LITERATURE REVIEW ON POLLUTION DEPOSITION PROCESSES

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ABSTRACT

An in-depth review of the literature related to deposition of gases and particulates by dry deposition and precipitation scavenging is reported. Recommendations are made on the hypotheses, algorithms or models considered to be most suitable for incorporation into a pollutant transport and diffusion model to be selected later. A review of field monitoring programs is also reported. A program is designed to provide data for calibrating the models recommended appropriate to the study area of the Alberta Oil Sands Environmental Research Program.

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1. INTRODUCTION

The Alberta Oil Sands Environmental Research Program (AOSERP) Policy and Direction document (November 1977) has been used to provide background information in this section. In many cases statements from that report are repeated verbatim but quotation marks have not been used.

1.1 PURPOSE AND OBJECTIVES

Objectives of the Air System are given as follows:

1. To establish data acquisition systems to effectively describe existing physical conditions and processes including: climatology, air quality, precipitation chemistry, lower atmosphere soundings, and inventory of emissions from all sources;
2. To describe major meteorological and air quality characteristics of the oil sands region based on historical and current data;
3. To apply physical models to processes of air pollutant dispersion, transport and deposition;
4. To develop systems for predicting levels of air pollution resulting from oil sands processing and the extent of dispersion and impingement on land and water; and
5. To provide advice and scientific support to other research sectors in areas relating to meteorology and air quality.

The objectives of this particular project apply to the *deposition* factor in Item 3 and to the *impingement on land and water* factor in Item 4. There are two principal work tasks required in the terms of reference.

The first task has been to carry out an in-depth review of the literature related to deposition of both gases and particulates in both non-precipitation and precipitation conditions, and to recommend the hypothesis, algorithm or model considered to be most suitable for incorporation into a transport and diffusion model still to be developed. The recommendations have been based on evaluation of the rationale of the theoretical and/or empirical treatment followed, a realistic appraisal of the ability to measure or calculate the input data required for model calibration in this specific study area, and the extent to which the model has been tested elsewhere. This work is reported in Section 2.

The second task has been to review various field monitoring programs that have been in operation elsewhere and to design a program for the AOSERP study area that will adequately provide data on which the recommended models can be calibrated and modified if required. This work is reported in Section 3. Section 4 relates to minimizing potential errors in sampling and analysis and suggests quality control procedures. Section 5 summarizes the principal findings and recommendations of the study.

1.2 APPROACH

To accomplish the objectives and tasks described, the work has been carried out to a considerable extent sequentially; i.e., the recommendations on the favoured deposition models were developed as the basis for the field program design. Some aspects, e.g., literature review, of both major tasks have been carried out in parallel and have been used as interchangeable information sources. Figure 1 shows the AOSERP study area and the location of meteorolgoical, ambient air quality and precipitation chemistry stations now being operated.

Section 6.1 is a list of papers, articles, texts, and proceedings that have been reviewed in the course of selecting deposition models for more intensive review. Thirty of these were examined in detail and these are evaluated in Tables 18 to 21 for the cases of both dry and wet deposition and gaseous and particulate species.

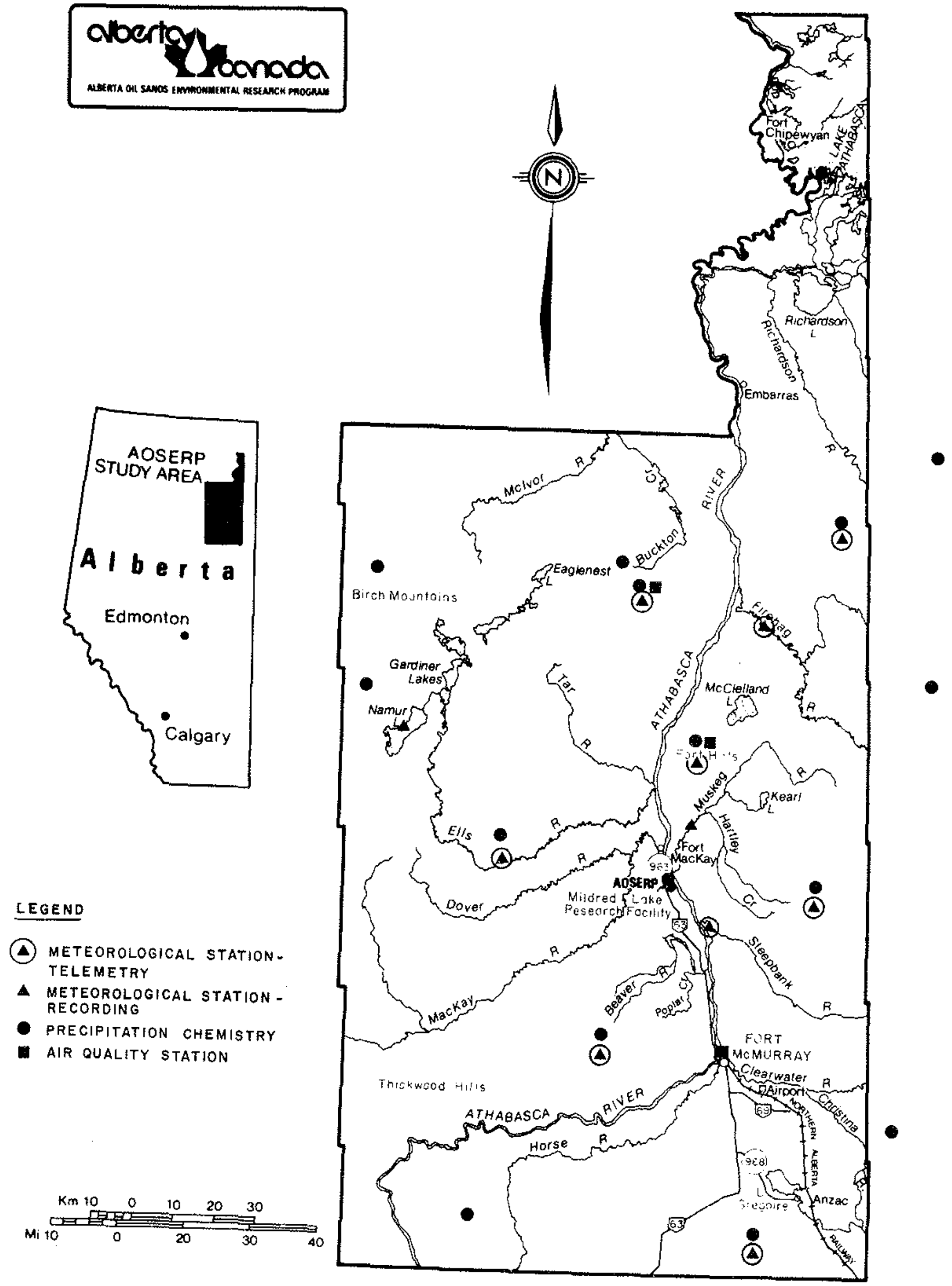

Figure 1. Meteorology and Air Quality Technical Research Committee--research sites.

Section 6.2 is a list of references that have been reviewed relating to design of field monitoring programs.

1.3 IDENTIFICATION OF CONTAMINANTS AND SOURCES

1.3.1 Existing And Committed Developments

Based on the Program Policy and Direction document (1977), the following developments are expected. At present there is one oil sands plant in operation--Great Canadian Oil Sands (GCOS). It may by permit, produce up to 65,000 bbl/day of synthetic crude and in the process release up to 300 tonnes/day SO_2 from the powerhouse stack and 48 tonnes/day SO_2 from the incinerator stack. In actual practice the plant operates at less than maximum continuous production, and 1976 SO_2 emissions were estimated to be about 60 percent of the total allowable. Amounts of other gases also produced in the course of normal plant operations during 1976 were estimated as follows:

H_2S	13×10^6 g
NO_x (as NO_2)	$5,934 \times 10^6$ g
CO	975×10^6 g
light hydrocarbons	303×10^6 g
heavy organics	$4,633 \times 10^6$ g

Particulates released through the powerhouse stack include elements present in the raw bitumen ore which come out with the solid material in the coking process and which are subsequently released to the atmosphere when the coke is burned as fuel. An analysis of fly ash revealed the following significant elements:

silicon	34 percent (by weight)
carbon	11 percent
aluminum	11 percent
iron	5 percent
vanadium	2 percent
nickel	1 percent

The Syncrude Canada Plant, which will start production in 1978, is designed to produce 125,000 bbl/day and will be permitted to release SO_2 to the atmosphere at the rate of 287 tonnes/day. Other gases to be emitted include CO_2, N_2, NO_x and H_2. Particulates produced in the fluid coking process and CO boiler will be nearly completely removed (95 percent) by electrostatic precipitators.

The town of Fort McMurray, which has a present population of over 15,000, produces atmospheric pollutants by domestic and industrial fuel consumption and road traffic. Total emissions for 1976 have been estimated as follows:

SO_2	35×10^6 g
CO	$1,142 \times 10^6$ g
NO_x	$1,126 \times 10^6$ g
light hydrocarbons	127×10^6 g
heavy organics	770×10^6 g

1.3.2 Future Developments

It is estimated that by 1985 there will be a third oil sands plant producing at 100,000 bbl/day. The population of the area at that time may approach 45,000.

By the year 2000 there could be five surface mining and two *in situ* recovery plants operating. Each will produce about 100,000 bbl/day.

The area population at that time will approach 90,000 and it is expected that a second major population centre may be established, probably in the vicinity of Fort MacKay. Table 1 summarizes the major features of future potential developments.

The total annual emissions of SO_2 in the year 2000 could therefore be in the order of 1.2×10^6 tonnes. This can be compared with annual emissions of 1.3×10^6 tonnes at Sudbury, 0.66×10^6 tonnes in Cleveland and 0.49×10^6 tonnes in the Sarnia-Port Huron complex.

Table 1. Summary of area development projects .

				Estimated Max. SO_2 Emission Rate		
Time	Area Population	Oil Sands Plants	Max. Daily Production (10^3 bbl)	at 70 tonnes/day per 100,000 bbl	average	at 250 tonnes/day per 100,000 bbl
Present	15,000	1	60		348	
1978	18,000	2	185		635	
1985	45,000	3	300	705	795	885
2000	90,000	5 open pit 2 *in situ*	700	985	1,435	1,885

2. DEPOSITION PROCESSES

2.1 INTRODUCTION

The basic objective of this part of the project was to review all relevant literature relating to depositional processes of gases and particulates. In our review, we place no restrictions on the processes to be considered and our analysis has proceeded within that framework. However, we do note, where possible, aspects of the models and algorithms that may restrict their use as an interlocking sub-model of the Gaussian process or Livermore Regional Air Quality model.

The approach that has been adopted in reporting the literature survey is first to discuss qualitatively in Section 2.2 the depositional processes, using the work of Hidy (1970, 1971, 1973) as a basis. Next, we attempt to classify the deposition models so that the vast amount of literature can be reported and reviewed logically in terms of historical development and processes involved. Sections 2.4 to 2.7 deal separately with particulate dry deposition, gaseous dry deposition, particulate wet deposition, and gaseous wet deposition considering for each model its theoretical basis, assumptions, limitations, and practical aspects. Probable errors are discussed for each model. Finally, in Section 2.8 recommendations are made regarding the favoured hypothesis, algorithm or model.

2.1.1 Atmospheric Diffusion Models

Two approaches to modelling the transport of atmospheric emissions from the processing plants of oil sands in Alberta are being considered. The first is based on the usual technique of the Gaussian model and would be used to determine ambient air quality and deposition loading up to 10 km from the source. The second approach, based on an Eulerian formulation of the mass continuity equation, caters for modelling effects over an area possibly up to an order of magnitude larger than the Gaussian procedure with complex topography and varying meteorological conditions.

The specific Gaussian model to be adopted is not known but the following typical one based on Gifford (1968:99) illustrates the essential characteristics

$$\bar{\chi}(x,y,z,H) = \frac{Q}{2\pi\sigma_y\sigma_z\bar{u}} \exp\left|-\tfrac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right| \cdot \left\{\exp\left|-\tfrac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right| + \exp\left|-\tfrac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right|\right\} \qquad (2.1)$$

where $\bar{\chi}$ = concentration (as 10-minute average),
Q = emission strength,
x,y,z = cartesian co-ordinates,
σ_y,σ_z = dispersion coefficients in y and z directions,
H = stack height plus plume rise,
$\bar{u}$ = average wind velocity.

To take into account dry deposition of airborne contaminants, Q is adjusted in the following manner (Van der Hoven 1968:202)

$$Q = Q' = Q_o \left\{\exp \int_o^x \frac{dx}{\sigma_z \exp\left|\tfrac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right|}\right\}^{-\left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{v_d}{\bar{u}}} \qquad (2.2)$$

where Q' = depleted source strength at distance x,
Q_o' = initial source strength,
v_d = deposition velocity.

Thus dry deposition loading would be given by

$$L_d = v_d\,\bar{\chi}\,(x,y,z_o,H) \qquad (2.3)$$

where $\bar{\chi}\,(x,y,z_o,H)$ = concentration at ground level.

Scavenging by precipitation is given as follows (Engelmann 1968:208)

$$L_w = \Lambda \int_0^H \chi(x,y,z,Q')dz \qquad (2.4)$$

where Λ = washout coefficient.

For the case where precipitation extends upstream to the source, washout becomes

$$L_w = \frac{\Lambda Q_o}{(2\pi)^{\frac{1}{2}}\bar{u}\sigma_y} \exp\left|-\tfrac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right| \exp\left|-\frac{\Lambda x}{\bar{u}}\right| \qquad (2.5)$$

Thus it is seen that the deposition process--wet or dry--can readily be taken into account by the parameters v_d and Λ.

The Livermore Regional Air Quality model (MacCracken et al. 1976) may be considered to be a numerical solution to the vertically integrated species continuity equation. The fundamental governing equation is

$$\frac{\partial}{\partial t}(\rho\bar{c}_i H) + \frac{\partial}{\partial x}\bar{u}\,\bar{c}_i\,(1+\beta_i)\rho H + \frac{\partial}{\partial y}\bar{v}\,\bar{c}_i(1+\beta_i)\rho H + w_i$$

$$= \frac{\partial}{\partial x}\left(K\frac{\partial}{\partial x}\rho\bar{c}_i H\right) + \frac{\partial}{\partial y}\left(K\frac{\partial}{\partial y}\rho\bar{c}_i H\right) + \bar{s}_i H + \rho H\bar{R}_i(\bar{c}_1, c_2, \ldots, \bar{c}_N) \qquad (2.6)$$

with $$w_i = \begin{cases} \rho w_H c_i(x,y,H,t) & w_H > 0 \\ 0 & w_H = 0 \\ \rho w_H c_{\tau_i} & w_H < 0 \end{cases}$$

and $$\beta_i = \frac{n}{n+1}\,\frac{b_i}{\bar{c}_i}$$

where ρ = atmospheric density,

$\bar{c}_i$ = vertically averaged concentration for species i,

H = inversion height,

$\bar{u},\bar{v}$ = vertically averaged horizontal velocity components,

x,y,z = cartesian co-ordinates,

w_H = vertical velocity at top of inversion layer,

n = coefficient in the power law velocity profile,

t = time,

K = horizontal turbulent eddy diffusion coefficients,

$\bar{s}_i$ = non-chemical source and sink rate density of species i,

$\bar{R}_i(\bar{c}_1, c_2, \ldots, \bar{c}_N)$ = change in concentration as a result of chemical and photochemical reactions among the N different species,

b_i = function which includes the emission source strength and deposition velocity.

It is noted that the model is vertically averaged and the equations are solved in the x and y directions after finite differencing. Because of vertical averaging, ground-level concentrations which will be based on the average profile values will be smaller in magnitude than those normally expected (Roth et al. 1975:A25). Using a washout coefficient approach, this limitation will not be serious but it may be for dry deposition values which are a function of ground-level concentrations. Furthermore, some of the more complex scavenging models are able to incorporate vertical concentration profiles and, if adopted, their full potential will not be realized. Notwithstanding these comments, in the case of v_d, the model modifies the average vertical concentration using the logarithmic profile assumption.

Operationally, the following inputs are required.

1. For a 1-h and 1-km scale, surface and elevated source emission data for each pollutant are required.
2. Atmospheric structure and winds must be specified. Using the MASCON numerical model (MacCracken et al. 1972; Dickerson 1978), which utilizes available observational data on surface winds and inversion levels, wind fields are generated consistent for complex topography and air mass conditions as input to the air quality model. The MASCON model also generates horizontal eddy and

vertical surface diffusion coefficients. It should be noted for the surface (1 m) vertical diffusion coefficient (K_z) that

$$K_z = 0.1\,\alpha\,u_1 \tag{2.7}$$

where α = Von Karman's constant (0.4),

u_1 = horizontal wind velocity at 1 m.

Therefore K_z is independent of surface type. This aspect may be limiting when dealing with surfaces which may range from water and snow through to forests.

3. The intensity of solar radiation is required to calculate photodissociation reaction rates.

2.2 DEPOSITION PROCESSES

The most extensive qualitative reviews of the deposition processes of particulate and gaseous pollutants are by Hidy (1970, 1971, 1973). In each, however, he is concerned with the removal rather than the deposition of pollutants and so includes processes that may only change the species of the pollutant within the atmosphere without necessarily removing it totally from the atmosphere. Nevertheless, we use Hidy's summaries as an outline of the many processes that can effectively remove particulates and gases from the lower atmosphere. In subsequent sections these processes will be examined in various levels of detail.

However, it is noted that deposition mechanisms can be arbitrarily divided into two processes--dry and wet. The dry process includes, for example, sedimentation or particle fallout, diffusion or inertial deposition on vegetation and surfaces at ground level, and collisions with other particles. Such collisions can take place by Brownian motion, by turbulence within the suspending gas as a result of differences in relative velocities during fallout, and by electrical and phoretic forces acting between particles. Also, there are chemical reactions including condensation or evaporation on existing particles that can significantly affect the size spectrum of particles, as well as produce particles in the atmosphere.

Wet processes include rainout from within the cloud, including collision mechanisms, phoretic forces, diffusiophoresis, and nucleation. Below the clouds, wet processes involve washout as well as chemical reactions between aerosols and hydrometeors.

Hidy (1970) has summarized the removal of gases and particulates from the lower atmosphere as follows.

Processes affecting removal of gases:

1. Homogeneous gas-phase reactions,
2. Particle-gas reactions,
3. Adsorption and absorption in aerosols,
4. Adsorption and absorption in hydrometeors,
5. Adsorption and absorption in vegetation,
6. Adsorption and absorption in oceans and lakes, and
7. Adsorption and absorption in buildings, rocks, etc.

Dry processes affecting removal of aerosols:

1. Sedimentation (fallout),
2. Diffusional and inertial deposition on vegetation, structures, etc.,
3. Collision with other particles with or without electrical charging, and
4. Chemical reactions on existing particles.

Wet processes affecting removal of aerosols:

1. Rainout from clouds: collision mechanisms without electrical charge,
   phoretic mechanisms,
   electrical charge,
   removal by nucleation,
2. Washout under clouds, and
3. Chemical reactions between aerosols and hydrometeors.

Therefore, it can be seen that removal of gases depends on mass transfer (convective diffusion) to surfaces, on physical and chemical adsorption on that surface, or on homogeneous chemical reactions to form particles. On the other hand, aerosol removal relies in part on actual dry fallout by sedimentation, on collision with other particles, including cloud droplets and raindrops, and on chemical reactions of a heterogeneous nature.

An interesting feature of aerosol behaviour relates to the development of phoretic forces associated with non-uniformities in the suspending medium. Two forces are of concern here--the aerosol thermal force proportional to temperature gradient and the diffusiophoretic force proportional to the concentration of gaseous species under consideration. Hidy (1970:362) suggests that, on the basis of thermal gradients and concentration gradients of water vapour expected near evaporating or condensing water droplets, these forces should be of second-order importance. This aspect is followed up in Section 2.4.4.

To gain some idea of the order of magnitude of the various processes listed above, Tables 2, 3 and 4 are reproduced from Hidy (1973). The tables show respectively the estimated removal rate or ageing rates of Aitken nuclei (mean radius of 0.05 μm), large particles (mean radius of 0.5 μm), and giant particles (mean radius 5 μm) at ground level (urban), near the cloud base, and in or above the clouds.

Analysis of the tables shows a number of aspects worth noting.

1. Relative to the other processes, sedimentation is not a significant contributor to the deposition process. Essentially, it only becomes of importance at the upper end of the size spectrum (≥50 μm) (Hidy 1971).
2. For Aitken nuclei, inertial and diffusional deposition is very significant, but is relatively unimportant for the larger particles.

Table 2. Estimated removal rates of Aitken nuclei in the troposphere (particles lost/cm^3/s).[a]

Process	Height Ground (urban) $N_i=10^5 cm^{-3}$	 Near cloud base (2km)$N_i=10^3 cm^{-3}$	 In or above clouds (6km)$N_i=10^2 cm^{-3}$
Sedimentation	10^{-6}	10^{-8}	10^{-9}
Inertial and diffusional deposition on obstacles at the surface (q_g=0.1 cm/s)	0.1	-	-
Convective diffusion ($D_T=10^4-10^3 cm^2/s$)	$10^{-1}-10^0$	10^{-4}	10^{-6}
Condensation of vapours on particles	10^4	10^0	10^{-1}
Thermal coagulation	10^0	10^{-4}	10^{-6}
Scavenging by differential settling[b,c] (R_2-10 μm)	10^{-3}	10^{-7}	10^{-9}
Turbulent coagulation[d]	10^{-3}	10^{-9}	10^{-11}
Washout by 1-mm spherical hydrometeors ($N_p=10^{-3} cm^{-3}$)	10^{-3}	10^{-5}	-
Rainout by cloud processes (nucleation + collisions) (R_p=10 μm)[e]	-	10^{-2}[f]	10^{-4}

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[a] Extracted from Hidy (1973).

[b] Brownian diffusion to surface included.

[c] Calculated for $\rho_p=1$ with 10-μm particle concentration, $N_2=10^{-1}cm^{-3}$, $N_2=10^{-3}cm^{-3}$, and $N_2=10^{-4}cm^{-3}$, respectively.

[d] Calculated for turbulence dissipation rate $\varepsilon=10^3 cm^2/s^3$, and $\varepsilon=0.1\ cm^2/s^3$, respectively.

[e] Calculated for $N_p=10^2/cm^3$, cloud base; $N_p=10\ cm^{-3}$ at 6 km.

[f] Aitken nuclei are assumed too small to be a factor in cloud droplet nucleation; Brownian diffusion is included in scavenging.

Table 3. Estimated removal rates of large particles (R_1=0.5 μm) in the troposphere (particles lost/cm^3/s).[a]

Process	Height		
	Ground (urban) $N_i=10^2/cm^3$	Near cloud base (2km)$N_i=1\ cm^{-3}$	In or above clouds (6km)$N_i=10^{-1}cm^{-3}$
Sedimentation	10^{-6}	10^{-7} to 10^{-8}	10^{-9}
Inertial and diffusional deposition on obstacles at the surface (q_g=0.01 cm/s)	10^{-5}	-	-
Convective diffusion ($D_T=10^5\ cm^2/s$)	10^{-3}	10^{-5}	-
Condensation of vapours on particles	10^{-1}	10^{-5}	10^{-6}
Thermal coagulation	10^{-4}	10^{-7}	10^{-9}
Scavenging by differential settling[b] (R_2=10 μm)	10^{-7}	10^{-11}	10^{-15}
Turbulent coagululation[b]	10^{-3}	10^{-9}	10^{-11}
Washout by 1-mm spherical hydrometeors ($N_p=10^{-3}cm^{-3}$)	10^{-8}	10^{-10}	-
Rainout by cloud process[b] (R_p=10 μm)	-	10^{-1}[c]	10^{-1}[c]

[a] Extracted from Hidy (1973).

[b] Same values of N_2 . ε, and N_p as used in Table 2.

[c] Assumed 0.1 particle/cm^3/s nucleates.

Table 4. Estimated removal rates of giant particles (R_1=5.0 μm) in the troposphere (particles lost/cm^3/s).[a]

Process	Height		
	Ground (urban) $N_i=10^{-1}cm^{-3}$	Near cloud base (2km) $N_i=10^{-3}cm^{-3}$	In or above clouds (6km) $N_i=10^{-4}cm^{-3}$
Sedimentation	10^{-7}	10^{-11}	-
Inertial and diffusional deposition on obstacles at the surface (q_g=0.1 cm/s)	10^{-6}	-	-
Convective diffusion ($D_T=10^5cm^2/s$)	10^{-6}	10^{-8}	-
Condensation of vapours on particles	10^{-6}	10^{-10}	10^{-11}
Thermal coagulation	10^{-6}	10^{-10}	10^{-12}
Scavenging by differential settling[b] (R_2=10 μm)	10^{-8}	10^{-12}	10^{-10}
Turbulent coagulation[b]	10^{-4}	10^{-10}	10^{-12}
Washout by 1-mm spherical hydrometeors ($N_p=10^{-3}cm^{-3}$)	10^{-7}	10^{-9}	-
Rainout by cloud processes (nucleation + collision)[b] (R_p=10 μm)	-	10^{-3}[c]	10^{-4}[c]

[a] Extracted from Hidy (1973.

[b] Same values of N_2 . N_p, and ε as in Table 2.

[c] Assumed 0.1 particle/cm^3/s nucleates if nuclei are present.

3. The same is true for convective diffusion.
4. Again for Aitken nuclei and for large particles, condensation of vapours on particles is extremely important at ground level, but becomes less near and within the cloud. For giant particles the ageing process, as a result of condensation of vapour onto particles, is very slow.
5. Thermal coagulation is important for the smaller size, but becomes less so as the particles become larger.
6. Except for Aitken particles near the ground, scavenging by differential settling is unimportant.
7. Turbulent coagulation is unaffected by particle size, but decreases with altitude.
8. Washout is not only an intermittent process, but as seen in the tables it appears to be less important than expected from the literature.
9. For large and giant particles, rainout through cloud droplet nucleation is the dominant process.

To summarize, for Aitken particles, condensation of vapours on particles, thermal coagulation, and inertial and diffusional deposition on obstacles at the surface are very important at ground level. Near the cloud base and within clouds, condensation of vapours and rainout are dominant. For large particles, condensation of vapours and convective diffusion are important near the ground, but rainout is the dominant process near and within the cloud. Relative to the ageing process of the smaller particles, those in the range of 5 μm are removed from the atmosphere very slowly.

2.3 CLASSIFICATION

Following the arbitrary division of the deposition mechanisms into wet and dry processes, and also distinguishing between particulates and gases, Figure 2 was devised. It lists the various formulae, algorithms, and models that have been proposed to model deposition mechanisms of air contaminants.

DEPOSITION MODELS

DRY DEPOSITION		WET DEPOSITION	
PARTICLES	GASES	PARTICLES	GASES
Empirical Deposition Velocity v_p (Gregory 1950) (Chamberlain 1953)	Empirical Deposition Velocity v_p (Gregory 1950) (Chamberlain 1953)	Empirical Scavenging Coefficient Λ_p	Empirical Scavenging Coefficient Λ_g
		Empirical Scavenging Ratio W (Chamberlain 1960)	
		Empirical Coefficient of Washout ∇ (Hutcheson & Hall 1974)	
Theoretical v_p (Slinn 1976b, 1977b)	Theoretical v_g (Hicks 1976c) (Slinn 1977b)	Theoretical Λ_p (Chamberlain 1953) (Slinn 1976a, 1977a)	Theoretical Λ_g (Chamberlain 1953) (Engelmann 1966)
		Theoretical W (Engelmann 1970)	
		Makhon'ko Washout-rainout Model (Makhon'ko 1967)	Makhon'ko Washout-rainout Model (Makhon'ko 1967)
		Modified Makhon'ko Model (Andersson 1969)	Modified Makhon'ko Model (Andersson 1969)
		Empirical Snow Model (Knutson & Stockham 1977)	
Slinn's Deposition Velocity Model (Slinn 1976b)	Gaseous Resistance Model (Chamberlain 1967) (Galbally 1974) (Wesely & Hicks 1976) (Garland 1977)	Numerical Washout Model (Kortzeborn & Abraham 1970) (Abraham et al. 1972)	SO_2-SO_4 Scavenging Model (Miller & de Pena 1971)
Sehmel's Integral Resistance Model (Sehmel 1970) (Sehmel 1971) (Sehmel 1973) (Sehmel & Hodgson 1976)	Gaseous Leaf Model (Bennett et al. 1973)	Modified Numerical Washout Model (Stensland & de Pena 1975)	EPAEC Model (Washout) (Hales 1972) (Dana et al. 1975) (Hales et al. 1973) (Slinn 1974a)
	Gaseous Air-Water Interface Model (Liss 1971) (Liss & Slater 1974) (Liss 1975) (Liss & Slater 1975)	Davis In-Cloud Scavenging Model (Davis 1972)	Improved Model of Reversible SO_2 (Barrie in press.)
		Stratiform In-Cloud Scavenging Model (Dingle & Lee 1973) (Lee & Dingle 1974)	Brookhaven Washout Model (Hill & Adamowicz 1977)

Figure 2. A classification of deposition models.

