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Estimates of the sulfate scavenging coefficient from sequential precipitation samples on Long Island

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ABSTRACT

By comparing deposition of sulfate in successive hours of precipitation samples taken over a 6-year period at Brookhaven National Laboratory (BNL) on Long Island in New York, we have estimated scavenging coefficients in air for sulfate under a variety of meteorological and seasonal conditions. The scavenging coefficients obtained are underestimated (typically up to 12%) because of liquid phase production of sulfate from SO_2 scavenged in air. The square root transformation of the scavenging coefficients $\lambda^{1/2}$, yields an approximately normal distribution. An interesting property of the distribution of scavenging coefficients is that the ratios of the mean value of $\lambda^{1/2}$ to its standard deviation cluster around the value 2.4; this property may limit the choice of stochastic models which describe the scavenging process. The mean value of the sulfate scavenging coefficient is 1.0×10^{-4} s^{-1}. A trend analysis of the relationship between the scavenging coefficients and rainfall rate indicates that the sulfate scavenging coefficient is virtually invariant for rainfall rates ≤ 5 mm h^{-1}.

1. Introduction

Removal of water soluble pollutants by precipitation is a major atmospheric cleansing process. In most atmospheric photochemical models, scavenging due to precipitation is parameterized by a first-order rate coefficient λ, where

$$\frac{dN}{dt} = -\lambda N, \tag{1}$$

where N is the amount of the species in a given volume of air and λ is called the scavenging coefficient. The solution of the above equation is

$$N(\Delta t) = N_0 \exp(-\lambda \Delta t), \tag{2}$$

where N_0 is the initial amount of the species in a designated volume of air. Estimates of the scavenging coefficient and its distributional properties are also required in analytical and statistical models of concentration and residence time of soluble pollutants (Junge and Gustafson, 1957; Rodhe and Grandell, 1972, 1981; Scriven and Fisher, 1975; Bolin and Persson, 1975; Henmi and Reiter, 1978; Omstedt and Rodhe, 1978; Venkatram et al., 1982, Fisher, 1982, 1983).

The purpose of this paper is to present a method of estimating the scavenging coefficient in air from the change in species deposition in successive samples of precipitation. This allows us to obtain a large number of estimates of λ using 6 years (June 1976–May 1982) of sequential hourly precipitation samples collected and analyzed at Brookhaven National Laboratory (BNL) on Long Island (Raynor and Hayes, 1982, 1983, 1984). The estimates of λ are used to study its distribution function and variation with rainfall rate, synoptic conditions and precipitation type.

It is noted that eq. (1) neglects the effect of advection on N. In order to interpret Eulerian data in terms of this equation it is necessary to assume that conditions in the precipitation system are horizontally uniform. The sensitivity of the results to this assumption is discussed later in this section. As the precipitation event progresses the amount of the pollutant in the column of air above the sampler decreases. Consequently the amount of the pollutant deposited in the sampling

bucket increases. The amount deposited in the sampler in time Δt is the difference between N_0, the initial amount of the species present in the atmospheric column, and N, the amount of the species present in that column after time Δt. The increase in the sampler is given by

$$M(\Delta t) = N_0[1 - \exp(-\lambda \Delta t)], \quad (3)$$

where $M(\Delta t)$ = the amount of the species present in the sampler after time Δt. We see that as $\Delta t \to 0$, there is no material in the sampler and as $\Delta t \to \infty$, the volume above the bucket will be scrubbed clean due to the in-cloud and below-cloud scavenging processes. Comparing two successive time intervals Δt_1, and Δt_2 of precipitation we have: $M(\Delta t_1) = N_0[1 - \exp(-\lambda \Delta t_1)]$, $M(\Delta t_2) = N(\Delta t_1)[1 - \exp(-\lambda \Delta t_2)]$ where $N(\Delta t_1) = N_0 \exp(-\lambda \Delta t_1)$, for air, eq. (2). Thus

$$\frac{M(\Delta t_1)}{M(\Delta t_2)} = \frac{[1 - \exp(-\lambda \Delta t_1)]}{\exp(-\lambda \Delta t_1)[1 - \exp(-\lambda \Delta t_2)]}, \quad (4)$$

when $\Delta t_1 = \Delta t_2$

$$\frac{M(\Delta t_1)}{M(\Delta t_2)} = \exp(\lambda \Delta t_1), \quad (5)$$

and the measured scavenging coefficient is:

$$\lambda = \frac{\ln\left|\frac{M(\Delta t_1)}{M(\Delta t_2)}\right|}{\Delta t_1}. \quad (6)$$

Note that the atmospheric burden of the pollutant species above the sampler does not appear in this equation and λ is estimated from precipitation samples only. The scavenging coefficients determined from eq. (6) do not distinguish between the rainout and washout processes but give an integrated value for the whole air column in and below the cloud.

