SOME CONSIDERATIONS ON THE WASHOUT OF SULFATE FROM STACK PLUMES

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ABSTRACT

A theoretical analysis of the contribution to rainwater sulfate concentration by precipitation scavenging of gaseous SO_2 and sulfate containing aerosols is presented. Aspects, such as the proper choice of mean raindrop diameter, are discussed in detail, and guidelines for their use are explored. Sample calculations are provided in which emissions from an hypothetical stack are considered as the source of the gaseous SO_2 and sulfate aerosol. The basic assumption of irreversible sorption behavior is discussed and utilized to obtain an upper limit to the resulting sulfate concentration.

The effect of raindrop diameter on the sulfate concentration is not consistent. However, for a given drop diameter the sulfate concentration decreases as the precipitation rate increases. The sulfate concentration resulting from aerosol scavenging depends on the particle diameter and the precipitation rate. The sulfate concentration shows a maximum with respect to particle size; at moderate distances from the source, it is maximum for particles having aerodynamic equivalent diameter of about 5 μm to 10 μm.

INTRODUCTION

The washout of sulfate from the atmosphere occurs by absorption of gaseous sulfur dioxide or by scavenging of sulfate containing aerosol particles. Both mechanisms have received considerable attention.

The data of Hales, Thorp, and Wolf (1971) showed no strong relationship between mean raindrop size and sulfate washout but did show an inverse relationship with background acidity of the rain (Hales, 1974). Hutcheson and Hall (1974) recently reanalyzed the field experimental data of Ensminger and Martin (1957). They concluded that

aerosol scavenging was not responsible for the sulfate washout, but that SO_2 absorption was the primary mechanism.

In this paper, we will present a theoretical analysis concerning the sulfate concentration of rainwater resulting from precipitation scavenging of gaseous SO_2 and sulfate containing aerosols emitted from an ideal emission source.

THEORETICAL CONSIDERATIONS

As already pointed out, the washout of sulfate from stack plumes occurs by absorption of gaseous SO_2 or by collection of sulfate containing particulates. These mechanisms act in parallel, and their effects on the resulting sulfate content of the rainwater are then additive.

ABSORPTION OF SO_2 BY RAINDROPS

The fundamental considerations of precipitation scavenging of soluble pollutant gases has been nicely summarized by Hales (1972). In that paper the author pointed out that the calculation of precipitation scavenging rates for trace gases is complicated by several factors. Some of these are reversible sorption behavior, liquid phase mixing, and chemical reactions in the liquid phase. Hales considered each of these factors.

If the absorption process is reversible, calculation of this type of scavenging can lead to substantial computational difficulties. Reversible absorption would be operative if the dissolved gas does not undergo any chemical reaction and can be desorbed into the gas phase in its original state. With such phenomena, there can be a redistribution of the pollutant in the atmosphere. Consider for the moment a plume that is approximately gaussian in the vertical. As a particular raindrop enters the plume it experiences an increasing concentration until the plume centerline is reached. For a high mass transfer rate, it is possible that the raindrop is nearly saturated at this point in its travel. As it proceeds below the plume centerline, the raindrop now experiences a decreasing concentration of the species in the gas phase; and the direction of the driving force for mass transfer is out of the drop. Slinn (1974a) has analytically considered reversible sorption behavior and the resulting redistribution of the plume. The influence of the reversible precipitation scavenging is that the plume diffuses about the effective source height corrected for a washdown speed. Slinn's results for small distances of travel (his Eq. 24) are similar to that obtained for irreversible first order scavenging (c.f., Heines and Peters (1973)).

Reversible sorption phenomena can be significant for species that undergo only slow chemical reactions in the liquid phase. This, however, may not be true of SO_2. Liss (1971) has theoretically shown that for waters having a pH > 4, the transfer of SO_2 from air into the liquid phase is gas phase controlled. Brimblecombe and Spedding (1972) have substantiated this for specific experimental conditions, and this is in agreement with the criteria of Hales (1972). He pointed out that the system is mass transfer controlled in the gas phase if $D_c k_r / 3K_g \mathfrak{H} >> 1$, where D_c is the raindrop diameter, k_r is the liquid phase reaction rate, K_g is the overall mass transfer coefficient based on the gas phase, and $\mathfrak{H}$ is Henry's Law constant. For SO_2, the hydration rate constant is on the order of $10^6 s^{-1}$, $\mathfrak{H} \approx 10^{-2}$, $D_c \approx 10^{-3} m$, and $K_g \approx 10^{-1} m/s$. Thus, $D_c k_r / 3K_g \mathfrak{H} \approx 10^6$. If this is the case, the annihilation of SO_2 as a dissolved species within the drop is so rapid that the liquid phase resistance is negligible, and the SO_2 exerts an insignificant back pressure.

However, the liquid phase oxidation cannot be considered infinitely fast, and in the consecutive processes, may be the rate limiting reaction rather than the prior hydrolysis rate of SO_2. As a result, this concept of the irreversible behavior of the SO_2 absorption may not be entirely accurate. The liquid phase oxidation is affected by numerous species. Johnstone and Coughanour (1958) found that the oxidation of SO_2 in a sulfate catalyst solution was relatively fast. However, as the pH was decreased to relatively low values the oxidation slowed. The pH of their acid solutions was probably lower than what one normally anticipates in raindrops. The analysis of Scott and Hobbs (1967), expanding on the experiments of Van den Heuvel and Mason (1963), indicated that the rate determining step is the liquid phase oxidation of the bisulfite (HSO_3^-) to the sulfate. The ammonium ion catalyzes this reaction by maintaining a high pH.

