

C-1. 3. 3 Studies on Evaluation of Dry Deposition Velocity of Aerosol Particles

Contact person Hiroshi Hara

Senior Research Scientist
Department of Community Environmental Sciences
National Institute of Public Health, Japan
Ministry of Health and Welfare
Shirokanedai 4-6-1, Minato-ku, Tokyo 108-8683
Tel: +81-3-3441-7111, Fax: +81-3-3446-4319

Total Budget for FY 1996-1998 8,911,000 Yen (FY 1998 2,920,000 Yen)

Abstract Dry deposition to forests plays an important role to discuss forest declines in a quantitative manner. This study focuses on the field measurement of concentration profiles for sulfate as well as sulfur dioxide in forests and a corn field in order to evaluate deposition velocity. Sulfur dioxide concentration showed a concentration profile that concentration decreased with decreasing height. Sulfate concentrations, however, were rather homogeneous irrespective of the height: the concentration did not decrease even near the surface. In the case of a coniferous (red pine) forest, the sulfate concentration decreased over the canopy top to yield negative deposition velocities for sulfate particles. The emission velocity, defined as a negative deposition-velocity, showed a high correlation with deposition velocity of ozone that was also measured in this collaboration work. This fact strongly suggested that sulfate was formed on the particles generated by the reaction between ozone and terpenes emitted from the leaves of red-pine into the atmosphere. The deposition velocity of sulfate

Key Words Dry Deposition, Aerosol, Sulfate, Concentration Profile, Forest

1. Introduction

“Acid rain” is a phenomenon that deposition of sulfuric and nitric acids from the atmosphere to the earth’s surface with subsequent adverse acidification impacts to ecosystems. The deposition is classified into wet and dry deposition. In wet deposition, acids are deposited in the form of aqueous solution such as rain, fog, and snow. Dry deposition is a delivery of gaseous and particulate acids to the earth’s surface associated with eddy diffusion, Brownian diffusion, and absorption and adsorption. Whereas wet deposition is easily measured with a conventional bucket, dry deposition is still difficult to measure on a routine basis. Dry deposition is generally estimated by several methods for research purposes. One of the common methods is inferential method where the deposition (F) is quantified as the product of air concentration (c) and deposition velocity (v_d) that is specific with a combination of atmospheric chemical species and receptor surface.

In this study, concentration profiles of sulfate particles were measured in deciduous and coniferous forests and a corn field in order to obtain insights on dry deposition velocities of sulfate particles for these receptor surfaces.

2. Experimental

2.1 Theoretical

Dry deposition velocity is evaluated by gradient method in this program. Concentration gradient measured over forest canopy and heat transport coefficient, simultaneously determined in the same field, would yield deposition velocity under the assumption that the coefficient is numerically identical with the corresponding eddy diffusion coefficient.

According to diffusion theory, the diffusion flux, F , is given by eq. (1) and deposition velocity, V_d , is defined as eq. (2) where K_d , c , and z are eddy diffusion coefficient, air concentration of a substance, and height from the surface, respectively.

$$F=Kd(\partial c/\partial z) \quad (1)$$

$$F=c V_d \quad (2)$$

Air concentrations, c_u and c_1 , at two different heights, z_u and z_1 , would provide concentration gradient and diffusion coefficient, K_d , can be assumed to be heat diffusion coefficient, K , V_d is eventually given by eq.(3),

$$V_d=K ((c_u -c_1)/(z_u -z_1))/c \quad (3).$$

2.2 Field Measurements

Filter pack method was applied to collect aerosol concentration at five or six heights in forests and corn field. An impactor was applied before the filter pack assembly in order to remove particles with diameters larger than $2.5 \mu\text{m}$. The sample filters were extracted in a ultrasonic bath with subsequent determination of sulfate ion by using ion chromatograph. The sample filters for a given sampling period were determined in one analytical run to eliminate or minimize possible instrumental drifts between analytical runs. Each sample was repeatedly injected to yield peak heights within 5% variation. The volume of sampled air was determined by reading the gas meter to the 0.1 liter. The air volume was corrected for different temperatures.

