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PRECIPITATION CHEMISTRY: ITS BEHAVIOR AND ITS CALCULATION

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Jeremy M. Hales

1. INTRODUCTION

As our understanding of the atmospheric sciences has evolved it has been marked increasingly by the compelling need to develop generalized and simple, yet reliable methods for assessing the impacts of man-made change. Development of such procedures has always been characterized by a trade-off between simplicity on the one hand and reliability on the other; and although limited accuracy and overextended application have continued to pose problems, some rather remarkable successes have been achieved. One has only to consider the extended application of the Gaussian plume model, as presented in Turner's Workbook of Dispersion Estimates (Turner (1970)), to illustrate this point.

Similar successes in the field of precipitation chemistry have been comparatively limited, owing to the complexity of the scavenging process. Some notably elegant inroads have been established (eg., Chamberlain (1953)), but these have focused on limited *subsets* of the overall scavenging problem, and cannot be extended for generalized, reliable usage. In aggregate, however, these assorted techniques compose a useful means of attacking the extended scavenging problem; and while it is probably unreasonable to ever expect a straight-forward "Turner's Workbook" type of document to emerge for

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scavenging calculations, one can at least look to a composite set of techniques which is generally useful on an applied basis.

The purposes of this paper are twofold. The first of these is to present a rational basis for examining this aggregate set of scavenging-calculation techniques, and for guiding the reader in his course toward choosing the most appropriate technique for his particular application. The second purpose of this paper is to present a somewhat brief survey of our current understanding of scavenging and precipitation chemistry. Both objectives will be implemented by a flowchart approach, which attempts to draw the various facets of scavenging calculations together and present a generalized approach to the problem in total.

The mathematical level of this paper is restricted to the presentation of the equations necessary to provide the reader with a basic appreciation of the fundamental concepts involved. References to more detailed mathematical treatments* are cited at appropriate juncture points, for the reader interested in more detailed pursuit. Within this format it is hoped that the present article will find extensive usage as a first reference, and will allow the user to scope his particular problem in a valid manner, which will direct him rapidly to the most expedient solution technique.

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*The chapter by Slinn (1980) in the DOE Publication Meteorology and Power Production is recommended as a key reference in this regard.

2. MATERIAL BALANCES: SOURCES OF SPATIAL AND TEMPORAL VARIABILITY

Since the preponderance of scavenging calculations is based on one sort of material balance or the other, it is appropriate at this point to examine briefly some qualitative aspects of the general material balance of pollution in the atmosphere. This is shown schematically in Figure 1, which depicts a given pollutant as it is emitted from a source, and ultimately delivered to a receptor, via the atmosphere. Important points to note from this diagram are the competing effects of wet and dry deposition, and the potential for reversible cycling of pollutants through various combinations of steps before ultimate delivery to the surface. It should be noted also that material balances can be formulated around various individual steps, substeps, and combinations of steps in Figure 1; and in assessing a particular type of scavenging calculation it is important to ascertain just what portion of this scheme has been covered.

Mathematical characterization of the processes in Figure 1 can be accomplished by defining some chosen volume of atmosphere, and then formally summing the effects of all of these processes over this space. Depending on the volume element chosen for this summation, the resulting characterization can be either integral or differential in form. Differential material balances are normally based on small volume increments and yield differential equations, which must be integrated subsequently to produce the desired computations of concentrations and removal rates. Integral balances typically are performed over much larger regions, and result either in integral equations or else algebraic forms derived from some sort of implied integration processes. Quite often material balances are mixed in nature,

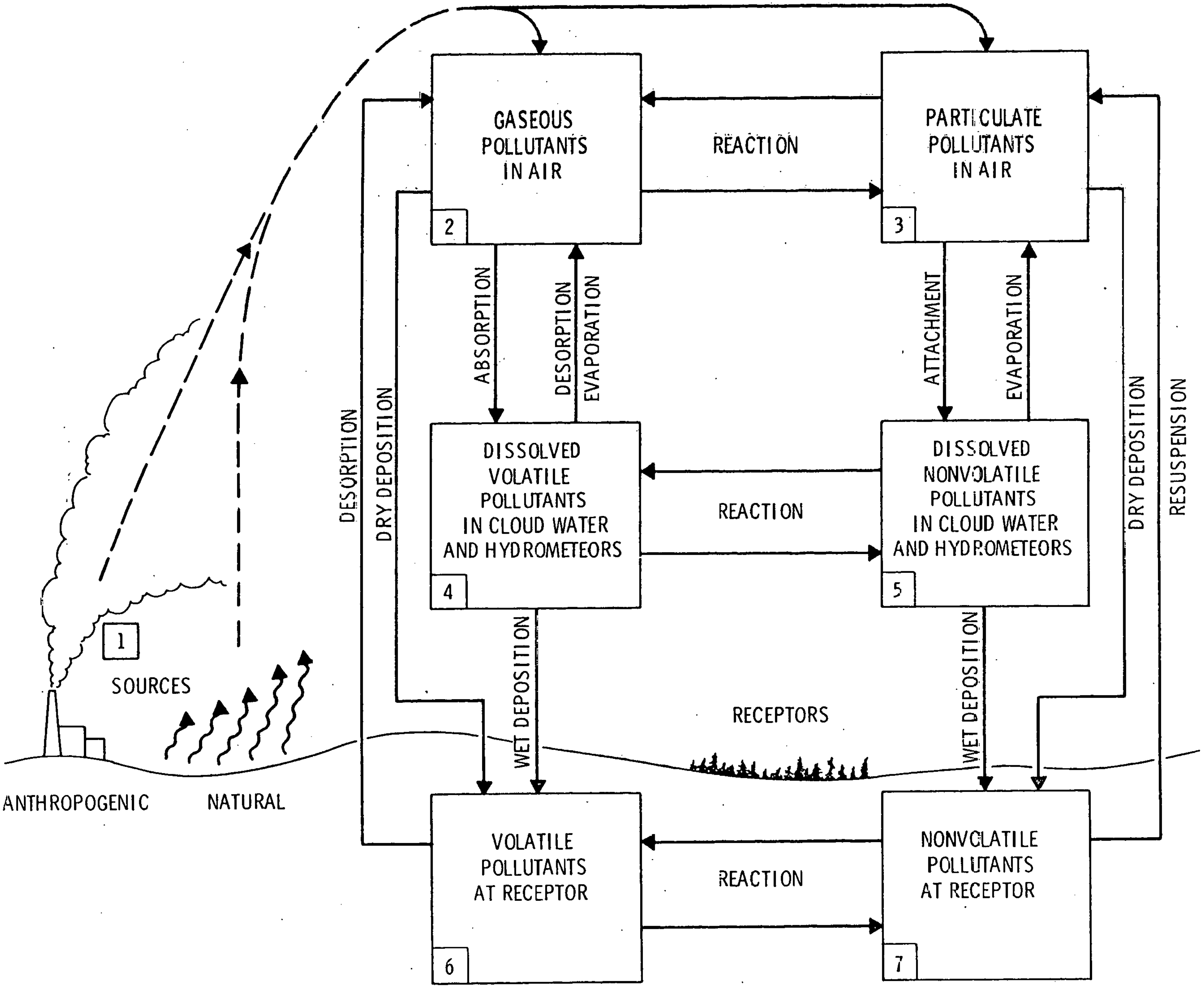

FIGURE 1 - Schematic Description of Material Balance for Pollution in the Atmosphere

and yield correspondingly mixed mathematical forms.

Examples of integral approaches are simple box models and storm-scale material balances. One particularly important result of the differential material balance can be expressed by the forms*

$$\frac{\partial c_{Ay}}{\partial t} = -\nabla \cdot c_{Ay}\tilde{v}_{Ay} - w_A + r_{Ay} \quad \text{(gaseous phase)} \qquad (1)$$

and

$$\frac{\partial c_{Ax}}{\partial t} = -\nabla \cdot c_{Ax}\tilde{v}_{Ax} + w_A + r_{Ax} \quad \text{(aqueous phase)} \qquad (2)$$

which describe the net input of some arbitrary pollutant A over a small volume increment of the atmosphere, as it is interchanged between the precipitation and the gaseous-phase medium (denoted here respectively by the subscripts x and y). In Equations 1 and 2 the rates of change in the concentrations of gaseous-phase and aqueous-phase pollutant are expressed in terms of

- transport across the boundaries of the element (divergence terms),
- transport between gaseous and aqueous phases within the element (w_A), and
- aqueous-phase and gaseous-phase chemical reaction within the element (r_{Ax} and r_{Ay}).

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*See Bird, et al. (1960), Hales (1972) or Slinn (1980) for a more detailed discussion.

$\tilde{v}_{Ax}$ and $\tilde{v}_{Ay}$ denote velocity vectors for pollutant A in the aqueous and gaseous phases, respectively. Many of the computational approaches to be discussed in this paper are based on various simplified forms of Equations 1 and 2.

From Figure 1 and the above equations one can identify several sources of variability, which may be expected to induce spatial and temporal differences in the chemical composition of precipitation:

- variability associated with source fluctuation and configuration,
- variability associated with normal atmospheric transport and mixing processes,
- variability induced by storm dynamics,
- variability caused by atmospheric transformation processes prior to the precipitation event,
- variability associated with microphysical cloud processes; physical attachment and aqueous-phase transformation, and
- variability caused by pollutant depletion via wet- and dry-removal processes.

These features are difficult to isolate , and their relative effects will vary, depending on the averaging times associated with the precipitation-chemistry measurements at hand. In performing and assessing scavenging calculations, however, it is important that one keep these factors in mind, and attempt to define the spatial and temporal averaging times appropriate to his own particular requirements.

So little is known presently with regard to spatial and temporal variability in precipitation chemistry that it is difficult to draw any really meaningful or helpful conclusions regarding its behavior. Some limited insight can be obtained, however, by considering some typical case examples. Figure 2, for instance, shows the results of a <u>sequential</u> sampling of rain from a particular precipitation event measured at the Brookhaven National Laboratory (Raynor (1978)). This is a relatively remote site located on upper Long Island; and while it reflects the presence of the east-coast megalopolis, it is considered to be a reasonably-valid representation of <u>regional</u> precipitation chemistry. Key features to note from this figure are the pronounced variability of concentration during storm passage, and the obvious continua of the time-concentration curves.

Figure 3* is a typical result of averaging precipitation-borne pollutant concentrations over entire precipitation periods, and plotting several events in sequence. Here discrete plotting is necessary, owing to the episodic nature of precipitation. The fact that large fluctuations exist in spite of the longer averaging times should not be surprising, in view of the introduction of additional sources of variability from the candidates itemized above.

Figure 4 pertains to an expanded data set that originated from this same sampling site, but now has been averaged over one-month

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*Data from MAP3S sampling site at State College, Pennsylvania (MAP3S (1980)).

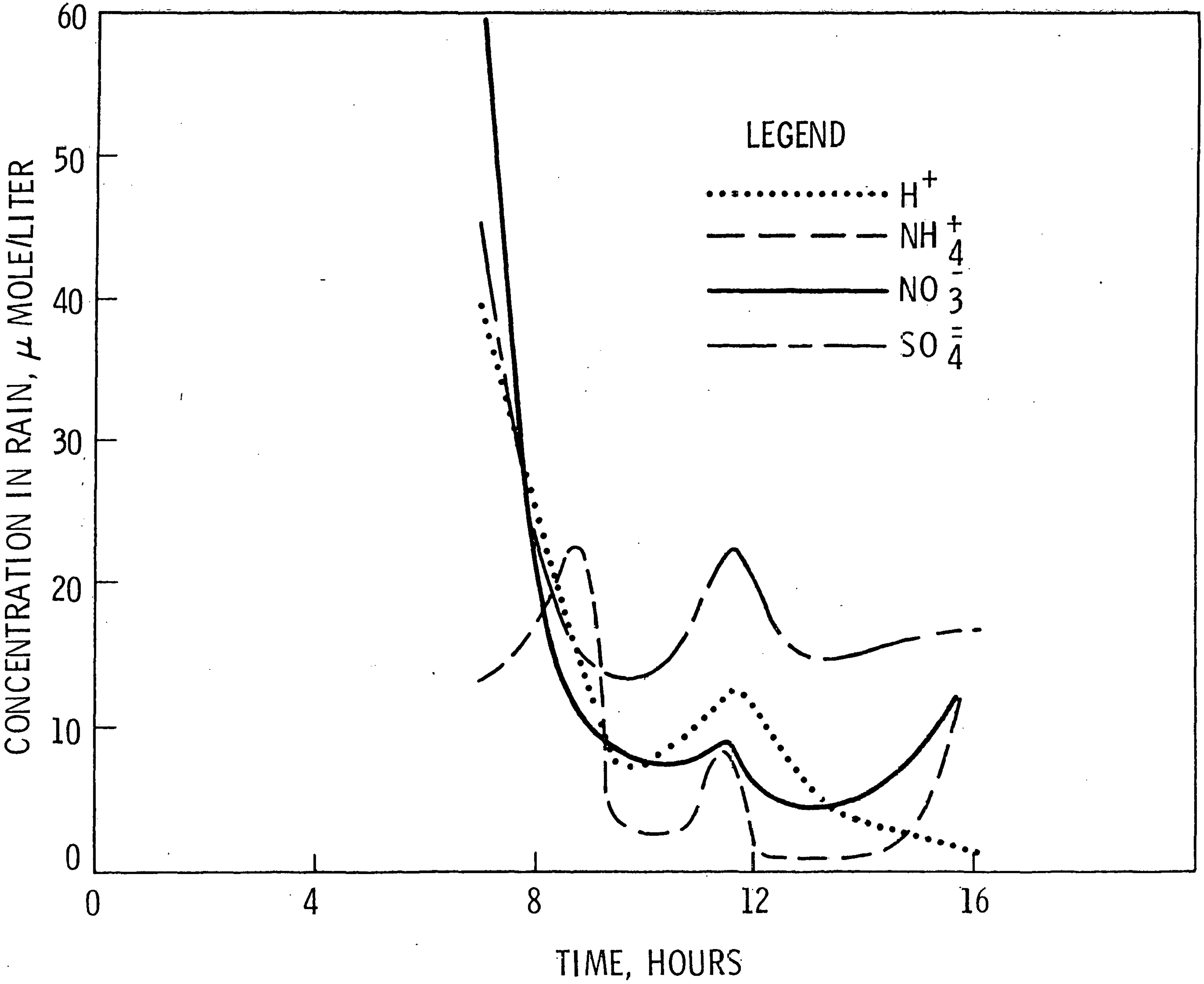

FIGURE 2 - Concentrations of Selected Chemical Species in Rain During A Rain Event at the Brookhaven MAP3S Site.

