A Method for Modeling the Deposition of Sulfur by Precipitation over Regional Scales[1]

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ABSTRACT

Radioactive fallout data suggest that the concentration of pollutants in rainfall, while highly variable, might be described on the average by about an inverse half-power dependence on the amount of precipitation. Recent measurements of sulfur concentrations in summer rainfall collected at Argonne National Laboratory tend to support this contention, as do preliminary results derived from operations of the DOE precipitation chemistry network. The concept is extended to develop a bulk removal rate for airborne total sulfur by precipitation for use in regional dispersion modeling.

1. Introduction

Concern about acid rainfall has led to an increased research effort in a number of related disciplines. At the same time, the need to develop better simulations of air pollution episodes has led to advanced studies of precipitation scavenging as a sink for atmospheric contaminants. Each of the major programs investigating regional-scale air pollution problems in North America[2] recognizes the importance of precipitation scavenging as a major sink for atmospheric sulfur; other sinks include dry deposition and transport out of the region of interest. Several precipitation-sampling networks have been set up in recognition of the need for more comprehensive data on the deposition of pollutants in rain and snow, but simple methods for the estimation of wet removal rates are required immediately for use in existing numerical simulations.

The need to develop computationally efficient numerical schemes in order to conduct sensitivity tests that are of practical relevance and the limitations in scale resolution of available meteorological data result in the requirement that formulations describing both dry and wet deposition processes should be relatively straightforward. For the case of dry deposition, the concept of a deposition velocity has gained considerable favor among modelers, although the simple expedient of assuming a surface flux proportional to the pollutant concentration in air at some conveniently low level is an oversimplification. For wet deposition there is considerable support for the "scavenging ratio" approach. This has had a large amount of exposure in recent years, mainly as a consequence of studies of the wet deposition of trace metals. In essence, scavenging ratios express the relationship between concentrations of material detected in precipitation and those measured in air at the same time. An alternative procedure is to employ some experimentally determined scavenging rate, usually expressed as a percentage removed per unit of rainfall (or of time) in an exponential decay scheme.

A recent reanalysis of natural radioactivity concentrations measured in rain collected during several storms at Argonne National Laboratory (ANL) indicated relatively constant values of the scavenging rate, which was assumed to be that appropriate for natural, background aerosol particles (see Hicks, 1978). However, published scavenging rates vary widely. Part of the apparent scatter can be associated with differences in terminology; some of the reported values apply only to the collection of aerosol by falling raindrops (mainly via impaction), whereas other evaluations represent the sum of this and in-cloud processes such as nucleation. The data presented earlier (in Hicks, 1978) suggest, therefore, that subcloud and in-cloud scavenging mechanisms combine to produce a relatively constant rate of removal. However, it is well known that the concentration of contaminants in light rains is much

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[2] Such as the Long Range Transport of Air Pollution study of the Atmospheric Environment Service of Canada, the Sulfur Transformation and Transport Experiment of the U.S. Environmental Protection Agency (EPA), the Sulfur Regional Experiment of the Electric Power Research Institute, and the Multistate Atmospheric Power Production Pollution Study (MAP3S) of the U.S. Department of Energy (DOE) and the EPA. The present work was performed under the auspices of MAP3S.

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TABLE 1. Some relationships between the amount of material (M) deposited in a rainfall of amount h (liters); a, b and c are constants.

$M = a[1 - \exp(-bh)]$	Damon and Kuroda (1954)
$M = ah - bh^2$	Szalay and Bere'nyi (1958)
$M = a[1 + bh - \exp(-ch)]$	Miyake *et al.* (1960)
$M = a(1 + bh^{1.2} - ch^{2.4})$	Moeken and Alderhout (1963)

greater than in more extensive rainfalls and for this reason a number of relationships describing the dependence of the effective average washout ratio on the amount of rainfall have been developed. Table 1 gives some examples of equations of this kind; these result from studies of radioactive fallout in rain. All of the tabulated formulations yield a net scavenging ratio which decreases with increasing rainfall amount but, unfortunately, there is little agreement otherwise. Some of the relationships are derived from data collected on an event basis, others apply to long-term averages. In order to incorporate wet removal in regional-scale numerical models it is necessary to develop a parameterization procedure similar to those tabulated, but applicable to the short-term precipitation data reported by the National Weather Service and suitable for use in simulations of atmospheric sulfur pollution. It is the present aim to address this need, starting with a review of some relevant results derived in studies of radioactive fallout and ending with a comparison with some recent measurements of sulfate in rainfall collected at ANL and with results generated by the DOE network of precipitation chemistry stations set up as part of the MAP3S program [as reported in summary form in Battelle Pacific Northwest Laboratories, PNL-2402 (1977); a description of the network is given by MacCracken (1978)].