3. Results

3.1 Concentration Profiles in Deciduous Forest

The concentration profiles were determined in a deciduous forest with a canopy top at 16 m for the height range of 2.0 m to 20.8 m above the surface (Figs. 1 and 2). Concentration profile for sulfate showed rather homogeneous patterns in summer and winter whereas the sulfur dioxide concentration decreased with decreasing height in all cases. In order to obtain more insight on the profile closer to the surface, the measurements were carried out for heights of 0.12 to 4.0 m. The similar results were obtained for sulfate and sulfur dioxide (Fig. 3).

3.2 Concentration Profiles in Corn Field

The concentration profile was measured up to a height of 4 m in a corn field of 1.6 m height in order to obtain an overall picture of the profile. In most cases, similar profile patterns were obtained for sulfate and sulfur dioxide to those in the deciduous forest (Fig. 4). In a limited cases, however, the sulfate concentration was likely to decrease near the surface although the sulfur dioxide illustrated a steep decrease as approaching to the surface (Fig. 5), which might happen during night time.

The deposition velocity for sulfate aerosol was tentatively calculated to fluctuate around zero with some maxima around 1 cm/s (Fig. 6).

3.3 Concentration Profiles in Coniferous Forest

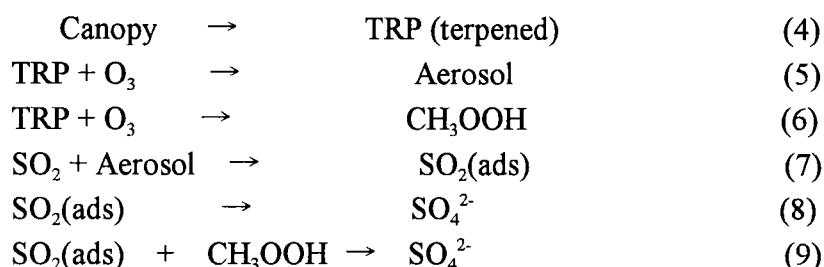
The measurements were conducted in summer in a field of coniferous forest of which decline is a matter of concern in Japan. Sulfate concentration profile proved rather homogeneous under the canopy (16 m) whereas the concentration evidently increased over the canopy (Fig. 7). This sort of pattern prevailed during the measurements. This profile over the canopy corresponded to emission of particles instead of deposition. Similar negative gradients were observed for sulfur dioxide. When the data quality of this gas is considered in terms of filter pack method, the concentration profile was not so convincing as those for sulfate aerosol. The sulfur dioxide concentration seemed to be too low for the blank levels of the alkali-impregnated filters.

4. Discussion

The results in the coniferous forest were discussed together with concurrently measured deposition velocity of ozone. The negative profile of sulfate concentration together with heat diffusion coefficient would yield negative deposition velocities which should be interpreted to be emission velocity of sulfate particles. Deposition velocity for ozone and emission velocity for sulfate showed a significant correlation. These velocities for a measurement period are shown in Fig. 8 (Koyama, 1999).

It is generally accepted that coniferous trees emit terpenes and that ozone reacts with this group of chemical species to form aerosol (Yokouchi and Ambe, 1985, Weschler and Shields, 1999). In the light of this atmospheric chemistry, the sulfuric acid is suggested to be yielded on the surface of particles formed through the ozone-terpene reactions.

A plausible mechanism is given below:



Terpenes species (TRP) are emitted into the atmosphere from the coniferous canopy, eq. (4) (Yokouchi et al., 1983, Isebrands, et al., 1999). Ozone is transported from a polluted air parcel where photochemical reactions took place to produce oxidizing agents including ozone, and react with terpenes over the canopy of the forest to produce aerosol particles, eq. (5). Ozone-terpene reactions will also generate methyl-peroxide to be dissolved in water film on aerosol particles, eq. (6). Sulfur dioxide is adsorbed onto the newly formed aerosol particles, eq. (7) to be catalytically converted to sulfuric acid, eq. (8) (Hara et al., 1994). Sulfuric acid is also formed in the water film through the reaction with methyl-peroxide when sulfur dioxide is dissolved into the water film, eq. (9). These oxidation is associated with emitting aerosol particles into the atmosphere. The negative gradient of sulfate concentration over the canopy could therefore be observed in deciduous forest in summer.

A close examination of the concentration profile of sulfate for summer deciduous forest could show a similar negative gradient over the canopy top (Fig. 1). This could be the case of aerosol formation associated with the ozone-terpene reactions because terpenes were probably emitted during this summer observation.