This type of classification was adopted as it allows the relative developments in each of the four processes to be compared. Furthermore, as one reads down the figure, one can see the historical development of the individual procedures and their relation to earlier ones. In general, it will be noted that as one moves down each column the models become more theoretical.

Clearly this figure does not contain all deposition models, but we are confident the major ones are included. The references associated with each model are only a guide to the source information. More details are given in the appropriate section. An extensive bibliography is included in this report.

2.4 DRY PARTICULATE MODELS

2.4.1 Introduction

From Figure 2 it is seen that except for the work of Sehmel and his colleagues and the theoretical work of Slinn (1977b) little progress has been made in theoretically modelling the depositional process of particulates. However, it will be noted in Section 2.4.3 that many laboratory and field experiments have been undertaken as a basis for empirical estimates of particulate deposition.

This introductory section is followed by a brief discussion of terminal velocity of particulates in the atmosphere. The next section deals with the concept of deposition velocity (v_p). Laboratory and field measurements of v_p will be tabulated. In Section 2.4.4, the theoretical aspects of deposition velocity will be outlined and the final sections will summarize the work of Slinn, Sehmel and colleagues in modelling v_p.

2.4.2 Terminal Velocity of Particles

The earth's gravitational field plays a significant role in the deposition of particulate matter on the earth's surface. The rate of descent of the particle depends on the balance between the aerodynamic drag force and the gravitational force exerted by the earth. For a smooth spherical particle and neglecting the effect of slip flow, terminal velocity may be expressed in the form of Stokes' equation as follows

$$v_t(r) = \frac{2r^2 g\rho(r)}{9\mu} \tag{2.8}$$

where $v_t(r)$ = terminal velocity for particle of radius r,

g = gravitational acceleration,

$\rho(r)$ = particle density, and

μ = atmospheric dynamic viscosity.

The terminal velocities of spherical particles in Stokes' low range at 10°C are (Chamberlain 1953)

Radius of particle (μ)	0.5	1	5	10	50	100	500
Terminal velocity for unit density of 2.5 (cm/s)	0.003	0.01	0.31	1.2	25	76	400

Clearly, particles of radius of the order of a micron (1 μm) or less are deposited very slowly by sedimentation--other processes of deposition predominate.

2.4.3 Deposition Velocity

The deposition rate of small particles to the ground can be greater than can be explained by the appropriate terminal velocity. This has focussed attention on non-gravitational and non-precipitation mechanisms of deposition.

In analyzing the deposition rate of spores to the ground, Gregory (1950) concluded that the rate was proportional to the immediate ground-level air concentration. Chamberlain in 1953 introduced the concept of deposition velocity (v_d) and defined it as the ratio of the deposition rate to the immediate ground-level concentration, thus

$$v_d = \frac{F}{\bar{\chi}(x,y,o)} \tag{2.9}$$

where F = amount of aerosol removed per unit time per unit area, and

$\bar{\chi}(x,y,o)$ = average concentration of aerosol.

The deposition velocity concept can be applied to a particle or gas, but strictly v_d should be defined relative to the height above the surface at which the volumetric measurement is made. Where the deposition surface is rough or has projections, the numerator in Equation (2.9) is taken as the amount deposited per unit area of ground plan and not per unit area of actual surface.

The concept of deposition velocity in no way explains the physics of the deposition process; nevertheless, it is a convenient way to express dry deposition phenomena. To utilize the concept, deposition velocities have been measured in the laboratory and field.

As part of this review, all papers that contain laboratory or field measured values of deposition velocity of particulates (v_p) were collated and results are summarized as Tables 5 and 6, respectively. Eleven papers dealing with laboratory experiments and 17 containing field information were found. Figure 3 includes more details of Sehmel (1973) and Sehmel and Sutter (1974) results than contained in Table 5. Figure 4 is a plot of combined laboratory and field data for a grass surface.

From these tables and figures a number of conclusions can be drawn.

1. Figure 4 illustrates the typical deposition velocity-particle diameter relationship. The variability for the large diameters greater than 10 μm results from various wind speeds and friction velocities used in the experiments. It also shows that the minimum of v_p occurs in the range 0.1 - 1 μm.
2. v_p is approximately a linear function of wind speed and friction velocity.

Table 5. Laboratory measurements of deposition velocities of particles.

Author (date)	v_p (cm/s)	Reference Height (m)	Particulate Diameter (μm)	Surface	Comments
Chamberlain (1967b)	0.03		0.1	grass	
	0.03		1		
	0.1		2		
	0.8		5		
Möller and Schumann (1970)	$v_g \propto D^{2/3}$				D = diffusion coefficient $2\times10^{-2} \geq D \geq 2\times10^{-5} cm^2 S^-$
Chamberlain and Chadwick (1972)	$v_d = 0.06 u_*$		20-30	cereal crops	dry Includes wind-tunnel and field data
	$v_d = 0.12 u_*$				wet
Clough (1973)	0.005	0.1	0.08	filter paper	v_p to copper also measured. v_p found to be a function of wind speed.
	0.003		0.5		
	0.3		5		
	2		20		
Sehmel (1973)	2×10^{-3}-10	0.01	0.1-28	smooth brass	see Figure 3
Sehmel and Sutter (1974)	5×10^{-3}-29	0.01	0.2-30	water	see Figure 3
Belot and Gauthier (1975)	$v_p \propto u^3$ $v_p \propto d^4$		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

Continued ...

Table 5. Concluded.

Author (date)	v_p (cm/s)	Reference Height (m)	Particulate Diameter (μm)	Surface	Comments
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		5×10^{-2}	short grass	
	0.02		0.2		

Table 6. Field measurements of deposition velocities of particles .

Author (date)	v_p (cm/s)	Reference Height (m)	Particulate Diameter (µm)	Surface	Comments
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 (1960)	0.7			ocean	chloride over Scandinavia
	1.6				
Small (1960)	0.5 (0.2-3.4)			land	Radioactive particles over Norway.
Neuberger et al. (1967)			Ragweed	coniferous forest	80% ragweed pollen removed from air by forest
White and Turner (1970)	5.6		Na	mixed deciduous woodland	1. Probable over-estimation of aerosol income, hence v_p. 2. Standard deviation varied between 65% and 95% of mean v_p.
	4.7		K		
	3.0		Ca		
	7.1		Mg		
	0.8		P		

Continued ...

Table 6. Continued.

Author (date)	v_p (cm/s)	Reference Height (m)	Particulate Diameter (μm)	Surface	Comments
Esmen and Corn (1971)	$v_p = 0.5 D$		0.1-10	filter paper millipore filters glass slide	
Chamberlain and Chadwick (1972)	$v_p = 0.06 u_*$ $v_p = 0.12 u_*$		20-30	cereal crops	dry Includes wet wind tunnel and wind data
Peirson et al. (1973)	0.1-0.6			land	v_p estimated for 23 trace elements based on several years of data
Cawse (1974)	1.3		Al		
	0.22		As		
	(0.45)		Cd		
	0.50		Cr		Extracted from Gatz (1975a) Values in parenthesis were estimated by Gatz from a relationship between particle size and v_d
	(0.50)		Cu		
	1.1		Fe		
	0.56		Mn		
	(0.45)		Ni		
	0.30		Pb		
	(1.0)		Ti		
	0.29		V		
	0.62		Zn		

Continued ...

Table 6. Continued.

Author (date)	v_p (cm/s)	Reference Height (m)	Particulate Diameter (μm)	Surface	Comments
Hart and Parent (1974)			Na Ca Mg K P NO_3	Douglas fir and junipers	deposition $\frac{\text{beneath trees}}{\text{open terrain}} = 3\text{-}16$
Clough (1975)	3.4		30	grass	dry $u_*=37$ cm/s
	7.3			grass	dry $u_*=87$ cm/s
	11.			grass	wet $u_*=87$ cm/s
	61.			dry moss	
	100.			wet moss	
	0.74		4	grass	dry $u_*=37$ cm/s
	1.1				
	0.75		3	grass	dry $u_*=37$ cm/s
	12.7			dry moss	
Abrahamsen et al. (1976)			$SO_4^=$	spruce and pines	deposition $\frac{\text{beneath trees}}{\text{open terrain}} = 2$
Dovland and Eliassen (1976)	0.16		atmospheric aerosol	snow	lead, $SO_4^=$; upper bound value
	0.68				

Continued ...

Table 6. Concluded.

Author (date)	v_p (cm/s)	Reference Height (m)	Particulate Diameter (μm)	Surface	Comments
Fritschen and Edmonds (1976)	0.07- 0.46		3	Douglas fir	
Prahm et al. (1976)	0.4		atmospheric aerosol	Atlantic Ocean	$SO_4^=$
Krey and Toonkel (1977)	0.5				^{90}Sr; HASL wet-dry collector
Wesely et al. (1977)	0.6	5	0.05-0.1	bare soil and grass	$u<2$ m/s; eddy correlation method

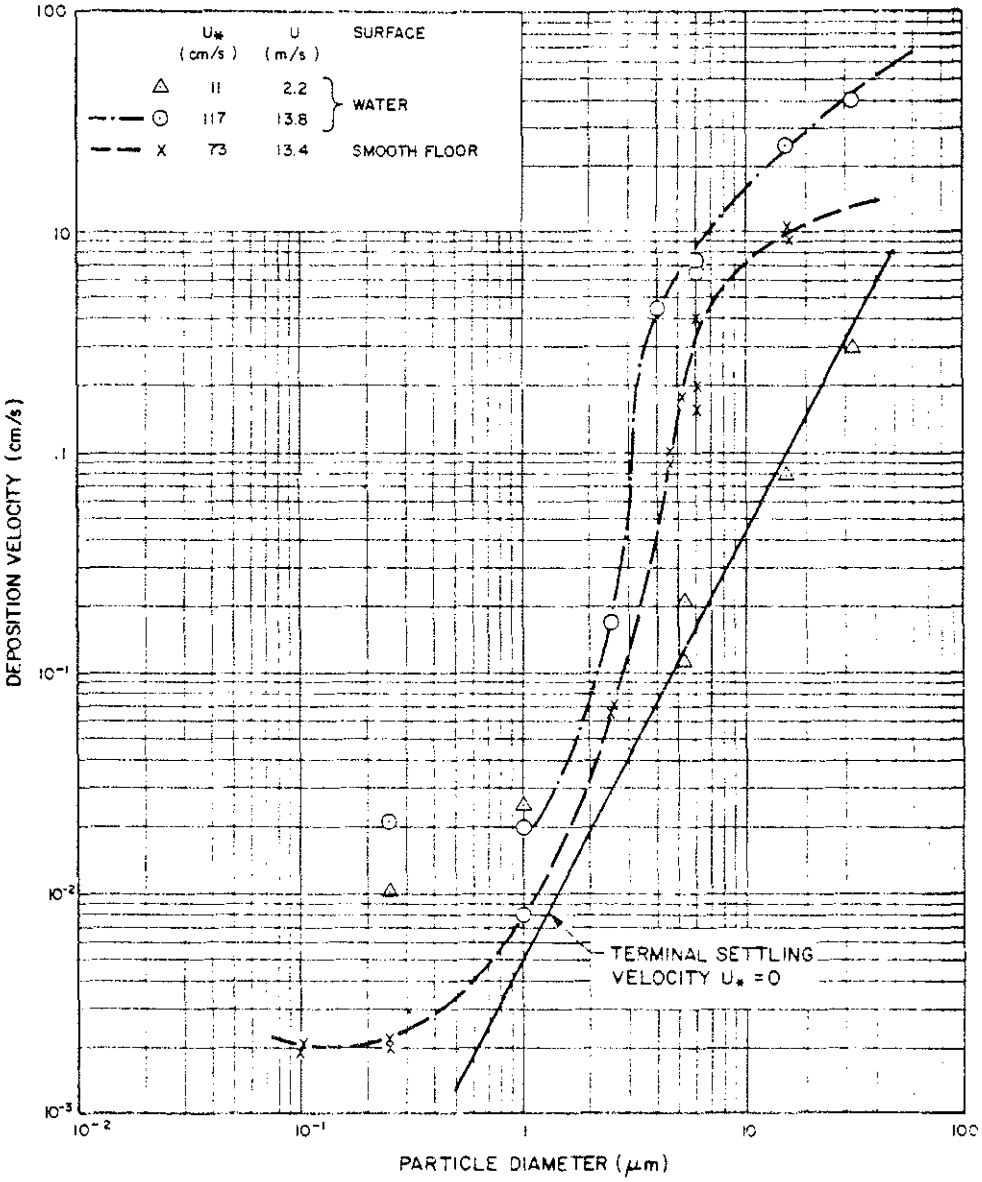


Figure 3. Laboratory measurements of deposition velocities of particles to a water surface and a smooth floor (extracted from Sehmel 1973 and Sehmel and Sutter 1974).

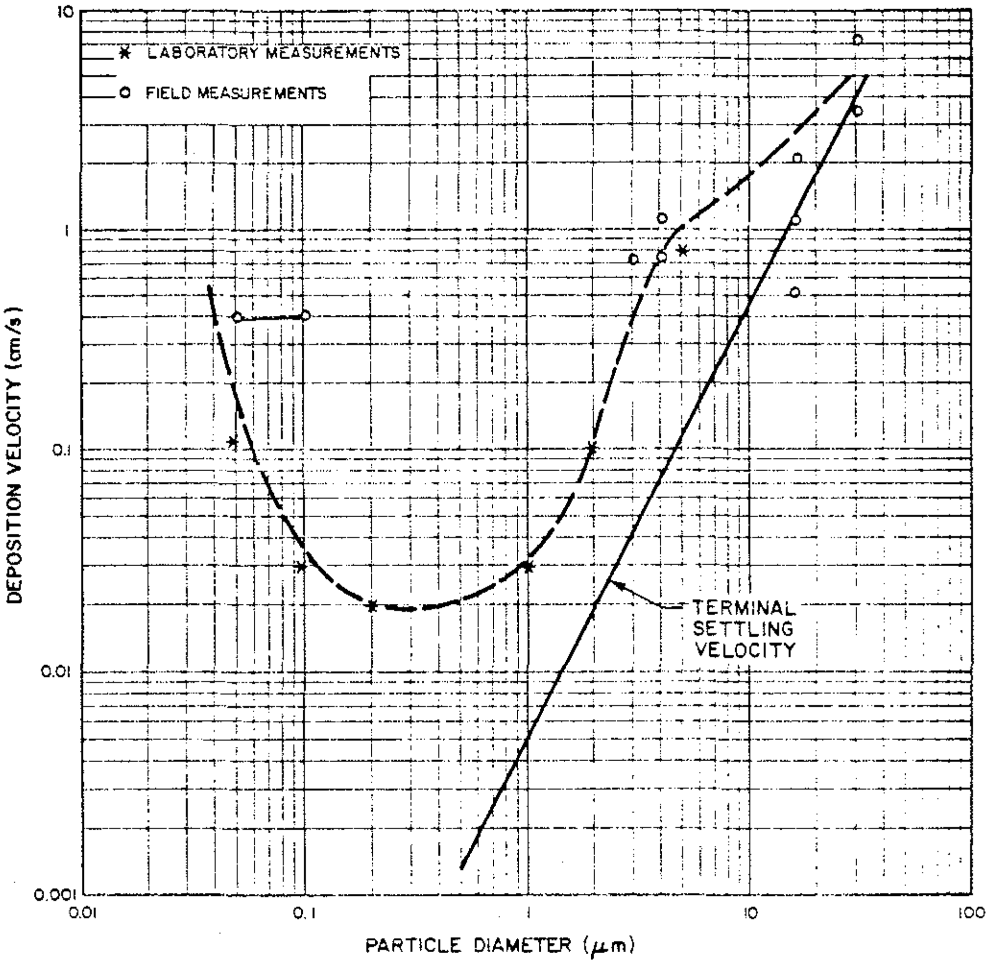


Figure 4. Laboratory and field measurements of deposition velocity of particles to grass.

3. Deposition of particulate matter beneath trees varies significantly with values ranging from 2 - 16 times that measured in adjacent open terrain.
4. Considerable care needs to be exercised in choosing a "typical" deposition velocity. v_p is a function of many factors and can vary by 2 orders of magnitude.

2.4.4 Theoretical Deposition Velocity

In dry deposition of particulates, we assume that atmospheric transport is always rate limiting. Furthermore, for our purpose it is sufficient to assume that the particles are not re-entrained into the atmosphere, unless winds are high (as in a dust storm).

Slinn (1977b) examines 2 basic theories for dry deposition of particles to a smooth surface. He rejects the approach by Friedlander and Johnstone (1957) and its variations (Chamberlain 1960; Davies 1966) and develops the suggestion of Owen (1969), namely that particles finally reach the surface by bursts of turbulence. From this picture he obtains deposition velocity as

$$v_p = v_s + 10^3 \overset{o}{m}'' + \frac{u_*^2}{\beta \bar{u}} E_j \tag{2.10}$$

where v_p = deposition velocity of particles,

v_s = settling velocity of particles,

$\overset{o}{m}''$ = water vapour mass flux (+ve if condensation),

u_* = characteristic or friction velocity,

$\bar{u}$ = mean wind speed,

β = empirical constant,

E_j = collection efficiency

$$= 10^{-3/S_t} + \frac{\beta}{\gamma} S_c^{-0.6} \tag{2.11}$$

S_t = particle Stokes number,

$$= \tau \, u_*^2 / \nu \tag{2.12}$$

τ = particle relaxation time,
ν = kinematic viscosity of air,
γ = empirical constant,
S_c = Schmidt number
= ν / D, and (2.13)
D = particle's diffusion coefficient.

The first term on the right-hand side of Equation (2.10) accounts for gravitational settling or sedimentation, while the second term takes into account the diffusiophoretic contribution to v_p for the case of water vapour evaporization or condensation. (Electrical effects and thermophoresis are assumed negligible.)

In Figure 5 (taken from Slinn 1977b, Figure 13), Equation (2.10) is plotted for $\beta = \gamma = 0.4$ and for different values of u_* and $\overset{o''}{m}$. (According to Slinn [1977b] a value of $\overset{o''}{m}$ = 1 mm/h is not an unreasonably high value for wet surfaces on warm days at moderate humidity). Figure 5 illustrates a number of important characteristics about v_p.

1. Minimum v_p occurs in the particle radius range of 10^{-1} μm and 1 μm. For comparison, note the location of the minimum of the observations in Figure 4.
2. For particle radii greater than 1 μm, the inertial impact effects become significant, increasing v_p by more than 2 orders of magnitude.
3. Below 10^{-1}-μm size, molecular diffusion becomes the dominating effect.
4. Diffusiophoresis can significantly influence dry deposition.
5. Theoretical curves seem to fit experimental results.

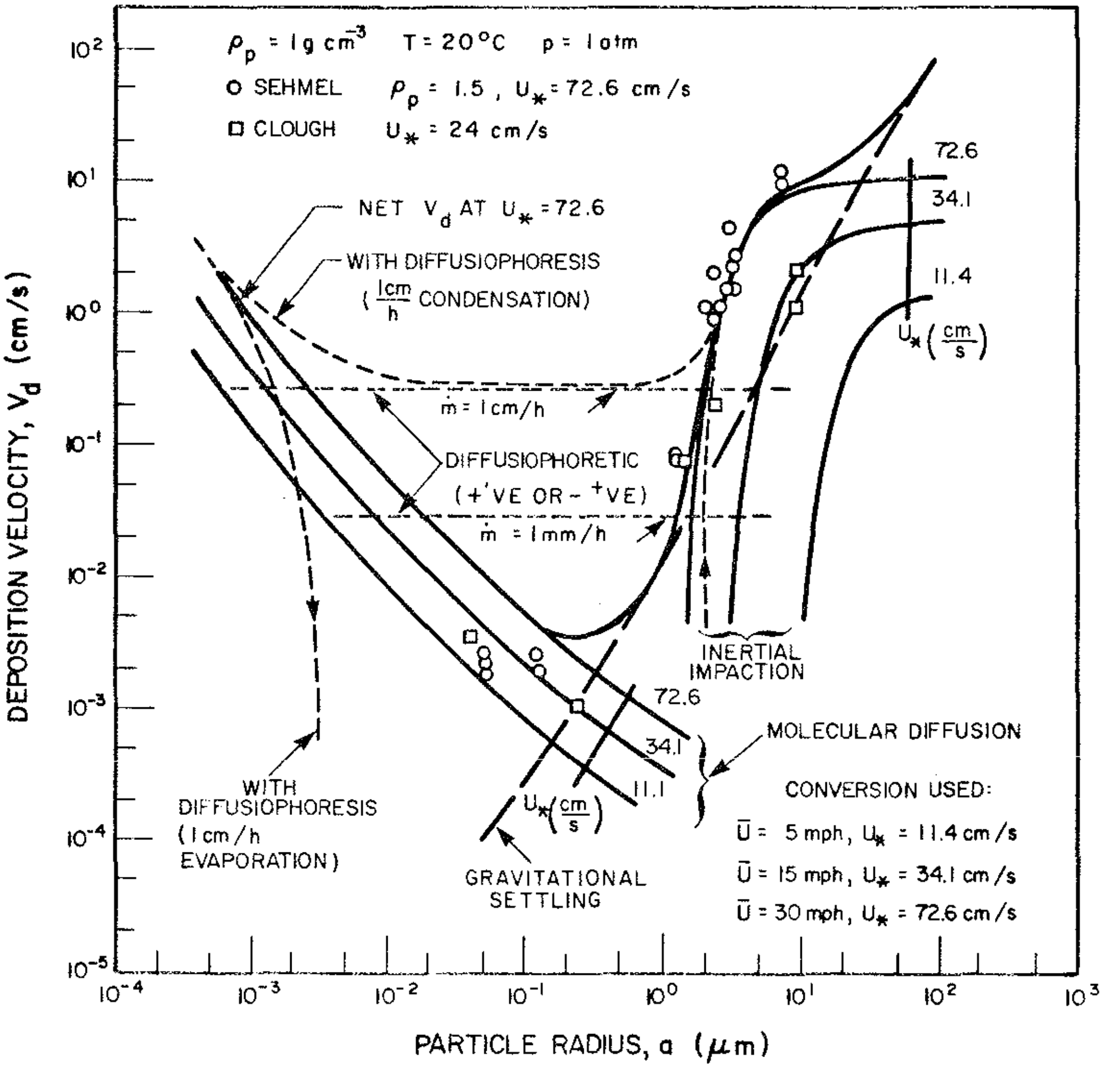


Figure 5. Dry deposition to smooth surfaces as a function of particle radius
(extracted from Slinn 1977b)

2.4.4.1 Deposition in a canopy. The previous discussion was concerned with particle deposition on a smooth surface. The introduction of a canopy presents added complexities. Slinn (1977b) has outlined a new theory for dry deposition in a canopy which may be represented by the following equation.

$$v_p = v_s - \frac{\delta u_*^2}{\beta \bar{u}_g} E_j + \frac{\alpha u_*}{\alpha u_* + CH} \left| CH + \frac{u_*^2 E_j}{\beta \bar{u}_g} \right| \qquad (2.14)$$

where v_p = deposition velocity within the canopy,

v_s = settling velocity,

u_* = friction velocity,

$\bar{u}_g$ = mean wind speed above the canopy,

E_j = collection efficiency (Equation 2.11),

C = fraction of particles of radius a that are filtered out per second,

H = thickness of canopy layer, and

$\alpha, \beta, \gamma, \delta$ = empirical constants, but insufficient field data are available to evaluate them.

Using the concept of canopy filtration efficiency, Slinn (1977b) defined C as follows :

$$C = \frac{\bar{u}_c B}{\lambda \bar{\rho}} \xi(a, \lambda) \qquad (2.15)$$

where $\bar{u}_c$ = mean wind speed within the canopy,

λ = typical length scale of individual fibres,

$\left(\frac{B}{\bar{\rho}}\right)$ = packing density of foliage,

B = biomass per unit volume

$$= \rho \int \lambda \Lambda \, N(A) dA, \qquad (2.16)$$

$\bar{\rho}$ = average mass density of foliage,

$\xi(a, \lambda)$ = collection efficiency of the canopy fibres.

The canopy infiltration effect, γ, is defined by:

$$\gamma = \frac{HB}{\lambda \rho} \qquad (2.17)$$

To illustrate the direction of the results, Equation (2.14) is plotted as Figure 6 (extracted from Slinn 1977b, Figure 16) with the infiltration parameter (γ) being the third variable. From this figure it is observed that :

1. There is a significant increase in v_d for particles smaller that 10 μm. Increases also occur with canopy height H and biomass B.
2. With decreasing size of the characteristic dimension of the collectors, there is an increase in v_d.

Regarding Figure 6, Slinn (1977b) also notes that v_d increases with increasing wind speed within the canopy.

Finally, it should be noted that according to Slinn there are not yet available sufficient data to test Equation (2.14) but the theory appears to be consistent with various experimental results.

2.4.5 Slinn's Deposition Velocity Model

Based on the concept of deposition velocity, we note that Equation (2.10) may be utilized as a particulate deposition velocity model.

To apply the model in practice, a number of variables and parameters would need to be known, namely :

$\overset{o}{m}''$ (water vapour mass flux)--this would be based on climatic data (temperature, humidity, wind, net radiation) measured at the field site;

u_* (friction velocity)--probably could be estimated knowing the surface characteristics but better to measure vertical wind profile; and

τ (relaxation time)--this is a drag coefficient, estimated as the settling velocity divided by the acceleration of gravity (Davies 1966, tables).

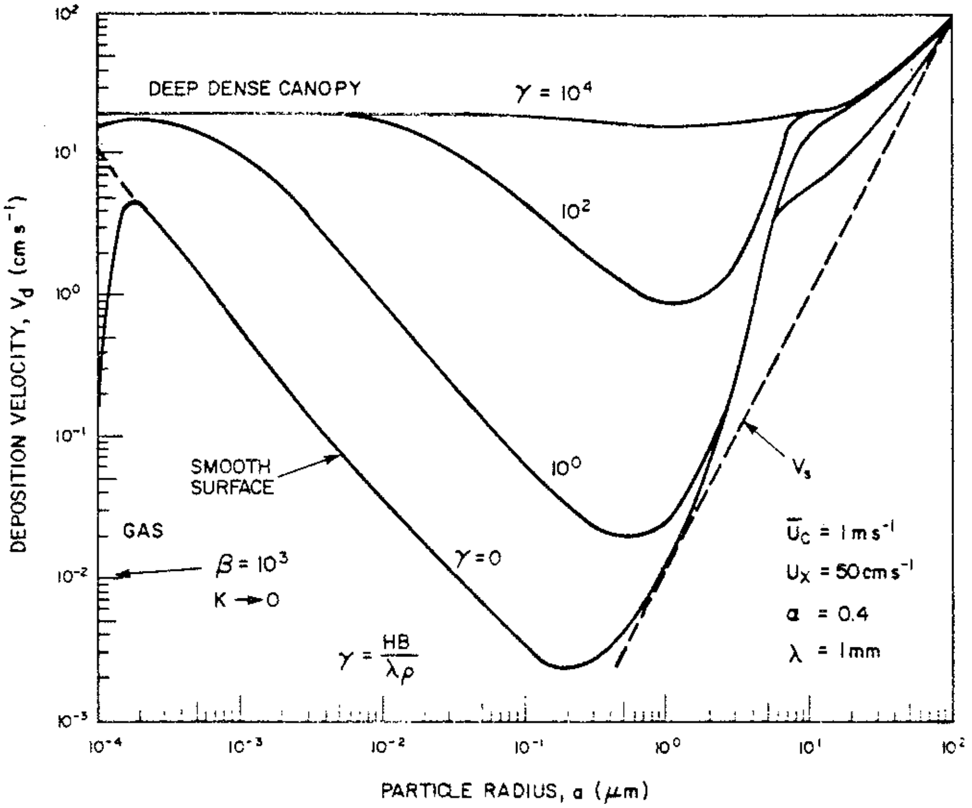


Figure 6. Dry deposition as a function of particle radius and various canopy characteristics (extracted from Slinn 1977b).

In addition, particle size spectrum and average wind speed would be required. As values of the parameters β and γ are not adequately known at present, field values of v_d would need to be measured along with other variables in Equation (2.10) so that typical values of β and γ for the field site could be ascertained.

