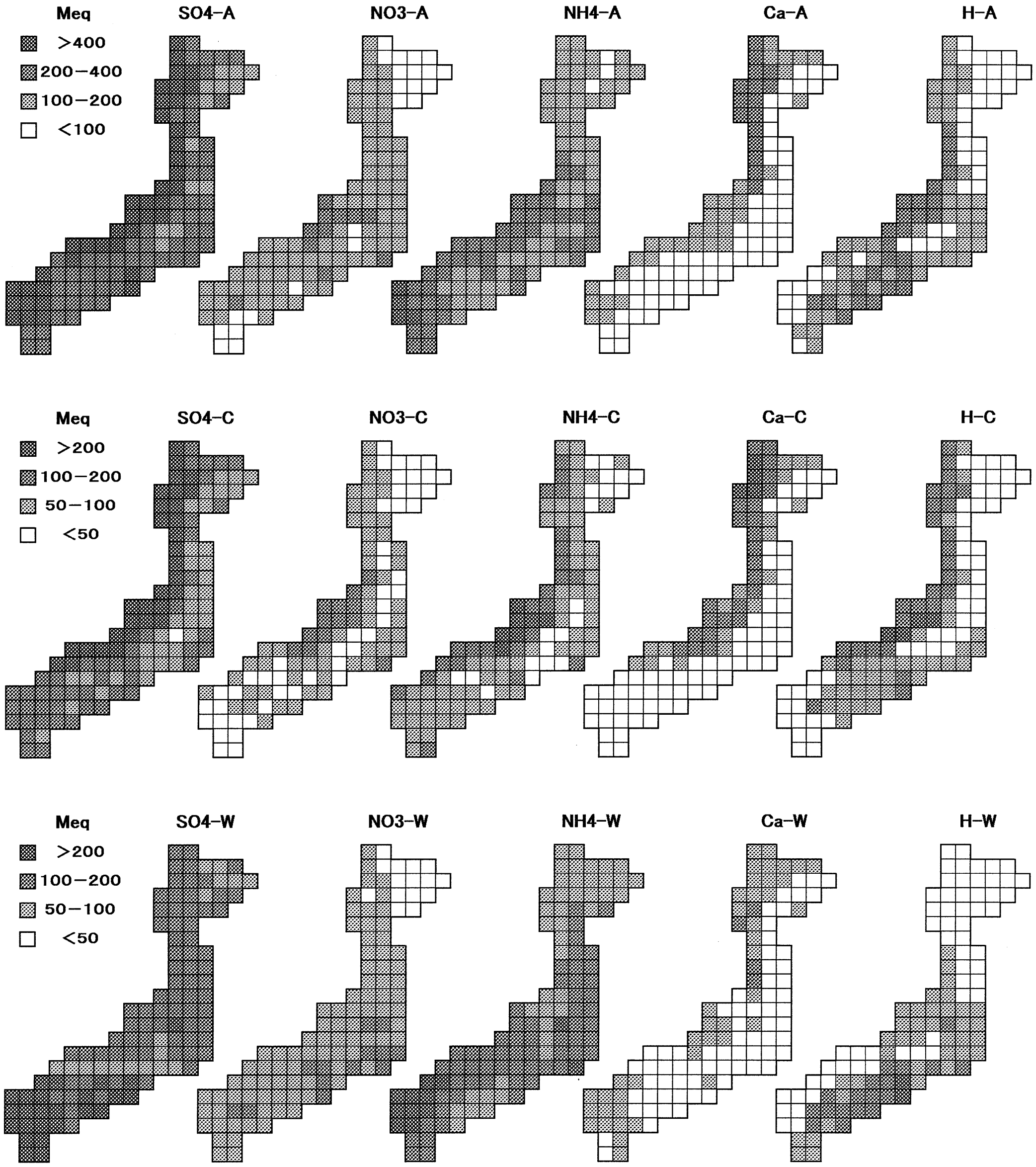

Fig. 4. Wet depositions of nss-SO_4^{2-}, NO_3^-, nss-Ca^{2+} and NH_4^+, and inferred H^+ per grid square during a period from October 1987 to September 1990. The upper charts indicate wet depositions for the annual average, the middle chart, for the cold season, and the lower chart, for the warm season.

