

Acid Deposition Chemistry in Japan

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The acid deposition issue in Japan was briefly addressed with respect to suspicions of its effects, precipitation chemistry, and research trends of related atmospheric chemistry. Acid deposition was not recognized in Japan until the episode of the skin and eye-irritation to people in 1975. Recently, dieback of Japanese cedar and pH decrease of freshwaters are discussed in terms of acid deposition. A survey of precipitation chemistry launched in 1983 by the Japan Environment Agency described nationwide characteristics of precipitation based on bulk samples: the volume-weighted annual mean pH for the twenty-nine stations was 4.7 with a range of 4.5 to 5.0. Sulfuric acid exceeded nitric acid, and more than half of these acids were considered to have been neutralized by ammonia and alkaline calcium species. Various studies are currently under way for the four elements of acid deposition: sulfur and nitrogen emissions, transport and transformation, wet and dry deposition, and adverse effects on ecosystems. Further studies including critical load evaluation and international monitoring in Asian region are also currently being reviewed.

Key Words acid deposition, sulfate, nitrate, pH, wet, dry, Japan

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1. INTRODUCTION

Attention has recently been focused heavily on global environmental issues. In Japan, "acid rain" is the subject of more public concern than climate change and stratospheric ozone depletion. The climate of Japan is so precipitious so that rain has become more closely related to daily life, and further to the Japanese culture. A number of citizen groups measure pH values of rainwater collected in their community. Newspapers cover their result with a map of pH distributions. The phrase, "acid rain" literally means acidification of rainwater, and,

public are likely to have an interest particularly in the pH values of rainwater.

However, "acid rain" is not altogether accurate though it makes newspaper copy¹⁾. Acid rain as an environmental issue is not the acidification of rainwater. It is the acidification of the atmosphere loaded with sulfuric and nitric acids and the resultant acidification of the environment. Sulfur dioxide (SO₂) and nitrogen oxides (NO_x) emitted into the atmosphere are converted to corresponding strong acids during the course of transport. The conversion takes place in the gas phase as well as in the aqueous phase. The acidic substances thus formed in the atmosphere are eventually deposited onto earth's surface. The atmospheric deposition is separated into two distinct mechanisms: wet deposition (in the form of rain, snow, and fog), and dry deposition (in the form of gases and particles). Plants, soils, and

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surface waters affected their activities by responding to chemical species deposited onto their surfaces.

The issue of "acid rain" consists of a series of phenomena: emission, transport and transformation, deposition, and adverse effects. Thus, we should describe this environmental issue by "acid deposition" or "acidification" in order to understand the whole view of its picture.

In this review, I address the physico-chemical aspects of acid deposition in Japan referring the recent results of the Japan Environment Agency (JEA) Acid Precipitation Survey and the research trends of atmospheric chemistry of acid deposition in Japan.

2. SUSPICIONS OF ADVERSE EFFECTS OF ACID DEPOSITION

2.1 Human effects: moist air pollution²⁾

In June, 1975, drizzling injured people's eyes and caused skin irritation in some areas on the Suruga Bay and in Yamanashi prefecture. Welsh onion, tobacco plant, cucumber, and Japanese egg-plant were also damaged. The pH was estimated to range from 2.0 to 3.5. In the following year, as many as 33,000 people in the Kanto Plain, the plain surrounding Tokyo, were affected in August 1976. JEA named this phenomenon "moist air pollution (acid rain)" and initiated in 1975 a five-year survey of precipitation chemistry in Kanto District in the rainy season³⁾. On the 25th of June of the year, 114 people were irritated in the eye and the skin with drizzling. According to JEA survey on this occasion, the lowest pH of 3.05 occurred at Kumagaya, 100 km to the north of Tokyo. Because of the precipitation pH in the affected areas was below 3.0, hydrogen ion was considered to be responsible for the irritation. Clinical experiments suggested that some other compounds including formaldehyde, hydrogen peroxide, and formic acid had caused these adverse effects.

2.2 Dieback of a Japanese cedar (*Cryptomeria Japonica*)

Sekiguchi⁴⁾ reported that the dieback of *cryptomeria japonica* was extended over a wide range covering the western and northwestern areas of the Kanto Plain. The affected area was compared with normal areas in terms of concentration and deposition of sulfur and nitrogen compounds as well as photochemical oxidant. He proposed that this phenomenon was due to the deposition of acidic substances and oxidants. This report provoked some surveys of JEA. Takahashi⁵⁾ also studied the dieback of the cedar in the Kanto Plain to confirm the extensive damage. The distribution pattern of affected areas overlapped that of the photochemical oxidant concentration. Recently, similarly affected forests were reported. The cause is discussed in terms not only of acidification of soils but also of other factors: magnesium deficiency, exposure to atmospheric ozone, excess supply of nitrogen compounds, and water deficiency⁶⁾.