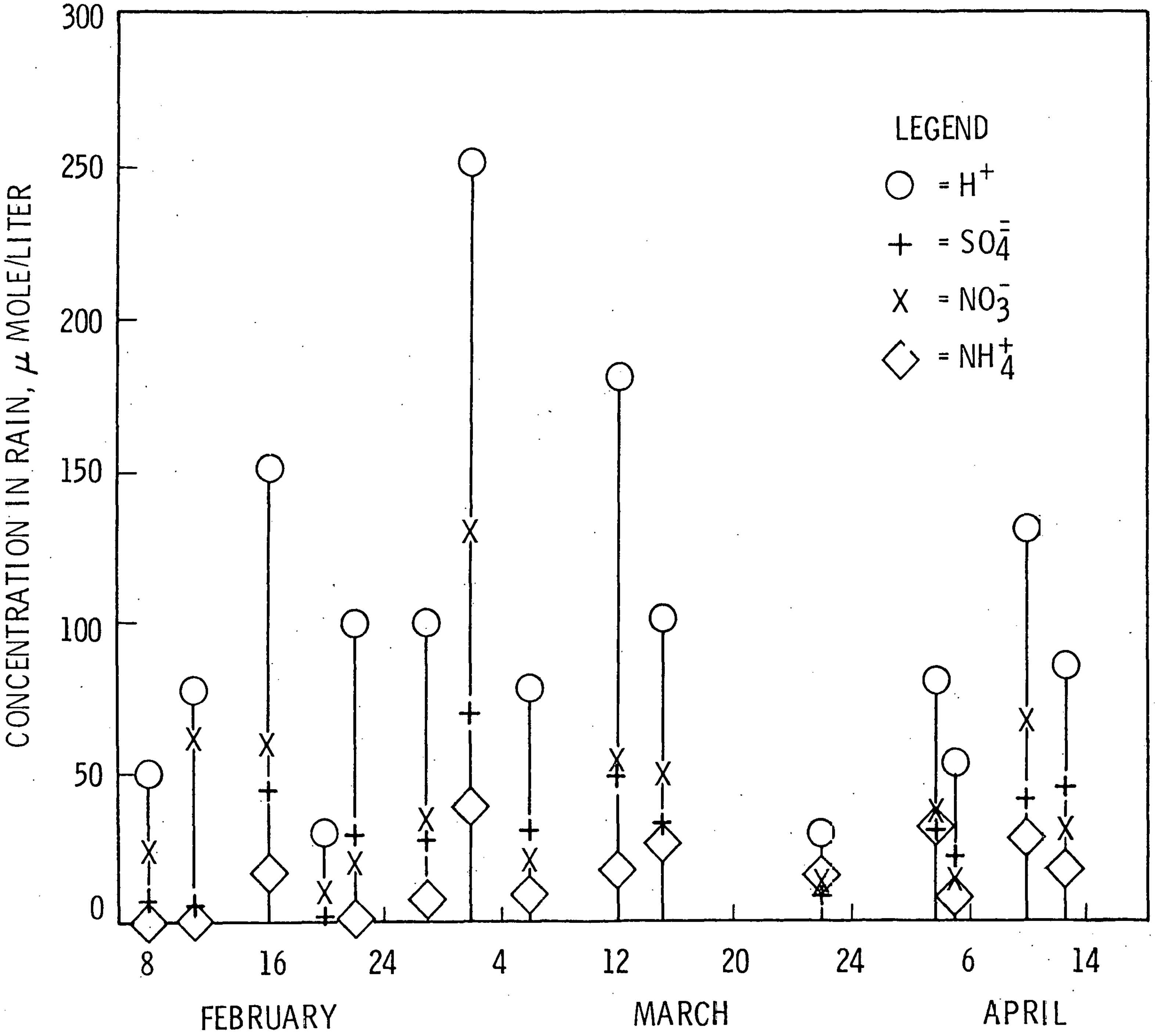

FIGURE 3 - Concentrations of Selected Chemical Species in Precipitation for Several Precipitation Events. Event-Averaged Concentrations from Penn State MAP3S Site.

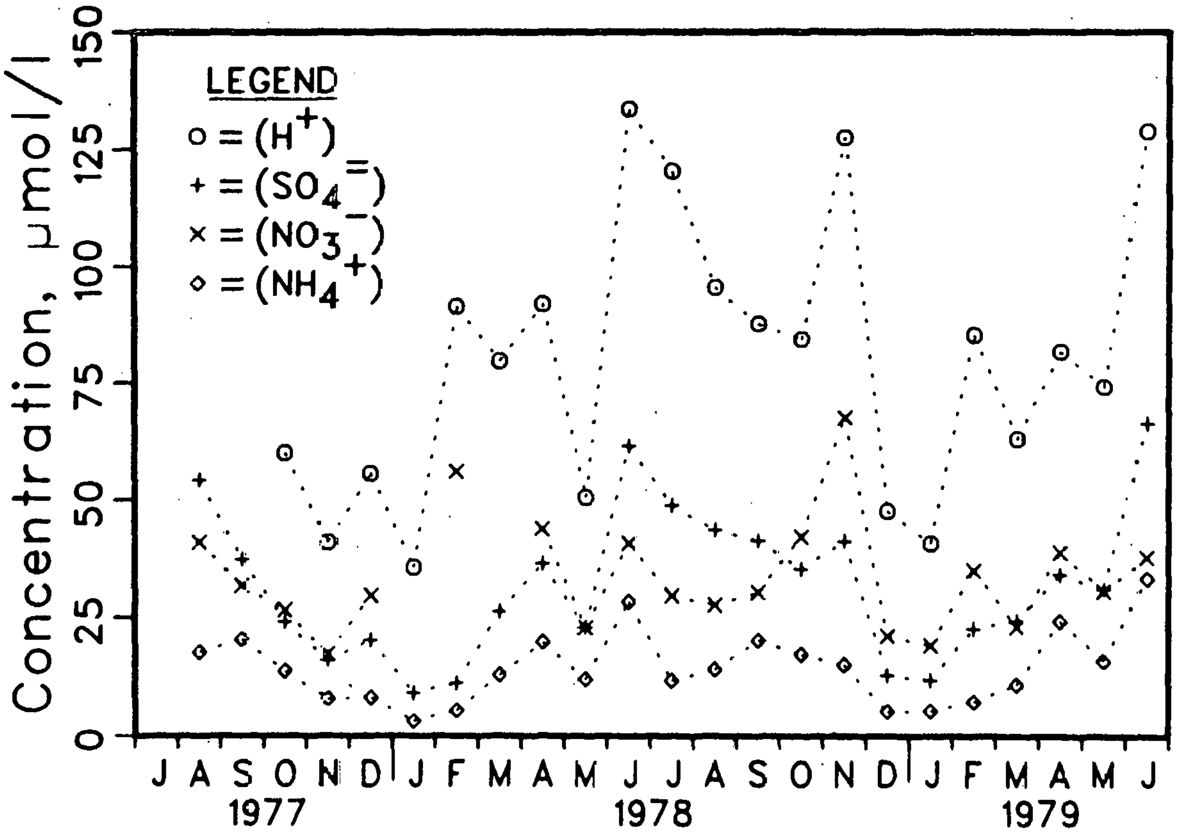

FIGURE 4 - Concentrations of Selected Chemical Species in Precipitation. Monthly-Averaged Concentrations from Penn State MAP3S Site.

periods.* At this point the averaging process appears to have smoothed the concentration excursions somewhat, and suggests a seasonal cycling of species such as $SO_2^=$, H^+ and NH_3^+. This apparent smoothing should be observed with some caution, however, in view of pronounced excursions typically observed from longer data sets. This is illustrated by some of the long-term European Air Chemistry Network data, as presented in Figure 5. From this it can be recognized that one must exercise appropriate caution in interpreting limited data sets such as given in Figure 4, *especially* for trend analysis.

In addressing *spatial* variability, it should be noted that point-to-point differences in rainborne pollutant concentrations will be strongly related to *temporal* variability in most cases. Although spatial variability has been considered carefully by Granat and his co-workers in siting studies (Granat (1978)), and several statistical interpretations of variability over regional networks have been presented (eg., Pack and Pack (1979), Munn and Rodhe (1971)), this whole question remains at a highly unresolved state. Figure 6, which is a concentration and rainfall map for a convective event in the vicinity of St. Louis, Missouri, indicates the type of complexity that can be observed in spatial structure.

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*Computed as $$\frac{\sum_1^N Ce\ Re}{\sum_1^N Re},$$
where Ce and Re are the concentrations and rainfall amounts associated with a particular event, and N is the number of events occurring during a particular month.

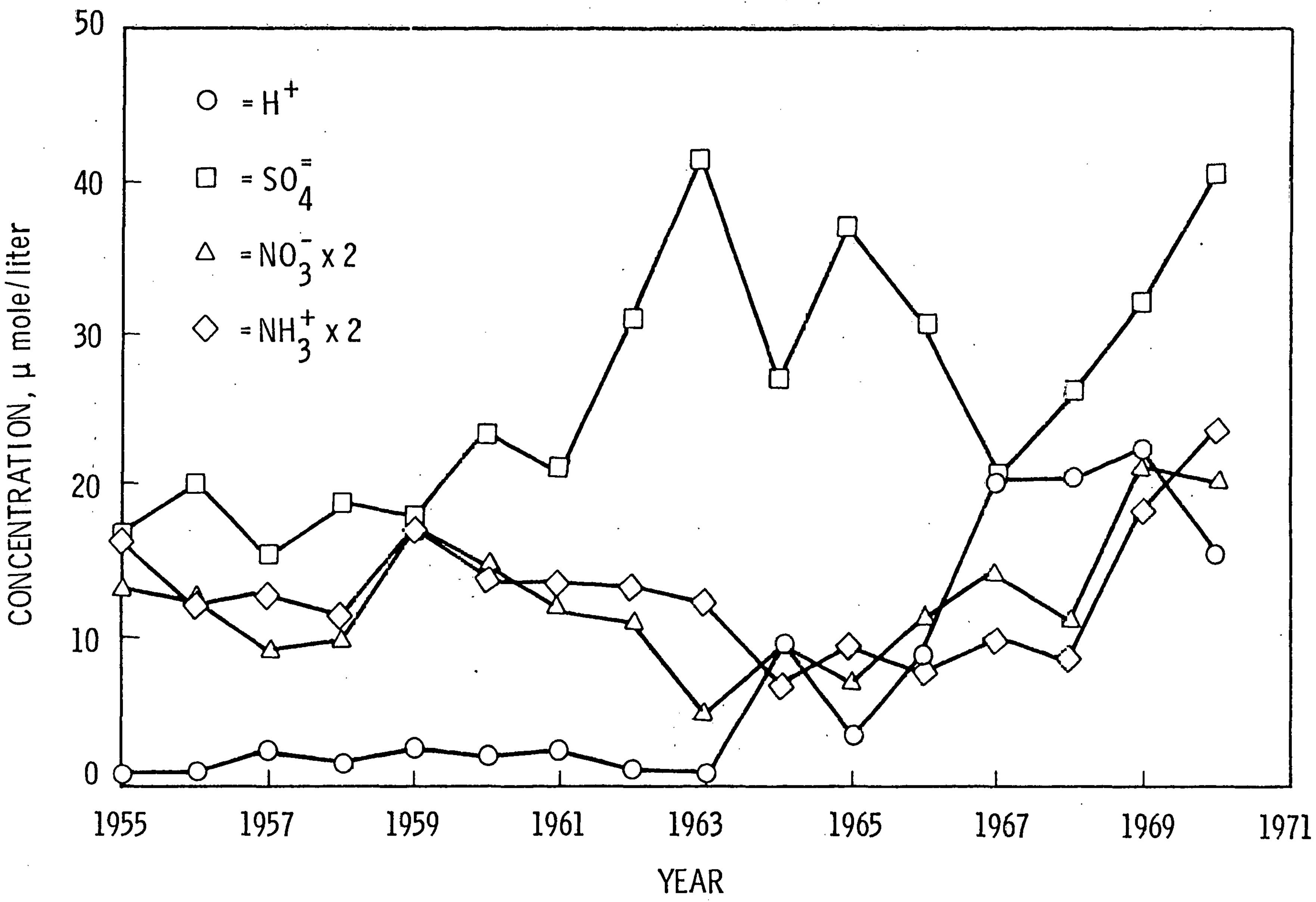

FIGURE 5 - Annually Averaged Precipitation Chemistry Data: EACN Arjeplög Site, North-Central Sweden.