WMO (1997) summarized precipitation concentration and deposition values for various regions of the globe using available monitoring data. Estimated median values of wet deposition for Europe and eastern North America were 15–30 mmol m^{-2} yr^{-1} for nss-SO_4^{2-}, 12–30 mmol m^{-2} yr^{-1} for NO_3^- and 11–35 mmol m^{-2} yr^{-1} for NH_4^+, respectively. Therefore, wet depositions of major ions over the Japanese Archipelago were on the same level as that observed in Europe and eastern North America.

Table 2. *Annual rainfall amount, wet deposition of nss-SO_4^{2-}, NO_3^-, nss-Ca^{2+} and NH_4^+, AC, BC and inferred H^+ over the Japanese Archipelago during the period from October 1987 and September 1990*

	Rainfall	Area	nss-SO_4^{2-}	NO_3^-	NH_4^+	nss-Ca^{2+}	AC	BC	H^+ inf
Climate region	mm yr^{-1}	10^9 km^2	meq m^{-2} yr^{-1}						
① NE. Hokkaido	1029	42.5	35.3	9.4	16.5	18.8	44.7	37.6	7.1
② SE. Hokkaido	1146	55.3	25.3	9.0	16.3	10.8	34.4	27.1	7.2
③ W. Hokkaido	1265	76.7	65.2	19.6	22.2	40.4	84.7	63.9	22.2
④ E. Tohoku	1287	72.5	33.1	17.9	27.6	12.4	51.0	40.0	12.4
⑤ W. Tohoku	1632	32.9	72.9	24.3	30.4	33.4	97.3	63.8	33.4
⑥ Kanto	1627	74.3	43.1	29.6	44.4	10.8	71.3	55.2	16.2
⑦ Hokuriku	2158	75.6	80.7	30.4	38.4	25.1	112.4	63.5	48.9
⑧ Tosan	1653	24.6	32.5	16.3	28.5	16.3	48.8	44.7	8.1
⑨ Tokai	1872	24.1	37.3	20.7	16.6	8.3	58.1	33.2	24.9
⑩ Kinki	1635	18.1	44.2	27.6	27.6	11.0	71.8	38.7	33.1
⑪ San-in	1821	42.9	69.9	25.6	51.3	18.6	93.2	69.9	23.3
⑫ Setouchi	1551	41.7	55.2	26.4	33.6	14.4	81.5	48.0	33.6
⑬ Nankai	2583	53.1	58.4	24.5	26.4	11.3	81.0	37.7	43.3
⑭ N. Kyushu	1900	53.2	73.3	18.8	63.9	16.9	94.0	82.7	11.3
⑮ S. Kyushu	2430	34.3	61.2	14.6	43.7	14.6	78.7	58.3	17.5
Annual	1691	721.8	54.0	21.3	33.5	18.7	75.4	52.4	23.0
Cold Season	628		26.9	10.0	13.4	10.7	36.9	24.2	12.6
Warm Season	1063		27.2	11.4	20.1	8.0	38.5	28.3	10.4

5. Discussion

As described above, the concentrations and wet depositions of nss-SO_4^{2-}, NO_3^-, NH_4^+, and nss-Ca^{2+} increase during the cold season. This tendency is found on the northwestern region of the central mountain range facing the continent across the Japan Sea. These features of temporal and spatial variations suggest that in-flow of chemical substances from outside the region plays an important rule in the wet deposition field of H^+ in Japan.

Many studies have been performed in order to analyze the chemical composition of precipitation in Japan (Kawaratani and Fujita, 1990; Yamaguchi et al., 1991; Tamaki and Koyama, 1991; Dokiya et al., 1995; Hara, 1993; Fujita et al., 2000). Studies conducted during the last decade suggest that concentrations of ions in precipitation are influenced mainly by two factors. The first is the meteorological conditions such as wind system and rainfall pattern due to Asian monsoons. The second factor is the geographical distribution of emission sources of chemical substances through natural and anthropogenic activities.

