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Air Quality Criteria for Particulate Matter and Sulfur Oxides --

Chapter 6: Atmospheric Transport, Transformation, and Deposition

Chapter 6 Was Inadvertently Omitted from the Volume III Printing.

NOTICE

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.

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Office of Health and Environmental Assessment
Office of Research and Development
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NOTE TO READER

The Environmental Protection Agency is revising the existing criteria documents for particulate matter and sulfur oxides (PM/SO_x) under Sections 108 and 109 of the Clean Air Act, 42 U.S.C. §§ 7408, 7409. The first external review draft of a revised combined PM/SO_x criteria document was made available for public comment in April 1980.

The Environmental Criteria and Assessment Office (ECAO) filled more than 4,000 public requests for copies of the first external review draft. Because all those who received copies of the first draft from ECAO will be sent copies of the second external review draft, there is no need to resubmit a request.

To facilitate public review, the second external review draft will be released in five volumes on a staggered schedule as the volumes are completed. Volume I (containing Chapter 1), Volume II (containing Chapters 2, 3, 4, and 5), Volume III (containing Chapters 6, 7, and 8), Volume IV (containing Chapters 9 and 10), and Volume V (containing Chapters 11, 12, 13, and 14) will be released during January-February, 1981. As noted earlier, they will be released as volumes are completed, not in numerical order by volume.

The first external review draft was announced in the Federal Register of April 11, 1980 (45 FR 24913). ECAO received and reviewed 89 comments from the public, many of which were quite extensive. The Clean Air Scientific Advisory Committee (CASAC) of the Science Advisory Board also provided advice and comments on the first external review draft at a public meeting of August 20-22, 1980 (45 FR 51644, August 4, 1980).

As with the first external review draft, the second external review draft will be submitted to CASAC for its advice and comments. ECAO is also soliciting written comments from the public on the second external review draft and requests that an original and three copies of all comments be submitted to: Project Officer for PM/SO_x, Environmental Criteria and Assessment Office, MD-52, U.S. Environmental Protection Agency, Research Triangle Park, N. C. 27711. To facilitate ECAO's consideration of comments on this lengthy and complex document, commentators with extensive comments should index the major points which they intend ECAO to address, by providing a list of the major points and a cross-reference to the pages in the document. Comments should be submitted during the forthcoming comment period, which will be announced in the Federal Register once all volumes of the second external review draft are available.

6. ATMOSPHERIC TRANSPORT, TRANSFORMATION, AND DEPOSITION

6.1 INTRODUCTION

Preceding chapters of this criteria document discussed the physical and chemical properities of sulfur oxides and particulate matter (Chapter 2); their sources and emissions (Chapter 4) and measurements of their ambient levels in urban and rural environments. (Chapter 5). These chapters in part, addressed material which is relevant to portions of the subject matter to follow. Whenever possible reference to detailed resource material in previous chapters is made so long as clarity of presentation is preserved.

The purpose of this chapter is to review our present knowledge of the physical and chemical processes contributory to the transport, transformation and deposition of particulate matter and sulfur oxides in the atmosphere and to discuss the theoretical approaches for integrating these processes with source emission contributions through the use of mathematical models. Such integrating approaches provide a vehicle for improved understanding and conceptualization of the complex processes operative in polluted atmospheres, and through these source receptor relationships provide a means to a sound, creditable scientific basis for determining the nature and extent of emission control required to meet specified ambient air quality levels.

The concentration of a pollutant species at some fixed point in time and space after being emitted from a source at a given distance away is dependent upon four fundamental factors. These factors are as follows: 1) emission--the rate of pollutant emitted and the configuration of its source; 2) transformation--the chemical and physical reaction processes which convert one pollutant species to another; 3) transport and diffusion--the movement and dilution of a pollutant species through time and space as a result of various meteorological variables; and 4) deposition--the removal of a pollutant species through their interaction with land and water surfaces (dry deposition) and through interaction with precipitation or cloud condensation nuclei (wet deposition).

The principal pathway processes of airborne pollutants are schematically illustrated in Figure 6-1. Ideally each of these processes should be treated explicitly in the air quality simulation model, but this is typically not the case. In this chapter three of the factors, transformation, transport and diffusion, and deposition are discussed in detail as they constitute major theoretical components of the air quality simulation model. Emissions, which can be viewed more as a model input, are discussed only in the context of their relevancy to air quality simulation modeling in the final section.

It should be noted, that the modeling approaches discussed within this chapter consider explicit treatments of the dynamic physical and chemical processes operative in the atmosphere to simulate the relationship between pollutant emission and ambient air quality. More implicit statistical-empirical approaches, which deduce source contribution through analysis of

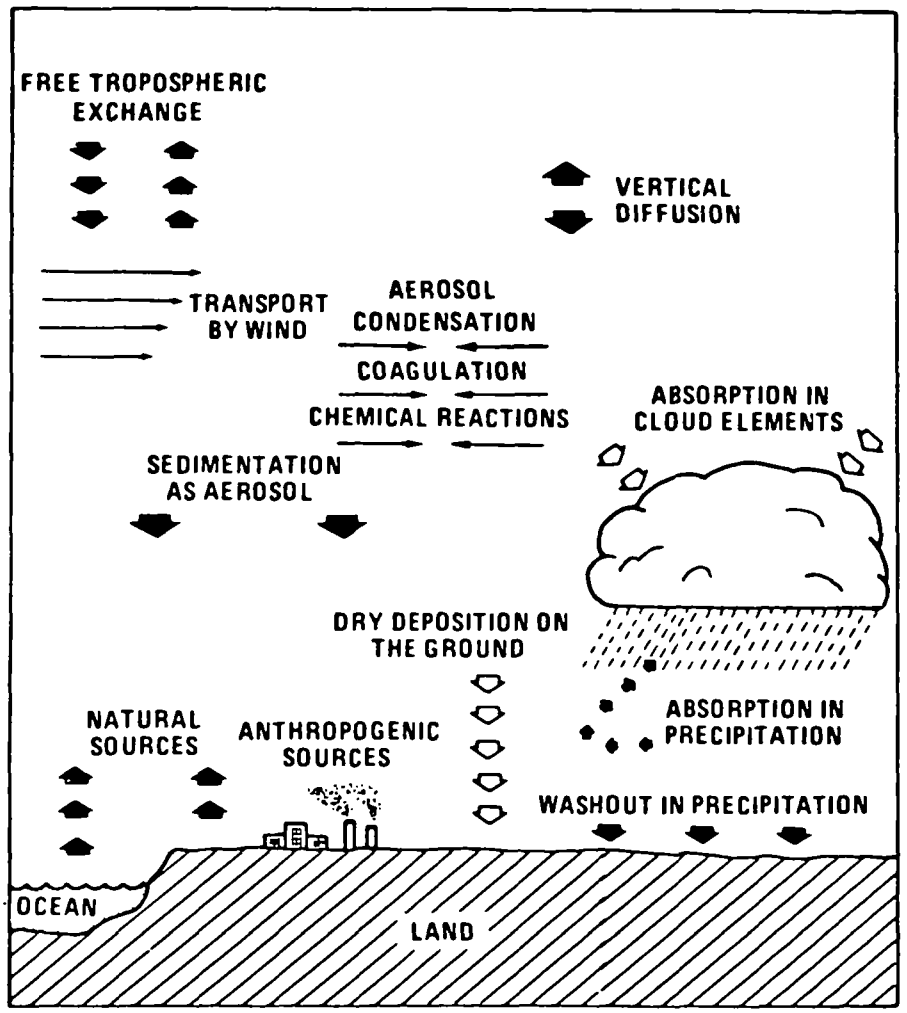

Figure 6-1. Pathway processes of airborne pollutants.

Source: Adapted from Drake and Barrager(1979).

empirical information only, are not within the purview of this chapter. One specific technique, chemical factor analysis, has shown considerable promise in developing source-receptor relationships for particulate matter and is discussed in Chapter 5.

6.2 CHEMICAL TRANSFORMATION PROCESSES

A detailed discussion of the chemistry of SO_2 and that of other gases reacting to form particulate matter in the atmosphere has been presented in Chapter 2. Section 6.2.1 provides a brief summary of the results on the atmospheric chemical transformation processes of SO_2 and particulate matter presented in Chapter 2. Section 6.2.2 reviews the status of field measurements on the rate of SO_2 oxidation in industrial and urban plumes; and their contribution to elucidating the transformation pathway processes of SO_2 oxidation.

6.2.1 Chemical Transformation of SO_2 and Particulate Matter

Present understanding of the homogeneous gas phase reactions of SO_2 indicates that the rate of SO_2 oxidation in the atmosphere is dominated by free radical reaction processes. The free radical species identified as important contributors to the SO_2 oxidation process are hydroxyl (HO), hydroperoxy (HO_2), methylperoxy (CH_3O_2) and other organic peroxy species (RO_2, $R'O_2$, etc.). The concentration of these radicals in the atmosphere are dependent on many factors, the more important of which are the concentration of volatile organic compounds and nitrogen oxides (NO and NO_2) in the atmosphere, temperature and solar intensity. Theoretical estimates have shown that maximum SO_2 oxidation rates of 4.0% h^{-1} are possible in polluted atmospheres. But, recent experimental rate constant determinations for the HO_2 and CH_3O_2 reactions with SO_2 indicate that these processes may not be as important as previously thought and that the maximum possible homogeneous SO_2 oxidation rate under optimum atmospheric conditions may only be of the order of 1.5% h^{-1}. This rate is a result of SO_2 reaction with hydroxyl radical only.

Present knowledge of heterogeneous pathways to SO_2 oxidation in the atmosphere indicates that the liquid phase catalyzed oxidation of SO_2 by Mn ion and carbon are potentially important processes. Theoretical estimates of atmospheric SO_2 oxidation rates via these processes are of the order of 10% h^{-1}. Unfortunately, a great deal of uncertainty surrounds the actual availability of these catalyzing substances in ambient fine particulate matter. The quantitative determination of rates of SO_2 oxidation via these processes has never been demonstrated under actual atmospheric conditions.

Organic and nitrate particulate matter forming processes are presently thought to be dominated by homogeneous gas phase reactions. In the case of atmospheric nitrates, a particularly significant production pathway is through reaction between hydroxyl free radical and nitrogen dioxide resulting in nitric acid ($HONO_3$) formation. The fate of nitric acid in the atmosphere is not well understood, though a portion of gaseous nitric acid is known to enter into an equilibrium with ammonia (NH_3) to form particulate ammonium nitrate (NH_4NO_3). Information on the production rates and mechanistic details of organic particulate matter is

very limited. The product information which is available indicates that oxidation reactions, involving the interaction of ozone, nitrogen oxides and hydroxyl free radicals with higher molecular weight organics represents a major pathway to organic particulate matter production.

6.2.2 Field Measurements on the Rate of SO_2 Oxidation

The majority of SO_2 oxidation studies in the atmosphere have been only carried out in recent years and of those, most have involved power plant plumes. One reason for the late start in this research area has been the lack of adequate measurement technology for particulate sulfur, but recent developments Huntzicker et al. (1978), Cobourn et al. (1978) seem to have alleviated this problem. A summary of SO_2 oxidation rates based on field measurements in power plant, smelter and urban plume studies carried out from 1975 to the present is given in Table 6-1. The rates of SO_2 oxidation in industrial plant plumes consistently range from 0 to 10%/h, with urban plumes showing only a slightly greater maximum rate of 13%/h. The pre-1975 studies', Gartrell et al. (1963), Dennis et al. (1969), Weber (1970) and Stephens and McCalden (1971), which observed conversion rates an order magnitude larger than more recent observations, must be considered suspect due to possible artifact formations in the sulfate analysis technique and limitations in the analytical methods in general.

Newman (1980) recently reviewed the majority of the power plant and smelter plume studies presented in Table 6-1 and arrived at the following conclusions.