2.3 Acidification of Fresh Waters

Kurita et al.⁷⁾ analyzed a seventeen-year record, 1972-1988, of monthly pH values for rivers and lakes in mountaneous areas of Central Japan. Some rivers and lakes showed pH decreases by approximately 0.6 pH unit in ten years, and others by 0.2 to 0.3. From a geological point of view, the watersheds with decreasing pH are composed of granite and rhyolite having low capacity of acid neutralization. In contrast, those without appreciable pH decrease are of andesite, torphyrite, and quartz diorite with rather high capacity of acid neutralization.

Precipitation pH data is not available for this period. But the pH of atmospheric deposit gauge samples in Ohmachi, a rural site in this area, showed no appreciable trends of pH in the same period. And the precipitation pH of this area would be estimated around pH 5.0 based on monitoring results in Nagano city, the prefectural capital, in 1975 and 1976. In the light of these findings, they attributed

the decrease of pH value of ambient waters to acid deposition to the watershed.

However, this interpretation of the pH decrease was criticized: 1) the alkalinity of the freshwater is sufficiently high so that the acid deposition to this extent would not cause such pH decrease, 2) similar pH decreases have been observed in about ten watersheds in Japan, which would be attributable to the suppressed activity of photosynthesis in the water bed because of recent changes in the utilization form of the watersheds⁷⁾. These interpretations are still open to further discussion.

3. A BRIEF HISTORY OF PRECIPITATION CHEMISTRY STUDY IN JAPAN

3.1 Early Studies before "Moist Air Pollution"

The adverse effect of acidification in Japan could date from the late days of the 19th century. Smoke from a copper mine in Yanaka-mura damaged forests in the areas 10 km distant from the smoke stacks⁸⁾. This is interpreted as adverse effects of dry-deposited sulfur dioxide derived from sulfur species originally contained in copper ore.

Precipitation chemistry in Japan was initiated at the end of the 19th century in regard to nutrient supply to agricultural crops. Kellner determined nitrate plus nitrite, and ammonium in precipitation in the period of 1888-1889 in Tokyo¹⁰⁾.

From the viewpoint of geochemistry, Miyake¹¹⁾ first reported in 1939 chemical parameters including pH in three cities: annual mean pHs, 4.1 (Tokyo), 5.2 (Kobe), and 5.6 (Hamamatsu) for 1936-1937. More recently, Kanazawa¹²⁾ measured pH of precipitation in Tokyo and Tsukuba, and reported that the overall mean pH values of 4.5 for both series of measurements. Twenty-six percent of samples in Tokyo had pH values less than 4.0 whereas 10% of those in Tsukuba.

From the angle of air pollution research, Yoshida et al. determined pH of precipitation in Yokkaichi, one of the major industrial cities in Japan, for 1960

-1967 to observe a decreasing trend of pH¹³⁾. In 1963, Okita determined concentrations of major ions including pH in rain and fogwater samples in Norikuradake, Shiobara, and Tsukuba¹⁴⁾. Nakai and Takeuchi¹⁵⁾ demonstrated that sulfate derived from anthropogenic sources in rainwater in industrial areas increased from 40-50% in 1960 to 70-75% in 1971-1973. In 1971, Komeiji et al. started precipitation chemistry measurements in relation with corrosion of metallic materials exposed to the atmosphere¹⁶⁾.

3.2 Moist Air Pollution and Related Studies

The survey of moist air pollution in 1975-1985 mentioned in section 2.1 was the first study of acid precipitation in Japan. This survey stimulated studies of acid precipitation chemistry in Japan. After the five-year survey by JEA, the survey was practically inherited by local governments in Kanto District¹⁷⁾. A number of prefectural institutes and some universities also collected a large quantity of data on pH and related chemical parameters.

Sekiguchi et al. observed a pH value of as low as 2.86 for the first 1-mm fraction of rainwater sampled in Maebashi in 1981, and further ensured this magnitude of hydrogen ion concentration in terms of ion balance and conductivity check¹⁸⁾.

Meanwhile, World Meteorological Organization (WMO) set up a station in Ryori, Iwate for WMO Background Air Pollution Monitoring Network (BAPMoN). Precipitation measurement in Ryori was initiated in 1976 as one of the BAPMoN activities. Another WMO station was located in MinamiTorishima in 1993, which will also start in 1994 measuring precipitation chemistry¹⁹⁾.