Figure 5 shows annual average rainfall amount (1988–1990) in East Asia and the positions of air mass 24 h before arrival at 850 hPa isobaric surface over Tsushima in the warm season and the cold season of 1990 (HYSPLIT4 Model, 1997). As shown in Fig. 5, the predominant wind system over Japan is different season by season. In the warm season, in which the subtropical high-pressure system over the Pacific is dominant, the predominant wind system over the site is southeasterly and southwesterly, from the Pacific Ocean and the East China Sea. In the cold season, the predominant wind system over the site is northwesterly from the Asian Continent. The run of wind during the period between December and February is particularly long.

A brief examination of precipitation over the land area reveals that the annual precipitation in East Asia tends to be high in the southeastern region and low in the northwestern region, excluding the northwest coast of Japan. With respect to seasonal changes, the monthly precipitation is generally high in summer under the warm humid air masses, and low in winter under the cold and dry air masses, excluding the northwest coast of Japan.

The origin of each chemical substance has not yet been clarified completely. However, on the basis of the information obtained to date, a brief distribution of these substances is as shown in Fig. 6 (Fujita et al., 2000). The emission source of basic dust is the desert and yellow ochre highland in the northwest of the continent (Ichikuni, 1978; Uematsu et al.,

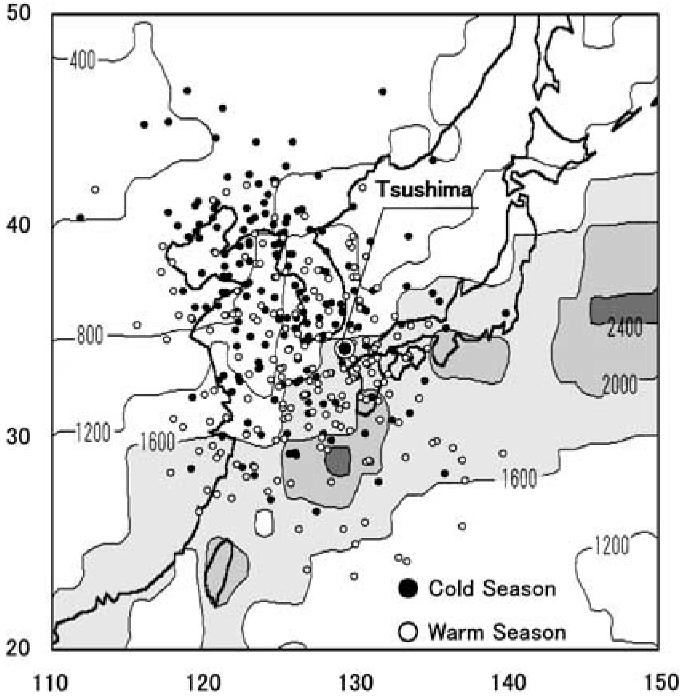

Fig. 5. Three-year average rainfall for East Asia (1988–1990) and the positions of air mass 24 h before arrival at a 850 hPa isobaric surface over Tsushima in the warm season (open circles) and the cold season (closed circles) of 1990.