2.4.6 Sehmel's Integral Resistance Model

In 1970 Sehmel examined a number of theories that had been advanced to explain turbulent deposition. But according to Sehmel, none of these models adequately accounted for experimental observations. These models were based upon the assumptions that particle transport across a boundary layer is caused by a combined effect of eddy diffusion followed by a final free flight to the deposition surface. In the models it is assumed that particle and air eddy diffusivities are equal and that the particle velocity at the start of free flight is related to the root mean square air velocity. Sehmel's work showed that the free flight velocity is a function of the particle relaxation time and not the previously assumed function of the root-mean-square air velocity and he outlined a model consistent with experimental data. In 1971 and 1973, this model was further developed to take into account the effects of gravity on deposition. Details of the Integral Resistance model, as we have called it, are given by Sehmel and Hodgson (1976).

The model predicts particulate deposition velocity based on a steady-state one-dimensional mass transfer process. Dimensionless integral mass transfer resistances are used for prediction.

The turbulent deposition of aerosol particles from an air stream to a surface is one means by which airborne particles are removed from the polluted atmosphere. The turbulent air eddies impart a directed motion to the particles. However, the particles have a much greater inertia than an equivalent volume of air. Thus the concept of deposition velocity is a measure of this effect, combined with all the others that can cause mass transport across a surface boundary layer (Sehmel 1971). These are listed below:

Brownian motion

- diffusiophoresis
- eddy diffusion
- electrical charge effects
- gravity
- impaction
- interception
- non-uniform surfaces
- thermophoresis
- turbulent gradients
- particle lift forces in uniform shear fields which might typify the laminar sub-layer.

Several limitations are evident in the deposition velocity concept. Firstly, experimental deposition velocities have been determined with limited experimental control. For example, particle diameters have been inadequately known and it is difficult to generalize to other field conditions. Secondly, particle (and gaseous) removal rates are non-steady state processes dependent upon the delivery capacity of the upper atmosphere as well as surface resistance. Normally, non-steady state mass transfer cannot be adequately defined by a single point concentration, and therefore most field determined deposition velocities only approximate surface mass transfer rates.

Sehmel and Hodgson (1976) postulate that the pollutant deposition can be described by a 3-box model. In Box 1, airborne pollutant plume movement is described by standard meteorological eddy diffusion. In the depositional process, the plume approaches and interfaces with Box 2. This idealized layer is just above the vegetative canopy or surface elements in the region where the transfer processes are modified by the presence of the canopy or surfaces. Box 3 is located within the canopy or surface elements.

Depositional velocities are predicted by calculating integral diffusion resistances in each of the 3 boxes. However, as diffusional resistance correlation exists only for small surface roughness, predictions are limited to surface elements with small roughness heights.

Basic assumptions in the Sehmel and Hodgson model are that:

1. Particles diffuse at a constant flux from a uniform concentration of particles,
2. A relationship for particle eddy diffusivity can be determined,
3. The effect of gravity can be described by the terminal settling velocity,
4. Particle agglomeration does not occur, and
5. Particles are completely retained by the surface.

For a detailed discussion on dry deposition and resuspension of aerosol particles, see Slinn (1977b).

Based on these assumptions, deposition flux, F, can be described by

$$F = -(\varepsilon + D)\frac{dC}{dZ} - v_t C \tag{2.18}$$

where F = deposition flux,
ε = particle eddy diffusion,
D = Brownian diffusivity,
C = particle concentration at surface, and
v_t = terminal settling velocity.

The deposition velocity is predicted from a dimensionless integral form of Equation (2.18)

$$-\int_{C_z}^{0} \frac{u_* dC}{F + v_t C} = \int_{z^+ \text{ at } C_z}^{r^+} \frac{dz^+}{\varepsilon/\nu + D/\nu} = \text{Int} \tag{2.19}$$

where ν = kinematic viscosity of air,

u_* = friction velocity, and

z^+ = dimensionless distance above the surface

$$= zu_*/\nu. \tag{2.20}$$

Integration limits are that particle concentration is a constant C_2 at a reference height of 2 cm and above, and that particle concentration is zero at a dimensionless particle radius r^+ from the deposition surface.

The integral Int can be sub-divided into 3 parts; thus

$$\mathrm{Int} = \int_{z^+ \mathrm{at}\ C_2}^{z^+_{1\text{-}2}} \frac{dz^+}{\varepsilon/\nu + D/\nu} + \int_{z^+_{1\text{-}2}}^{z^+_{2\text{-}3}} \frac{dz^+}{\varepsilon/\nu + D/\nu} + \mathrm{Int}_3 \tag{2.21}$$

where the first integral is Int_1 and the second is Int_2.

The limits of integration are between the adjoining box interfaces.

Surface integral resistances Int_3 were evaluated by Sehmel and Hodgson from deposition velocities determined in a wind tunnel for a range of surface, particle sizes, friction velocities, and roughness heights as follows

$$\begin{aligned}\mathrm{Int}_3 = -\exp\Big\{ & -23.667 + 5.555 \ \ln d/z_o - 0.007681 \ (\ln u_*/v_t \\ & + 0.03799 \ (\ln u_*/v_t)^2 - 2.54 \ \ln D/(u_* \ z_o) \\ & - 3.724 \ \ln \frac{\rho_p \ u_* d^2}{18 \ \mu \ z_o}\Big\}\end{aligned} \tag{2.22}$$

where d = particle diameter,

z_o = roughness height,

ρ_p = particle density of 1.5 g/cm^3, and

μ = air viscosity.

For Int_3, the reference concentration height for defining the deposition velocity was 1 cm above the deposition surface, which corresponds to Box 3.

Restistance integrals Int_2 and Int_1 for heights greater than 1 cm were evaluated using Equation (2.21) and atmospheric diffusion correlations for stable, neutral, and unstable conditions. The assumption was made that particle eddy diffusivity was equal to the eddy diffusivity of air momentum. Since these correlations do not include any canopy effect on eddy diffusivity in Box 2, Int_2 and Int_1 were combined into a single resistance integral. Details are given in an appendix to Sehmel and Hodgson's paper. Results as a function of stability are shown as Figure 7.

Deposition velocities (v_z) at height Z are related to the sum of the surface integral resistances and the integral resistances above 1 cm as follows

$$v_z = \frac{v_t}{1 - 1/\alpha} \tag{2.23}$$

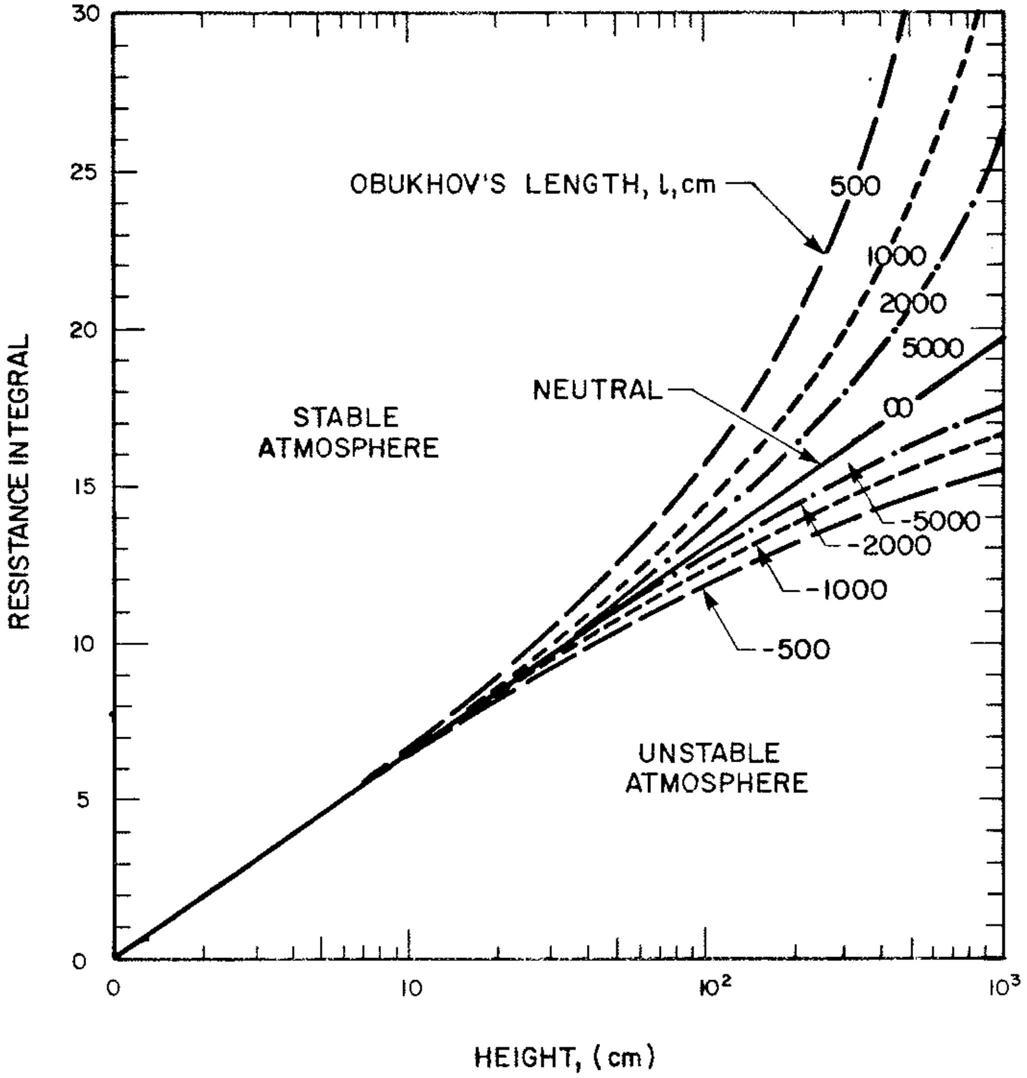
where
$$\alpha = e^{-\frac{v_t \mathrm{Int}}{u_*}} \tag{2.24}$$

Note that as Int becomes large (it is a negative number), K_z approaches v_t, the gravitational settling velocity.

In summary, the Integral Resistance model for estimating deposition velocity consists of Equation 2.23, which in turn depends on Equations (2.24) and (2.21). Int_3 in Equation (2.21) is solved from an empirically derived Equation (2.22) and Int_1 and Int_3 are combined and determined from Figure 7.

In order to ulitize this approach, the following field data are required:

1. Particle size spectrum,
2. Particle density, and



OBUKHOV'S LENGTH IS DEFINED AS $\frac{U_* \rho C_p T}{k g H}$ WHEN U_* IS THE FUNCTION VELOCITY, ρ IS THE DENSITY OF AIR, Cp IS HEAT CAPACITY OF AIR AT CONSTANT PRESSURE, T IS THE ABSOLUTE TEMPERATURE, k IS THE VON KĀRMĀN CONSTANT (0.41), g IS THE ACCELERATION DUE TO GRAVITY, AND H IS THE VERTICAL FLUX OF SENSIBLE HEAT.

Figure 7. Resistance integrals (Int_1 and Int_2) for heights greater than 1 cm is a function of atmospheric stability (extracted from Sehmel and Hodgson 1976).

3. Vertical wind and temperature profiles (to determine roughness height, friction velocity, particle eddy diffusivities, and atmospheric stability as Obukhov's length).

Sehmel advised (personal communication, Battelle Pacific Northwest Laboratories, January 1978) that deposition velocities from the model compared satisfactorily with those measured during a small field experiment. He also suggested that the model could be used for forest cover, but noted that the empirical Equation (2.22) had not been developed for such high roughness.

2.5 DRY GASEOUS MODELS

2.5.1 Introduction

Like dry particulate models, dry gaseous models rely on the concept of deposition velocity as the basis of modelling. Thus, the next section is concerned with the concept of deposition velocity as applied to gases (v_g) and presents measured results of v_g. Section 2.5.3 considers theoretical estimates of v_g and rate limiting effects. The sections that follow then deal respectively with the Gaseous Resistance model (Section 2.5.4), the Gaseous Leaf model (Section 2.5.5) and the Gaseous Air-Water Interface model (Section 2.5.6).

2.5.2 Deposition Velocity of Gases

Chamberlain (1953) defined dry deposition velocity of a gas (v_g) as

$$v_g = \frac{F}{\chi(z_1)} \tag{2.25}$$

where F = mass flux of gas, and

$\chi(z_1)$ = concentration of gas at height z_1 above the deposition surface.

Therefore, dry deposition flux of gases is considered to be proportional to the ground-level concentration (at some reference height).

Chamberlain further showed that an upper bound value of v_g could be found from an analogy with the momentum flux to the surface. However, two boundary conditions need to be fulfilled, namely:

1. That the surface acts as a 'perfect sink' for the gas, so that the vapour pressure of the deposited matter is negligible, and
2. That the gas concentration is effectively constant in the horizontal plane, and the gas cloud extends to a great height vertically.

If these conditions are fulfilled, and the vertical eddy diffusion coefficient for matter and momentum is assumed to be equal, then the two analogous equations for the vertical distribution of momentum and matter are respectively

$$K(z)\,\frac{\delta(\rho u)}{\delta z} = \tau \text{ with } u = 0 \text{ when } z = 0 \tag{2.26}$$

$$K(z)\,\frac{\delta \chi}{\delta z} = F \text{ with } \chi = 0 \text{ when } z = 0 \tag{2.27}$$

where τ = shearing stress assumed constant with height, and
F = vertical flux and equals the rate of deposition per unit area of ground.

Thus
$$\chi(z) = \frac{F\,u(z)}{\tau/\rho} \tag{2.28}$$

But
$$v_g = \frac{F}{\chi(z_1)} \tag{2.25}$$

and
$$\tau/\rho = u_*^2 \tag{2.29}$$

where u_* = friction velocity

Substituting in Equation (2.28) for $z = z_1$ gives

$$v_g = u_*^2/u(z_1). \tag{2.30}$$

Typical values of u_* for long grass is 50 cm/s, and for a wind speed u = 500 cm/s gives v_g = 5 cm/s. Therefore, this value sets the upper limit on deposition velocity for the conditions examined assuming that Reynold's analogy holds. Slinn (1977b:874) notes that experimental results indicate that the limiting value of v_g given by Equation (2.30) is rarely attained except for very reactive gases such as I_2.

Tables 7 to 10 set down laboratory and field measurements of v_g for sulphur dioxide and other gases separately. It is difficult to summarize the results because of the many factors affecting the estimates--experimental method, reference height, type of surface, moisture condition of surface, and atmospheric conditions. Nevertheless, the average results tabulated below as v_g in cm/s seem to exhibit a fair degree of consistency. The values in parenthesis indicate the number of separate studies used to obtain average deposition velocity.

Laboratory SO_2	
Alfalfa	1.2 (2)
Sandy soil	0.6 (2)
Clayey soil	0.8 (2)
Field SO_2	
Grass	1.1 (13)
Alfalfa	1.0 (1)
Soil	1.0 (3)
Land	1.3 (3)
Forest	1.6 (4)
Water	1.1 (6)
Snow	0.3 (2)
Field Ozone	
Diabatic condition	0.6 (4)
Neutral condition	1.1 (3)
Field Iodine (as I_2, I^{131} or elemental I)	
Grass	1.6 (7)
Other surfaces	1.0 (3)

Table 7. Laboratory measurements of deposition velocities of sulphur dioxide.

Author (date)	v_g (cm/s)	Reference Height (m)	Surface	Comments
Thomas et al. (1943)	1.0	1	alfalfa	growth chamber (Chamberlain 1975)
Spedding (1969)	1.5		barley leaves	results adjusted for field plant morphology
Hill (1971)	2.5	1	alfalfa	wind tunnel
Bromfield (1972)	1.0	1	mustard	glasshouse
Cowling et al. (1973)	0.62	1	rye grass	growth chamber (Chamberlain 1975)
Payrissat and Beilke (1975)	0.19-0.55 0.38-0.60	soil chamber	soils	r.h. 37-57% n.h. 70-80% found v_g to be a function of pH
Hill and Chamberlain (1976)	2.8		vegetation	
Judeikis and Stewart (1976)	2.5		cement I	
	2.0		ready-mix cement	
	1.8		exterior stucco I	
	1.6		cement II	
	0.86		exterior stucco II	
	0.66		clay soil	
	0.65		sandy load soil	
	0.04		asphalt	

Continued ...

Table 7. Concluded.

Author (date)	v_g (cm/s)	Reference Height (m)	Surface	Comments
Judeikis and Wren (1977)	3.9		F_2O_3	
	0.9		adobe clay soil	
	0.6		sand loam soil	

Table 8. Field measurements of deposition velocities of sulphur dioxide.

Author (year)	v_g (cm/s)	Reference Height (m)	Surface	Comments
Katz and Ledingham (1939)	0.7-1.3		alfalfa	
Meetham (1950)	1.3		land	Britain (Chamberlain 1973)
Meetham (1954)	0.7		London fog	Chamberlain (1973)
Chamberlain (1960)	1.8		land	Britain (1939-1944)
Saito et al. (1971)	1.3	2	grass	v_g found to be function of wind speed
Chamberlain (1973)	0.83	1	short grass	
	0.84		bare soil	
Garland et al. (1973)	1.2	1	grass	radioactive tracer
	0.8			gradient method
Fowler and Unsworth (1974)	0.3	1	wheat	v_g varies during night and day
Garland et al. (1974)	0.55	1	short grass	
Owers and Powell (1974)	0.7	0.2	grass	wet and dry similar
	2.6	0.05	grass	$u = 5.2$ m/s
	3.5	0.05	grass	base of hedge
	1.6	0.05	grass	leeward side of hedge
	0.7	0.05	grass	$u = 1.8$ m/s
	0.9	0.2	water	
	0.5	0.05	water	

Continued ...

Table 8. Continued.

Author (year)	v_g (cm/s)	Reference Height (m)	Surface	Comments
Belot et al. (1974)	1			based on uptake of SO_2 to pine and oak shoots
Shepherd (1974)	0.8 0.3	0.2	grass	summer autumn } profile method
Whelpdale and Shaw (1974)	2.6	2	grass	for neutral stability--values for other stabilities given in paper
	2.2		water	
	0.5		snow	
Martin and Barber (1975)	≈2		pine trees	
Dovland and Eliassen (1976)	0.13		snow	upper bound value
Garland (1976)	0.55		short grass	
	1.19		medium grass	radioactive method
	0.77		medium grass	gradient method
	1.1		soil	
	0.46		water	
Petit et al. (1976)	1.8 3.7		mixed forest	
Prahm et al. (1976)	2		Atlantic Ocean	

Continued ...

Table 8. Concluded.

Author (year)	v_g (cm/s)	Reference Height (m)	Surface	Comments
Garland (1977)	<2		Scots pine forest	gradient method
	0.3			radioactive method
Garland (1977)	0.85	1	short grass	gradient method
	0.89		medium grass	
	1.19		medium grass	radioactive method
	1.2		bare calcareous soil	gradient method
	0.41		water	
Garland and Branson (1977)	0.2-0.6		pine trees	at night, v_g = 0.05 cm/s.

Table 9. Laboratory measurements of deposition velocities of gases except sulphur dioxide.

Author (date)	v_g (cm/s)	Reference Height (m)	Gas	Surface	Comments
Chamberlain (1953)	1.2		I^{131}	flat plate	u = 2 m/s
	0.3				u = 0.4 m/s
Hill and Chamberlain (1976)	0.0		CO	vegetation	included for comparison
	0.1		NO		
	0.33		CO_2		
	0.63		PAN		
	1.67		O_3		
	1.90		NO_2		
	2.07		Cl_2		
	2.83		SO_2		
	3.77		NF		
Israel (1974)	1.6		HF	alfalfa and orchard grass	fumigation experiment
Garland (1977)	1.8		ozone	soil	4% water content
	0.84			sand	27% water content
	1.4			peat	43% water content
	0.46			peat	74% water content
	0.55			grass	
	0.74			grass	in presence of SO_2
Judeikis and Wren (1977)	0.02		H_2S	adobe clay soil	
	0.02		H_2S	sandy loam	
	0.3		DMS	adobe clay soil	
	0.06		DMS	sandy loam	

Table 10. Field measurements of deposition velocities of gases except sulphur dioxide.

Author (date)	v_g (cm/s)	Reference Height (m)	Gas	Surface	Comments
Chamberlain (1953)	2.5		I^{131}	grass	
Regener (1957)	0.35		ozone		diabatic condition
	0.7				neutral condition
Chamberlain (1960)	1.8		I^{131}	ground	
	0.7			leaves	
	2.8			field	
Chamberlain and Chadwick (1966)	1.4		I^{131}	vegetation	
Bunch (1968)	1.0		I^{131}	irrigated grasses	
Galbally (1968)	0.4		ozone		diabatic condition
	1.4				
Kelley and McTaggart Cowan (1968)	1.4		ozone		neutral condition
Galbally (1969)	0.95		ozone		diabatic condition
	0.1				unstable condition
Galbally (1971)	1.2		ozone		neutral condition
	0.2				diabatic condition
Turner et al. (1973)	0.5	0.025	ozone	bare fine sandy loam	

Continued ...

Table 10. Concluded.

Author (date)	v_g (cm/s)	Reference Height (m)	Gas	Surface	Comments
Vogt et al. (1973)	0.59	1	I_2	grass	mass balance
Israel (1974)	3.1		HF	alfalfa and orchard grass	
Heinemann et al. (1976)	0.8 1.2	1	iodine vapour	grass clover	
Vogt et al. (1976)	1.5		elemental I	grass	

2.5.3 Theoretical Deposition Velocity

Hicks (1976c) provides a basis for theoretical examination of gaseous v_g. His approach simply assumes that the contaminant is effectively removed upon reaching the surface and he relates the rate of removal to a gross measure of the surface roughness appropriate to the bulk transfer of the material of interest. A number of assumptions are required:

1. Transfer of any contaminant in air near the surface is governed by flux gradient relationships appropriate for the flux of sensible heat and water vapour;
2. Over smooth terrain the eddy and molecular diffusivities can be added and the desired roughness length can be parameterized in terms of the friction velocity and the appropriate molecular diffusivity; and
3. Over rougher surfaces, the appropriate roughness follows the same form of relationship as has been determined for the transfer of sensible heat.

Based on these assumptions, Hicks shows that the eddy deposition velocity is given by

$$v_e = k^2 u_z / (\{\ln[(z - d_p) / z_p] - \Psi_p\} \cdot \{\ln[(z - d)/z_o] - \Psi_M\}) \quad (2.31)$$

where k = von Karman's constant ($\simeq 0.4$),

u_z = wind speed at height z,

d_p = zero plane displacement for the transfer of the quantity p,

z_p = roughness length appropriate to the flux F_p,

d = zero plane displacement for momentum transfer,

z_o = roughness length for momentum transfer,

Ψ_p = integrated departure from neutral of ϕ_p,

ϕ_p = dimensionless gradient of quantity p,

Ψ_M = integrated departure from neutral of ϕ_M, and

ϕ_M = dimensionless wind gradient.

As presented, v_e represents an upper limit on v_g for gaseous compounds assuming that the surface is highly efficient (that is, the concentration of the gas at zero plane is many times less than the concentration at height z).

Assuming a wind speed of 5 m/s at reference height 10 m, computed values of v_e for sulphur dioxide are listed in Table 11.

Except for the forest values, these data appear to be consistent with field observations.

Another aspect that needs to be taken into account is the combination of rate limiting processes. According to Slinn (1977b), for most gases the flux to the ground or to vegetation is rate limited by the conversion of the gas to a less volatile compound, by diffusion into groundwater, or by passage of the gas through plant membranes. In the case of gas deposition to lakes, the atmosphere may be rate limiting for reasonably reactive gases, since mixing in the water body may promote transfer in the sink.

To illustrate these general aspects, Slinn (1977b) considered a model for dry deposition of gases to a stationary water body. Details are not given in the reference but Figure 8 from Slinn shows the end result. It demonstrates that dry deposition can be rate limited by slow mixing in the groundwater, low solubility or slow reaction rate.

2.5.4 Gaseous Resistance Model

Theoretical models describing dry deposition of gaseous pollutant to vegetative surfaces are not well advanced. All models concerned with vegetative surfaces include qualitative terms describing the mechanisms of uptake of gaseous material at the surface. Generally, component resistances are assumed additive (Bolin et al. 1974; Chamberlain 1975) in the following manner (Wesely and Hicks 1976)

Table 11. Values of v_e for sulphur dioxide. (Wind speed 5 m/s, reference height 10 m.)

Surface	Stability $(z/L)^a$	v_e (cm/s)
Tilled soil	-1	1.1
	0	0.8
	1	0.3
Short grass (z_o = 2.3 cm)	-1	2.4
	0	1.6
	1	0.5
Forest (z_o = 50 cm	-1	7.2
	0	6.1
	1	4.7

[a] L = Monin Obukhov length

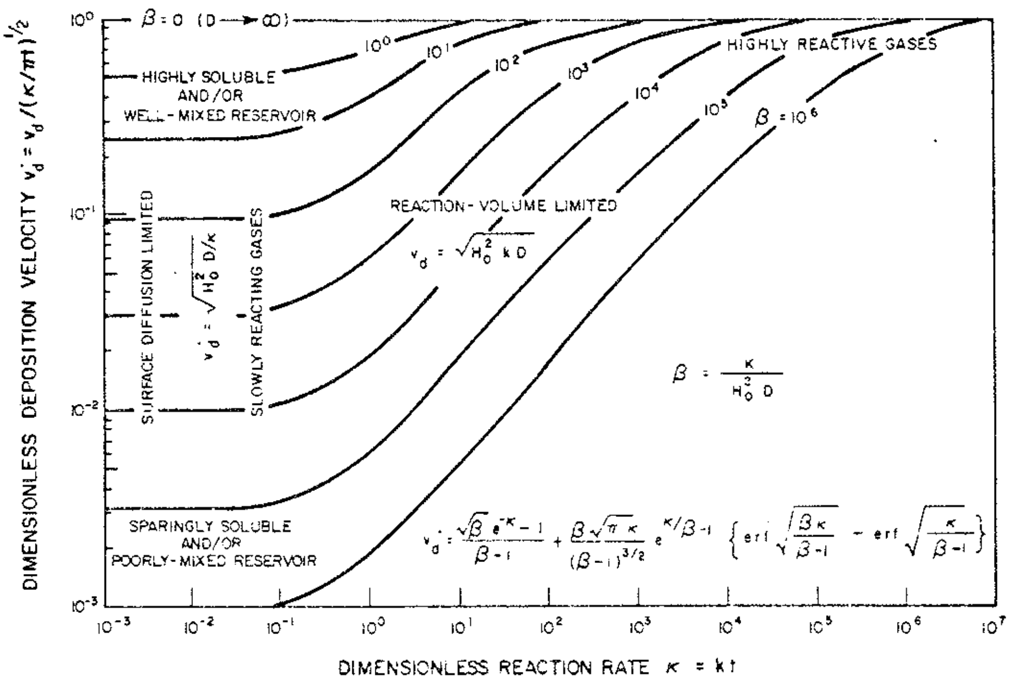


Figure 8. Effect on deposition velocity of phenomena other than atmospheric diffusion limitations (extracted from Slinn 1977b).

$$r = r_a(z) + r_b + r_c + r_m = 1/v_g \tag{2.32}$$

where r = total resistance and is defined as the inverse of transport velocity (or more commonly called deposition velocity),

$r_a(z)$ = aerodynamic resistance at height z determined by the nature of the turbulence above the surface,

r_b = surface resistance to transfer in the nearly-viscous air layer (laminar sub-layer) immediately in contact with the plant surface,

r_c = canopy stomatal resistance, and

r_m = mesophyll resistance.

Based on the work of Hicks and Liss (1976), Wesely and Hicks (1976) adopted the following equation for aerodynamic resistance which is the resistance between the reference height and the height corresponding to the surface roughness length

$$r_a = \frac{1}{(k^2\bar{u})} [\ln(z/z_o) - \Psi_c] [\ln(z/z_o) - \Psi_m] \tag{2.33}$$

where z = height above the displacement height of the plant canopy,

z_o = surface roughness length,

k = von Karman's constant,

$\bar{u}$ = mean wind speed, and

Ψ_m, Ψ_c = diabatic corrections (see Dyer and Hicks 1970)

The resistance r_b is added to correct for the difference between momentum, and heat and mass transfer processes. It is considered that this term arose because heat and mass transfer involve molecular diffusion in laminar layers surrounding roughness elements, whereas momentum transfer is affected largely by pressure forces. The additional resistance is expressed as

$$r_b = B^{-1} u_*^{-1} \qquad (2.34)$$

where B = sub-layer Stanton number.

B has been found to be a function of Reynolds and Schmidt numbers (Garland 1977) but the approach adopted by Shepherd (1974) and used by Wesely and Hicks (1976) is followed here. Shepherd parameterized the gross canopy surface by

$$B^{-1} = 2/k \qquad (2.35)$$

hence

$$r_b = 2/ku_* \qquad (2.36)$$

where u_* = surface friction velocity.