1) The diurnal average oxidation rate of sulfur dioxide to sulfate is probably less than 1% per hour.
2) Little or no oxidation of sulfur dioxide occurs from early evening through to early morning.
3) Maximum oxidation rates of sulfur dioxide to sulfur of 3% per hour can occur under midday conditions.
4) The contribution of homogeneous and heteorogeneous mechanisms to sulfur dioxide oxidation in plumes cannot be elucidated from the present studies.

It should be noted that the reported SO_2 oxidation rates are estimates based on analyses of measured physical and chemical parameters and in many instances have incorporated within them certain simplifying assumptions which are not totally substantiated. Typical uncertainties in reported values are 50%, but may be greater if inappropriate assumptions have been used. Even with these uncertainties in mind, the overall consistency in the observed range of SO_2 oxidation rates is gratifying.

6.3 PHYSICAL REMOVAL PROCESSES

The removal of particulate matter and gases from the atmosphere occurs predominantly via two physical processes. These are dry deposition, the removal of chemical species from the atmosphere at the air surface interface, and precipitation scavenging, the removal of chemical species from the atmosphere by interaction with various types of precipitation such as rain, snow, etc. These processes prove to have both a positive and negative impact with respect to

TABLE 6-1. FIELD MEASUREMENTS ON THE RATES OF SO_2 OXIDATION IN PLUMES*

Plume Type Location	SO_2 Oxidation Rate ($\%h^{-1}$)	Method	Reference
Keystone (Pennsylvania)	0-10	$^{32}S/^{34}S$ ratio, change with oxidation	Newman et al. (1975)
Labadie (Missouri)	0.41-4.9	Total change in particle volume	Cantrell and Whitby (1978)
Four Corners (New Mexico)	0.27-0.84	Sub-micron sulfate and SO_2 - change of ratio with time	Ursenbach et al. (1977)
Labadie and Portage des Sioux (Missouri) Muscle Shoals (Alabama) Kyger Creek (Ohio)	0-5	Particulate sulfur to total sulfur ratio	Forrest and Newman (1977)
Labadie (Missouri)	0-3	Particulate sulfur to total sulfur ratio	Gillani et al. (1978)
Four Corners (New Mexico)	2-8	CCN production (CCN to SO_2 ratios)	Pueschel and Van Valin (1978)
Labadie (Missouri)	0-4	Particulate sulfur to total sulfur ratio	Husar et al (1978)
Cumberland (Tennessee)	0-7	Particulate sulfur to total sulfur ratio	Meagher et al. (1978)
Great Canadian Oil Sands (Alberta, Canada)	0-3	Particulate sulfur to total	Lusis et al. (1978)
Keystone (Pennsylvania)	0-5	Particulate sulfur to total sulfur ratio	Dittenhoefer and dePena (1978)
Centralia (Washington) Four Corners (New Mexico)	0-6	Total change in particle volume	Hobbs et al. (1979)
Four Corners (New Mexico)	0.15-0.5	CCN production (CNN to SO_2 ratios)	Mamane and Pueschel (1980)

TABLE 6-1 (Continued).

Plume Type	SO_2 Oxidation	Method	Reference
Leland-Olds (North Dakota) Sherburne County Minnesota Big Brown (Texas)	0-5.7	Total change in particle volume	Hegg and Hobbs (1980)
Smelter			
INCO Nickel (Copper Cliff Canada)	0-7	Particulate sulfur to total sulfur rates	Lusis and Wiebe (1976)
INCO Nickel (Copper Cliff, Canada)	1.2-5.2	Particulate sulfur to total sulfur rates	Forrest and Newman (1977)
Mt Isa Mines (MTISA, Australia)	0.25†	Particulate sulfur to lead ratio	Roberts and Williams (1979)
Urban			
Los Angeles California	1.2-13	Particulate sulfur to total sulfur ratio	Roberts and Friedlander (1975)
St. Louis Missouri	7-12.5	Particulate sulfur to total sulfur ratio	Alkezweeny and Powell (1977)
St. Louis Missouri	3.6-4.2	Particulate sulfur to total sulfur ratio	Chang (1979)

*Adapted in part from Hegg and Hobbs (1980)
†diurnal average rate

environmental air pollution issues. On the one hand, they constitute the major mechanisms by which the polluted atmosphere cleanses itself, lowering ambient air concentrations of pollutant species and thereby reducing health related risks, but on the other hand the deposited pollutant materials may introduce increased risks to our terrestrial and aquatic ecosystems.

Since wet and dry removal processes significantly affect the lifetime of SO_2 and particulate matter in the atmosphere and thereby affect the distance traveled and concentration of these species, understanding these processes is essential if proper assessment of their environmental significance is to result. The removal of pollutant species by dew fall has not been studied and remains for future research to determine if this process is an important removal mechanisms for atmospheric contaminants.

In the sections to follow, discussion on dry deposition and precipitation scavenging are presented with emphasis on experimental data bases and theoretical treatment.

6.3.1 Dry Deposition

Extensive surveys in the area of particle and gas dry deposition have been performed over the years, several recent examples are reviews by Sehmel (1980), McMahon and Denison (1979), Chamberlain (1980) and Garland (1978). The dry deposition of sulfur dioxide and particulate matter, as with other atmospheric species is governed by three major components: meteorological variables, properties of the depositing pollutant and surface variables. These components are influenced by specific parameters which interact in complex ways that in many instances are not completely understood.

The most important meteorological processes affecting dry deposition are transport related phenomena. These transport processes are governed by the wind and temperature profiles, by eddy diffusion and by sedimentation across the boundary layer to the canopy. They are strongly influenced by two meteorological parameters, the friction velocity, u_* and the aerodynamic surface roughness, z_0. Both of these parameters are used to describe the wind speed profile above a given surface under given conditions of atmospheric stability. Typically these two variables are determined empirically by fitting wind speed data as a function of height. The strong diurnal dependence of dry deposition is linked to the formation of a stable layer of air at the earth's surface at night (nocturnal inversion) which affectively inhibits the vertical transport of pollutant species to the canopy surface. The formation of the nocturnal inversion and its affect on other atmospheric processes is discussed in the section on transport and diffusion.

Important properties influencing the dry deposition of a pollutant are its solubility in water and for particulate matter, specifically, its size distribution density, morphology and composition. Important properties of the surface include: 1) the moisture content of the surface which in conjunction with the solubility of the pollutant species will govern the overall sticking efficiency of the deposited material; and 2) the physiological state of the

vegetation surface, most importantly the the opening and closing of stomata pores, where the rate of pollutant uptake is thought to be strongly governed.

Chamberlain and Chadwick (1953) introduced a convenient way to express the rate of dry deposition of both gases and particles in the form of a velocity term. Dry deposition velocity, defined as the downward flux F of the species, divided by its ambient concentration x at some specified height (typically 1-2 meters above the surface), is the standard form in which all measured deposition rates are reported. Dry deposition velocities are typically reported in units of cm s^{-1}.

$$v_d = \frac{-F}{x}$$

Dry deposition velocity is positive by convention and therefore requires a minus sign on F, the downward flux which is defined as negative.

Measurement techniques for the dry deposition of pollutant species have been recently reviewed and critiqued by Hicks et al. (1980). In this work measurement methods were sorted into three major categories: 1) estimates of accumulation, 2) flux monitoring, and 3) flux parameterization.

Though none of the experimental techniques developed to date has proven to be a panacea in dry deposition measurements, a consensus of opinion on the overall accuracy of the methods and their suitability for specific applications has generally been reached. Based on Hicks et al. (1980) the three categories are described briefly with general comments on their limitation.

Estimates of accumulation maybe considered using atmospheric radioactivity or mass balance methods. Radioactive techniques compare ambient concentration of selected radioactive species with concentrations in water bodies vegetation, etc. to evaluate the rate of input of the material into the ecosystem over long term periods. The technique is typically limited to small particle uptake of long lived species and has difficulty distinquishing between dry and wet removal and resolving short term variations. Mass balance studies attempt to measure the various inflow and outflow processes in the ecosystem, with the exception of the dry deposition, which is then determined through a budget calculation. The major limitation of the method is that the dry deposition is inferred by indirect measurements which in themselves are difficult to measure accurately.

Flux monitoring considers the direct measurements of total deposition over a well defined surface for set periods of time. Several types of deposition surfaces have been used with this general category including: open pots, flat filters, flat plates and shallow pans, fiber filters and sticky films. Overall, the methods are limited due to their lack of standardization, unrepresentativeness of natural surfaces and potential for contamination by locally resuspended particles.

Flux parameterization includes a variety of methods, one of which, eddy correlation has shown significant promise as a measurement standard for the dry deposition of gases. The

technique requires the simultaneous measurement of the concentration of pollutant species and the vertical component of the wind velocity at a sufficiently fast enough rate to determine the turbulent flux of the pollutant concentration. A significant limitation of the technique is the lack of adequate fast-response instrumentation for many of the pollutant species of interest. In addition, particle flux due to gravitational settling is not detected and can produce invalid results if significant particle resuspension is occurring. Also considered under the flux parameterization category are laboratory methods including chamber and wind tunnel studies. In these controlled experimental studies, plants, leaves, or simulated canopy surfaces, etc. are exposed to known amounts of pollutant concentration. Measurements in the change in concentration, which can be accomplished by a variety of methods, is then used to determine pollutant uptake.

6.3.1.1 Sulfur Dioxide Dry Deposition--The dry deposition of SO_2 to grass, crops, forests, soil and building surfaces has been reviewed in recent years by Sehmel (1980), McMahon and Denison (1979) Chamberlain (1980) and Garland (1978). Compilations of dry deposition laboratory and field measurements of SO_2 have been presented in McMahon and Denison (1979). A review of these results indicates measured dry deposition velocities ranging from 0.04 to 3.7 cm-sec^{-1}, but with the majority residing in the range 0.3 to 1.6 cm-sec^{-1}. The apparently wide range of dry deposition values is not particularly disconcerting when the variety of surfaces, meteorological conditions, and experimental methods is taken into consideration.

A summary of the average dry deposition velocity by surface type is presented in Table 6-2.

TABLE 6-2. AVERAGE DRY DEPOSITION VELOCITY OF SO_2 BY SURFACE TYPE

Surface	Laboratory Measurement, v_g(cm sec^{-1})	Field Measurement, v_g(cm sec^{-1})
Alfalfa	1.2 (2)	1.6 (2)
Grass	-	1.1 (14)
Wheat	-	0.4 (3)
Forest	-	1.4 (5)
Sandy Soil	0.6 (2)	-
Clayey Soil	0.8 (2)	-
Soil	-	1.2 (4)
Land	-	1.2 (4)
Water (Fresh)	-	1.1 (6)
Ocean	-	0.5 (2)
Snow	-	0.3 (2)

Note: Values in parenthesis indicate the number of separate studies used to obtain the average deposition velocity.

In reviewing predominantly the same set of data Garland (1978) concluded that the mean deposition velocities for SO_2 over surfaces ranging from water and soil through short grass to forest were very similar and suggested a value of about 0.8 cm s^{-1} to be quite applicable to large areas of Europe.

Sheih et al. (1979) in a more detailed effort to estimate dry deposition velocities of sulfur dioxide and particulate sulfate over the eastern half of the United States, southern Ontario and nearby oceanic regions, computed deposition velocities as a function of land use characteristics, surface roughness scale lengths and surface resistances to pollutant uptake. Gridded dry deposition velocities maps of sulfur dioxide and sulfate corresponding to half degree increments of longitude and latitude were computed for a range of atmospheric stabilities. The results indicate that deposition velocity distributions for sulfur dioxide are rather nonuniform for the less stable atmospheric conditions. For very unstable, Pasquill category A, atmospheric conditions dry deposition velocities over the eastern U.S. ranged from 0.4 to 0.9 cm s^{-1} (excluding water surfaces) for sulfur dioxide, with a mean area wide dry deposition velocity of approximately 0.6 cm s^{-1}. Under the same conditions sulfates ranged from 0.7 to 0.9 cm s^{-1} with a mean value of approximately 0.8 cm s^{-1}. Sheih et al. (1979) note that under near calm conditions at night, stability classification schemes do not adequately represent the nocturnal inversion formed at the surface and recommend that a dry deposition velocity of 0.07 cm s^{-1} be assumed for both sulfur dioxide and sulfate particles.