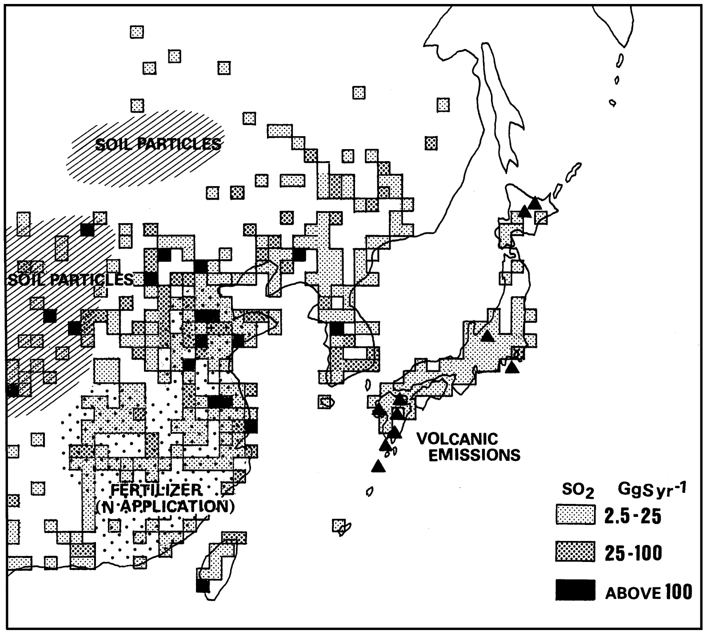

Fig. 6. Annual emission of anthropogenic sulfur dioxide per grid square as of 1990 superimposed on the geographical distribution of emission sources of volcanic sulfur, soil particles and ammonia in East Asia.

1983; Nishikawa et al., 1991; Hao, 1993). According to analyses for the dry region of the continent, atmospheric calcium exists mostly in the form of $CaCO_3$, or sometimes in the form of $CaSO_4$ (Hseung and Jackson, 1952; Okada and Kai, 1995). Calcium is also emitted into the atmosphere through production and combustion processes. Potential candidates would be $CaSO_4$ from desulfurization equipment and CaO from coal combustion. Emissions of calcium from cement factories in Beijing cannot be ignored (Hao, 1991). The effect of road pavement wear was significant in snowfall regions of Japan in the past (Noguchi et al., 1995). Although few data are available concerning the chemical form and emission of calcium in East Asia, as shown in Fig. 6, the major broad emission sources of nss-Ca^{2+} in precipitation are considered to be located in the dry region of the continent, the desert regions at latitude 40°N or higher and the yellow ochre plateaus at latitude 40°N or lower. This assumption should be evaluated by future quantitative discussion.

The major emission sources of ammonia are application of chemical fertilizer, livestock and energy consumption. The largest source in East Asia is the agricultural regions of southeastern China (Zhao and Wang, 1994; Murano et al., 1996). The annual emission of ammonia for the region covering China, Japan and South and North Korea is estimated to be approximately 814 Gmol yr^{-1} (Zao and Wang, 1994). On the other hand, annual emission of ammonia in Japan is estimated to be approximately 29 Gmol yr^{-1}; the greatest contribution, approximately 65% of the total, comes from the agricultural sector, while approximately 29% of the total is attributed to urban activities (Kannari et al., 2001).

The annual emission of SO_2 from fossil-fuel combustion in East Asia is estimated to be approximately 375 Gmol yr^{-1} (Fujita et al., 1991; Akimoto et. al., 1994). Although emission sources for SO_2 are distributed throughout the region, the emission rate in the coastal region near Bohai Bay and the Yellow Sea is particularly high. The annual emission of non-sea salt sulfur compounds in Japan is estimated to be approximately 32 Gmol yr^{-1}. The greatest contribution, approximately 50% of the total, comes from volcanic activity, while the contribution of stationary sources accounts for 34% of the total, mobile sources, for 9%, and biogenic activities in land and coastal sea areas, for 7% (Fujita, 1996). The emission of SO_2 due to volcanic activity is concentrated in climate region no. 15 (S. Kyushu), where Sakurajima is located. There are no active volcanoes on the Chinese Continent or the Korean Peninsula.

The annual emission of NO_x from fossil fuel combustion in East Asia is estimated to be approximately 200 Gmol yr^{-1}. Although the distribution of emission sources of NO_x is similar to that of SO_2, the major sources are separately located large metropolitan areas (Akimoto and Narita, 1994). The annual emission of NO_y ($=NO + NO_2 + HNO_3 + NO_3^-$) in Japan is estimated to be approximately 35 Gmol yr^{-1} (Kannari et al., 2001).