The process of entrainment of sulfates into water drops and snow may be considered to be irreversible. This is indicated by the washout ratio, the equilibrium ratio of sulfate concentration in the captured phase to its concentration in air. Huebert et al. (1983) measured the washout ratio for snow to be ~ 1000. Cawse (1974) observed the washout ratio to be in the range 570–24,000 from analysis at seven locations in Britain.

As mentioned above, this expression for λ is valid only if the scavenging process occurs at a uniform rate in the horizontal direction, so that there is no net flux of the species into the air column being sampled. To limit the errors introduced by the inevitable heterogeneity in the atmosphere we have restricted the choices of precipitation samples to be used in estimating λ. The conditions imposed are as follows.

(1) The precipitation type in the two successive hours of comparison must be the same.
(2) The synoptic type in the two successive hours of comparison must be the same.
(3) The amount of material deposited in a given hour of precipitation must be less than that deposited in the previous hour. A contrary condition indicates that a net import of material has taken place in the volume of air above the sampling unit and eq. (1) is not applicable.

Thus we try to limit ourselves to an air mass which has had a common previous history for the estimation of each λ.

2. Sulfate scavenging

Sulfate, SO_4^{2-}, is generated in the atmosphere by oxidation of SO_2 in the gas phase, on the surfaces of aerosols and in the liquid phase of droplets in clouds and fog. The sources of sulfate in precipitation samples thus include in-cloud and below-cloud scavenged gaseous and aerosol sulfates with a contribution from in-solution oxidation of SO_2 scavenged from air. Several estimates of the rates of precipitation scavenging of sulfate and SO_2 have been reported in the literature. Garland (1978) concludes that the rate of sulfate scavenging by precipitation is $\sim 10^{-4}$ s^{-1}, ten times faster than the rate of removal of SO_2. Chan et al. (1983) estimate the sulfate scavenging coefficient to be $\sim 0.5 \times 10^{-4}$ s^{-1} in winter and 1.9×10^{-4} s^{-1} in summer due to precipitation scavenging from a deposition study at the INCO Nickel Smelter at Sudbury, Ontario. Huebert et al. (1983) made 11 independent estimates of the aerosol sulfate scavenging coefficient with a 2 – 4 h sampling time and found it to range from $(-0.6 - 2.5) \times 10^{-4}$ s^{-1} with the mean value of 0.9×10^{-4} s^{-1}. Lacaux and Warburton (1983) have estimated precipitation scavenging coefficients for submicron size par-

ticles [sulfate is predominantly submicron in size (Whitby, 1978)] released into convective clouds. Based on the amount of material deposited as compared with the amount released over a given sampling region over time period Δt, they conclude the sulfate scavenging coefficient to be $\sim(0.3-2)\times10^{-4}$ s^{-1}. Scott (1982) modelled the uptake of soluble aerosol particles, such as sulfate, by nucleation scavenging in cloud water and estimated $\lambda\sim10^{-4}$ s^{-1}. His model also suggests that λ should be a function of precipitation rate and type. From precipitation samples from the East Midlands in UK, Maul (1978) estimates the washout coefficient of SO_2 to be $\sim3\times10^{-5}$ s^{-1}. The field data of Dittenhoefer and DePena (1980), Dana et al. (1975), Granat and Söderlund (1975), and Granat and Rodhe (1973) indicate the SO_2 scavenging coefficient to be $\sim10^{-5}$ s^{-1}. Kumar (1985) estimates the SO_2 scavenging rate to be $\sim2\times10^{-5}$ s^{-1} based on an Eulerian model for the scavenging of pollutants by raindrops.

These studies suggest that the mean rate of scavenging of sulfate in precipitation is about 10^{-4} s^{-1} and is nearly an order of magnitude faster than the mean rate for SO_2. It appears therefore that the scavenging coefficient λ determined by comparing sequential samples of sulfate in precipitation (eq. (6)) refers primarily to scavenging of sulfate from air. However there is some contribution from SO_2 scavenged in air and converted to sulfate in the liquid phase. We now present a rough estimate of the error in the sulfate scavenging coefficient estimated from eq. (6) due to the scavenging of SO_2.

