Analysis of Four-Year Results of Acid Precipitation
Based on a Wet-Only Sampling Network in Japan

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Abstract

Precipitation chemistry in Japan was discussed based on a wet-only event-basis dataset from five sites from April 1984 to March 1988. The annual average pH at each site ranged from pH4.5 to 5.1. Non-seasalt (nss-) sulfate and nitrate concentrations ranged from 30 to 63 $\mu\text{mol/L}$ and from 19 to 79 $\mu\text{mol/L}$, respectively. The pH was higher for the concentration levels of nss-sulfate and nitrate. This was attributable to the probable neutralization of the input acidity by additional alkaline species, gaseous ammonia and particulate calcium species. This was discussed in terms of pH and pAi defined as $-\log([\text{nss-SO}_4^{2-}] + [\text{NO}_3^-])$.

Key words: acid deposition, sulfate, nitrate, ammonium, calcium

1. Introduction

In October, 1983, the Japan Environment Agency (JEA) initiated acid precipitation monitoring as a part of the Phase-I Survey of Acid Deposition, from April 1984-March 1987. This survey was the first nationwide precipitation chemistry monitoring that employed identical sampling procedures and subsequent chemical analyses. In 1988, the Phase-II Survey succeeded the Phase-I with different sites, samplers, and sampling schedule. Because the Phase-II Survey is not yet completed, the Phase-I results are the only currently available dataset for precipitation chemistry in Japan. The monitoring included wet-only sample collection at seven of the stations of the network. Because the mechanisms of the wet-only sampler prevented the other two stations from obtaining winter time data, the results for five stations are discussed preliminarily. In this paper, the five-site data were analyzed in terms of concentration and deposition, and further, the chemistry was briefly compared with that for some other regions.

2. Experimental

Wet-only samples were collected on an event basis at five sites in Japan: Tokyo, Nagoya, Osaka, Hiroshima, and Nagasaki. Locations are reported elsewhere (Hara et al., 1990). From the global viewpoint, all these stations must be classified as urban (Tokyo, Nagoya, and Osaka) and suburban (Hiroshima and Nagasaki). Data quality was assessed by calculating the ratio of the cation sum to anion sum, and observed to calculated conductivity. Ratios different from unity by more than 20% led to re-analysis of the samples involved to resolve the discrepancy. Non-seasalt components were calculated in the usual way by assuming sodium ion to be a conservative tracer for seasalt, and estimating seasalt contributions from the known ionic ratios in seawater (Millero, 1974).

3. Results and Discussion

The mean values of the major parameters are summarized in Table 1. The mean pH did not vary among these sites: pH4.35-4.77. Although the number of sites is very limited, the spatial variation of the concentration was found to be different among ions in terms of the ratio of the standard

deviation to the mean, σ/m : nss-SO_4^{2-} ; 0.31, NO_3^- ; 0.56, NH_4^+ ; 0.55, nss-Ca^{2+} ; 0.80, and H^+ ; 0.43. Non-seasalt sulfate and hydrogen ion concentrations may be regarded as rather uniform compared with the other ions, which is in accordance with a similar suggestion based on the two-year results of bulk samples at 29 sites in Phase-I Survey. (Hara, 1991).

In urban sites, nitric acid exceeded sulfuric acid on an equivalent basis in urban sites provided that the acidity was assumed to originate from either nitric and sulfuric acid whereas sulfuric acid was dominant in suburban sites. Nitrogen oxides exceeded sulfur dioxide in these urban sites and nitrogen oxides levels were also high. Nitrogen oxides are generally converted in the atmosphere to nitric acid more rapidly than sulfur dioxide. These conditions would have resulted in a dominance of nitric acid of these sites.

Gatz has recently summarized the urban data of precipitation chemistry (Gatz, 1991). The major ion concentrations in the wet-only sample are summarized for six urban sites in the U. S. (Seattle, Chicago, New York City, Detroit, and two sites in Los Angeles), and one site in Greece, Athens. In comparison with the concentration levels of these urban sites, nss-sulfate and hydrogen ion levels are comparable. Nitrates in Tokyo were two times higher, and Nagoya nitrate levels are greater than the highest level of his seven sites. Ammonium levels in Osaka and Nagasaki were comparable to those of the U. S. and Greek sites, but the other sites in Japan recorded fairly more elevated concentration levels. As for nss-calcium ion, the concentrations generally increased more than that in the U. S. urban sites whereas Athens showed exceptionally high concentrations, ca. $140 \mu\text{eq/L}$.