5. Conclusion

Although this work initially was intended to determine dry deposition velocities of sulfate particles to deciduous and coniferous forest, the concentration profiles of sulfate would have proved to be different from what is generally assumed at least for the height regions around the canopy top. The concentration profile was negative over the canopy in almost all cases in this study. Deposition velocities and reactivity of ozone could explain this profile was associated with terpenes emitted from the forest with subsequent ozone reaction forming aerosol particles. Ozone would play an important role in the dry deposition of gases susceptible to oxidation.

References

- Hara, H., Nakasato, S., and Hatakeyama, S.. (1994) Aqueous-phase oxidation of S(IV) by CH_3OOH at pH1-2. *In* Abstracts of the 8th CACGP Symposium on the IAMAP Commission on Atmospheric Chemistry and Global Air Pollution, 5-9 September, 1994, Fuji-Yoshida, Japan. p. 116.
- Isebrands, J. G., Buenther, A. B., Harley, P., Helming, D., Klinger, L., Vierling, L., Zimmerman, P., and Geron, C. (1999) Volatile organic compound emission rates from mixed deciduous and coniferous forests in Northern Wisconsin, USA. *Atmos. Environ.*, 33, 2527-2536.
- Koyama, A. (1999), Master Thesis, Tokyo University of Agriculture and Technology, 1999.
- Weschler, C. J. and Shields, H. C. (1999) Indoor ozone/terpene reactions as a source of indoor particles. *Atmos. Environ.*, 33, 2301-2312.
- Yokouchi, Y., Okaniwa, M., Ambe, Y. and Fuwa, K. (1983) Seasonal variation of monoterpenes in the atmosphere of a pine forest. *Atmos. Environ.*, 17, 743-750.
- Yokouchi, Y. and Ambe, Y. (1985) Aerosols formed from the chemical reaction of monoterpenes and ozone. *Atmos. Environ.*, 19, 1271-1276.

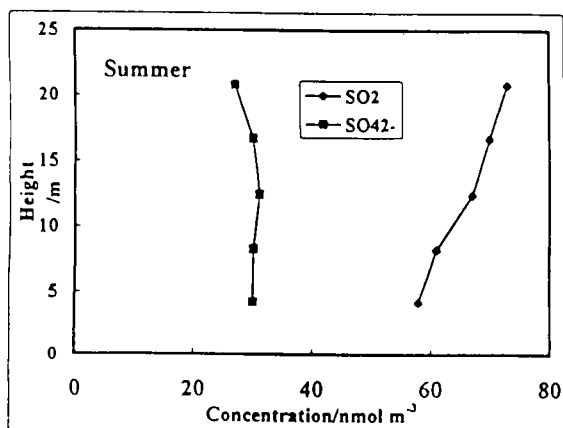


Fig. 1 Concentration profiles for SO_4^{2-} and SO_2 in deciduous forest

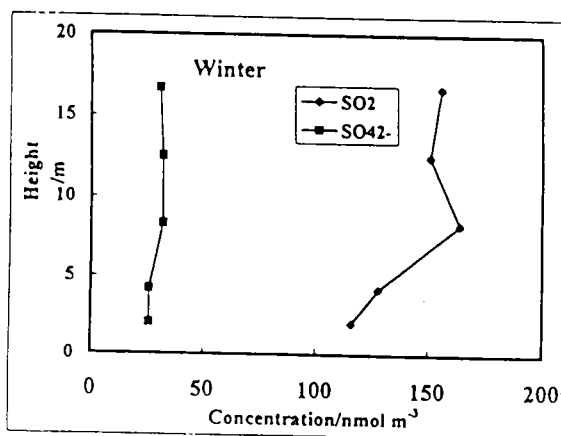


Fig. 2 Concentration profiles for SO_4^{2-} and SO_2 in deciduous forest.