2.1. *Error in the sulfate scavenging coefficient due to liquid phase production from dissolved SO_2*

The error introduced in estimating the sulfate scavenging coefficient from precipitation samples may be investigated by adding another term in eq. (3) to take account of sulfate production in the liquid phase from SO_2. Assuming that all scavenged SO_2 is converted to SO_4^{2-} we have:

$$M(\Delta t_1)=N_0^1[1-\exp(-\lambda_1\Delta t_1)]+N_0^2[1-\exp(-\lambda_2\Delta t_1)], \quad (7)$$

where $M(\Delta t_1)$ is the total deposited SO_4^{2-} in time Δt_1. N_0^1 is the initial amount of sulfate present in the volume of air above the sampler, scavenged at rate λ_1 and N_0^2 is the initial amount of SO_2 present in the air above the sampler scavenged at rate λ_2. Comparing two successive time intervals Δt_1 and Δt_2 of precipitation we have, analogous to eq. (4):

$$\frac{M(\Delta t_1)}{M(\Delta t_2)}=\frac{N_0^1[1-\exp(-\lambda_1\Delta t_1)]+N_0^2[1-\exp(-\lambda_2\Delta t_1)]}{N_0^1\exp(-\lambda_1\Delta t_1)[1-\exp(-\lambda_1\Delta t_2)]+N_0^2\exp(-\lambda_2\Delta t_1)[1-\exp(-\lambda_2\Delta t_2)]}. \quad (8)$$

We now take $\Delta t_1=\Delta t_2=3600$ s, which is the sampling time for the BNL Sequential data, and assume that $\lambda_1=10^{-4}$ s^{-1} and $\lambda_2=10^{-5}$ s^{-1}, which is generally consistent with previous estimates of mean sulfate and SO_2 scavenging coefficients discussed above. Eq. (8) then becomes:

$$\frac{M(\Delta t_1)}{M(\Delta t_2)}=\frac{1}{0.698+0.1128\varepsilon}+\frac{1}{5.96/\varepsilon+0.965}, \quad (9)$$

where $\varepsilon=N_0^2/N_0^1$, the initial ratio of the air concentrations of SO_2 and SO_4^{2-}. Measurements of air concentrations were not made in tandem with the precipitation samples at BNL. However we investigate the role of SO_2 scavenging in eq. (9) by using measurements of sulfate and SO_2 air concentrations in other industrial regions, such as given by Charlson et al. (1983). Their Table 1 shows that ε may be expected to range between 0.25 and 1 for a site like BNL which is in the vicinity and mostly downwind of the New York City-New Jersey industrial area. We have used eq. (6) and eq. (9) to calculate the error

Table 1. *The error in estimating the sulfate scavenging coefficient due to oxidiation of SO_2 scavenged from air*

ε	$\bar{\lambda}_1$ (s^{-1})	Error
0	1.00×10^{-4}	0%
0.25	0.97×10^{-4}	3%
0.5	0.94×10^{-4}	6%
0.75	0.92×10^{-4}	9%
1	0.89×10^{-4}	12%
1.5	0.85×10^{-4}	18%

The sulfate scavenging coefficient is increasingly underestimated for greater SO_2/SO_4^{2-} air concentrations (increasing ε).

introduced in the estimate of the sulfate scavenging coefficient for various values of ε and present it in Table 1. The ratio $M(\Delta t_1)/M(\Delta t_2)$ of sequential sulfate deposition in precipitation samples determines the scavenging coefficient. We see that for $\varepsilon = 0$ we recover our assumed value of the sulfate scavenging coefficient, 10^{-4} s^{-1} using eq. (6). For increasing values of ε the sulfate scavenging coefficient determined from the deposition of sulfate in precipitation samples underestimates the actual sulfate scavenging coefficient by $\leqslant 12\%$, for $0.25 < \varepsilon < 1$.

2.2. *Sample and data acquisition*

Precipitation samples were obtained using an automatic sequential precipitation sampler designed and built at Brookhaven National Laboratories (Raynor and McNeil, 1978, 1979; Raynor and Hayes, 1984). Upon the onset of precipitation a sensor is activated which opens the cover on a sampler and allows precipitation collection for 1 h (or less if precipitation ends within the hour). After 1 h the system rotates to allow precipitation to be collected in the next sampler bucket. A new collecting bucket is introduced every hour until the precipitation ceases. The beginning and ending times for each collected sample were automatically recorded. The sampler is capable of collecting solid and liquid precipitation. A tipping-bucket rain gauge recorded the amount of precipitation to the nearest 0.25 mm. Solid precipitation amount was indicated by a weighing rain gauge.