3.3 JEA Acid Precipitation Survey: Phase I.

Acid deposition was realized to be a global environmental issue as well as global warming and ozone-layer depletion. In 1983, JEA organized the Committee of Acid Deposition to launch a five-year project of the precipitation chemistry monitoring throughout the year (Phase-I Survey), which was

the first nationwide survey of precipitation chemistry to employ identical sampling procedures and subsequent chemical analysis²⁰⁻²⁶.

A. Mean pH

Figure.1 illustrates the volume-weighted annual mean composition of precipitation samples collected with bulk sampler at 29 stations in the period of April 1986 to March 1988 (Fig. 2). Table 1 summarizes annual mean values of pH and concentrations of major ions. The pH ranged from 4.5 to 5.2 with a mean of 4.7, significantly lower than 5.0 that was regarded as a tentative criterion of acid rain as annual average pH value²⁶. These results were obtained with bulk samplers which remained open during both wet and dry periods. Dry deposited alkaline dust might have affected the pH of sample to some extent, which have yielded higher pH values by about 0.1 pH unit²⁰.

B. Seasalt Contribution

Approximately 60% of the ions were derived from seaspray in terms the relative concentrations of sodium and chloride ions (Fig. 1). This is ascribed to the nature of locations: all of the stations except one (HRS2) were situated in coastal areas. Further, each of seasalt and non-seasalt (nss-) fractions were calculated assuming sodium ion to be a conservative tracer for seasalt. The dotted lines in Fig. 1 partition the concentration into non-seasalt (left) and seasalt (right) fractions.

C. Nitrate-to-Sulfate Ratio

Sulfuric acid exceeded nitric acid provided that

the acidity is assumed to originate from either sulfuric or nitric acid. The equivalent ratio of nitrate to nss-sulfate (N/S ratio) was maximum to be 0.83 in Tokyo which is exceptionally higher than the others. Concentrations of the major ions are summarized in Table 1. The ratio except that for TKY2 (Musashino, Tokyo) ranged from 0.19 to 0.57 with a mean of 0.30. Sulfuric acid was concluded to contribute to the free acidity of precipitation in most part of Japan. The maximum ratio observed in TKY2 will be ascribed to the high levels of nitrogen oxides (NO_x) and high ratio of NO_x to sulfur dioxide (SO₂) in Tokyo area. Further, probably, the difference in the oxidation rate of NO_x and SO₂ in the gas phase has intensified this ratio. Nitrogen oxides generally undergo oxidation one order of magnitude faster than sulfur dioxide. Distance between emission sources and the station is so short that it had not permitted NO_x to be converted to HNO₃ during its transport.

D. Neutralization of Input Acidity

The pH of an aqueous solution is generally deter

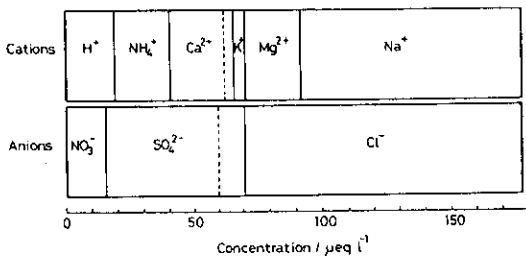


Fig.1 Volume-weighted mean ionic composition of precipitation in JEA Phase-I Survey²⁰.

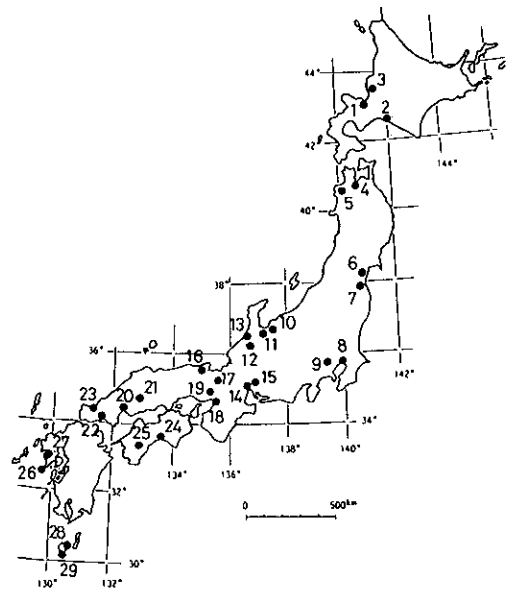


Fig.2 Monitoring Stations of JEA Phase-I Survey²⁰.