According to Garatt and Hicks (1973) the numerical coefficient of 2 is appropriate mainly for water vapour. Wesely and Hicks (1976) recommend a value of 2.6 for SO_2 and ozone.

The value of r_c is determined by summing, after weighting according to leaf areas and positions in the canopy, the stomatal resistances of individual leaves. However, it is more appropriate for our purposes to adopt measured resistances because of the wide range of environmental conditions that affect stomatal resistances of a particular plant, age, and condition. For example, for healthy dense uniform canopies of soybeans and maize the minimum value of r_c for transfer of water vapour from such crops is about 0.4 s/cm. Equivalent values for SO_2 and ozone would be 0.75 s/cm and 0.65 s/cm, respectively (Wesely and Hicks 1976:79).

For gases like SO_2 and ozone that are highly soluble in the water solution enveloping the mesophyll cells, the gases are quickly removed and r_m, the mesophyll resistance, is assumed to be zero. For CO_2, r_m = 6 s/cm was determined by Gaastra (1963).

Thus the gaseous deposition velocity at height z is given by

$$v_g = 1 / [r_a(z) + r_b + r_c] \qquad (2.37)$$

Experimental estimates of stomatal resistance are tabulated in Table 12. In this table, stomatal resistance is defined as

$$r_s = (1/v_g) - r_a(z) - r_b \tag{2.38}$$

$$= r_c + r_m \tag{2.39}$$

Sometimes it is defined as $(1/v_g) - r_a(z)$. For this situation, values in Table 12 are designated by

$$r_s' = r_b + r_c + r_m \tag{2.40}$$

The results in Table 12 may be summarized as follows.

From this review, the Gaseous Resistance model, Equation (2.32) appears to be a satisfactory algorithm for estimating the deposition velocity to vegetation. The aerodynamic component $r_a(z)$ can be estimated from mean wind speed, surface roughness length, and published diabatic corrections Ψ_m and Ψ_c. Wind speed and roughness values can be obtained from representative vertical profile of temperature and wind speed measured at the ground surface. From such data an estimate of surface friction velocity can be obtained to determine r_b in Equation (2.36). Average stomatal resistance estimates can be adopted from the values given in Table 12 or a field program embarked upon to determine the appropriate values of r_c and r_m.

2.5.5 Gaseous Leaf Model

This model is based on an analogy between a leaf and an electrical analogue simulator. Figure 9 shows the electrical analogue with the circuitry superimposed. The basic algorithm describing the exchange of gas between air and leaf is as follows

$$Qa = (Ca - C_{int}) \cdot \left(\frac{1}{ra_1 + (1-X_1)R\ell_1} + \frac{1}{ra_2 + (1-X_2)R\ell_2} \right) \tag{2.41}$$

Table 12. Experimental estimates of stomatal resistance to gaseous deposition.

Author (date)	Resistances[a] (s/cm)	Gas	Plant Surface	Comments
Gaastra (1963)	$r_s' = 35\text{-}40$	CO_2		stomata closed
	$r_s' = 3$			stomata open
	$r_m = 6$			
Spedding (1969)	$r_s' = 33\text{-}175$	SO_2	barley beans	stomata closed
	$r_s' = 1.6\text{-}6.3$			
	$r_m = 2.8$			
Unsworth et al. (1972)	$r_s = 6\text{-}7$	SO_2	bean plants	fully watered; Younger beans had smaller resistances
	$r_s = 11\text{-}17$			dry
Chamberlain (1973)	$r_s = 0.1\text{-}4$ average 1	SO_2	grass	
Garland et al. (1973)	$r_s' = 0.71$	SO_2	grass	
	$r_s' = 0.95$			
Fowler and Unsworth (1974)	$r_s' = 3.9$	SO_2	wheat	dry
	$r_s' = 0.41$			wet

Continued ...

Table 12. Continued.

Author (date)	Resistances[a] (s/cm)	Gas	Plant Surface	Comments
Garland et al. (1974)	$r_s \approx 1.5$	SO_2	grass	
Owers and Powell (1974)	$r_s' = 0.75$	SO_2	grass	u = 2.6 m/s rh 65%
	$r_s' = 0.01$			u = 5.2 m/s rh 77%
	$r_s' = 0.73$			u = 1.8 m/s rh 80%
Shepherd (1974)	$r_s = 0.8$	SO_2	grass	summer
	$r_s = 3.0$			winter
Garland (1976)	$r_s = 0.56$	SO_2	short grass	
	$r_s = 0.41$		medium grass	
	$r_s = 0.88$		medium grass	
	$r_s = 0.06$		soil	
	$r_s = 0.4$		water	
	$> \approx 0.5$			
Unsworth and Fowler (1976)	$r_s = 0.46$	SO_2	wheat	dry
	$r_s = 0.21$			wet

Continued ...

Table 12. Concluded.

Author (date)	Resistances[a] (s/cm)	Gas	Plant Surface	Comments
Garland (1977)	$r_s = 0.34$	SO_2	short grass	gradient method
	$r_s = 0.66$		medium grass	
	$r_s = 0.45$		medium grass	radioactive method
	$r_s = 0.01$		bare calcareous soil	gradient method
	$r_s = 0.56$		fresh water	
	$r_s \geq 0.5$		Scots pine	
Garland and Branson (1977)	$r_s = 1.5\text{-}5$	SO_2	pine forest	day
	$r_s \simeq 20$			night

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[a] For definition of r_s and r_s' see Section 2.5.4

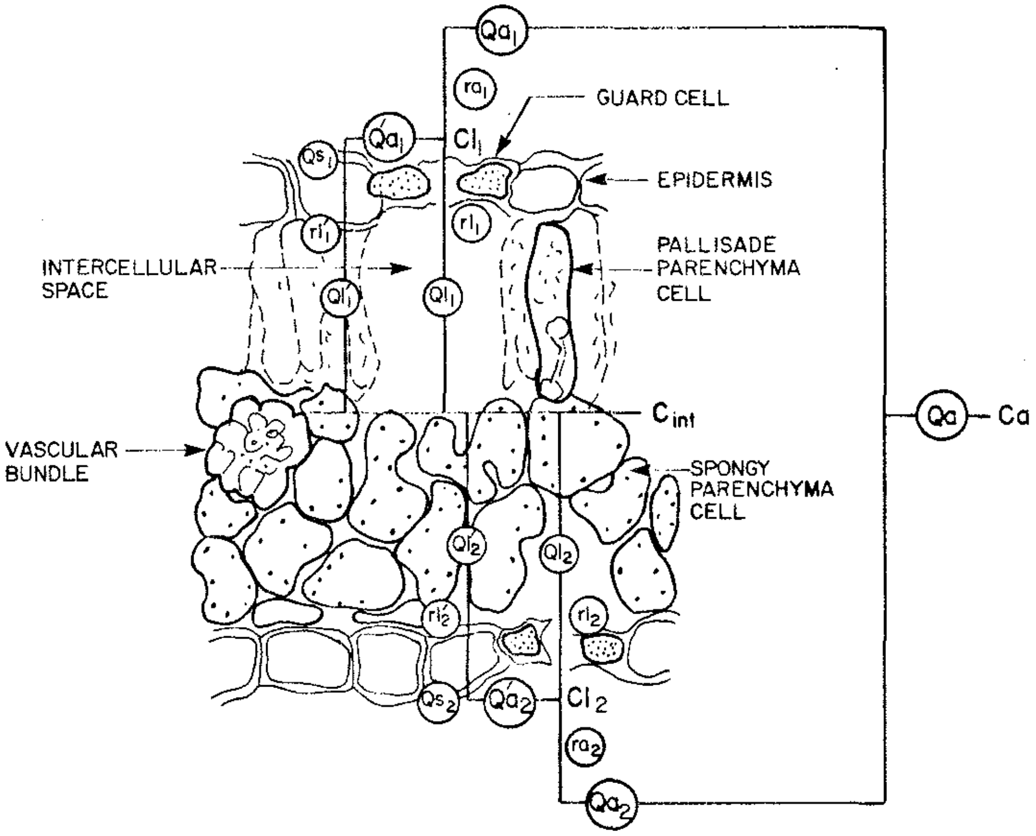

Figure 9. Electrical analogue simulator of pollutant exchange between leaf and surrounding air (after Bennett et al. 1973).

where Qa = total flux,

Ca = pollutant concentration in air surrounding leaf,

C_{int} = average internal gaseous concentration at the mesophyll-intercellular air interface,

ra_1, ra_2 = air (boundary layer) resistance to the upper and lower leaf surface,

X_1, X_2 = defined as the ratio of the fluxes due to sorption, decomposition or desorption by upper or lower leaf surfaces to the upper and lower total fluxes respectively,

$$\frac{1}{R\ell_1} = \frac{1}{r\ell_1} + \frac{1}{r\ell_1'} \tag{2.42}$$

$$\frac{1}{R\ell_2} = \frac{1}{r\ell_2} + \frac{1}{r\ell_2'} \tag{2.43}$$

$r\ell_1, r\ell_2$ = stomatal + internal diffusion resistances from the upper and lower leaf surfaces

$r\ell_1', r\ell_2'$ = cuticular + internal resistances from the upper.

This model then may be regarded as a more refined version of the gaseous resistance approach, but in it more details about the characteristics of the leaf are required. Utilization of Equation (2.41) in practice would require a knowledge of the area of leaves per ground surface area. Unless these details are readily available, this approach is not recommended.

2.5.6 Gaseous Air/Water Interface Model

From considerations of solubility and chemical reactivity of SO_2 , Liss (1971) evaluated the gas and liquid components of the total resistance to exchange of SO_2 across air/water interfaces. In 1974 Liss and Slater extended this approach to the transfer of other gases across the air/sea interface. Liss in 1975 considered the special case of lake surfaces.

Liss utilizes the two-layer model of the interface as shown in Figure 10. In the model, the fluid is assumed to remain homogeneous as a result of turbulent mixing process. A gas crossing between the two phases experiences the most resistance to transfer in the regions immediately adjacent to the interface. Transfer through the interfacial layers is by molecular processes. The derivation of the model is given in Liss and Slater (1974) and results in the following relationship which shows how the resistances of the individual phases combine to give the overall resistance

$$\frac{1}{K_l} = \frac{1}{k_l} + \frac{1}{Hk_g} \tag{2.44}$$

and

$$R_l = r_l + r_g \tag{2.45}$$

where K_l = overall exchange coefficient (expressed on a liquid phase concentration basis),

k_l = liquid phase exchange coefficient,

k_g = gas phase exchange coefficient,

H = Henry's law constant,

$$= \frac{\text{equilibrium concentration in gas phase}}{\text{equilibrium concentration of unionized dissolved gas in liquid phase}} \tag{2.46}$$

(Values of H for several gases including SO_2 are given in Liss and Slater 1974).

R_l = overall resistance,

r_l = liquid phase resistance, and

r_g = gas phase resistance.

In order to apply the model to calculate deposition flux (F) to a water surface we utilize the formula

$$F = K_l \, \Delta C \tag{2.47}$$

where ΔC = concentration difference for the gas across the layer system.

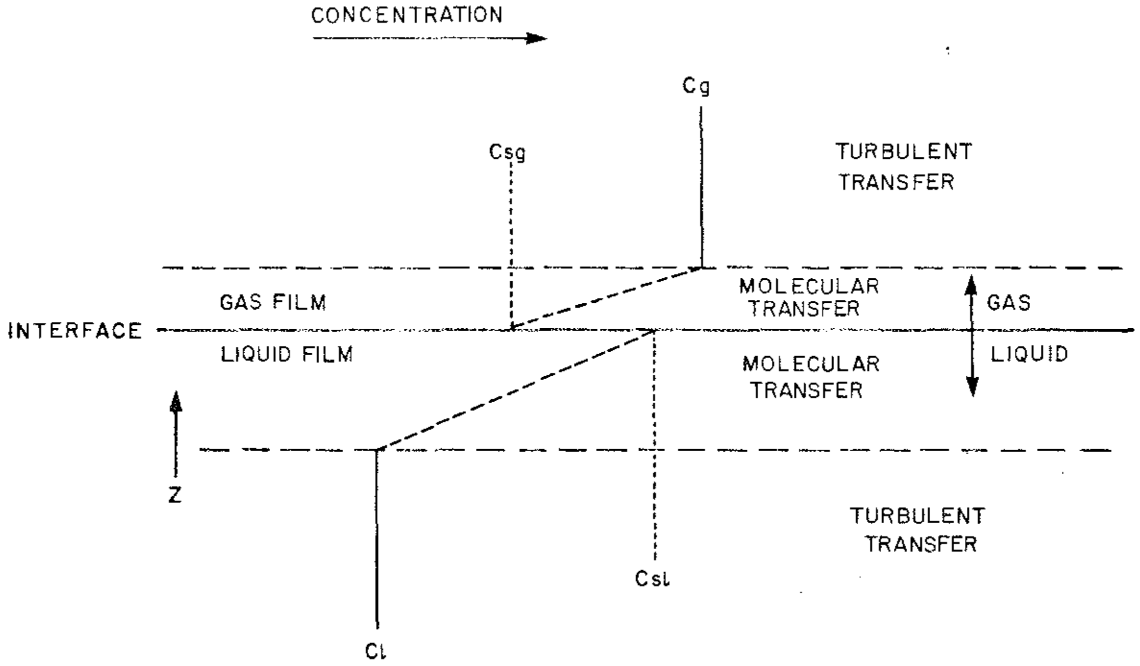

Figure 10. Two-layer model of a gas-liquid interface (extracted from Liss and Slater 1974).

Thus appropriate values of the exchange coefficients must be obtained. Based on studies in Lakes Michigan (Hicks 1972) and Ontario (Smith 1974), a value of k_g equal to 3,200 cm/h may be adopted. Liss (1971) suggests k_g for SO_2 be taken as 3,000 cm/h. However, for air/sea interface problems, Liss and Slater (1974) recommend for gases other than H_2O that k_g for H_2O be adopted (3,000 cm/h for sea-water) and a correction be applied as follows

$$k_g \text{ (for any gas)} = k_g(H_2O)\left(\frac{18}{\text{molecular weight of gas}}\right)^{\frac{1}{2}} \qquad (2.48)$$

This approach is not mentioned in Liss (1975) for lake surfaces, but it is assumed to be applicable.

Values of k_l are not readily available for fresh water. Nevertheless for sparingly soluble gases, which are not chemically reactive in the aqueous phase, a value of k_l equal to 5 cm/h seems appropriate (Liss 1975). Gases in this category would include N_2O, CO, CH_4, CCl_4, CCl_3F, MeI, $(Me)_2S$, and generally CO_2 (Liss and Slater 1974).

For chemically reactive gases, processes other than molecular diffusion may enhance transfer across the liquid film. Such gases include SO_2, NH_3, NO_2, HF, and HCl (Liss 1975). The degree of enhancement is predicted by the following equations (Liss 1971)

$$k_{l(\text{reactive})} = \alpha\, k_{l(\text{inert})} \qquad (2.49)$$

where $$\alpha = \frac{\tau}{(\tau-1) + \left\{\tan h\left|\left(\frac{k^*\tau}{D}\right)^{\frac{1}{2}} \frac{D}{k_{l(\text{inert})}}\right| \Big/ \left(\frac{k^*\tau}{D}\right)^{\frac{1}{2}} \frac{D}{k_{l(\text{inert})}}\right\}} \qquad (2.50)$$

α = ratio of the k_l values for a reactive and an inert gas exchanging under identical conditions,

τ = ratio of total to ionic forms of the gas in solution,

k^* = hydration rate constant for the gas, and

D = molecular diffusivity of the dissolved gas molecules.

Values of $k_{l(inert)}$ are not readily available. Liss (1971) suggests a value of 10 cm/h for SO_2. However, in his 1975 paper, Liss does not explain how to obtain $K_{l(inert)}$ for any chemically reactive gases. For the air/sea interface problem, Liss and Slater (1974) recommend that

k_l (for any gas) = 20 cm/h

so long as the molecular weight of the gas is greater than 15 and less than 65, otherwise one should use

$$k_l = 20 \left(\frac{44}{\text{molecular weight of gas}}\right)^{\frac{1}{2}} \tag{2.51}$$

Thus, to use the Gaseous Air/Water Interface model it is necessary to estimate k_g and k_l for the water body and to calculate the overall exchange coefficient and then apply Equation (2.47).

2.6 WET PARTICULATE MODELS

2.6.1 Introduction

Based on Figure 2, it is observed that in recent years considerable effort has gone into developing models of particulate scavenging by precipitation. Fortunately, most of the work has directly involved sulphate particles or, at least, they have been used in validating the models. A good deal of field information is also available from simple empirical models which involve scavenging coefficients and ratios. Furthermore, the wet deposition processes of particles, although complex in nature, have been extensively studied from a theoretical point of view by Slinn and others.

Following this section, we first deal with theoretical aspects of collision efficiency. This is followed by an empirical and theoretical discussion of particulate scavenging processes. The last sections deal with several in-cloud and below-cloud scavenging models.

2.6.2 Collision Efficiency of Particles by Rainfall Scavenging

In the last few years a number of important theoretical studies dealing with particulate collision efficiency have been undertaken (Slinn 1977a, 1977b; Beard 1977; Williams 1977). This measure is important because it is used in several of the fundamental models of precipitation scavenging by particles.

Collection efficiency is defined as the proportion of aerosols removed from an air stream by an obstacle--in this case a raindrop. But collection efficiency is made up of two factors--collision efficiency and retention efficiency as follows

$$\text{collection efficiency} = \text{collision efficiency} \times \text{retention efficiency} \tag{2.52}$$

However, retention efficiency is normally taken as unity. Esmen (1972) carried out some preliminary work and confirmed this fact at least for washout by rainfall (below-cloud scavenging). Therefore, collection and collision efficiency are normally equated.

Slinn (1977b) has extensively explored this subject and has developed a semi-empirical expression for the collision efficiency between raindrops and particles as a function of particle size; the expression accounts for diffusion, interception, and inertial impaction. The result is given in the following equation and summarized in Figure 11.

$$E = \frac{4}{P_e}(1 + 0.4\ R_e^{\frac{1}{2}} S_c^{\frac{1}{3}}) + 4\kappa[\kappa + \frac{1+2V\kappa}{(1+VR_e^{-\frac{1}{2}})}] + (\frac{s-s*}{s+c})^{\frac{3}{2}} \tag{2.53}$$

where E = collision efficiency,

P_e = Péclet number (the ratio of convective to diffusional transport)

$= R_e S_c$, (2.54)

$R_e = Rv_t/\nu$ = Reynolds number, (2.55)

$S_c = \nu/D$ = Schmidt number, (2.56)

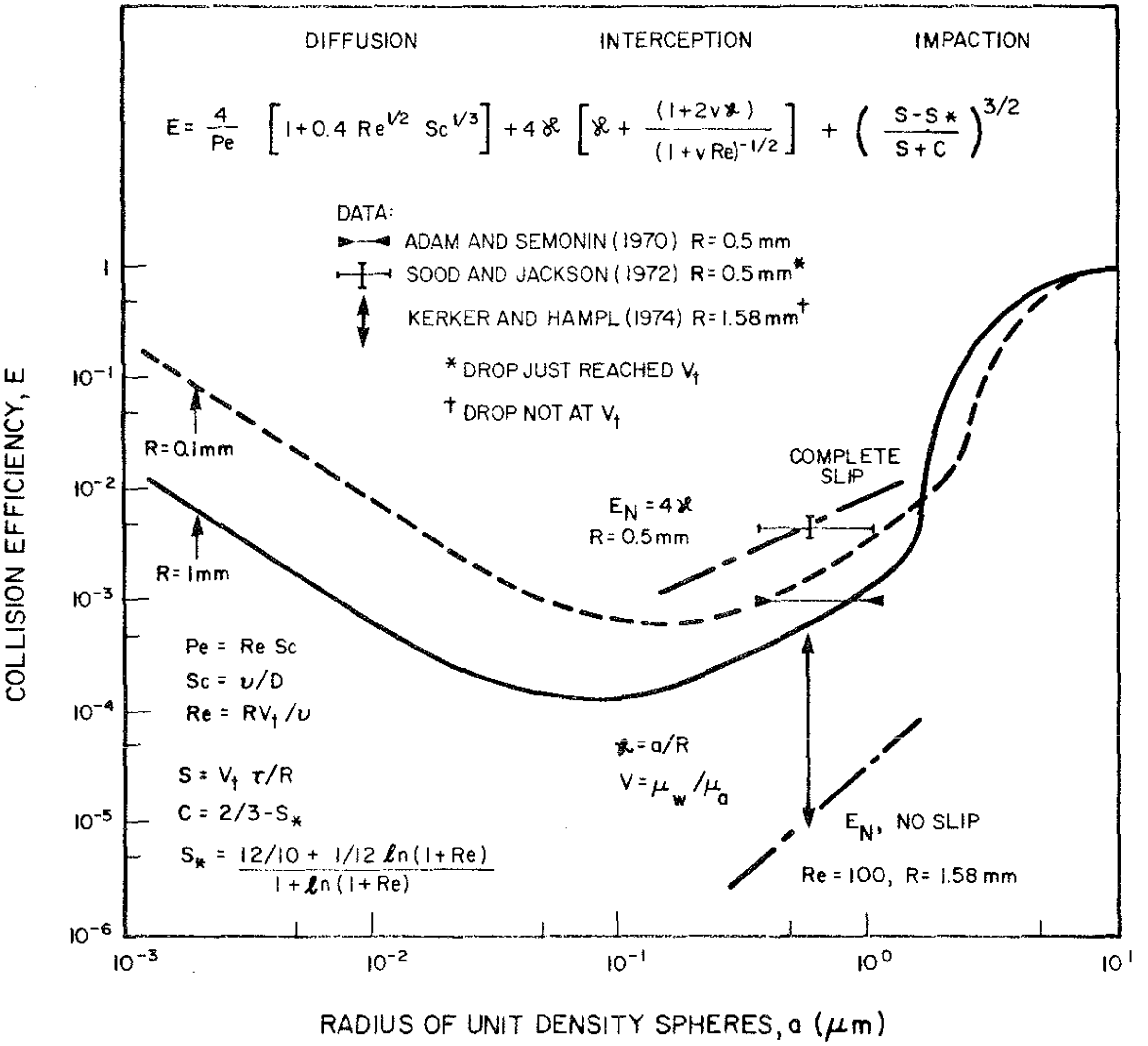

Figure 11. Slinn's collision efficiency-particle size relationship for rainfall scavenging (extracted from Slinn 1977b).

κ = a/R = interception parameter, (2.57)

$V = \mu_w/\mu_a$, (2.58)

μ_w, μ_a = coefficients of viscosity for air and water ($\mu_w/\mu_a \simeq 60$),

R = radius of raindrop,

v_t = terminal velocity of raindrop,

ν = kinematic viscosity of air,

D = diffusivity of the particle,

a = radius of particle,

$s = v_t\ \tau/R$, (2.59)

τ = relaxation of the particle,

s_* = critical Stokes number, (2.60)

$$= \frac{\frac{12}{10} + \frac{1}{2}\ \ell n\ (1+R_e)}{1 + \ell n(1+R_e)},$$

$$c = \frac{2}{3} - s_* \qquad (2.61)$$

In proposed Equation (2.53), Slinn (1977b) noted a number of points.

(a) Raindrop flattening is considered to be unimportant.

(b) Internal circulation may be important.

(c) The form of Equation (2.53) depends on diffusion (first term on right-hand side), interception (second term), and impaction (third term). However, a number of effects have not been included, such as:

1. Turbulence, especially during heavy rainstorms when drops themselves generate significant small-scale turbulence through wake shedding;
2. Thermophoresis and diffusiophoresis; for an evaporating drop the result is to enhance collisions;
3. For water vapour condensation, collisions are inhibited;

4. Electrical effects are considered to be negligible; and
5. Retention efficiency is usually assumed to be unity.

Only a few experimental data points are available to check Figure 11 and these only cover the range 5×10^{-1} to 10^{0} µm. Slinn (1976b:861) considers the diffusion and impactive portions of the curves to have sufficient experimental support to suggest that the corresponding terms in Equation (2.53) are reliable to within a factor of 2 or 3.

This conclusion seems to be consistent with the theoretical studies by Beard (1977). He calculated numerical collision efficiency from particle trajectories in a numerical flow field of a rigid sphere. The results are shown in Figure 12.

Outside the range 0.1 to 1.0 µm particle radius, the results compare well with Figure 11 which is based on Slinn's results. However, within the range, Beard's results show variations of 2 orders of magnitude. Beard stresses that any estimate of E in this range would be speculative, but that curves a and b of Figure 12 should be regarded as lower and upper bounds. It is noted that Slinn's curve falls within these limits.

A number of points should be observed on Figure 11:

1. E varies from unity for large particles ($>10^{1}$ µm) to about 10^{-4} for particles with radii about 10^{-1} µm;
2. Below 10^{-1} µm, the effect of diffusion becomes significant and collision efficiencies rise by 2 orders of magnitude; and
3. For particles <1 µm, small raindrops are more efficient scavengers than larger ones.

The recent experimental results of Radke et al. (1977) are important relative to the above conclusions. They have been superimposed on Figure 11 and reveal collection efficiencies 2 orders of magnitude larger than those of Slinn and 1 order of

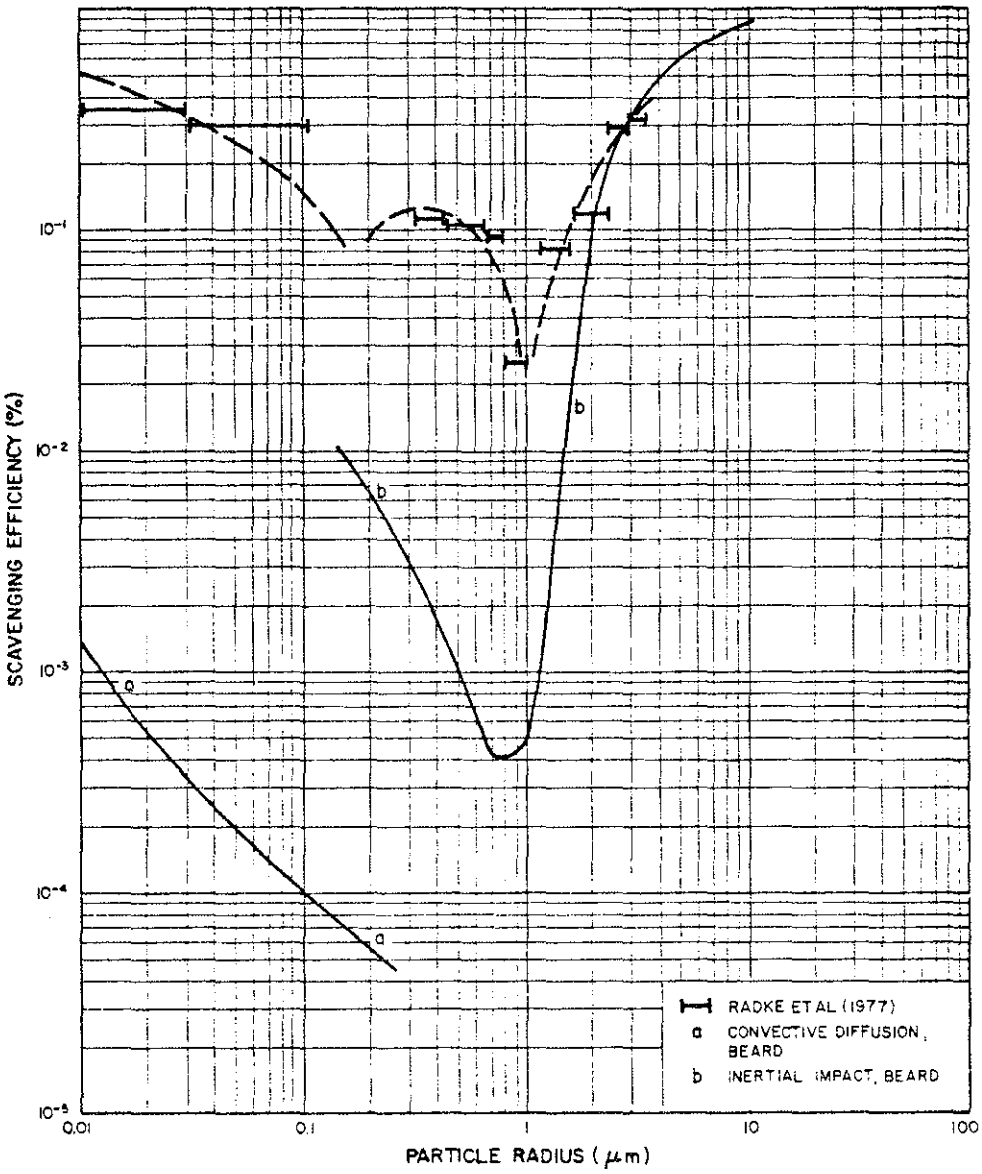

Figure 12. Radke et al. (1977) experimental data compared with Beard's collision efficiency-particle size relationship for rainfall scavenging (extracted from Beard 1977).

magnitude larger than Beard's upper bound. Consequently the whole question of collection efficiencies of precipitation scavenging is still unresolved.