On the basis of the above analytical results, the molar ratios of wet deposition to total emission over the Japanese Archipelago have been calculated. Estimated deposition/emission ratios for the 3-yr average rainfall amount were 0.59 for nss-SO_4^{2-}/SO_x, 0.43 for NO_3^-/NO_y and 0.83 for NH_4^+/NH_3, respectively. In the case of sulfur and oxidized nitrogen, these ratios are considered to be ratios of precipitation sulfate and nitrate to the sums of restrictive oxidized sulfur and nitrogen species in the gas phase when NO_3^- in NO_y represents particulate nitrate in the atmosphere. In the case of reduced nitrogen, atmospheric ammonium salts such as ammonium sulfate and ammonium nitrate are considered to be incorporated into water droplets. Although the meanings of emission/deposition ratios of oxidized and reduced nitrogen species are different, these calculations indicate that the wet depositions of sulfate, nitrate and ammonium in Japan are apparently of similar magnitude and lower than emissions of these precursors in this area. When assuming a steady state, part of difference between wet deposition and emission may be explained by the dry deposition of gaseous and particulate substances within the region.

The dry deposition of sulfur compounds in Japan was calculated for 80 km × 80 km grid squares by the product of near-surface sulfur concentration and the deposition velocity (Fujita, 1996). For Japan as a whole, the dry deposition of sulfur is estimated to be approximately 14 Gmol yr^{-1}; approximately 90% of the total comes from sulfur dioxide, while the contribution from particulate sulfate is as small as 10%. For the climate region no. 7 facing the continent across the Japan Sea, the ratio of total (wet + dry) deposition to total (anthropogenic + natural) emission is approximately 3.3, which indicates that in-flow from outside the region plays an important rule in the budget of sulfur in the region. Since the appropriate atmospheric concentration fields for HNO_3 and NH_3 are not available, it is difficult to obtain a value for the dry deposition of nitrogen compounds in Japan.

As described above, the predominant wind system over the Japanese Archipelago is northwesterly in the cold season and southwesterly in the warm season. The broad emission sources of precursors constituting BC and AC are considered to be mostly located in the northwest region for calcium, and in the southeast region for ammonia and volcanic sulfur. Major emission sources for anthropogenic SO_2 and NO_x are distributed throughout the region, some of which overlap those of calcium and ammonia. Therefore, the ratio of BC/AC in precipitation in East Asia decreases exponentially with distance from northern China to the Pacific Ocean, indicating that the average residence time differs between bases (reduced nitrogen and calcium salts) and acid gases (sulfur and oxidized nitrogen) in the lower atmosphere (Fujita et al., 2000).

The strong northwesterly wind from the Siberian high-pressure system over the continent carries a dry air mass over the sea. This air mass receives moisture, and becomes unstable as it passes over the Japan Sea. When the wet air reaches the central mountain range of the Japanese Islands, heavy snowfall results on the Japan Sea side. The chemical substances emitted from the continent and carried over the sea are incorporated into snow clouds in this process. Since the production of sea salt is related to wind speed, sea salt sulfate and sea salt calcium produced from the sea are also incorporated into snow clouds or scavenged by snowflakes below cloud layers, and deposited with non-sea salt substances on the Japan Sea. With respect to sulfate and calcium in the coastal regions during the period from December to February, the wet deposition of sea salt origin and that of non-sea salt origin are of similar magnitude. After losing part of its content in this way, the dry air mass passes over the central mountain range to the Pacific Ocean. Although there are various complex causes of precipitation in East Asia, wet deposition is basically a flux that is determined by the product of the ionic concentration and the rainfall amount. The wet deposition of nss-SO_4^{2-}, NO_3^-, nss-Ca^{2+} and NH_4^+, which showed high concentrations on the Asian Continent and low concentrations over the Pacific Ocean, is canceled by precipitation, which showed low amount on the Continent and high amount over the Ocean, resulting in relatively small differences between the sites compared with that of sea-salt ions.

6. Conclusion

The wet deposition of acid and some major ions over the Japanese Archipelago was estimated on the basis of the CRIEPI's regional monitoring data at 21 sites between October 1987 and September 1990. The country was divided into 15 climatic regions with 114 grid squares, and the annual and the seasonal fluxes of non-sea salt sulfate, nitrate, ammonium and non-sea salt calcium were calculated.