Table 1. pH and Concentrations of Major Ions (JEA, 1990)

No.	Site Code	Rainfall mm y ⁻¹	pH	NH ₄ ⁺	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	nss-SO ₄ ²⁻	nss-Ca ²⁺
						[μeq L ⁻¹]							
1	SPR1	1171	5.0	21.6	72.4	5.4	30.4	138.8	11.0	74.3	178.0	57.6	66.3
2	SPR2	725	5.2	22.7	38.4	4.6	17.3	72.6	16.6	49.3	84.1	40.6	35.2
3	SPR3	971	4.8	17.2	30.9	6.1	25.5	127.5	13.2	57.5	144.7	42.1	25.3
4	AOM1	1104	5.1	32.2	87.3	29.7	63.3	229.2	24.5	121.8	342.4	94.2	77.2
5	AOM2	1486	4.9	26.6	51.4	15.3	53.5	200.0	18.4	94.9	302.1	70.9	42.6
6	SDI1	840	4.7	27.2	56.9	2.1	9.9	54.4	23.6	50.2	53.0	43.6	54.5
7	SDI2	1117	4.7	62.1	49.4	3.6	10.7	37.8	29.4	64.1	69.7	59.6	47.7
8	TKY1	1199	5.1	49.9	63.4	2.3	18.9	35.7	38.2	71.4	59.0	67.1	61.8
9	TKY2	1179	4.8	47.7	57.4	1.0	10.7	19.1	45.3	56.6	79.3	54.3	56.5
10	TYM1	1958	4.9	48.2	35.9	5.9	30.4	120.1	17.4	89.5	156.8	75.0	30.6
11	TYM2	1865	4.7	31.0	31.4	5.9	34.6	136.2	17.9	77.9	175.7	61.4	25.4
12	ISK1	2616	4.7	17.7	15.5	4.9	28.8	121.8	13.9	54.3	138.8	39.7	10.1
13	ISK2	2099	4.6	19.4	16.5	6.7	33.7	140.9	15.5	63.3	161.3	46.3	10.3
14	NGY1	1201	4.9	29.4	31.9	1.5	6.6	20.9	23.1	54.6	30.2	52.0	31.0
15	NGY2	1310	4.7	21.6	13.5	1.5	4.1	16.1	19.5	37.3	22.0	35.3	12.8
16	KYT1	1841	4.7	24.4	39.9	9.0	47.7	209.2	18.1	88.3	262.9	63.0	30.7
17	KYT2	1431	4.6	12.8	14.5	2.1	6.6	27.4	13.6	37.5	31.0	34.2	13.3
18	OSK1	1605	4.5	37.7	49.9	3.1	6.6	24.4	25.0	66.6	53.9	63.7	48.8
19	OSK2	1166	4.6	22.7	19.5	1.5	4.1	17.4	19.7	42.5	23.7	40.4	18.7
20	HRS1	1497	4.5	19.4	25.0	1.5	6.6	20.0	19.8	56.4	31.9	54.0	24.1
21	HRS2	1337	5.2	42.7	23.5	2.3	9.1	29.1	14.7	47.5	29.6	44.0	22.2
22	OMG1	1911	4.7	17.2	18.0	3.3	10.7	43.9	11.9	47.1	48.5	41.8	16.0
23	YMG2	1847	4.9	15.5	23.0	5.1	20.6	92.7	12.4	45.0	88.0	33.8	18.9
24	KCH1	2224	4.6	8.9	7.5	1.8	4.1	17.4	6.5	30.4	24.8	28.3	6.7
25	KCH2	2335	4.7	13.9	9.0	2.3	5.8	23.5	9.2	29.8	29.3	26.9	8.0
26	NGS1	1906	4.7	8.9	15.0	5.4	23.0	92.7	8.2	47.7	115.1	36.5	10.9
27	NGS2	2101	4.6	12.2	13.5	2.3	12.3	49.6	8.1	45.8	62.9	39.8	11.3
28	KGS1	3685	4.7	8.9	13.5	4.1	33.7	145.7	10.1	50.4	159.9	32.8	7.1
29	KGS2	5721	4.7	7.8	7.0	3.3	18.1	82.2	8.1	35.6	98.7	25.7	3.4
	Mean	1755	4.7	21.6	26.0	4.6	21.4	85.7	15.5	55.0	107.8	44.6	22.2
	max/min		5.0*	8.0	12	20	15	14	7.0	4.1	14	3.7	23

*Ratio in term of hydrogen ion concentration.

mined by the nature and relative proportion of acids and bases in solution²⁷⁾. In the light of current understanding of atmospheric chemistry, nss-sulfate and nitrate in precipitation exist as sulfuric and nitric acids when they are initially formed in the atmosphere. Before being deposited to the earth's surface, these acids are subjected to neutralization to some extent. In Japan, atmospheric ammonia and

non-seasalt calcium species neutralized more than half of the original acidity.

