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Analysis of Two-Year Results of Acid Precipitation Survey within Japan

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Precipitation chemistry within Japan has been assessed in order to judge both the magnitudes of the concentrations and the deposition of major ions: H^+, NH_4^+, Ca^{2+}, K^+, Mg^{2+}, Na^+, SO_4^{2-}, NO_3^-, and Cl^-. A data set was obtained through an acid precipitation survey by Japan Environemet Agency at 14 stations from April 1984 to March 1986. The annual average pH at each site ranged from 4.5 to 5.1 with a mean value of 4.7. The free acidity was derived both from sulfuric and nitric acids; sulfuric acid was found to contribute to 67—83% of the free acidity. The acidity was apparently lower than that expected from SO_4^{2-} and NO_3^- levels, mainly because alkaline species, such as NH_3, and Ca^{2+} species neutralized a certain fraction of the original acidity. This neutralization would certify the fact that SO_4^{2-} and NO_3^- deposition were comparable to, or smaller than those in eastern North America, but the Ca^{2+} and NH_4^+ deposition within Japan exceeded that within the U. S.

Acid deposition has recently become a subject of widespread concern.[1–5] This concern is derived largely from its effects on natural terrestrial and aquatic ecosystems.[2,4] In Japan, this phenomenon was recognized to be significant when it was found that drizzling injured people's eyes and caused skin irritation during the rainy seasons from 1973 to 1975 in the Kanto District (Metropolitan Tokyo and its surrounding prefectures) and in Shizuoka prefecture.[6,7] On one occasion, as many as 33,000 people complained of irritation. In 1975 Japan Environment Agency (JEA) started a five-year precipitation chemistry monitoring program which collected data for two weeks during the mid-rainy season in Kanto District.[7]

The acid-rain problem has become a global environmental issue. Thus, JEA organized in 1983 the Committee on Acid Precipitation to launch a five-year acid precipitation chemistry monitoring throughout the year (JEA Phase-I Study).[8] This monitoring system involved fourteen stations throughout Japan; fifteen stations were added in 1985. The JEA Phase-I Study is the first survey of acid precipitation within Japan to employ identical sampling procedures and subsequent chemical analysis. Meanwhile, several studies have been reported concerning the chemical composition of precipitation in a number of sites within Japan.[9–16] Most studies had limited objectives and involved different sampling periods and various types of samplers.

In this paper, in order to describe the present state of acid deposition within Japan, precipitation chemistry is addressed on the basis of results for the first two years (April 1984 to March 1986) which are opened to the public. The 1983 results, however, were precluded to appear in the present analysis because they were preliminary and covered only a half-year period.[8] The annual mean concentration and deposition of the major ions are presented, and the results briefly compared with those in the United States and some other countries.

Procedures

Monitoring Sites. Monitoring was carried out in cooperation with seven prefectural research institutes involved in