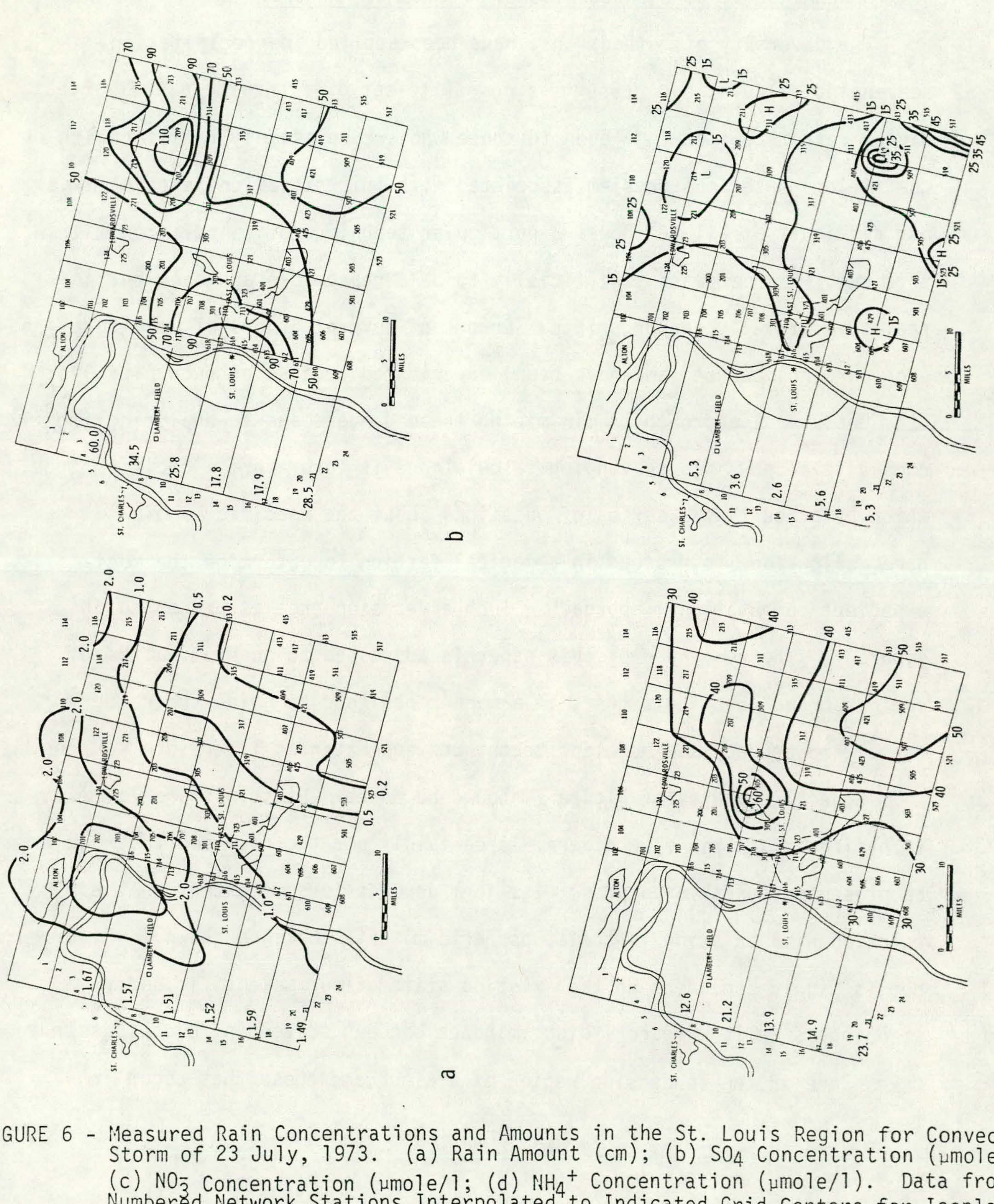

FIGURE 6 - Measured Rain Concentrations and Amounts in the St. Louis Region for Convective Storm of 23 July, 1973. (a) Rain Amount (cm); (b) SO_4 Concentration (μmole/l); (c) NO_3^- Concentration (μmole/l; (d) NH_4^+ Concentration (μmole/l). Data from Numbered Network Stations Interpolated to Indicated Grid Centers for Isopleth Analysis. From Hales and Dana (1979).

3. GENERAL SCAVENGING CALCULATIONS: FLOWCHART APPROACH

The diversity of methods that have been applied in precipitation-scavenging calculations presents a composite set of alternate pathways that can be rather bewildering, even to those who are relatively familiar with the field. A serious problem associated with this situation is that it is not difficult at all to choose a particular technique of calculation within this set, which appears superficially to be a reasonable approach but in reality is totally inappropriate. Errors of several orders of magnitude (and even in sign) can be (and have been) experienced because of such pitfalls.

One useful approach to minimizing these dangers and to analyzing the composite of possible scavenging calculations is to prepare a decision tree, which, by presenting a series of questions about the specific problem at hand, allows one to proceed in a logical fashion to determine the most expedient computational approach. Such a decision tree is presented in Figure 7. The remainder of this paper is addressed to an examination of various branches of this tree, in a manner designed to guide the reader rapidly to appropriate modeling techniques and extended literature sources.

Several features of Figure 7 should be noted. First, it should be emphasized that this flow diagram is certainly not the <u>only</u> one that could be presented for this purpose. Its form depends to some extent on the relationships existing in the atmospheric material balance shown in Figure 1, but is highly dependent on the existing state of our scientific understanding as well. Figure 1 discriminates between scavenging processes that take place in the condensing region of a cloud and those that occur in

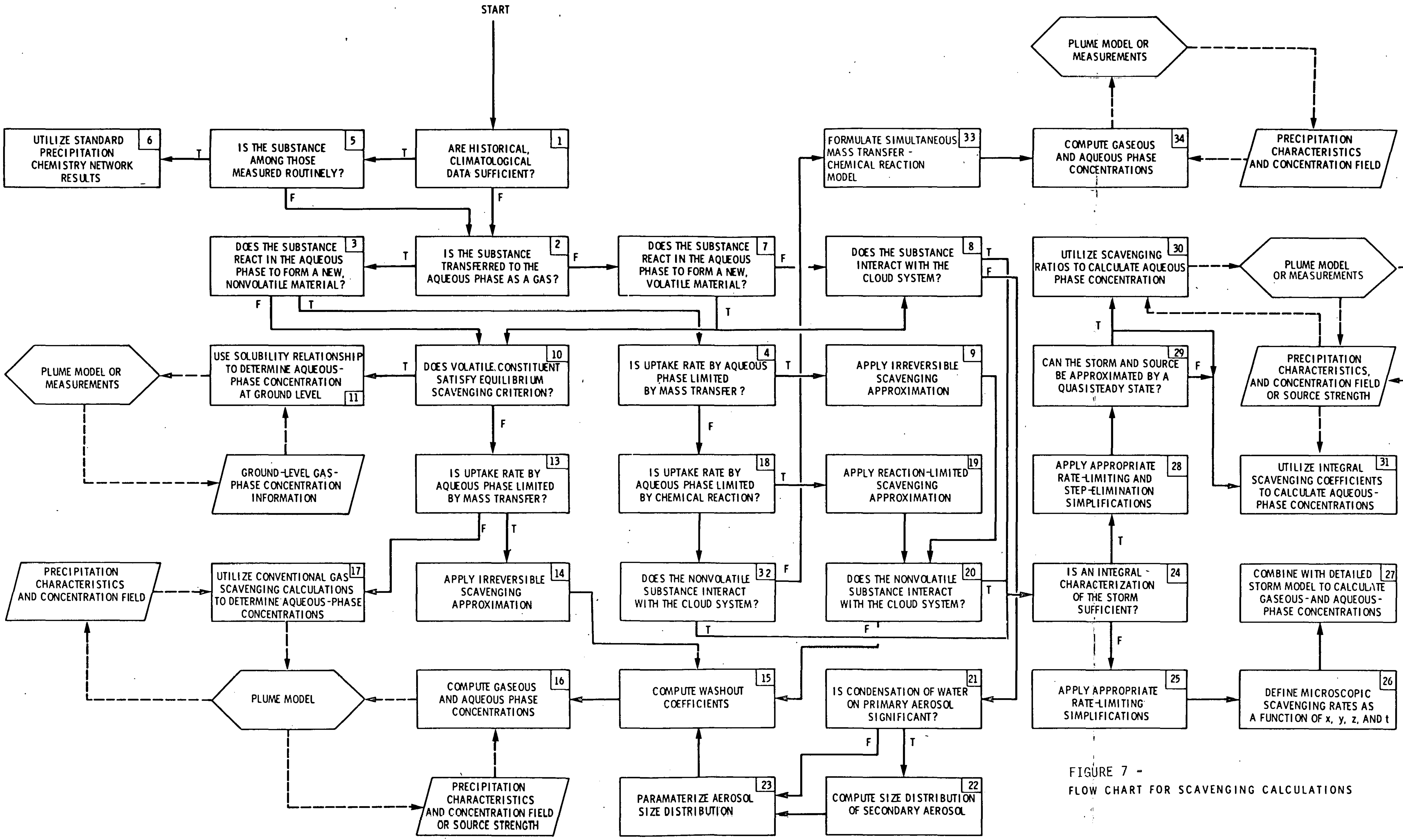

FIGURE 7 -
FLOW CHART FOR SCAVENGING CALCULATIONS

precipitation falling through clear air. This is somewhat artificial in a scientific sense, because common physical mechanisms are operative in both types of systems; but it presents a rather convenient format in view of most traditional approaches to scavenging assessment. Finally it should be noted that, while Figure 1 is addressed primarily to mathematical material-balance applications, it provides a route for climatologically-based predictions as well. Although this latter class of predictions must be utilized with careful consideration of the variability described in Section 2, it provides an expedient route for many types of evaluative applications, and should be considered seriously as an alternative candidate to the more modeling-oriented approaches.

3.1 Pathway 1-5-6: Use of Climatological Precipitation Chemistry Data

There are many circumstances where one is interested in obtaining reasonable estimates for actual values of wet deposition or concentration, and is not at all concerned about long-term trends or the impacts of new, localized sources. Under such conditions it is often appropriate to disregard any potential model application, and base precipitation-chemistry estimates solely on climatological data. In the absence of any better information one could, for example, estimate that the average rainborne sulfate concentration at State College, Pennsylvania for the month of July 1981 will be roughly equal to that shown in Figure 4 for July 1978. Obviously one must beware of the potential pitfalls involved in making such a prediction; but given the present uncertainties in regional modeling procedures, such an application of climatological persistance is often the most logical and productive approach.

Data sources for this purpose are somewhat difficult to access; and although there are current plans to implement a centralized precipitation-chemistry data repository within the United States,* one must currently obtain data directly from the individual sources in most cases. Table 1 itemizes some of the major sources of such data for North America and western Europe; a more detailed listing of North American networks is provided in the recent report by Niemann and his co-workers (1979).

3.2 Pathway 2-7-8-21-23-15-16: Below-Cloud Scavenging of Inert Aerosols

The scavenging of inert aerosol by falling raindrops is a comparatively straight-forward problem, and thus is a logical starting point for this overview of modeling techniques. The major problem envisioned here is the determination of the local rate of uptake of aerosol by the raindrops (particles per unit volume per unit time), as characterized by the term w_A in Equations 1 and 2. The terms r_{Ax} and r_{Ay} are zero (inert aerosol), and we shall assume for the time-being that other features of these equations are sufficiently well-known to permit final computation, once the nature of w_A is established. Some simple examples of such computations are presented later in this section.

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*This repository is currently intended to become a component of the EPA SAROD system.

TABLE 1. SELECTED SOURCES OF REGIONAL PRECIPITATION CHEMISTRY DATA

Network	Location	Sample Period	Contact
EPA/NOAA/WMO	US	Monthly	John Miller NOAA/ARL 8060 13th Street Silver Spring, MD 20910
MAP3S	Eastern US	Event	Terry Dana Battelle-Northwest PO Box 999 Richland, WA 99352
NADP	US	Weekly	James Gibson Natural Resources Ecology Lab Colorado State University Fort Collins, CO 80523
CANSAP	Canada	Monthly	Douglas Whelpdale Atmospheric Enviornment Service 4905 Dufferin Street Downsveiw, Ontario M3H 5T4 CANADA
European Air Chemistry Network	Western Europe	Monthly	Lennart Granat Meteorological Institute Stockholm University Stockholm, Sweden
LRTAP*	Western Europe	Event	Director of Information, OECD 2, rue Andre-Pascal 75775 PARIS CEDEX 16 FRANCE

*Operational 1972 through 1975.

Despite the relative simplicity indicated above, some rather troublesome features emerge during the application of aerosol-scavenging computations. These stem primarily from particle-size modifications during the scavenging process and from the size distributed nature of the raindrop and aerosol size spectra. Because of these features, the following discussion will be presented sequentially, starting with the relatively simple system involving a homogeneous aerosol.

3.2.1. Homogenous Non-Nucleating Aerosol

The simple case of homogeneous aerosol collection by raindrops can be analyzed most conveniently by visualizing a volume element of air as shown in Figure 8. If a single raindrop falls through this element, one can define a collection efficiency in terms of the total aerosol existing in the pathway of the drop, and the amount actually collected during the raindrop's passage through the element; that is,

$$E(R,a) = \frac{\text{mass of particles collected during drop's passage through element}}{\pi R^2 \Delta z m} \qquad (3)$$

where R is the raindrop's projected radius, a is the (effective) aerosol particle radius, and m is the mass of particles per unit volume existing within the element prior to the drop's passage.