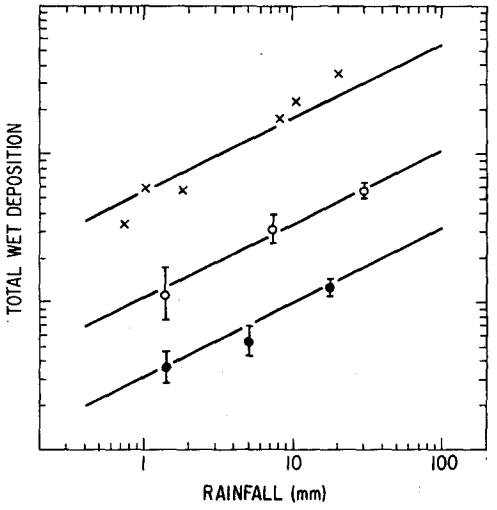

FIG. 1. The dependence of wet deposition on rainfall amount, using weekly averaged radioactivity data obtained in Australia, during 1960 and 1961 (solid circles), per-event data obtained in Oklahoma during 1964 [open circles; see Hall (1965)], and per-event sulfate measurements made at Argonne during 1975 (crosses).

2. Total beta-emitter concentrations

There is a paucity of experimental data suitable for investigating the relationship between the wet deposition of atmospheric sulfur and sulfur concentrations in the air. A number of studies have been initiated, however, and later some preliminary data obtained in two of them will be considered. First, we consider some results derived from studies of radioactive fallout, since it is known that airborne radioactivity is associated with the same "accumulation size range" particles that carry most of the atmosphere's particulate sulfur. The wet removal characteristics of fallout material can thus be considered to be indicative of those of sulfate particles, but care should be taken in extending the analogy to the case of total sulfur, since in practice sulfur in precipitation might also be derived from gaseous precursors through some in-cloud oxidation process.

The period of intensive testing of nuclear weapons during the 1950's provided an opportunity for thorough study of the physical processes associated with the wet removal of atmospheric radioactivity. However, investigations of the factors that control the concentrations in precipitation were hampered by the repeated injection of new material. In the Northern Hemisphere, the frequent testing of weapons made interpretation of radioactive fallout observations exceedingly difficult, and even in the Southern Hemisphere considerable difficulty was encountered. Accordingly, the declaration of a weapons testing moratorium in the early 1960's resulted in a spate of studies intended to capitalize on the existence of large quantities of trace material held in a stratospheric reservoir. In Fig. 1, solid circles illustrate the results obtained from an investigation of beta emitters deposited in weekly rainfall at Aspendale, Victoria, Australia, between September 1961 and May 1962. For the present purpose, these moratorium data have been combined into groups and plotted as means and standard errors. Only material deposited in rain is considered. The data suggest a net dependence on about the half-power of the weekly rainfall amount, as indicated by the line drawn by eye through the data points. In terms of concentration, a net inverse half-power relationship follows as a direct consequence. Data suitable for testing the behavior deduced from the Australian observations are rare. We may, however, consider the results published by Hall (1965) who reports on a study of radioactivity concentrations in three extensive squall-

TABLE 2. Event sulfate data from the MAP3S precipitation chemistry network during 1977. Days are selected on which three or more stations reported rainfall. Occasions for which there are apparent discrepancies between the amounts of rain reported by standard raingauges and by the rain chemistry collectors are excluded. Sulfate quantities A are in μg; rainfall amounts h are in liters. Data normalized with respect to geometric means calculated for each occasion are shown in parentheses.

