

## Experimental Studies on Wet Scavenging of Atmospheric Aerosols by Rain Drops

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### Abstract

Wet scavenging by rain drops is a most important removal process of air pollutants. In order to study the scavenging mechanisms of aerosol particles, the characteristics of chemical components in the rain water were examined as a function of the amount of rainfall. Rain water were collected continuously and separated into the soluble and insoluble components. The elemental concentrations in both components were determined by a PIXE analysis. The physical and chemical characteristics of atmospheric aerosols during the rainfall events were measured simultaneously.

The elemental concentrations in rain water decreased substantially just after rain started and then gradually declined in subsequential rain fall exceeding 1.0 mm. The large particles were scavenged more easily than the fine particles. Fe, Ti and Si in rain water were in high insoluble state. Contrarily, almost whole of S was dissolved in rain water.

**Key words :** Wet deposition, Atmospheric aerosols, Elemental concentration, PIXE analysis

### 1. INTRODUCTION

In the last several decades, the significance of global environmental problems including acid rain has been recognized at world wide. Atmospheric aerosols play an important role in such a problem in particular. Physical and chemical properties of the atmospheric aerosols as well as the rain drops are essential to understand the wet scavenging of atmospheric aerosols by rain water.

A lot of research groups have studies relationships between chemical compositions in rain water and

the amount of rainfall, and on the solubility of each elements of the aerosol particles caught by the rain drops (Kim *et al.*, 2003; Jickells *et al.*, 1992; Kim *et al.*, 1992; Seto *et al.*, 1992; Tanaka *et al.*, 1981). Most of them, however, have been mainly discussed using the mean values of rain water collected for relatively long time such as a whole rain event or on monthly basis.

A remarkable progress has been model in micro-analytical technique during the last two decades. A Particle Induced X-ray Emission (PIXE) is one of the most powerful analytical method. The analysis of atmospheric aerosol is one of the most feasible fields of the PIXE analysis. The PIXE technique has been applied to the micro-analysis of the various

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kinds of environmental samples such as rain water, polluted water and sediments as well as the atmospheric aerosols (Park *et al.*, 2001; Johansson *et al.*, 1995).

In this study, the rain drops were continuously collected from the beginning to the end of each rain event. Collected rain water was separated into the soluble and insoluble fractions. The elemental concentrations were determined by the PIXE analysis. The physical and chemical characteristics of atmospheric aerosols before the rain were compared to those of rainfall.

## 2. METHODS

### 2.1 Sampling of rain water and atmospheric aerosols

The sampling of rain water and atmospheric aerosols was carried out on the roof of 5-story building in the Uji campus of Kyoto University. The sampling site is in the residential area of the middle town being located at 10 km south-east of Kyoto city.

Rain water was sampled using four funnels with 30 cm diameter which could collect 28.3 mL of rain water for 0.1 mm rainfall. The frequency of sampling was planned as follows;

from 0.0 to 0.5 mm of rainfall	every 0.1 mm
5 samples	
from 0.5 to 1.5 mm of rainfall	every 0.2 mm
5 samples	
from 1.5 to 6.5 mm of rainfall	every 0.5 mm
10 samples	
from 6.5 mm to the end of rain	not divided
1 sample	

The pH value and electrical conductivity (EC) of rain water measured immediately after sampling. And then, rain water was filtered by passing through a 25 mm diameter Nuclepore filter with 0.2  $\mu\text{m}$  pore-size to divided into the soluble and insoluble components. Filtrate and residue were considered to be the soluble and insoluble components, respectively.

The gravimetric mass of the dried filtrate was

measured with an electron microbalance permitting readings in 0.01 mg. And then, it was stored in a desiccator until the PIXE analysis. The samples for the PIXE analysis of soluble components were prepared after storing in a refrigerator till just before the PIXE analysis. That is, 20  $\mu\text{L}$  of filtrate was dropped on the polycarbonate thin film (non-hole Nuclepore) by using a micropipet and dried by an infrared lamp. In total, one to 10 drops were repeatedly dropped and dried according to the concentration level estimated from the color of the residue. The size of sample was limited to 4 mm diameter so that whole of the sample could be bombarded by ion beam having 6 mm diameter.