The samples were then chemically analyzed for H^+, SO_4^{2-}, N in $NO_3^- + NO_2^-$, N in NH_4^+, Na^+, and Cl^- concentrations, usually within two weeks. A quality assurance program involving periodic checks of sample analysis with the MAP3S programs was in place. The lower limit of sulfate measurement capability was 20 μeq/liter until February 5, 1978 and 10 μeq/liter after that date. Sulfate concentrations below these values have been excluded from our analysis. We refer the reader to Raynor and Hayes (1984) for further details of data acquisition, analysis and methods. Estimates of the scavenging coefficients of ammonium compounds and of nitrates from these data have been presented by Sperber (1985).

3. Results

Ideally when estimating a value of λ from two successive precipitation samples we would require the rainfall rates of the two hours to be equal. This would help insure that the in-cloud and below-cloud processes would be occurring at a uniform rate in the 2 h. In order to enlarge the number of estimates of λ, we have considered successive hours for which the rainfall rates are within a given percentage of each other.

The sensitivity of the estimated scavenging coefficients to the allowed variability in rainfall rate is shown in Table 2. Note that the results are given in terms of the square root of the scavenging coefficient $\lambda^{1/2}$ because, as discussed in Subsection 3.1, its distribution approximates the normal distribution. The square of the mean value of the normally distributed variable $(\overline{\lambda^{1/2}})^2$, is shown in the first column of Table 2. Table 2 indicates that when the rainfall rate is allowed to vary by $\pm 50\%$ in the two hours the number of estimates of λ increases from 102 to 336.

We find that the difference in the mean values of $\lambda^{1/2}$ between the $\pm 0\%$ and $\pm 50\%$ data sets is not significant at the 95% confidence level. All statistical tests reported in this paper are at the 95% confidence level. Comparison between the $\pm 0\%$ and $\pm 100\%$ rainfall rate variability, however, indicates that the difference in the values of $\overline{\lambda^{1/2}}$ is statistically significant. We will therefore

Table 2. *Properties of the distribution of sulfate scavenging coefficients for various rainfall rate variabilities*

$\pm$% relaxation rainfall rate	$(\overline{\lambda^{1/2}})^2$ (s^{-1})	$\overline{\lambda^{1/2}}$ ($s^{-1/2}$)	σ ($s^{-1/2}$)	No. of cases
0	0.81×10^{-4}	0.90×10^{-2}	3.99×10^{-3}	102
50	0.92×10^{-4}	0.96×10^{-2}	4.08×10^{-3}	336
100	1.12×10^{-4}	1.06×10^{-2}	4.39×10^{-3}	593

Table 3. *Sensitivity of the sulfate scavenging coefficient to wind velocity for ±50% rainfall rate variability*

Windspeed (m s^{-1})	$\overline{\lambda^{1/2}}$ ($s^{-1/2}$)	σ ($s^{-1/2}$)	No. of cases
0–2	1.07×10^{-2}	3.83×10^{-3}	13
>2–4	0.94×10^{-2}	4.51×10^{-3}	37
>4–6	0.97×10^{-2}	4.36×10^{-3}	57
>6–8	0.89×10^{-2}	3.95×10^{-3}	43
>8	0.93×10^{-2}	3.73×10^{-3}	107

Table 4. *Sensitivity of the sulfate scavenging coefficient to wind direction for ±50% rainfall rate variability*

Wind direction	$\overline{\lambda^{1/2}}$ ($s^{-1/2}$)	σ ($s^{-1/2}$)	No. of cases
$\leqslant \pm 5°$	0.95×10^{-2}	3.85×10^{-3}	210
$\geqslant \pm 10°$	0.97×10^{-2}	4.45×10^{-3}	126

report results from the set of λ values obtained with ±50% variability in the rainfall rate.

Advection may be expected to be more important if strong winds are present. The sensitivity of the estimated scavenging coefficients to wind velocity measured at a height of 88 m and averaged over the sample period is given in Table 3. Restricting the data in terms of the prevailing wind velocity does not have a significant effect on $\overline{\lambda^{1/2}}$ values.

If the wind direction in the two successive hours differ, the estimated λ value may be in error since the two sampled air masses may have had different origins. Table 4 gives the values of $\overline{\lambda^{1/2}}$ and the standard deviation σ when the hourly averaged wind direction varied by $\leqslant \pm 5°$ (the resolution of the measurements) and by $\geqslant \pm 10°$. No significant differences in the means occur when a constraint is imposed on wind direction.

The error in the estimated λ values due to advection may be expected to be greatest at the leading and trailing edges of a storm due to input air from non-precipitating regions. We have repeated the analysis by omitting the data from the initial and last hours of precipitation events. The mean of the square roots of the 251 resulting scavenging coefficients is 9.34×10^{-3} $s^{1/2}$ (with $\sigma = 4.05 \times 10^{-3}$ $s^{1/2}$) not statistically different from the unconstrained data set.