6.3.1.2 Particle Dry Deposition--The dry deposition of particulate matter is considerably less understood from the viewpoint of measurements for pollutant species of interest. In the reviews by Sehmel (1980) and McMahon and Denison (1979), deposition velocities for particle species are compiled for both artificial and natural surfaces. Unfortunately, with the exception of lead particles from automotive exhaust, virtually no data existed for the other important particulate pollutants, such as sulfates, nitrates, and carbon containing particles. An additional problem arises in the interpretation of the relationship between deposition measurements on fallout collectors to that of dry deposition rates on natural surfaces. Fallout collectors which were used in a significant portion of the measurements reported, typically do not have the characteristics of the surfaces they are attempting to simulate.

Tables 6-3 and 6-4 from McMahon and Denison (1979) present a compilation of literature values for the deposition velocities of particles measured under laboratory and field conditions. The data cover a range of surface variables, particle sizes and composition, and meteorological conditions. A review of the data indicate:

- -- Deposition in nature varies considerably via processes which are not totally understood.
- -- The minimum deposition velocity for a particle is in a size range of 0.1 to 1.0 μm diameter.
- -- Deposition velocities are often reported for particle diameters and size distributions that do not reflect typical atmospheric particulate matter characteristics.

TABLE 6-3. LABORATORY MEASUREMENTS OF DEPOSITION VELOCITIES OF PARTICLES

Author (date)	v_g (cm s^{-1})	Reference height (m)	Particulate diameter (μm)	Surface	Comment
Chamberlain (1967)	0.03 0.03 0.1 0.8		0.1 1 2 5	Grass	
Möller and Schumann (1970)	$v_g \propto D^{2/3}$				D = diffusion coefficient $2 \times 10^{-2} \geq D \geq 2 \times 10^{-5}$ cm^2 s^{-1}
Chamberlain and Chadwick (1972)	$v_g = 0.06u_*$ $v_g = 0.12u_*$		20–30	Cereal crops	Dry Wet Includes wind-tunnel and field data
Clough (1973)	0.005 0.003 0.3 2	0.1	0.08 0.5 5 20	Filter paper	v_g to copper also measured. v_g found to be a function of wind speed.
Sehmel (1973)	2×10^{-3}–10	0.01	0.1–28	Smooth brass	See Fig. 1
Sehmel and Sutter (1974)	5×10^{-3}–29	0.01	0.2–30	Water	See Fig. 1
Belot and Gauthier (1975)	$v_g \propto u^3$ $v_g \propto d^4$		1–10	Shoots of pine and oak trees	u = wind speed d = particle diameter
Klepper and Craig (1975)	0.0035		0.8	Bean leaves	
Craig *et al.* (1976)	0.01		0.1–1	Smooth	Wind-tunnel
Wedding *et al.* (1976)					Deposition rate on pubescent leaves of sunflower was nearly 7 times that of the non-pubescent leaves of tulip poplar.
Little and Wiffen (1977)	0.11 0.02		5×10^{-2} 0.2	Short grass	
Little (1977)	0.5 0.04 0.3		2.75	Nettle Beech White Poplar	These data are for whole shoots for wind speeds of 2.5 m s^{-1}. Data for other wind speeds and separate plant surfaces are given in reference.
	0.9 0.1 0.3		5	Nettle Beech White Poplar	
	1.5 0.3 0.8		8.5	Nettle Beech White Poplar	

TABLE 6-4. FIELD MEASUREMENTS OF DEPOSITION VELOCITIES OF PARTICLES

Author (date)	v_g (cm s^{-1})	Reference height (m)	Particulate diameter (μm)	Surface	Comment
Chamberlain (1953)	2.1	0.3–0.9	16	Grass	u = 9.2 m/s
	1.1	0.3–0.9	16		u = 3.2 m/s
	0.5	0.3–0.9	16		u = 1.1 m/s
Eriksson (1959)	0.7			Ocean	Chloride over Scandinavia
	1.6			Land	
Small (1960)	0.5 (0.2–3.4)			Land	Radioactive particles over Norway
Neuberger *et al.* (1967)			Rag-weed	Coniferous forest	80% rag-weed pollen removed from air by forest
White and Turner (1970)	5.6		Na	Mixed deciduous woodland	1. Probable overestimation of aerosol income, hence v_g. 2. Standard deviation varied between 65 and 95% of mean v_g.
	4.7		K		
	3.0		Ca		
	7.1		Mg		
	0.8		P		
Esmen and Corn (1971)	$v_g = 0.5D$		0.1–10	Filter paper, Millipore filter, Glass slide	
Chamberlain and Chadwick (1972)	$v_g = 0.06u_*$		20–30	Cereal crops	Dry, Wet: Includes wind-tunnel and field data.
	$v_g = 0.12u_*$				
Pierson *et al.* (1973)	0.1–0.6			Land	v_g estimated for 23 trace elements based on several years of data
Cawse (1974)	1.3		Al		Extracted from Gatz (1975). Values in parentheses were estimated by Gatz from a relationship between particle size and v_g.
	0.22		As		
	(0.45)		Cd		
	0.50		Cr		
	(0.50)		Cu		
	1.1		Fe		
	0.56		Mn		
	(0.45)		Ni		
	0.30		Pb		
	(1.0)		Ti		
	0.29		V		
	0.62		Zn		
Hart and Parent (1974)			Na, Ca, Mg, K, P, NO_3	Douglas fir and junipers	$\frac{\text{Deposition beneath trees}}{\text{open terrain}} = 3–16$
Clough (1975)	3.4		30	Grass	Dry $u_* = 37$ cm s^{-1}
	7.3			Grass	Dry $u_* = 87$ cm s^{-1}
	11			Grass	Wet $u_* = 87$ cm s^{-1}
	61			Dry moss	
	100			Wet moss	
	0.74		4	Grass	Dry $u_* = 37$ cm s^{-1}
	1.1				
	0.75		3	Grass	Dry $u_* = 37$ cm s^{-1}
	12.7			Dry moss	
Abrahamsen *et al.* (1976)			SO_4^{2-}	Spruce and pines	$\frac{\text{Deposition beneath trees}}{\text{open terrain}} = 2$
Dovland and Eliassen (1976)	0.16		atmospheric aerosol	Snow	Lead
	0.68				SO_4^{2-}: upper bound value
Fritschen and Edmonds	0.07		3	Douglas fir	
	0.46				
Prahm *et al.* (1976)	0.4		atmospheric aerosol	Atlantic ocean	SO_4^{2-}
Krey and Toonkel (1977)	0.5				90_w: HASL wet-dry collector
Wesley *et al.* (1977)	0.6	5	0.05–0.1	Bare soil and grass	$u < 2$ m s^{-1}; Eddy correl method.

The large experimental uncertainties associated with particle dry deposition velocity measurement has stimulated the development and application of theoretical models for simulating the dry deposition process and predicting dry deposition velocities given specific meteorological data, Sehmel (1980), Slinn (1978, 1977), and Davidson and Friedlander (1978). The models describe only the physical processes of bringing the particle to the depositing surface. No consideration has been given to particle shapes other than spherical, to particle composition, or to surface properties with regard to particle retention. Particle size, an important property in the aerodynamic flow of particles to surfaces, is considered. The typical model result, shows predicted deposition velocities to increase as surface roughness and/or friction velocity increases and to be nearly independent of atmospheric stability. The deposition velocity for particles passes through a minimum in the 0.1 to 1 μm diameter particle range.

Figure 6-2 (Sehmel 1980) presents predicted deposition velocities at 1 meter from the surface, for $u_* = 30$ cm s^{-1} and particle densities of 1,4, and 11.5g cm^3, ($g/cm^3 = \mu g/m^3$).

In Table 6-5 the range of predicted deposition velocities at a height of 10 meters is presented for two particle size regions and for a range of aerodynamic surface roughness lengths, mean wind speeds, and calculated friction velocities. These results are based on data presented in Sehmel (1980) and should be fairly representative of the majority of meteorological and surface conditions encountered in the environment.

6.3.2 Precipitation Scavenging

As with dry deposition, precipitation scavenging or wet removal results from a series of complex physical and chemical interactions involving properties of the scavenging media and the species removed. Research in the area has continued for over the past thirty years, focusing on the removal of radioactive debris from the atmosphere introduced by nuclear weapons testing Bowen, (1960), Engelmann, (1968) and Volchok, et al. (1971), and in conjunction with material balance or budget studies on the removal of various elemental species from the atmosphere, Robinson and Robbins (1970), Rasmussen et al. (1975) and Junge (1972, 1974).

The fundamentals of the theory of precipitation scavenging have been researched and reviewed over the years, by Engelmann (1968), Postma (1970), Hales (1972), Slinn, et al. (1978) and Slinn (1981). Though our understanding of the details of the complex processes operative in precipitation scavenging is less than complete, significant progress has been made in elucidating the general scavenging pathways and developing appropriate parameterizations for their quantitative treatment. As pointed out by Slinn (1981) and others, the removal of trace constituents from the atmosphere by precipitation scavenging is dependent on four basic factors: 1) the position of the trace constituent relative to the scavenging media; 2) the physical form of the scavenging media; 3) the chemical and physical properties of the trace constitutent; and 4) the specific physical/chemical process that is operative. These basic factors are schematically illustrated in Figure 6-3.