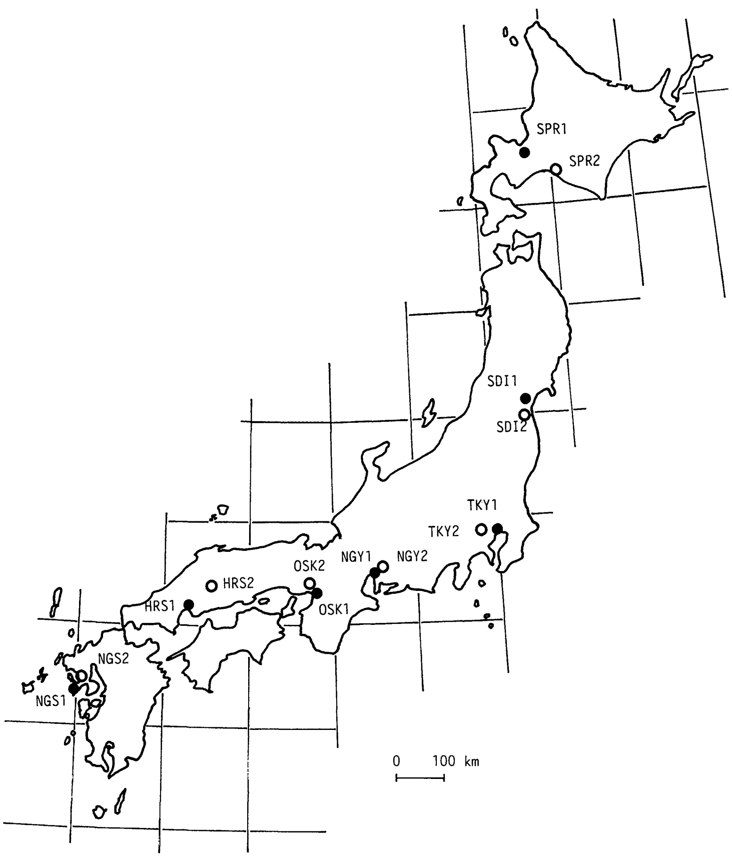

Fig. 1. Sampling stations in this survey. Closed and open circles designate sites 1 and 2 of each prefecture, respectively.

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Table 1. Sampling Stations

Station code	Station	Distance km	Population $\times 10^{-3}$	Longitude E	Latitude N	Altitude m
SPR1	Sapporo	0	1614	141°20′	43°04′	12
SPR2	Mukawa	70	7	141°54′	42°36′	6
SDI1	Sendai	0	870	140°54′	38°16′	34
SDI2	Ohgawara	25	20	140°44′	38°02′	21
TKY1	Koto-ku, Tokyo	0	8296	139°49′	35°40′	21
TKY2	Musashino, Tokyo	25	139	139°34′	35°43′	70
NGY1	Minami-ku, Nagoya	0	2143	136°55′	35°05′	1
NGY2	Meito-ku, Nagoya	10		137°00′	35°08′	52
OSK1	Osaka	0	2649	135°32′	34°40′	18
OSK2	Ikeda	21	103	135°27′	34°49′	79
HRS1	Hiroshima	0	1073	132°27′	34°23	27
HRS2	Shobara	72	23	133°01′	34°51′	273
NGS1	Nagasaki	0	449	129°48′	32°47′	80
NGS2	Ohmura	20	71	129°57′	32°54′	30

environmental science. Each prefecture set up two stations: an urban station (site 1) within the prefecture and a reference station (site 2), as shown in Table 1 and Fig. 1. The distance between two stations ranged from 10 to 70 km.

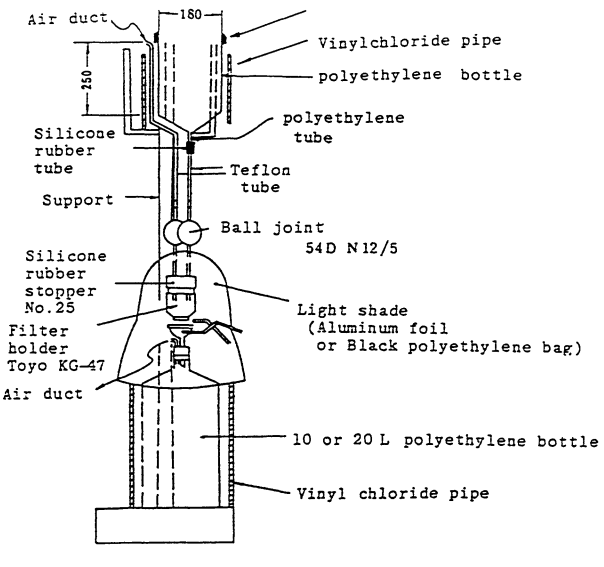
Samplers. Two types of samplers were employed in the monitoring:[17] bulk samplers and wet/dry samplers. This paper, however, deals with the results from bulk sampler data since bulk samplers were distributed to all of the stations, whereas the wet/dry samplers were only provided to one of the two stations in each prefecture.

Two types of bulk samplers were employed in this monitoring: a rain collector and a snow collector, both of which were developed in Japan. The rain collector, (Fig. 2(a)) comprised essentially three parts: a collection funnel, a storage bottle, and a membrane filter (Millipore MFAA, of 47 mm diameter) at the interface between the other two parts.[17] The membrane filter had three roles: to separate the soluble fraction of collected precipitation from insoluble substances; to prevent bacteria-induced chemical transformations of the filtrates; and to minimize the vaporization of rainwater in the storage bottle. During the snow season, the snow sampler was employed at the SPR1, SPR2, SDI1, and SDI2 stations. As depicted in Fig. 2(b),[17] this sampler was comprised a cylindrical funnel and a storage bag.