From Equation 3 and Figure 8, it is obvious that the accumulation rate of particle mass by the falling drop should be

$$-\pi R^2 v_z m E(R,a) \ ,$$

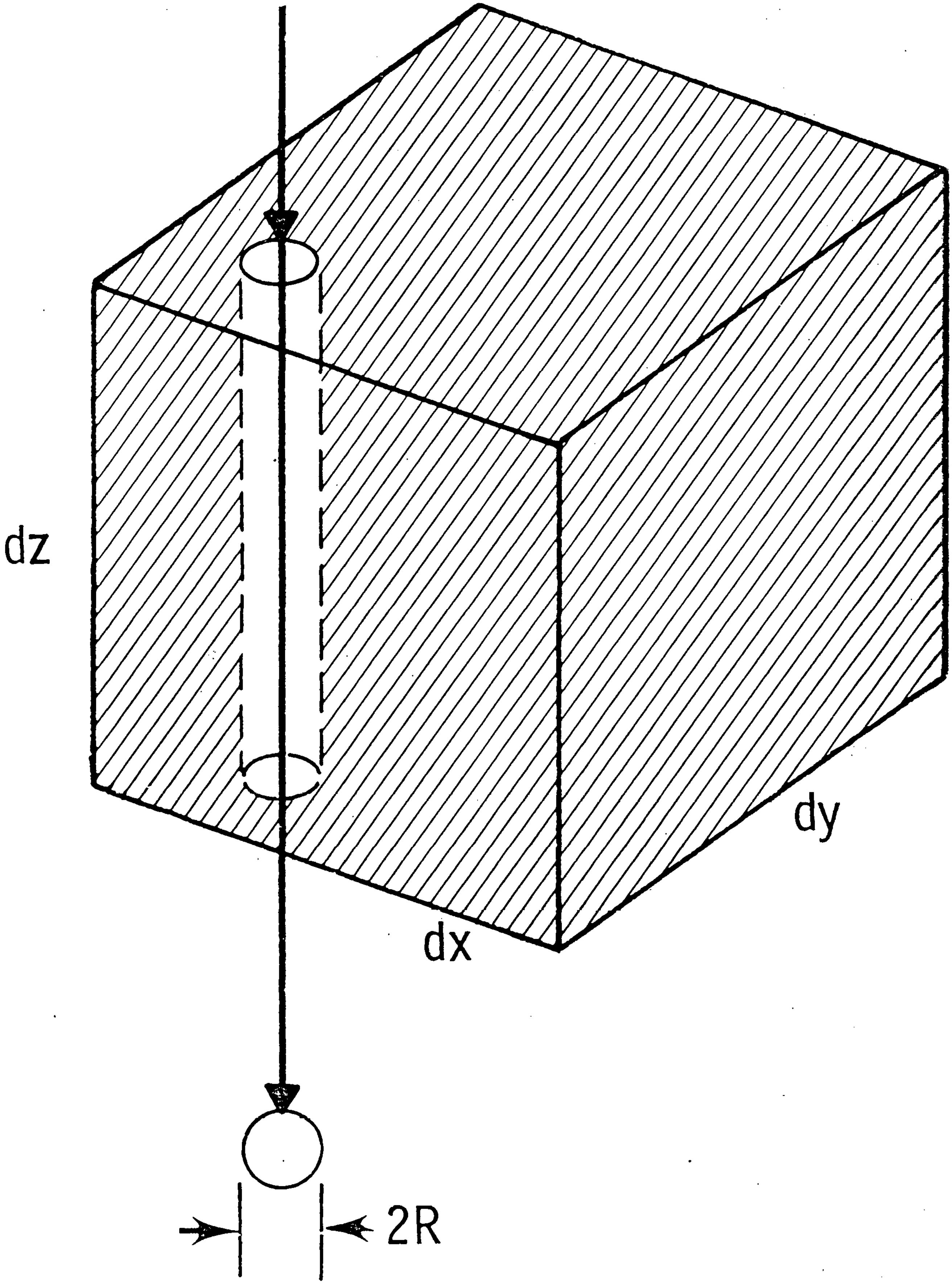

FIGURE 8 - Schematic of Raindrop Penetrating Unit Volume Element of Atmosphere.

where v_z is the vertical velocity of the raindrop (negative downward). Now for an ensemble of raindrops falling through the element, whose size distribution is characterized by the probability-density function $f_R(R)$, the total rate of pickup can be derived by integration over the total range of raindrop sizes. This total pickup rate is by definition equal to minus the interphase transport rate (w_A in Equations 1 and 2), thus:

$$w_A = -\pi N_T m \int_0^\infty R^2 \, v_z(R) \, E(R,a) f_R(R) \, dR, \tag{4}$$

where N_T is the total number of raindrops resident in the unit volume element. This relationship also can be expressed in terms of a <u>washout coefficient</u>, Λ, defined as

$$w_A = \Lambda m \tag{5}$$

From Equation (4),

$$\Lambda = -\pi N_T \int_0^\infty R^2 \, v_z(R) \, E(R,a) \, f_R(R) dR, \tag{6}$$

relating the washout coefficient to the efficiency.

From Equation 4 one can in principle compute the desired scavenging rate, w_A, if the entities E, v_z, and f_R are known; these will be discussed separately in the following paragraphs.

3.2.1.1 E(R,a). The efficiency term E(R,a) depends upon a host of possible collection mechanisms. These include:

- impaction of aerosol particles on the raindrop,
- interception of particles by the raindrop,

- Brownian motion of particles to the raindrop,
- nucleation of a water drop by the particle,
- electrical attraction,
- thermal attraction (thermophoresis), and
- diffusiophoresis,

and have been discussed at length by numerous previous authors (eg. Dingle and Lee (1973), Hidy (1973)). The last three of these mechanisms are of secondary importance in the case of below-cloud scavenging, except for rather special circumstances (cf. Wang, et al. (1978)). The nucleation mechanism, while potentially significant in many applications, is disregarded in the present context on the presumption that the aerosol in question is hydrophobic, and thus will maintain its fixed particle size a. Slinn (1977) has analyzed the first three of these mechanisms, and has suggested the following three formulae for computing the corresponding component efficiencies:

$$e_{\text{impaction}} = [(S-S_*)/(S+C)]^{3/2} \qquad (7)$$

$$e_{\text{impaction}} = 3a/R \qquad (8)$$

$$e_{\text{diffusion}} = 4\,Sh/(Re\,Sc) \qquad (9)$$

Here the Sherwood Number can be calculated from the Froessling Equation

$$Sh = \frac{2k_y R}{Dc} = 2 + 0.6\ Re^{1/2}\ Sc^{1/3} \qquad (10)$$

where

S (Stokes Number) $= \frac{-2a^2\rho_p v_z}{9R\rho_a \nu}$

S_* (Critical Stokes No.) $= (1.2 + L/12)/(L + 1)$

Sc (Schmidt Number) $= \frac{\nu}{D}$

Re (Reynolds Number) $= -2Rv_z/\nu$

$C = 2/3 - S_*$

$L = \ln(1 + Re/2)$

c = molar concentration of air molecules

D = molecular (Brownian) diffusivity

k_y = mass-transfer coefficient

ν - kinematic viscosity of air

ρ_a = density of air

ρ_p = density of the aerosol particle

More refined and involved estimates of these component efficiencies are available in the more recent literature (Slinn (1980)).

The corresponding numerical values of E(R,a) obtained by summing Equations 7, 8, and 9 exhibit the well-known tendency to become large for both very large and very small particle sizes, and to become low at intermediate sizes in the range of 0.1 microns (cf. Figure 9). Since contributions of secondary mechanisms are neglected in this approach, E(R,a) values computed in this manner can be considered to be conservatively low estimates of actual behavior. One can, of course, establish a corresponding upper-limit estimate of E(R,a) by simply setting it to unity. Since this practice can lead in some cases to efficiency-values three orders of magnitude higher than those obtained from Equations 7 through 9, it is somewhat limited in value- at least in the present context where nucleation is assumed unimportant. Because of this, Equations 7 through 9 are recommended for practical use under these conditions.

3.2.1.2 v_z. Estimation of the fall velocity of raindrops is complicated by the presence of temperature and pressure gradients, and internal circulations and deformations within the drop (cf. Pruppacher and Klett (1978)). For practical application, however, empirical fits to measured data provide the most practical means for characterization. The equations of Dingle and Lee (1972), given by the forms

$$v_z = 27.2692 - 1206.2884R + 348.0768R^2$$
$$(0.05 \leq R \leq 0.7 \text{ mm}) \tag{11}$$

and

$$v_z = -155.6745 - 613.4914R + 123.3392R^2$$
$$(0.7 \leq R \leq 2.9 \text{ mm}) \tag{12}$$

provide a balance between simplicity and accuracy, and are recommended as a starting point for use in below-cloud calculations.

3.2.1.3 $f_R(R)$. Owing to the complexity of rain-formation processes, no really satisfactory formulation exists to describe raindrop size spectra in a totally comprehensive manner. Undoubtedly the most-often applied probability-density function for raindrop size distributions is that of Marshall and Palmer (cf. Pruppacher and Klett (1978)):

$$f_R(R) = \frac{1}{C_2} \exp(-C_2R). \tag{13}$$

Here $C_2 = 8.2\ J^{-.21}\ \text{mm}^{-1}$ is a rainfall-rate dependent parameter (J = rainfall rate in mm/hr). It is suggested also in this context that the total number-concentration of raindrops, N_T, should lie close to $1950J^{.21}$ drops/m^3.

Equation 13 is recommended for initial calculations in conjunction with Equations 4 and 6. If more comprehensive computations are desired, one may choose to utilize other types of spectral equations, or employ field measurements of the actual rain spectra for the specific case at hand.

3.2.2 Size-Distributed, Non-Nucleating Aerosol

When (as is the usual case) both the raindrop and aerosol spectra are size-distributed, an extention of Equation 4 is required. If the aerosol mass concentration is described by the probability density function $f_m(a)$, then

$$w_A = -\pi N_T m \int_0^\infty \int_0^\infty R^2 v_z(R) E(R,a) f_R(R)\, f_m(a) dR da; \tag{14}$$

$$\Lambda = -\pi N_T \int_0^\infty \int_0^\infty R^2 v_z(R) E(R,a) f_R(R) f_m(a) dR da. \tag{15}$$

It should be noted that in Equation 15 Λ is defined as a mass washout coefficient. If one were interested in actual numbers of particles washed out, one could define a number washout coefficient simply by inserting a number-density function in place of $f_m(a)$ in Equation 15. Several examples of washout coefficient curves for various rain and aerosol spectra are given by Dana and Hales (1976).

Although size-distributed aerosol systems do not cause any great computational difficulty in principle, they do tend to pose extreme complications in practice. Calculations using Equation 15 demonstrate that aerosol scavenging rates are in general strongly dependent on both particle size, and spread of the particle-size distribution. Thus, there is a definite tendency for $f_m(a)$ (and thus Λ) to change radically during the course of a rain event, simply by action of the washout process. This combined with the fact that aerosol size distributions are seldom known with any acceptable degree of certainty, even before washout commences, imposes rather large limits of uncertainty in associated washout computations in a majority of practical applications.

3.2.3 Condensational Growth of Aerosols and Its Influence on Below-Cloud Scavenging

The discussion of below-cloud scavenging in Sections 3.2.1 and 3.2.2, which is based on the presumption that aerosol particles do not change their sizes during the scavenging process, is somewhat unrealistic. Most common aerosol particles do indeed act as nuclei for water condensation at high humidities (Junge (1963)), and appreciable changes in their sizes can be expected to occur as a result. This combined with the rather radical changes in E with particle size predicted from Equations 7 through 9 (compare lower curve of Figure 9), suggests that considerable modifications of below-cloud scavenging rates can occur via the condensation process.

Size and growth rates for nucleated droplets depend on the nature of the nucleating particle and the water-vapor content of its surrounding environment. At high humidities, growth can be very rapid for small droplet sizes; as the droplets become larger, however, the process shows significantly. Given a supersaturation of one precent, for example, a one-micron droplet will double its size via condensation within a few seconds; for a ten-micron particle the corresponding doubling time is of the order of several minutes (cf. Mason (1971)).