While the question of reversibility of the sorption phenomenon cannot be answered with certainty at this time, it does appear that one cannot consider the scavenging of SO_2 as a simple reversible hydrolysis behavior in pure water (Hales and Sutter, 1973). At this time, it seems more extensive studies on the oxidation of SO_2 in the water phase containing typical contaminants is warranted to answer fully this question of reversible sorption behavior. Nevertheless, the assumption of irreversible absorption provides an upper limit to precipitation scavenging of gaseous SO_2. For this case, the system is first order and irreversible; and the first order loss constant, k, can be described in terms of the gas phase mass transfer coefficient. If each raindrop size contributes to k independently, one can write, considering the normalized distribution of raindrops sizes as $f(D_c)$,

$$k = \int_{D_c^0}^{D_c^\infty} N f(D_c)\ \pi D_c^2 k_g(D_c)\ dD_c \qquad (1)$$

where N is the total number of raindrops per unit volume, $k_g(D_c)$ is the gas phase mass transfer coefficient, and D_c^0 and D_c^∞ represent the smallest and largest raindrop sizes present, respectively. For spherical drops, the Froessling equation (c.f., Skelland, 1974) is most frequently used to estimate k_g,

$$Sh = 2.0 + 0.6\ Re_c^{1/2}\ Sc^{1/3} \qquad (2)$$

where $Sh = k_g D_c/\mathscr{D}$, $Re_c = \rho D_c U_t/\mu$, and $Sc = \mu/\rho\mathscr{D}$. Equation (2) can be imagined to be comprised of a molecular diffusion contribution (2.0) and a convective contribution ($0.6\ Re_c^{1/2}\ Sc^{1/3}$).

It is generally not convenient to use Equation (1) in the integral form but rather to employ some mean diameter. One might ask which mean diameter is appropriate. Equation (2) shows that k_g varies as $1/\sqrt{D_c}$ at high Re_c where the contribution of the constant 2.0 is not substantial. Thus, the appropriate mean diameter is intermediate to the length mean diameter and the area mean diameter. In order to evaluate this factor more completely, Equation (1) was numerically integrated, assuming the raindrop size is logarithmic-normally distributed, and this value of k was compared to the value calculated if the root mean square of the length mean diameter and the area mean diameter ($\bar{D}_{\sqrt{1a}}$) were used.

It should be noted that the raindrops were assumed to be falling at their terminal velocity. The error resulting from this approximation is shown in Table 1 for several values of the number median diameter ($\bar{D}_g^1$) and the geometric standard deviation (σ_g)†. The error is quite small, and it is considerably greater if either the length or area mean diameter is employed. Under the conditions evaluated the absolute error can be 26% using the length or area mean diameter, and as large as 90% if one would use the volume (or mass) mean diameter.

Table 1
Percent Error in Estimating k by Using $D_{\sqrt{1a}}$

σ_g \ $\bar{D}_g^1$	0.6mm	1.0mm	1.4mm	1.8mm	2.2mm
1.2	-1.3	-1.3	0.3	-0.5	-0.6
1.4	-4.4	-2.4	-0.6	-1.7	-2.0
1.6	-7.1	-2.6	-2.1	-3.0	-3.4
1.8	-7.2	-0.6	-2.0	-2.9	-3.3
2.0	-4.2	2.1	0.3	-0.5	-0.8

†$D_{\sqrt{1a}}$ can be obtained from $\bar{D}_g^1$ and σ_g as

$$\ln D_{\sqrt{1a}} = \ln \bar{D}_g^1 + 0.75 \ln^2 \sigma_g.$$

SULFATE AEROSOL SCAVENGING BY RAIN

Sulfates are in the form of aerosol particles, and particulate scavenging by rain is a well known phenomenon. Unlike deposition due to sedimentation which depletes only the lowest layers of the cloud, rain scavenging removes particulates below the entire rain forming layer. The mechanism of particulate capture in below-cloud scavenging can be by inertial impaction, by interception, or by diffusive collection of the dust particles by the raindrops. Let us consider each of these mechanisms separately.

The efficiency of collection by inertial impaction can be characterized in terms of the dimensionless Stokes number; i.e.,

$$St = \frac{C_f \rho_p D_p^2 U_t}{9\mu D_c} \tag{3}$$

where C_f is the Cunningham correction factor for the particulates, ρ_p is the density of the particles, D_p is the diameter of the particles, U_t is the relative velocity of the drops with respect to the particles, and μ is the gas phase viscosity. There have been several correlations suggested to estimate the efficiency of impaction, but one of the simplest is (Walton and Woolcock, 1960)

$$\eta_{Imp} = \frac{1}{(1 + 0.7/St)^2} \tag{4}.$$

This scavenging process is more efficient for larger sized particles, and thus affects the particle size distribution.

In the case of interceptive collection, a simple formula has been suggested for a potential flow field about the spherical raindrop (c.f., Fuchs, 1964); i.e.,

$$\eta_{Int} = (1 + \kappa)^2 - \frac{1}{1 + \kappa} \tag{5}$$

where κ is the interception parameter, and it is the ratio of the particle diameter to the collector raindrop diameter. The applicability of Equation (5) is somewhat limited due to the displacement of the particles by the boundary layer which is not accounted for in the potential flow field assumption. Slinn (1974b) has discussed this limitation. However, Equation (5) does provide a reasonable starting point to estimate η_{Int}.

