MEASUREMENTS OF ATMOSPHERIC SO_2 AND SO_4^{2-}, AND DETERMINATION OF THE WET SCAVENGING COEFFICIENT OF SULFATE AEROSOLS FOR THE WINTER MONSOON SEASON OVER THE SEA OF JAPAN

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Abstract—In order to determine the scavenging coefficient of oxides of sulfur in winter monsoon over the Sea of Japan both air and precipitation concentrations of sulfur dioxide and sulfate were measured on Sado Island on the Sea of Japan coast. The measurements were taken during the period between 28 January and 3 February 1992. The atmospheric concentrations of SO_4^{2-} were 0.57–1.11 $\mu g\,S\,m^{-3}$ whereas those of SO_2 were below 0.27 $\mu g\,S\,m^{-3}$, much lower than SO_4^{2-} concentration. A back trajectory analysis showed that these sulfur species would have been transported from Eurasian continent over the Sea of Japan. A layer-average scavenging coefficient, k, for sulfate by precipitation including snow, graupel and rain was determined on the basis of the equation $k = HP/h$, where H, P and h are the scavenging ratio, precipitation intensity and mixing layer height, respectively, under the assumption of a uniformly mixed layer over the warm sea current along the Sea of Japan coast. The scavenging coefficients were calculated to be 3.5×10^{-5}–$2.9 \times 10^{-4}\,s^{-1}$ for precipitation intensities of 0.13–3.1 $mm\,h^{-1}$. A regression analysis of these datasets gave a k value for submicron SO_4^{2-} aerosol over the Sea of Japan of $k = 1.38 \times 10^{-4} P^{0.74}$, where P is precipitation intensity. These values are very close to a recently obtained result by Jylhä for radioactive aerosols. Summarizing the measurements taken by the authors and other investigators the wet scavenging coefficient k may be represented by $k = aP^b$ where a is around 10^{-4}, and b is between 0.67 and 0.76. Copyright © 1996 Elsevier Science Ltd

Key word index: Wet deposition, long-range transport of pollutants, SO_2 and SO_4^{2-} concentration, mixing layer.

INTRODUCTION

Wet scavenging means the attachment of gaseous and aerosol pollutants to cloud droplets, ice crystals and raindrops followed by droplet removal from the atmosphere to the earth's surface by rain or snow. For aerosols and gases that are irreversibly captured by hydrometeors, wet deposition can be considered as an exponential decay process. In this case, the rate of change in concentration C of aerosols or gases in the air is given by $dC/dt = -k_{local}C$, where the proportionality factor k_{local} is the wet scavenging coefficient (s^{-1}).

Usually, a layer-average wet scavenging coefficient k is used in long-range transport and deposition models. Therefore, in this paper, we focus on the average coefficient k.

During the investigations by one of the authors, of long-range transport and deposition of oxides of sulfur in East Asia, using a computer simulation model (Okita and Kobayasi, 1990) it was found that the model output was highly sensitive to the wet scavenging coefficient.

Numerous researchers have sought to determine wet scavenging coefficients, particularly for SO_2 and SO_4^{2-} (for example, see Davies, 1983; Eliassen and Saltbones, 1983; Golomb et al., 1983; Kleinman, 1983; Ragland and Wilkening, 1983; Endlich et al., 1984; Renner et al., 1985; Ellenton et al., 1985, 1988; Iversen, 1989). These data are generally based on model calculations, or measurements of the scavenging ratio, or merely estimated. Few field studies have been conducted to determine the wet scavenging coefficient directly. The authors attempted to derive the scavenging

coefficients for SO_2 and SO_4^{2-} with particular emphasis on determining their dependence on precipitation intensity during the winter monsoon season. These results will serve to improve acid deposition simulation modeling of the East Asia region (Okita, 1993).

A large air–sea temperature difference is always observed when the winter monsoon winds blow from the Eurasian continent over the relatively warm sea surface of the Sea of Japan. A temperature difference of more than 20 °C is not unusual over the warm Tsushima sea current which flows along the Sea of Japan. Consequently, the polar-continental air mass blowing over the Sea of Japan is significantly modified due to this large air–sea temperature difference. Active cumulus convection develops in the moist and unstable stratification caused by heating and water vapor supply from the underlying sea surface. This cumulus convection results in intense snowfall over the coastal area of the Sea of Japan.