Our theoretical capability to deal with the prospect of nucleation and condensational growth in below-cloud scavenging is presently at an unsatisfactory state. Slinn (1980) has taken the rather straight-forward approach of:

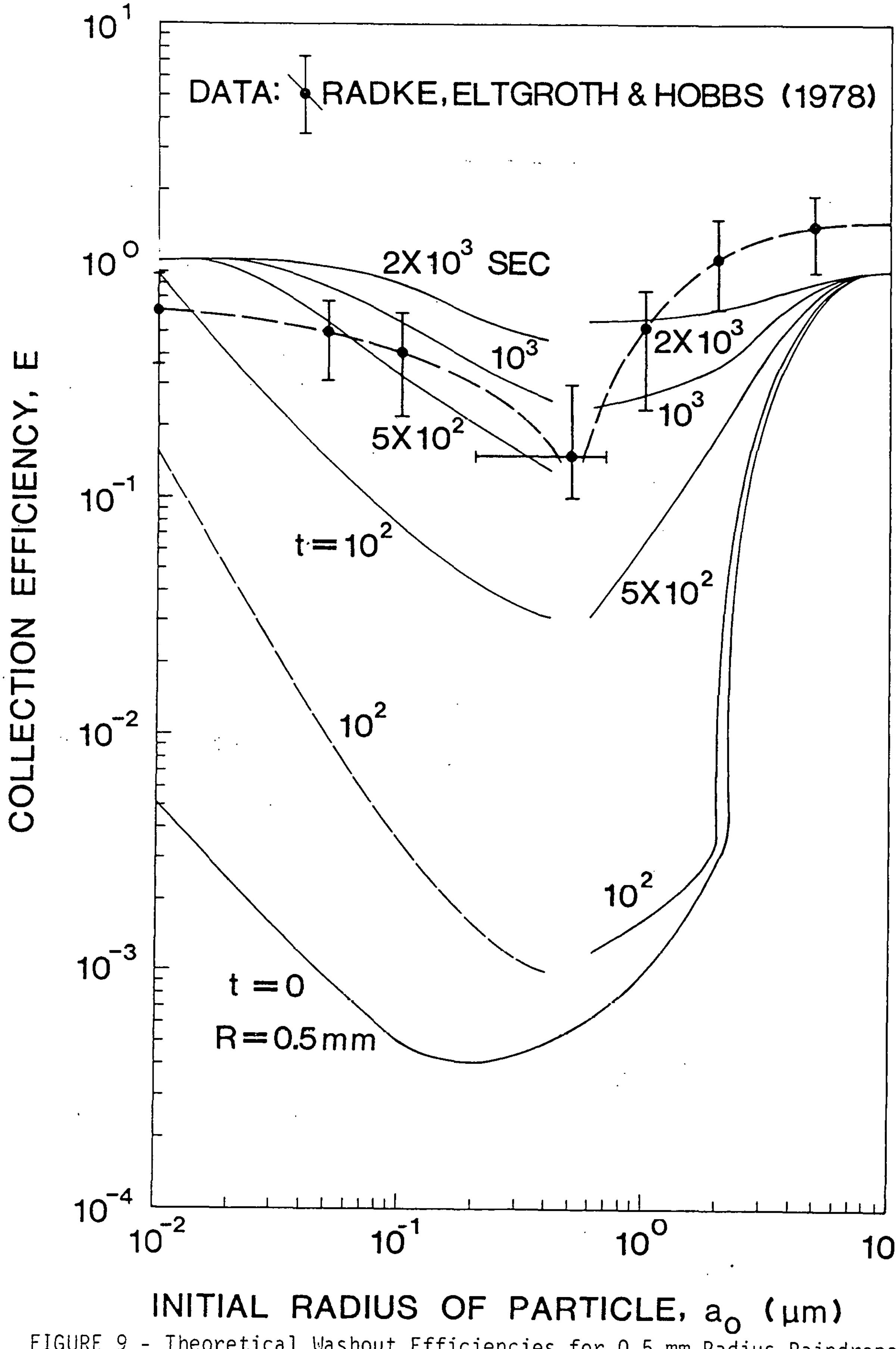

FIGURE 9 - Theoretical Washout Efficiencies for 0.5 mm Radius Raindrops, For Nucleating Aerosols. Calculations of Slinn (1980).

1. selecting an aerosol particle of dry size a_o,
2. calculating the size of the particle as it grows by condensation, assuming specific growth conditions,
3. calculating revised values of E as a function of time, corresponding to the increasing size of the droplet,

and 4. repeating the procedure over a range of dry particle sizes,

to obtain the revised efficiency curves shown in Figure 9. Here the bottom curve corresponds to a dry aerosol, and is essentially that which would be computed from Equations 7 through 9. The higher curves pertain to washout efficiencies of a growing aerosol, after the indicated growth times.

The efficiency curves on the right-hand side of Figure 9 are relatively simple, owing to the fact that particles in this size range do not interact significantly with each other via the Brownian diffusion process. They do, however, interact strongly with smaller aerosol particles, and thus the collection efficiencies of the latter are altered appreciably. Slinn has attempted to account for this in preparing the left-hand curves in Figure 9; his efforts have been limited, however, by the assumptions needed with regard to the characteristics of the large-particle end of the droplet spectrum. This has led to the variety of curves and the discontinuities that appear on the figure.

All of the above uncertainties, plus the generally unknown time-humidity history of an air parcel in a below-cloud scavenging environment add up to the fact that we have very little competence in prediction of below-cloud scavenging rates of areosols under conditions where nucleation occurs. This effect undoubtedly serves to push scavenging efficiencies in the direction of the upper "asymptote" (E=1) condition mentioned in Section 3.2.1.1. Just how effective this process is, however, is understood very poorly. Rather comprehensive analyses of aerosol growth with condensation are available (cf. Mason (1971), Fitzgerald (1974) and Johnson (1979)), and some fragmentary field measurements of plume scavenging exist (Radke, et al (1978)), but much remains to be accomplished before a really satisfactory understanding of this phenomenon is attained.

3.2.4 Below-Cloud Scavenging of Aerosols by Snow

The irregular and varied geometries of snow particles lead to difficulties in assessment of their size distributions, fall velocities and scavenging efficiencies; thus the computation of below-cloud scavenging by snow emerges as a problem fraught by even more difficulty than that described previously for rain. The usual mathematical approach to this problem is to define some sort of "efficiency", which is comparable to that defined in Equation 3, and is based on an equivalent diameter of one type or another. Slinn (1980) suggests:

D_e = diameter of sphere circumscribing the snow particle,

and proceeds to express a corresponding washout coefficient by the form

$$\Lambda = -\frac{\pi N_T}{4}\int_0^\infty D_e v_z(D_e)E(D_e,a)f_{D_e}\,dD_e \tag{16}$$

(cf. Equation 6). Combining this with an expression describing equivalent precipitation rate J in terms of D_e, he proceeds to the simplified form

$$\Lambda = \gamma J \, E(D_e, a)/D_m$$

where γ is a constant of the order of unity, and D_m is a characteristic length scale whose numerical values are summarized in Table 2.

TABLE 2. Characteristic Lengths of Ice Crystals for Use in Equation 17. From Slinn (1980)

Crystal Type	D_m(cm)
Graupel	0.014
Rimed Plates and Stellar Dendrites	0.0027
Powder Snow and Spatial Dendrites	0.001
Plane Dendrites	0.00038
Needles	0.0019

Slinn also provides a semi-empirical equation for E (not given here), which is similar in form to Equations 7 through 9. An upper asymptote for the system, of course, is simply E=1.

An alternative approach to snow-scavenging calculations, which is based on a more empirical framework, is that outlined by Knutson and Stockham (1977). These authors give explicit expressions for Λ which are functions of J, a, and temperature, and are based upon direct experimental observations.

In comparing the above results as well as the computations and measurements by additional investigators, it becomes readily apparent that several orders of magnitude uncertainty exist in typical applications of snow-scavenging calculations. Much more research needs to be accomplished, especially in the area of physical measurements of E, before a satisfactory computational capability will exist in this area.

3.2.5 Example Integrations of Continuity Equations for Aerosol Scavenging

Thus far this text has been addressed to evaluation of the microphysical processes leading to the <u>microscopic</u> features of the pollution material-balance equations. Usually, however, the desired products of a scavenging calculation are <u>macroscopic</u> features, such as delivery fluxes and concentrations. These features are typically calculated via solution of the material-balance equations, and it is appropriate at this point to illustrate this procedure using some rather simplified, yet practical examples.

3.2.5.1 Example 1: Scavenging Through a Gaussian Plume. If below-cloud scavenging occurs through an aerosol plume which is distributed in a Gaussian manner, and furthermore the scavenging interaction is characterized by the constant coefficient Λ, then

$$w_A = \Lambda c_{Ay} ;$$

and the solution to Equation 1, subject to appropriate restrictions and boundary conditions, is (Slade (1960)):

$$c_{Ay} = \frac{Q}{2\pi\sigma_y\sigma_z u} \exp\left(\frac{-y^2}{2\sigma_y^2}\right) \left\{ \exp\left[- \frac{(z-h)^2}{2\sigma_z^2}\right] + \exp\left[- \frac{(z+h)^2}{2\sigma_z^2}\right] \right\} \exp\left(- \frac{\Lambda x}{u} \right) \qquad (17)$$

where Q and h are the plume's source strength and release height, u is the wind velocity, and σ_y and σ_z are the plume spread parameters.

If one assumes constant, vertical rainfall with homogeneous drop size, then the corresponding reduced form of Equation 2 is

$$-v_{Axz} \frac{dc_{Ax}}{dz} + \Lambda c_{Ay} = 0. \tag{2a}$$

The average rainborne pollutant concentration c_{Ax} can be calculated at any point x,y,z simply by inserting Equation 17 into Equation 2a and integrating. In particular, c_{Ax} at ground level is

$$c_{Ax} = \frac{-\Lambda Q}{\sigma_y v_{Axz} u\sqrt{2\pi}} \exp\left(\frac{-y^2}{2\sigma_y{}^2}\right) \exp\left(\frac{-\Lambda x}{u}\right). \tag{18}$$

One should be careful to note here that c_{Ax} is the concentration of rainborne pollutant in terms of <u>total space</u> occupied by both the gaseous and aqueous phases. The relationship between c_{Ax} and the concentration of pollutant in collected rain, $\hat{C}_A$, can be derived by considering once again the ensemble of raindrops in the volume element of Figure 8. If $\hat{c}_A(R)$ is the aqueous-phase concentration of pollutant (pollutant per unit volume of water) associated with size-R hydrometeors, then

$$c_{Ax} = N_T \int_0^{\infty} V(R)\, \hat{c}_A(R) f_R(R) dR . \tag{19}$$

Here V(R) is the volume associated with size-R raindrops. Now $\hat{C}_A$ can be expressed simply as the vertical flux of rainborne pollutant, ie.

$$c_{Ax} v_{Ax} ,$$

divided by the vertical flux of rain:

$$\hat{c}_A = \frac{N_T \int_0^{\infty} V(R)\hat{c}_A(R)v_z(R)f_R(R)dR}{N_T \int_0^{\infty} V(R)v_z(R)f_R(R)dR} \tag{20}$$

Under the present special conditions of uniform raindrop size, the vertical velocity of rainborne pollutant is equal to the rainfall velocity, ie,

$$v_{Axz} = v_z \quad ,$$

and Equation 20 reduces to the form

$$\hat{c}_A = - \frac{c_{Ax} \, v_z}{J}$$

where J is the rainfall rate (ℓ/t), giving

$$\hat{c}_A = \frac{\Lambda Q}{J \, \sigma_y u \, \sqrt{2\pi}} \, \exp\left(\frac{-y^2}{2\sigma_y^{\,2}}\right) \, \exp\left(\frac{-\Lambda x}{u}\right) \tag{21}$$

upon application to Equation 12.

By studying this simple example, one can note that direct solution of Equation 2 can become extremely cumbersome if the hydrometeor system is size-distributed in nature. Under such conditions it is often much more expedient to approximate a partial solution to Equation 2 by abandoning the use of the washout coefficient, and utilizing instead a material balance over a single droplet. If one defines a particle-mean efficiency $\overline{E}(R)$, then from Section 3.2.1 this balance becomes

$$\frac{d\hat{c}_A(R)}{dz} = - \frac{3c_{Ay}\overline{E}(R)}{4R} \tag{22}$$

By repeated integrations of Equation 22 in conjunction with a descriptor of c_{Ay} (such as Equation 17), and with subsequent distribution according to Equation 20, one can compute a corresponding concentration in collected rain. This type of solution technique will be discussed further in conjunction with the discussion of gas scavenging in Section 3.3.

3.2.5.2 Example 2: Scavenging Through a Uniform Air Mass. Perhaps the simplest example of a scavenging process is that where there are no gradients in the gas-phase pollutant concentration and no chemical reaction, thus reducing Equation 1 to the form

$$\frac{dc_{Ay}}{dt} = - w_A = - \Lambda c_{Ay} \tag{23}$$

This can be integrated immediately to obtain the form

$$c_{Ay} = c_{Ay}\Big|_{t=0} \exp(-\Lambda t) . \tag{24}$$

Corresponding solutions of Equation 2 can be obtained as well, if desired. For example, integration of Equation 2a for the situation of (homogeneous distributed) rain falling a distance z_0 into a uniformly distributed plume of concentration c_{Ay} gives

$$c_{Ax} = -\frac{\Lambda z_o}{v_z} c_{Ay} \tag{25}$$

$$\hat{C}_A = \frac{\Lambda z_o}{J} c_{Ay} \tag{26}$$

Although often applied for atmospheric modeling purposes, Equation 23 is usually too restrictive to be a truly useful or accurate descriptor. In general the divergence terms in Equation 1 are important, and their truncation in this manner is not usually justified. One should note as well that Equation 23 is *not* a *definition* of Λ; rather, it is a mathematical description of a highly specialized set of circumstances. Confusion of this point has led to erroneous applications in some past efforts.

3.3 Scavenging of Non-reactive Gases

3.3.1 Pathway 2-3-10-13-17: General Conditions. In the preceeding discussion of aerosol scavenging it was assumed, tacitly that interphase transport of pollutant between the atmosphere and a falling drop was *irreversible*; that is, once collected the aerosol could not escape back to the air from the aqueous phase. This feature is reflected in Equations 4 and 5, which imply that w_A is always positive, that is, interphase transport should always be *from* the gas phase *to* the drop.