Four years is not sufficiently long for detailed temporal trend analysis. At some site, however, temporal trends seemed to be appreciable for certain ion concentrations. Nitrates in Tokyo, for example, increased steadily from $46.7 \mu\text{eq/L}$ to $96.2 \mu\text{eq/L}$ for this period.

Because Japan is an industrialized country and is long and slender groups of islands, very few sites could be regarded as rural. On the other hand, other networks such as NAPAP and EMEP are composed mostly of rural sites. A close comparison of the present dataset with those of these networks might not be erroneous, but a qualitative comparison would be significant.

The pH was rather high when considering the concentration levels of nss-SO_4^{2-} and NO_3^- which are comparable to those in Europe. (Schaug et al., 1987) and North America (Olsen and Watson, 1984). As Tsuruta (1988) has already suggested, this is attributable to probable neutralization by atmospheric alkaline species including gaseous ammonia and particulate calcium carbonate.

The 1987 annual deposition of nss-sulfate in Tokyo 83.4 meq/m^2 (was comparable to that in Kane (Pennsylvania, U. S. A.) (91.3 meq/m^2). Because the annual rainfall amount happened to be almost the same (Tokyo; 1370 mm/y and Kane; 1338 mm/y), the mean chemical compositions of the precipitation are illustrated in Fig. 1. As discussed earlier, the ratio of hydrogen ion to the sum of nss-sulfate and nitrate was 0.10 in Tokyo whereas 0.72 in Kane where Morgan (1982) defined this sum as input acidity. This difference in the precipitation chemistry will be explained in terms of neutralization of input acidity.

Many investigators have discussed the degree of neutralization by introducing several quantitative measures (Morgan; 1982, Daum et al.; 1984, Chang et al.; 1987, Tsuruta; 1988). In order to include the pH value

explicitly which is one of the most basic parameters in acid deposition, the author proposes another measure, pAi defined as below.

$$pAi = -\log([nss-SO_4^{2-}] + [NO_3^-]).$$

This measure, pAi, physically means that the hypothetical pH of precipitation water, if any neutralization took place in the fate of sulfuric and nitric acids. This should be discussed together with pH.

Figure 2 shows a plot of pAi versus pH for annual means for each stations of the Phase-I Survey. Also plotted in the same figure data from other networks: North America (NAPAP)(Erb et al., 1989), Europe (EMEP)(Schaug et al., 1987), China (Zhao et al., 1984), and global backgrounds (Dayan et al., 1985). The plot on the broken line corresponds to no neutralization, and the neutralization proceeded to greater extents as the plot deviates rightward horizontally. In North America, neutralization seems to proceed to a lesser extent whereas to a greater extent in Europe. The sites in China were classified into two groups: acid-rain and non-acid-rain region. Data for both regions showed similar pAi's but different pH, which can be attributable to the neutralization by alkali calcium species. Data for global backgrounds are located above or on the broken line. This may be due to the contribution of organic acid to the free acidity.

In some cases, nss-sulfate is also emitted in the form of CaSO₄ directly into the atmosphere from desulfurization plants (Tsurumi et al., 1991), where pAi corresponds to the lower limit of pH in the absence of neutralizing agents in the atmosphere. Nevertheless a combination of these two measures, pH and pAi will be a useful tool in understanding the chemical characteristics of precipitation.

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Table 1 Mean chemical parameters in the survey period

Stations	RF* mm/y	nss-SO ₄ ²⁻ μmol/L	NO ₃ ⁻ μmol/L	NH ₄ ⁺ μmol/L	nss-Ca ²⁺ μmol/L	pH
Tokyo	1441	63.0	79.3	91.9	61.2	4.73
Nagoya	1338	43.8	49.4	55.2	27.7	4.56
Osaka	1509	29.8	32.3	27.6	15.7	4.35
Hiroshima	1694	38.8	30.6	59.8	14.9	4.77
Nagasaki	1700	34.3	18.6	21.4	10.1	4.37
mean(μ)		42.0	42.0	51.2	25.9	30.3**
s.d.(σ)		12.9	23.6	28.2	20.8	13.1**
σ/μ		0.31	0.56	0.55	0.80	0.43

*RF: rainfall amount. **mean and s.d. for H⁺ concentration.

Fig. 1 Ionic Depositions at Kane (a) and Tokyo(b) in 1987.

Fig. 2 Relationship between pAi and pH. ○; Japan, □; Europe, ●; North America, ■; China, △; global background sites.