

# D-5 ACID-BASE CHEMISTRY OF KOREAN PRECIPITATION

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## INTRODUCTION

The issue of acid precipitation has recently drawn significant public and scientific attention in the Northeast Asia due to the region's ever and fastly increasing acidic gas emission. As of 1990, the emission of SO<sub>x</sub>, the most abundant acidic gas, amounts to about 20 million tons(1) which is almost equivalent to that of North America or Europe, most seriously acidified areas on earth. And it is expected that Asian emission will soon exceed that of the above areas. In Korea, from the year of 1988 to 1993, the emission of SO<sub>2</sub> and NO<sub>x</sub> was increased from 1.1 to 1.5, from 0.4 to 0.7 million tons respectively. It is not only the emission amounts, but the geographical distribution that makes the issue complicated. That is, the biggest emission country is located upwind causing a potential transboundary problem.

Since 1983, the Korean Environmental Administration and Forrest Research Institute of the Ministry of Agriculture, Forrest, and Fishery began to monitor the pHs and conductivities of precipitations on a national scale. The results of both event-based monitoring showed a wide variation of pH ranging from less than 4 to higher than 7. However, the annual mean pHs were around 5.0 with no distinct spatial or temporal variation(2). Due to the lack of other chemical information on precipitation, it was difficult to understand the causes and characteristics of the region's acid-base precipitation chemistry. Therefore, to fill this gap, we have launched a nationwide precipitation chemistry monitoring in which not only pH and electrical conductivity, but all the major ions were determined. In 1993, we had started to monitor at Seoul only, and the following year we added five additional stations including two remote island. Preliminary results are to be presented herein.

## METHODS

Monitoring sites are shown in Fig. 1. Precipitations were collected using automatic wet-only samplers at all sites except Seoul, where both wet-only and bulk samples were collected. Wet-only samples were recovered at daily or

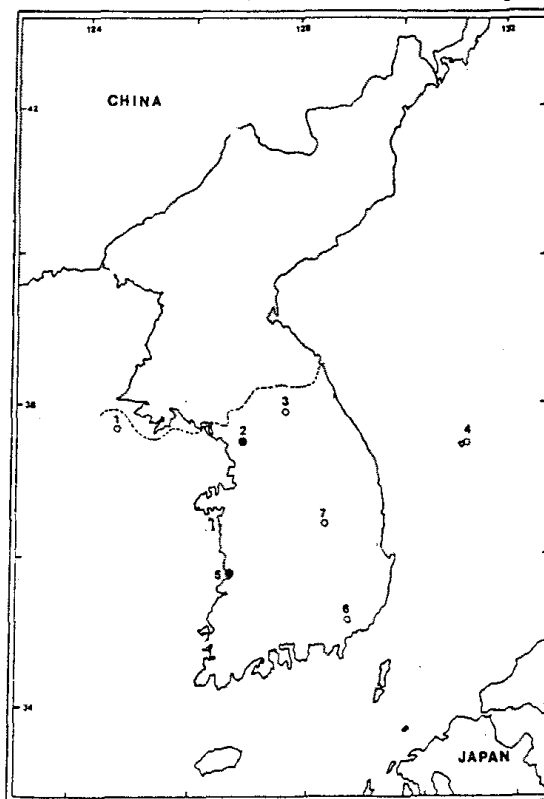


Fig. 1. Sampling sites for this study.

1. Sochung, 2. Seoul, 3. Chuncheon,
4. Ulling, 5. Kunsan, 6. Changwon
7. Jumchon,

event base, whereas bulk samples were recovered on the next morning of every rainy day. Thus, for some bulk samples, sampling duration was as long as three weeks. The recovered samples were stored in refrigerators until shipping to the laboratory for chemical analysis. In the laboratory, about 50ml aliquots were taken for immediate pH and conductivity measurements using an Orion pH meter and a conductivity detector of a Dionex DX-500 Ion Chromatograph, respectively. The remaining samples were filtrated and the filtrates were kept in refrigerators for major ion analysis, which were usually performed within 8 weeks by ion chromatography.

## RESULTS

There was a good correlation between cation and anion sums and calculated and measured conductivities :  $r^2 = 0.95$  for both cases.

Means and standard deviations of major ion concentrations are summarized in Table 1. The volume-weighted mean pHs ranged from 4.7 to 4.9. Though there were no distinct difference in the pHs between the sites or sample types, pH of every event varied greatly. Event pH of Seoul rain ranged from 4 to 7.8. It is quite common to observe pHs above 6. Most extreme values are generally observed in springtime when yellow sand storm occurs, indicating its strong influence on the region's precipitation pH.

