

STUDY ON MODELING PARAMETERS FOR DISTRIBUTION OF WET DEPOSITION OF SULFATE IN EAST ASIA

Daichi Takahashi, Yoshika Sekine, Shinichiro Hashimoto

Department of Chemistry, School of Science, Tokai University,
1117 Kitakaname, Hiratsuka, Kanagawa, 259-1292 Japan,
3ascm006@keyaki.cc.u-tokai.ac.jp, sekine@keyaki.cc.u-tokai.ac.jp

1. INTRODUCTION

A major air pollutant in the early 1990s in China has been sulfur dioxide (SO_2) emitted from coal combustion effluents. Its high atmospheric concentrations resulted in acidic wet depositions which caused damages not only on ecosystem but also on economics through agricultural products. Large emissions of SO_2 in the continental cities could affect air quality of other countries by long range transport beyond borders. Therefore, common understanding on SO_2 and related problem should be needed among eastern Asian countries.

In a previous study, authors have shown distribution and decreasing tendency of SO_2 concentration in China since 1990s based on data analysis and multi-grid box model estimates [1, 2]. Those studies also aimed to predict future changes of SO_2 concentration by inputting SO_2 emission rate predicted along with significant scenarios. The SO_2 emissions per year have been estimated by economic models such as I-O technique, and often used as air pollution index for certain administrative districts (nationwide, province, city or so) [2,3]. Subsequently, questions were raised about changes of precipitation pH influenced by sulfate contamination in near future.

While a number of numerical modeling studies were conducted on the global or regional acid deposition assessments [eg.4], authors have planned to develop a site-specific empirically-based model which describes prospective distribution of precipitation pH and wet depositions of sulfate in eastern Asian cities, using the SO_2 concentration as a variable. In this study, feasible modeling parameters were investigated by deriving from 2-year compiled monitoring data of Intergovernmental Meeting on the Acid Deposition Monitoring Network in East Asia (EANET) covering wet and dry depositions at 43 sites in 10 countries.

2. MODELING POLICY AND THEORY

A simulation model, which forecasts precipitation pH as a function of atmospheric SO_2 concentration, is based on two assumptions. The first assumption is that SO_4^{2-} in rain mostly can be associated with that in atmospheric aerosols. The second is that SO_4^{2-} represents sulfur species in the rain. Then, atmospheric SO_2 concentrations were related to atmospheric SO_4^{2-}

concentration in aerosols and subsequently wet deposition of SO_4^{2-} . The secondary aerosols result primarily from oxidation processes of SO_2 : homogeneous gas-phase reactions involving free radicals and heterogeneous reactions in droplet phase and on aerosol particles.

The relationship between atmospheric concentrations of SO_2 and SO_4^{2-} was simply defined in the modified form of the gas-particle distribution factor, F by Grosjean and Friedlander [5] and Kadowaki [6] :

$$F = \frac{[SO_4^{2-}]_a}{[SO_2]_g + [SO_4^{2-}]_a} \quad (1)$$

where $[SO_2]_g$ is atmospheric SO_2 concentration in $\mu g/m^3$ and $[SO_4^{2-}]_a$ is airborne particulate sulfate concentration in $\mu g/m^3$. The gas-particle distribution factor has been known to be dependence on meteorological conditions (temperature, humidity, light intensity) and active chemical species, typically oxidants.

A scavenging ratio practically parameterizes a diversity between concentrations of chemical species in rain and aerosol phases [7,8]. The coefficient is generally defined in dimensionless ratio of the concentration of sulfate in the precipitation and in the aerosol as follows,

$$W = \frac{96 \times 10^3 [SO_4^{2-}]_r \rho}{[SO_4^{2-}]_a} \quad (2)$$

where $[SO_4^{2-}]_r$ is precipitation sulfate concentration in mol/L and ρ is the density of air ($1200 g/m^3$). The scavenging ratio also depends of meteorological conditions (cloud type, phase contact time, precipitation intensity, etc.) and on the microphysical conditions (size and hygroscopy of the particles, number of condensation nuclei and so on).