2.6.2.1 Collision efficiency of particles by snow scavenging. According to Slinn (1977b), approximations for the removal rate of pollutants by ice crystals are, at the present time, cruder than those introduced for rain scavenging. He suggests the following equation for collision efficiency, but notes that it is little more than an intelligent guess

$$\varepsilon \simeq \left(\frac{D}{\nu}\right)^{a} + \{1 - \exp[-(1 + R_{e\ell}^{\frac{1}{2}})\frac{a^2}{\ell}]\} + \left(\frac{s-c_*}{s+c}\right)^{\frac{3}{2}} \qquad (2.62)$$

where ε = collision efficiency of snow, and

ℓ = characteristic dimension of the collecting element of the ice crystal.

Equation (2.62) is plotted in Figure 13. Data relating to Figure 13 are given in Table 13. It should be noted there are some experimental data for large particles and the tentative equation fits well.

2.6.3 Scavenging Coefficient of Particles

Wet deposition, which consists of rainout (within cloud scavenging) and washout (below cloud scavenging), may be considered as an exponential decay process, thus

$$\chi_t = \chi_o e^{-\Lambda_p t} \qquad (2.63)$$

where χ_t = atmospheric concentration of particles at time t,

χ_o = atmospheric concentration of particles at time zero, and

Λ_p = scavenging coefficient for particles (in units of time^{-1}).

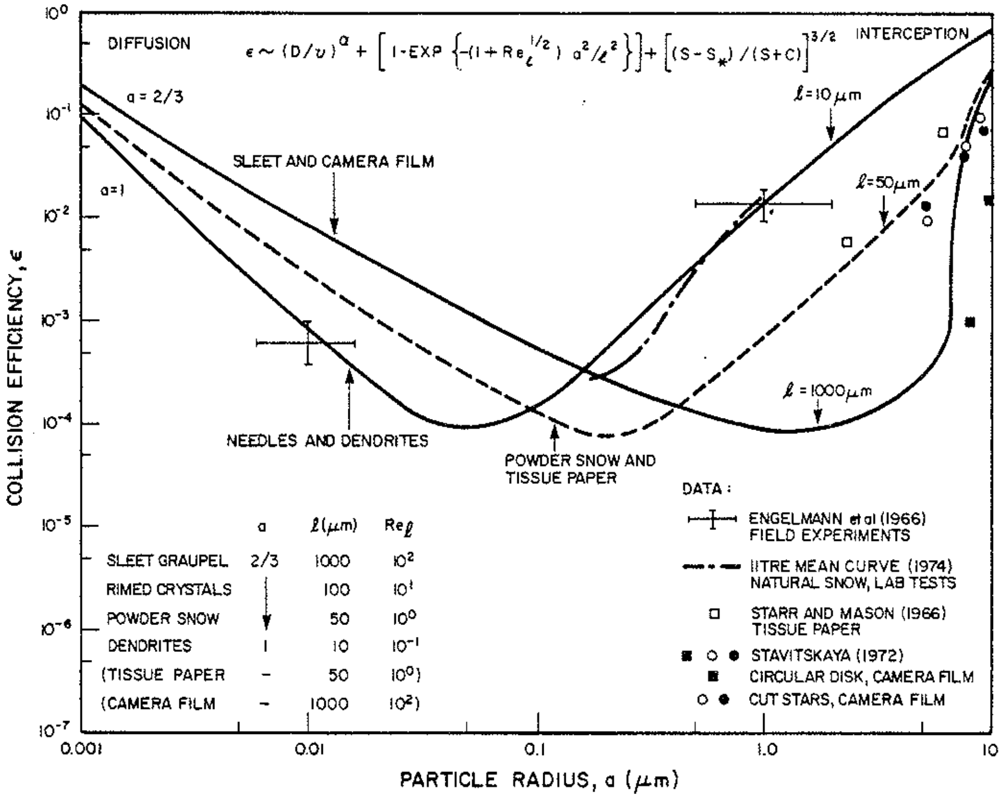

Figure 13. Slinn's collision efficiency-particle size relationship for snow scavenging (extracted from Slinn 1977b).

Table 13. Data relating to Figure 13 (particle size relationship for snow scavenging, Slinn 1976a).

	a	ℓ (μm)	$R_{e\ell}$
Sleet, graupel	2/3	1,000	10^2
Rimed crystal	↓	100	10^1
Powder snow		50	10^0
Dendrites	1	10	10^{-1}
Tissue paper	-	50	10^0
Camera film	-	1,000	10^2

The loading or deposition rate is then

$$L_{wet} = \bar{\chi} \Lambda H t \tag{2.64}$$

where L_{wet} = deposition rate due to wet scavenging,

$\bar{\chi}$ = average concentration of particles throughout H, and

H = scavenging height.

The scavenging coefficients (washout coefficient or rainout coefficient) are of practical significance. Because they are dependent on many aerosol and scavenging characteristics, often it is more realistic to begin a solution of a problem by modifying a previously measured or predicted coefficient rather than considering the more basic variables. These will be discussed in Section 2.6.6.

In Table 14 we have compiled a comprehensive list of field measurements of wet scavenging coefficients of particles. At first glance these values show little consistency. In Figure 14, the results obtained by Radke et al. (1977) have been plotted from his Figure 3.

Values in Table 14, which have particle size data available, are also superimposed. In the 5 cases shown by circles the values are a function of rainfall intensity. A common value of 5 mm/h was adopted. For the sixth case, shown as a cross, the particle size was given as less than 1 μm and so 0.5 μm was adopted. Overall, the points show satisfactory agreement with Radke's data. The figure illustrates the importance of particle size as a major factor in determining wet scavenging coefficients.

Table 14. Field measurements of scavenging coefficients of particles .

Author (date)	Λ_p (s^{-1})	Particulate size (μm)	Comments
Kalkstein et al. (1959)	$2x10^{-5}$	SO_4, NH_4	rainout (Makhon'ko 1967)
	$2x10^{-5}$	Cl, NO_3	washout
Georgii (1963)	$4x10^{-5}$	dissolved	rainout
	$22x10^{-5}$	inorganic	rainout
	$4x10^{-5}$	containment	washout
Banerji and Chatterjee (1964)	$0.4x10^{-5}$	radon	rainout (Makhon'ko 1967)
Makhon'ko (1964)	$2x10^{-5}$	fission products	rainout
	$\leq 1x10^{-5}$		washout
Shirvaikar et al. (1960)	$7x10^{-5}$	atmospheric dust	rainout (Makhon'ko 1967)
Peterson and Crawford (1970)	$16x10^{-5}\ J^{0.8}$	5	based on Engelmann's data (1965)
Makhon'ko and Dmitrieva (1966)	$20x10^{-5}$	fission products	rainout
Makhon'ko (1967)	$7x10^{-5}$	atmospheric dust	rainout plus washout
Wolf and Dana (1969)	$0.5x10^{-5}\ J$	0.5	Snow; Knutson and Stockham (1977)
Bakulin et al. (1970)	$3x10^{-5}$		^{212}Pb; washout from thunderstorm

Continued ...

Table 14. Continued.

Author (date)	Λ_p (s^{-1})	Particulate size (μm)	Comments
Burtsev et al. (1970)	$15\times10^{-5}\ J^{0.5}$	≈0.2	washout
	$20\times10^{-5}\ J^{0.5}$	≈0.2	rainout
Dana (1970)	$13\times10^{-5}\ J$	7.5, 3	Uranin and rhodamine particles, respectively
Perkins et al. (1970)	300×10^{-5}	atmospheric aerosol	rainout
Esmen (1972)	0.4×10^{-5}	atmospheric aerosol	includes rainout
Rodhe and Grandell (1972)			suggest Λ proportional to rainfall density
Acres-ESC (1974)	0.7×10^{-5}	atmospheric aerosol	includes rainout
Graedel and Franey (1975)	$\Lambda_{snow}=25-50\Lambda_{rain}$	0.4-1	see Slinn (1976c)
Hicks (1976a)	50×10^{-5}	<1	rainout

Continued ...

Table 14. Concluded.

Author (date)	Λ_p (s^{-1})	Particulate size (μm)	Comments
Graedel and Franey (1977)	19×10^{-5}		condensation nuclei
	18×10^{-5}	0.3-0.5	
	28×10^{-5}	0.5-0.7	
	43×10^{-5}	0.7-0.9	snow
	65×10^{-5}	0.9-1.5	
	92×10^{-5}	1.5-3	
Radke et al. (1977)			see Figure 14

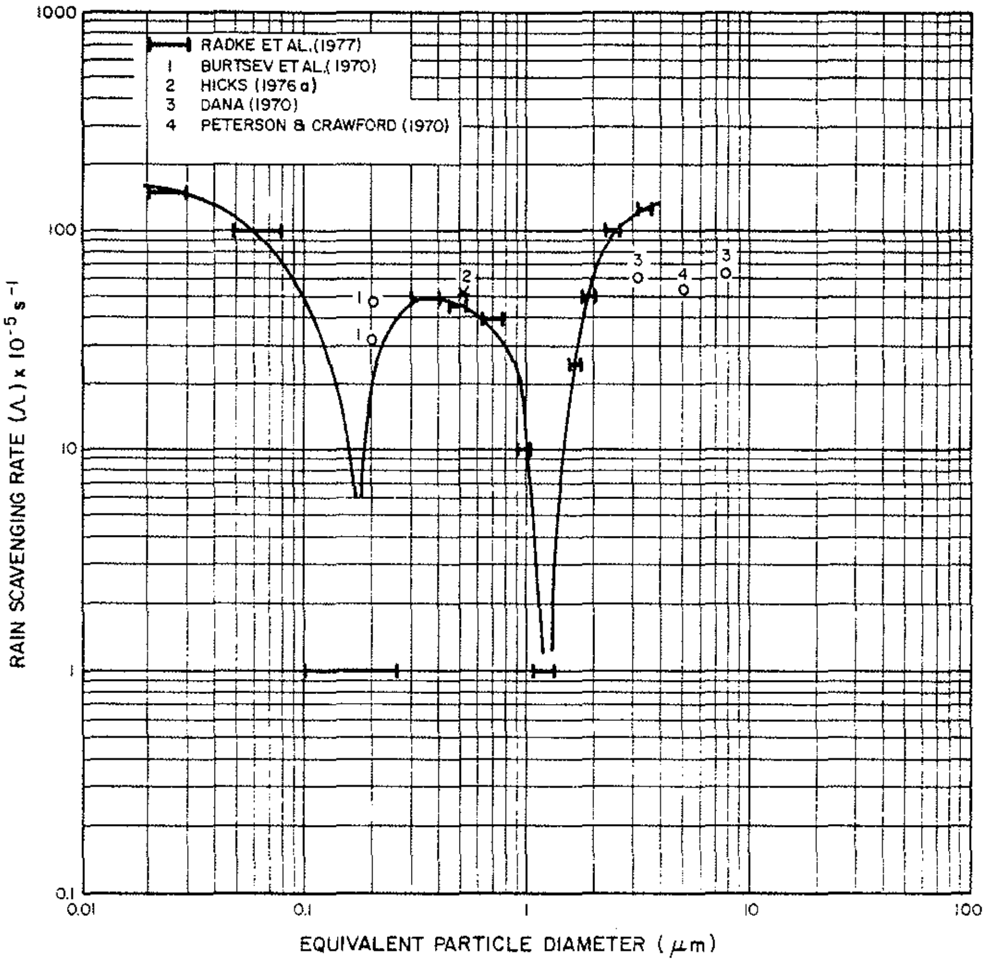

Figure 14. Relationship between rain scavenging rates and particle size.

2.6.4 Scavenging Ratios

The scavenging ratio (or washout ratio) is an alternative expression to scavenging coefficients for wet deposition and has been defined as the ratio of the mass contaminant in precipitation falling through a column of air compared with the mass in the column of air (Chamberlain 1960)

$$W = \frac{k\rho}{\chi} \tag{2.65}$$

where W = scavenging ratio,
k = concentration of contaminant in precipitation ($\mu g/g$),
χ = concentration of contaminant in unscavenged air ($\mu g/m^3$), and
ρ = density of air (1,200 g/m^3).

Wet deposition rate is then given by

$$L_{wet} = W \chi J/\rho \tag{2.66}$$

where J = rainfall rate.

The value of W is normally adopted from field observations and Table 15 has been included, which lists all such observations.

Like wet scavenging coefficients, scavenging ratios have been found to be a function of particle size and rainfall intensity. Generally, scavenging ratios decrease with precipitation amount but increase with particle size (Gatz 1975b). Gatz also observed that W increases with distance from the emission source. All these aspects indicate that localized measurements are desirable when using scavenging ratios.

2.6.5 Coefficient of Washout

The coefficient of washout is defined by Hutcheson and Hall (1974) as the fraction of the available pollutant washout per inch of rain. It is an empirically derived value and may be computed as follows.

Table 15. Field observations of washout ratios.

Author (date)	Ratio (Mass bases)	Contaminant	Precipitation	Comments
Hinzpeter (1958)	1,250	β	0.1	rain (mm/day)
	710		1.0	
	400		10	
	1,100		0.15	snow (equivalent water mm/day)
	620		1.0	
	290		10	
Chamberlain (1960)	230	^{137}Cs		air concentration at 1,200 m
	130	^{95}Zn		
	430	^{210}Pb		
Small (1960)	4,000	β		October 1956
	470			September 1959
	1,100			average (3 years)
Peirson and Keane (1962)	560	^{137}Cs		air near ground
	520	^{148}Co		
	480	^{140}Ba		
	500	^{95}Zr		
	420	^{131}I		
Peirson and Cambray (1965)	600-800	^{137}Cs		annual means

Continued ...

Table 15. Continued.

Author (date)	Ratio (Mass bases)	Contaminant	Precipitation	Comments
Pelletier et al. (1965)	475-2,100	β		Jan. 1963 - June 1964
Gatz (1966)	1,100-9,200	Pollen	rain 0.15-3.6 mm/h	surface area
Georgii and Beilke (1966)	190 19	SO_2	0.3 mm 11-20 mm	rainstorm
Crawford (1968)	100-2,700	^{131}I		snow
Van de Westhuizen (1969)	$W=9{,}000P^{-0.59}$	^{137}Cs		P = mm rainfall per 3 months
Health and Safety Laboratory (1970)	160-18,000	Pb		
Perkins et al. (1970)	1,500-5,500	^{38}Cl	rain 0.1-8.0 mm/h	
Gatz (1972)	751	Cu		sampled rain days
	951	Fe		
	169	Pb		
	1,212	Mg		
	698	Mn		
	671	Zn		
Peirson et al. (1973)	380 - 2,900	23 elements		

Continued ...

Table 15. Concluded.

Author (date)	Ratio (Mass bases)	Contaminant	Precipitation	Comments
Gatz (1975b)	375	Al		
	110	As		
	125	Cd		
	150	Cr		
	140	Cu		
	250	Fe		
	125	Ni		
	76	Pb		
	325	Ti		
	110	V		
Prahm et al. (1976)	4 000	S		Includes both wet
	24 000	Na		and dry deposition
Gatz (1977)	457	Mg		
	548	K		METROMEX, 1971-72
	352	Ca		Scavenging ratios vary
	370	Mn		with particle size--
	253	Fe		see also Gatz (1975b)
	179	Zn		
	76	Pb		
Krey and Tonkel (1977)	$970P^{-0.17}$	^{90}Sr		
	$1,400^{-1.1}$	Pb		

$$\nabla = bt^{0.85}[0.07^{\frac{1}{3}} + (J-0.07)^{\frac{1}{3}}] \tag{2.67}$$

where ∇ = washout coefficient,

b = empirical constant varying seasonally (based on an analysis of washout from a coal-fired power plant, Hutcheson and Hall [1974] found b to range from 1.9 to 2.3),

t = travel time (distance/wind speed), and

J = precipitation rate (in/h).

2.6.6 Theoretical Particulate Scavenging Coefficient

Chamberlain (1953) showed that rain scavenging rate is given by

$$\Lambda = \int_0^\infty \int_0^\infty N(R)\ \pi R^2\ E(a,R)\ v_t(R)\ dRda \tag{2.68}$$

where Λ = rain scavenging rate,

$N(R)$ = number of drops of radius R per unit volume of air,

$E(a,R)$ = collision efficiency of raindrops of radius R with particles of radius a, and

$V_t(R)$ = terminal velocity of drop radius R.

Here we assume that retention efficiency is unity and integrating over all drops, that the drops act independently. According to Slinn (1977a), the latter assumption is probably true because the mean distance between drops is quite large.

Slinn (1977a, 1977b) further argued that because drop size distribution is difficult to define, because collection efficiencies are not adequately known, and because we do not know the properties of the pollutant, Equation (2.68) may be approximated by

$$\Lambda(a) = \frac{c\ J_o\ E(a,R_m)}{R_m} \tag{2.69}$$

where $\Lambda(a)$ = rain scavenging rate of a particle of size **a** (s^{-1}),

$c = \frac{1}{2}$ (Slinn indicates that it is of the order of unity but adopts $\frac{1}{2}$),

J_o = rainfall rate (mm/h), and

R_m = mean-volume radius and using Mason's result (1971)

$$= 0.35\ (J_o)^{\frac{1}{4}}. \tag{2.70}$$

It should be noted that in this reduced form Λ is still given as a function of particle size, a significant point noted in Figure 14.

Slinn tested Equation (2.69) with field data given by Dana (1970) and was satisfied with the comparison.

2.6.6.1 Theoretical scavenging coefficient of snow. Slinn (1977a,1977b) has suggested the following algorithm to represent the removal rate of snow

$$\Lambda_s(a) \simeq 10^6 \frac{J_s}{v_t^2} \varepsilon(a,\ell) \tag{2.71}$$

where $\Lambda_s(a)$ = snow scavenging for particle size a (s^{-1}),

J_s = snowfall rate (rainfall equivalent)

v_t = average terminal velocity of snow particle,

$\varepsilon(a,\ell)$ = particle crystal collection efficiency (Equation 2.62), and

ℓ = characteristic dimension of the collecting element in the ice growth.

Field data are inadequate to test this formulation.

2.6.6.2 Effect of polydispersity and particulate growth. Taking into account polydispersity of the aerosol and on the time for attachment and condensational growth, Slinn (1977a) illustrated the strong dependence of the mass average removal rate on these factors.

Dana and Hales (1976, 1977) have examined analytically the importance of taking into account the polydisperse nature of aerosols. They showed that for particles in the range 0.5×10^{-2} μm to 1 μm there is up to 2 orders of magnitude difference in the washout coefficient between results based on monodispersed particles and those based on polydispersed particles. They strongly recommended that, in experiments designed to determine scavenging coefficients, both particle and rain spectra be measured.

2.6.7 Theoretical Scavenging Ratio

Englemann (1970) argues that the concept of a cloud as a box in which pollutants are removed to the cloud elements at some fractional rate (rainout coefficient) is not useful since sustained precipitation will not occur without a continued supply of moisture and unscavenged air. Therefore Englemann proposed an in-cloud scavenging model utilizing the scavenging ratio concept. He related the scavenging ratio to the fraction of pollutant that nucleates to the efficiency of the cloud precipitation process and to the humidity as follows

$$\left(\frac{k}{\chi}\right)_v = \frac{n}{q\ E_2} + \frac{1-n}{q}\ \rho\alpha \tag{2.72}$$

where $\left(\frac{k}{\chi}\right)_v$ = washout ratio on a volume basis,

ρ = density of water,

n = fraction of pollutant which nucleates and is subsequently removed by precipitation,

q = absolute humidity of the entraining air,

E_2 = efficiency of the cloud at removing water as precipitation from the air it processes, and

α = reactivity factor.

E_2 varies within the range of 0.05 to 0.65 depending on cloud and precipitation type, entrainment and the temperatures at cloud base and cloud top. Summers (1970) relates E_2 to the liquid-water content of the cloud. This relationship is based partly on data for convective storms in Alberta.

The reactivity factor α covers collection differences between the pollutant and water vapour. Ignoring any below cloud effects, Englemann notes that α should be approximately unity.

Equation (2.72) applies at the cloud base. Below-cloud scavenging contributes to the deposition of the pollutant by $H\chi\Lambda$ (see Equation 2.64) and to the concentration in the precipitation by $H\chi\Lambda/J_o$ where H = height of the cloud base, χ = concentration of pollutant in the air, Λ = washout coefficient, and J_o = rainfall rate.

Therefore, Equation (2.72) can be modified to provide scavenging ratio at the ground

$$\left(\frac{k}{\chi}\right)_v = \frac{\rho n}{qE_2} + \frac{1-n}{q}\rho\alpha + \frac{H}{J_o} \tag{2.73}$$

This assumes that the air concentration between the ground surface and the cloud base is represented by χ.

2.6.8 Makhon'ko Washout-Rainout Model

This model, Equation (2.74) below, describes the variation in concentration of radio-active particles with time resulting from the attachment of particles to cloud droplets and to below-cloud scavenging by rainfall.

$$C_t = \chi_o\left(\alpha + \beta e^{-\Lambda_r t} + \gamma e^{-\Lambda_w t}\right) \tag{2.74}$$

where C_t = contaminant concentration in the rainwater at time t,

χ_o = contaminant concentration in sub-cloud layer at t=0,

α,β,γ = parameters depending on vertical air velocity, cloud thickness and rainfall intensity,

t = precipitation duration,

Λ_r, Λ_w = parameters characterizing the removal rate and are respectively rainout (in-cloud) scavenging coefficient and washout (below-cloud) scavenging coefficient.

The model is based on a number of assumptions, namely:

1. Cloud water remains constant and consists of monodispersed droplets with a number density of $300/cm^3$;
2. Contaminant particles are also monodispersed; and
3. Particles attached to cloud droplets are immediately removed from the cloud to the ground.

Parameters α, β, and γ would have to be determined from localized measurement. Λ_r and Λ_w could also be measured locally or values adopted from Table 14 or Figure 14.

2.6.8.1 Modified Makhon'ko model. Andersson (1969) modified Makhon'ko's model to the form

$$C_t = \chi \left(a + \beta e^{-\Lambda_r t} + \frac{H'}{H} \gamma e^{-\Lambda_w t} \right) \tag{2.75}$$

where H = height of the cloud base,

$$H' = \frac{1}{a}(e^{aH} - 1), \text{ and} \tag{2.76}$$

a = constant determining the vertical profile of contaminant concentration.

In Makhon'ko's model, χ_o is assumed constant with height. However, in Equation (2.75) it is assumed that contaminant concentration decreases exponentially with height.

2.6.9 Empirical Snow Scavenging Model

Knutson and Stockham (1977) developed an aerosol scavenging model by snow using empirical expressions for the scavenging efficiency of single snowflakes, their size distribution, and their mass-gross size relations. The empirical model for the scavenging coefficient is given by

$$\Lambda_s = a\ J_s^{\ b}\ f(T,D_p) \tag{2.77}$$

where Λ_s = scavenging coefficient for snow (s^{-1}),

J_s = precipitation intensity (mm/h),

a,b = empirical coefficients which are a function of snow type (these are tabulated below),

$f(T,D_p)$ = effective scavenging cross-section defined as the number of aerosol particles caught by a snowflake in unit fall distance divided by aerosol concentration,

$$f(T,D_p) = \text{antilog}\ [-3.17 + 0.0187T + 3.41 \log D_p - 7.20\ (\log D_o)^3], \tag{2.78}$$

T = temperature (^oF), and

D_p = particle diameter (μm).

Another term used to describe snow scavenging is the specific cross section, s. This is defined as the sum of the effective scavenging cross-section for all snowflakes in a litre of melted snow and is given by

$$s = cf(T,D_p)/J_s^{\ d} \tag{2.79}$$

where c,d = empirical coefficients which are a function of the type of snow.

Values of the coefficients a, b, c, and d in Equations (2.78) and 2.79) are tabulated in Table 16.

Knutson and Stockham compared results from the Empirical Snow model to field measurements. The comparison was hampered by lack of data on J_s and D_p. Nevertheless, the model agreed with field data to within a factor of 3 in most cases.

Table 16. Values of coefficients a, b, c, and d in Equations (2.78) and (2.79) .

Type of Snow	a	b	c	d
Lump graupel	0.21	0.188	675	1.0
Densely rimed dendrites	0.40	0.266	1,309	0.934
Densely rimed radiating assemblages of dendrites	0.32	0.305	1,044	0.895
Aggregates of unrimed radiating assemblages of dendrites or dendrites	0.41	0.57	1,336	0.623

2.6.10 Early Particulate Scavenging Models

To complete this review several of the early particulate scavenging models are included. Greenfield (1957) presented a theoretical model of monodispersed particles and droplets and showed that particles greater than 2 μm are captured by raindrops under the influence of inertial impact. Smaller particles become attached to cloud droplets by diffusion. This is particularly effective for particles less than 0.05 μm but ineffective for larger ones. Palomares (1970) extended Greenfield's approach by incorporating Best's (1950) raindrop distribution, but had to assume rainfall intensity to be constant in order to derive a solution.

In 1962 Facy developed a multi-rate model of in-cloud scavenging. According to Slinn (1974b), this approach has been extended by Dingle and Lee (see Section 2.6.13). The contributions of other workers including Makhon'ko, Chamberlain, and Engelmann have been included earlier.

2.6.11 Numerical Washout Model

This model was first published in 1970 by Kortzeborn and Abraham, and later by Abraham et al. (1972). Primarily, it is a model for computing time dependent behaviour of raindrop size distributions for a variety of conditions. The model includes a spatially varying atmospheric profile and takes into account evaporation and coalescence of raindrops on a dynamic basis.

The basic assumptions in the model are that:

1. The atmosphere is constant in time and one-dimensional; that is, ambient temperature, pressure, and relative humidity are functions only of altitude; vertical and horizontal winds are assumed zero;
2. The raindrops fall vertically at their terminal velocities, and their water vapour and heat transfer rates are governed by Best's (1950) differential equations.

3. The transient evaporation and coalescence processes are considered simultaneously.

The model utilizes a numerical solution to the basic equations and determines the raindrop size distribution function and raindrop temperature for radii, altitudes and times of interest. It requires as input:

1. The temperature, pressures, and relative humidity profiles of the atmosphere, and
2. The raindrop size distribution function and raindrop temperature at the cloud base.

To illustrate the potential of the raindrop spectrum output of the model, washout of monodisperse aerosol particles (2 μm to 20 μm) is included as part of the model. The washout process is based on an exponential decay at the scavenging rate Λ, where

$$\Lambda = \int_0^\infty N\ V\ E\ A\ d\ R \qquad (2.80)$$

where N = concentration of raindrops in the air at the level under consideration,
V = terminal velocity of drops,
A = cross-sectional area of drops,
R = raindrop radius, and
E = collision efficiency of drops for particles of prescribed diameter (the model uses a linear interpolation of the Langmuir efficiencies).

In its present form the model has two major limitations. Firstly it is developed only for monodisperse particles. However, this limitation could probably be overcome by numerically solving Equation (2.80) for a discrete set of particle sizes. The second limitation is of more concern. The model requires an estimate of E, but until a more definitive function than that available in Section 2.6.2 can be found, this model is of limited value.

2.6.11.1 Modified numerical washout model. This model is concerned with large particles (>1 μm) of NaCl and takes into account only inertial capture. It is a further development of the model of Abraham et al. (1972) described in the previous section. That model accounted for raindrop evaporation and coalescence, spatially varying atmospheric profile, monodisperse aerosol, and release of captured particles back to the atmosphere as raindrops evaporate away. The modified version of Stensland and de Pena (1975) includes the following additional aspects:

1. Polydisperse aerosol,
2. Hygroscopic aerosol (hence one that changes with relative humidity),
3. Recapture of released particles by raindrops, and
4. Output consisting of the prediction of the rainwater concentration as a function of time.

The assumptions in the model are:

1. The Marshall-Palmer (1948) raindrop distribution begins falling from the cloud base;
2. Scavenging occurs in a series of sub-cloud layers containing an initial distribution of NaCl particles which have no significant settling velocity and are not replenished with time;
3. No horizontal winds exist, but an updraft may be present;
4. The temperature profile, the relative humidity profile, and rainfall intensity at cloud base are assumed constant in time; and
5. Raindrop coalescence is not considered.

Details of the method may be found in Stensland and de Pena's (1975) paper. To demonstrate the method, NaCl particles were considered and results were found to compare satisfactorily with experimental data.

A major drawback with this model as published is that it takes into account only inertial capture of particles and hence it has a restricted particle range of application.