Atmospheric aerosols were collected using a two stacked filter sampler before, during and after the rain. The two stacked filter sampler consist of two filters with different pore-size of 8.0 and 0.4  $\mu\text{m}$  which were connected in series and could classify the aerosol particles into the fine and coarse fractions. Nuclepore filter was selected for the reasons of less generation of bremsstrahlung X-rays, less impurity and high endurance against the ion beam bombardment. The sampling flow rate is not only concerned with the time resolution of the sample but also the cutoff size of filter. The sampling flow rate of 30 L/min (surface velocity = 24 cm/s) was adopted. Under these sampling conditions, the 50% cutoff size of 8  $\mu\text{m}$  pore-size filter was estimated to be about 1.1 ~ 1.2  $\mu\text{m}$  depending upon the particle density (Park *et al.*, 1999; Kasahara *et al.*, 1993a). Sampling time of two hours was required in order to keep the accuracy of PIXE analysis. The total sampling air volume was around 3.6 m<sup>3</sup>. Furthermore, the particles size distribution of each element was measured with a 12 stages Anderson cascade impactor to examine the effect of particles size on the wet scavenging of aerosol particles.

### 2.2 PIXE analysis

Elemental concentrations were determined by the PIXE analysis. It was performed with a 2.0 MeV proton beam from a tandem accelerator of the Department of Nuclear Engineering, Kyoto University. Beam intensities from 10 to 100 nA were employed

**Table 1. Summary of rain water sampling between January and November, 1995.**

Run	Date	Time (start-stop)	Rainfall (mm)	No. of sample	Min. pH	Max. pH	Max. E.C. ( $\mu\text{S}/\text{cm}$ )	Note
1	Jan. 22	3:52~9:50	2.07	11	3.9	4.9	106	
2	Feb. 12	15:45~19:45	4.99	16	3.7	4.6	109	
3	Feb. 28	20:40~22:44	4.94	16	4.0	5.1	78	
4	Apr. 22	1:00~8:30	1.70	10	5.2	6.6	41	
5	May 25	16:10~5:00	8.64	21	4.5	6.9	62	Yellow Sand
6	Jun. 8	10:50~23:50	7.88	21	4.9	6.3	30	
7	Jun. 30	23:20~12:55	20.18	21	5.0	6.5	32	
8	Sep. 24	7:00~8:50	3.39	14	5.8	6.5	13	Typhoon
9	Oct. 24	11:00~20:30	20.64	21	4.0	5.7	102	
10	Nov. 7	14:35~21:53	12.47	21	4.1	5.0	81	
11	Nov. 14	12:40~21:29	15.96	20	4.0	4.8	82	

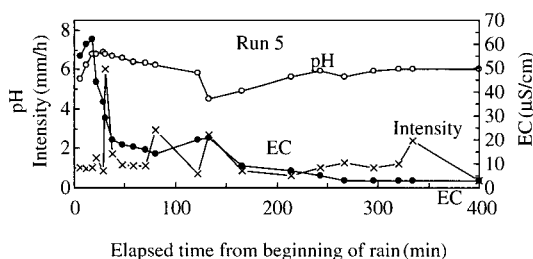
and the total dose was about 5~20  $\mu\text{C}$ . X-rays with an energy of 1.4~14.8 keV emitted from the target were detected by a Si (Li) detector which had a resolution of 152 eV at 5.9 KeV. An absorber of 39.3  $\mu\text{m}$  thick Mylar film was set between the sample and detector to control the counting efficiency of lighter elements. The counting rates for X-rays were kept below 500 pulses per second. The calibration was carried out with the 18 single element standard samples at each experimental set up as described previously in detail (Kasahara *et al.*, 1993b). The concentrations of 14 elements (Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb) were determined in this study.

### 3. RESULTS AND DISCUSSION

#### 3.1 The concentration change with the amount of rainfall

The rain water was collected at 11 rain events between January 22 and November 14, 1995. The sampling condition is summarized in Table 1. The lowest pH ranged from 3.7 to 5.8 and the sampling time to them differed the from rain to rain. The range of the highest electrical conductivity (EC) was from 13 observed at the rain during the typhoon to 109  $\mu\text{S}/\text{cm}$ .