Daum et al. defined fractional acidity to be $[H^+]/([nss-SO_4^{2-}] + [NO_3^-])$ ²⁸⁾: the numerator is the resulting hydrogen ion concentration (acidity) whereas the denominator is interpreted to be the original acidity. Several reports deal with similar discussion on the neutralization of original

acids²⁸⁻³²). This neutralization in Japan was confirmed by the nationwide monitoring data.

In order to include explicitly the pH value, one of the most basic parameters in acid deposition, the author proposed another index, pA_1 defined as below³³: $pA_1 = -\log([nss-SO_4^{2-}] + [NO_3^-])$.

This measure, pA_1 , physically means that the hypothetical pH of precipitation water if no neutralization took place in the fate of sulfuric and nitric acids. This should be discussed always together with pH.

Figure 3³³ shows a plot of pA_1 versus pH of wet-only samples for annual means at five stations of the Phase-I Survey. Also plotted in the same figure data from other networks: North America (NAPAP)³⁴, Europe (EMEP)³⁵, China³⁶, and global backgrounds³⁷. The plot on the broken line corresponds to no neutralization, and the plot deviates rightward horizontally as the neutralization proceeds to a greater extent. In North America, neutralization seems to proceed to a lesser extent whereas to a greater extent in Europe than in Japan. The measurement sites in China were classified into two groups: acid-rain and non-acid-rain region.

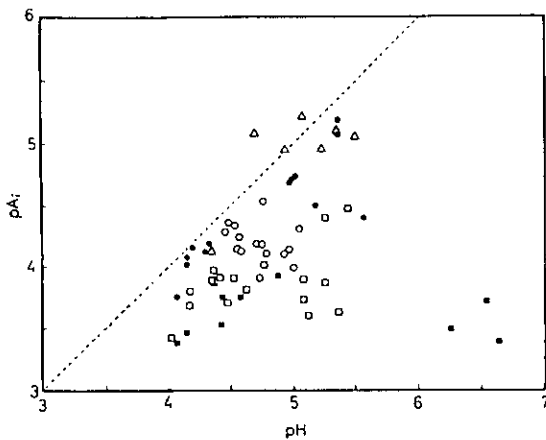


Fig. 3 pH vs pA_1 ³³
 (○; Japan, □; Europe, ●; North America, ■; China, △; global backgrounds).

Data for both regions showed similar pA_1 s but different pHs, which will be attributable to the neutralization by alkali calcium species. Data for global backgrounds are located above or on the 1 : 1 broken line. This would be due to the contribution of organic acid to the free acidity³⁶.

F. Deposition

The deposition of major ions were compared with those of North America. The annual flux of nss-sulfate and nitrate in Japan was shown to be comparable to those in North America. However, fluxes of acid neutralizing ammonium and nss-calcium species exceeded corresponding North American fluxes resulting in higher pH values in Japan for its high level of deposition of the original acidity. A typical contrast is given as below.

The ionic composition and rainfall amount is compared between Koto-ku, Tokyo and Kane, Pennsylvania (Fig. 4³³). Kane showed the highest deposition intensity in nss-sulfate in North America, and Koto-ku also recorded the maximum among the seven stations equipped with wet-only sampler. Because the rainfall amount happened to be almost the same, the nss-concentration was of the same level. The input acidity was considerably neutral-

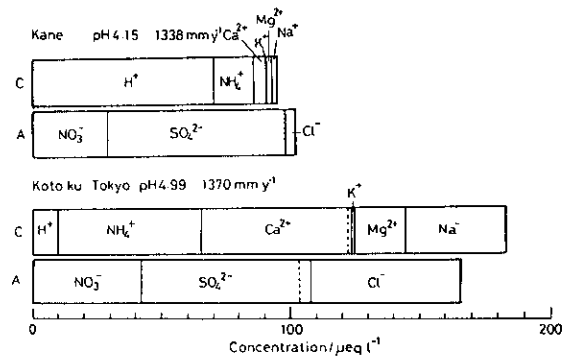


Fig. 4 Rainfall Amount and Ionic Composition of Precipitation in Tokyo (Koto-ku) and Kane, U.S.³³

ized in Tokyo but its substantial fraction was conserved in Kane.