The authors determined the wet scavenging coefficient based on measurements taken on Sado Island on the Sea of Japan (cf. Fig. 1).

MEASUREMENTS ON SADO ISLAND

Ambient air and precipitation measurements of SO_2 and SO_4^{2-} were conducted at the Aikawa Acid Precipitation Monitoring Station on Sado Island. This monitoring station was recently constructed by the Japan Environment Agency and is located on a 100 m high hill about 700 m inland from the northwestern coast of the island. An atmospheric gas and aerosol sampler and two plastic buckets were mounted on a roof of the one-story building of the station.

The sampler was a tandem filter in which SO_4^{2-} aerosol and SO_2 gas were collected on a AF07P fluoropore filter and a Na_2CO_3 impregnated cellulose filter, respectively, with a sampling flow rate of $20 \ell \, min^{-1}$. The mouth diameter of the precipitation sampling bucket was 25 cm and a tetrachloromercurate solution was placed in one of the buckets to keep S(IV) in the precipitation sample from oxidizing after its collection. The mass size distribution of SO_4^{2-} aerosol was measured using an Andersen sampler. The samplings of gas, aerosol and precipitation were conducted between 28 January and 3 February 1992.

S(IV) collected on the impregnated filter was oxidized to S(VI) using an H_2O_2 solution and SO_4^{2-} on the filters was extracted into water, and both were analyzed using an ion chromatograph. SO_4^{2-} and S(IV) in the precipitation water were determined by ion chromatography and colorimetry, respectively.

Precipitation intensity was recorded by an automatic precipitation recorder at the station. RHI radar data were obtained from the Niigata Local Meteorological Observatory, which is located about 80 km from the station (cf. Fig. 1). This was used to estimate the height of precipitation cells, which the authors assumed was the height of the top of the uniformly mixed layer. Cloud base height was usually about 500 m or lower as observed from the base height of the clouds covering mountains on Sado Island.

RESULTS OF MEASUREMENTS

The vertical distributions of potential temperature observed at Wajima Weather Station, which is located on the coast of the Sea of Japan about 130 km
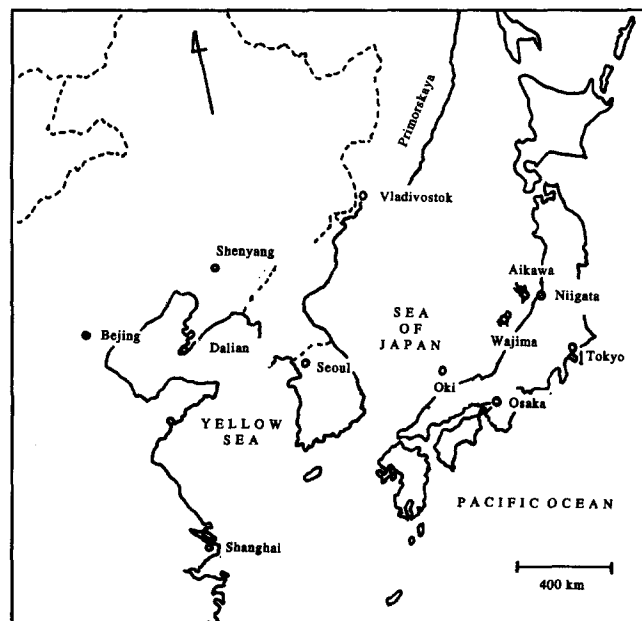

Fig. 1. Map of East Asia.

WSW from the Aikawa station (cf. Fig. 1) are shown in Fig. 2. They indicated that at a height below about 2 km there existed a well mixed layer, and that the main body of convective cloud was found within this layer.