The results of these sensitivity studies do not, of course, show that advection does not influence our estimates of λ. They merely point out that the variability in the deposition data is large enough to hide the effects of advection. The various factors contributing to the variability may possibly be separated by improving the time resolution of observations.

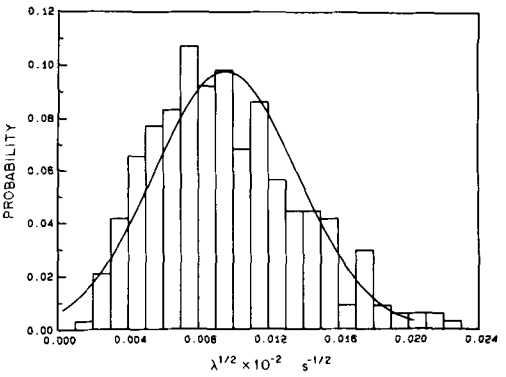

Fig. 1. Histogram of the probability distribution function of the square root of the sulfate scavenging coefficient for ±50% rainfall rate variability. The superimposed curve is the ideal normal distribution for the mean and standard deviation of the data set.

3.1. *Frequency distribution of* λ

Upon transforming λ by taking the square root we find that the frequency distribution of $\lambda^{1/2}$ approximates a normal distribution. Presented in Fig. 1 is the histogram of the probability distribution of $\lambda^{1/2}$ for the ±50% rainfall rate variability data set. The superimposed curve is the ideal

Table 5. *Properties of the sulfate scavenging coefficient based on season, synoptic and precipitation type*

Condition	$(\overline{\lambda^{1/2}})$ ($s^{-1/2}$)	σ ($s^{-1/2}$)	$(\overline{\lambda^{1/2}})/\sigma$	No. of cases
Spring	0.92×10^{-2}	3.73×10^{-3}	2.47	88
Summer	1.01×10^{-2}	5.10×10^{-3}	1.98	47
Fall	0.96×10^{-2}	3.89×10^{-3}	2.47	87
Winter	0.96×10^{-2}	4.03×10^{-3}	2.38	114
Low	0.95×10^{-2}	3.34×10^{-3}	2.84	38
Warm	0.92×10^{-2}	4.03×10^{-3}	2.28	153
Cold	1.08×10^{-2}	4.59×10^{-3}	2.36	57
Occluded	0.94×10^{-2}	3.92×10^{-3}	2.41	38
Stationary	0.91×10^{-2}	3.94×10^{-3}	2.31	42
Squall	1.20×10^{-2}	4.80×10^{-3}	2.50	7
Rain	0.92×10^{-2}	3.87×10^{-3}	2.38	259
Rainshower	1.18×10^{-2}	4.61×10^{-3}	2.57	25
T. shower	1.39×10^{-2}	4.48×10^{-3}	2.85	8
Snow	0.96×10^{-2}	3.67×10^{-3}	2.63	37
Whole set	0.96×10^{-2}	4.08×10^{-3}	2.35	336

normal distribution for the mean and standard deviation of the data set. We find that the sets of scavenging coefficients obtained with $\pm 0\%$ and $\pm 100\%$ rainfall rate variability (Table 2) have distributions very similar to Fig. 1 with the mean values and standard deviations given in the table.

Table 5 gives the mean values, standard deviations and ratios of these quantities for groups of scavenging coefficients divided according to seasons, synoptic conditions and precipitation types. We note that the ratio of the mean value and the standard deviation varies in a restricted range around the mean value of 2.35, independent of how the groups of λ values are chosen.

A question raised by Table 5 is whether or not the number of λ values obtained for each group is large enough to allow the conclusion that the mean and standard deviations of $\lambda^{1/2}$ are not independent of each other. This needs to be checked by further observations of λ at Brookhaven National Laboratory and at other locations. If such a relationship can be shown to be generally valid, it may be useful in two important aspects. First, it would indicate that the distribution of $\lambda^{1/2}$ is determined essentially by only one parameter — thus limiting the choice of stochastic models which may describe the scavenging process. Second, it would help to resolve the sampling problem, i.e., it would suggest the number of λ values which must be known to obtain an adequate representation of its distribution function.