4. TRENDS OF ATMOSPHERIC RESEARCH OF ACID DEPOSITION

4.1 Emission Inventories

Since Asia is one of the major sulfur emission region from the global point of view, the emission inventory for sulfur and nitrogen oxides was of great valuable. Fujita et al³⁹⁾ produced a map of anthropogenic sulfur emissions in East Asia with a total emission of approximately 11 Tg-Sy^{-1} , where S denotes both sulfur dioxide and sulfate on an elemental sulfur basis. Asian emission intensity is comparable to those in Europe and North America. Fujita et al. also estimated nitrogen oxides emissions to be 3.3 Tg-Ny^{-1} for East Asia where N denotes nitrogen oxides on an elemental basis. More recently, Kato and Akimoto⁴⁰⁾ calculated sulfur and nitrogen emissions for twenty-five countries east of Afghanistan and Pakistan to show emissions of sulfur dioxide and nitrogen oxides are 23.4 and 10.7 Tg in 1987, respectively for East Asia.

Volcanos are significant emission sources of sulfur dioxide in Japan. Annual emission intensities from major twelve volcanos were evaluated by the correlation spectrometry⁴³⁾ on the basis of averaged daily emission during the survey period. The sum of the sulfur dioxide emission from the volcanos was estimated to exceed $1.0 \text{ Tg-SO}_2\text{y}^{-1}$, which is comparable to or larger than those from anthropogenic sources in Japan.

4.2 Long-Range Transport

The Japan Sea coastal area in wintertime is characterized by heavy precipitation amounts and northwesterly monsoon over Japan Sea. Kitamura⁴²⁾ and Oizumi et al⁴³⁾ pointed out that the potential winter-time transport of nss-sulfate from the Asian Continent on the basis of observations at Ishikawa and Niigata prefectures on Japan Sea coast, respectively. Using the dataset of Phase-I

Survey, Hara et al. plotted⁴⁴⁾ the nss-deposition at stations on this coast against rainfall amount both for summer and winter months. The deposition was markedly heavier in winter than in summer and its concentration on this coast was also significantly elevated. More recently, Hara and Akimoto⁴⁵⁾ assembled the available datasets on precipitation chemistry in order to generate isopleth maps of concentrations and deposition of major ions. The increased nss-sulfate deposition on this in winter was further evidenced. These studies strongly suggested contributions of long-range transport to nss-sulfate deposition along Japan Sea coastal areas.

Katatani et al. studied long-range transport of sulfur species in East Asia by using an three-dimensional grid model⁴⁶⁾. Comparisons of their calculated results with the available observations showed the consistency between them was fairly good and that the rough estimates of volcanic sulfur emissions were likely to cause the main source of errors.

4.3 Wet Deposition (1): Monitoring

JEA Acid Precipitation Survey is now in its Phase-II. Monitoring of acid deposition is the basis of acid deposition surveys. In this phase, the monitoring stations were entirely altered to those for Japanese Nation Air-pollution Surveillance Network (NASN) and additional stations were included in remote islands. Samplers were replaced by wet/dry ones equipped with automatic pH and conductivity measurement devices for every 0.5-mm precipitation depth.

Interim results of Phase-II Survey were released in 1992. The pH distribution is illustrated also in Fig. 5⁴⁷⁾. The pH value ranged from 4.3 to 5.3. No appreciable pH changes were observed between the two surveys, although changes in the measurement system might have introduced biases in the datasets.

These data are compared with those in Europe (Fig. 7³⁵⁾) and North America (Fig. 8⁴⁸⁾) whose data are based on wet-only sampler observations. In