Table 1 shows the atmospheric concentrations of SO_2 and SO_4^{2-} measured at Aikawa station. Back trajectories of air parcels at the 850 hPa level arriving at Aikawa at 9:00 and 21:00 JST were calculated.
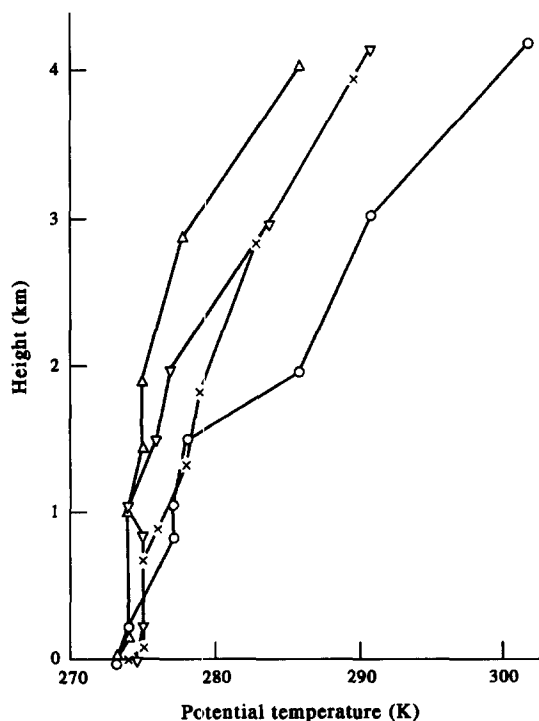

Fig. 2. Vertical profiles of potential temperature observed at Wajima, Japan. ×: 1 February, 0900 JST, △: 1 February, 2100 JST, ▽: 2 February, 0900 JST, ○: 2 February, 2100 JST.

Figure 3 shows the trajectories between 28 January and 3 February. These figures indicate that during this period the air masses came predominantly from the Eurasian continent.

Figure 4 shows the mass size distribution of SO_4^{2-} aerosol. The figure indicates that the fraction of supermicron SO_4^{2-} aerosol was much less than that of submicron particles.

Even in a well mixed layer such as that shown in Fig. 2, various microphysical processes take place at different heights (Murakami et al., 1994), so that k_{local} depends on cloud layer height. But, under the assumption of a uniformly mixed layer, the layer-average coefficient k of scavenging of oxides of sulfur due to precipitation may be given by the formula

$$k = HP/h \qquad (1)$$

where H is the scavenging ratio $= C_w/C_a \times 10^6$ in which C_w is the chemical species concentration $(mg\ell^{-1})$ in precipitation water, and C_a the species concentration $(\mu g\,m^{-3})$ in air; P is the precipitation intensity $(cm\,s^{-1})$, and h the height (cm) of convection cell as measured by radar because, here, we consider wet scavenging in the mixing layer.

Table 1 shows that, usually, SO_4^{2-} concentrations far exceeded SO_2 concentrations in air, and particularly when air of both above and below the 850 hPa layer came from the Eurasian continent the average SO_2 and SO_4^{2-} concentrations were found to be 0.08 and $0.86\ \mu g\,S\,m^{-3}$, respectively. Further, no sulfite was detected in the precipitation samples. Therefore, equation (1) is used to derive an approximate value for the wet scavenging coefficient of submicron SO_4^{2-}.

Table 2 shows the value of k derived using equation (1). During the winter monsoon season most of the precipitation is in the form of snow and graupel, so that the Bergeron process would operate together with collisional growth of precipitation elements for the production of the precipitation.

Table 1. Concentrations of SO_4^{2-} and SO_2 at Sado station

Period			Concentration ($\mu g\,S\,m^{-3}$)		Remarks[a]
			SO₄	SO₂	
1 1/28	10:28–15:05		0.87	0	North Korea,[b] northeast China
2 1/28	15:17–1/29	9:01	1.11	0.60	North Korea, northeast China
3 1/29	9:11–15:10		0.69	0.70	North Korea,[b] northeast China
4 1/29	15:15–1/30	9:09	1.29	0.84	North Korea, northeast China
5 1/30	9:13–15:10		0.76	0.16	North Korea,[b] northeast China
6 1/30	15:15–1/31	9:07	0.53	0.08	Vladivostok, northeast China
7 1/31	9:14–15:20		1.11	0	Vladivostok,[b] northeast China
8 1/31	15:23–2/1	9:23	0.79	0.13	Primorskaya, northeast China
9 2/1	9:28–16:00		1.03	0.14	Primorskaya,[b] northeast China
10 2/1	16:03–2/2	9:10	0.57	0.27	Primorskaya,[b] northeast China
11 2/2	9:18–14:52		0.77	0	North Korea,[b] northeast China
12 2/2	14:56–2/3	8:46	0.84	0.11	Wajima, North Korea, northeast China
13 2/3	8:59–14:30		1.10	0	Wajima, Yellow Sea,[b] Dalian

[a] Area, sea and city shown in remarks are those over which air trajectory arriving at Aikawa on that day passed.