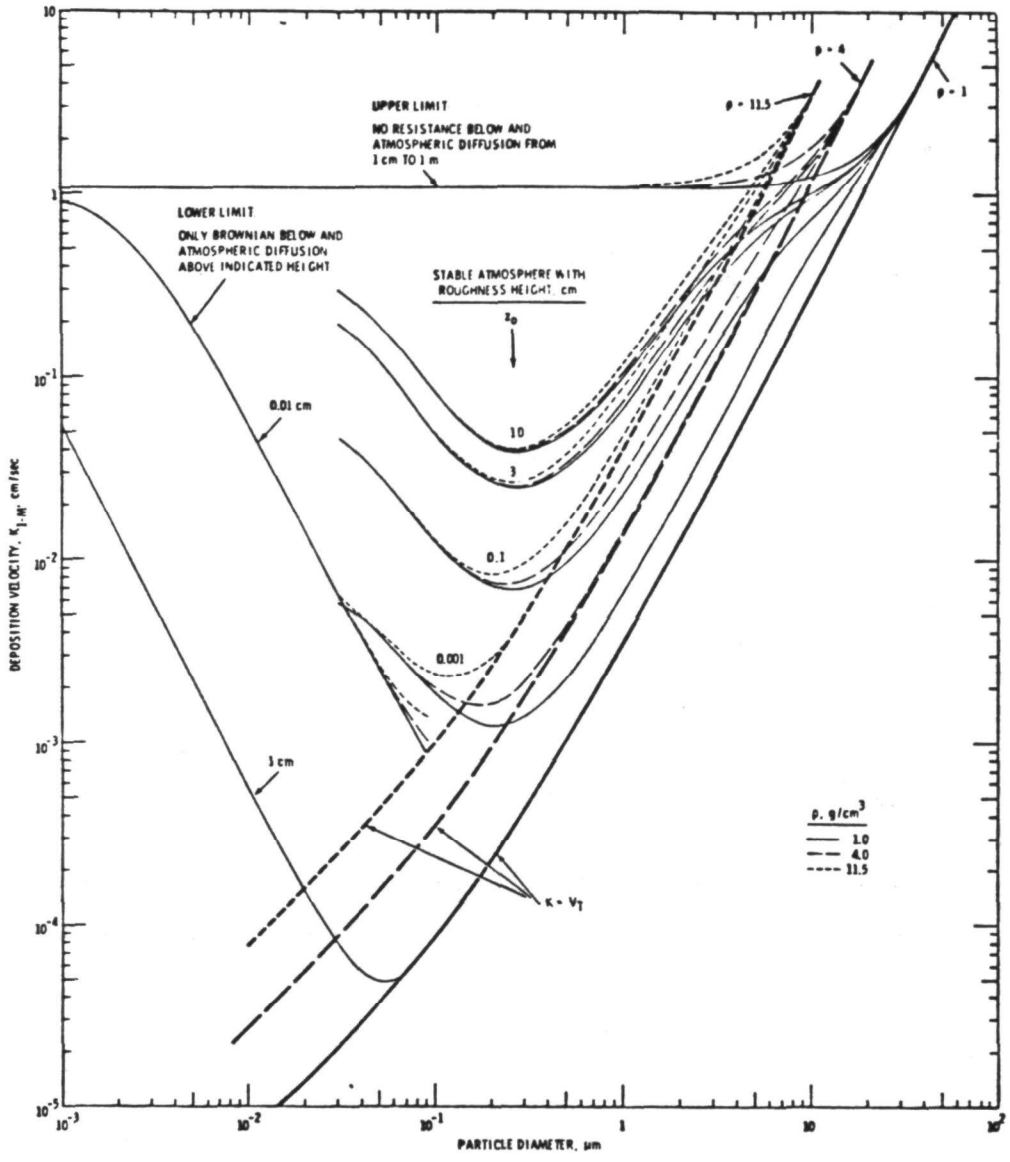

Figure 6-2. Predicted deposition velocities at 1 m for $\mu_* = 30$ cm s^{-1} and particle densities of 1, 4, and 11.5 g cm^{-3}.

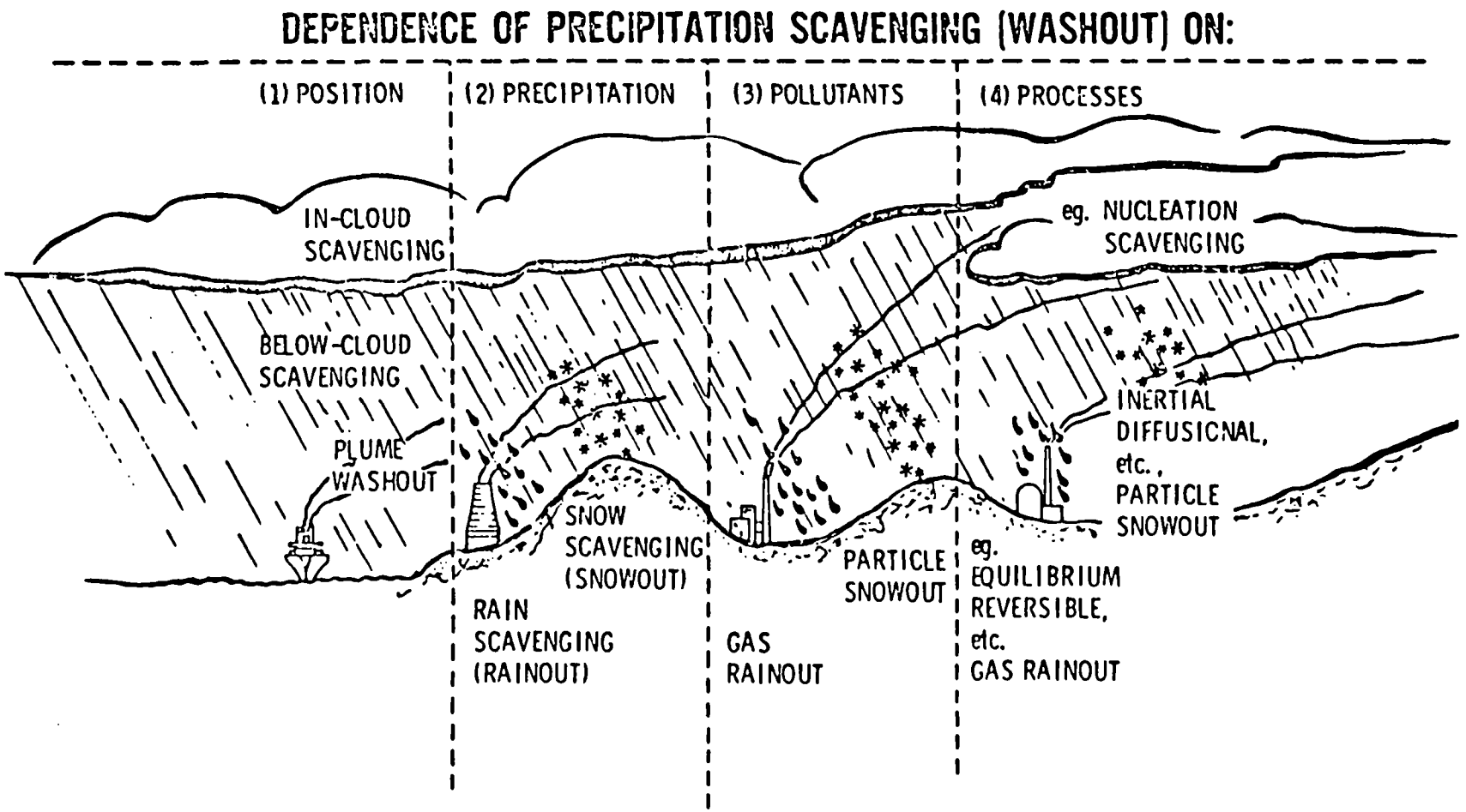

Figure 6-3. Basic factors influencing precipitation scavenging.

TABLE 6-5. PREDICTED PARTICLE DEPOSITION VELOCITIES†

z_0 cm	u/u_* m-sec/cm-sec	Deposition Velocity Range†† Particle Diameter 0.1 to 1μ cm s^{-1}	1μ to 1μ cm s^{-1}
0.1	2.3/10	$1.5X10^{-2}$ - $5.0X10^{-2}$	$5.0X10^{-2}$ - 4
10	1.2/10	$9.0X10^{-2}$ - $1.5X10^{-1}$	$1.5X10^{-1}$ - 4
0.1	11.5/50	$2.0X10^{-2}$ - $5.5X10^{-2}$	$5.5X10^{-2}$ - 4
10	5.8/50	$1.0X10^{-1}$ - $2.0X10^{-1}$	$2.0X10^{-1}$ - 4

†Based on model predictions in Sehmel (1980)
††particle density of 11.5 mg/m^3

A convenient practice in the field of precipitation scavenging has been to distinguish between below-cloud and in-cloud scavenging processes. Unfortunately, the commonly used terminology used in describing these processes, rainout for in-cloud and washout for below cloud, has lead to considerable confusion. The elucidation of the contribution of these processes to the total scavenging in a precipitation event is extremely difficult. Washout, being more amenable to experimental study, has received the most attention from the scientific community. Also in many experimental studies, distinction of the two processes has been ignored and only the total precipitation scavenging has been considered. The theoretical approaches to be discussed in the section to follow are for washout processes only, while empirical parameterization discussed consider total gas and particle scavenging.

The parameterization of the precipitation scavenging process has generally taken the form of a loss rate per unit volume and has evolved from various assumptions applied to the continuity equation, Slinn (1977). Parameterizations for the removal of gases by rain and the removal of particles by rain and by snow are considered in the following sections. The formalism and technical rigor used in their development, can be found elsewhere, Hales (1972, 1978) Slinn (1977), and is beyond the scope of this work.

6.3.2.1 SO_2 Wet Removal--The removal of sulfur dioxide from the atmosphere by rain is governed by basic physical processes that describe the absorption and desorption of the SO_2 molecules from the hydrometeor, Hales (1972, 1978), and by a series of chemical reactions, Postma (1970), Hill and Adamowicz (1977), Barrie (1978), which account for the liquid phase oxidation of SO_2. From a purely physical process viewpoint, the rate of scavenging of a gas by rain is a function of the size spectrum of the raindroplets, the fall path of the raindroplet to the ground, the rainfall rate, and the solubility of the gas. General expressions have been

developed, Hales (1978) and Slinn et al. (1978), for computing the scavenging of SO_2 and other gases given simplifing assumptions regarding the characterization of the precipitation and solubility of the gas. As pointed out in Chapter 2, the liquid phase oxidation of SO_2 is very complex and not adequately understood at present. Several recent studies, Hill and Adamowicz (1977), Barrie (1978), Garland (1978), Gravenhorst, et al. (1978) have considered the SO_2 - bisulfite oxidation process, Scott and Hobbs (1967) in predicting wet removal rates of SO_2 under various atmospheric conditions. The solution phase chemistry for SO_2, based on the mechanism of Scott and Hobbs (1967) as used in the SO_2 washout model by Barrie (1978) is discussed here as an illustrative example.

Sulfur dioxide exists in solution as physically dissolved SO_2 ($SO_2 \cdot H_2O$), which follows a linear Henry's Law relationship with gas phase SO_2, bisulphite (HSO_3^-), and sulfite (SO_3^-). The equilibria describing the process are as follows:

$$(SO_2)g + (H_2O)_\ell \rightleftharpoons (SO_2 \cdot H_2O)_\ell$$

$$K_H = \frac{[SO_2 \cdot H_2O]_\ell}{[SO_2]_g} \qquad (1)$$

$$SO_2 \cdot H_2O_\ell \rightleftharpoons H^+_\ell + HSO_3^-{}_\ell$$

$$K_1 = \frac{[H^+]_\ell [HSO_3^-]_\ell}{[SO_2 \cdot H_2O]_\ell} \qquad (2)$$

$$HSO_3^-{}_\ell \rightleftharpoons H^+_\ell + SO_3^={}_\ell$$

$$K_2 = \frac{[H^+]_\ell [SO_3^=]_\ell}{[HSO_3^-]_\ell} \qquad (3)$$

The K's are equilibrium constants, with K_H being the Henry's Law constant for SO_2, and the square brackets represent chemical activities which are effectively concentrations for the dilute conditions present. It has been established Beilke and Lamb (1975) that the dissociation of $SO_2 \cdot H_2O$ and HSO_3^- are very rapid, thereby introducing a non-linear relationship between gas phase SO_2 and total dissolved SO_2 which is strongly dependent on pH (see Figure 6-4 Barrie, 1978) and only weakly dependent on temperature. The effect of temperature is a shift in equilibria to the left for increasing temperatures, resulting in a slight shifting to the right of the curves in Figure 6-4. Within the pH range of precipitation, pH 3 to 6, over 90% of the dissolved SO_2 exists as bisulfite, with less than 10% existing as sulfite. This result indicates that equilibrium equation (7) can be neglected, without significantly effecting the washout calculation. Barrie assumed that SO_2 oxidation in the raindrops could be neglected due to the limited time for reaction (0-5 min) and the low pH's encountered, Beilke et al.

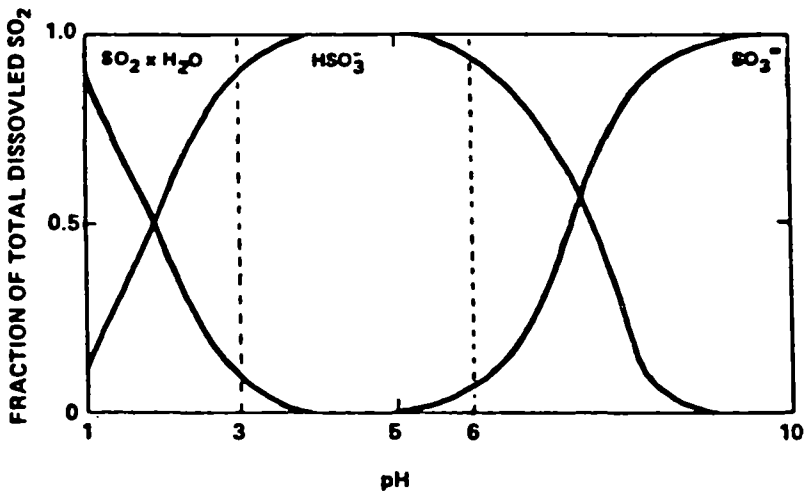

Figure 6-4. Abundance of dissolved SO_2 species as a function of pH (25°C).