The concentrations of these ions in precipitation increased during the cold season, and this tendency was noted on the northwestern region facing the continent across the Japan Sea. The total wet depositions of ions over the Japanese Archipelago (area 722 000 km^2) were estimated approximately as: nss-SO_4^{2-}, 54 meq m^{-2} yr^{-1}; NO_3^-, 21 meq m^{-2} yr^{-1}; NH_4^+, 34 meq m^{-2} yr^{-1}; and nss-Ca^{2+}, 19 meq m^{-2} yr^{-1}, respectively. If the concentration difference AC − BC was converted into the wet deposition of H^+, it was approximately 23 meq m^{-2} yr^{-1}, or the total deposition over the Japanese Archipelago was approximately 17 Geq yr^{-1}. For Japan as a whole, wet deposition of H^+ in the warm season (April–September) and the cold season (October–March) was 45% and 55%, respectively. In the warm season, the major receptor of acid was the climate regions facing the Pacific Ocean, while in the cold season it was the climate regions facing the Japan Sea. The wet deposition over the Japanese Archipelago was influenced by two factors: meteorological conditions such as wind system and rainfall pattern due to Asian monsoons, and the geographical distribution of emission sources of chemical substances through natural and anthropogenic activities in East Asia. Meteorological and geographical analyses suggested that in-flow of chemical substances from outside the region plays an important role in the budget of acid over the Japanese Archipelago.

7. Acknowledgments

We thank Yoichi Ichikawa, Hiroshi Hayami and Tomoaki Odaira for helpful comments and suggestions regarding this work. Part of this program was carried out under a contract with the Ministry of International Trade and Industry, Japan.

REFERENCES

Akimoto, H., and Narita, H. 1994. Distribution of SO_2, NO_x and CO_2 emissions from fuel combustion and industrial activities in Asia with 1° × 1° resolution. *Atmos. Environ.* **28A**, 213–225.

Dokiya, Y., Miyakoshi, N., Hirooka, T., Yamashita, J., Ishikawa, S., Ohya, M. and Sugaya, J. 1995. Long range transport of sulfur compounds over the Western North Pacific: Deposition samples obtained on islands. *J. Meteorol. Soc. Jpn.* **73**, 873–881.

Fujita, S. 1996. An estimation for atmospheric sulfur budget over the Japanese archipelago, *Environ. Sci.* **9**, 185–199.

Fujita, S., Ichikawa, Y., Kawaratani, R. K. and Tonooka, Y. 1991. Preliminary inventory of sulfur dioxide emissions in East Asia, *Atmos. Environ.* **25A**, 1408–1409.

Fujita, S., Tonooka, Y. and Ohta, K. 1992. Annual contribution of volcanic sulfur emissions on the atmosphere in Japan. *J. Jpn. Soc. Air Pollut.* **27**, 336–343.

Fujita, S., Takahashi, A., Weng, J. H., Huang, L. F., Kim, H. K., Li, C. K., Huang, T. C. and Jeng, T. J. 2000. Precipitation chemistry in East Asia, *Atmos. Environ.* **34**, 525–537.

Fujita, S., Takahashi, A., Hayami, H. and Sakurai, T. 2001. Long-term trends in the chemical composition of precipitation over western Japan, *Water, Air, and Soil Pollution* **130**, 415–420.

Galloway, J. N., Zhao, D., Xinng, J. and Likens, G. E. 1987. Acid rain: China, United States, and remote areas. *Science* **236**, 1559–1562.

Hao, Q. 1991. Present status of acid rain problem in China and tasks for the period. *J. Jpn. Soc. Air Pollut.* **26**, 283–291.

Hao, Q. 1993. The study on the sand/dust storms in northwest China and high-altitude transportation path of Kosa aerosol. *Environ Sci.* **14**, 43–50.

Hara, H. 1993. Acid deposition chemistry in Japan. *Bull. Inst. Public Health* **42**, 1–12.

HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model, 1997. Web address: http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Research Laboratory, Silver Spring, MD.

Hseung, Y., and Jackson, M. L. 1952. Mineral composition of the clay fraction of some main soil groups of China, *Soil Sci. Soc. Am. Proc.* **16**, 97–110.