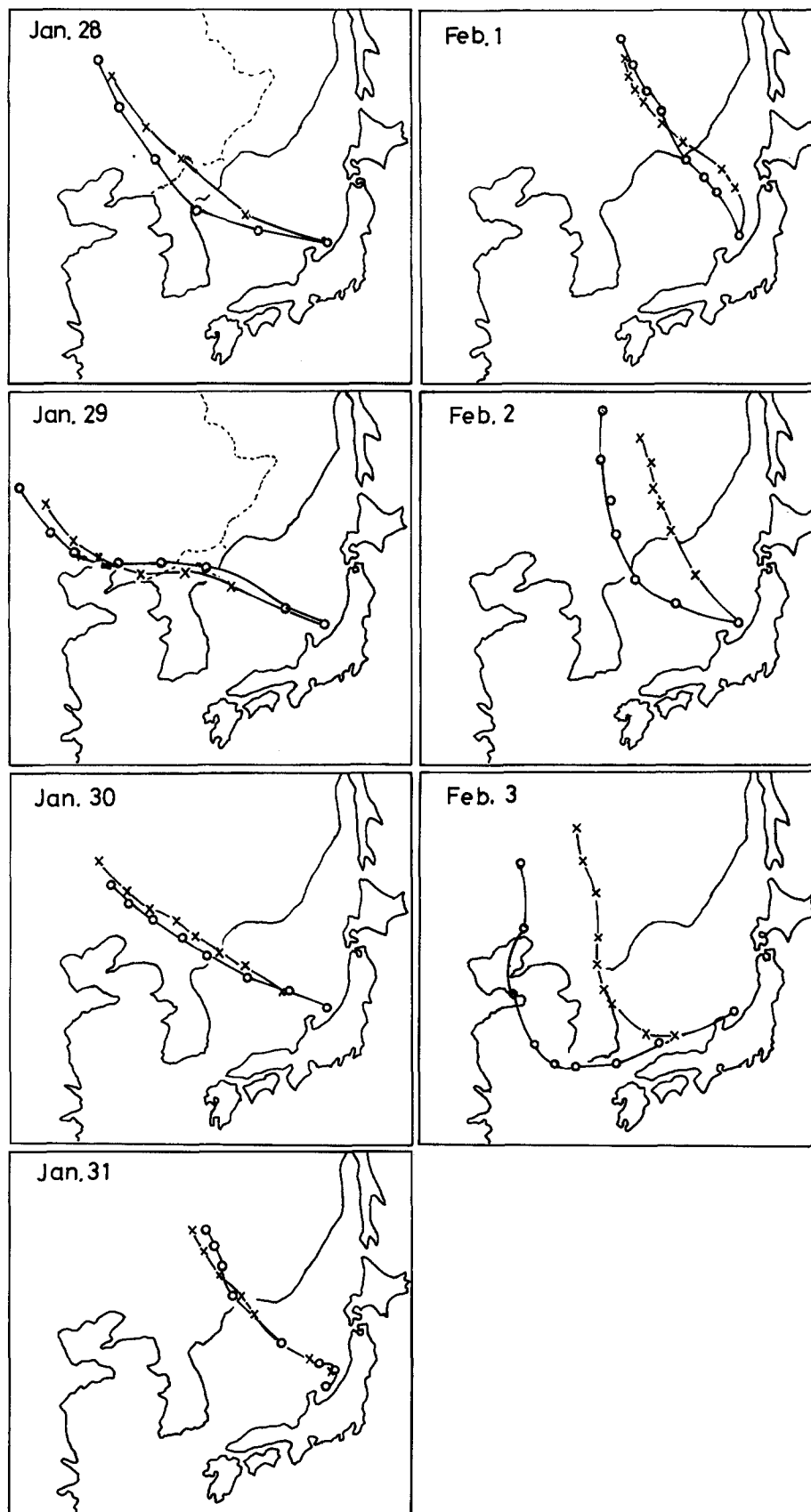[b] Surface wind direction is the same as that at 850 hPa layer.