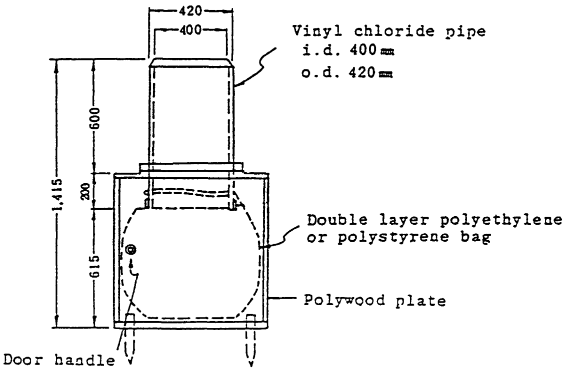
Samples were sent back weekly to each prefectural laboratory for chemical analyses.

Sample Analysis. A number of chemical parameters and rainfall amounts were measured for the precipitation samples including pH, specific conductance, and the concentration of the major ions[17] (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{2+}, K^+, Mg^{2+}, and Na^+), which are considered to determine the characteristics of precipitation.[18]

All of the measurements were made in laboratories: the pH and specific conductance were determined by a pH electrode and a specific conductance meter, respectively. The anions were analyzed by ion chromatography, and Ca^{2+}, K^+, Mg^{2+}, and Na^+ by atomic absorption spectrometry. Ammonium ions were measured by a phenol-hypochlorite method.



(a) Rain collector.



(b) Snow collector.

Fig. 2. Bulk samplers:[17] a) rain collector, b) snow collector.

Details of the analytical procedures have been described elsewhere.[17]

Correction of Contribution of Seasalt. Sulfate and Ca^{2+} in precipitation are derived either from seasalt or from a non-seasalt origin, such as anthropogenic and natural emissions. We, thus, must discriminate seasalt SO_4^{2-} and Ca^{2+} from non-seasalt (nss-) SO_4^{2-} and nss-Ca^{2+} for further discussion. The nss-SO_4^{2-} and Ca^{2+} were evaluated from the Na^+ concentration under the assumption that all of the Na^+ ions originated from seasalt with the conserved weight ratios of SO_4^{2-}/Na^+ (0.251) and Ca^{2+}/Na^+ (0.038) in the seawater.[8]

Results and Discussion

Mean Ionic Composition of Rainwater in This Monitoring. In order to understand the gross features of the ionic composition of the rainwater collected within this network, the mean ionic composition was calculated, as illustrated in Fig. 3. This corresponds to the composition of all the rainwater samples within Japan collected in a huge hypothetical bucket.

The mean pH at 14 stations was 4.7, well below 5.6 which is the "natural" acidity of rainwater in the form of pH.[19] Approximately one third of the ionic components originated from seasalt, since all of the stations except Shobara were situated in coastal areas (Fig. 1, and Table 1). Sulfuric acid exceeded nitric acid in the present results, provided that the acidity is assumed to be derived from either sulfuric or nitric acid, a reasonable assumption in the light of our current knowledge concerning atmospheric chemistry.[20,21] The precipitation pH, as well as that of other aqueous solutions, is determined by the nature and relative proportion of acids and bases in solution.[20,22,23] As Tsuruta has already pointed out,[5] these acids in Japan are ascertained to have been titrated with bases such as NH_3 and Ca^{2+} species in the atmosphere, which resulted in the higher pH for the SO_4^{2-} and NO_3^- levels. If it were not for these alkaline species in the precipitations, the resulting pH would have been 4.3, a decrease of 0.4 pH unit.