(1975). In cases where SO_2 is the dominant species contributing to the acidity of the rain droplet, an expression relating the gas phase SO_2 concentration to the bisulfite ion concentration in equilibrium with the gas is as follows:

$$[HSO_3^-]_\rho^{eq} = \{K_H K_\rho [SO_2]_g^{eq}\}^{1/2} \quad (4)$$

Incorporating this expression with a physical model for gas transfer to the droplet, Barrie (1978) modeled the washout of SO_2 from a plume under varying meteorological and SO_2 concentration conditions. He concluded that the fractional plume washout rate (%/mm rain) is inversely proportional to the plume concentration and thickness. For heavy rain (25 mm/h) washout from a 1000 ppb(v) SO_2 plume of 20 m thickness occurs at a rate of 56% hr^{-1}, while under drizzle conditions (0.5 mm/h) for a 300 pph(v) SO_2 plume of 50 m thickness the rate was 2% h^{-1}. Barrie assumed that the pH of the raindrop was governed by the dissolution of the SO_2. In a more definitive model of SO_2 washout, Hill and Adamowicz (1977) included estimates for SO_2 oxidation within rain droplets and for the pH dependence of the precipitation. They indicated that pH can be quite variable (over six orders of magnitude) at SO_2 ambient levels of 10 ppb and less. As SO_2 levels increase, the variability in background pH decreases. The SO_2 oxidation rate of 3.6% h^{-1} used in the calculations is based on the catalytic oxidation studies of Brimblecombe and Spedding (1974). In a typical calculation of the rate of SO_2 washout, Hill and Adamowicz assumed various ambient SO_2 concentrations to be well mixed through a layer 1 kilometer in depth and a rainfall rate of 1 mm/h with a predominant drop radius of 0.5 mm and pH of 7. Calculated washout rates of SO_2 under these conditions were 2.6%/h and .8%/h for ambient SO_2 levels of 10 ppb and 100 ppb, respectively.

A convenient empirical expression for the wet removal of gases takes the form of an exponential decay process, where the time constant for decay (scavenging coefficient for the gas), determined in field and laboratory studies, is a function of the rainfall intensity. The expression takes the form

$$x_t = x_0 e^{-\Lambda pt} \quad (5)$$

where x_t and x_0 are the atmospheric concentrations of the gas at time t and zero, respectively, and Λ_g is the scavenging coefficient for the gas. Estimates of the scavenging coefficients for sulfur dioxide have been determined by Chamberlain (1953), Beilke (1970), Hales et al. (1971), Dana et al. (1975) and others. calculated scavenging rates of SO_2 using these coefficients can range typically from 2% h^{-1} to 22% h^{-1}.

6.3.2.2 Particle Wet Removal--The study of precipitation scavenging of particles has predominantly focused on theoretical studies, Semonin and Beadle, (1977), Slinn (1977), Grover et al. (1977), Wang et al. (1978), but with considerable emphasis in experimentel work taking hold in

recent years (Dana and Hales, 1976 ; Radke et al., 1980 ; Gatz, 1977). The wet removal of sulfate particulate matter in the ambient environment has been of particular interest, (Scott, 1978 ; Hales, 1978 ; Dana, 1980) due to the acidic tendency of these particles and the increased concern in the phenomenon termed "acid rain". Chapter 7 of this criteria document discusses acid precipitation and its associated scientific issues and is not a specific topic for consideration in this section.

Important parameters affecting the particle scavenging rate by precipitation, as with gases, are the size spectrum of the rain droplets, the fall path of the rain droplet to the ground, and the rainfall rate, but also include in addition, the size distribution and composition off the particulate matter. As with gases, general expressions have been developed (Slinn, 1977) for computing the scavenging of particles given certain simplifing assumptions.

A practical operational approach in predicting the wet removal of particles as mentioned previously for gaseous has been through the measurement of empirical scavenging coefficients.

A comprehensive list of field measurements of wet scavenging coefficients of particle has been compiled by McMahon and Denison (1979) and presented in Table 6-6. A cautionary note is in order. The scavenging coefficients are dependent on the rain fall rate, the mean rain drop radius, and the particle size. When these factors are taken into consideration, the scavenging coefficients reported in Table 6-6 show reasonable consistency as demonstrated by Figure 6-5 taken from McMahon and Denison (1979).

Recent airborne measurements by Radke et al. (1980) on precipitation scavenging of aerosol particles greater than 0.01 μm diameter in aged air masses, coal fired power plant plumes, a Kraft paper mill, and a plume from a volcanic eruption were quite encouraging in supporting theoretical estimates of wet removal for aerosol particles greater than 1.0 μm. Marked differences were observed in the submicron particle region, where measured scavenging efficiencies for submicron aerosol particles were typically an order of magnitude greater than theoretical predictions; and the scavenging gap, that portion of the aerosol particle size range where scavenging collection efficiencies are at a minimum, was observed to be much narrower than predicted by theory. Radke et al. (1980) offer some explanations for the discrepancies including deliquescent growth and nucleation scavenging of the submicron particles in convective clouds. Considering the varied aerosol particle sources and precipitation studied the measurements showed marked continuity, (see Figure 6-6), Radke et al. (1980).

6.4 TRANSPORT AND DIFFUSION

Pollutant substances emitted into the atmosphere are transported and diffused as a result of a series of complex physical interactions which describe the mean motion of air and its fluctuating components. Transport and diffusion have associated with them spatial and temporal scales. The selection of the spatial or temporal domain of interest directly influences what specific physical phenomena will predominantly affect the transport and diffusion process.

TABLE 6-6. FIELD MEASUREMENTS OF SCAVENGING COEFFICIENTS OF PARTICLES

Author (date)	Λ_p (s^{-1})	Particulate size (μm)	Comment
Kalkstein *et al.* (1959)	2×10^{-5} 2×10^{-5}	SO_4, NH_4 Cl, NO_3	Rainout Washout } Makhon'ko (1967)
Georgii (1963)	4×10^{-5} 22×10^{-5} 4×10^{-5}	Dissolved inorganic contaminent	Rainout Washout
Banerji and Chatterjee (1964)	0.4×10^{-5}	Radon	Rainout Makhon'ko (1967)
Makhon'ko (1964)	2×10^{-5} $\leq 1 \times 10^{-5}$	Fission products	Rainout Washout
Shirvaikar *et al.* (1960)	7×10^{-5}	Atmospheric dust	Rainout Makhon'ko (1967).
Makhon'ko and Dmitrieva (1966)	20×10^{-5}	Fission products	Rainout
Makhon'ko (1967)	7×10^{-5}	Atmospheric dust	Rainout plus washout
Wolf and Danz (1969)	$0.5 \times 10^{-5} J$	0.5	Snow; Knutson and Stockham (1977)
Bakulin *et al.* (1970)	3×10^{-5}		^{212}Pb; washout from thunderstorm
Burtsev *et al.* (1970)	$15 \times 10^{-5} J^{0.5}$ $20 \times 10^{-5} J^{0.5}$	$\simeq 0.2$ $\simeq 0.2$	Washout Rainout
Dana (1970)	$13 \times 10^{-5} J$	7.5, 3	Uranin and rhodamine particles respectively
Perkins *et al.* (1970)	300×10^{-5}	Atmospheric aerosol	Rainout
Peterson and Crawford (1970)	$16 \times 10^{-5} J^{0.8}$	5	Based on Engelmann's data (1965)
Esmen (1972)	0.4×10^{-5}	Atmospheric aerosol	Includes rainout
Rodhe and Grandell (1972)			Suggest Λ proportional to rainfall intensity
Acres-ESC (1974)	0.7×10^{-5}	Atmospheric aerosol	Includes rainout
Graedel and Franey (1975)	$\Lambda_{snow} = 25\text{-}50\Lambda_{rain}$	0.4-1	See Slinn (1976)
Hicks (1976)	50×10^{-5}	<1	Rainout
Graedel and Franey (1977)	19×10^{-5} 18×10^{-5} 28×10^{-5} 43×10^{-5} 65×10^{-5} 92×10^{-5}	 0.3-0.5 0.5-0.7 0.7-0.9 0.9-1.5 1.5-3	Condensation nuclei Snow
Radke *et al.* (1977)			See Fig. 8

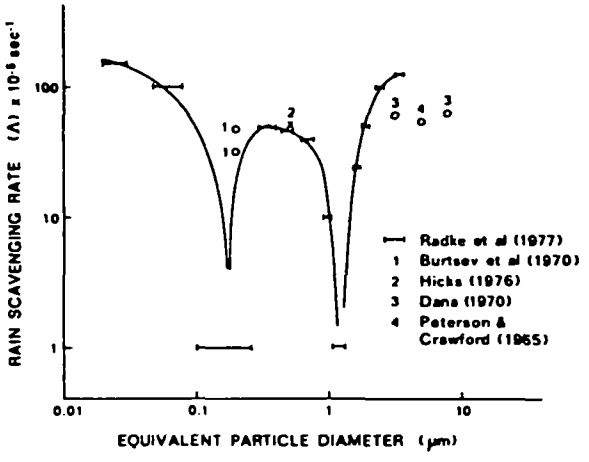

Figure 6-5. Relationship between rain scavenging rates and particle size.

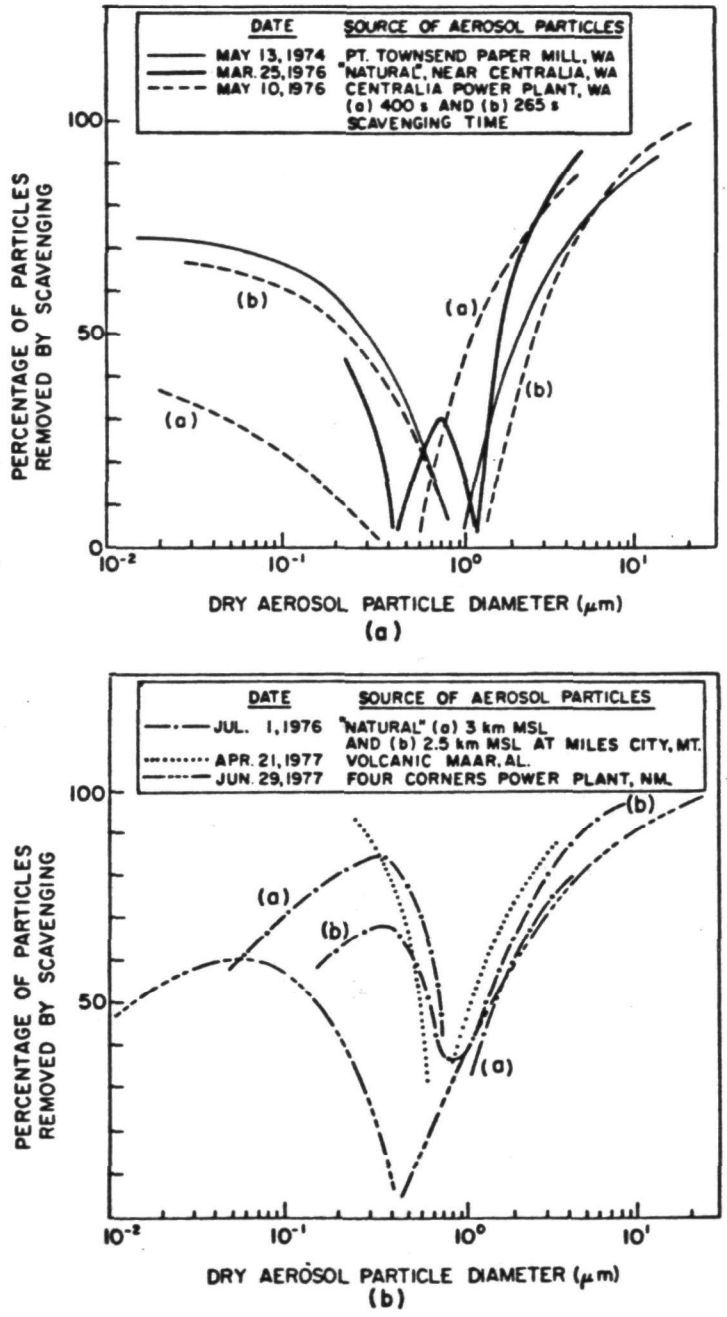

Figure 6-6. Percentages of aerosol particles of various sizes removed by precipitation scavenging.