On the other hand, the hydrogen ion concentration, and thereby pH, in precipitation is determined by the balance between acidic and alkaline species [4]. The molar concentration of H^+ in rain can be approximately estimated from eq.(3)

$$[H^+]_r = 2[SO_4^{2-}]_r + [NO_3^-]_r + [Cl^-]_r - [NH_4^+]_r - 2[Ca^{2+}]_r - [Na^+]_r - 2[Mg^{2+}]_r - [K^+]_r \quad (3)$$

Combining eqs.(1)-(3) gives the final equation, describing the site-specific hydrogen ion concentration in precipitation as a function of $[SO_2]_g$.

$$[H^+]_r = \frac{2WF[SO_2]_g}{96 \times 10^3 \rho(1-F)} + [NO_3^-]_r + [Cl^-]_r - [NH_4^+]_r - 2[Ca^{2+}]_r - [Na^+]_r - 2[Mg^{2+}]_r - [K^+]_r \quad (4)$$

3. DATA CITED

EANET is performing the monitoring of precipitation, gas and aerosol in the atmosphere, and publishing annual data report describing annual mean and monthly mean observation

results. In this study, the previous data for the period 2000-2001 were cited from ref. [9]. The monitoring method that EANET has employed is briefly described below.

Precipitation (wet deposition)

Monitoring interval: every 24 hours or every precipitation event

Major parameters: pH, electrical conductivity, concentrations of sulfate (SO_4^{2-}), nitrate (NO_3^-) and other ions.

Gas and Aerosol (dry deposition)

Monitoring interval: every two week to one month (when measured by Filter pack method), or every hour (when measured by Automatic monitoring method).

Major measurements: gaseous (SO_2 , HNO_3 , etc.) and particulate components (SO_4^{2-} , NO_3^- , etc.) (when measured by Filter pack method), or SO_2 , NO_2 , NO , O_3 , and particulate mass concentration (PM_{10} , $\text{PM}_{2.5}$, TSP) (when measured by Automatic monitoring method).

Since this study required particulate SO_4^{2-} concentration for calculation of F and W, we picked up the EANET data sets from the 11 sampling sites in 5 countries where the filter pack methodology was employed for the aerosol monitoring. The annual mean and monthly maximum and minimum of precipitation pH, $[\text{SO}_2]_g$, $[\text{SO}_4^{2-}]_a$, and $[\text{SO}_4^{2-}]_r$ of the 11 sites are highlighted in Table 1.

Table 1 Summary of monitoring data on pH, $[\text{SO}_2]_g$, $[\text{SO}_4^{2-}]_a$ and $[\text{SO}_4^{2-}]_r$ at selected sites.

Country	Name of sites (Characteristics)	year	pH			$[\text{SO}_2]_g (\mu\text{g}/\text{m}^3)$			$[\text{SO}_4^{2-}]_a (\mu\text{g}/\text{m}^3)$			$[\text{SO}_4^{2-}]_r (\mu\text{mol/L})$		
			Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
Malaysia	Petaling Jaya (urban)	2000	4.35	4.65	4.12							23.5	33.0	9.7
		2001	4.25	4.41	3.98	14	17	10	3.6	5.3	1.6	22.2	31.0	23.7
	Tanah Rata (remote)	2000	4.79	5.34	4.30	0.2	0.3	<0.3	1.2	2.3	0.7	4.1	6.6	<1.0
		2001	4.90	5.16	4.56	0.2	0.3	<0.3	0.7	1.1	0.2	3.7	12.6	2.2
Mongolia	Ulaanbaatar (urban)	2000	6.26	7.51	6.09	3.9	5.6	1.9	2.1	2.7	1.3	24.3	103	14.8
		2001	6.19	7.07	6.01	4.4	6.9	2.7	2.6	3.5	1.4	25.2	108	17.0
	Tereelj (remote)	2000	5.52	7.26	4.96	1.0	3.2	<0.3	1.1	1.7	0.4	16.4	36.5	7.8
		2001	6.04	6.27	5.89	1.4	3.5	0.5	1.6	2.3	1.0	9.7	14.4	5.1
Philippines	Metro Manila (urban)	2000	5.48	7.99	5.16	13	17	9.6	2.0	3.0	1.1	23.4	105	12.7
		2001	5.41	8.10	5.05	11	17	4.8	1.9	3.9	<0.1	37.3	105	11.9
	Los Banos (rural)	2000	5.44	6.29	4.63	2.0	3.2	1.3	0.5	0.5	0.5	10.5	19.9	2.4
		2001	5.53	7.54	4.84	1.9	5.9	<0.3	0.9	2.5	<0.1	15.6	82.4	5.7
Russia	Mondy (remote)	2000	5.26	6.62	5.02	0.3	0.8	<0.3	0.5	1.1	0.2	7.2	35.7	1.0
		2001	5.50	6.57	5.34	0.6	1.3	<0.3	0.8	1.8	0.2	11.0	23.1	3.8
	Listvyanka (rural)	2000	5.07	5.78	4.64	2.7	8.5	0.5	1.4	3.6	0.4	15.4	35.1	1.2
		2001	4.96	5.56	4.63	5.7	20	0.3	2.5	4.0	1.0	13.4	23.6	10.6
	Ikutsk (urban)	2000	5.11	6.59	4.80	9.1	36	0.3	2.4	9.3	<0.1	30.1	127	14.5
Vietnam		2001	5.28	7.30	4.94	8.0	32	0.8	3.8	7.8	0.2	29.6	186	9.9
	Hanoi (urban)	2000	5.45	6.41	4.63				1.1	2.8	0.3	30.1	586	6.1
		2001	5.83	6.08	5.32	9.3	15	0.3	1.4	4.0	0.3	13.3	41.9	7.4
	Hoa Binh (rural)	2000	5.11	6.69	4.20				2.2	4.8	0.4	16.3	144	8.3
		2001	5.04	6.95	4.52	6.8	10	1.1	2.6	6.7	0.1	14.1	72.4	4.2