3.2. *Variation of the scavenging coefficient with season, precipitation type and synoptic type*

The precipitation type of each hourly sample was recorded for this 6-year data set. Of the 26 precipitation categories defined only 3 categories yielded greater than 10 estimates of λ. At BNL the most frequent precipitation type is rain, with rain showers a distant second followed by snow and thundershowers, respectively (Raynor and Hayes, 1984). The majority of the scavenging coefficients were derived from rain events, followed by rainshowers and snow. The main reason for thundershowers yielding so few estimates of λ is the failure to meet the criterion that deposition in hour i be greater than in hour $i+1$. This may be ascribed to the more violent nature of the storm, i.e., the non-homogeneity due to entrainment of material from updrafts. The considerable variability of rainfall rate from hour to hour also reduced the number of estimates of λ for thunderstorms because it violated the requirement that rainfall rates be within $\pm 50\%$ of each other. Rain type events generally have steadier rainfall rates and are usually due to altostratus clouds. Rain showers emanate from cumulus clouds which have a greater vertical extent than altostratus clouds because of greater updraft velocities. The differences among the $\overline{\lambda^{1/2}}$ values for different seasons and for different precipitation categories in Table 5 are not statistically significant. It may be noted, however, that the trends in these differences are the same in the three data sets of 0%, 50% and 100% rainfall rate variabilities (Table 2). The experimental results of Knutson et al. (1976) indicated that snow is a more efficient scavenger of aerosol particles than rain, when based upon equal weights of precipitation. It may be noted, however, in the BNL data base that the classification of precipitation as snow or rain in the data set we are using is based on surface observations. It is probable, especially in winter, that the raindrops observed at the surface were in the solid phase at cloud level.

The majority of precipitation event at BNL

were associated with warm fronts (Raynor and Hayes, 1982). Other frontal systems which yielded more than five estimates of λ were cold fronts, occluded fronts, stationary fronts, low pressure systems and squall line.

The differences in the $\overline{\lambda^{1/2}}$ values between cold and warm fronts and between cold and stationary fronts are statistically significant. This raises the possibility that the differences among the seasonal and precipitation categories in Table 5 may also be statistically significant for larger data sets.

3.3. *Dependence of the scavenging coefficient on rainfall rate*

The possibility of a dependence of λ on rainfall rate is investigated using the scatterplot shown in Fig. 2. Since the rainfall rate in the two successive hours of precipitation from which λ is estimated may differ by up to $\pm 50\%$, the independent variable is taken to be the average rainfall rate in these two hours. λ values obtained for snow are excluded from Fig. 2.

Trends are shown on the scatterplot using the technique of moving statistics discussed by Kleiner and Graedel (1980) and Cleveland and Kleiner (1975). This method of enhancing scatter plots has been found to be useful in detecting trends in noisy data when the density of data points is not uniform. The method also has the advantage of indicating if the distribution of the dependent variable changes with the independent variable.

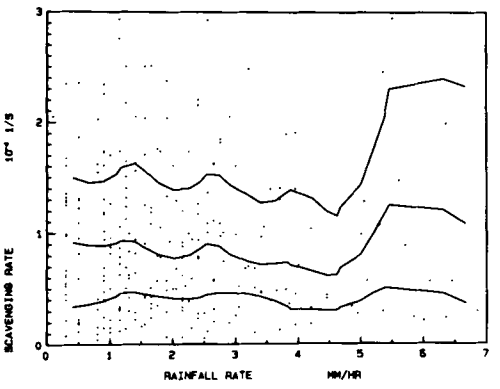

Fig. 2. Scatterplot with superimposed moving statistics of the dependence of the sulfate scavenging coefficient on rainfall rate. The figure indicates that the sulfate scavenging coefficient does not increase with the rate of precipitation in a systematic manner as suggested by theoretical models.

Estimates of λ which lie in a predetermined interval of the rainfall rate, chosen to be 0.8 mm h^{-1}, mainly as a balance between smoothness of the resultant curve versus obliteration of any possible trend, are sorted in increasing order. From this set of λ values are plotted 3 points, the lowest point is the lower semi-midmean, the middle point is the midmean and the upper point is the upper semi-midmean, all plotted at the midmean of the rainfall rates from the interval. The midmean is the mean of the sorted variable computed after the upper and lower quartiles are excluded. The lower (upper) semi-midmeans are the midmeans of the values below (above) the median. The moving statistics were computed for succeeding intervals of 0.8mm h^{-1} in the rainfall rate which are displaced by 0.2 mm h^{-1} from each other. Intervals with fewer than 6 data points were excluded. The resulting curves were further smoothed by the iterative application of the Hanning technique until the values of successive iterations were $\pm 3\%$ of each other; generally less than seven iterations were required (Kleiner and Graedel, 1980). The resulting scatterplot with superimposed moving statistics is presented in Fig. 2. Scott (1982), Slinn (1977) and Pruppacher and Klett (1978) estimate on a theoretical basis that the sulfate scavenging coefficient increases with rainfall rate in an approximately linear fashion.