The collection of particles by diffusion to spherical collectors is frequently based on Equation (2) evaluated for an aerosol system. While the correlation expressed by Equation (2) is, for the most part, based on the low to moderate Schmidt numbers usually experienced in liquid-liquid systems and gas-liquid systems, its applicability has been

generally assumed for the large Schmidt number aerosol case. If this extrapolation can be assumed, the diffusive collection efficiency can be written as (c.f., Strauss, 1966)

$$\eta_{Dif} = \frac{8}{Re_c Sc} + \frac{2.4}{Re_c^{1/2}\ Sc^{2/3}} \qquad (6).$$

Other equations showing similar predictions have been suggested.

The question of how to combine the individual collection efficiency contributions to estimate an overall value is almost always raised. It would be most gratifying if the problem were solved by dimensional analysis in a manner similar to that for cylindrical collectors (Pascari and Friedlander, 1960). In the absence of such a correlation, however, we prefer to assume that the collection mechanisms act in series and write (Strauss, 1966)

$$\eta = 1 - (1 - \eta_{Imp})(1 - \eta_{Int})(1 - \eta_{Dif}) \qquad (7).$$

Equation (7) affords the appropriate limit that $\eta < 1$ if the individual collection efficiencies are all less than unity.

The scavenging of particulates is essentially an irreversible and first order process; and if one assumes that each collision is effective and that the raindrops act independently, the rate constant is

$$k(D_p) = \int_{D_c^0}^{D_c^\infty} Nf(D_c)\ \frac{\pi}{4}\ D_c^2\ \eta(D_c) U_t(D_c)\ dD_c \qquad (8).$$

The question of chemical reaction irreversibility in the liquid phase is generally not considered since the scavenging is of the sulfate.

It should be noted that Equation (8) is written for a single particle size, and if the overall effect of a particle size distribution is sought a second integration is required; i.e.,

$$k = \int_{D_p^0}^{D_p^\infty} N_p g(D_p) k(D_p)\ dD_p \qquad (9).$$

For the moment, however, we will just consider Equation (8) and $k(D_p)$. The error in using a simplified form of Equation (8) with a mean raindrop diameter was also evaluated assuming the raindrop size to be logarithmic-normally distributed. If one uses an appropriate mean diameter, the error can be maintained relatively small. For the smaller particles -- on the order of 1.0 μm aerodynamic equivalent diameter and smaller -- where interceptive collection and to a lesser extent the

diffusive mechanism become increasingly important, $\bar{D}_{\sqrt{1a}}$ seems to be the most appropriate choice. This is understandable since η_{Int} varies roughly as $1/D_c$ and U_t varies roughly as $\sqrt{D_c}$ for the raindrops larger than about 1.3 mm. As a result, the integral is approximately

$$\int_{D_c^0}^{D_c^\infty} f(D_c)\ D_c^{3/2}\ dD_c$$

multiplied by a constant.

On the other hand for the larger particles where inertial impaction dominates, the area mean diameter,† $\bar{D}_a$ appears to be the proper choice. This is also reasonable since $k(D_p)$ is increasing and is in the range where η_{Imp} varies approximately as $1/\sqrt{D_c}$.

CONCENTRATION OF POLLUTANT FROM A POINT SOURCE WITH HOMOGENEOUS SCAVENGING ACTIVE

Chamberlain (1953) performed calculations employing an exponential correction to Sutton's (Sutton, 1932) plume model equation. Other investigators (Engelmann, 1968) have also studied this problem by evaluating the overall washout. However, it is our intent to evaluate the effect of this type of rain scavenging on the resulting sulfate content of the rain.

The eddy diffusion model concept can easily handle scavenging processes occurring either within the plume or at ground level. Consider the behavior to be steady state with the understanding that the eddy diffusivity accounts for the turbulent fluctuations of time scale less than that of the averaging time. Furthermore, presume that the positive x-axis is aligned with the wind field averaged over the same time period. Finally, note that only first order irreversible loss terms are operative. For transport in the x-direction dominated by convection, the governing partial differential equation is (Heines and Peters, 1973)

$$U \frac{\partial c}{\partial x} = A_y\, x^q \frac{\partial^2 c}{\partial y^2} + A_z\, x^n \frac{\partial^2 c}{\partial z^2} - kc \qquad (10).$$

In Equation (10), kc represents any homogeneous first order loss terms. Chemical reaction, of course, is the most obvious example. However, if the time averaged species concentration is considered to be

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†$\bar{D}_a$ can be obtained from $\overline{D_g^1}$ and σ_g as

$$\ln \bar{D}_a = \ln \overline{D_g^1} + 1.0 \ln^2 \sigma_g.$$

averaged over a large spatial volume, then other scavenging and production mechanisms can be treated as being homogeneous even though they are heterogeneous by physico-chemical behavior. A large spatial volume is a relative term. For chemical reactions, one is limited by the number of molecules in the volume, whereas for absorption of a gas by rain the number of raindrops in the volume is limiting. Therefore, the large volume for these two scavenging mechanisms is decidedly different. For example, 40 cm^3 of air will contain on the order of 10^{15} molecules of a species in the ppm concentration range, but only on the order of 10^0 raindrops. As a result, the fluctuation of a species at a concentration of 1 ppm would be due to the turbulence and may only be a few percent, whereas the fluctuation of the number of raindrops could be on the order of fifty percent or so. Thus, the criterion that should be used to establish the volume required for averaging is related to the degree of fluctuation that one might expect in the atmosphere process variable.