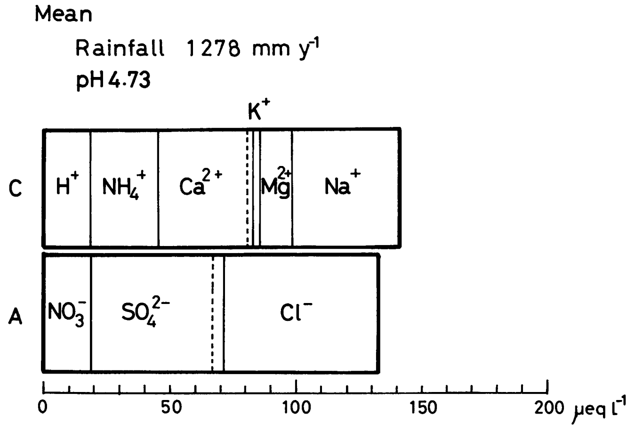


Fig. 3. Mean ionic composition of precipitations at 14 stations over Japan.

pH and Concentrations of the Major Ions. Table 2 gives the precipitation-weighted mean of value each chemical parameter for each site provided with a bulk sampler. The pH values range from 4.5 to 5.1. No distinguished spatial patterns have been noted over the country, although some sites in western Japan seem to have lower pH values than those in northern Japan: SPR1, SPR2, SDI1, and SDI2.

The NO_3^- level at TKY2 was found to be remarkably high (2.52 mg L^{-1}) compared with those at the other stations (0.56—1.58 mg L^{-1}); this matter will be discussed later.

Non-seasalt Ca^{2-} concentration were considerably more elevated at SPR1 (2.15 mg L^{-1}) than those at the other stations. We interpret the results as an indication that this site is highly affected by local emissions, such as the road dust produced by studded tires during the winter months.

An analysis of the entire data of the present five-year survey would help in ascertaining this interpretation of the probable spatial distribution.

The present bulk sampler data was preliminarily compared with those from other regions of the world. It should be noted, however, that data based on different type of samplers (wet-only or bulk) cannot be directly compared, since the collected materials might not be regarded as always being identical with each other.

However, a preliminary comparison of the rain collector with the wet/dry sampler showed that the rain collector gave a 0.1 pH-unit higher pH value unit on the average than that did with the other type of sampler; also, the bulk sampler collected 60—80%, dependent upon the ionic species of the deposition, compared with the wet/dry sampler.[24] As long as we note these discrepancies, it is still meaningful at present to make a brief comparison with corresponding data sets.

A data set for the U. S. (regional annual average of 1980[25]), Europe (EMEP network),[26] and China (several site data during 1981—1984)[27] are shown in Table 2. Regarding the European network, EMEP determined mean annual pH values of 4.1 to 5.4. The regions with the lowest precipitation pH were found in the central parts of Europe and in Southern Scandinavia. In China, the pH ranged form 4.1—4.9 (acid-rain areas) to 6.3—6.7 (non-acid-rain areas); a low pH occurs in the southern part of the country.

The pH of the present survey corresponds to those between Northeastern U. S. (4.1—4.2) and Northwestern U. S. (5.1—5.2), and is somewhat lower than in Western-Midwestern U. S. (5.0—5.5).

The nss-SO_4^{2-} level within Japan is nearly comparable to the SO_4^{2-} level of Northeastern U. S. (Table 2), but is somewhat lower than nss-SO_4^{2-} within Europe.

Regarding the NO_3^-, the concentration at TKY2, the highest concentration in this survey, corresponded