The moving statistics presented in Fig. 2 indicate that the sulfate scavenging coefficient decreases slightly with rainfall rate over the range ~ 1 mm h^{-1} to ~ 4.5 mm h^{-1}. The increase for rainfall rates > 4.5 mm h^{-1} to ~ 5.5 mm h^{-1} for the midmean and upper semi-midmean is based upon few data points and must be viewed with caution until further results become available.

In the laboratory Lai et al. (1978) have observed the scavenging coefficients of submicron size aerosols to be virtually independent of the precipitation rate which were set at 2, 3, and 15 mm h^{-1}. This may be considered to be in general agreement with the results presented here for rainfall rates $\leqslant 4.5$ mm h^{-1} since sulfate aerosols are also predominantly of submicron size (Whitby, 1978). Lai et al. (1978) hypothesize that this behaviour may be explained by the decreased

collection efficiencies of large drops at large precipitation rates.

4. Discussion

It has been shown in this paper that chemical sampling of two successive intervals of precipitation allows us to estimate the scavenging coefficient of a soluble species in air. Six years of sequential data samples with hourly resolution collected at Brookhaven National Laboratory were used to obtain lower limit estimates of the sulfate scavenging coefficients at this location. The relatively large number of estimates of λ obtained in this manner allowed us to study its distribution function and its variation with season, precipitation type and rainfall rate.

The main source of error in our analysis is the assumption of horizontal homogeneity in the precipitation system between the two successive hours of sampling from which λ is estimated. Sensitivity studies were carried out to gauge the impact of this assumption and some precautionary measures were taken to exclude samples in which the probability of error was considered to be high. Nevertheless it is difficult to make a priori estimates of the error in the estimated λ values due to the lack of horizontal homogeneity. This error may be reduced by decreasing the sampling time. Currently a large number of stations worldwide collect precipitation samples for chemical analysis (e.g., MAP3S precipitation chemistry network). However, the time resolution of sampling at most of these stations is greater than one hour. The results presented in this paper suggest that useful information on precipitation scavenging of soluble species in air may be obtained at these networks of stations by improving the time resolution of sampling.

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REFERENCES

Bolin, B. and Persson, C. 1975. Regional dispersion and deposition of atmospheric pollutants with particular application to sulfur pollution over western Europe. *Tellus 27*, 281–309.

Cawse, P. A. 1974. A survey of atmospheric trace elements in the UK (1972–1973). AERE-R 7669, H.M.S.O., London U.K.

Chan, W. H., Ro, C. U., Vet, R. J., Tang, A. J. S. and Lusis, M. A. 1983. Precipitation scavenging and dry deposition of pollutants from the INCO nickel smelter in Sudbury. In: *Precipitation scavenging, dry deposition and resuspension*, Pruppacher, H. R., Semonin, R. G. and Slinn, W. G. N., eds. Elsevier, New York.

Charlson, R. J., Vong, R. and Hegg, D. A. 1983. The sources of sulfate in precipitation (2). Sensitivities to chemical variables. *J. Geophys. Res. 88*, 1369–1374.

Cleveland, W. S. and Kleiner, B. 1975. Enhancing scatterplots with moving statistics. *Technometrics 17*, 447–454.

Dana, M. T., Hales, J. M. and Wolf, M. A. 1975. Rain scavenging of SO_2 and sulfate from power plant plumes. *J. Geophys. Res. 80*, 4119–4129.

Dittenhoefer, A. C. and DePena, R. G. 1980. Sulfate aerosol production and growth in coal-operated power plant plumes. *J. Geophys. Res. 85*, 4499–4506.

Fisher, B. E. A. 1982. The transport and removal of sulphur dioxide in a rain system. *Atmos. Environ. 16*, 775–783.

Fisher, B. E. A. 1983. A review of the processes and models of long-range transport of air pollutants. *Atmos. Environ. 17*, 1865–1880.

Garland, J. A. 1978. Dry and wet removal of sulphur from the atmosphere. *Atmos. Environ. 12*, 349–362.

Granat, L. and Rodhe, H. 1973. A study of fallout by precipitation around an oil-fired power plant. *Atmos. Environ. 7*, 781–792.

Granat, L. and Söderlund, R. 1975. *Atmospheric deposition due to long and short distance sources*, Report AC-32. University of Stockholm, Department of Meteorology.