Fig. 3. Trajectories of air mass at 850 hPa level between 28 January and 3 February, 1992. ×: trajectories arriving at Aikawa at 0000 JST. ○: trajectories arriving at Aikawa at 1200 JST. Distance between successive marks indicates air mass movement during 12 h.
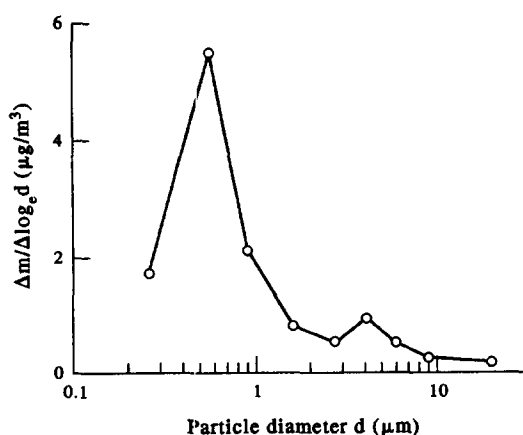
Fig. 4. Size-distribution of SO$_4^{2-}$ aerosol mass m sampled at Aikawa station.

Fig. 5. Relation between wet scavenging coefficient and precipitation intensity.

Figure 5 shows the relationship of k vs precipitation intensity P, and indicates a good correlation between the two. The regression analysis indicates the relation $k = aP^b$, where $a = (1.38 \pm 0.18) \times 10^{-4}$ and $b = 0.74 \pm 0.12$, respectively, for precipitation intensities of 0.13–3.1 mm h^{-1}. It should be recalled that this relation is obtained for precipitation during the winter monsoon season over the warm sea current along the Sea of Japan coast.

DISCUSSION

1. Atmospheric concentrations of SO$_2$ and SO$_4^{2-}$ at Aikawa

As shown in Fig. 3, during the period from 28 January to 3 February 1992, the air mass at 850 hPa arriving at Aikawa always originated from the Eurasian continent. Table 1 shows that when the ground level wind direction was the same as that at 850 hPa, the SO$_2$ concentration was low, that is, below 0.27 μg S m^{-3}. On the other hand, under the same wind conditions, SO$_4^{2-}$ concentrations were 0.57–1.11 μg S m^{-3}. Therefore, as a general rule, SO$_4^{2-}$ concentrations were much higher than SO$_2$ concentrations in the air mass which passed over the Sea of Japan during the winter monsoon season. Although the Aikawa station was located close to the sea coast, as shown in Fig. 4, the contribution of SO$_4^{2-}$ from sea-salt particles in a mechanical production mode was much less than those of submicron particles produced in a coagulation mode (i.e. produced by conver-
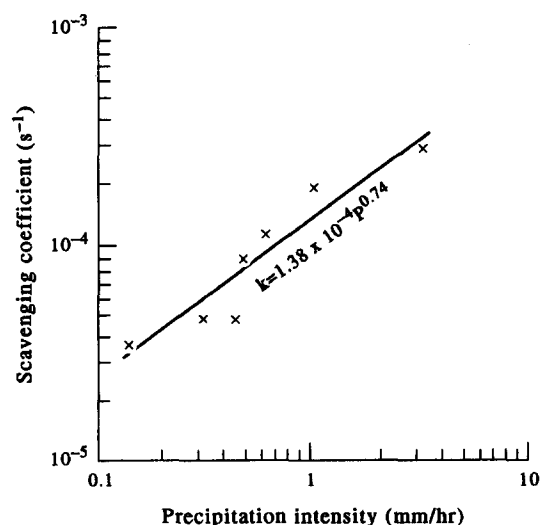
sion of SO$_2$ to SO$_4^{2-}$ during long-range transport of the air mass).

According to the measurement of aerosol components conducted by Mukai et al. (1990) at Oki Island (cf. Fig. 1), during the period from 1983 through 1988, the mean SO$_4^{2-}$ concentration range in January and February was 0.7–1.0 μg S m^{-3}. Thus, the SO$_4^{2-}$ concentrations at Aikawa were slightly lower than those at Oki Island probably because Sado Island is located at greater distance from major emission source areas on the continent.