In this paper, analytical results of the rain water collected from May 25/16 : 10 to May 26/05 : 00 (Run 5) are mainly discussed. The changes of pH,



**Fig. 1. Changes of pH, electrical conductivity (EC) and rainfall intensity as a function of the elapsed time from beginning of rain.**

EC and the intensity of rainfall are shown as a function of elapsed time after rain began in Figure 1. The accumulated amount of rainfall reached to be 6.5 mm after 334 min (May 25/21 : 44) from the beginning of rain. Since then, the rain water of 2.14 mm rainfall was collected without separation until the end of rain (May 26/05 : 00). The pH value was 5.5 at the beginning of rain and changed randomly between 4.5 and 6.9 and reached 6.0 at the end of rain. The EC decreased quickly at the beginning of rain and then decreased gradually.

The changes of the total mass concentration of the insoluble component (Inso) and elemental concentrations of Si and Fe are illustrated as a function of the accumulated rainfall amount from the beginning of rain in Figure 2a), and changes of EC and the elemental concentrations of S, K and Ca in the soluble component in Figure 2b).

The values of EC, Insoluble and the elemental concentrations were normalized by dividing by their initial values. The normalized EC, Insoluble and the

concentrations of S and Fe are plotted as a function of the accumulated rainfall amount in Figure 3.

As a general tendencies, the concentrations of 14 elements in both soluble and insoluble components decreased quickly from the beginning of rain to about 1.0 mm rainfall and then decreased gradually. After 2.0 mm rainfall, their concentrations decreased to less than 20% of the initial concentrations. The electrical conductivity and the total mass concentration of the insoluble component varied in the similar way with the change of elemental concentration. This suggests that the scavenging of aerosol particles by rain drops advance very effectively at the beginning of the rainfall.

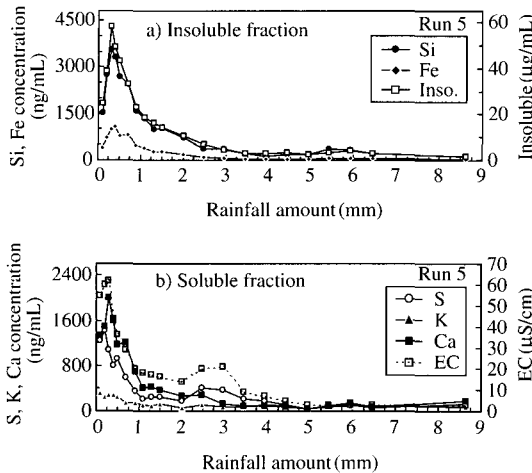


Fig. 2. Changes of insoluble (Inso) and elemental concentration in rain water as a function of the rainfall amount.

### 3.2 The total concentration and insoluble fraction

The total (soluble + insoluble components) concentrations of 14 elements are illustrated as the averaged value of 0~0.5, 0.5~1.1, 1.1~2.0, 2.0~3.0 and 3.0~6.5 mm rainfall in Figure 4a). Since the concentrations of Si, Ca and Fe were relatively