Henmi, T. and Reiter, E. R. 1978. Regional residence time of sulfur dioxide over the eastern United States. *Atmos. Environ. 12*, 1489–1495.

Huebert, B. J., Fehsenfeld, F. C., Norton, R. B. and Albritton, D. 1983. The scavenging of nitric acid vapor by snow. In: *Precipitation scavenging, dry deposition and resuspension*. Pruppacher, H. R.,

Semonin, R. G. and Slinn, W. G. N., eds. Elsevier, New York, pp. 293–303.

Junge, C. E. and Gustafson, P. E. 1957. On the distribution of seasalts over the United States and its removal by precipitation. *Tellus 9*, 164–173.

Kliener, B. and Graedel, T. E. 1980. Exploratory data analysis in the geophysical sciences. *Rev. Geophys. Space Phys. 18*, 699–717.

Knutson, E. O., Sood, S. K. and Stockham, J. D. 1976. Aerosol collection by snow and ice crystals. *Atmos. Environ. 10*, 395–402.

Kumar, S. 1985. An Eulerian model for scavenging of pollutants by raindrops. *Atmos. Environ. 19*, 769–778.

Lacaux, J. P. and Warburton, J. A. 1983. Precipitation scavenging of submicron particles released by rockets into convective clouds. In: *Precipitation scavenging, dry deposition and resuspension*. Pruppacher, H. R., Semonin, R. G. and Slinn, W. G. N., eds. Elsevier.

Lai, K.-Y., Dayan, N. and Kerker, M. 1978. Scavenging of aerosol particles by a falling water drop. *J. Atmos. Sci. 35*, 674–682.

Maul, P. R. 1978. Preliminary estimates of the washout coefficient for sulphur dioxide using data from an east midlands ground level monitoring network. *Atmos. Environ. 12*, 2515–2517.

Omstedt, G. and Rodhe, H. 1978. Transformation and removal processes for sulfur compounds in the atmosphere as described by a one-dimensional time-dependent diffusion model. *Atmos. Environ. 12*, 503–509.

Pruppacher, H. R. and Klett, J. D. 1978. *Microphysics of clouds and precipitation*. D. Reidel Publishing Company, 714 pp.

Raynor, G. S. and Hayes, J. V. 1982. Variation in chemical wet deposition with meteorological conditions. *Atmos. Environ. 16* 1647–1656.

Raynor, G. S. and Hayes, J. V. 1983. Differential rain and snow scavenging efficiency implied by ionic concentration differences in winter precipitation. In: *Precipitation scavenging, dry deposition and resuspension*. Pruppacher, H. R., Semonin, R. G. and Slinn, W. G. N., eds. Elsevier, New York, pp. 249–262.

Raynor, G. S. and Hayes, J. V. 1984. *The sequential precipitation chemistry sampling program at Brookhaven National Laboratory with an analytical summary of 1976–1982 data*. Report BNL 51819. Brookhaven National Laboratory, Upton, New York, 69 p.

Raynor, G. S. and McNeil, J. P. 1978. *The Brookhaven automatic sequential precipitation sampler*. BNL 50818.

Raynor, G. S. and McNeil, J. P. 1979. An automatic sequential precipitation sampler. *Atmos. Environ. 13*, 149–155.

Rodhe, H. and Grandell, J. 1972. On the removal time of aerosol particles from the atmosphere by precipitation scavenging. *Tellus 24*, 442–454.

Rodhe, H. and Grandell, J. 1981. Estimates of characteristic times for precipitation scavenging. *J. Atmos. Sci. 38*, 370–386.

Scott, B. C. 1982. Theoretical estimates of the scavenging coefficient for soluble aerosol particles as a function of precipitation type, rate and altitude. *Atmos. Environ. 16*, 1753-1762.

Scriven, R. A. and Fisher, B. E. A. 1975. The long-range transport of airborne material and its removal by deposition and washout—1. General considerations. *Atmos. Environ. 9*, 49–58.

Slinn, W. G. N. 1977. Some approximations for the wet and dry removal of particles and gases from the atmosphere. *J. Water, Air, Soil Pollut. 7*, 513–543.

Sperber, K. R. 1985. Characteristics of removal and deposition of soluble species by precipitation. M.S. Thesis. State University of New York, Stony Brook, N.Y.

Venkatram, A., Ley, B. E. and Wong, S. Y. 1982. A statistical model to estimate long-term concentrations of pollutants associated with long-range transport. *Atmos. Environ. 16*, 249–257.

Whitby, K. T. 1978. The physical characteristics of sulfur aerosols. *Atmos. Environ. 12*, 135–160.