Specifically, gas absorption and particulate scavenging by raindrops can be modeled as homogeneous loss terms. We consider k to be based on the appropriate mean diameter as discussed previously. Heines and Peters (1973) have shown the solution to Equation (10) with the appropriate boundary conditions and a deep mixing depth to be

$$c = \frac{Q\sqrt{\frac{(n+1)(q+1)}{A_y A_z}}}{4\pi x \frac{(n+1)+(q+1)}{2}} \exp\left[-\frac{(q+1)Uy^2}{4A_y x^{q+1}}\right]$$

$$\cdot\left\{\exp\left[-\frac{(n+1)U(H-z)^2}{4A_z x^{n+1}}\right] + \exp\left[-\frac{(n+1)U(H+z)^2}{4A_z x^{n+1}}\right]\right\}$$

$$\cdot\exp\left[-\frac{kx}{U}\right] \qquad (11).$$

Some workers have ignored the exp[-kx/U] term in Equation (11) in developing precipitation scavenging models (c.f., Hales et al., 1973).

The rate of irreversible scavenging of a pollutant at a particular point in the x, y, z space is kc. The amount of the species transferred from the air to the rain water in a column having area in the x, y plane of A and below the rain forming layer at altitude H' is

$$R = \int_0^{H'} \int_A kc \, dA dz \qquad (12).$$

It should be noted that using Equation (9) to represent the overall washout coefficient of many particle sizes is only meaningful if the concentration of all aerosol sizes present is the same. Otherwise, one must recognize that both c and k depend on D_p, and a third integration

of the product kc over all particle diameters present is necessary.

In most cases, H' will be large relative to the plume spread in the z-direction, and H' can be assumed to be nearly infinite. Then for k being independent of spatial position, $A \to 0$, and $H' \to \infty$,

$$R = \frac{kAQ\sqrt{\frac{(q+1)}{\pi UA_y}}}{2x^{(q+1)/2}} \exp\left[-\frac{(q+1)Uy^2}{4A_y x^{q+1}}\right] \exp\left[-\frac{kx}{U}\right] \qquad (13).$$

One should note that R does not depend on the source height H nor on the plume spread in the z-direction. This is not unexpected since the total pollutant material above a point in the horizontal plane depends only on the rate of dispersion in the y-direction and the scavenging rate.

SULFATE CONCENTRATION IN THE RAIN WATER

The homogeneous loss constant, k, must account for all washout processes that contribute to the sulfate content of the rain water. Since the effects are first order and parallel, their individual contributions to the sulfate concentration are additive. Consider that the emissions of gaseous SO_2 and sulfate containing particulate from the source can be represented as Q_{SO_2} and Q_p, respectively. It should be noted that Q_{SO_2} will be expressed as mass of SO_2 emitted per unit time. Furthermore, Q_p will consist of aerosol particles of various sizes, D_p. Thus, if $g(D_p^3)$ represents the normalized mass size distribution relationship,

$$Q_{p_i} = Q_p g(D^3_{p_i}) \qquad (14).$$

It should be noted that to readily obtain some indication of the sulfate concentration several idealizations are required at this point. First, we will ignore any gas phase aerosol formation processes by SO_2. In the absence of any other species that can result in gas phase reactions, this seems reasonable. Secondly, it is presumed that the particle size distribution of the sulfate aerosol is only affected by precipitation scavenging. This means that particle size changes by coagulation and/or water vapor condensation growth can be neglected. These assumptions are difficult to completely justify, especially since cooling of the water vapor laden stack plume could lead to supersaturation, and subsequent aerosol growth. However, since the supersaturation, except under extreme circumstances, would be limited by the rapid dilution enhanced by plume dispersion, the submicron size particles should not grow much beyond 0.5 μm. Particle size change by coagulation is most efficient for small aerosol sizes; and again, except for long plume travel times, the particle growth due to rapid coagulation should not be too important

for the larger particles.

We are now in a position to relate Q and k to the individual washout processes that are occurring. Let η_i represent the collection efficiency of particles of size D_{pi}. If Q_{SO_2} represents the emissions of gaseous SO_2, then correcting for the molecular weight of $SO_4^=$, the emissions are $1.5Q_{SO_2}$ on a sulfate basis. Therefore, Equation (13) can be written for sulfate removal as

$$R = \frac{\pi D_c^2 NA\sqrt{\frac{q+1}{\pi UA_y}}}{2x^{(q+1)/2}} \exp\left[-\frac{(q+1)Uy^2}{4A_y x^{q+1}}\right]\left\{1.5k_g Q_{SO_2}\right.$$

$$\left.\exp\left[-\frac{\pi D_c^2 Nk_g x}{U}\right] + \frac{U_t}{4}\sum_{i=1}^{m}\eta_i Q_{p_i}\exp\left[-\frac{\pi D_c^2 U_t \eta_i x}{4U}\right]\right\} \qquad (15).$$

Now R mass of $SO_4^=$ is transferred to the rain water by the time the drop reaches ground level. Let P be the precipitation rate. Then R mass of $SO_4^=$ is transferred to PA volume of rainwater in a unit time. Thus, the resulting sulfate concentration of the rainwater, $[SO_4^=]$, is simply R/PA.