Dissolved ion concentrations are comparable to those of Japan(3) and North America(4), but ion compositions are largely different particularly from those of North America. In North America, the most abundant cation is proton which accounts for more than 50% of total cation concentration. In Korea, however, proton accounts only for as little as 10%: the most abundant ion is ammonium and the next is calcium. Sulphate was the dominant anion: sulfur/nitrogen ratio was about 4, much higher than that of Japan or North America, suggesting that sulfur dioxide is the dominant acid precursor in Korea.

Table 1. Volume weighted average of pH and chemical component of rain

Sampling Site	Period	pH											
			Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	H <sup>+</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	nss-Ca <sup>2+</sup>
			μeq / ml										
Seoul(Bulk)	93.2~	4.9	22.0	41.0	142	13.5	12.4	111	6.89	13.1	99.8	140	99.2
Seoul(Wet)	94.5~	4.9	15.5	27.5	86.7	13.9	8.67	85.6	3.19	6.59	41.3	85.6	40.9
Sochung	94.5~	5.0	54.9	18.4	51.5	9.80	40.3	50.0	5.49	17.6	39.6	46.6	37.8
Chunchon	94.4~	4.7	15.6	19.4	42.3	20.9	9.45	39.4	2.50	6.42	24.1	48.5	23.7
Kunsan	94.8~	4.9	39.6	27.4	116	14.0	32.2	61.8	6.90	15.6	69.8	112	67.6
Kwanak mt.	94.8~	4.8	28.0	34.1	95.0	15.5	20.1	63.3	8.88	12.1	63.5	92.6	62.6

From the above ion composition data, it is evident that acid precursors introduced in atmospheric environment in Korea were well neutralized before they reached the ground. The degree of neutralization is demonstrated in Fig. 3, in which pHs and pAis for all precipitation samples are plotted. Here pAi represents the hypothetical pH of precipitation when no neutralization takes place:  $pA_i = -\log([nss-SO_4^{2-}] + [NO_3^-]) / 5$ . The broken line corresponds to the case of no neutralization, and the more neutralization proceeds, the further the plots deviate to the right of the figure.

Ammonia is believed to be the most important neutralizer in this region. Our recent measurement of gaseous ammonia revealed highly elevated concentration in order of tens of part per billions. Alkaline carbonate from the yellow sand dust appear to be an another important neutralizer. For example, one of 1993 was measured to have an alkalinity of 670  $\mu\text{eq/l}$ . Another the pH of the precipitation was 7.75, the alkalinity equivalent pOH amounts to about 4, not 6. It should be noted, however, that this neutralization is effect only for long effects such as acidification of lakes or soil due to extreme sporadic while the acute effects are still remain.

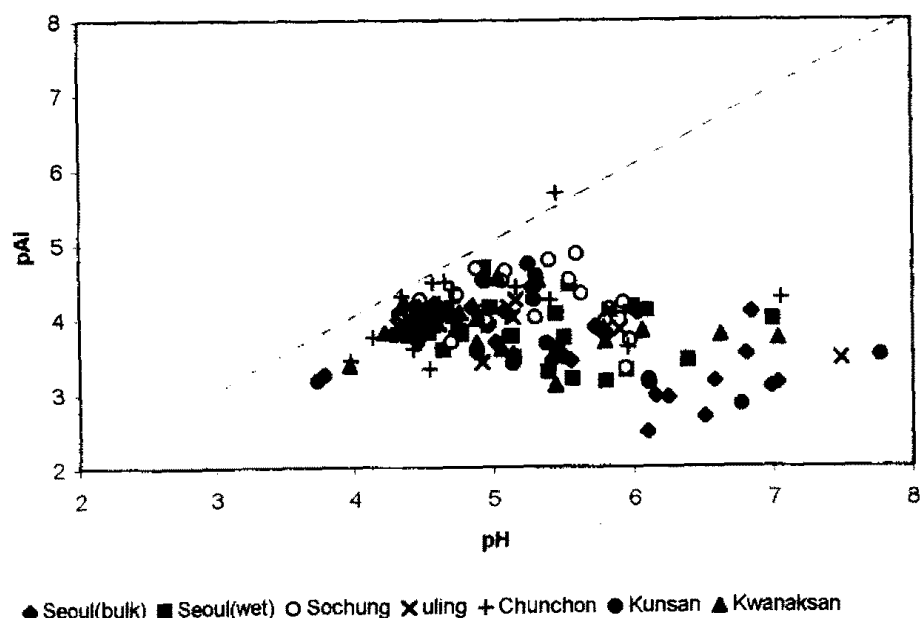


Figure 2. Correlation between pHs and pAis.

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