2.6.12 Davis In-Cloud Scavenging Model

The Davis approach to in-cloud scavenging is based on a 3-phase model:

1. Transfer of material from the air to cloud water,
2. Removal of material from the cloud water by rain and snow, and
3. Transfer of material by rain and snow to the ground.

The 3 algorithms representing each phase follow. However, as it was derived for examining scavenging of cosmogenic radionuclides, for our purpose the production rate of radionuclides and their decay have been set to zero in the equations

$$N_a = N_{ao} e^{-\lambda t} \qquad (2.81)$$

$$N_w = N_{wo} e^{-\psi t} + N_{ao} e^{-\lambda t_o} [e^{-\lambda t} - e^{-\psi t}] \qquad (2.82)$$

$$\frac{dN_g}{dt} = \psi N_w \qquad (2.83)$$

where N_a = air concentration,

N_{ao} = N_a for $t = 0$

= free air concentration at $t = 0$,

λ = attachment rate (s^{-1}) (Slinn's [1974b] term),

N_w = cloud water concentration,

N_{wo} = cloud water concentration at $t = 0$,

ψ = dilution rate or removal rate (s^{-1}),

t_o = in-cloud time before precipitation begins, and

$\frac{dN_g}{dt}$ = rate of deposition on ground.

In deriving the model a number of assumptions are made:

1. Clean air concentration is known,
2. Process of in-cloud attachment and removal are continuous, and
3. Evaporation and below-cloud scavenging can be ignored.

Slinn (1974b) has used this model to examine in a generalized quantitative manner the rate of limiting aspects of in-cloud scavenging. He assumed

$$\psi \text{ (removal rate)} = \frac{\rho J_o}{wb} \tag{2.84}$$

where ρJ_o = precipitation flux, and

w = liquid water content within the rain forming region of the cloud which has thickness b.

Slinn further assumed the attachment rate (λ) to be a function of particle size. The results, shown in Figure 15, indicate how rainout varies qualitatively with particle size and other factors.

Lee and Dingle (1974) in examining the Davis and earlier models (Makhon'ko 1967; Engelmann 1968) note a number of limitations:

1. The assumption of uniform cloud droplets and particle size;
2. The size-time independent attachment rate constant, and the size-time independent removal rate constant;
3. The lack of distinction between the attachment rate constant and the removal rate constant; and
4. The integral estimation of contaminant removed by precipitation using unrealistic parameterization of the microphysical processes.

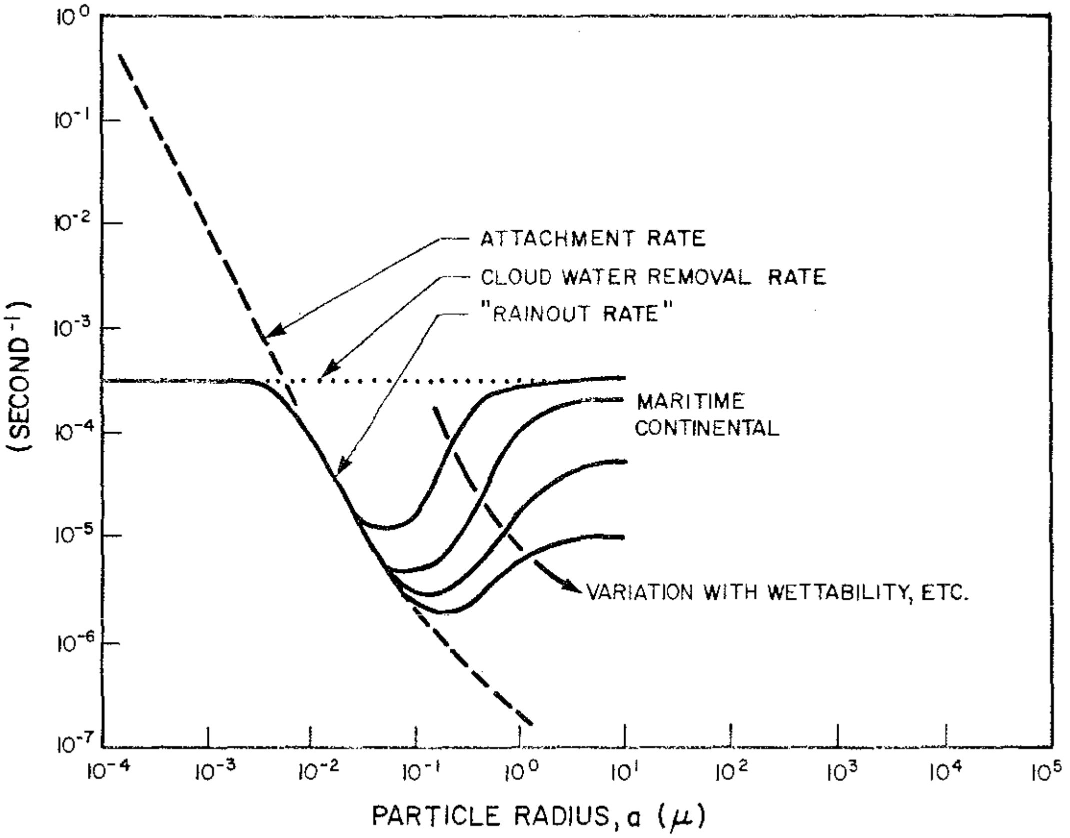

Figure 15. Rainout as a function of attachment and removal rates (extracted from Slinn 1974b)

2.6.13 Stratiform In-Cloud Scavenging Model

This model, developed by Dingle and Lee (Dingle and Lee 1973; Lee and Dingle 1974) is a model of the in-cloud scavenging process and is primarily based on continuity equations incorporating diffusive attachment, impaction, and accretion processes and takes into account particle and droplet size spectra. However, phoretic and electrical influences are neglected.

In the model the cloud is considered to be an assemblage of droplets intermingled with a particulate contaminant, some of which is free floating in the cloud air and some of which is attached to the cloud droplets. Rain, independently generated, removes the contaminant from both classes. The basic algorithms are as follows

$$Na(t) = N_a(0)e^{-\alpha t_c} e^{-(\alpha + \beta + \gamma)^t} \qquad (2.85)$$

$$N_c(t) = [N_c(0) + N_a(0)(1 - e^{-\alpha t_c})]e^{-\bar{\lambda} t} + \frac{N_a(0)e^{-\alpha t_c}}{\bar{\lambda} - (\alpha + \beta + \gamma)} \cdot$$

$$[e^{-(\alpha + \beta + \gamma)t} - e^{-\lambda t}] \qquad (2.86)$$

$$N_r(t) = [N_c(0) + N_a(0)] (1 - e^{-\bar{\lambda} t}) + \frac{N_a(0)e^{-\alpha t_c}}{\bar{\lambda} - (\alpha + \beta + \lambda)}$$

$$[e^{-\bar{\lambda} t} - e^{-(\alpha + \beta + \lambda)}] \cdot [\lambda + \beta + \lambda] \qquad (2.87)$$

where N_a = number density of contaminant particles in the cloud air,

N_c = number density of contaminant particles attached to cloud droplets,

N_r = number density of contaminant particles removed by raindrops,

α = diffusive attachment rate between particles and droplets,

β = diffusive attachment rate between particles and raindrops,

γ = impact collection rate for particles by raindrops,

= mean accretion rate of droplets by raindrops, and

t_c = time for contaminant to interact with the cloud before precipitation occurs.

The rate constants α, β, γ, and $\bar{\lambda}$ are evaluated in terms of the respective physical processes. The diffusive attachment rate (α) is considered as the sum of Brownian diffusion (based on Byers 1965) and turbulent contribution. For the latter, Levich formulation (Levich 1962) was used. In addition the size spectra of contaminant particles and cloud droplets are required. Dingle and Lee utilized the approach of Khrgian and Mazin (1952) and the log-normal distribution respectively.

To determine the diffusive attachment rate between particles and raindrops (β), the Marshall-Palmer (1948) raindrop size distribution was adopted with the above Brownian diffusion and turbulent terms.

To determine the impact collection rate, the authors used the equation

$$\gamma = \sum [\pi R^2 \; E(R,r)(V_R - V_r)N_R \; \Delta R] \qquad (2.88)$$

for each i and k

where V_R = terminal velocity of raindrops of radius R,

V_r = terminal velocity of particles of radius r,

$E(R,r)$ = collision efficiency,

$N_R \; \Delta R$ = number of raindrops per unit volume in the range R to R + ΔR,

i = particle size index, and

k = raindrop size class index.

Values of E(R,r) were derived from Mason (1971).

The removal of cloud droplets by rain is given by Equation (2.88), where r denotes the cloud droplet size and $\bar{\lambda}$ is substituted for γ.

For computational purposes the model has been modified. For example, a weighted mean accretion rate ($\bar{\lambda}$) is adopted rather than a value dependent on raindrop and cloud droplet size. It is also assumed that the cloud spectrum and size distribution of pollution are assumed to be time independent for each time step. Further, α, β, γ, and $\bar{\lambda}$ remain constant during each time step.

Based on the above formulation and a small amount of testing by the authors, this model of in-cloud scavenging of particles is considered to be satisfactory.

2.6.14 Sulphate Washout Model

Peters (1976) developed an algorithm for computing the sulphate concentration of rainwater down-wind of a point source. In development of the method, Peters assumed:

1. Irreversible absorption behaviour of gaseous SO_2; this assumption provides an upper limit to precipitation scavenging of gaseous SO_2 (see Section 2.6.7);
2. Error in adopting a mean raindrop diameter rather than the spectrum of drops is not too large;
3. Steady-state behaviour;
4. First order irreversible loss;
5. Governing partial differential equation is

$$U \frac{\partial c}{\partial x} = A_y x^q \frac{\partial^2 c}{\partial y^2} + A_z x^n \frac{\partial^2 c}{\partial z^2} - k c \qquad (2.89)$$

where U = wind velocity in x direction,
c = concentration in air,
A_y = eddy diffusivity coefficient in y direction,
A_z = eddy diffusivity coefficient in x direction,

q = eddy diffusivity exponent in y direction,

n = eddy diffusivity exponent in z direction, and

k = first order homogeneous loss constant;

6. Gas absorption and particulate scavenging by raindrop can be modelled as a homogeneous loss term;
7. Gas phase aerosol formation by SO_2 is negligible; and
8. Particle size distribution of sulphate aerosol is only affected by precipitation scavenging.

Thus solving Equation (2.89) with appropriate boundary conditions and a deep mixing layer (Heines and Peters 1973), adopting a first-order loss process, and considering both gaseous SO_2 and sulphate aerosol, Peters derived the following equation to determine the sulphate concentration of rainwater

$$[SO_4^=] = \frac{\sqrt{\dfrac{g+1}{\pi\ U\ A_y}}}{D_c\ U_t\ x^{(q+1)/2}} \exp\left[- \frac{(q+1)\ Uy^2}{4\ A_y\ x^{q+1}} \right] \cdot \left\{ 4.5\ \frac{k_g Q_{SO_2}}{\beta_g} \exp\left[- \frac{6\ P\ k_g x}{D_c\ U_t\ U\ \beta_g} \right] + \frac{3U_t}{2} \sum_{i=1} \frac{\eta_i\ Q_{pi}}{\beta_{pi}} \exp\left[- \frac{3P\ \eta_i\ x}{D_c\ U\ \beta_{pi}} \right] \right\} \tag{2.90}$$

where D_c = diameter of raindrop,

U_t = relative velocity of raindrops with respect to particle,

k_g = gas phase mass transfer coefficient (see Section 2.7.5),

Q_{SO_2} = strength of point source emission of gaseous SO_2,

β_{pi}, β_g = correction factors relating to mean drop size,

P = precipitation rate,

η_i = collection efficiency of particles of size i, and

Q_{pi} = strength of point source emission of particles size i.

Collection efficiency (η_i) of particles was based on the assumption that the deposition mechanisms act in series. Three mechanisms were involved--inertial impact, interception, and diffusion. The equations adopted for each differ from those outlined in Section 2.6.2 and are, therefore, included here for completeness.

The equation for inertial impact is

$$\eta_{Imp} = \frac{1}{(1+0.7/S_t)^2} \qquad (2.91)$$

where η_{Imp} = inertial impact efficiency,

S_t = dimensionless Stokes' number

$$= \frac{C_f\ \rho_p\ D_p\ U_t}{q\ \mu D_c}, \qquad (2.92)$$

C_f = Cunningham correction factor for particles,

ρ_p = density of particles,

D_p = diameter of particles, and

μ = gas phase viscosity.

The equation for interception is:

$$\eta_{Int} = (1 + \kappa)^2 - \frac{1}{1 + \kappa} \qquad (2.93)$$

where η_{Int} = interception efficiency, and

κ = interception parameter

= ratio of the particle diameter to the collector raindrop diameter.

The equation for diffusion is:

$$\eta_{Dif} = \frac{8}{R_e S_c} + \frac{2.4}{R_e^{\frac{1}{2}} S_c^{\frac{2}{3}}} \qquad (2.94)$$

where η_{Dif} = diffusion efficiency,

R_e = Reynold's number for raindrops, and

S_c = Schmidt number for raindrops.

Combining the efficiencies of the three mechanisms by series gives

$$\eta = 1 - (1 - \eta_{Imp})\ (1 - \eta_{Int})\ (1 - \eta_{Dif}). \qquad (2.95)$$

Using Equation (2.90), Peters made a number of theoretical predictions.

1. Sulphate concentration in rainwater decreases with distance from the source.
2. The effect of increasing precipitation rate is to decrease the sulphate concentration. The dependency of the sulphate concentration on the precipitation rate is more pronounced for the smaller raindrop sizes.
3. The magnitude of the effect of precipitation rate on the rainwater sulphate concentration is dependent on the raindrop and particle diameters. This dependence on precipitation rate becomes less as the raindrop size increases and as the particle size decreases.

4. The contribution of particles to the rainwater sulphate concentration is a maximum in the 3-µm to 10-µm range at moderate distances from the source.

2.7 WET GASEOUS MODELS

2.7.1 Introduction

Very little empirical information about simple scavenging models is available. In fact, only two field studies were found in the literature, compared with 35 for dry gaseous deposition. Some detailed theoretical work by Hales is available, but it is concerned with gaseous scavenging from a mass transfer point of view. The alternative chemical model approach assumes that mass transfer is infinitely rapid. Following an examination of simple empirical and theoretical models, procedures for modelling gaseous scavenging by these two approaches are reviewed.

2.7.2 Scavenging Coefficients of Gases

Like particulate scavenging, wet deposition of gases may be considered as an exponential decay process and we define a gaseous scavenging coefficient as follows

$$\chi_t = \chi_o \, e^{-\Lambda_g t} \qquad (2.96)$$

where χ_t = atmospheric concentration of gas at time t,

χ_o = atmospheric concentration of gas at time zero, and

Λ_g = scavenging coefficient of gases (in units of time^{-1}).

Using this concept, the loading or deposition rate of the gas due to scavenging is

$$L_{wet} = \bar{\chi}\ \Lambda_g\ Ht \tag{2.97}$$

where L_{wet} = deposition rate, and

H = scavenging height.

Compared with the other empirical parameters examined-- v_p, v_g, and Λ_ρ--few laboratory or field estimates of Λ_g have been measured. Values are tabulated in Table 17.

2.7.3 Theoretical Gaseous Scavenging Coefficient

Based on the assumption that the rate of gaseous absorption of a raindrop is solely controlled by the rate of diffusion of the gas to the raindrop, Chamberlain (1953) showed that

$$\Lambda_g = \int_0^\infty \pi\ Y\ S_h\ D\ N\ dD \tag{2.98}$$

where Λ_g = gaseous below-cloud scavenging (washout) coefficient,

Y = coefficient of molecular diffusivity,

D = diameter of raindrops,

N = concentration of drop in air, and

S_h = Sherwood (or Nusselt diffusion) number.

The Sherwood number for spheres is given by

$$S_h = 2 + 0.6\ R_e^{\frac{1}{2}}\ |\nu/Y|^{\frac{1}{3}} \tag{2.99}$$

where R_e = Reynolds number, and

ν = kinematic viscosity of air.

Using Equations (2.98) and (2.99), Chamberlain related Λ_g for SO_2 to rainfall intensity. Analysis of these results suggest

$$\Lambda_g \text{ for } SO_2 = 10 \times 10^{-5}\ J^{0.53} \tag{2.100}$$

where J = rainfall intensity in mm/h.

Table 17. Laboratory and field measurements of scavenging coefficients of gases.

Author (date)	Λ_g (s^{-1})	Gas
Laboratory Results		
Beilke & Georgii (1968)	$\Lambda_g = 50 \times 10^{-5}\ P^{-0.54}$	SO_2 P = total rainfall < 1 mm
Beilke (1970)	$17 \times 10^{-5}\ J^{0.6}$	SO_2
	$\Lambda_{NO_2} = 1/4\ \Lambda_{SO_2}$	SO_2
Field Data		
Makhon'ko (1967)	6×10^{-5}	SO_2
Hales et al. (1970)	2×10^{-5}	SO_2 Small scale experiment
	0.4×10^{-5}	SO_2 Large scale experiment - lower value of Λ_g attributed to evaporation of SO_2 from water drops.

This latter equation gives estimates of Λ_g for SO_2 midway between the laboratory and field estimates tabulated in Table 17.

2.7.4 Makhon'ko Washout-Rainout Model

Makhon'ko's model (Makhon'ko 1967) and its modification to account for the variability of initial contaminant with height (Andersson 1969) could be used for gaseous deposition. These models are explained in Section 2.6.8. For gaseous deposition washout and rainout coefficients for the particular gases would be used instead of the particulate scavenging coefficients.

2.7.5 Theory of Gaseous Scavenging by Rain

This section is based on Hales' (1972) fundamental paper on gaseous scavenging by rainfall. Gaseous pollutant molecules, in order to be captured, must first migrate from the atmosphere to the surface of the liquid. From here they normally pass through the vapour-liquid interface, and then migrate into the liquid interior where they may react chemically or simply exist as unreacted dissolved gas molecules. The existence of dissolved gas molecules constitutes a concentration of gas in the liquid and, because of the finite solubility of the gas, it will be characterized by a vapour pressure. Thus, there will be a tendency for gas molecules to desorb from the liquid back to the atmosphere.

Based on simplified film theory (Figure 16), the mass transfer coefficients are as follows

$$\frac{1}{K_y} = \frac{m_y}{k_x} + \frac{1}{k_y} \tag{2.101}$$

where K_y = overall mass transfer coefficient (expressed on gas phase basis),

k_y = mass transfer coefficient in gas phase,

k_x = mass transfer coefficient in liquid phase, and

m_y = liquid water content.

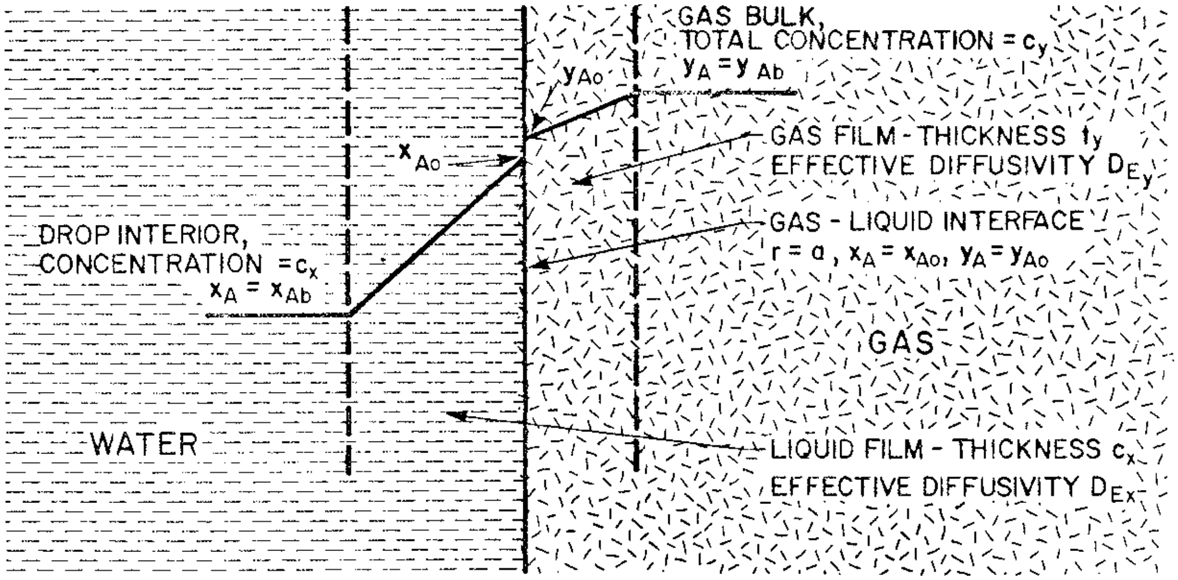

Figure 16. Schematic of film-theory approach (after Hales 1972).

For systems that obey Henry's law, $m_y = H$.

If K_y is constant and independent of y_{Ab} and y_{Ae} (gas phase mole fraction of contaminant for bulk and equilibrium conditions, respectively) the process is said to be *first order*. On the other hand, if the gas is annihilated completely upon contacting the drop surface, $y_{Ae} = 0$, the washout process is said to be *first order irreversible*.

Based on the continuity equations for pollutant in the gaseous and liquid phases in the atmosphere the rate of removal per unit volume of air by washout (w) is

$$w = 4\pi \int_o^\infty a^2 f(a)\ K_y(a)\ (y_{Ab} - y_{Ac})\ da \qquad (2.102)$$

where a = raindrop radius, and

f(a) = probability density function describing the size distribution of raindrops existing in the volume element.

Most previous analyses of atmospheric washout have assumed total retention of pollutant by the drop; thus,

$$w = \Lambda_i\ y_{Ab}\ C_y \qquad (2.103)$$

where Λ_i = overall washout coefficient for irreversible process, and

C_y = total concentration of gas.

Generally, irreversibility is a poor approximation for gaseous washout, and Hales recommends that the washout coefficient be defined in terms of a reversible process

$$w = \Lambda_r (y_{Ab} - y_{Ae})\ C_y \qquad (2.104)$$

Thus, the collection rate for pollutant captured by raindrops into a collection of unit area (Z),

$$Z = 4\pi N \int_o^\infty a^2 f(a)\ v_z(a) \cdot \left(\int_C^a \frac{k_y(y_{Ab} - y_{Ae})}{v_a^2}\ v_t\ dr_a \right) da + Z_o \qquad (2.105)$$

where N = number of raindrops in a unit volume,
a = raindrop radius,
$f(a)$ = probability density function of raindrops size distribution,
v_z = vertical velocity of raindrops,
v_a = wind velocity,
v_f = individual raindrop vector velocity,
r_a = position vector originating at the collector and tracing out the trajectories of different sized droplets, and
Z_o = total amount of pollutant captured per unit time by the rain prior to its passage through the plume.

Equation (2.105) shows how K_y is used to calculate wet deposition. If K_y were known, one could employ Equation (2.105) to calculate Z given rainfall, wind, plume-concentration and solubility data. However, by measuring Z, K_y cannot be determined on the basis of k_y unless other information about the nature of k_y is known.

To estimate the gas-plume mass-transfer coefficients we use the Fröessling equation which is defined as follows:

$$S_h = 2 + 0.6\, R_e^{\frac{1}{2}}\, S_c^{\frac{1}{3}} \qquad (2.106)$$

where S_h = Sherwood number

$$= \frac{2k_y a}{D_{Ay}\, C_y}, \qquad (2.107)$$

D_{Ay} = diffusion coefficient in the gas,
R_e = Reynold's number

$$= -\frac{2\, a\, v_z}{\nu}, \qquad (2.108)$$

v_z = terminal velocity of the raindrop

ν = kinematic viscosity of air

s_c = Schmidt number

$$= \nu/D_{Ay} \cdot \qquad (2.109)$$

However, compared with the above, the liquid-phase mass-transfer coefficient is very difficult to determine, because of surface film effects on the drop and chemical reaction in the liquid phase. If rapid convection occurs, the liquid mass-transfer coefficient becomes large and $K_y = k_y$. This is an upper limit. For zero convection, diffusion is the sole mechanism of transport. Equations are given in Hales (1972) for the systems that respectively obey and do not obey Henry's law.

The consequences of chemical reactions are complex. These are dealt with in Hales (1972).

2.7.6 SO_2-SO_4^{-2} Scavenging Model

Miller and de Pena (1972) adopted the approach of Scott and Hobbs (1967) and later McKay (1971) for the formation of sulphate in water drops. They assumed that the solution of SO_2 in water occurs at the rate measured by Wang and Himmelblau (1964). The rate of oxidation was based on their own experimentation. The developed model was applied to rainout and washout of SO_2 by using a profile of SO_2 below a cloud that represented a highly concentrated plume. Both rainout and washout were incorporated into the model.

Throughout the development stage of a cloud, SO_2 is absorbed, ionized, and oxidized to sulphate ions. The sulphate ions act as condensation nuclei as well as being captured by cloud droplets. These within-cloud processes are called rainout. On the other hand, the process of gas and particulates captured by falling raindrops is called washout.

The fundamental algorithms of the model are given in Figure 17. The droplets remain in the cloud for 1/2 hour before they begin to fall as rain. During this time SO_2 is absorbed by the cloud droplets and some sulphate is formed.

The first step in application of the model to rainout and washout is to adopt concentration values of CO_2, NH_3, and SO_2. It is assumed that during the few seconds between condensation on a cloud nucleus and growth to the size of a cloud droplet, the droplet achieves chemical equilibrium with NH_3 and CO_2 at the assumed partial pressures.

Next, Equation (1), Figure 17, is used to calculate the initial (H^+) concentration. At time T=0, the droplets begin to absorb SO_2. The next step involves computing (HSO_3^-), (SO_3^{-2}) and (SO_4^{-2}) concentrations using Equations (2) to (8), Figure 17. Then (H^+) is calculated and the process repeated for 1,800 seconds.

In the washout process, it is envisaged that the rain falls through a series of boxes placed between the cloud base and the ground. The amount of water entering each box is fixed by holding the intensity of precipitation constant. No SO_2 was allowed to enter the boxes during the rain episode. Thus, the SO_2 in each box was depleted with each time step.

Sulphate particles (as ammonium sulphate) were included in the model by assuming that they act as condensation nuclei in the formation of the cloud. Below the cloud it was assumed that the distribution of particles was uniform in the vertical plume. As the raindrops fell through each box they collected particles simultaneously as they absorb SO_2. For washout, the method of Junge (1963) was applied as follows:

$$K = \Sigma K_i \tag{2.110}$$

$$K_i = \frac{3}{4}(H/r_d)\ n_i\ (ml)_i \tag{2.111}$$

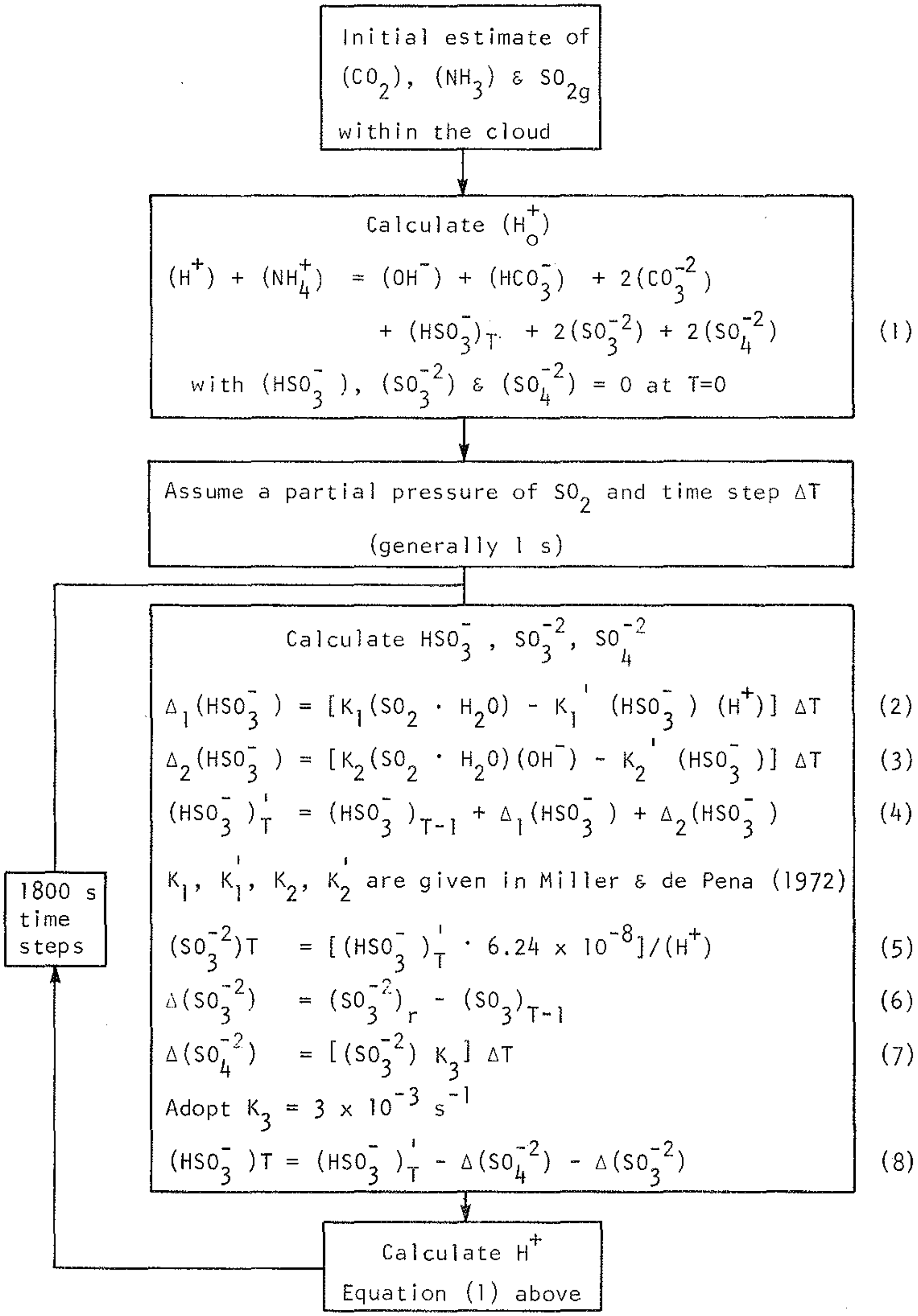

Figure 17. Model to compute sulphate concentration in raindrops.

where K = total concentration of sulphate in the raindrop,

K_i = concentration of sulphate in the rainwater obtained by collecting particles in the size interval i,

H = height of the cloud base,

r_d = radius of collecting drop,

η_i = collection efficiency based on Langmuir (1948)

$(ml)_i$ = mass of particles in the class interval i.