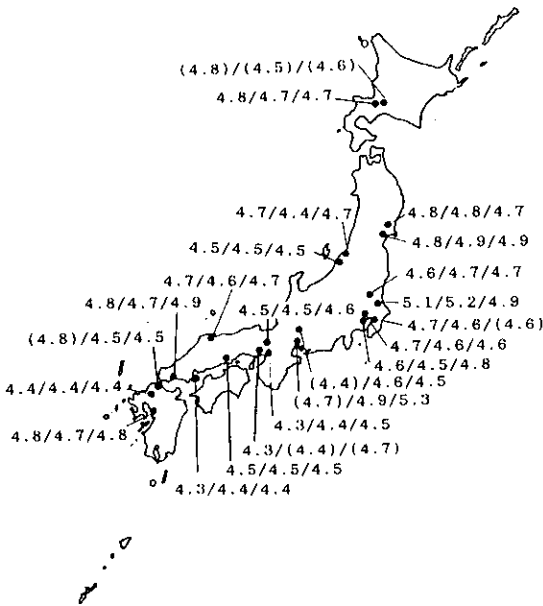


Fig. 5 pH determined in the Phase-II Survey⁴⁷⁾

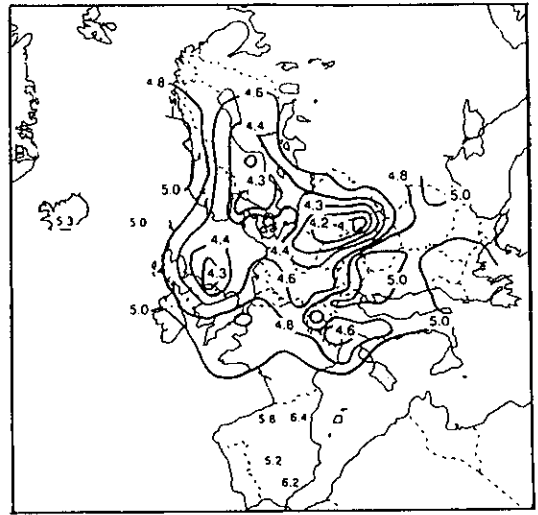


Fig. 6 pH in Europe⁵⁵⁾

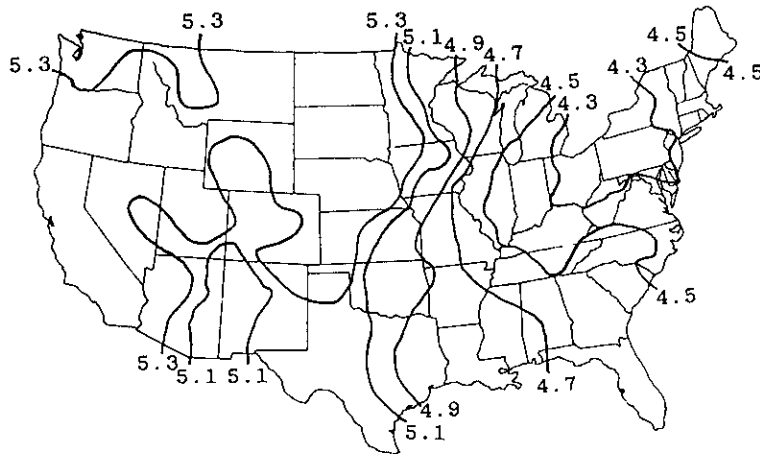


Fig. 7 pH in North America⁴⁸⁾

Europe, pH ranged approximately from 4.4 to 6.5 whereas from 4.2 to 5.6 in North America. The lower pH values for Japan was comparable to those for these two regions.

During the period of JEA surveys, some other monitoring networks started their operation. In June, 1984, Fujita and Kawaratani⁵⁵⁾ conducted a twelve-month monitoring of precipitation chemistry

at a uniformly distributed network of twenty stations in western Japan which encompassed Seto Inland Sea. Discussions were given especially to nss-sulfate in terms of spatial distribution, seasonal variation, relationships between deposition, and rainfall amounts and other related subjects.

In 1987, Central Research Institute of Electric Power Industry (CRIEPI) started its own nationwide

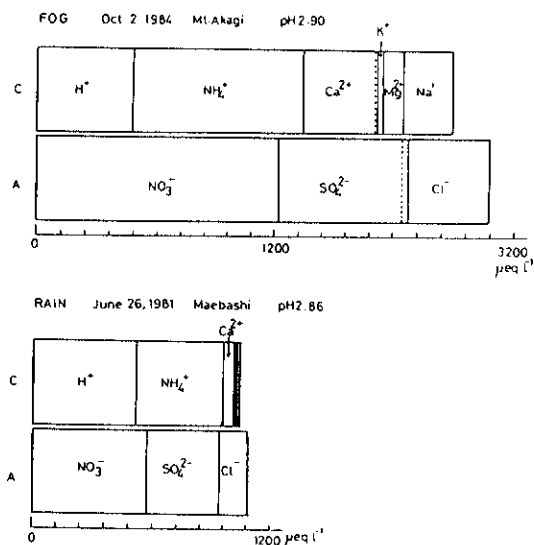


Fig. 8 Ionic Composition of Rainwater and Fogwater⁴⁹⁾.
rain water: Maebashi, June 26, 1981, pH2.86,
fogwater: Mt. Akagi, Oct. 2, 1984, pH2.90.

monitoring network⁵⁶⁾. This network has been operated to collect fundamental data on temporal and spatial distribution of acid deposition and to provide basic data for assessing the effects of acidification on terrestrial ecosystems. Precipitation are sampled with wet-only precipitation chemistry collectors every ten days at 21 stations including 5 remote islands. Gaseous SO_2 and major particulate ions including sulfate and nitrate are also monitored in this network.