In the case of gases, which can both *absorb in* and *desorb from* water, the irreversibility assumption is generally invalid; and under such conditions it is usually necessary to reformulate expressions for w_A which take reversibility into account. This is done most conveniently by discontinuing use of the efficiency concept (as expressed in Equation (3)) and employing instead a corresponding expression for *flux* of pollutant from the falling hydrometeor:

$$F = -\frac{K_y}{c}\left(c_{Ay} - h'\hat{c}_A\right). \qquad (27)$$

Here K_y is an overall mass-transfer coefficient, and h' accounts for the solubility of the gas. One should note that both absorption and desorption are predicted by Equation 27, depending on the relative magnitudes of c_{Ay} and $h\hat{c}_A$. One should observe also that, because of small molecular masses and relatively high diffusivities of gaseous pollutants, diffusion predominates as an interphase transport mechanism; and thus all mechanisms in Section 3.2.1.1 other than diffusion become insignificant.

Diffusive transport in <u>both</u> the gaseous and aqueous phases is important in determining gas scavenging rates, and it is usually convenient to consider these effects individually in terms of gas- and liquid-phase coefficients k_y and k_x, such that

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{h'}{k_x} \tag{28}$$

(cf. Bird, et al. (1960)). k_y can be estimated from Equation 10. Evaluation of k_x is somewhat more difficult, although for many gases of high or moderate solubility (small h') its relative effect in Equation 28 is small and it can be neglected (cf. Barrie (1978) and Hales (1972)).

On the assumption of spherical raindrops, Equation 27 can be integrated to provide a general expression for the interphase transport rate, which is a gas-scavenging conterpart to Equation 4:

$$w_A = \frac{4\pi N_T}{c} \int_0^\infty R^2 f_R(R) K_y(R) [c_{Ay} - h\hat{c}_A (R)] dR \tag{29}$$

3.3.2 Example Integrations of Continuity Equations for Gas Scavenging

Equation 29 can be incorporated with Equations 1 and 2, and utilized to calculate spatial concentration fields and delivery fluxes in a manner similar to that described previously for aerosol washout. The increased complexity of the coupling term w_A requires that additional attention be focused on the interactive nature of the rain and the gas-phase plume, and one often is forced to make further simplifying assumptions, or else increase the complexity of the calculation appreciably. This plus the size-distributed nature of the rain spectrum often discourages direct solution of Equation 2, in favor of an approximation in terms of individual hydrometeors, similar to that described in Section 2.3.5.1.

From Equation 27 the single-drop material balance (cf. Equation 22) is

$$\frac{d\hat{c}_A(R)}{dz} = \frac{3K_y}{v_z Rc} \left(c_{Ay} - h'\hat{c}_A\right) . \tag{30}$$

specific applications of this equation are presented in the following paragraphs.

3.3.1.1 Example 1: Scavenging Through a Gaussian Plume. In the event that scavenging does not deplete the plume appreciably, the conventional Gaussian plume equation (Equation 17) (with $\Lambda = 0$) may be incorporated with Equation 30, and the results integrated to obtain the following expression for pollutant concentration in raindrops at ground level:

$$\hat{c}_A(R) = \frac{Q\xi}{2\sqrt{(2\Pi)}\sigma_y u} \exp\left(-\frac{y^2}{2\sigma_y^2} + \frac{\sigma_z^2\zeta^2}{2}\right)$$

$$x \left\{\exp(\zeta h)\left[1 - \operatorname{erf}\left(\frac{-\sigma_z^2 - h}{\sigma_z\sqrt{(2)}}\right)\right]\right. \tag{31}$$

$$\left.\exp(-\zeta h)\left[1 - \operatorname{erf}\left(\frac{-\sigma_z^2 + h}{\sigma_z\sqrt{(2)}}\right)\right]\right\}$$

where

$$\zeta = \frac{3K_y h'}{cv_z R}$$

and

$$\xi = \frac{3K_y}{v_z R}$$

This may be considered to be a gas-scavenging counterpart of Equation 21 although it is somewhat more restrictive because the coupling term w_A was removed from the gas-phase equation (cf. Hales, et al (1973)).

A more comprehensive model of this type, which allows numerical computations to be performed for general plume types, non-linear solubility behavior, and nonvertical rainfall has been presented by Drewes and Hales (1980). An elegant analytical solution of Equations 1 and 2 which does not decouple the equations and thus accounts for plume distortion via the absorption-desorption process, has been given by Slinn (1974).

3.3.1.2 Example 2: Scavenging Through a Uniform Air Mass. A gas-scavenging counterpart to Equation 26 can be derived via simple integration of Equation 30 for an initially clean drop as it is allowed to fall through a uniformly-distributed pollutant gas of concentration c_{Ay} from height z_o. The result is

$$\hat{c}_A(R) = \frac{c_{Ay}}{h'}[1-\exp(\zeta z_o)] \qquad (32)$$

It is of some interest to observe the differences between Equation 32 and its irreversible counterpart, Equation 26. Visual inspection of Equation 32 shows that a raindrop falling through a uniformly distributed polluted gas will approach a limiting concentration c_{Ay}/h'. Equation 25, on the other hand, suggests that the raindrop should scavenge pollutant indefinitely as long as it is able to fall. This difference can result in orders-of-magnitude deviations in computed values. Accordingly, one must exercise proper care in performing such calculations to ensure that the formulations employed are appropriate to the specific pollutant of interest.

3.3.2 Pathway 2-3-10-11: Equilibrium Scavenging

Under the special conditions where the raindrops are known to be at a state of solubility equilibrium with regard to the pollutant, scavenging computations become especially simple. If c_{Ay} is the ground-level gas-phase concentration, then

$$\hat{c}_A = c_{Ay}/h' \tag{33}$$

can be employed immediately for scavenging calculations. Situations where Equation 33 is known to hold are referred to as <u>equilibrium scavenging conditions</u>. These conditions, promoted by short relaxation times for the absorption-desorption process, and slowly varying gas-phase concentration fields in the vicinity of the falling drops, are observed to occur whenever the dimensionless group

$$\Gamma_{eq} = \frac{3K_y h' \, c_{Ay}}{v_z \, Re \, dc_{Ay}/dz} \tag{34}$$

becomes greater than about 10 (Hales 1972). Here the term dc_{Ay}/dz should be interpreted conservatively as the maximum gas-phase concentration gradient experienced by the raindrop throughout its fall.

3.3.3 Pathway 1, 2, 3, 4, 9: Mass-Transfer Limited Gas Scavenging

One situation where the assumption of irreversible capture may be valid, even in the case of gases, is that where the pollutant is highly soluble or reactive. Under these conditions gas-phase mass transfer is the sole limiting factor, and Equations 4 - 6 (with $E = e_{diffusion}$) still apply. HCl is a prime example of a gas having a sufficiently high solubility to provide mass-transfer limited conditions under a large variety of circumstances. (cf. Pellet 1977)

3.4 Scavenging of Reactive Ceases

The prospect of chemical reaction of a dissolved gas in rainwater introduces the possibility of several alternate types of behavior, which are itemized below:

1. If the chemical reaction is rapid and reversible with a nonvolatile product, i.e.

$$A \rightleftharpoons B,$$

then the scavenging interactions usually can be treated as a psuedophysical absorption process (cf. Sherwood and Pigford 1952). With this treatment pathways 2-3-10-11 or 2-3-10-13-17 can be utilized directly for calculation, as long as an appropriate means for describing solubility is available. Dimensionless criteria describing conditions acceptable for psuedophysical absorption calculations are available (Hales 1972).

2. If the chemical reaction is rapid, irreversible, and leads to a nonvolatile product, then mass transfer to the raindrop's surface usually can be considered as the rate-limiting step in the scavenging process. Under such conditions pathway 2-3-4-9-20-15 can be employed for direct calculations. Dimensionless criteria (Hales 1972) for fast-reaction mass-transfer limited conditions are available.

3. With relatively slow chemical reactions (eg. $SO_2 \rightarrow SO_4^=$), two modes of below-cloud scavenging may be isolated. These correspond to the nonreactive

pickup of gas by physical (or psuedophysical) absorption and the reactive depletion of gas within the drop. If relaxation times for the absorption step are short compared to those for reaction, then the first of these modes may be treated via steps 3-10-11 or 3-10-13-17 in a quasi-independent manner. Likewise, the reactive mode can be simplified under some circumstances to allow a relatively straightforward calculation to be performed. Again, dimensionless criteria may be derived (Hales 1972) to describe conditions where such assumptions are allowable.

4. In the more general case, involving the possibility of multiple reactions, competitive effects, or volatile reaction products, one usually has little choice other than formulating a detailed mathematical description of the mass-transfer - chemical-reaction process (pathway 3-4-18-32-33-34). A generalized numerical framework for scavenging calculations of this class has been reported by Drewes and Hales (1980). Specific computations for the SO_2 - $SO_4^=$ system in well-mixed environments have been presented by Overton, et al (1979) and Hill and Adamowicz (1977).

3.5 In-Cloud Scavenging of Gases and Aerosols

As indicated previously, common mechanisms contribute to the scavenging process regardless of whether or not it occurs within a visible cloud system; and thus the distinction between in- and below-cloud scavenging is somewhat artificial. There is, however, a definite shift in the relative importance of these mechanisms. Readdressing the collection pathways itemized in Section 3.2.1.1, it seems obvious that, for cloud environments where condensation is occurring, nucleation should play a much more dominant role in contacting the pollutant with condensed water. Also, because of the importance of evaporation-condensation cycles in typical cloud systems, electrical, thermal, and diffusiophoretic forces should be expected to become relatively important (cf. Dingle and Lee (1973)). Interception and impaction, on the other hand, can be expected to become insignificant for the attachment of primary pollutant particles to cloud droplets, although they definitely remain important as mechanisms of accretion of pollutant-laden droplets to falling hydrometeors.

In-cloud scavenging computations tend to become highly involved, owing to the complex flows that typically occur in condensing and evaporating systems. The previous discussion of below-cloud scavenging was based on the rather casual assumption that flow-fields were defined, or at least could be estimated with adequate precision; this assumption is usually invalid for in-cloud systems, however, and quite often one is faced with the additional need to derive these flow fields via modeling of storm-dynamics processes. Such modeling entails solving the appropriate equations of conservation for energy, momentum and mass of the storm system, and lends significant increases to the complexity of the problem.

Because of the involved nature of this subject, it is convenient to subdivide the in-cloud scavenging process into a number of sequential steps, which can be treated individually to isolate key aspects of the process. These are portrayed in the simplified visualization shown in Figure 10, and can be itemized as

1. Transport of the pollutant to the cloud system from its source,
2. Transport of pollutant within the cloud system,
3. Interphase transport of airborne pollutant to the aqueous phase,

and 4. Removal of the pollutant-laden cloud water as precipitation.

Typically the first of these events is treated in terms of a transport model, or else it is ignored, assuming that the pollutant is already in the region of the storm. Numerous models of this type exist, ranging from rather straightforward trajectory calculations (Wendell, et al (1976), Samson (1980), Hefter (1980), Bolin and Persson (1975)), to detailed numerical solutions of variants of Equation (1) and its momentum- and energy-conservation counterparts (Kreitzburg and Leach (1978)). While such trajectory modeling efforts are being performed rather routinely at the present time, it is important to note that, owing to the complexities associated with air motions near precipitation regions, these calculations must be conducted with due care to produce meaningful results.

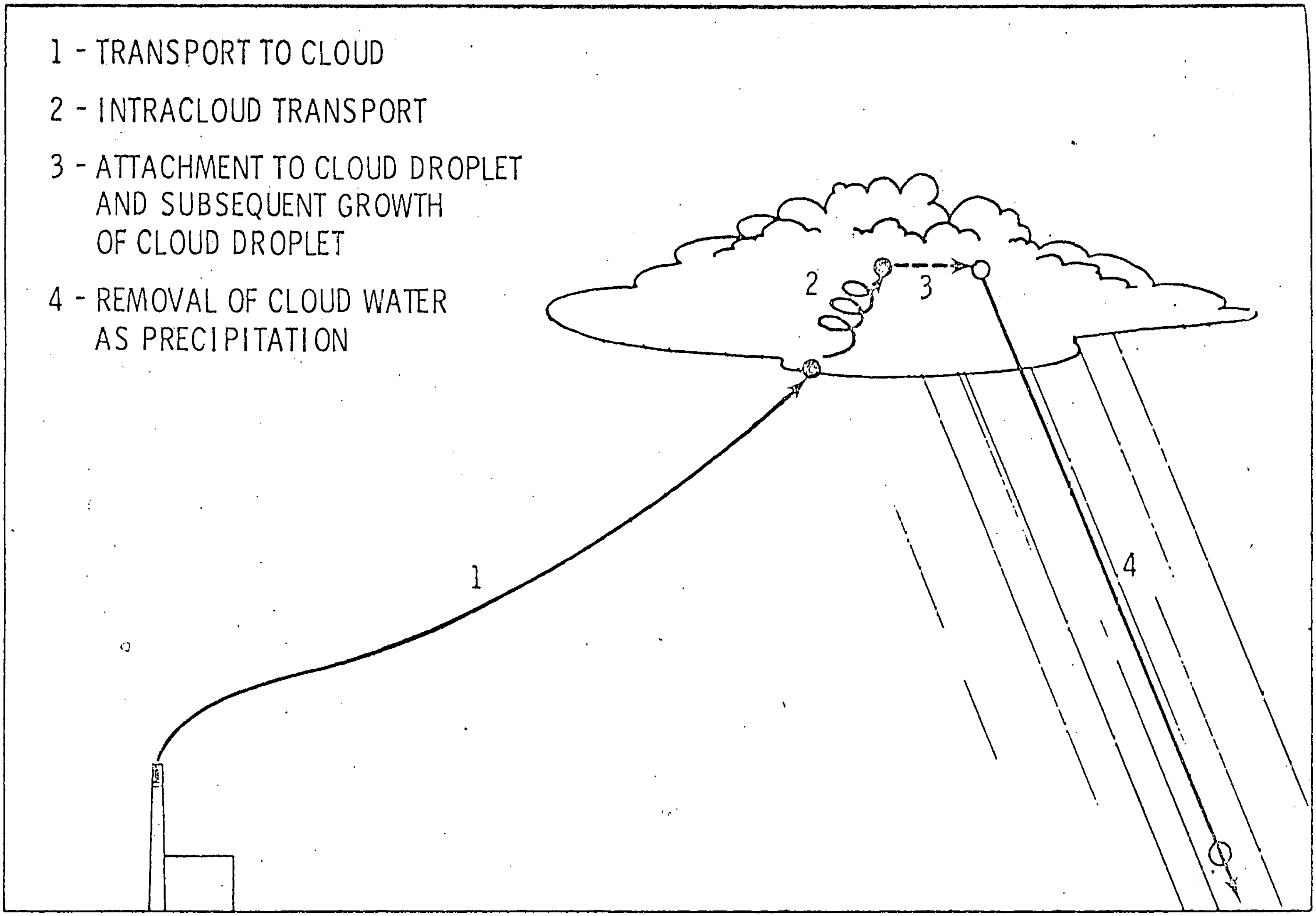

FIGURE 10 - Steps in the Overall In-Cloud Scavenging Process

Other approaches to the analysis of source-cloud transport have been statistical in nature, and are potentially useful if general climatological analysis, rather than specific source-receptor information, is required. The reader is referred especially to the paper of Rodhe and Grandell (1972) for an example of this type of analysis.