4. RESULTS AND DISCUSSION

4.1 Gas-particle distribution factor

Gas-particle distribution factors between SO_2 and sulfate were calculated according to eq.(1),

putting 2-year data together at each site. Fig.1 shows plots of F against latitude. The factors ranged from 0.15 to 0.81 in 2-year average and showed site specific feature: relatively higher in high latitude areas. Besides, the factors in the rural and remote areas were larger than those in the urban areas. This is roughly because larger emissions of active air pollutants together with SO_2 from anthropogenic sources (fossil fuel combustion) caused the oxidation of SO_2 . It is generally recognized that there are two most important atmospheric oxidation processes: homogeneous gas-phase reactions

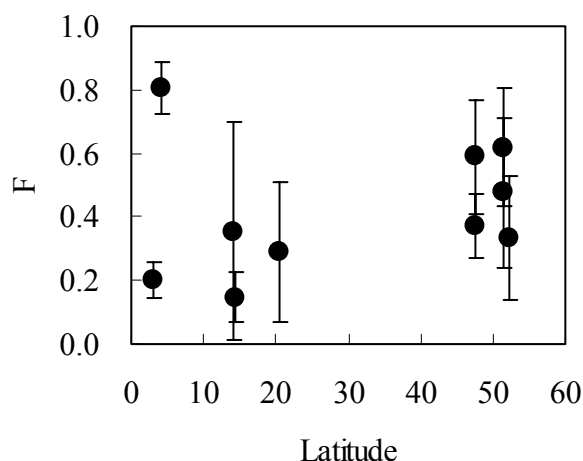


Fig.1 Plots of gas-particle distribution factor against latitude (●: 2-year average, bars: standard deviations of the monthly data.)

involving free radicals such as OH and heterogeneous reactions in droplet phase. Kadowaki [6] has noted the latter process in case of SO_2 oxidation because of a good correlation found between F and relative humidity (RH), when RH was more than 75%, in an urban area, Japan. Therefore, dependence of F on the RH was considered. In rural and remote areas of the EANET site, significant correlation between F and RH was found at RH above 75% with $r=0.6$ at 1% confidence level (Fig.2(a)), as previously reported [6]. On the other hand, as shown in Fig.2(b), the factors did not depend on RH in urban area, even higher than 75%. This means gas-phase chemistry is also important in the area where oxidants concentration in the atmosphere might determine the distribution factors.