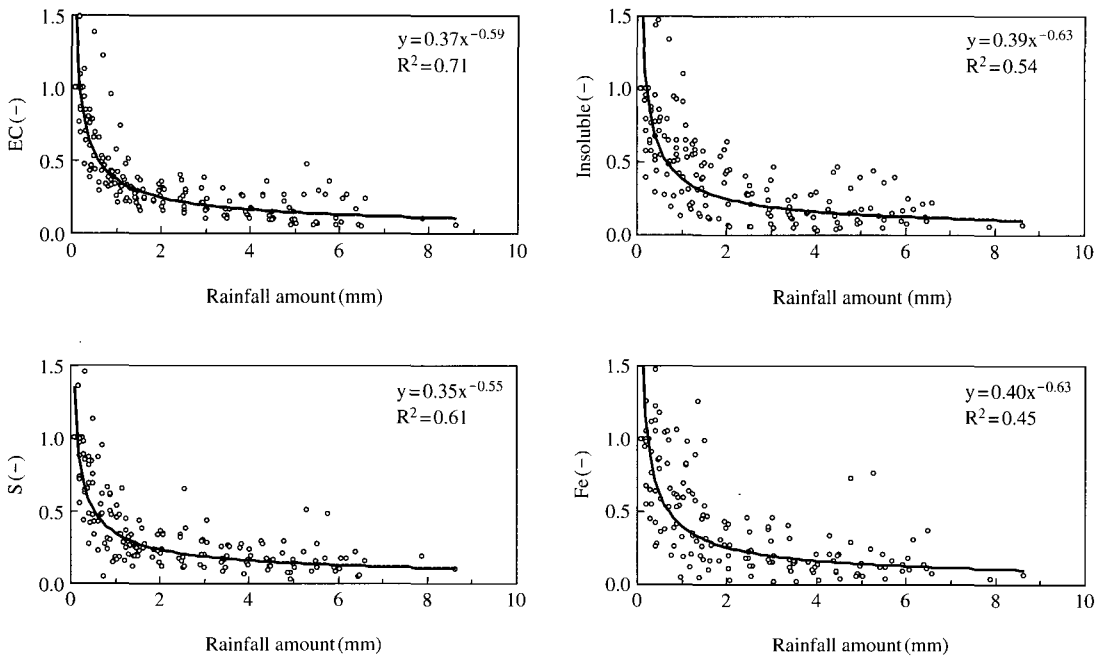


Fig. 3. Changes of the normalized EC, Insoluble and elemental concentrations as a function of the rainfall amount.

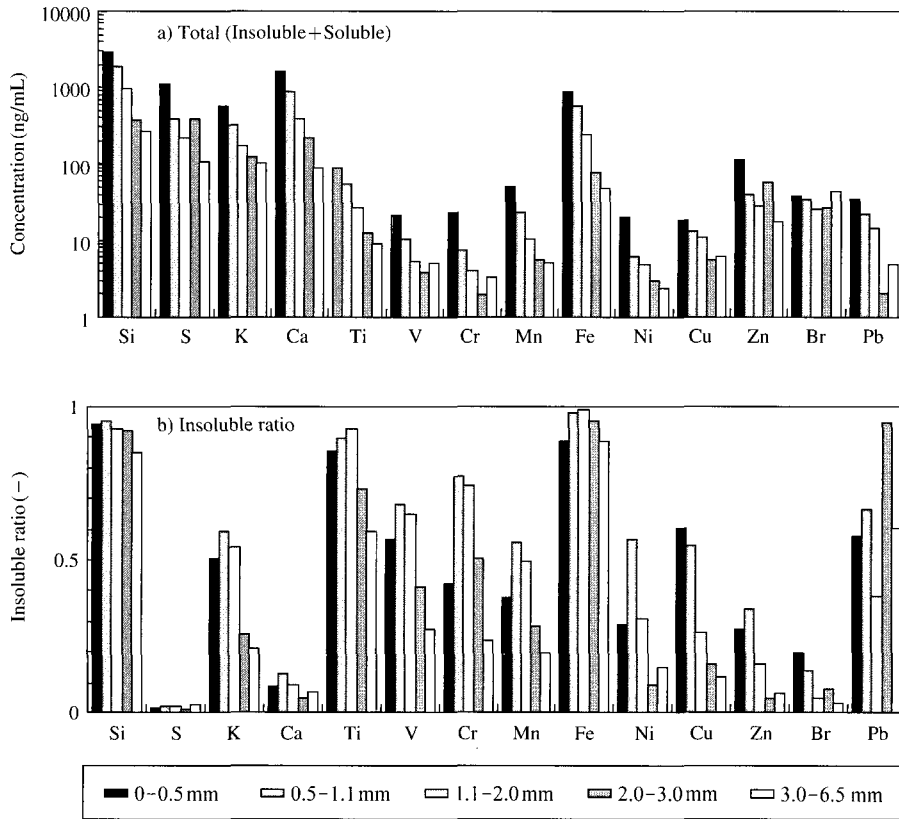


Fig. 4. The total (soluble+insoluble) concentrations and insoluble fraction of 14 elements in subsequential rainfall.

high as compared with other season, it was supposed that Yellow Sand dust was flying to Kyoto area during sampling period of Run 5.

Figure 4b) shows an Insoluble fraction defined by the ratio of the concentration of insoluble component to the total concentration. The insoluble fractions of Fe, Ti and Si originated mainly in the soil dust were large with exceeding 0.75. On the other hand, the insoluble fractions of S, Ca, Br and Zn were smaller than about 0.2 throughout the whole rain. Especially, almost entire fraction of S was dissolved in rain water. The insoluble fraction had generally a decreasing tendency with the rainfall amount. It means that the insoluble components are more easily caught by rain drops. The qualitative tendency of the insoluble fraction of each element was roughly similar to the data in the literature

(Giusti *et al.*, 1993).