The <u>second</u> event of the above sequence often can be simplified, since pollution is generally well mixed in the atmosphere and usually enters the cloud system in the same manner as the water vapor from which the cloud is formed. An example of where this might *not* be the case is that of a plume that mixes into an already-existing cloud system by diffusion from below. Since the attachment process can occur through the cloud volume, and also since the plume particles will themselves affect cloud microphysics and thus scavenging, it is not unreasonable to expect that their removal will depend upon their intracloud mixing to some degree. Such cases are of relatively minor importance, however, and the remainder of this discussion shall be based upon the assumption that pollutant and cloud-makeup water are introduced to the storm system in the same manner and are thus intimately mixed throughout.

The <u>third</u> event, that of the microphysical attachment of aerosol particles to cloud droplets and hydrometeors, has been the subject of extensive debate over the past three decades. Despite the noted profusion of mechanisms, however, there seems to be a rather general consensus that the primary attachment pathway for aerosol particles in the 0.1 to 1 micron range is nucleation. Junge (1963), for example, estimates that anywhere from fifty to eighty percent of the mass of a general continental aerosol will be active as condensation-nucleus material in a typical storm situation.

As noted in Section 3.2.3, the times required for growth of nucleated droplets via the condensation process are sufficiently long to make this step a potential rate-influencing feature of the overall scavenging process.

This combined with additional known complexities of cloud processes results in a rather involved picture of the in-cloud attachment phenomenon. Quite obviously mechanisms such as coalescence serve as additional factors to modify the size distribution of cloud particles. Moreover the natural fluctuations in supersaturation within typical clouds tend to complicate matters considerably (Junge 1963), and it seems obvious that even with the simplistic notion that all attachment occurs via nucleation, the problem of rigorous mathematical characterization becomes overwhelming.

An important feature to note from this discussion, however, is that many of the mechanisms for extraction of pollutant in storm systems (eg. nucleation, coagulation, accretion) are related intimately to those for removal of water. This is a feature that can be used to advantage in many practical scavenging calculations, and will be considered in more detail in the following discussion.

The fourth event in the in-cloud scavenging sequence--that of removal of pollutant-laden cloud water as precipitation--quite obviously involves a close relationship between scavenging and water removal as well. Those cloud particles that have grown sufficiently by condensation and coalesence to achieve significant fall velocity drop through the cloud, accreting other droplets and finally emerging as precipitation, carrying their associated pollutant burden to the ground. Owing to the size-distributed nature of the cloud and precipitation elements the mathematical description of this process can become rather complex, although simplified parameterizations have been formulated (Mason 1971). It is sufficient for this discussion to note, however, that here again is a process that takes sufficient amounts of time to be a significant rate-influencing step in the overall scavenging process.

The calculation of in-cloud scavenging rates can be simplified appreciably if one or more of the events in the above sequence can be disregarded. As indicated previously, one way to accomplish this is simply to begin the modeling process at a late point in the sequence, thus assuming that the consequences of all previous steps are already known, or else have been predicted by other models. Quite obviously this approach demands specific information regarding either concentrations at the beginning of the modeled sequence, or else the rates of a concurrent phenomenon, such as rain production.

A second possible way to disregard steps in the sequence is to establish events that occur slowly compared to others and thus can be considered as rate limiting. If such steps are, indeed shown to exist, the remaining ones can be ignored, thus simplifying the modeling problem. This is a procedure identical to that employed in chemical reaction-rate modeling, and has been examined previously in the context of events 3 and 4 by Slinn (1974). In view of the above discussion it appears unlikely that either event 3 or event 4 will become rapid enough in a sufficiently large number of cases to permit their general neglect as rate-influencing steps. In formulating working models, therefore, one must either begin at event 3 (or earlier) and model and process through to completion, or else utilize additional information to permit a beginning at event 4.

Regardless of this starting point, most practical assessments of this situation can be categorized into a manageable number of classes, depending on whether:

1. The material balance used for calculation is integral or differential in nature

and

2. The derivation requires explicit solution of momentum and/or energy equations to derive thermodynamic and/or flow features.

The following discussion of calculation methods will be subdivided according to these classes.

3.5.1 Pathways 20-24-28-29-30 and 20-24-28-29-31: Integral Material Balances

Perhaps the most straightforward example of an integral material-balance approach to in-cloud scavenging analysis is the derivation of washout ratios. This is a particularly appealing approach, because it allows most of the essential features to be lumped into a small number of parameters; and although these are difficult to estimate from first principles, they can be force-fit to experimental observations in a rather convenient manner.

The washout ratio is defined as

$$\xi = \frac{\hat{C}_A}{c_{Ay}} \quad . \tag{35}$$

Its basic features can be derived (cf. Engelmann 1971) by assuming that the storm can be characterized as a quasi steady-state phenomenon, and then by performing a material balance over a total precipitating cloud system for both the pollutant and water. If one denotes the overall extraction efficiencies for the storm as ε_w (water vapor) and ε_p (pollutant), then it can be shown (Hales and Dana (1979)) from such a balance that

$$\xi = \frac{\varepsilon_p \rho_w}{\varepsilon_w H} ; \tag{36}$$

where ρ_w is the density of water, and H is the mass concentration of water vapor entering the cloud with the pollutant.

Considerable effort has been placed on the elucidation of ε_p and ε_w. Based on the concept of common mechanisms for water and pollutant removal (eg. nucleation, accretion) it has been suggested that ε_p and ε_w should be roughly equal to one-another, giving

$$\xi = \frac{\rho_w}{H} \tag{37}$$

which typically assumes numerical values in the range of 10^5.

Field measurements have shown that washout ratios of this order of magnitude often occur (Gatz 1972, Engelmann 1971). The associated variability is rather large, however, and this combined with more detailed examination of the scavenging mechanisms suggests that Equation 37 is applicable only as a general rule-of-thumb, and then only for particulate pollutants and rather specialized storm types.

Scott (1978) has recently extended scavenging-ratio theory by providing a more sophisticated model of mechanisms operating within the cloud environment. In this model a pollutant aerosol is attached to cloud droplets via a nucleation step, with subsequent incorporation into snow or rainwater via the processes of coagulation and accretion. The relative values of ε_p and ε_w depend on storm type and intensity, and Scott has subdivided his derived scavenging ratios into three following storm types:

- warm rain storms
- cold storms, where the Bergeron process is important in defining the character of the precipitation
- convective storms

Scott's initial calculations are summarized in Figure 11, which indicates that significant differences in ε should occur as a function of storm type. While these curves are extremely convenient for applied calculations, they are based strongly on assumed nucleating capabilities of the pollutant aerosol. They therefore should be applied with some caution, especially if the pollutant tends to be hydrophobic or distributed as a very fine aerosol with a correspondingly low nucleating capability. It also should be applied with caution in circumstances where competitive mechanisms may contribute to the presence of pollutant in percipitation. Examples of the occurence of competitive

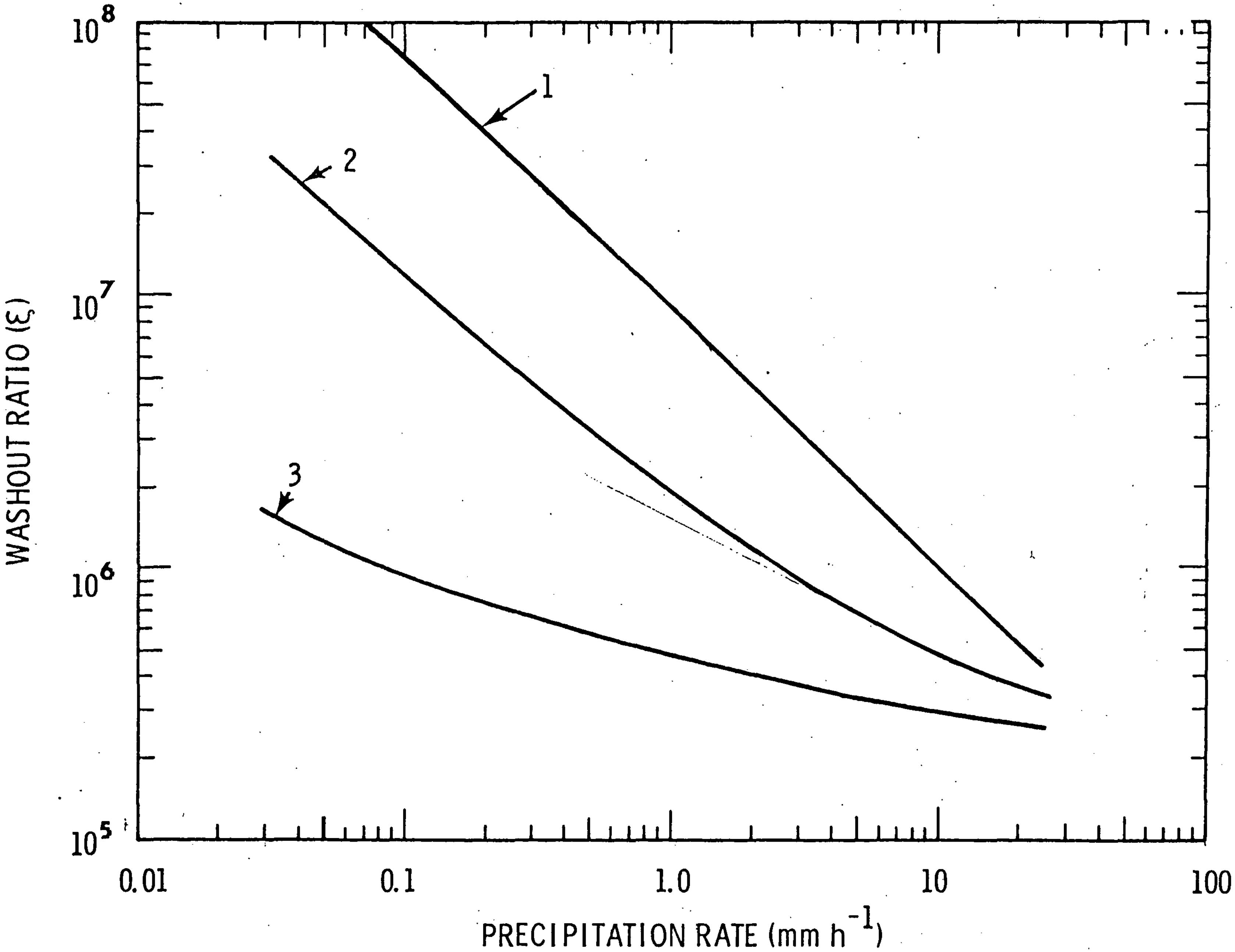

FIGURE 11 - Washout Ratios for Aerosols for Different Storm Types: 1) Convective Storms; 2) Warm-Rain Process Storms; 3) Bergeron-process Storms. Adapted from Scott (1978)

mechanisms include the processes leading to the presence of sulfate and nitrate in precipitation, which include both aerosol scavenging and the uptake of reactive gases.

In a subsequent analysis Scott (1979) has extended the above treatment to nonreactive gas scavenging via snowstorms*. Here the primary gathering mechanism is expected to be dissolution of the gas in supercooled droplets near the cloud base. From the equilibrium scavenging criterion given by Equation 34, the extent of this dissolution should be dictated simply by a solubility relationship. Subsequent delivery of SO_2 to the surface occurs by accretion of the supercooled droplets via a riming process.

Since the amount of supercooled cloudwater in a snowstorm is inversely related to temperature, Scott's model suggests that gas scavenging should be comparatively limited for storms occurring in very low temperature environments; this type of behavior has been observed experimentally in the case of SO_2 scavenging (Hales, et al 1971).