The study of air pollution transport and diffusion is typically treated on the basis of the extent of the horizontal scale. Therefore, high level pollutant concentrations which occur in the vicinity of a major emission source are dominated by physical processes that are operative on a local horizontal scale of the order of 1 to 5 kilometers, or approximately one hour of transport. Since the majority of criteria pollutants are emitted directly into the atmosphere by major sources, a predominance of interest with respect to air pollution regulation has resided on this scale. But, as air pollution issues are raised with regard to pollutants of a more ubiquitous nature, having appreciable long life-time and in some cases forming through secondary reaction processes, the horizontal scale of interest expands considerably. Sulfur dioxide and particulate matter span a horizontal scale ranging from local to global. A brief review of the physical processes contributing to transport and diffusion is presented in section 6.4.1, while section 6.4.2 considers pollutant residence times and their long distance transport.

6.4.1 The Planetary Boundary Layer

The primary vehicle for the transport of pollutants within the atmosphere is the mean wind within approximately the first 1000 meters above the earth's surface. The mean wind is determined primarily by the interaction of three forces governed by thermodynamic and mechanical processes. These are: the force due to the horizontal pressure gradient produced by differential solar heating of the earth's surface; the Coriolis force due to the earth's rotation; and the friction force due to the texture of the earth's surface. The planetary boundary layer is defined as that portion of the atmosphere within which surface frictional effects have a substantial impact on the mean wind. Typically, this layer is hundreds of meters in depth and varies diurnally.

Diffusion in the planetary boundary layer, which governs the spreading of pollutants perpendicular to the transport flow, is regulated by turbulence. Turbulence, which is comprised of a complex spectrum of fluctuating motion superimposed on the mean wind, is generated through the interaction of directional and speed differences (Shear) in large scale atmospheric motions and perturbations introduced in the mean flow by the roughness of the earth's surface, as well as by heating of this surface by the sun.

The theory of the mean vertical structure of the planetary boundary is fairly well understood, Haugen (1973) and its characterization is possible through the measurement of basic meteorological parameters. The description of the turbulent properties within the mean motion, which govern diffusion, has proven to be more elusive. Detailed theoretical approaches to turbulence encounter solution problems resulting from having more unknown parameters than equations. The introduction of higher order closure techniques, which apply assumptions that permit new unknowns to be expressed in terms of others in such a way as to allow solution of the equation set, have limited practical application due to their intensive computer and data requirements. As a consequence the practical treatment of atmospheric diffusion to air pollu-

tion related processes is based on highly parameterized theories which depend strongly on basic experimental data sets.

Practical approaches to the treatment of atmospheric diffusion have been derived from three principal sources: statistical theory, similarity theory and gradient transport or K-theory (Pasquill, 1974). A brief description of these approaches and their utility to air pollution related problems is presented below. More definitive discussions on the theories can be found in the annotated references.

Statistical theory considers the time history of the motion of a single fluid "particle", relative to a fixed co-ordinate axis (Taylor, 1921), and of groups or clusters of such particles relative to their centroid (Batchelor, 1953). The theory provides the basis for the development of the Gaussian diffusion formulation and provides an effective means to correlate empirical dispersion data. As a result, diffusion equations for various emission source types have been developed (Gifford, 1968, 1975 ; Turner, 1970 ; Pasquill, 1974, 1975). A practical limitation of this approach is that it makes the fundamental assumption of turbulence homogeneity, whereas boundary-layer turbulence is inhomogeneous, especially in the vertical.

The similarity theory of diffusion relates the mean position and other properties of diffusing clouds and plumes to the characteristic parameters of the surface layer, by dimensional reasoning. Results (Monin and Yaglom, 1971) are reasonably complete for the surface layer. But extension to the entire boundary layer introduces further parameters, which limit their practical use.

The gradient-transport, or K-theory of diffusion is historically the oldest; it originated with Fick (1855) and Boussinesq (1877). Atmospheric applications have been most successful at large scales, including global diffusion. At boundary-layer scales the behavior of K is quite complicated. Useful results can be obtained (Pasquill, 1974 ; Yaglom, 1975 ; or Csanady, 1973), but the mathematics required tends to be fairly elaborate. The essential problem is to account for the strong space-time scale-dependence of eddy-diffusivity, which was first demonstrated by Richardson (1926). Berlyand (1974) has based a comprehensive system of air pollution analysis entirely on a form of K-theory.

The parameterization of atmospheric diffusion was shown by Obukhov (1941) to follow a form of Richardson's law of diffusion where the total amount of turbulent energy dissipation and the pollutant spreading is proportional to the diffusion time to the 3/2 power. Data on the instantaneous values of the spreading of plumes and puffs (i.e., on relative diffusion) shows that this law describes diffusion up to t on the order of an hour (Gifford, 1976a). On the other hand the time-average spreading of plumes was shown by Taylor (1921) to obey the asymptotic laws $\sigma \propto t$ for small t-values and $\sigma \propto t^{1/2}$ in the limit of large t-values. Diffusion depends both on travel time from source to receptor, and on the sampling time, that is, the time over which the concentration is averaged at the receptor point. The situation is made more complicated by the fact that cross-wind diffusion behaves markedly different from vertical

diffusion in the boundary layer because of the inhibiting effect on vertical turbulence fluctuations imposed by the presence of the ground, and because of the strong damping effect of stability on vertical turbulent motions.

A number of attempts have been made to express horizontal and vertical boundary layer diffusion for flat uniform terrain, as measured by the lengths σ_y and σ_z, to more or less easily measured quantities that characterize boundary layer thermal and mechanical turbulence properties. Extensive surveys of the literature on the subject, have been undertaken by Gifford (1976b) and Weber (1976). The former stressed the common logic underlying various and sometimes seemingly conflicting schemes, as well as the need to evaluate many exceptional cases that arise in practical applications.

Based on these analyses and those of Pasquill (1975, 1976), the diffusion parameterization originally suggested by Pasquill (1961) is valid for sources located at or fairly near the surface, for uniform underlying terrain, and for receptors up to several kilometers distance. Extension to greater distances, varying surface roughness, and other generalizations have been discussed Smith (1972) as well as relations to surface-layer turbulence parameters, Golder (1972) and Draxler (1976). The difficulties that have arisen in applying this methodology to practical air pollution problems have centered around, cases for which the turbulence is produced or modified by factors which extend beyond the purely thermal and mechanical components that control the local boundary layer turbulence.

6.4.2 Horizontal Transport and Pollutant Residence Times

The horizontal distance over which a pollutant is transported is strongly influenced by its overall lifetime or residence time in the atmosphere, the characteristics of the mean wind, and the time of day and height at which the pollutant is emitted into the atmosphere.

Residence times for pollutants, are governed by the extent of wet and dry removal and chemical transformation the pollutant species undergoes in the atmosphere. Depicted in Figure 6-7 are estimated residence times for typical pollutants and their associated characteristic horizontal meteorological scale. Average wind speeds of 5 m/sec were assumed in approximating the distance scale. Residence time estimates are based on Junge (1972, 1974).

Transport scales for pollutants such as SO_2 which have appreciable dry deposition velocities, will be sensitive to the relative height at which the pollutant is emitted. Pollutant distributions also will be sensitive to the stability of the atmosphere which will govern the extent of vertical mixing to the surfaces.

Industrial facilities emitting large quantities of SO_2 have tried to take advantage of these natural meteorological phenomena to reduce ambient levels of SO_2 in the vicinity of their stacks. By building taller effluent stacks, emitting facilities succeed in injecting SO_2 at higher levels in the atmosphere, allowing the pollutant more time to disperse and transport before reaching ground level, thereby affectively reducing ground level concentra-

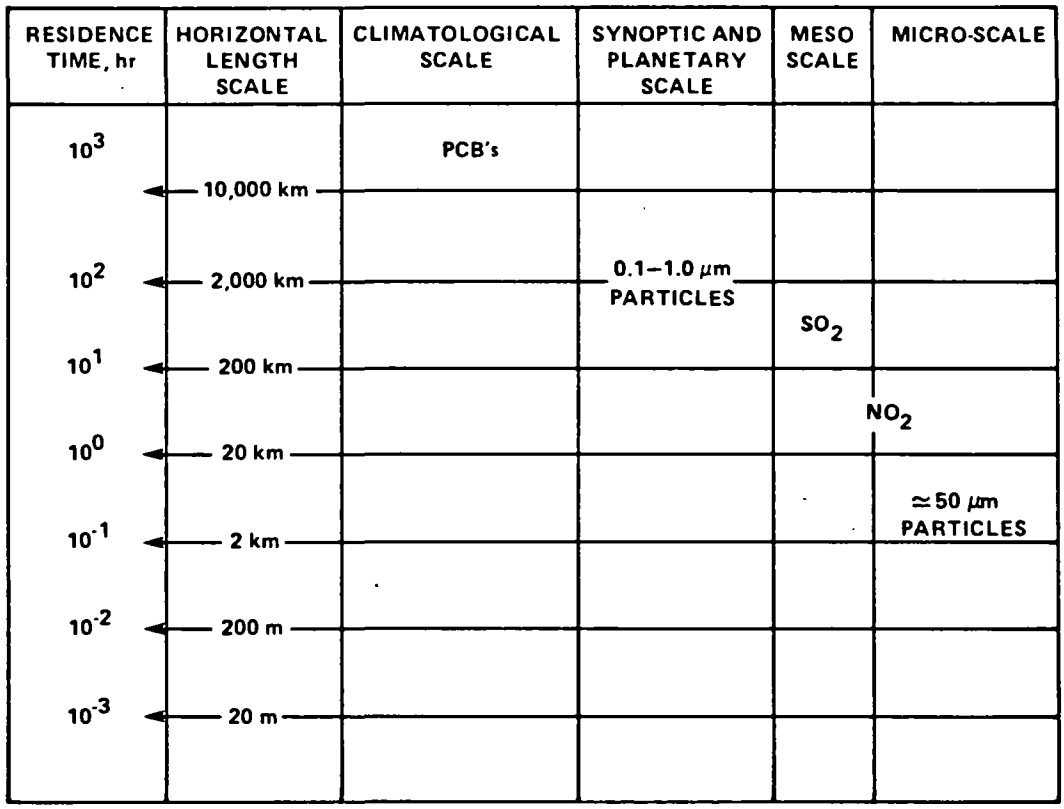

Figure 6-7. Estimated residence times for select pollutant species and their associated horizontal transport scale.

tions of SO_2 as a result. A great deal of controversy arose regarding this approach and as to whether it was circumventing the intent of the Clean Air Act. As a result of the Clean Air Act Amendments of 1977 the Environmental Protection Agency requires that the degree of emission limitation necessary for control of any air pollutant can not be achieved through the construction of stacks higher than would be considered appropriate using good engineering practice design standards. An interesting corollary of the tall stack issue is the potential for such sources to enhance the production of particulate sulfate. As a result of SO_2 being emitted at higher levels in the atmosphere the probability of its removal by dry deposition is lowered, extending its lifetime in the atmosphere and subsequently enhancing its probability to transform through chemical reaction to particulate sulfate.