Date (1977)	Whiteface Mountain		Ithaca, NY		Pennsylvania State University		University of Virginia	
	h	A	h	A	h	A	h	A
25 February	1.06 (1.30)	885 (0.94)	—	—	0.89 (1.15)	1540 (1.63)	0.49 (0.63)	618 (0.65)
5 March	0.64 (0.83)	613 (0.36)	—	—	1.52 (1.95)	2480 (1.45)	0.48 (0.62)	3270 (1.92)
21 March	0.13 (0.30)	175 (0.24)	1.40 (3.27)	2550 (3.55)	0.43 (1.01)	833 (1.16)	—	—
29 March	0.44 (3.5)	344 (0.81)	—	—	0.66 (3.67)	1390 (3.28)	0.02 (0.11)	159 (0.38)
10 June	0.09 (0.42)	346 (0.51)	—	—	0.72 (3.37)	1250 (1.83)	0.15 (0.70)	744 (1.09)
22 August	0.54 (1.58)	1560 (1.02)	0.62 (1.81)	2080 (1.35)	0.12 (0.35)	1120 (0.73)	—	—
24 August	0.73 (1.15)	766 (0.41)	0.01 (1.59)	5330 (2.84)	—	—	0.35 (0.55)	1620 (0.86)
1 December	0.47 (0.61)	388 (0.34)	0.78 (1.01)	1120 (1.11)	1.27 (1.64)	2690 (2.68)	—	—

line storms in Oklahoma in 1964. A network of rain samplers provided about 10 separate samples from each occurrence. The resulting data have also been grouped and plotted in Fig. 1. There appears to be excellent support for extending the half-power relationship from weekly averages to events.

Pelletier *et al.* (1965) present results of reanalyses of published data, originally obtained in Norway and Russia, which tend to support the present findings (see their Fig. 4). However, a slightly greater value of the power-law exponent is required to explain data obtained in England. Pelletier *et al.* are mainly concerned with monthly averages, and so it is not clear that the relationships derived in their investigations directly address the questions being asked here. Nevertheless, it is of interest to note that they find considerable support for an exponential behavior essentially the same as that of Damon and Kuroda (1954, see Table 1), which is then found to provide a good description of monthly fallout deposition measured in the vicinity of Lake Erie.

3. Sulfate concentrations in rainfall

A set of sulfate concentration measurements in individual precipitation events at ANL during 1975 provides an opportunity to test the power-law relationship with data directly applicable to the main subject of interest here. Data collected during a three-week period from 18 October to 10 November are plotted in Fig. 1. A value obtained later (20 November) does not fit the overall picture and seems to be representative of an entirely different situation, but the six plotted sulfate determinations appear to confirm the beta-activity results reasonably well. More data would be required before it could be concluded that the best-fitting power-law relationship is different from that deduced from the beta-activity data.

Results obtained by the DOE network of precipitation sampling stations offer another opportunity to test the applicability of a half-power approximation. A recent Battelle Pacific Northwest Laboratory report (PNL-2402, July 1977) presents results of chemical analyses performed on aliquots of samples collected at sampling sites in central Virginia (University of Virginia), central Pennsylvania (Pennsylvania State University), and two locations in New York (State University of New York at Whiteface Mountain, and Cornell University at Ithaca). To minimize the influence of large-scale changes in air concentration, data have been used only when simultaneous daily precipitation was reported by at least three of the four sampling stations. Occasions in which the measured sample volume disagreed (by 25% or more) with the prediction based on conventional raingage records have been omitted. The remaining acceptable data are listed in Table 2. These data have been normalized according to geometric means calculated for every event, and combined into groups for presentation in Fig. 2. On the whole, the network sulfate data

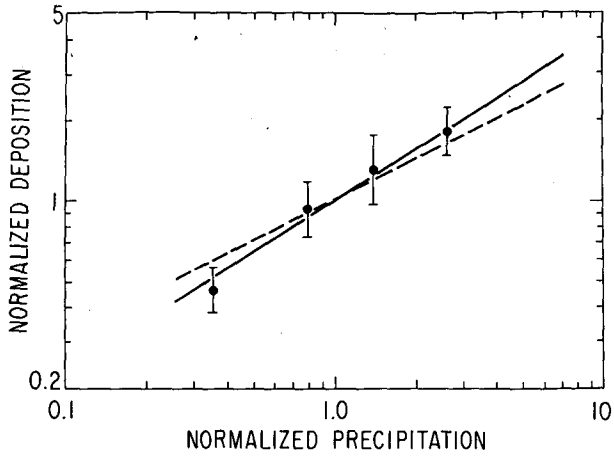

FIG. 2. The dependence of the normalized deposition of sulfate in daily precipitation on the normalized rainfall quantity in the northeastern United States. Data were derived from the DOE network of stations at Charlotte, Virginia; State College, Pennsylvania; Albany, New York; and Whiteface Mountain, New York. The solid best-fitting line is not statistically different from the half-power law relationship (dashed) anticipated on the basis of radioactivity data.

appear to support the half-power relationship; the best fitting line determined by regression has an exponent (0.61 ± 0.13) that is not significantly different from the expected square-root relationship.