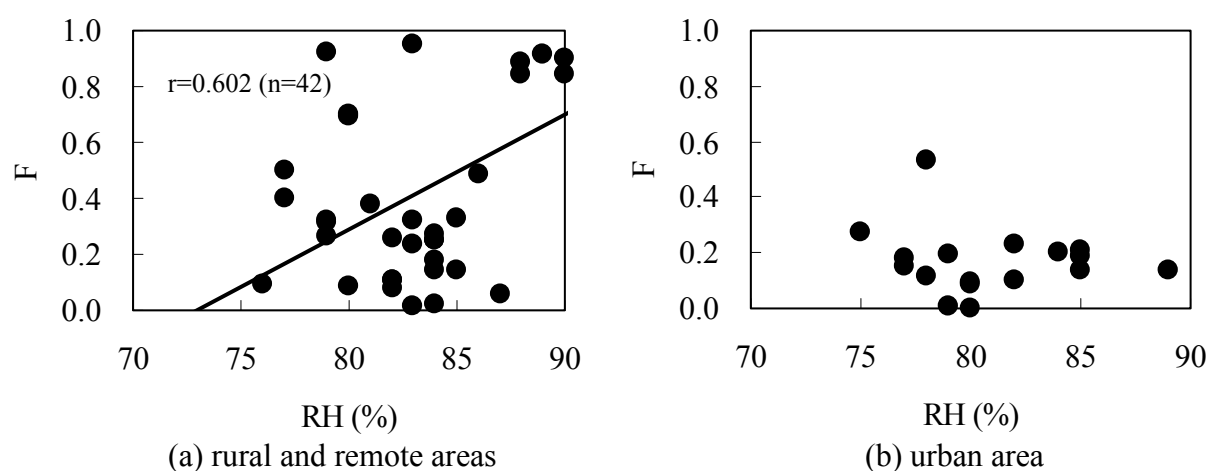


Fig.2 Scatter diagram of relative humidity and monthly calculated conversion factor observed at EANET stations. Data sets less than 75% RH were excluded.

4.2 Scavenging ratio

Fig.3 shows plots of scavenging ratios (W) against latitude. The ratio ranged from 700 to 8000: higher in the urban areas of the Philippines, Russia, and Vietnam, where relatively higher atmospheric concentrations of sulfur species were observed. The scavenging ratio depends on the precipitation intensity as shown in Fig.4. Large precipitation dilutes sulfate concentration in rain, resulting in lower W. To exclude this dilution effect of rain water, products of W and precipitation were obtained and plotted against monthly precipitation (P) as shown in Fig.5. The result showed a slight linear relationship between both two parameters, with $r=0.556$ at 1% confidence level, despite using monthly basis data. Regarding the products represent absolute scavenging ability of rain water, deviations may be caused by variation of rainfall intensity and its interval within a month.

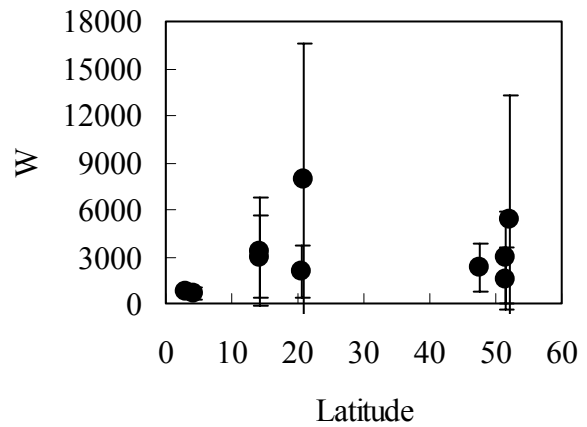


Fig.3 Plots of scavenging ratio against latitude (●: 2-year average, bars: standard deviations of the monthly data.)

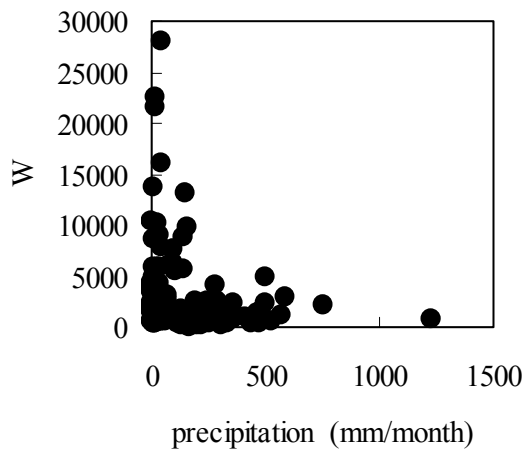


Fig.4 Dependence of scavenging ratio on the precipitation per month.