Of particular importance to horizontal transport is the strength and time of formation of the nocturnal inversion, a stable layer of air formed at the surface due to the differential cooling of the earth's surface relative to the air at night. The depth of this stable layer can vary from approximately 50 m to 500 m depending on meteorological conditions. At the onset of the nocturnal inversion all pollutants present in the well mixed layer from that day's emission are cut off from the surface by this stable layer of air. No major mechanisms for transport through this layer exist; so dry deposition processes virtually stop, leaving the pollutant reservoir aloft free to transport long distances with negligible losses. In addition, horizontal mean winds are typically enhanced in layers aloft due to the reduction in frictional drag at the earth's surface as a result of the presence of the stable nocturnal layer. Associated with this overall process is a phenomenon of the particular importance to nighttime transport, the nocturnal jet. Blackadar (1957) described the mechanism for the formation of the nocturnal jet as due to decoupling of winds previously restrained by frictional forces at the surface, and now free to accelerate in response to existing pressure gradients; as a result some overshooting in wind speed occurs as the flow attempts to establish a new balance with inertial forces. Bonner (1968) examined two years of upper level wind data from the National Weather Services rawinsonde network to determine the frequency and geographical distribution of the low-level jet. Recently, high-resolution measurements of wind profiles collected over central Illinois, Sisterson And Frenzen (1978), showed that nocturnal, low-level wind maxima occur more frequently than indicated in the analysis performed by Bonner. In these studies, low-level wind maxima were observed on 24 out of a total of 30 nights for which meteorological field experiments were conducted in the summers of 1975 and 1976. Typical average wind speed profiles observed under the decoupled conditions showed wind speeds of the order of 1-2 m s^{-1} near the surface increasing to maximum values of 8 m s^{-1} at 100-200 meters above the surface.

It is quite apparent that the nocturnal jet and nighttime flows in general are significant factors in the transport of pollutants over long distances.

Definitive studies on the long range transport of atmospheric tracers have been primarily associated with radioactive debris, Islitzer and Slade (1968), and in many instances at height levels not of particular interest for air pollution related work. Some analyses of ambient data have been performed to provide qualitative indications of the long range aspects of certain pollutant species, Altshuller (1976), Lyons and Husar (1976), Rodhe et al. (1972), Brosset and Akerstrom (1972), but very few quantitative studies exists. The major reason being lack of appropriate experimental data. Recent monitoring and field study programs designed to address the long range transport air pollution phenomenon, should alleviate this problem somewhat, Perhac (1978), MacCracken (1978), Schiermeier et al. (1979).

6.5 AIR QUALITY SIMULATION MODELING

The principal role of the air quality simulation model is to describe quantitatively the relationship between emissions distribution and ambient air quality in time and space. Air quality simulation models provide a vehicle for improved understanding of the physical and chemical processes operative in polluted atmospheres, and a means to sound, creditably based scientific decisions on the nature and extent of emission control required to meet specified ambient air quality.

The development of the air quality simulation model (AQSM) has its origins as far back as the early 1930's when Sutton (1932) introduced his basic theory on diffusion in the atmosphere, which established the foundation for the Gaussian equations used in describing the dispersion of effulents in the atmosphere. The evolution of AQSM's has continued since then, treating increasingly complex air pollution problems and utilizing advanced theoretical approaches in describing the details of the physical and chemical processes operative in the atmosphere. The use of mathematical models for air quality impact analysis associated with SO_2 and total suspended particulate matter, both criteria pollutants, has been a standard practice over the years, though discretionary, prior to the passage of the Clean Air Act Amendment in 1977. With the passage of the 1977 amendments, the Environmental Protection Agency is now required to take certain regulatory steps related to the use of air quality simulation models. The work horse of operational air quality simulation modeling has been the single and multiple source Gaussian plume models. The predominant use of these models has been the prediction of ground level concentrations in the immediate vicinity to several kilometers downwind of the effluent source. Many reviews on dispersion modeling are available, see for example, Gifford (1968), Strom (1976) and Turner (1979). Section 6.5.1 provides a brief discussion on the status of the Gaussian modeling techniques, while Section 6.5.2 discuss the scientific basis and status of air quality simulation modeling over long distance scales and their impact on furthering our understanding of the physical and chemical processes affecting the fate of SO_2 and particulate matter in the air environment. In Section 6.5.3, a discussion of model evaluation and data bases is provided.

6.5.1 Gaussian Plume Modeling Techniques

The Gaussian diffusion formulation used in a variety of air quality simulation modeling approaches is a result of the Gaussian or normal distribution function being a fundamental solution to the Fickian diffusion equation, which strictly speaking applies only in the limit of large diffusion time and for homogeneous, stationary conditions.

The Gaussian diffusion formulation for a continuous point source emitting pollutants at height h and calculated receptor concentrations at ground level is given by

$$x(x,y) = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\left(\frac{y^2}{2\sigma_y^2} + \frac{h^2}{2\sigma_z^2}\right)\right] \qquad (1)$$

where χ is the time-averaged ground-level concentration at horizontal coordinates (x,y), Q the continuous source strength, u the time-averaged magnitude of the wind velocity in the x direction (considered constant and unidirectional over the height interval between the source and the ground), and σ_y and σ_z are the standard deviations of the concentration distribution in the y and z directions. The horizontal dispersion coefficient, σ_y and the vertical dispersion coefficient, σ_z are functions of atmospheric stability and empirically derived. The above formulation assumes perfect ground reflection by the pollutant species. The formulation may be altered to include a reduction factor to consider surface absorption. Graphical and analytical expression for σ_y and σ_z are available as a function of downwind distance from the source and atmospheric stability, based on experimental observation of smoke and pollutant releases, see for example, Turner (1970).

The Gaussian modeling approach has been applied to point, line and area source emissions configurations. When applied to multiple source problems, contributions from individual sources to a receptor concentration can be calculated separately and added to give the total contribution to the receptor region. The simplicity of the Gaussian technique, its low operational costs, ease of use and general utility in air pollution applications has resulted in its extensive use over the years. Applications utilizing Gaussian plume model formulations have not been without criticism. Aside from the fundamental disadvantages in the Gaussian formulation, such as, inability to treat spatially varying meteorological parameters, discontinuity under calm wind conditions, and inability to treat nonlinear reactive pollutants, the major criticisms have been related to the improper application of the models through the use of inadequate or inappropriate input data. As pointed out by Turner (1979), the ease in using the Pasquill-Gifford dispersion estimates rather than collecting recommended on-site meteorological data for developing inputs to the model has lead to applications beyond the scope intended for the dispersion schemes. Turner (1979) indicates that a significant improvement in dispersion modeling estimates would be achieved through the collection and use of on-site measurements including: hourly averaged wind speed and direction at 10 m; standard deviation

of horizontal wind fluctuations; bulk Richardson number as determined from temperature, 10 m wind speed and 2 and 10 m temperature differences; height of surface boundary layer under unstable conditions; and the top of the inversion under stable atmospheric conditions. Additional improvements will be gained as existing theories and experimental data bases are drawn together in a unified scheme for estimating dispersion parameters as a function of stability, effluent release height and surface roughness.

A variety of operational Gaussian air quality dispersion models, used for the majority of SO_2 and total suspended particulate matter regulatory applications, are available through EPA's UNAMAP, User's Network for Applied Modeling of Air Pollution. A brief description of these models can be found in Turner (1979).

Finally, an additional important aspect to dispersion modeling calculations is the prediction of the effective height of the effluent release, so called "plume rise", which strongly affects the predicted ground level concentration of pollutants. Significant research into the processes affecting plume rise and its prediction has been underway for over the past twenty years. Recently, Briggs (1975) reviewed the physics of plume rise and its prediction and presented basic formulations for calculating the height to which plumes rise as a function of atmospheric stability and several standard stack parameters. He indicates that the greatest need for further investigation, concerns plume rise limited by ambient turbulence under convective atmospheric conditions.

6.5.2 Long Range Air Pollution Modeling

The growing interest in the long range transport of air pollutants in recent years has resulted in several extensive reviews on the subject, Bass (1980), Eliassen (1980), Pack et al. (1978), Smith and Hunt (1978). Long range is defined here as horizontal scales of the order of 1000 km resulting in transport times of the order of several days. Typical model spatial resolutions on this scale range from 20 to 100 km. As concluded by Bass (1980), the majority of long range transport models are Lagrangian based. The Lagrangian approach represents an emitting source element by a series of discrete pollutant parcels which are advected and diffused by a time and space dependent wind field. In principle, the individual pollutant parcels can treat time-dependent chemical transformation, dry deposition and precipitation scavenging processes. Fixed space-time averages of pollutants are generated by superimposing all elements that pass a specified point over the averaging time of interest. The Lagrangian models, although all cut from the same basic theoretical fabric, have developed various nuances in their evolution.

In reviewing the models, very little consensus of opinion surfaces with regard to standard treatments for: 1) wind field analysis; 2) choice of wind height level for trajectory; 3) mixing height variations; and 4) dry and wet removal and chemical transformation rates. Even the basic generation of discrete air parcels is viewed from four different approaches: puff super-position, segmented plume, square puff, and statistical. Three of the approaches which

are readily depicted, Figure 6-8 Bass (1980), are contrasted to the idealized continuous plume they are attempting to represent.

Eulerian or grid-based approaches have been less prevalent in long-range transport air pollution modeling. This may to some extent result from problems associated with the numerical integration of the advection equation which give rise to pseudo-diffusion effects. But a more likely reason is the increased complexity and enhanced data base and computational requirements of the Eulerian models.

Table 6-7 provides a representative sampling of long-range transport models discussed in the available literature and presents for each referenced model: a brief description of the modeling approach, including characteristic averaging times; approaches to dry and wet removal and chemical transformation; and pollutant species modeled.

A review of the models presented in Table 6-7 indicates that sulfur dioxide and sulfates have been the species of major interest. This stems from the fact that many of the models were developed with the specific intent of addressing the acid rain phenomenon. These sulfur species have been identified as major contributing factors in the acidification of precipitation. Though none of the models as presently configured consider primary emitted particulate matter, their inclusion would be reasonably straightforward given the availability of appropriate emission inventories. The far more difficult tasks of considering the gas to particulate matter forming processes of nitrates and organic species, aerosol dynamic processes and size distributions remain for future research to resolve. Until these basic processes as well as gas-liquid phase transfer and solution phase chemistry of rain droplets are adequately treated within the models, significant skepticism as to the scientific creditability and utility of the models will remain.

In a similar manner, regional visibility impairment, which results from the physical interaction of sunlight with light absorbing gases and particulate matter and light scattering aerosols, requires the consideration of many of the process indicated above. Though several empirical analysis techniques have been developed recently which provide a qualitative understanding of the scope and general meteorological characteristics of the visibility impairment problem, no adequate quantitative relationships presently are available for emission control strategy assessments.

Although verification studies of long range transport models are limited, it has been recognized for some time that errors in observed wind direction, Pack et al. (1978) and the specification of wind fields in general, Sykes and Hatton (1976), Smith and Hunt (1978), and Draxler (1979) can result in drastic errors in spatial predictions over long range travel distances.