Table 2. pH and Concentrations of Major Ions

Site code	pH	NH_4^+	Ca^{2+}	K^+	Mg^{2+}	Na^+	NO_3^-	SO_4^{2-}	Cl^-	nss-SO_4^{2-}[a)]	nss-Ca^{2+}[a)]
							mg L^{-1}				
SPR1	4.9	0.36	2.30	0.34	0.45	3.84	0.89	4.29	7.00	3.31	2.15
SPR2	5.0	0.26	0.46	0.13	0.19	1.35	0.87	2.07	2.38	1.73	0.41
SDI1	4.6	0.65	1.02	0.15	0.13	0.81	1.33	2.38	2.29	2.17	0.99
SDI2	4.8	1.27	1.51	0.33	0.16	0.80	1.34	2.81	2.49	2.60	1.48
TKY1	4.9	0.53	1.23	0.09	0.19	0.80	1.58	2.83	2.06	2.64	1.20
TKY2	4.5	0.57	0.65	0.07	0.09	0.45	2.52	2.22	1.59	2.11	0.64
NGY1	4.8	0.49	0.70	0.06	0.09	0.51	1.36	2.89	1.11	2.70	0.67
NGY2	4.6	0.39	0.31	0.07	0.06	0.45	1.29	2.16	0.87	2.01	0.29
OSK1	4.5	0.64	0.92	0.18	0.08	0.53	1.32	2.88	1.90	2.75	0.90
OSK2	4.7	0.33	0.40	0.08	0.07	0.52	1.02	1.83	1.04	1.70	0.38
HRS1	4.8	0.28	0.77	0.06	0.08	0.48	1.06	2.72	1.10	2.57	0.75
HRS2	5.1	0.65	0.40	0.08	0.09	0.65	0.95	2.35	1.62	2.16	0.37
NGS1	4.8	0.31	0.33	0.21	0.27	2.05	0.56	2.51	3.61	1.99	0.26
NGS2	4.6	0.23	0.34	0.11	0.16	1.07	0.64	2.21	2.04	1.89	0.29
Mean	4.7	0.48	0.74	0.13	0.15	0.99	1.16	2.54	2.15	2.28	0.70
Max/Min	5.5[b)]	5.5	7.4	5.7	7.5	8.5	4.5	2.3	8.0	2.0	8.3
Regional annual average of the U. S., 1980[25)]											
NW[c)]	5.1—5.2	0.02—0.04	0.04—0.06				0.1—0.2	0.2— 0.5			
W-MidW[c)]	5.0—5.5	0.2 —0.7	0.2 —0.7				0.9—1.9	1.0— 1.5			
NE[c)]	4.1—4.2	0.3 —0.4	0.2 —0.3				1.9—2.2	3.0— 4.0			
Europe, 1985[26)]											
	4.1—5.4	0.1 —2.7					0.9—4.4			0.6—8.4	
China[27)]											
AR[d)]	4.1—4.9	0.9 —1.9	0.1 — 4.6				1.0—2.0	5.4—19			
NAR[d)]	6.3—6.7	2.3 —4.0	5.7 —15.2				1.8—5.0	7.8—16			

a) nss: non seasalt. b) Ratio in term of hydrogen ion concentration. c) NW: Northwestern, W-MidW: Western to Mid-Western, NE: Northeastern. d) AR: Acid rain areas, NAR: Non acid rain areas.

to that in Northeastern U. S., while the other Japanese stations found the same concentration levels as those in Western-Midwestern U. S. The NO_3^- levels in Europe are likely to be higher than those in Japan and the U. S., and to be as high as that in China, where SO_4^{2-} concentrations are exceptionally high among all countries and regions.

As for alkaline species, such as NH_4^+ and Ca^{2+}, Japan has medium levels among the U. S., Europe, and China (Table 2). Concentrations higher than those in the U. S. were observed for NH_4^+ and Ca^{2+}.

The term, "acid precipitation," sometimes implies too much the significance of the pH level, that pH might be misunderstood to be the single measure of acid precipitation. However, in light of the discussion so far, the entire ionic composition should be carefully examined, for example, by using the ionic composition diagram shown in Fig. 3.

Futher analysis of the present survey data, together with the remaining two-year data of this survey covering fifteen additional stations in other areas of Japan is needed, whereby it may be ascertained whether or not this view applies to most areas of Japan. If they do occur, the sources of these major components need to be determined.

Maximum/Miminum Ratios of Ionic Concentrations. The number of stations was so limited that detailed spatial distributions could not be determined. However, the ratio of the maximum to the minimum concentration for each ion would display a degree of spatial variability: When the concentration of an ionic species is rather uniform within Japan, this ratio does not exceed unity to a great extent. These ratios are also summarized in Table 2. On a basis of this ratio, the ionic components could be divided into three classes: high (larger than seven), low (smaller than approximately two), and medium. The high-ratio class covers five components: Ca^{2+}, nss-Ca^{2+}, Mg^{2+}, Na^+, and Cl^-, while the low ratio class comprises SO_4^{2-} and nss-SO_4^{2-}. Since the non-seasalt contribution accounted for more than 80% of SO_4^{2-} and Ca^{2+}, as is shown in Fig. 3, it is only reasonable that the total (seasalt plus non-seasalt) and non-seasalt component should belong to the same class.

In contrast to ions of high and medium ratios, the lower-ratio components, SO_4^{2-} and nss-SO_4^{2-}, are strongly suggested to be rather uniformly distributed within Japan.