P can be easily related to the raindrop size distribution, N, and U_t as

$$P = \int_{D_c^0}^{D_c^\infty} Nf(D_c)\,\frac{\pi}{6}\,D_c U_t(D_c)\,dD_c \qquad (16).$$

Again it is not convenient to use the raindrop size distribution, and it is generally more suitable to base the determination on a mean drop diameter. An appropriate mean diameter can be found by evaluating Equation (16) using the drop size distribution. However, it is not useful to employ different mean diameters as the bases for the first order loss constant and the precipitation rate. We will adopt the mean raindrop diameter appropriate for the first order loss constant as the basis. As a result, the precipitation rate must be corrected by a factor β and is

$$P = \beta N\,\frac{\pi}{6}\,\bar{D}_c^3 U_t(\bar{D}_c) \qquad (17),$$

where $\bar{D}_c$ represents the appropriate mean. A plot of β versus σ_g is shown in Figure 1 for the cases of $\bar{D}_c$ being $\bar{D}_{\sqrt{1a}}$ or $\bar{D}_a$. There is very little dependence of β on $\bar{D}_g^I$, and its effect can be safely ignored if $\bar{D}_g^I$ is between 0.8 mm and 2.4 mm.

By employing Equations (15) and (17), the sulfate concentration can

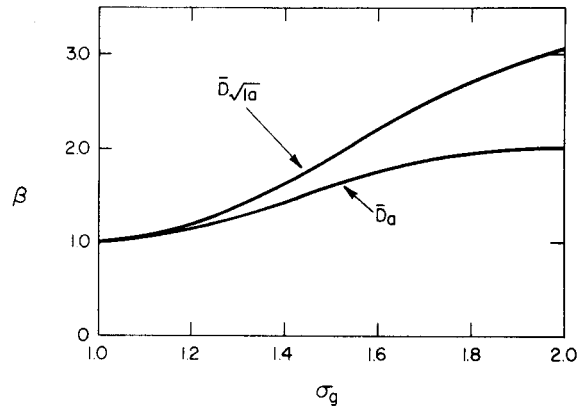

Figure 1. Correction factor to calculate the precipitation rate based on $\bar{D}_{\sqrt{1a}}$ or $\bar{D}_a$ for a logarithmic normal raindrop size distribution.

be obtained assuming gaseous SO_2 emissions and particulate emissions of m discrete aerosol sizes are present.

$$[\overline{SO_4^=}] = \frac{\sqrt{\frac{q+1}{\pi U A_y}}}{D_c U_t x^{(q+1)/2}} \exp\left[-\frac{(q+1)Uy^2}{4A_y x^{q+1}}\right]\left\{4.5\ \frac{k_g Q_{SO_2}}{\beta_g}\right.$$

$$\left.\cdot\exp\left[-\frac{6Pk_g x}{D_c U_t U \beta_g}\right] + \frac{3U_t}{2}\sum_{i=1}^{m}\frac{\eta_i Q_{p_i}}{\beta_{p_i}}\exp\left[-\frac{3P\eta_i x}{D_c U \beta_{p_i}}\right]\right\} \qquad (18)$$

Equation (18) shows that the resulting sulfate concentration of the rainwater should be distributed in a gaussian manner about the direction of the time averaged wind. Furthermore, the maximum sulfate concentration in the rain occurs very close to the stack before significant plume spread in the crosswind direction occurs.

It is believed that the form of the raindrop size distribution should not greatly affect the general conclusions. For example, the single parameter Marshall-Palmer distribution† (Marshall and Palmer, 1948) was also evaluated, and the results indicated that the error introduced by using $\bar{D}_{\sqrt{1a}}$ for gas scavenging is generally within 15% except for extremely small raindrop sizes. In acutality, the use

†The normalized Marshall-Palmer distribution can be written as

$$f(D_c) = \gamma e^{-\gamma D_c}.$$

of $(\bar{D}_1 \bar{D}_a^2)^{1/3}$ predicts a much smaller error, but its use is hardly warranted until a much better predictive model is required. Since the Marshall-Palmer distribution is frequently used, a plot of β versus γ for this distribution is shown in Figure 2.

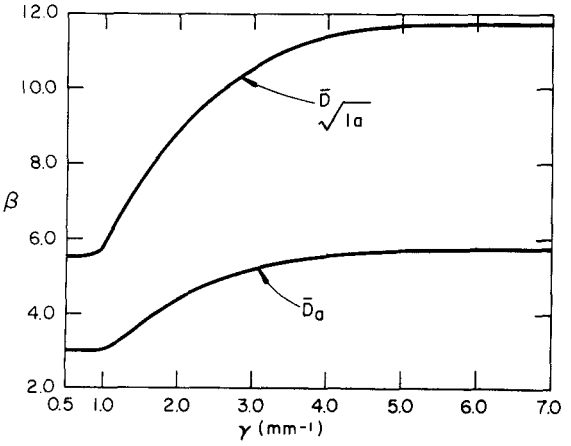

Figure 2. Correction factor to calculate the precipitation rate based on $\bar{D}\sqrt{1a}$ or $\bar{D}_a$ for the Marshall-Palmer Raindrop Size distribution.

DISCUSSION OF THEORETICAL PREDICTIONS

To illustrate the theoretical predictions, we will consider hypothetical meteorological conditions where $q = 0.5$, $A_y = 0.7$, and $U = 4.0$ m/s. Furthermore, let $y = 0$ and for simplicity consider $\beta = 1.0$. This latter consideration implies that the rain consists of a single drop size. While this is an obvious simplification, the results obtained are nevertheless very instructive. Even with this simplification, it will be seen that it is not advisable to make broad generalizations about the effects of raindrop size and precipitation rate on the resulting rainwater sulfate concentration.