Zenkoku Kogaiken Kyogikai⁵⁷⁾, the association of the prefectural and municipal institutes of environmental science, initiated precipitation chemistry monitoring at as many as 158 sites in 1990 with bulk samplers in order to obtain information on their monitoring activities and the state of acidification of precipitation. In a few years, the number of stations will be reduced to be approximately 50 with emphasis of selected subjects including long-range transport.

4.4 Wet Deposition (2): Fog and Snow Chemistry

Snow and fog also consist significant wet deposi-

tion channel. Snow chemistry is investigated also with respect to snow on the ground, and snow melts. As the snow deposited on the ground underwent melting, the ionic contents of the major ions were demonstrated to decrease. The snowmelt, on the other hand, was confirmed to be enriched with the major ions⁴⁷⁾.

Several groups study fog chemistry. Sekiguchi⁴⁹⁾ observed fog water with a pH of 2.90 on Mt. Akagi, approximately 100 km north to Tokyo. The ionic composition was compared with that of rainwater with comparable pH and that fogwater contained much higher concentrations of sodium, calcium, and potassium ions (Fig. 8). An interpretation of this result is obtained if the fogwater had incorporated aerosol particles at the ground level.

Ikeda et al. performed a modelling study of fog chemistry on the basis of the measurements on the top and at the foot of Mt. Akagi⁵⁰⁾. They reported that both oxidation of dissolved sulfur dioxide by hydrogen peroxide and incorporation of sulfate aerosol in the atmosphere were responsible for the sulfate in the fog. Nitrate was concluded almost entirely due to incorporation of nitrate aerosol.

4.5 Dry Deposition

Dry deposition of sulfur species to Japan Sea coastal areas were estimated⁵¹⁾ by using the inferential equation, $F = c v_d$ where F , c , and v_d represent dry deposition flux, air concentration of depositing sulfur, and deposition velocity, respectively. The coastal area was divided into five climatological regions. Dry deposition was shown to be significantly comparable to the wet deposition in every region (Table 2). Deposition of sulfur dioxide accounted for more than 90% of those of sulfur compounds, both sulfate and sulfur dioxide.

Although dry deposition cannot be directly monitored, dry deposition fluxes will be estimated as above. Air concentrations can be monitored by using conventional techniques with least modification. The fourth phase of EMEP⁵²⁾ includes measure-

Table 2. Estimated deposition and emission of sulfur species on Japan Sea coast areas⁵¹⁾

Areas	Rainfall Amount mm y ⁻¹	Deposition*		Emission*	
		Wet	Dry	Man-made	Natural
Western Hokkaido	1200	0.06	0.04	0.03	
Western Tohoku	1600	0.04	0.02	0.03	
Hokuriku	2300	0.11	0.07	0.04	
Western San-in	2100	0.06	0.04	0.01	
Northwestern Kyushu	2000	0.08	0.05	0.05	
Total		0.35	0.22	0.16	<0.02 ?

*Tg·S y⁻¹

ments of SO₂, SO₄²⁻, HNO₃+NO₃⁻, NH₃+NH₄⁺, NO₂, and O₃. In Japan, both gaseous and particulate sulfur and nitrogen species should be monitored on a nationwide scale.

4.6 Integrating Study in the JEA Phase-II Survey

In JEA Phase-II Survey, efforts were also directed to integrate monitoring results in order to predict adverse effects of acid deposition upon freshwater, and vegetation.

5. Further Studies

JEA has recently launched a critical loads evaluation program. Critical loads are defined as the highest deposition of hydrogen ions or acid anions, principally sulfate and nitrate, to environmental elements that will not cause harmful effects⁵³⁾. Critical loads generally differ from location to location, reflecting the different sensitivity to acid deposition of soils, freshwaters, and other environmental elements with different buffering capacities, which needs specific investigations in Japan.

In JEA Phase-III Survey, monitoring method will be improved in terms of siting criteria, sampling and chemical analysis, and quality control and quality assurance. The monitoring network will be rearranged being classified into three groups: remote, rural, and urban sites in Japan.

As Okita⁵⁴⁾ lately proposed an international

monitoring network in East Asia possibly including Southeast Asia, tentatively named "Asian Monitoring and Evaluation Programme (AMEP)" after the European programme, EMEP. JEA considers that some stations of JEA network will also be involved in such an international network. Further collaborations between Asian countries will play an important role in understanding what is and will be happening in this region, and is measures against the environmental acidification.

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