Relative Importance of NO_3^- and nss-SO_4^{2-} to Acidity. Assuming that precipitation acidity originates primarily from sulfuric and nitric acids, the ratios of NO_3^-/nss-SO_4^{2-} (the N/S ratio), expressed as equivalents, would display the relative importance of their contributions to precipitation acidity.[28,29] These acids in precipitation are originally formed in the atmosphere through pertinent gas- or aqueous-phase chemistry.[21] Atmospheric alkaline species, mainly NH_3, neutralize a certain portion of these acids, yielding ammonium salts such as $(NH_4)_2SO_4$ and NH_4NO_3. From the viewpoint of atmospheric acidity,[30,31] the original acidity is conserved as the amount of SO_4^{2-} and NO^{3-} anions. As Table 3 shows, the N/S ratio ranges from 0.21 to 0.50, except at the TKY2 station. Thus, sulfuric acid would contribute 67—83% to the free precipitation acidity within Japan.

The highest ratio, 0.93, was obtained at the TKY2 station, situated about 20 km inland from the coast. Both nitric and sulfuric acids equally contributed to the precipitation acidity at this point. As we discussed before, the NO_3^- concentration peaked at this station. Because the nss-SO_4^{2-} level was rather uniform within Japan, the high N/S ratio resulted from the NO_3^- peak, which may be ascribed to the high NO_x levels and high ratios of NO_x to SO_2 within the Tokyo area. Further, possibly, the difference in the oxidation rates of SO_2 and NO_x intensified the NO_x/SO_2 ratio,

Table 3. Equivalent Ratios of Major Ions

Site code	(Cl/Na) / $(Cl/Na)_{ss}$	nss-SO_4^{2-} / SO_4^{2-}	nss-Ca^{2+} / Ca^{2+}	NO_3^- / nss-SO_4^{2-}	$(NH_4^+ +$nss-$Ca^{2+})$ / $(NO_3^- +$nss-$SO_4^{2-})$	NH_4^+ / nss-Ca^{2+}
SPR1	1.02	0.77	0.94	0.21	1.53	0.19
SPR2	0.98	0.84	0.89	0.39	0.70	0.70
SDI1	1.57	0.91	0.97	0.48	1.28	0.73
SDI2	1.73	0.93	0.98	0.40	1.90	0.95
TKY1	1.43	0.93	0.98	0.46	1.11	0.49
TKY2	1.97	0.95	0.99	0.93	0.75	0.99
NGY1	1.21	0.93	0.96	0.39	0.78	0.81
NGY2	1.08	0.93	0.94	0.50	0.58	1.49
OSK1	2.00	0.96	0.98	0.37	1.02	0.79
OSK2	1.11	0.93	0.95	0.47	0.72	0.97
HRS1	1.28	0.95	0.97	0.32	0.75	0.42
HRS2	1.39	0.92	0.93	0.34	0.90	1.95
NGS1	0.98	0.79	0.79	0.22	0.70	1.32
NGS2	1.06	0.86	0.85	0.26	0.55	0.88
Mean	1.21	0.90	0.95	0.39	0.93	0.76