It was assumed that 50 percent of particles were acid. This acidity must be taken into account in Equation (7), Figure 17, by adding the additional sulphate ion to Equation (1), Figure 17.

Testing of the model as published (Miller 1972) is considered to be totally inadequate. Using sulphate concentration in rainwater, a comparison was made between data published in the literature from 23 papers and results adopting "reasonable conditions" in the model. Although the model gave values within the range of published data, these ranged over 2 orders of magnitude and little was known about the prevailing conditions. Before any confidence can be placed in the model, further testing and evaluation will be required.

2.7.7 EPAEC Washout Model

The EPAEC Washout model (Dana et al. 1975) was developed for predictions of the reversible washout of SO_2 emitted from power station plumes and other sources. The approach is based on the integration of coupled conservation equations in the gaseous (atmospheric) and liquid (rain) phases; thus,

$$\frac{\partial \rho_y}{\partial t} = - \nabla \cdot \rho_y V_y - W + R_y \qquad (2.112)$$

$$\frac{\partial \rho_x}{\partial t} = - \nabla \cdot \rho_x V_x + W + R_x \qquad (2.113)$$

where ρ_y, ρ_x = molar densities of gas (y) and liquid (x) phase pollutant, respectively,

V_y, V_x = average velocity vectors for pollutant in the gas and liquid phases, respectively,

R_y, R_x = terms for generation of pollutant by chemical reactions, and

W = time rate of gain of pollutant mass in the liquid phase by washout.

Equations (2.112) and (2.113) are expressed in terms of individual drops and are simplified for modelling purposes by assuming:

1. W in Equation (2.112) is small compared with the divergence term and therefore neglected (in Equation [2.112] only),
2. Steady-state conditions,
3. No liquid phase reaction, and
4. Spherical non-interacting drops.

Adopting these simplifying assumptions, Equation (2.113) can be reduced to the following which expresses the rate of change of concentration within a raindrop

$$\frac{dc}{dz} = \frac{3K_y}{v_z a} (y_b - H'c) \qquad (2.114)$$

where c = average concentration of scavenged material into a raindrop of radius a at height z,

y_b = mixing ratio of gas-phase pollutant,

K_y = mass-transfer coefficient,

v_z = terminal fall velocity of raindrop, and

H' = solubility parameter.

Equation (2.114) is solved in the EPAEC model by finite difference approximations for discretized spectra of raindrop sizes. The gas phase mixing ratio $y_b(x, y, z)$ is supplied by solution of Equation (2.112). A Pasquill-Gifford bivariate normal model is currently adopted which allows for a first-order irreversible gas phase reaction; that is, the mass transfer coefficient, K_y, and the effective Henry's law constant H' are invariant with concentration (Hales et al. 1973). Steady-state conditions and negligible W are assumed in Equation (2.112).

Ground-level concentration of each raindrop size is combined to give a mixed average concentration of SO_2 in incident rainwater. Essentially this is a solution of Equation (2.113) for the ground-level point of interest.

Inputs to the model include the mass-transfer coefficient K_y, using Fröessling's equation (Equation 2.106) and H', the solubility parameter, which has been determined by Hales and Sutter (1973) experimentally. Some circulation will be occurring within the falling drop. This, combined with other mixing factors, for example oscillation and thermal perturbation, will effect a transfer of material within the drop. Such a mechanism is difficult to analyze theoretically, so Hales et al. (1973) considered the 2 limiting cases of zero convection (stagnant droplet) and an infinitely rapid convection (well-mixed droplet) within the drop.

For the well-mixed drop, liquid mass transfer becomes large and therefore

$$K_y = k_y \tag{2.115}$$

where k_y = gaseous-phase mass transfer coefficient.

Analysis of the stagnant drop condition is complex. Hales et al. (1973) recommends

$$K_y = \frac{k_y}{1 + \frac{aHk_y}{5c_x D_{Ax}}} \qquad (2.116)$$

where a = raindrop radius,

H = Henry's law constant,

c_x = concentration in liquid phase, and

D_{Ax} = diffusion coefficient of pollutant A in liquid.

A documented version of the EPAEC model is available (Hales et al. 1973).

Hales and colleagues also developed two additional solutions to Equations (2.112) and (2.113). The first of these is a linearized version of the EPAEC model, assuming vertical rainfall and constant transport and solubility properties.

The second additional model (Slinn 1974a) is similar to the linearized version except that the washout term remains, thus maintaining a 2-way coupling of the gaseous and liquid phase equations to determine plume washdown.

A detailed discussion of probable errors in the model are given by Hales et al. (1973). It is important that inadequacies in the plume model, uncertainties in chemical reaction behaviour, and improper solubility estimates are probably the major sources of error in the general application of the EPAEC model. Inadequacies in the plume model are often serious. The authors believed that a majority of the errors observed in the EPAEC model have arisen from corresponding errors in the plume model.

Kinematic mechanisms, particularly for SO_2 oxidation in power plant plume, are poorly understood. In the model, a first-order rate law is assumed. This seemed to be satisfactory for the data used to test the model (Hales et al. 1973).

The studies by Slinn (1974a) indicated that neglecting W in Equation (2.112) (that is, assuming zero scavenging *en route*) is a reasonable assumption. However, for studies that are concerned with deposition near the limits of Gaussian models (10 km from source), neglecting W may not be a reasonable assumption.

Estimates of solubility of trace gases are difficult to determine, especially if values are extrapolated from measurements at higher concentrations to those being studied. It is important that appropriate estimates be known. Hales and Sutter (1973) experimentally determined values of H' in Equation (2.114).

Another source of error relates to the gas-phase mass-transfer coefficients--these could be in error by a factor of 2 or more. However, this becomes less serious as equilibrium scavenging conditions are encountered. Lastly, it is necessary that an adequate description of the raindrop size spectra be obtained.

2.7.7.1 Improved model of reversible SO_2. In the EPAEC model 2 extreme conditions were modelled--absorption by a stagnant drop and also by a well-mixed drop. From one extreme to the other, the predicted concentration of SO_2 in rain varied by up to an order of magnitude. Barrie (in press) has developed a model which more accurately describes the absorption and desorption of falling drops and takes account of the micro-physical effects of internal circulation.

Barrie's model is based on a 2-system liquid gas interface approach (like Figure 16). In solution, SO_2 diffuses as bisulphate across the liquid-diffusion layer; thus,

$$F_L = \frac{D_L}{\delta_L}\left([HSO_3^-]_L^{\,\prime} - [HSO_3^-]_L\right) \tag{2.117}$$

where F_L = flux of SO_2 to rain droplet,

D_L = binary-salt diffusion coefficient calculated from the mobility of the hydrogen and bisulphate ions (for SO_2 at $10^{o}C$, $D_L = 1.83 \times 10^{-5}$ cm/s),

δ_L = thickness of the liquid-phase diffusion layer (Barrie adopted $\delta_L = 0.1$ drop radius),

$[HSO_3^-]_L^{'}$ = concentration of bisulphite in the liquid phase at the interface

$$= \frac{-1 + \sqrt{\{1 + 4ZB[HSO_3^-]_L + Z[SO_2]_g\}}}{2ZB}, \qquad (2.118)$$

$$Z = \frac{D_g \ \delta_L}{\delta_g \ D_L}, \qquad (2.119)$$

$$B = a \ / \ K_1 K_H \ , \qquad (2.120)$$

D_g = diffusivity of SO_2 in air ($D_g = 0.141$ cm^2/s),

$$\delta_g = 2r/S_h \ , \qquad (2.121)$$

r = droplet radius,

K_1 = equilibrium constant ($K_1 = 2.42 \times 10^{-5}$ mole/cm^3),

K_H = equilibrium constant ($K_H = 51.1$ mole/cm^3),

S_h = Sherwood number

$$= 1.56 + 0.616 \ R_e^{\frac{1}{2}} \ S_c^{\frac{1}{3}} \qquad (2.122)$$

for $0.002 \leqslant r \leqslant 0.06$ cm

$$= 2 + 0.6 \ R_e^{\frac{1}{2}} \ S_c^{\frac{1}{3}} \qquad (2.123)$$

for $r > 0.06$ cm,

$[HSO_3^-]_L$ = concentration of bisulphite outside liquid phase diffusion layer

$$= \{K_H \ K_1 [SO_2]_g\}^{\frac{1}{2}}, \qquad (2.124)$$

$[SO_2]_g$ = concentration of gaseous SO_2 procedure.

To incorporate this procedure in plume washout, Barrie used a numerical approach in which a raindrop spectrum and Equation (2.117) were used. Based on a one-dimensional vertical model, rain fell vertically and continuously through a column of air considered as a number of layers with an initial SO_2 distribution. Reversible SO_2 exchange was permitted between the raindrops and each layer. Raindrop spectrum was based on Best's formulae (1950) as follows

$$1 - S = \exp\{-(2r/a)^{2.25}\} \tag{2.125}$$

$$a = 1.30\ J^{0.232} \tag{2.126}$$

$$W = 67\ J^{0.846} \tag{2.127}$$

where S = fraction of rainwater in drops of radius less than r,

J = precipitation intensity (mm/h)

W = concentration of rainwater in air (mm^3/m^3).

The model has not been validated by comparing computed values with experimental results.

2.7.8 Brookhaven Washout Model

This model described by Hill and Adamowicz (1977) is a combination of the physical models of mass transfer exemplified by the work of Hales and his colleagues (Section 2.7.7) and of chemical models in which mass transfer is taken to be infinitely rapid.

A simple chemical system is used as a basis of the model. Hill and Adamowicz consider a well-mixed layer of atmosphere adjacent to the surface of the earth. Rain is formed above the layer and prior to entering the layer attains a background concentration of a strong acid or a strong base or zero in the absence of both.

The chemical system treated involves a simple dissociation of SO_2 in rain containing a strong acid or strong base. No other atmospheric gases or background solutes are present.

Other assumptions in the model include:

1. Mass transfer is infinitely rapid (with this assumption, the model will estimate an upper limit on the rate of SO_2 uptake);
2. Except for SO_2, no other atmospheric gases or background solutes are present;
3. Raindrops are spherical and fall at their terminal velocities;
4. Henry's law determines the SO_2 gas-liquid distribution at the air-water interface; and
5. Production of sulphate ion results from bisulphate oxidation.

The washout model equations are as follows:

$$\frac{1}{K_1}\left\{2[H^+] - 2[SO_4^{2-}] - [Ex] + K_1\left(1 + \frac{K_w}{[H^+]^2}\right)\right\}\frac{d[H^+]}{dz}$$

$$- \frac{1}{K_1}\left(2[H^+] + K_1\right)\frac{d[SO_4^{2-}]}{dz}$$

$$= \frac{3k_g}{v_t R}\left\{[SO_{2,g}] - \frac{H}{K_1}[H^+]\left([H^+] - 2[SO_4^{2-}] - [Ex] - \frac{K_w}{[H^+]}\right)\right\} \qquad (2.128)$$

$$\frac{d[SO_4^{2}]}{dz} = \frac{k_{ox}}{v_t}\left([H^+] - [Ex] - 2[SO_4^{2-}] - \frac{K_w}{[H^+]}\right) \qquad (2.129)$$

where z = fall distance,

K_1 = ionization constant for equilibrium

$$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^-, \qquad (2.130)$$

$[H^+]$ = concentration of H^+,

$[SO_4^{2-}]$ = concentration of SO_4^{2-},

$[Ex]$ = concentration of background excess acid or base in raindrops,

K_w = constant for water ionization,

k_g = gas-phase mass transfer coefficient,

v_t = raindrop terminal velocity,

R = raindrop radius,

$[SO_2,g]$ = concentration of SO_2 pollutant in the atmosphere,

H = Henry's law constant for molecular SO_2,

k_{ox} = rate constant for bisulphite oxidation.

These equations are solved subject to the initial conditions

$$z = 0,\ [H^+] = [H^+(0)],\ [SO_4^{-2}] = 0$$

where $[H^+(0)]$ = concentration of hydrogen ion in the rain above the mixed layer, using a fourth order Runge-Kutta-Gill method. After obtaining $[H^+]$ and $[SO_4^{-2}]$, $[HSO_3^-]$ and then $[SO_2]$ are found from the following equations

$$[HSO_3^-] = [H^+] - [Ex] - K_w / [H^+] \qquad (2.131)$$

$$[SO_2] = [H^+][HSO_3^-] / K_1 \qquad (2.132)$$

where $[HSO_3^-]$ = concentration or HSO_3^-

The above calculations are for single drop size. To obtain the composition of rain from a full spectrum of drop sizes, we sum over all drop sizes and divide by the rainfall rate; thus,

$$\langle [S_T(h)] \rangle = \frac{1}{J} \int_0^\infty v_t(R)\ [S_T(R,h)]\ w\ f(R)\ dR \qquad (2.133)$$

where $\langle [S_T(h)] \rangle$ = mixed average total sulphur content of rain at ground level,

h = raindrop fall distance,

J = rainfall rate,

w = volume fraction of rain in air,

$f(R)$ = Best (1950) drop size distribution function, and

$[S_T]$ = total sulphur content

$$= [SO_2] + [HSO_3^-] + [SO_4^{-2}] \tag{2.134}$$

As presented, this model does not contain any procedure for spatial integration of washout. Furthermore, the results from the model have not been compared with experimental results. In this context it is worth noting that the washout coefficient from the model is given by

$$\Lambda = \frac{JK_1}{hH[Ex]} \tag{2.135}$$

For a typical set of data, Hill and Adamowics found the washout coefficient calculated by Equation (2.135) to be approximately 2 orders of magnitude less than the equivalent value calculated from Equation (2.100) which was based on Chamberlain's results. The authors suggest that this difference results from assuming in Equation (2.100) that initial rates of SO_2 uptake are maintained at all times, whereas in the present theory equilibrium is maintained. In discussing this problem, Hales (1972) states that washout coefficients based on so-called *irreversible* washout, that is, those based on initial rates, should not be used in connection with gaseous washout.

2.8 SUMMARY AND RECOMMENDATION OF DEPOSITION MODELS

Tables 18 to 21 provide for the 4 deposition categories--dry particulate models, dry gaseous models, wet particulate models, and wet gaseous models--summary information about 29 models discussed in the foregoing material. For each model, data requirements, details of model tests, and an estimate of probable errors are summarized. For some models in which error data were not available from the reference material, errors were estimated by comparison with similar procedures.

Table 18. Summary of dry particulate models.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Empirical deposition velocity, v_p (2.4.3)	Ground-level concentration Deposition surface Particle size	Ground-level concentration Particle size spectrum	Empirical model	Up to 1 order of magntidue	Minimal computational effort
Theoretical deposition velocity to smooth surface (2.4.4)	Ground-level concentration Particle size and density Particle settling velocity Particle relaxation time Friction velocity Wind effect Particle diffusion coefficient Kinematic viscosity of air Water vapour mass flux Empirical constants	Ground-level concentration Particle size spectrum Vertical surface wind profile Vertical surface temperature profile Humidity Net radiation	Some testing mainly for particles >0.1 µm	Appear to be within 1/2 order of magnitude	

Continued ...

Table 18. Concluded.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Theoretical deposition velocity in a canopy (2.4.4)	As for previous model plus thickness of canopy layer mean wind speed with canopy length scale of canopy fibres packing density of foliage biomass per unit volume average mass density of foliage	As for previous model plus forest height mean wind speed within forest botanical characteristics of forest	Not tested	Larger than previous model	Too many unknown factors
Sehmel's Integral Resistance Model (2.4.6)	Ground-level concentration Particle size & density Particle settling velocity Roughness height Friction velocity Particle diffusion coefficient Air viscosity Obukhov length	Ground-level concentration Particle size spectrum Vertical surface wind profile Vertical surface temperature profile Ambient air temperature	One field test	±100%	Satisfactory

Table 19. Summary of dry gaseous models.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Empirical deposition velocity v_g (2.5.2)	Ground-level concentration Deposition surface	Ground-level concentration	Empirical model	Grass ±70% Water ±80%	Satisfactory
Theoretical deposition velocity (2.5.3)	Ground-level concentration Wind speed Roughness length Richardson number von Karman's constant	Ground-level concentration Vertical surface wind profile Vertical surface temperature profile	Not tested	Upper limit of v_g, error unknown	May be useful for forests
Gaseous resistance model (2.5.4)	Ground-level concentration Wind speed Surface friction velocity von Karman's constant Stomatal resistance Diabatic corrections	Ground-level concentration Vertical surface wind profile Vertical surface temperature profile	Empirical model	Same order as v_g	Satisfactory

Continued ...

Table 19. Concluded.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Gaseous leaf model (2.5.5)	Ground-level concentration Internal leaf gaseous concentration Leaf density Boundary layer resistance of leaf surface Stomatal and internal diffusion resistance Cuticular and internal resistance	Ground-level concentration Internal leaf gaseous concentration Leaf density	Not tested	Unknown	
Gaseous Air-Water Interface model (2.5.6)	Water-surface concentration Gas phase exchange rate Liquid phase exchange rate Molecular diffusivity of gas Henry's law constant Hydration rate constant Ratio of total to ionic forms of gas in solution	Water-surface concentration	Some general comparisons found satisfactory	Probably similar to v_g	Satisfactory

Table 20. Summary of wet particulate models.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Empirical[a] coefficient Λ_p (2.6.3)	Average concentration of particles in atmosphere Particle size Scavenging height Duration of rainfall	Vertical concentration profile of particles Particle size spectrum Height of plume Rainfall duration	Empirical model	For particles <0.1 μm, up to factor of 3; other sizes, up to 1½ orders of magnitude	Alternatively, measured Λ_p in field
Scavenging ratio (2.6.4)	Concentration of particles in atmosphere Particle size Type of particles Rainfall rate Duration of rainfall Density of air	Vertical concentration profile of particles Particle size spectrum Chemical analysis Rainfall intensity and duration	Empirical model	½-1 order of magnitude	Alternatively, measure W in field
Coefficient of washout ∇ (2.6.5)	Concentration of particles in atmosphere Rainfall amount Wind speed Empirical coefficient	Vertical concentration profile of particles Rainfall intensity and duration Wind speed	Empirical model	Based only on one test	Alternatively, measure ∇ in field

Continued ...

Table 20. Continued.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Theoretical scavenging coefficient (2.6.6)	Average concentration of particles in atmosphere Scavenging height Rate and duration of rain Collection efficiency Particle size Parameter	Vertical concentration profile of particles Particle size spectrum Height of plume Rainfall intensity and duration	Satisfactory using one field data set	Because based on collection efficiency, could be 1-2 orders of magnitude in error--see Figure 12	
Theoretical scavenging coefficient of snow (2.6.6)	Average concentration of particles in atmosphere Scavenging height Rate and duration of snow Collection efficiency of snow Particle size Terminal velocity of snow crystals	Vertical concentration profile of particles Particle size spectrum Depth of plume Snowfall intensity and duration Snowflake crystal type	Not tested	Snow scavenging collection efficiency process inadequately understood. Errors probably greater than for rainfall	

Continued ...

Table 20. Continued.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Theoretical scavenging ratio (2.6.7)	Concentration of unscavenged particles Rainfall duration and rate Absolute humidity of entraining air Fraction of pollutant that nucleates Efficiency of cloud precipitation process Reactivity factor (≃1)	Vertical concentration profile of particles Rainfall intensity and duration Upper air humidity data Pollutant nucleation	Not tested	Unknown	
Makhon'ko washout rainout model (2.6.8)	Pollutant concentration prior to rain Rainfall duration and rate Cloud thickness Wind speed Scavenging coefficients	Vertical concentration profile of pollutant Rainfall intensity and duration Cloud thickness Wind speed	Empirical model	Large errors unless parameters are defined in field	
Modified Makhon'ko model (2.6.8)	As above plus height of cloud base	As above plus height of cloud base		As above	

Continued ...

Table 20. Continued.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Empirical snow washout model (2.6.9)	Average concentration of particles in atmosphere Scavenging depth Snowfall duration and rate empirical constants Temperature Particle size	Vertical concentration profile of particles Depth of plume Snowfall duration and rate Type of snow Temperature Particle size spectrum	Field tested	Within factor of 3	Satisfactory
Numerical washout model (2.6.11)	Average concentration of particles in atmosphere Duration of rainfall Scavenging height Best's rainfall distribution Terminal velocity of raindrops Collision efficiency (Langmuir)	Vertical concentration profile of particles Rainfall duration Scavenging height	Not tested	Unknown	Limited to 2-20 μm particles
Modified numerical washout model (2.6.11)	Similar to above plus particle size	Similar to above plus particle size	Not tested	Unknown	Limited to particle >1 μm. Model developed for NaCl

Continued ...

Table 20. Continued.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Davis in-cloud scavenging model (2.6.12)	Atmospheric concentration of particles prior to rain Rainfall rate and duration Initial cloud water concentration Cloud thickness Cloud liquid water content Removal rate)Data are not Attachment)readily rate)available	Vertical concentration profile of particles Rainfall intensity and duration Initial cloud water concentration Cloud thickness Cloud liquid water content	Not tested	Unknown	
Stratiform in-cloud scavenging model (2.6.13)	Intensity and duration of rain Type of cloud Temperature Raindrop size (Marshall-Palmer) Particle size Terminal velocity of raindrops Terminal velocity of particles Collision efficiency (Mason) Various constants	Rainfall intensity and duration Type of cloud Temperature Particle size spectrum	Some testing	Unknown, but may be large because of use of collision efficiency	Feasible procedure

Continued ...

Table 20. Concluded.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Sulphate washout model (2.6.14)	Source strength of SO_2 Rainfall duration and rate Source strength of particles Particle size and density Terminal velocity of raindrops Terminal velocity of particles Gas phase mass-transfer coefficient Gas phase viscosity Empirical correction parameters	SO_2 stack emission Rainfall intensity and duration Particle stack emission Particle size spectrum	Not tested	Unknown, but may be large because of utilization of collision efficiencies	Complete model of transport, diffusion, and deposition

Table 21. Summary of wet gaseous models.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Empirical scavenging coefficient Λ_g (2.7.2)	Average concentration of gas in atmosphere Scavenging height Duration of rainfall	Vertical concentration profile of gas Depth of plume Rainfall duration	Empirical model	Too little field data to estimate Λ_g	Determine field value
Theoretical scavenging coefficient (2.7.3)	As above plus raindrop size molecular diffusivity concentration of raindrop in air Sherwood number	As above plus raindrop size spectrum	Satisfactorily compared with limited field and laboratory data	Assumes an irreversible process--hence upper bound value	Satisfactory as a first upper bound approximation
Makhon'ko rainout models (2.7.4)					See Table 20

Continued ...

Table 21. Continued.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
SO_2 - SO_4^{-2} scavenging model (2.7.6)	Initial atmospheric concentration of CO_2, NH_3, and SO_2 Height of cloud base Wind speed Rainfall intensity and duration Particle size Raindrop size Collection efficiency (Langmuir) Reaction rate constants	Atmospheric concentration estimates of CO_2, NH_3, and SO_2 Height of cloud base Wind speed Rainfall intensity and duration Particle size spectrum Raindrop size spectrum	Inadequate	Unknown	
EPAEC washout model (2.7.7)	SO_2 emission strength Dispersion coefficients Stack characteristics Wind speed Ambient temperature Rainfall rate and duration Raindrop size Gas phase mass-transfer coefficient Henry's law constant Gaseous diffusion coefficient in liquid	SO_2 stack emission Atmospheric stability Ambient temperature Wind speed Rainfall intensity and duration Raindrop size spectrum	Field tested for various conditions	Within factor of 2 for greater than 100 m from stack	Satisfactory; complete model of transport, diffusion and deposition

Continued ...

Table 21. Concluded.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Improved model of reversible SO_2 (2.7.7)	Vertical profile of SO_2 Rainfall intensity and duration Raindrop size spectrum (Best) Diffusion coefficients Equilibrium constants	Vertical concentration profile of SO_2 Rainfall intensity and duration	Not tested	Expect to be little more accurate than EPAEC model	Satisfactory
Brookhaven washout model (2.7.8)	Concentration of SO_2 in atmosphere Background concentration of raindrops Raindrop size distribution (Best) Rainfall intensity and duration Height of cloud Raindrop terminal velocities Gas phase mass transfer coefficient Henry's law constant Equilibrium and rate constants	Vertical concentration profile of SO_2 Acidity of background raindrops Rainfall intensity and duration Height of cloud	Not tested	Unknown	Dr. F.B. Hill suggests model too complex for field applications

Based on this summary and our detailed review, we recommend that the following deposition models be considered for incorporation into the Gaussian approach or the Eulerian formulation using the Livermore Air Quality model. It should be pointed out, however, that the more complex particulate and gaseous scavenging models may not be compatible with the proposed structure of the Livermore model. Therefore, the recommendations include alternative approaches to wet deposition using a scavenging parameter. Furthermore, for each of the four categories we have recommended which model should be used in preliminary analysis.

(a) <u>Dry Particulate Deposition</u>

1. Preliminary analysis.
   Empirical deposition velocity (Section 2.4.3).
2. Detailed analysis.
   Sehmel's Integral Resistance model (Section 2.4.6)

(b) <u>Dry Gaseous Deposition</u>

1. Preliminary analysis.
   Empirical deposition velocity (Section 2.5.2).
2. Detailed analysis.
   Gaseous Resistance model for land surfaces (Section 2.5.3).
   Gaseous Air-Water Interface model for water surfaces (Section 2.5.6).

(c) <u>Wet Particulate Deposition</u>

1. Preliminary analysis.
   Empirical scavenging coefficient or ratio (Sections 2.6.3, 2.6.4).
2. Detailed analysis.
   Empirical Snow Washout model (Section 2.6.9).
   Stratiform In-cloud Scavenging model (Section 2.6.13)
   Empirical scavenging coefficient or ratio approach (Sections 2.6.3, 2.6.4) if other recommended procedures are not compatible with adopted transport-diffusion models.

(d) Wet Gaseous Deposition

1. Preliminary analysis.
   Empirical scavenging coefficient (Section 2.7.2)
2. Detailed analysis.
   Improved model of reversible SO_2 (Section 2.7.7)
   Empirical scavenging coefficient approach (Section 2.7.2) if the other procedure is not compatible with the adopted transport-diffusion model.

In this latter category, it is recommended that the EPAEC Washout model (Section 2.7.7) be also considered mainly because the computer program is documented and available. It is a complete model of transport, diffusion, and deposition and, therefore, the results from it could be used in a comparative way with those from the adopted model to estimate wet gaseous deposition.