4. A procedure for use in simulations

Table 3 lists data obtained during a study of rainout of radioactivity, conducted at ANL in 1966 (Hicks, 1978). Values of the scavenging ratio and the ratio of concentration in rain (C_r) to that in air (C_a), are tabulated, as well as estimates of the modified scavenging ratio ξ corrected for the amount of rainfall h (liters), i.e.,

$$\xi = C_r h^{1/2}/C_a, \tag{1}$$

as suggested by the previous discussion (after allowing for the obvious equality between total deposition and the product $C_r h$). For these calculations measurements of C_a made near the surface have been employed. Two different fission products have been selected for use here; each is easily identified and measured through the detection of distinctive gamma emissions.

The values listed in Table 3 indicate that for this particular data set there is relatively little statistical benefit to be derived from the use of the present half-power-law relationship instead of the more conventional method. However, the value of the constant ξ seems to be determined to $\pm 30\%$ accuracy; in mass units, the value of the constant is about 2000 $mm^{1/2}$. On the other hand the conventional scavenging ratio is ~900, which is much the same as would be expected for the case of sulfate rainout [Garland (1978) presents values ranging from ~500–1500, after a single value of 24 000 is omitted; these evaluations are attributed to Cawse (1974)]. Thus the anticipation that radioactivity rainout data will be indicative of sulfate rainout does indeed appear to be verified.

5. Application in numerical models

Although perhaps outwardly attractive to modelers who wish to include some simple parameterization of precipitation scavenging in numerical simulations, the present half-power relationships should be employed only after a considerable amount of thought has been given to the nature of the problem itself.

Precipitation, particularly rain in summer convection, may have spatial and temporal scales of a few kilometers and 20–30 min, while the minimum resolutions in a numerical model of regional air pollution dispersion and associated objectively analyzed precipitation fields may be 50–100 km and 1–6 h. Formulas and coefficients developed from measurements in individual rain events may require considerable modification and calibration for use in regional dispersion models.

In some long-term regional dispersion models (e.g., Sheih, 1977; Shannon, 1979a) concentrations of sulfur dioxide and sulfate at a given time and location are not estimable. However, the airborne mass of total sulfur represented by a puff coincident with precipitation is known. It is computationally convenient to deposit a portion of the sulfur mass as a function of the amount of precipitation reported. We can express (1) as

$$\xi = \frac{M_{sr}}{M_r}\frac{M_a}{M_{sa}} h^{1/2}, \tag{2}$$

where M_a and M_r are masses of air and rain, respectively, and M_{sa} and M_{sr} are the masses of

TABLE 3. Scavenging ratios (dimensionless) and values of the "constant" ξ ($mm^{1/2}$) derived from measurements of Ce-141 and Zr-95 concentrations in air and rain at Argonne during 1966.

Date	h (mm)	Scavenging ratios		ξ	
		Ce-141	Zr-95	Ce-141	Zr-95
20 May	2.0	13000	3600	18000	5100
13 June	1.5	2300	2300	2800	2800
5 July	3.1	240	600	420	1100
11 July	5.9	2800	1200	6800	2900
13 July	4.6	600	840	1300	1800
18 July	0.8	360	2800	320	2500
26 July	97.3	480	480	4700	4700
1 August	6.3	240	120	600	301
10 August	13.6	720	360	2700	1300
Geometric mean	4.9	890	870	1970	1930
Standard error		56%	44%	57%	34%
Combined geometric mean		880		1950	
Combined standard error		32%		30%	

sulfur in each. In dispersion models M_a is usually taken to be a constant determined by the depth of the modeled atmosphere. If we are considering a unit area, M_r is directly proportional to rainfall h. Thus, we can express R, the ratio of the mass of sulfur deposited to that originally airborne, as

$$R = \frac{M_{sr}}{M_{sa}} = \xi \frac{M_r}{M_a} h^{-1/2} \approx Ch^{1/2}, \quad (3)$$

where C is a proportionality constant. There is no general agreement about how much of the sulfur burden would be deposited by a given rainfall, but a removal rate R, where

$$R = \begin{cases} (J/4)^{1/2}, & J \leq 4, \quad (4a) \\ 1 & J > 4, \quad (4b) \end{cases}$$

and J is expressed in millimeters per hour, has given reasonable results in simulations in which temporal resolution of precipitation is hourly and the depth of the modeled atmosphere is 2000 m (Shannon, 1979b).