Ichikawa, Y. and Fujita, S. 1995. Analysis of wet deposition of sulfate using a trajectory model for East Asia, *Water, Air, and Soil Pollution* **85**, 2015–2020.

Ichikawa, Y., Hayami, H. and Fujita, S. 1998. A long-range transport model for East Asia to estimate sulfur deposition in Japan, *J. Appl. Meteorol.* **37**, 1364–1374.

Ichikuni, M. 1978. Calcite as source of excess calcium in rainwater, *J. Geophys. Res.* **83**, C12, 6249–6252.

Ikeda, Y. and Higashino, H. 1997. The estimation of acid deposition in East Asia focused on the ratio of sources contribution on the deposition. *J. Jpn. Soc. Atmos. Environ.* **32**, 175–186.

Kannari, A., Baba, T. and Hayami, H. 1998. Estimation of ammonia emissions in Japan. *J. Jpn Soc. Atmos. Environ.* **36**, 29–38.

Kawaratani, R. K. and Fujita, S. 1990. Wet deposition of volcanic gases and ash in the vicinity of Mount Sakurajima, *Atmos. Environ.* **24A**, 1487–1492.

Miles, L. M. and Yost, K. J. 1982. Quality analysis of USGS precipitation chemistry data for New York. *Atmos. Environ.* **18**, 2889–2898.

Morgan, J. J. 1982. Factors governing the pH, availability of H^+, and oxidation capacity of rain. In: *Atmospheric chemistry* (ed. E. D. Goldberg), Springer, Berlin, 17–40.

Murano, K., Hatakeyama, S., Kuba, N., Lee, D. S. and Lee, T. Y. 1996. Grid ammonia emission fluxes in Japan and Korea. Proceeding of the Int. Symp. on Acid Deposition and its Impact, 10–12, Dec. 1996, Tsukuba, Japan, 134–140.

Nishikawa, M., Kanamori, S., Kanamori, N. and Mizoguchi, T. 1991. Ion equivalent balance in water-soluble constituents of Kosa aerosol. *J. Aerosol Res. Jpn.* **6**, 157–164.

Noguchi, I., Kato, N., Akiyama, M., Otsuka, H. and Matumoto, Y. 1995. The effect of alkaline dust decline on the precipitation chemistry in northern Japan. *Water, Air, and Soil Pollution* **85**, 2357–2362.

Okada, K., and Kai, K. 1995. Features and elemental composition of mineral particles collected in Zangye, China. *J. Meteorol. Soc. Jpn.* **73**, 947–957.

Okita, T. 1983. Acid precipitation and related phenomena in Japan. *Water Quality Bull.* **8**, 101–108.

Saito, R. 1957. The climate of Japan and her meteorological diastors. *Geophys. Mag.* **28**, 89.

Takahashi, A., and Fujita, S. 2000. Long-term trends in nitrate to non-seasalt sulfate ratio in precipitation collected in western Japan. *Atmos. Environ.* **34**, 4551–4555.

Tamaki, M. and Koyama, I. 1991. The acid rain observed on ground level in Japan; A review of major issues and problems. *J. Jpn. Soc. Air Pollut.* **26**, 1–22.

Tsuruta, H. 1989. Acid precipitation in Eastern Asia. *Kagaku* **59**, 305–315.

Uematsu, M., Duce, R. A., Prospero, J. M., Chen, L., Merrill, J. T. and McDonald, R. L. 1983. Transport of mineral aerosol from Asia over the North Pacific Ocean. *J. Geophys. Res.* **88**, 5343–5352.

WMO (World Meteorological Organization). 1997. Global acid deposition assessment. WMO Global Atmosphere Watch No. 106 (ed. D. M.Whelpdale and M. S. Kaiser), 241 pp.

Yamaguchi, K., Tatano, T., Tanaka, F., Nakao, M. and Gomyoda, M. 1991. An analysis of precipitation chemistry measurements in Shimane, Japan. *Atmos. Environ.* **25A**, 285–291.

Zhao, D. and Wang, A. 1994. Estimation of anthropogenic ammonia emissions in Asia. *Atmos. Environ.* **28A**, 689–694.