In Figure 3, the ratio of the sulfate concentration of the rainwater due to absorption of gaseous SO_2 to the SO_2 source strength is plotted versus distance from the source for raindrop diameters of 0.5 mm, 1.0 mm, and 3.0 mm with precipitation rates of 0.2 μm/s, 1.0 μm/s, and 2.0 μm/s. As expected, the sulfate concentration in the rainwater decreases with distance from the source which is apparently consistent with the data of Ensminger and Martin (1957) and the data of Dana et al. (1973).

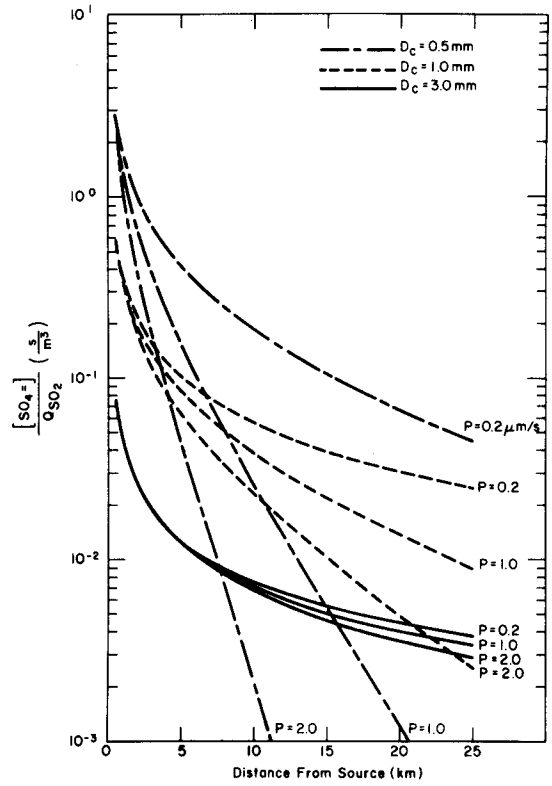

Figure 3. Rainwater sulfate concentration due to precipitation scavenging of gaseous SO_2.

The effect of drop diameter on the sulfate concentration is not always the same; i.e., for a fixed precipitation rate the sulfate concentration with the 0.5 mm drop may or may not be greater than with the 1.0 mm and 3.0 mm drop, depending on the distance from the source. This is consistent, at least qualitatively, with the observations of Hales, Thorp, and Wolf (1971). The effect of increasing the precipitation rate is to decrease the sulfate concentration. This is better illustrated in Figure 4 where the sulfate concentration at x = 10 km is shown as a function of precipitation rate. The dependency of the sulfate concentration on the precipitation rate is more pronounced for the smaller raindrop sizes. The apparent reason for this trend is as follows. For the larger drop, the average volume of air that each drop occupies is so large that it appears essentially infinite in extent. On the other hand, the entire volume occupied by the greater number of smaller raindrops is affected by the absorption process. As the precipitation rate increases, this average volume of air per drop decreases so that the available SO_2 in the volume is limiting.

Typical results of similar calculations for sulfate containing aerosol of size 0.1 μm, 1.0 μm, and 10. μm are shown in Figures 5 thru 8.

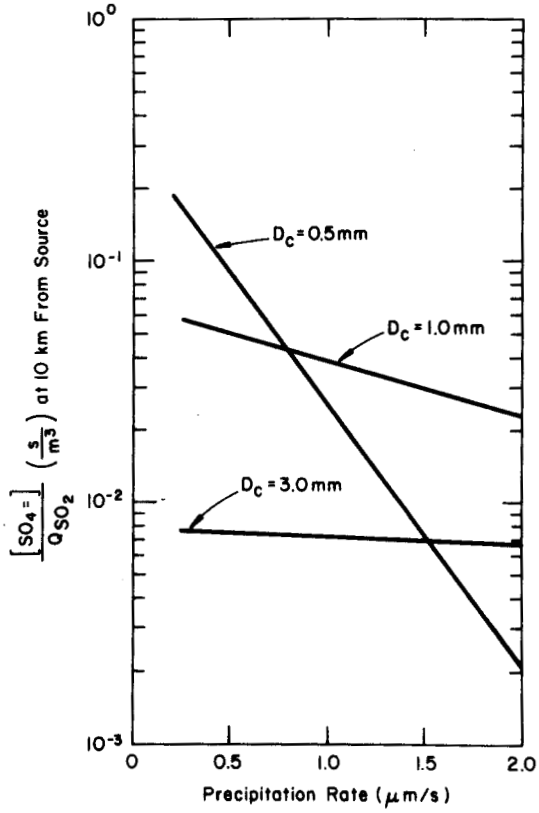

Figure 4. Rainwater sulfate concentration from SO_2 absorption as a function of precipitation rate.