### 3.3 Elemental concentration change of atmospheric aerosol during rain

In order to investigate the wet scavenging of aerosol particles by rain drops, it is essential to measure simultaneously the characteristics of atmospheric aerosols as well as the rain drops. The fine and coarse fractions of atmospheric aerosols were sampled every two hours prior to rain event and continue until it stopped. Sampling time of two hours was required to maintain the accuracy of PIXE analysis. Figure 5 shows the concentration changes of 14 elements in both coarse and fine particles during sampling period of Run 5. Initial and 2 hr in the explanatory notes mean the samples collected before rain and two hours after beginning of

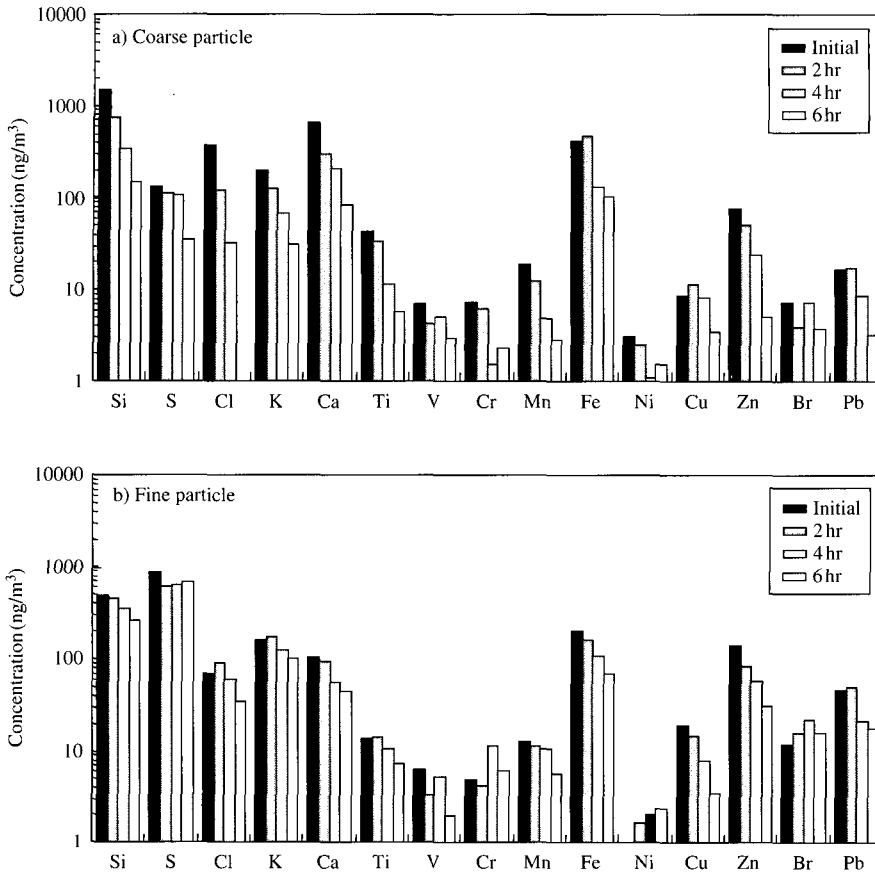


Fig. 5. Changes of the elemental concentrations of aerosol particles classified into the coarse and fine fractions which were collected during the rain event.

rain, respectively.

It is well known that the collection efficiency of aerosols by rain drops depends closely on the particles size. Both large and very small particles are easily captured by the initial and diffusional attachment and the intermediates sizes around 0.1 ~ 1 μm particle diameter has the minimum collection efficiency. The mass of the particles smaller than 0.1 μm is negligibly small. It suggests that the coarse particles larger than 1 μm can be scavenged more easily than fine particles. In the present study, it was confirmed, as shown obviously in Figure 5, the elemental concentrations of the coarse particles decreased more quickly with time than those of the fine particles.

Table 2. Reduction rate of elemental concentration of atmospheric aerosol during rain.