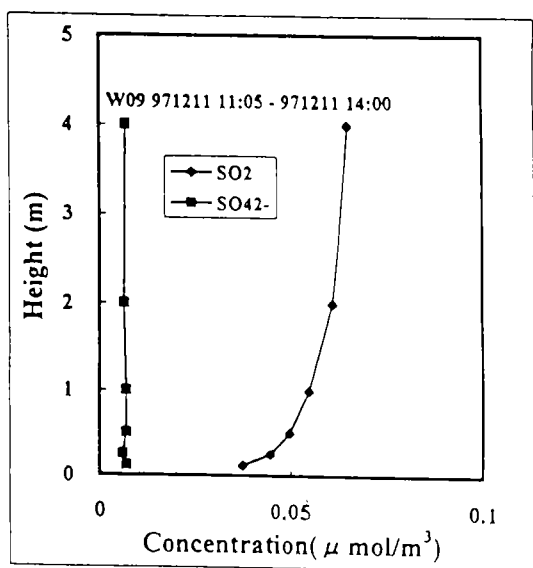


Fig. 3 Concentration profiles for SO_4^{2-} and SO_2 in deciduous forest.

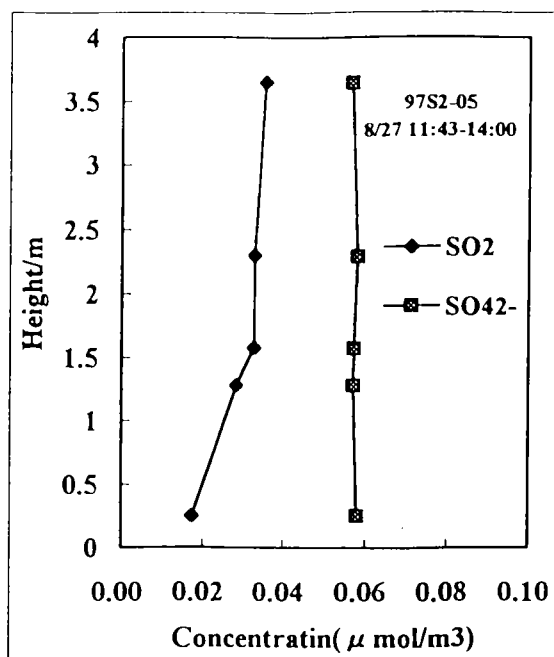


Fig. 4 Concentration profiles for SO_4^{2-} and SO_2 in corn field.

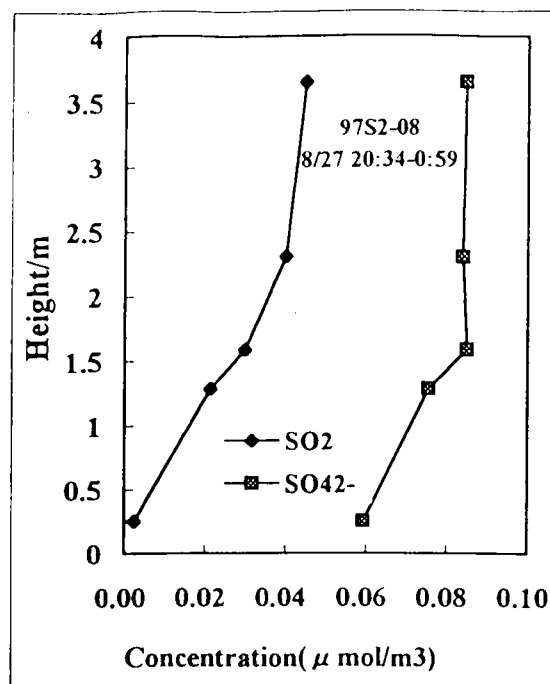


Fig. 5 Concentration profiles for SO_4^{2-} and SO_2 in corn field.