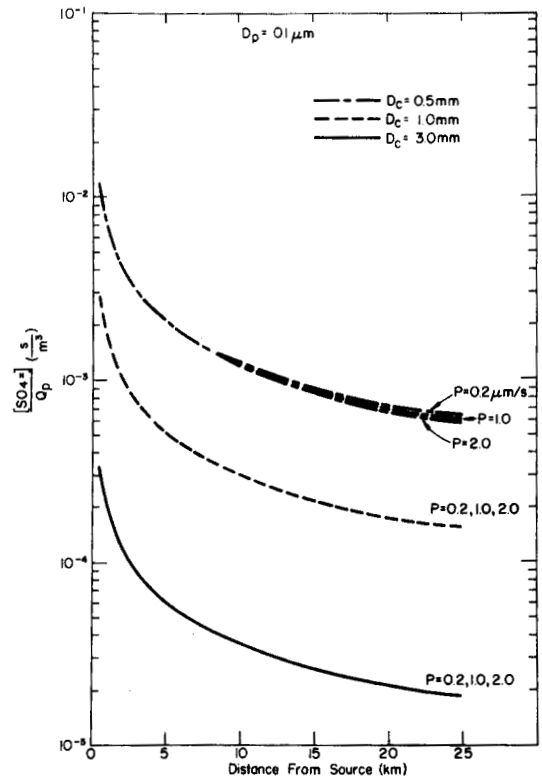

Figure 5. Rainwater sulfate concentration due to precipitation scavenging of 0.1 µm AED sulfate aerosol.

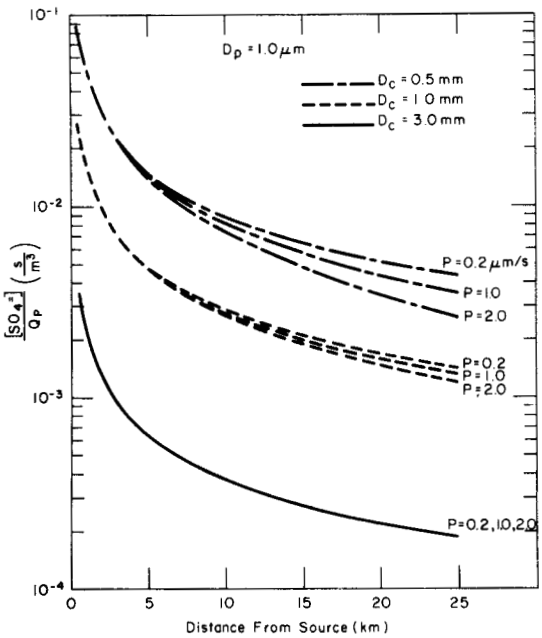

Figure 6. Rainwater sulfate concentration due to precipitation scavenging of 1.0 μm AED sulfate aerosol.

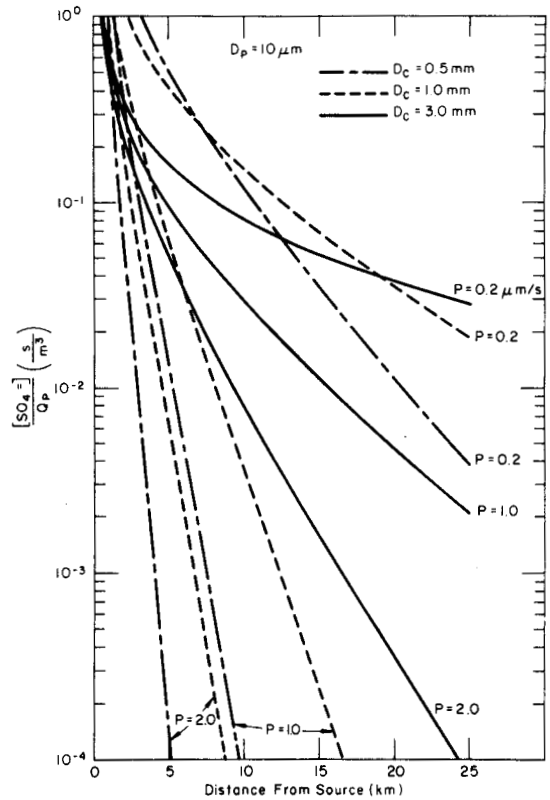

Figure 7. Rainwater sulfate concentration due to precipitation scavenging of 10. μm AED sulfate aerosol.

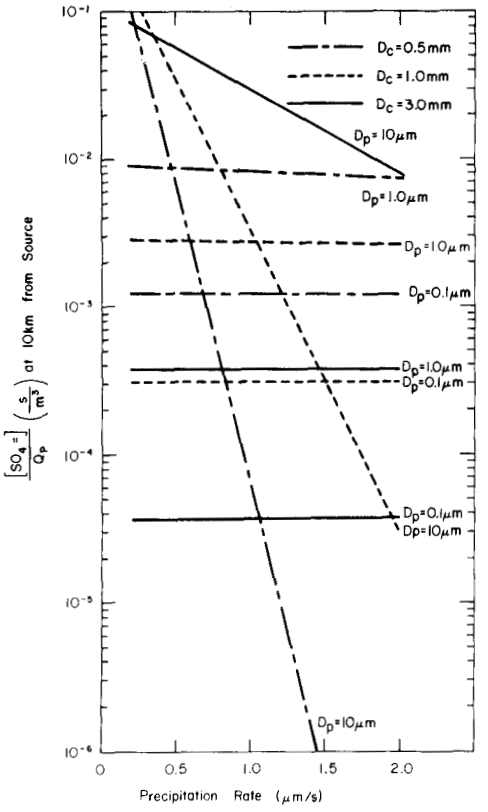

Figure 8. Rainwater sulfate concentration from scavenging of aerosols as a function of precipitation rate.

Effects similar to that observed for gaseous SO_2 absorption are noted. The magnitude of the effect of precipitation rate on the rainwater sulfate concentration is dependent on the raindrop and particle diameters. For the smallest particle size evaluated, the effect of precipitation rate is very slight. This dependence on precipitation rate becomes less as the raindrop size increases and as the particle size decreases. This is more clearly shown in Figure 8.