	Si	Ca	Fe	S	Zn	Pb
Pre-rain period	1	1	1	1	1	1
0-2 hr average	0.60	0.52	1.00	0.72	0.63	1.07
2-4 hr average	0.35	0.34	0.38	0.73	0.39	0.48
4-6 hr average	0.21	0.17	0.27	0.72	0.17	0.33

As mentioned before, the collection efficiency depends strongly on the particle size. The particle size distribution of each element differs according to their production and transformation processes. In general, the mass size distributions of Si, Ca and Fe skew to the larger size range and those of S, Zn and Pb skew to the smaller size range (Horvath *et al*,

**Table 3. Movement of each element from atmospheric aerosol into rain water and estimated effective height.**

	S	K	Si	Ca	Mn	Fe	Cu	Zn	Pb
Amount in aerosol pre-rain period [ng/m <sup>3</sup> ]	990	360	1960	760	31	630	28	212	63
Amount in aerosol 4-6 hr ave. [ng/m <sup>3</sup> ]	720	130	410	130	8	170	7	36	21
Amount of aerosol scavenged [ng/m <sup>3</sup> ]	280	230	1550	630	23	460	21	176	42
Amount in rain water : 0-5.7 hr [μg/m <sup>2</sup> ]	1760	1110	4780	2230	69	1240	21	224	62
Effective height [m]	6300	4800	3100	3500	3000	2700	1000	1300	1500

1996). They have roughly one peak in the coarse and fine particle region, respectively. Therefore, it is supposed that the mass concentration of Si, Ca and Fe in the atmospheric aerosols decreased faster than those of S, Zn and Pb. The relative concentration normalized by the initial concentration were calculated with each sampling time step and is shown in Table 2. It is obvious that Si, Ca and Fe were scavenged faster than S and Pb by rain.

The atmospheric aerosols scavenged by rain drops are moved into rain water. The concentration change on each element of the atmospheric aerosols and those in rain water scavenged are listed in Table 3. The amount of scavenged aerosols was estimated from the difference of the average concentration of aerosols sampled prior to rain and in the middle of rain event. On the other hand, the amount of element deposited during 5.7 hr from the beginning of rain, equivalent to 6.5 mm of rainfall, was obtained from the elemental concentration in rain water and the rainfall amount collecting rain water sample. Assuming a vertical distribution of the atmospheric aerosols to be uniform, the falling height of rain drops, which is called an effective height in this paper, was determined from the amount of element scavenged by rain drops and the amount of element deposited into rain water. The estimated effective height was indicated in Table 3. The effective heights of Cu, Zn and Pb were around 1,300 m as against about 3,000 m of Si, Ca, Mn and Fe which are mainly originated in the soil dust. The high values of Si, Ca, Mn and Fe is thought to be caused by the higher concentrations of Yellow Sand dust at the high altitude than those at the ground surface. On the other hand, since the concentration of Cu, Zn and Pb are supposed to decrease with the altitude,

the real falling distance of rain drops is presumably longer than the estimated effective height of 1,300 m. The effective height of S became 6,300 m. It is considered as the main causes of such an extremely high value of S that the small particle consisting of surface acts as a nuclei in the production process of cloud droplet (rainout) and that gaseous S as well as particulate S is scavenged by both rainout and washout. Furthermore, it is supposed from 6,300 m effective height of S as compared with 1,300 m of Cu, Zn and Pb that the washout effect of the particulate S is smaller than the other effects.

#### 4. CONCLUSIONS

In order to study the scavenging mechanisms of aerosol particles, the characteristics of chemical components in the rain water were examined as a function of the rainfall amount. The physical and chemical characteristics of atmospheric aerosols were measured simultaneously. The principal conclusions are as follows;

- 1) The elemental concentrations in rain water decreased quickly until about 1.0 mm of rainfall from the beginning of rain and then gradually as the rainfall continued.
- 2) The elements consisting mainly of the larger particles such as Si, Ca and Fe were scavenged more easily than the elements consisting mainly of the fine particles such as S and Pb.
- 3) Fe, Ti and Si in the aerosol particles exists in high insoluble state in rain water. Contrarily, almost whole of S was dissolved in the rain water.
- 4) From the evaluation of the effect height of each element, it is supposed that there exist the high

concentration layer of Yellow Sand dust at the high altitude and that the washout effect of the particulate S is smaller than the other effects such as the rainout of particulate S and washout of gaseous S.

5) The time resolution in the analysis of atmospheric aerosols was two hours against the several minutes of the rain water in the present study. In order to investigate in detail the wet scavenging mechanisms of aerosols particle, it is required that the sensitivity in the analysis of atmospheric aerosols increase at least ten times by the improvement of sampling and analytical conditions.

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