A significant contribution to uncertainties in transport prediction resides in the sparse temporal and spatial resolve of upper level wind information. The National Weather Service

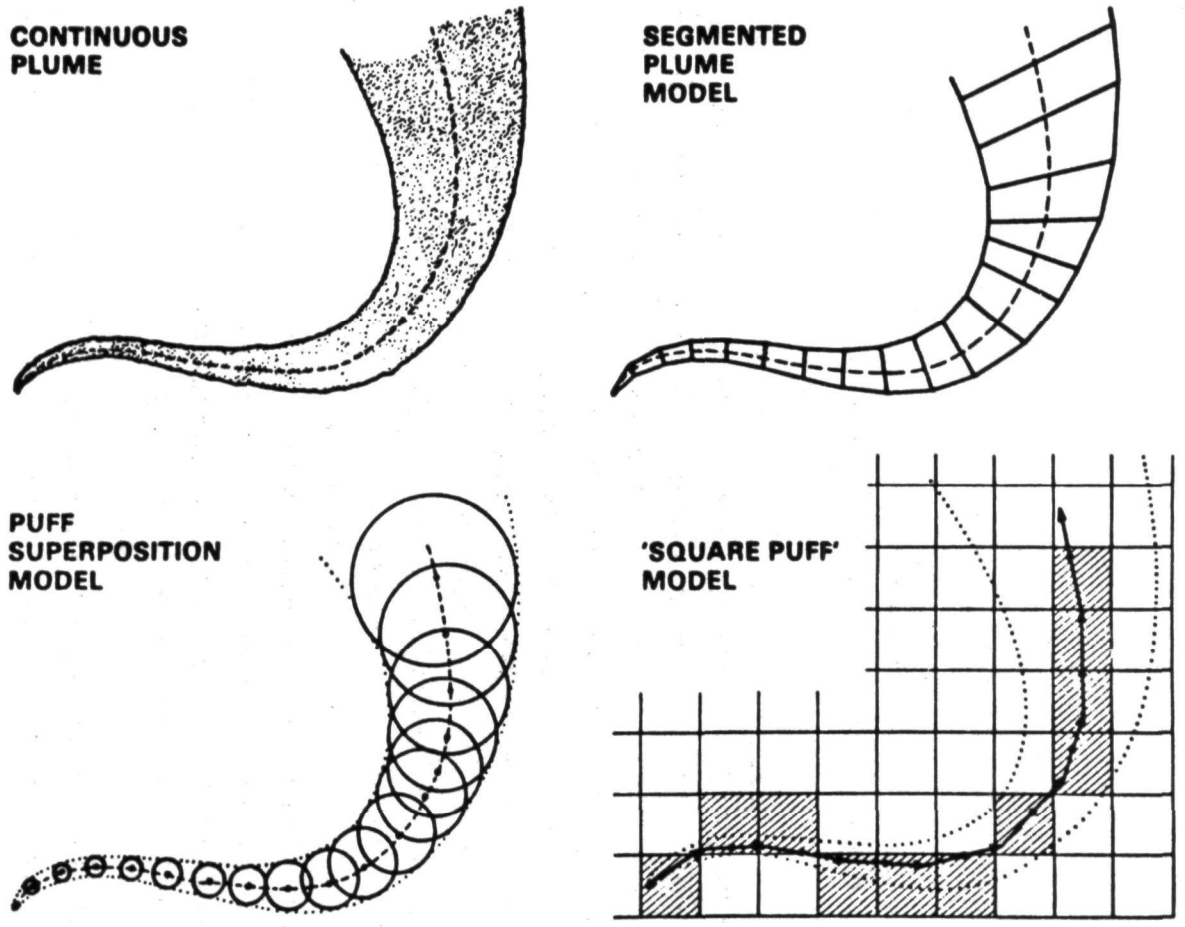

Figure 6-8. Trajectory modeling approaches.

TABLE 6-7. SUMMARY OF SELECT LONG RANGE TRANSPORT AIR POLLUTION MODELS

Model	Description					Reference
	Type	Averaging Time	Removal Process	Chemical Process	Pollutant Species	
ARL-ATAD[1]	puff trajectory	daily to yearly	first order wet and dry removal	none	Inert Substances	Heffter et al. (1975) Heffter (1980)
EURMAP-1,-2[2] ENAMAP-1	puff trajectory	daily to yearly	first order wet and dry removal	SO_2 first order decay	SO_2 and $SO_4^=$	Johnson et al. (1978) Mancuso et al. (1979) Bhumralkar (1980)
MESOPUFF[3]	puff trajectory	daily to yearly	first order dry removal	SO_2 first order decay	SO_2 and $SO_4^=$	Benkley and Bass (1979a)
MESOPLUME[4]	plume segment trajectory	daily to yearly	first order dry removal	SO_2 first order decay	SO_2 and $SO_4^=$	Benkley and Bass (1979b)
ASTRAP[5]	statistical trajectory	monthly to yearly	diurnal and seasonal dependent dry removal first order wet removal	diurnal and seasonal dependent SO_2 first order decay	SO_2 and $SO_4^=$	Shannon (1979) Shieh (1977)
AIRSOX	puff trajectory/ vertical-finite difference	daily to yearly	first order wet and dry removal	SO_2 first order decay	SO_2 and $SO_4^=$	Meyers et al. (1979)
MESO GRID[6]	grid	daily to monthly	first order wet and dry removal	typically SO_2 first order decay	SO_2 and $SO_4^=$	Morris et al. (1979)

[1] see also model by Start and Wendell (1974).

[2] see also models by Eliasen (1978), Nordo (1976) and Eliasen and Saltbones (1975).

[3] see also models by Draxler (1977, 1979).

[4] see also models by McNaughton (1980), Hales et al. (1977) Pendergast (1979) and Henmi (1980).

[5] see also models by Bolin and Persson (1975), Fisher (1975, 1978) and Scriven and Fisher (1975).

[6] see also models by Lui and Durran (1977), Rao et al. (1976), Lavery et al. (1980) and Carmichael and Peters (1979).

rawinsonde network provides vertical wind speed and direction, temperature, and moisture profiles every 12 hours at seventy sites across the continental U.S. This provides upper-level winds at a horizontal resolution of the order 400 kilometers, considerably less resolved than the 20 to 80 kilometer grid spacing required in air quality simulation modeling techniques. Increased temporal resolution in upper level winds should also diminish tranport prediction uncertainties.

6.5.3 Model Evaluation and Data Bases

The evaluation/verification of long range transport models through comparisons of model predictions with observation has been almost nonexistent. The major deterent has been insufficient or in many cases, inappropriate monitoring data for the spatial scales of interest. Long range transport models predict ambient pollutant concentrations that are representative of horizontal spatial averages of the order of 10^3 square kilometers. Standard monitoring networks, established for local high level concentration measurements within the vicinity of the emission sources do not provide representative data for long range models. Some routine monitoring data for SO_2 and $SO_4^{=}$ from the EPA Storage and Retrieval of Aerometric Data (SAROAD) system has had some utility in model testing (Bhumralkar, 1980) but in general has proven less than adequate. The SURE air quality network (Perhac, 1978) which operated over the period August 1977 to October 1978, has provided to date the most extensive SO_2 and SO_4 data base for long range transport model evaluation. But even these data collected over this limited period are only sufficient during the intensive study periods, August 1977, October 1977, mid-January to mid-February 1978, April 1978, July 1978 and October 1978, when an extended 54 site monitoring network was activated. During the SURE study period, data also exist from the MAP3S precipitation chemistry network (MacCracken, 1978) which had at least four sites operational during the program. No dry deposition data are available for the study period. Since the data have only recently become available, they have had limited use, but future long-range transport model evaluations are certain to consider their use.

Another limitation in model evaluation studies is the quality of the emission inventory. Until recently a national gridded emission inventory did not even exist. Clark (1980) prepared on annual gridded emissions inventory for the United States and Southern Canada east of the Rocky Mountains utilizing data compiled by the U.S. Environmental Protection Agency and the Ontario Ministry of the Environment and Environment Canada. In preparing the gridded inventory, he found significant errors in many of the U.S. point source records which had to be corrected. Models, like chains, are only as strong as their weakest link. Certainly emission inventories must be viewed as candidates in this role.

As mentioned at the outset, long-range transport model evaluations are extremely limited, but two recent studies should be noted.

Mancuso et al. (1979) evaluated a trajectory puff model using monthly averages from the OECD monitoring program. They generated two sets of evaluation results. The first considered

model predictions versus observations using parameters originally specified for the model. This resulted in root mean square (RMS) differences of 12.9 and 4.8 $\mu g/m^3$ for SO_2 and SO_4, respectively. In the second evaluation, half of the data was used to optimize model parameters through a regression analysis technique and then the remaining half of the data was used to evaluate the model. This resulted in RMS differences of 7.7 and 2.9 $\mu g/m^3$ for SO_2 and SO_4 and correlation coefficients of 0.72 both for SO_2 and SO_4, a marked improvement in the model's performance. None of the optimized parameters assumed values which were physically unrealistic. Lavery et al. (1980) evaluated a grid model using data from the SURE monitoring network and based on 24-hour averaged concentrations. Four days were selected for parameter "adjustments" and "fine tuning" and additional three days were used for the model evaluation. RMS differences for SO_2 ranged from 6.9 to 23.4 $\mu g/m^3$ for the three days, with a mean value of 14.1 $\mu g/m^3$. RMS differences for SO_4 ranged from 5.2 to 14.4 $\mu g/m^3$ with a mean value of 9.3 $\mu g/m^3$. Mean correlation coefficients for SO_2 and SO_4 for the three days tested were 0.31 and 0.53, respectively.

Overall, the results from both models are encouraging. Evaluation of a trajectory puff model for the U.S., Bhumralkar (1980), using the SURE data base is also showing promising results.

6.5.4 Atmospheric Budgets

Atmospheric budgets have proven a convenient technique for evaluating on a quantitative basis the overall source and sink contributions of specified pollutant species within a selected region of interest. The budget is formulated by estimating the various input and output processes associated with the region, as anthropogenic and natural emissions, pollutant concentration inflow and outflow, and wet and dry removal. Budget analyses provide a general indication over the long-term of the significant factors contributing to the pollutant burden in a given region. Sulfur budgets have been of greatest interest both in Europe, Rodhe (1972, 1978), Garland (1978) and in North America, Galloway and Whelpdale (1980), primarily due to sulfur's association with the acid precipitation phenomenon. Conclusions drawn from the eastern North American sulfur budget by Galloway and Whelpdale (1980) were that man-made emissions exceed natural ones by a factor of 10; wet and dry deposition over the region are approximately equivalent; and at least one-quarter of the emissions leaves the region via the atmosphere to the east. As with western Europe the North American budget showed that man's activities dominates the regional atmospheric sulfur cycle.

6.6 SUMMARY

The processes governing the transport and diffusion, chemical transformation and wet and dry removal of sulfur dioxide and particulate matter in the atmosphere are extremely complex and not completely understood. The oxidation rates of SO_2 observed in industrial plumes and urban atmospheres range from 0-15% h^{-1} and would seem to be only partially accounted for through homogeneous gas phase reactions. Liquid phase catalytic oxidation reactions involving Mn and carbon are possible contributing sources to the observed oxidation rates, but further

research is required to quantify these processes under typical atmospheric conditions.

The dry deposition of SO_2 is fairly well understood as a result of extensive measurements over various canopies. Particle dry deposition has focused more on the physical aspects of the deposition process, that is the aerodynamic and has very little supportive measurement data on particles with compositions typical of those found in the polluted atmosphere.

Our understanding of the wet removal of SO_2 has progressed considerably in recent years, including the consideration of solution phase chemistry within rain droplets. While particle removal, as with gases, is extremely dependent on the physical characterization of the precipitation events which may in many instances be the determining factor in accurate wet removal prediction.

The characterization of the dynamics of the planetary boundary layer is essential to an adequate understanding of pollutant transport and diffusion over all spatial scales. Though considerable advances have been made in this area, our ability to predict mean transport and diffusion over long distance scales is less than adequate. This in part is due, no doubt, to the sparse spatial and temporal resolution of the upper air wind observation network used to generate the transport winds.

Present generation long range transport air pollution models consider simple parameterization for chemical transformation and wet and dry removal, and varying degrees of sophistication in the treatment of transport and diffusion. None of the models adequately treat the dynamics of the planetary boundary. Evaluations of long range transport models, though limited because of lack of data bases, have shown that with further research and development these models should prove to be adequate tools in addressing air pollution issues associated with the movement of pollutant emission over long distance scales.

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