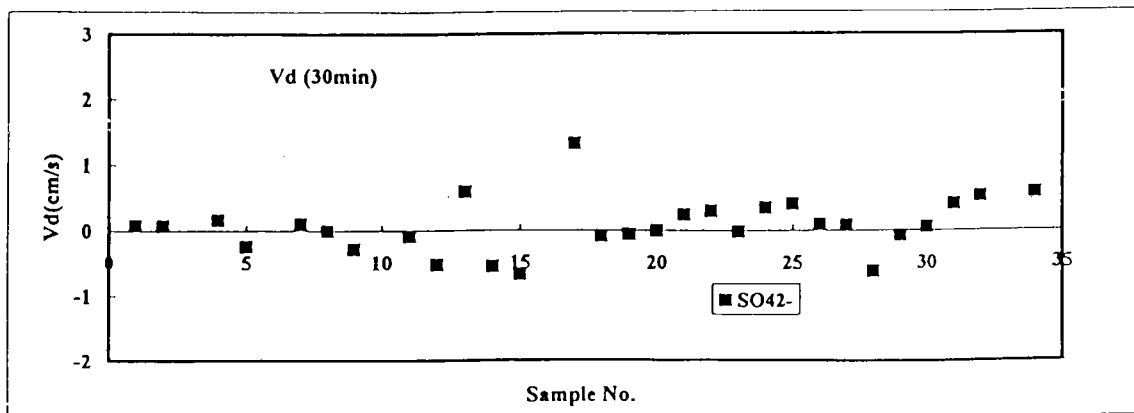


Fig. 6 Deposition velocity for SO_4^{2-} aerosol in corn filed.

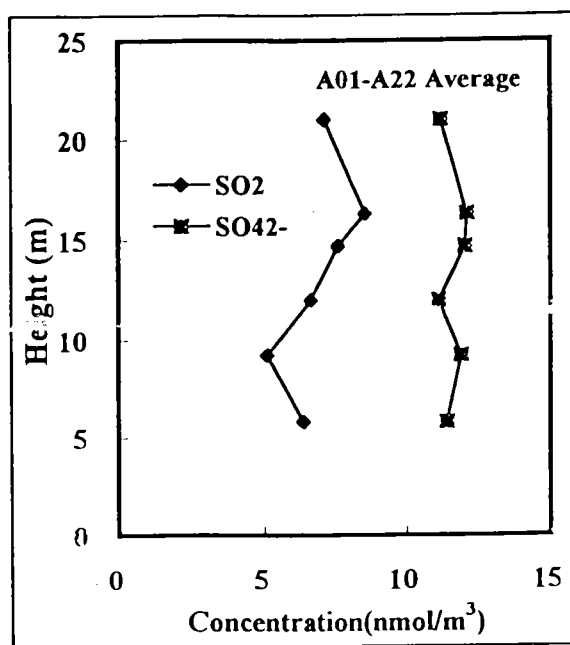


Fig. 7 Concentration profiles for SO_4^{2-} and SO_2 in coniferous forest.

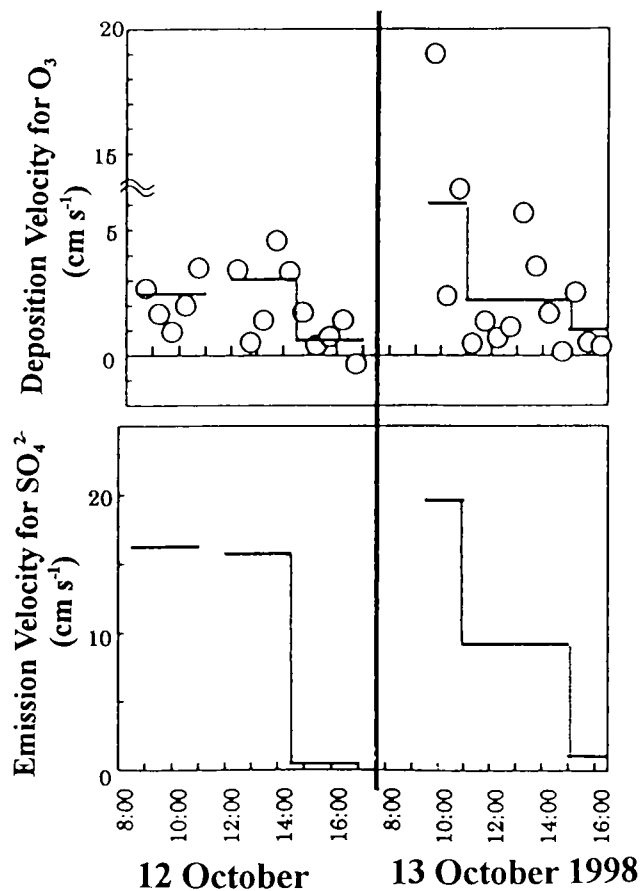


Fig. 8 Deposition velocity for O_3 and emission velocity for SO_4^{2-} in coniferous forest.