The dramatic decreases in the rainwater sulfate concentration at moderate distances from the source due to the scavenging of 10. μm aerosol particles is apparently due to the very efficient removal of these particles near the source. Particles of that size are so effectively removed near the source that only very low particle concentrations are present at further distances. Thus, the low numbers of these particles at the 10 to 15 km distance from the source can contribute little to the sulfate concentration. If prior plume washout is ignored, this predicted decrease is not nearly so substantial.

The effect of aerosol particle diameter on the sulfate concentration is more clearly shown in Figure 9 for D_c = 1.0 mm. This shows that

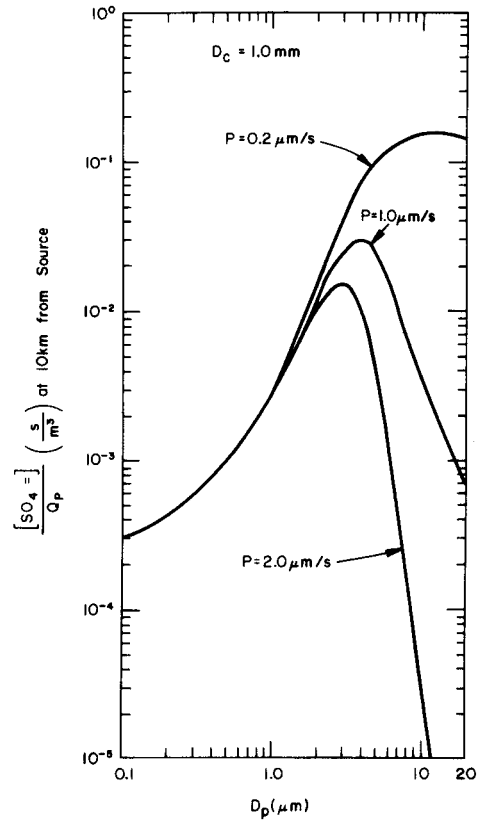

Figure 9. Dependence of rainwater sulfate concentration on aerosol size.

the contribution of particles to the rainwater sulfate concentration is maximum in the 3 μm to 10 μm range at moderate distance from the source. This contribution does not continue to increase with D_p as other workers have suggested. This is due to prior plume washout and the very efficient particulate removal near the source for these particle sizes. For equivalent rates of sulfate emission from the source, the contribution to the sulfate concentration at 10 km from the source by 1.0 μm aerosol particles can be two orders of magnitude less than that from 5 μm to 10 μm particles for low precipitation rates. Furthermore, the sulfate concentration is maximum for scavenging particles of 4 μm to 6 μm diameter at the high precipitation rates.

SUMMARY

Results of calculations are presented that show the effect of precipitation rate and raindrop size on sulfate washout from stack plumes. Both gaseous SO_2 absorption and scavenging of sulfate aerosols are considered. For equivalent mass emission rates both effects are important and neither can apparently be ignored, especially if the emitted sulfate containing particles are in the 3 μm to 10 μm range.

One must remember that these theoretical calculations are based on several idealizations and should recognize the limitations of the results. For example, aerosol coagulation, growth and formation processes in the plume have been neglected. Furthermore, ideal plume behavior and constant precipitation rates were used in the analysis. Nevertheless, the underlying physico-chemical treatment is sound, and the author feels that the model should provide reasonable guidelines for the refinement of such calculations. In addition, one should note that realistic confirmation of precipitation scavenging models is only possible when the physical parameters such as raindrop size distribution, particle size distribution, and precipitation rate are accurately known. Inaccuracies in these parameters of twenty to thirty percent and even higher are not unexpected in field evaluations, and these can result in order of magnitude errors in the rainwater sulfate concentration.

NOMENCLATURE

Latin Letters

A_y	coefficient in y-direction eddy diffusivity
A_z	coefficient in z-direction eddy diffusivity
c	concentration in the air
C_f	Cunningham correction factor
D_c	diameter of collector raindrop
$\bar{D}_a$	area mean diameter
$\bar{D}_l$	length mean diameter
$\bar{D}_{\sqrt{la}}$	root mean square of the length mean and area mean diameters
$\bar{D}_g^l$	number median diameter in logarithmic-normal distribution
D_p	diameter of particle
$\mathcal{D}$	molecular diffusivity of pollutant species in air
H	effective stack height

H'	height of rain forming layer
$\mathcal{H}$	Henry's law constant
k	first order homogeneous loss constant
k_g	gas phase mass transfer coefficient
k_r	first order reaction rate constant
K_g	overall mass transfer coefficient based on overall gas phase driving force
n	exponent in z-direction eddy diffusivity
N	number density of raindrops
q	exponent in y-direction eddy diffusivity
Q	strength of point source emissions
R	amount of pollutant species transferred from the air to the rain
Re_c	collector raindrop Reynolds number
Sc	Schmidt number
Sh	Sherwood number
St	Stokes number
U	wind velocity in the positive x-direction
U_t	relative velocity of the raindrops with respect to particles
x	downwind direction
y	crosswind direction
z	vertical direction

Greek Letters

β	correction factor defined by Equation (17)
γ	parameter in Marshall-Palmer distribution
μ	viscosity of the air
ρ	density of air
ρ_p	density of particle
σ_g	geometric standard deviation in logarithmic normal distribution

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