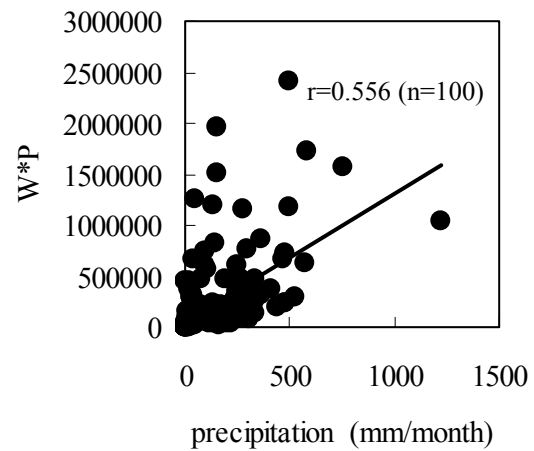


Fig.5 Plots of products of W and P against the precipitation per month.

4.3 Reconstruction of precipitation pH

Using F and W obtained above, precipitation pH was reconstructed according to eq.(4). Fig.6 shows a scatter diagram between calculated pH and observed pH in every month at each site. The calculated pH tended to increase with an increase in observed pH. However, a good agreement was not found. To inspect cause of the uncertainty, eq.(3) was used to reconstruct precipitation pH inputting observed $[\text{SO}_4^{2-}]_r$ into the equation. Fig.7 illustrates comparison of observed precipitation pH (obs-pH), calculated precipitation pH (cal-pH) from eq.(4) using F

and W, and pH value obtained from eq.(3) using observed $[\text{SO}_4^{2-}]_r$ (eq3-pH) at 9 sites on 2-year averaged data basis. While effectiveness of F and W was suggested in the results of Malaysia (Petaling Jaya, Tanah Rata) and Mongolia (Ulaanbaatar), differences between cal-pH and eq3-pH in Russia (Mondy, Listvyanka, and Irkutsk) and Vietnam (Hoa Binh) required further consideration of correction of F and W by influential factors such as humidity, precipitation intensity, oxidants concentration and so on. Disagreement between eq3-pH and obs-pH should be carefully considered because it also depends on analytical accuracy.

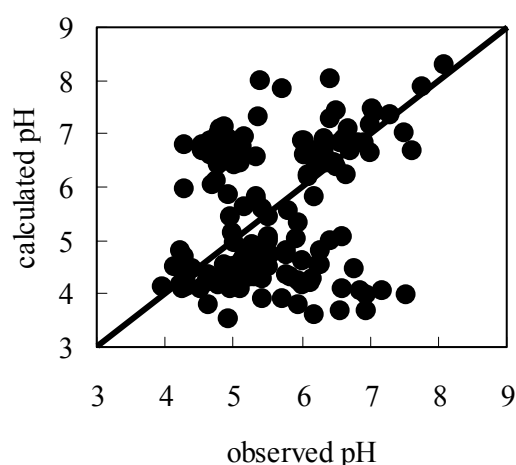


Fig.6 Scatter diagram of calculated pH and observed pH in every month at each site.

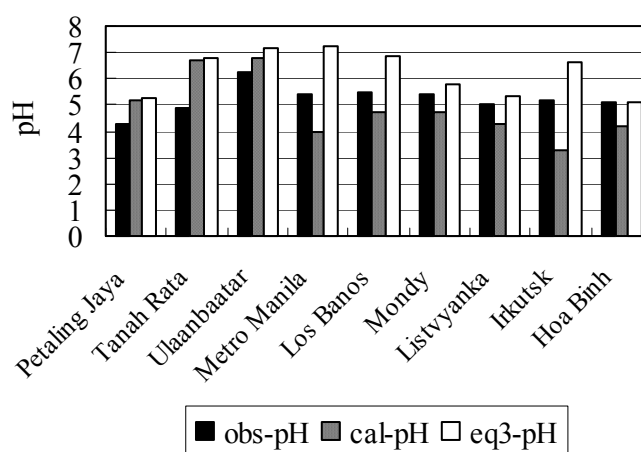


Fig.7 Comparison of precipitation pH at selected sites using 2-year average data.

5. CONCLUDING REMARKS

In order to predict precipitation pH by change of SO_2 concentration in the atmosphere, the empirical modeling parameters, F and W were introduced into the reconstruction formula of hydrogen ion concentration in rain. The results required further consideration of correction of these parameters based on RH, precipitation intensity, oxidants concentration and so on, and QA/QC evaluation and development of the monitoring data.

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