Table 4. Mean Deposition of Major Ions

Site code	Rainfall	H^+	NH_4^+	Ca^{2+}	K^+	Mg^{2+}	Na^+	NO_3^-	SO_4^{2-}	Cl^-	nss-SO_4^{2-}	nss-Ca^{2+}
	$mm\ y^{-1}$						$g\ m^{-2}\ y^{-1}$					
SPR1	981	0.012	0.35	2.25	0.33	0.44	3.77	0.88	4.21	6.87	3.25	2.11
SPR2	788	0.008	0.20	0.37	0.10	0.15	1.06	0.69	1.63	1.88	1.36	0.33
SDI1	1042	0.024	0.68	1.06	0.16	0.14	0.84	1.38	2.47	2.39	2.26	1.03
SDI2	995	0.014	1.26	1.50	0.33	0.16	0.79	1.33	2.79	2.50	2.59	1.47
TKY1	1234	0.016	0.66	1.52	0.12	0.24	0.99	1.92	3.49	2.55	3.24	1.48
TKY2	1270	0.036	0.72	0.83	0.09	0.12	0.58	3.20	2.82	2.02	2.68	0.81
NGY1	1189	0.020	0.58	0.83	0.08	0.10	0.61	1.61	3.43	1.32	3.20	0.80
NGY2	1256	0.028	0.49	0.39	0.09	0.07	0.57	1.62	2.71	1.09	2.52	0.37
OSK1	1191	0.034	0.77	1.09	0.21	0.10	0.63	1.56	3.38	2.24	3.23	1.05
OSK2	1404	0.031	0.46	0.56	0.11	0.10	0.73	1.41	2.52	1.44	2.56	0.53
HRS1	1387	0.023	0.39	1.07	0.08	0.11	0.66	1.48	3.77	1.52	3.56	1.04
HRS2	1498	0.013	0.97	0.60	0.11	0.14	0.97	1.43	3.51	2.43	3.23	0.56
NGS1	1693	0.025	0.52	0.56	0.35	0.46	3.47	0.95	4.25	6.10	3.36	0.43
NGS2	1962	0.052	0.45	0.66	0.21	0.31	2.10	1.25	4.11	4.00	3.52	0.57
Mean	1278	0.024	0.61	0.95	0.17	0.19	1.27	1.48	3.22	2.74	2.88	0.90
Max/Min	2.5	4.3	6.3	6.1	4.4	4.6	6.6	4.6	2.6	6.3	2.6	6.4

resulting in the higher N/S ratios: NO_2 generally undergoes oxidation one order of magnitude more rapidly than does SO_2.[32] Since the TKY1 station is located in an industrialized area, the distance between emission sources and the station seems so short that it does not permit a conversion of the emitted NO_2 to NO_3^- during the transport processes.

Depositons of the Major Ions. Depositon, defined as the product of the concentration and the rainfall amount, is another major quantity in evaluating the acid depositon phenomenon. The annual mean depositon of major ions is summarized in Table 4, together with the rainfall amounts.

Similar variations in the deposition were noted for major ions to the concentration. The depositions of NO_3^- and Ca^{2+} peaked at TKY2 and SPR1, respectively.

The magnitudes of the depositons were tentatively compared with an available data set of the United States.[33] The nss-SO_4^{2-} deposition levels within Japan (1.36—3.56 $g\ m^{-2}\ y^{-1}$) were comparable to those of eastern North America, the highest level of which was 3.0—4.8 $g\ m^{-2}\ y^{-1}$. Nitrate deposition at the Tokyo stations (1.92 and 3.2 $g\ m^{-2}\ y^{-1}$ for TKY1 and TKY2, respectively) corresponded to the heavy deposition area of eastern North America (2.0—3.1 $g\ m^{-2}\ y^{-1}$). The deposition of alkaline species within Japan (NH_4^+; 0.20—1.26 $g\ m^{-2}\ y^{-1}$, and Ca^{2+}; 0.37—2.25 $g\ m^{-2}\ y^{-1}$), however, exceeded those of eastern North America (NH_4^+; 0.4—0.9 $g\ m^{-2} y^{-1}$, Ca^{2+}; 0.30—0.54 $g\ m^{-2}\ y^{-1}$) in the area with heavy SO_4^{2-} and NO_3^- depositions.

It should be noted that Japan has a greater amount of rainfall than most European countries and North America: the U. S. rainfall is, on an average, less than half that of Japan.[34] When the concentration level of Japan is comparable to that of these countries, our deposition magnitude will surely be larger than those of the others, which should be kept in mind when evaluating acid deposition within Japan.

Conclusion

A general picture of precipitation chemistry within Japan was obtained based on two years of monitoring: pH; 4.5—5.1 with a mean of 4.7, nss-SO_4^{2-}; 1.70—3.31 $mg\ L^{-1}$, NO_3^-; 0.56—2.52 $mg\ L^{-1}$, NH_4^+; 0.26—1.27 $mg\ L^{-1}$; Ca^{2+}; 0.33—2.30 $mg\ L^{-1}$. Though the depositon levels of nss-SO_4^{2-} and NO_3^- are somewhat high, more NH_4^+ and Ca^{2+} are deposited per unit area within Japan, resulting in a partial neutralization of sulfuric and nitric acids.

It is important to emphasize the preliminary nature of these results. Further analysis of the data, including results from an addtional fifteen stations, would help us to ascertain the present interpretation.

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