6. Transfer to the free troposphere

A further complication arises from the recognition that convective storms constitute a means for distributing pollutants throughout the troposphere. Byers and Braham (1948) present an eloquent description of the growth and decay of a typical thunderstorm, supported by evidence that demonstrates the low-level convergence feeding the convective updraft in the early stages of cell development. During the entire life cycle, a convective cloud represents a path for interchange between the mixed layer below its base and the free troposphere above. However, rain falls to the surface for only a portion of the cloud life cycle. Thus, the usual simplification of considering dry and wet deposition of pollutants to the surface underneath as the only pollutant removal mechanisms might be quite erroneous, since whenever precipitation is reported we must expect leakage from the mixed layer to the atmosphere aloft. Even in the presence of nonprecipitating clouds, transfer through the top of the mixed layer might well take place when suitable cloud development occurs. It is not known whether this loss of material from the mixed layer constitutes a major error in existing simulations. As a first estimate, we might suspect from consideration of the updraft velocities reported for typical convective cells and from the relatively short periods for which rain actually falls that the deep convective mechanism sometimes constitutes as great a "sink" for mixed-layer pollution as does wet deposition itself. It also seems likely that the mechanism will not be unique to the convective case considered above, but might also be important when frontal and orographic mechanisms dominate.

From the point of view of regional-scale numerical simulations, which usually consider only the lowest few kilometers of the atmosphere, material injected into the free troposphere will be lost. In reality, this material will enter into new, longer term circulation patterns that will be characterized by residence times substantially longer than the few days normally thought of for sulfur in the mixed layer. (At ~40° latitude, the residence time of radioactive fallout in the troposphere is known to be ~10 days.) The pollutants will be transported for relatively great distances in stratified flow. As in the case of radioactive fallout, the major removal mechanism will then be scavenging by clouds and deposition in precipitation, although dry deposition could be a factor if mesoscale or regional-scale subsidence causes the layers containing the pollutants to descend to the mixed layer. However, at this time the mechanisms and rates involved are not sufficiently well known to permit them to be realistically incorporated in numerical simulations.

7. Discussion and conclusions

The estimation of sulfur deposition by wet processes as a function of the half-power of the amount of precipitation, while computationally efficient and able to utilize routinely available meteorological data, is intended as an interim measure, primarily for long-term simulations of atmospheric sulfur pollutants. It is fully expected that better relationships, particularly for episodic simulations, will be developed as more precipitation chemistry data become available. However, it seems evident that use of a constant scavenging ratio can be misleading, since the average concentration in collected precipitation will decrease with increasing rainfall amount, and will follow an approximate negative half-power relationship.

Scott (1978) has reported on models of the washout ratio for sulfate which indicate that the relationship between the washout ratio and rainfall quantity might be strongly dependent upon the type of storm. The curves plotted in his Fig. 2 predict that the amount of material deposited will be almost independent of the quantity of precipitation for intense convective storms ($R \approx h^{0.07}$), but will be strongly influenced in cases in which the Bergeron process (of ice growth in the cloud) is applicable ($R \approx h^{0.75}$). For the case of synoptic-scale warm rain, the power law exponent (for sulfate) derived from his Fig. 2 ranges from about 0.15 to 0.7. On the basis of these results, MacCracken (1979) recommends that a power law exponent of ~0.6 be employed as an average value.

The individual experiments reported here draw considerable scatter in the value of the exponent. The Southern Hemisphere fallout data indicate a value of 0.5, as do the data of Hall (1965). How-

ever the Argonne sulfate data would be better fitted by a value of ~0.57 and the MAP3S precipitation chemistry results indicate ~0.64. Thus it could be argued that a value of ~0.6 might indeed be better for purposes of sulfate scavenging parameterization, since it is possible that the fallout results might not be completely appropriate in this regard. However, at this time there seems insufficient evidence to choose one value rather than the other. From the viewpoint of the numerical simulations that are the main subject of interest here, the question is a nicety with relatively little practical impact.

The half-power formulation for sulfur deposition should be applied with considerable caution, since the data on which it is based are very limited. For example, only midlatitude convective rainfall is considered. In addition, the spatial and temporal resolution of meteorological and air quality data used or estimated by a particular model can strongly affect resulting simulations. Clearly, the results of contemporary precipitation sampling networks will eventually provide the crucial test of this and other models of precipitation scavenging.

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