Other types of integral material balances have adopted the concept of a storm-averaged scavenging coefficient. If for example one expands the size of the volume element used for deriving the microscopic equations (1) and (2) so that it encompasses a total cloud system, then the interphase transport rate can be expressed in terms of an averaged scavenging coefficient and an average concentration:

$$\overline{w} = \overline{\Lambda}\ \overline{c_{Ay}}$$

By defining corresponding macroscopic terms for the divergence and (if necessary) the reaction terms, one can proceed directly to formulate an expression for

---

*In-cloud scavenging of nonreactive gases by <u>rainstorms</u> is usually a nonessential problem, owing to the reversible nature of the scavenging process, which focuses primary emphasis on processes that occur close to the ground.

the total system, which may be applied directly for practical use.* Before this is possible, however, one must determine appropriate values for $\overline{\Lambda}$.

A few examples of modeling efforts leading to storm-averaged scavenging coefficients are available. Slinn (1977) for example, begins with a rather general form of equation (1), inserts terms appropriate to describe the above-noted microphysical attachment mechanisms, and then averages over space and particle size to obtain a space-particle average scavenging coefficient. The resulting expression takes the form

$$\overline{\Lambda} = \frac{J\overline{\varepsilon}}{2\overline{R}_m} \tag{39}$$

where $\overline{\Lambda}$ is a spacially-averaged scavenging coefficient, J is the rainfall rate, and $\overline{R}_m$ is the volume-mean raindrop size at ground level. $\overline{\varepsilon}$ is given by a rather complicated expression reflecting particle-attachment and droplet growth behavior, and is predicted to vary with time. Although very few data exist to test Slinn's expression, tracer-release tests have been shown to fit Equation 39 reasonably well with an $\overline{\varepsilon}$ value of 1/3.

A second expression for a storm-average scavenging coefficient has been derived by Klett (1977) in his analysis of wet removal of nuclear debris. Basically this author has assumed complete attachment of pollutant to cloud particles of a given size distribution, and has integrated expressions for droplet capture by accretion to obtain formula for the scavenging coefficient and the rain rate. Combining these Klett arrives at the expression

$$\overline{\Lambda} = 4.2 \times 10^{-4}\ \overline{E}\ J^{0.79} \quad (\mathrm{sec}^{-1}) \tag{40}$$

---

*A simple example of such an expression is that for a spatially-homogeneous storm system, stationary in space, and involving a constant wind speed $\overline{u}$. Under such conditions the governing equation is

$$\frac{dc_{Ay}}{dx} = - \frac{\overline{\Lambda}}{\overline{u}}\ \overline{c}_{Ay}$$

where $\overline{E}$ is an average scavenging efficiency and the rainfall rate is expressed in units of mm/hr. Comparing with numerical solutions of the accretion equation for assumed cloud droplet spectra Klett suggests an $\overline{E}$-value of 0.83.

Integral material-balance approaches using storm-averaged scavenging coefficients offer some advantage over washout-ratio applications, because the former do not depend intrinsically on the assumption of a steady state. Moreover, the scavenging-coefficient approach is somewhat more satisfactory when vertical gradients of c_{Ay} are pronounced. Both approaches have had virtually no serious application for cases where reactive scavenging of gaseous materials occurs; although there have been some attempts to guess at values of ξ and $\overline{\Lambda}$, where the chemical conversion rate r_{Ax} has been rather crudely lumped with the physical removal terms of the governing equations. Much remains to be accomplished in this important research area.

3.5.2 Differential Material Balances

Given flow-field and thermodynamic properties one can integrate Equations 1 and 2, subject to appropriate initial and boundary conditions, and compute scavenging features that are more detailed than those made possible via the integral approach. Several examples of such computations exist (eg. Lange and Knox 1977, Watson, et al 1977). These tend to be mathematically involved and require machine computation; and up to the present time they have been limited by uncertainties regarding the local interphase transport term w_A. These uncertainties stem from the multitude of possible attachment mechanisms, and the usual procedure is simply to choose some constant value for the scavenging coefficient and incorporate into the overall formulation. The errors associated with this process are usually of such a magnitude that gross scavenging rates computed by this method are not significantly superior to those obtained from the simpler, integral formulations. Increased resolution of spatial and temporal variability provided by this modeling approach can be useful in specific situations, however, especially in the case of diagnosing physical behavior in field experiments. As with the integral approaches, very little progress has been made to date in the field of reactive-scavenging analysis.

3.5.3 Scavenging Models Involving Storm-Dynamics Computations

The material-balance approaches described in Sections 3.5.1 and 3.5.2 were based largely on the presumptions that velocity and/or temperature features of the storm systems were known in sufficient detail to allow essential computations to be performed. There are in existence, however, a number of rather detailed storm models which generate these features explicitly, and thus can be utilized potentially for more detailed scavenging analysis. Owing to relatively large computation requirements, the application of such models to date has not been extensive. Molenkamp (1977) has performed some limited scavenging calculations for aerosol using a one-dimensional convective-storm model, and Hane (1978) has utilized a two-dimensional model for this same purpose. Kreitzburg and Leach (1978) have performed more extensive scavenging computations using a detailed mesoscale model, which provides significant new insights regarding the characteristics of cyclonic storm systems.

As with the differential material balances described in Section 3.5.2, these models have been constrained largely to computations based on rather gross assumptions regarding interphase transport rates. Future applications with more detailed treatment of microphysical extraction mechanisms can be expected to provide some noteworthy advances to our understanding during future years.

3.6 Composite Regional Models

Thus far, this discussion has centered mainly on phenomena occuring in the vicinity of precipitating systems. This focus has allowed a much more detailed examination of the individual mechanisms of the scavenging process; and while the discussion has been conducted at a somewhat superficial level, some idea of the complexities of these mechanisms has emerged.

Against this backdrop it is of interest to consider the evolving set of regional models of pollution behavior. Because of their large time and distance scales, these models cannot afford the luxury of concentrating on one particular atmospheric pathway, such as wet removal; indeed, all pathways including long-range transport, chemical reaction, and dry deposition must be considered simultaneously.

The necessarily composite nature of such models introduces several new areas of uncertainty, and these combined with the mathematical complexity of solving equations such as (1) and (2) over extended distances has generally forced the characterization of most processes in highly parameterized form. In particular, wet removal has been treated principally in terms of simplified expressions for washout coefficients or washout ratios.

In principle there is nothing particularly limiting about the expression of wet removal in terms of Λ and ξ in such models. These parameters can vary with time and space as computation proceeds, and as long as one stipulates the correct values of these parameters at each computation point, valid results can be obtained. The challenge, of course, is in the selection of these values- a task which can be guided to some extent by the considerations in the preceeding text.

Regional-scale modeling is currently developing at an extremely rapid rate, and several examples exist where wet removal is treated in terms of different expressions for either ξ or Λ , as functions of storm type, precipitation rate, chemical species, and so forth. Many of these models are summarized in the recent review by Drake and his coworkers (1979).

The question regarding whether to select washout coefficients or ratios as a parameterization basis depends to some extent on the particular model being used, and also on the pollutant species in question. Regional scavenging of nonreactive (or psudeononreactive) gases such as SO_2 is usually treated most appropriately in terms of washout ratios, because of the natural relationship between ξ and the equilibrium-scavenging expression, Equation (33). Nonreactive aerosol scavenging, at the present state of understanding, can be treated equally well using either approach, unless serious vertical stratification of the gaseous-phase pollutant exists. Under such conditions the washout coefficient, which allows specific vertical integrations to be performed, is usually more appropriate. When reactive scavenging is involved, both techniques of parameterization are on rather uncertain grounds. Certainly reactive removal can be treated more specifically in terms of a non-integrated parameter such as Λ ; but thus far there has been little progress in this area, other than the practice of fitting values empirically to observed precipitation chemistry data. Much remains to be accomplished on this important research topic.

4. CONCLUSIONS

This paper has provided an overview of scavenging calculation techniques, and has summarized our present state of knowledge in this area of the atmospheric sciences. Obviously, there is much that is needed to be learned before we can attain a totally satisfactory capability in this regard; and in concluding this presentation it is worthwhile to reconsider the data shown in Figures 2-6, with the following question:

> Given the techniques for wet-removal calculation that currently exist, how well can we explain and/or predict the observed concentrations and their variability?

The answers to this question are somewhat mixed. Certainly the techniques discussed in Section 3, if used appropriately, are capable of order-of-magnitude determinations in many circumstances; and under restricted conditions they can even generate predictions having factor-of-two accuracy or better. Moreover, there is ample explanation in existing theories of wet removal to account easily for the spatial and temporal variability exemplified in Figures 2-6.

These capabilities, however, cannot be considered to be very satisfactory in the context of current needs. The noted ability to explain spatial and temporal variability on a semiquantitative basis has not resulted in any real competence in predicting such variability in specific instances. Moreover, we possess very little competence in identifying specific sources responsible for wet deposition at a given receptor site. Finally, the order-of-magnitude predictive capability noted above hardly can be judged satisfactory for most assessment purposes. In reviewing the discussion of Section 3 against the backdrop of these deficits, several research needs become apparent. The most important of these are itemized in the following paragraphs.

- Much more definitive information is needed with regard to the scavenging efficiencies of submicron aerosols, for both rain and snow. Especially important in this regard is the effect of condensational growth of such aerosols in below-cloud environments.

- We need to know much more about aqueous-phase conversion processes, which are potentially important as alternate mechanisms resulting in the presence of species such as sulfate and nitrate in precipitation. Since virtually nothing is known presently regarding the chemical formation of such species in clouds and precipitation, there is a tendency to lump these effects with physical removal processes in most modeling efforts, expressing them in terms of psuedo scavenging coefficients or collection efficiencies. Such phenomena must be resolved in finer mechanistic detail than this before a satisfactory treatment is possible, and this requires a knowledge of chemical transformation processes that is much more advanced than existing at the present time.

- Much more extensive understanding of the competitive nucleation capability of aerosols in in-cloud environments is needed, especially for those substances that do not compete particularly well in the nucleation process. The influence of aerosol-particle composition- especially for "internally-mixed*" aerosols- is particularly important in this regard.

- The identification of specific sources responsible for chemical deposition at a given receptor location requires that we possess a much more accomplished capability to describe long-range pollution transport. Progress in this area during recent years has been encouraging, but much more remains to be achieved before we have a proficiency that is really satisfactory for reliable source-receptor analysis.

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*Those containing individual particles composed of mixture of chemical species.

- We still need to enhance our understanding of the detailed microphysical and dynamical processes that occur in storm systems. Besides providing required knowledge of basic physical phenomena, such research is important in providing valid parameterizations of wet-removal for subsequent use in composite regional models.

As a final note, it is useful to reflect on the fact that scavenging modeling research- as treated in the context of this report, at least- has been in a rather continuous state of development over the past 30 years (cf. Fuquay (1970)). While progress has been indeed significant during this period, a number of important and unsolved problems still exist. Accordingly, one must be cognisant of this perspective in judging our rate of advancement during future years. Reasonable progress in resolving the above items can be expected over the next decade; but the complexity of these problems demands that a serious and sustained effort be applied to this purpose.

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NOMENCLATURE

a	Aerosol particle radius, l
A	Component identifier
c	Molar concentration of air, moles/l^3
c_{Ax}	Concentration of pollutant A associated with the aqueous phase, moles per unit volume of total space
c_{Ay}	Concentration of pollutant A associated with the gaseous phase, moles per unit volume of total space
$\hat{c}_A$	Concentration of pollutant A in a single raindrop, moles per unit volume of water
$\hat{C}_A$	Concentration of pollutant A in collected rainwater, moles per unit volume of water
D	Molecular (or Brownian) diffusivity, l^2/t
D_e	Diameter of sphere circumscribing a snow particle, l
E	Collection efficiency
f	Probability-density functions, l/l
F	Pollutant flux from a drop surface, moles/l^2t
h	Emission height, l
h'	Solubility parameter
H	Mass concentration of water vapor m/l^3
J	Precipitation rate, l/t (or flux, l^3/l^2t)
k_x	Aqueous-phase mass-transfer coefficient, moles/l^2t
k_y	Gaseous-phase mass-transfer coefficient, moles/l^2t
K_y	Overall mass-transfer coefficient, moles/l^2t
m	Mass concentration of aerosol particles, m/l^3
N_T	Number concentrations of raindrops, drops/l^3
Q	Pollutant sources strength, moles/t
r_{Ax}, r_{Ay}	Aqueous- and gaseous-phase chemical reaction rates, moles/l^3t
R	Raindrop radius, l
Re	Reynolds Number
S	Stokes Number
S_*	Crictical Stokes Number
Sc	Schmidt Number
Sh	Sherwood Number

t	Time, t
u	Wind velocity, l/t
v	Velocity, l/t
$\tilde{v}_{Ax}$	Velocity vector of aqueous-phase pollutant, l/t
$\tilde{v}_{Ay}$	Velocity vector of gaseous phase pollutant, l/t
v_{Axz}	Vertical component of aqueous-phase pollutant velocity vector, l/t
v_z	Hydrometeor fall velocity (negative downward), l/t
w_A	Interphase transport rate of pollutant to the aqueous phase from the gaseous phase, moles/l^3t
x	Coordinate, l; also aqueous phase designation
y	Coordinate, l; also gaseous phase designation
z	Coordinate, l
ε_w, ε_p	Cloud extraction efficiencies for water and pollutant
Γeq	Dimensionless group defining equilibrium scavenging conditions
ζ	Parameter used in equations (31) & (32), l/l
ξ	Washout ratio; also parameter used in equation (31), moles/l^4
Λ	Washout coefficient, l/t
σ_y, σ_z	Plume-spread parameters, l
ρ	Density, m/l^3
$\nabla.$	Vector divergence operator, l/l

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