2. Wet scavenging coefficient of SO$_4^{2-}$

As shown in Table 2 the hydrometeors found during sampling of precipitation were rain, snow and graupel. According to the detailed study of the microphysical structure of snow clouds over the Sea of Japan conducted by Murakami et al. (1994), both ice nucleation-freezing of cloud droplets, and warm rain type of accretion between ice particles and supercooled droplets took place in the clouds.

As described previously, the scavenging coefficient formulation presented in this study was mainly for submicron SO$_4^{2-}$ aerosols.

In Table 3, the scavenging coefficient of SO$_4^{2-}$ aerosols measured in the present study is compared with other measured, model calculated, and estimated coefficient for aerosol particles. The majority of the measurement results presented in this table were derived from the scavenging ratio. Only the dependency of the coefficient on precipitation intensity is given in these cases. Although these scavenging coefficients

Table 2. Precipitation forms, cloud top heights and wet scavenging coefficients of sampled precipitations

Period		Precipitation form	Cloud top height (m)	k (s^{-1})
Jan. 29	1:30–6:00	Rain	3000	2.9×10^{-4}
Jan. 29	15:30–21:00	Rain	2000	8.9×10^{-5}
Jan. 31	1:30–2:30	Snow	2500	4.6×10^{-5}
Jan. 31	22:00–Feb. 1 13:00	Snow	2600	4.6×10^{-5}
Feb. 1	13:30–14:30	Graupel	2000	1.8×10^{-4}
Feb. 1	18:45–Feb. 2 1:48	Graupel	3600	1.1×10^{-4}
Feb. 3	5:30–9:40	Rain	2700	3.5×10^{-5}

Table 3. Comparison of wet scavenging coefficients for aerosols

Investigators	Species s^{-1}	Scavenging coefficient	Remarks
Georgii and Weber (1960)	SO_4^{2-}	$\propto P^{0.67}$	M
Gatz (1977)	Zn	$\propto P^{0.76}$	M
Fisher (1978)	SO_4^{2-}	10^{-4}	E
Garland (1978)	SO_4^{2-}	10^{-4}	E
Scott (1978)	SO_4^{2-}	$5.8' \times 10^{-6} P^{0.70}$	C
Eliassen and Saltbones (1983)	SO_4^{2-}	4×10^{-6}	E
Golomb et al. (1983)	SO_4^{2-}	10^{-4}	E
Ragland and Wilkening (1983)	SO_4^{2-}	$1.22 \times 10^{-4} P^{0.63}$	E
Van Dop (1983)	SO_4^{2-}	$1.0 \times 10^{-4} P$	E
Barries (1985)	SO_4^{2-}	$\propto P^{0.67}$	M
Ellenton et al. (1988)		$3 \times 10^{-4} P$	E
Jylhä (1991)	radioactive material	$1.0 \times 10^{-4} P^{0.64}$	M
Present study	SO_4^{2-}	$1.38 \times 10^{-4} P^{0.74}$	M

P: Precipitation intensity $(\mathrm{mm\,h^{-1}})$.
M: Measurement, C: Model calculation, E: Estimation.

vary widely, it seems that recent measurement results converge to an equation of the form $k = aP^b$ where a is around 10^{-4} and b is between 0.67 and 0.76.

CONCLUSION

During the period between 28 January and 3 February 1992 measurements of oxides of sulfur in the air and precipitation water were conducted at Aikawa on Sado Island on the Sea of Japan coast during the winter monsoon season. Atmospheric SO_2 and SO_4^{2-} concentrations were below 0.27 and between 0.57 and $1.11\ \mu\mathrm{g\,S\,m^{-3}}$, respectively. According to back trajectory analysis these pollutants were transported from the Eurasian continent over the Sea of Japan.

The wet scavenging coefficient of precipitation for submicron SO_4^{2-} aerosols over the Sea of Japan in which the form of precipitation is snow, graupel or rain was calculated to be $k = 1.38 \times 10^{-4} P^{0.74}$. This value is close to that recently obtained by Jylhä for radioactive aerosol. It is also interesting that the coefficient estimated by Ragland and Wilkening is close to the measured ones. In conclusion, it seems that in general the wet scavenging coefficient can be determined from an equation $k = aP^b$, where a is around 10^{-4} and b is between 0.67 and 0.76.

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