3. FIELD OPERATIONS

3.1 FIELD PROGRAM TO TEST MODELS

The purpose of this section is to develop a field program to test the choices of deposition models proposed in Section 2. In some cases, such as SO_2, enough information has been gathered that a reasonably sophisticated study can be proposed. In other situations, such as snow scavenging, both theory and field measurement development are lacking (Slinn 1977). In this latter situation, a simple approach must be proposed. This is in keeping with recommendations of Section 2 which suggest a simple approach coupled with a more sophisticated "probably workable" approach. The form and specific parameters are directly and indirectly important to the field program and analysis. Gas, solid and liquid phases must obviously be considered separately but, in addition, the form and reactivity of the parameter must be considered directly or indirectly. For example, Gatz (1976) obtained similar results for washout ratios in event samples for metals in METROMEX compared to the "soluble" (filtered) values obtained by Cawse at Chilton, U.K. in bulk samples. The results for METROMEX event samples deviated a great deal, however, from the results for total metals in the U.K. study. Similarly, one must attempt to consider the significance of the deposition of a small mass of small sized particles with a large reactive surface compared to a gross mass flux estimate. These considerations are inherent if not stated explicitly in the following discussions.

3.1.1 Review of Models Selected and Parameters Required

The recommendations of Section 2 are summarized in Table 22 with reference to the following sections. They are rearranged so that the simplest approaches for wet and dry deposition are grouped together followed by more complicated considerations.

Table 22. Summary of parameters which must be measured for simple and sophisticated deposition model testing. The first four entries represent a simple approach[a], and the subsequent entries represent a sophisticated approach[b].

Type	Section 2 Model Ref.	Section 3 Measurement Ref.	Parameters
Dry-particulate	2.4.3	3.3.2, 3.3.4	Flux - F_p
			particulate conc - χ_p
			deposition velocity - V_p
Dry-gaseous	2.5.2	3.3.6	Flux - F_g
			gas concentration - χ_g
			deposition velocity - V_g
Wet-particulate	2.6.3	3.3.4	Flux - F_w
		3.3.5	particle spectrum - N(p)
			rainfall duration - t
			rainfall intensity - J
Wet-gaseous	2.7.2	3.3.3	vertical gas gradient - $\frac{\Delta\chi_g}{\Delta z}$
			plume depth
			rainfall duration - t

Continued ...

Table 22. Continued.

Type	Section 2 Model Ref.	Section 3 Measurement Ref.	Parameters
Dry-particulate	2.4.6	3.3.3	vertical wind gradient - $\frac{\Delta \bar{u}}{\Delta z}$
			vertical temp. gradient - $\frac{\Delta \theta}{\Delta z}$
		3.3.5	particle spectrum - N(p)
		3.3.11	ambient surface temp. - $N(\theta)$
Dry-gaseous	2.4.6	3.3.3	vertical wind gradient - $\frac{\Delta \bar{w}}{\Delta z}$
			vertical temp. profile - $\frac{\Delta \theta}{\Delta z}$
Dry-gaseous (air water interface)	2.5.6	3.3.11	concentration in water - χ_L
Wet-particulate (snow)	2.6.9	3.3.5	vert. part. spectrum grad. - $\frac{\Delta N(p)}{\Delta z}$
		3.3.7	plume depth - H
		3.3.8	snowfall duration - t_s
			snowfall rate - J_s
			type of snow - ST
		3.3.11	ambient temperature - $N(\theta)$
		3.3.5	particle size spectrum - N(p)
Wet-particulate	2.6.13	3.3.9	rainfall intensity - J
			rainfall time - t
		3.3.11	ambient temperature - $N(\theta)$
		3.3.5	particle size spectrum - N(p)

Continued ...

Table 22. Concluded.

Type	Section 2 Model Ref.	Section 3 Measurement Ref.	Parameters
Wet-particulate	2.6.14	3.3.9	rainfall intensity - J
		3.3.9	rainfall time - t
		3.3.5	particle size spectrum - N(p)
		3.3.11	stack emissions gas particulates, size - SP (stack parameters)
Wet-gaseous	2.7.7	3.3.11	atmospheric stability
		3.3.11	SO_2 emissions - SP
		3.3.11	ambient temperature - N(θ)
		3.3.3	wind speed gradient - $\frac{\Delta u}{\Delta z}$
		3.3.9	rainfall intensity - J
		3.3.9	rainfall duration - t
		3.3.9	raindrop spectrum - N(R)
Wet-gaseous	2.7.7	3.3.3	vertical gas conc. grad. - $\frac{\Delta \chi_g}{\Delta z}$
		3.3.9	rainfall intensity - J
		3.3.9	rainfall duration - t

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[a] Snow also requires addition to the category, type of snow, (3.3.8) under "Wet Deposition".

[b] Measurements of "simple model" must be added to this listing.

Reference to pertinent sections in theory (Section 3.3) and measurement are given along with the appropriate symbol used in Section 3.4.

Parameters required for the simple approach are: ground-level concentrations of particulates, gases and rainfall; particle size spectrum; precipitation record; and plume depth. For a more sophisticated study, these parameters, plus the following, must be known: vertical wind, vertical temperature, vertical gas, and particle concentration profiles; ambient temperature; rainfall intensity; raindrop size spectrum; type of cloud; snow duration; and rate and type of snow.

3.1.2 Chemical Parameters to be Measured

Table 23 is a compilation of the parameters to be considered for measurement in the field program. In constructing the table, gas, solid and liquid phase partitioning must be taken into account. Differentiation of occurrence in a phase will affect the scavenging coefficients (V_p, $V_w\Lambda$, W) greatly as is shown in Gatz (1976).

Discussion of techniques of analysis is found in Sections 3.3.6 and 4.2. The following discussion relates to the forms in the scavenging process.

The important components of the gas phase are SO_2, NO_x, NH_3, H_2O, H-NH_4 SO_4 species and organics. SO_2 oxidizes to SO_4^{-2} aerosols; NO_x is reduced to NH_3, and H^+ is associated with SO_2 and NO_x reactions. NO_x occurs as N_2, N_2O, NO, NO_2, HNO_2, HNO_3, and organic nitrogen (Soderlund and Svensson 1976). SO_2 occurs in the gas phase as predominantly SO_2, with small amounts of H_2S, SO_3, dimethyl sulphide, and organic sulphur gases (Granat et al. 1976). Typical nonurban background concentrations of SO_2 are about 0.2 μg S/m^3 (0.06 ppb [V]); whereas background remote area concentrations of NO_x are about 0.1 μg NO_2/m^3 (0.2 ppb [V]); NO_3^- and SO_4^{-2} are much more concentrated in liquid and solid phases. H-NH_4-SO_4 species occur as submicrometre aerosols as H_2SO_4, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, and $(NH_4)_2SO_4$, depending upon H^+, SO_4^{-2}, NH_3, and H_2O concentrations.

Table 23. Chemical parameters to be considered in field measurements.

Parameter	Phases
Gases:	
SO_2	g, L, P[a]
NO_x	g, L, P
NH_3	g, L, P
H_2O	g, L
Organics	g, L, P (see Table 3.3)
Condensed:	
Ca^{+2}	L, P
Mg^{+2}	L, P
K^+	L, P
Na^+	L, P
H^+	L, P
Cl^-	L, P
HPO_4^-	L, P
HCO_3^- (alkalinity)	L, P
Acidity	L, P
Specific conductance	L
Trace metals (Pb, V, Zn, Fe), etc.	L, P

[a] g = gas, L = liquid, P = solid.

Organics have been measured in the atmosphere as gases, in precipitation, adsorbed on particulates, and generally at ng/L (liquid) levels. GC/MS techniques have been used to analyze samples of air, snow, and rain. Most precipitation is concentrated up to an order of magnitude compared to surficial waters. Organic compounds are common near urban areas (Grob and Grob 1971; Raymond and Guiochon 1974; Bertsch et al. 1974), and they should be a significant component of emissions in this study area. Table 24 summarizes the results for 22 samples from remote areas in Norway (Lunde et al. 1976). The values cited should be taken as very rough indicators of organics present in a non-urban background which receives input from distant sources. PCB's were determined in all samples; a typical sample will have 30 - 100 GC peaks, and perhaps 20 - 60 components. Neutral fractions consist mainly of alkanes, polycyclic aromatic hydrocarbons, phthalic acid esters, and fatty acid ethylesters, stated more or less in decreasing occurrence and concentration. Acidic components consist mainly of fatty acids and dicarboxylic acids. PCB's are found in all samples and occur about equally with filtered and particulate components.

Common ions and trace metals occur in the liquid and particulate phase in precipitation. This is also true for sulphate and nitrogen compounds. Generally, there is a greater concentration in the particulate than the soluble phase. Differentiation between solid and liquid is usually defined by 0.4 µm filtration, although this size has been shown to be somewhat arbitrary when comparison studies using ultrafilters (*circa* 0.001 µm) or finer filters (0.02 µm) are used. Normally, all major ionic components are measured, so that an electroneutrality balance can be carried out. Furthermore, the measurement of specific conductance can be compared with a calculated specific conductance if all major ions are measured. This is discussed in detail in Section 4.2.

Table 24. Some groups of organic compounds found in remote areas of Norway.[a,b]

		Phase Concentration		
Acidity	Compound	Water	Particulate	Occurrence
Neutral	$C_{15}H_{32}$ - $C_{20}H_{42}$		present	rare
Neutral	$C_{21}H_{44}$ - $C_{31}H_{64}$	present	present	common
Neutral	Fluoranthene	present	present	common
Neutral	Benzopyrene	low	present	common
Neutral	Dibutylphtalate	low	low	common
Neutral	Dioctylphtalate	variable	variable	common
Neutral	$C_{15}H_{31}COO\ C_2H_5$	50-200 ng/L		common
Acid	n - $C_9H_{19}COOH$	medium	low	common
Acid	n - $C_{13}H_{27}COOH$	variable	variable	common
Acid	n - $C_{15}H_{31}COOH$	variable	variable	common
Acid	$C_{17}H_{33}COOH$	abundant	variable	common
Acid	n - $C_{17}H_{35}COOH$	variable	variable	common
Acid	n - $C_{27}H_{55}COOH$	absent	abundant	rare
Acid	Dehydroabietic acid	low	variable	common
Acid	Benzoic	absent	variable	rare-common
	Polychlorinated biphenyls	N.D.-6.7 $\bar{X}$ = 2.3	N.D.-4.1 ng/L $\bar{X}$ = 2	always present

---

[a] These may be considered as approximately background.

[b] Trace substances are not included.

Acidity and alkalinity can be used to derive some of the N-H-S soluble species in precipitation and condensate reactions. This technique is discussed further in Section 4.2.

There are a large number of trace metals found in precipitation and rainfall samples. The selection of specific trace metals for consideration often depends upon the method of analysis. The trace metals listed in Table 23 are commonly found in the atmospheric samples and represent a common occurrence from smallest diameter to largest size. Often aluminum or silicon are analyzed to use as a reference for contributions from re-entrainment of soils. An enrichment factor, EF, is defined as:

$$EF = \frac{(X/R)_{air}}{(X/R)_{soil}}$$

where $(X/R)_{air}$ is the ratio of the concentration of the trace metal, X to reference metal R, (Al or Si), in air, compared with the ratio $(X/R)_{soil}$ for the soil.

Often average crustal rock abundances or average soil abundances are used to obtain $(X/R)_{soil}$, but in this study it would be more correct to obtain soil values in the vicinity of the field measurement.

3.1.3 Time and Spatial Scales

The overall size of the Langrangian model is approximately 150 km x 150 km with a 10-km x 10-km grid. Time resolution is approximately 1 h. These scales may be compared with:

1. Scavenging rates of SO_2 for Alberta (Summers 1977) of $\Lambda = 10^{-7}\ s^{-1}$ for snow to $8 \times 10^{-4}\ s^{-1}$ for heavy thunderstorms ($\Lambda = -\ln \chi/t$);
2. Precipitation intensity ranges of about 0.1 mm/h for light snow to 25 mm/h for heavy thunderstorms;
3. SO_2 oxidation rates (Lusius et al. 1977) of $\leq 0.005\ h^{-1}$ to $0.03\ h^{-1}$; and
4. Dry deposition velocities from ≤ 0.01 cm/s to 1.5 cm/s.

3.2 METEOROLOGICAL AND TOPOGRAPHICAL MESOSCALE INFLUENCES

The Alberta Oil Sands Environmental Research Program, Air System Research Report, Mann (1978), gives an excellent summary of wind, precipitation, fog, and sunshine conditions in the study area, parameters of principal significance for the transport, transformation, diffusion, and deposition of air pollutants. This information is repeated in the following with changes made only to section, figure, and table numbering to match the format of this report.

3.2.1 Wind

The general upper level circulation at this latitude is from WNW to SSE as illustrated by the 850-mb air trajectory study by Denison (1976). Due to disturbances caused by topography, frontal systems, and major pressure systems, the pattern of surface winds is far more complex. For instance, a low pressure system moving from west to east will cause south then southwest winds which will finally veer to northwest as the system moves into Saskatchewan. A high pressure area centered over the Prairies in winter will give persistent southeast winds in the area (Figure 18).

Local topography exerts a strong influence on winds. Prominent hills or mountains will deflect the air flow, and valleys will have a channelling effect. For this reason, the wind record at the Fort McMurray airport, although it has a long history, may not represent other areas. In Figure 18, the topographic effects of both Muskeg Mountain to the north-northwest and Stony Mountain to the south can be seen. In Figure 19, the frequency distribution for Embarras shows the effect of the Birch Mountains to the west. Lac La Biche winds in Figure 20 show no significant topographic effects.

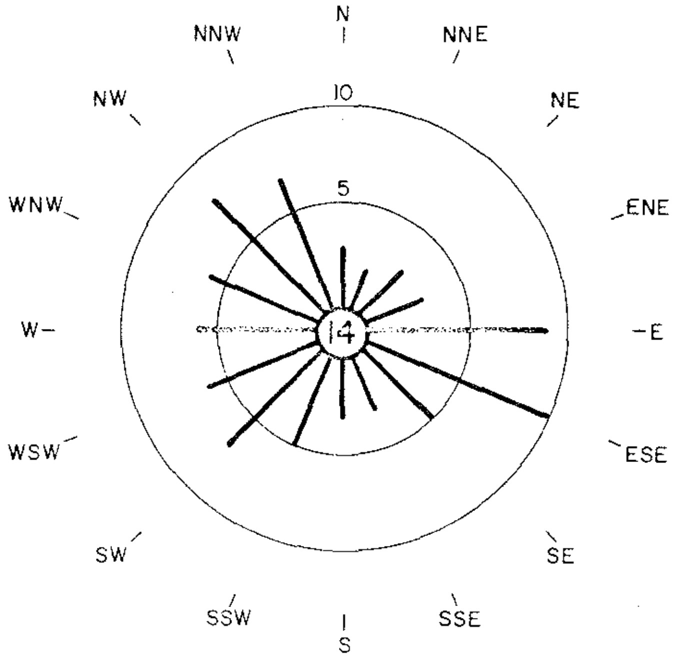
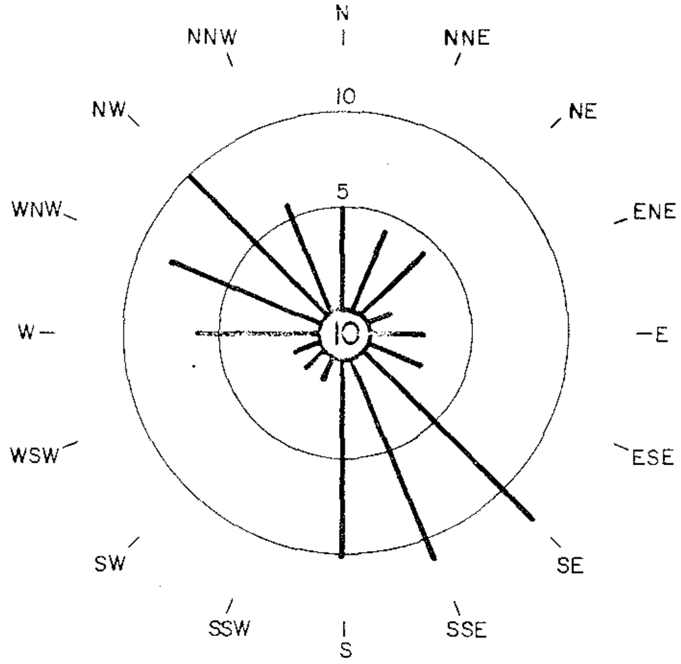


Figure 18. Annual percentage frequency of wind, Fort McMurray, 1955 - 1966.



NOTE: NUMBER IN CENTRE IS FREQUENCY OF CALM CONDITIONS

Figure 19. Annual percentage frequency of wind, Embarras, 1955 - 1962.

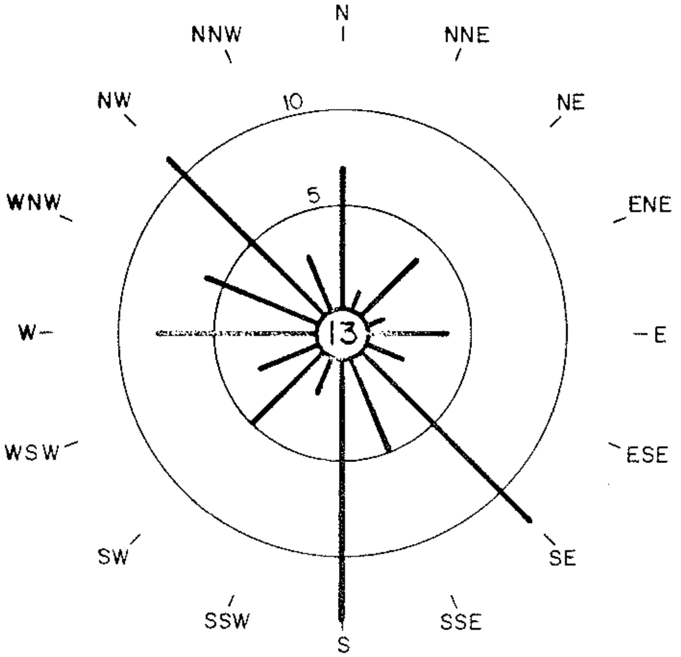
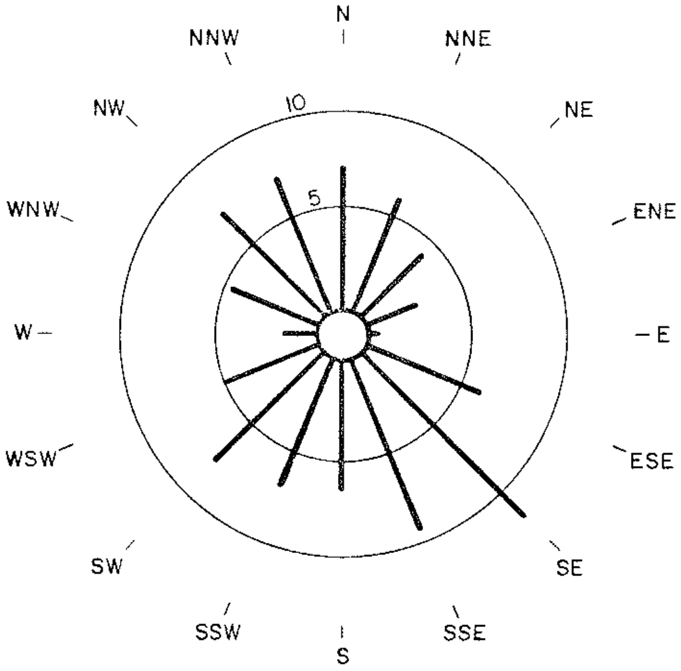


Figure 20. Annual percentage frequency of wind, Lac La Biche (A), 1944 - 1962.



NOTE: NUMBER IN CENTRE IS FREQUENCY OF CALM CONDITIONS

Figure 21. Synthesized annual percentage frequency of wind, Mildred Lake, 1963 - 1975.

Figure 21 represents a synthesis of short-term records at Mildred Lake with the long history at Fort McMurray. The effect of the Athabasca Valley is evident as is the slight channelling caused by the depression between the Fort Hills and Muskeg Mountain.

3.2.2 Precipitation

Figure 22 shows the relative monthly precipitation and number of days with precipitation at Fort McMurray and Edmonton. It can be seen from this that, while the patterns are similar, Edmonton has slightly more rain and days with rain in the summer than does Fort McMurray. In the fall and early winter, the situation is reversed.

Maximum precipitation events shown in Figure 23 tend to occur later in the season at Fort McMurray, and mid-summer peaks are less marked.

One of the largest precipitation events in the area occurred in August 1976 when Fort McMurray recorded 95.7 mm in 24 hours and Stony Mountain, 119.8 mm.

According to established records, a storm of this magnitude could be expected to occur once in 50 to 75 years. Although this was a significant event, its effects were localized and the meteorological stations at Birch Mountain and Firebag recorded only nominal amounts.

Snowfall in the area follows about the same pattern as Edmonton, although the first permanent snow arrives about 10 days earlier, and the last snow leaves about 15 days later. Higher areas receive more snow which remains longer.

The probability of precipitation as computed from long-term records yields information of considerable interest. The low probabilities in April-May and in October relate to the precipitation days and total precipitation in Figure 24.

3.2.3 Fog

In general, extensive fog in the area is rare. Valley fog, however, occurs frequently in the fall due to night-time

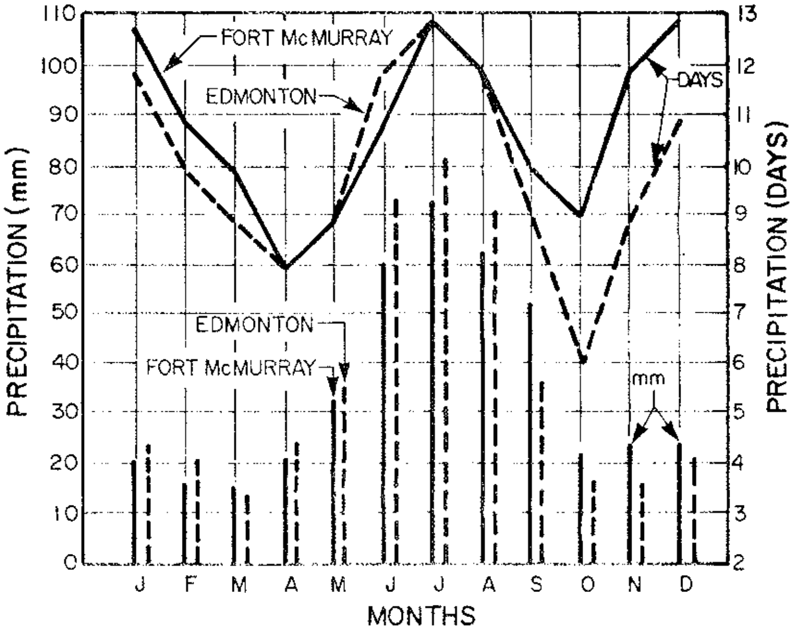


Figure 22. Monthly mean precipitation and days with precipitation at Fort McMurray and Edmonton.

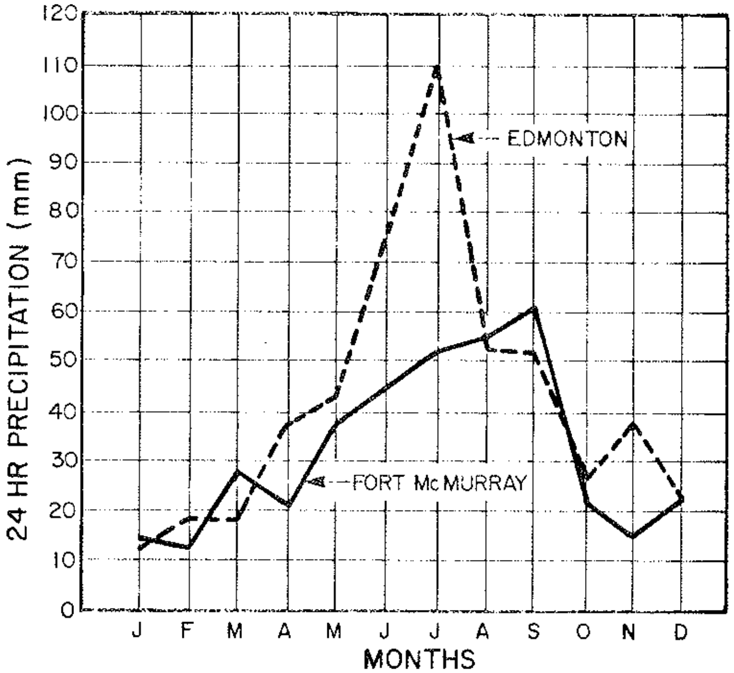
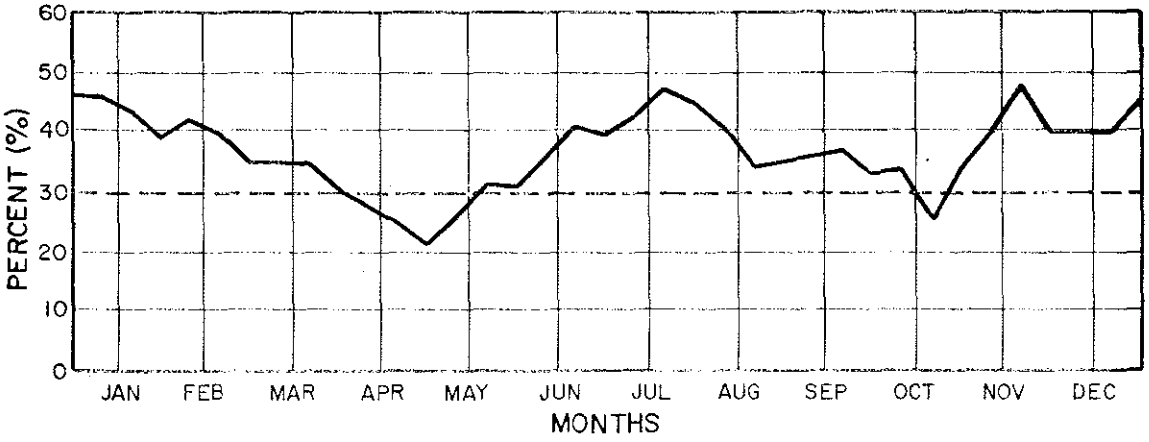
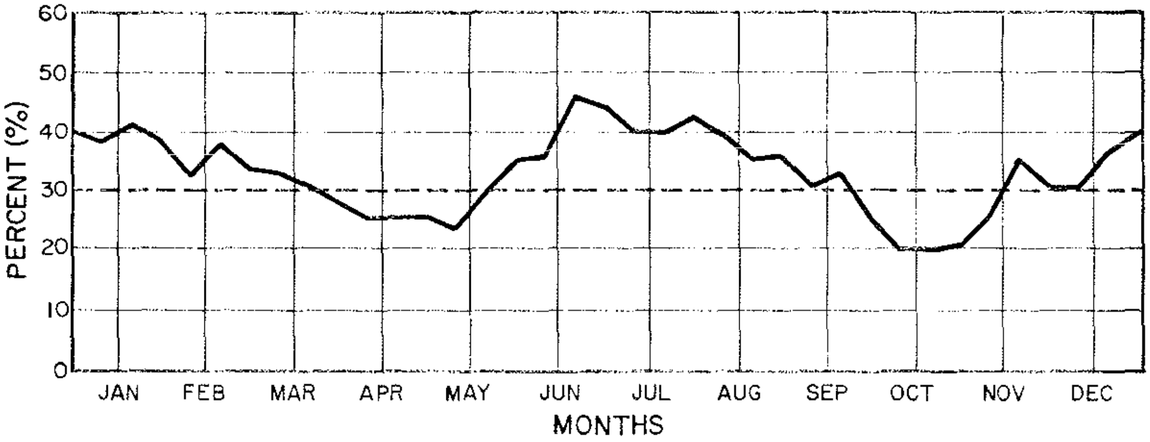


Figure 23. Monthly maximum precipitation events.



FORT McMURRAY



EDMONTON

Figure 24. Probability of precipitation.

cooling of the air over the relatively warmer water of the Athabasca River. It rarely moves out of the valley but may interfere with highway traffic near river level. Fog normally dissipates by 0900 to 1000 h as a result of the sun's heat and circulation.

Ice fog may occur during periods of very low temperature below -35°C. Under normal circumstances, there will be less than 10 occurrences a year (Croft et al. 1977). It is more likely to form in the vicinity of sources of water vapour such as open water storage area, human habitation, and cooling towers.

3.2.4 Sunshine

The AOSERP study area receives about the same number of sunshine hours as Edmonton: a total of 2,114 h per year at Fort McMurray versus 2,247 for Edmonton. One of the sunniest locations in Alberta, Lethbridge, receives 2,387 h a year on the average. Figure 25 shows the monthly average sunshine hours at Fort McMurray and Edmonton.

3.2.5 Meteorological and Topographical Mesoscale Considerations

Field experiments and sampling must consider variations in synoptic weather and ground features. Mann (1978) have summarized general surface level wind patterns and precipitation, and this information has been reviewed in Sections 3.2.1 and 3.2.2. The upper level winds are generally from WNW and they are modified into surface winds from west and south due to topographic funnelling. Lower level winds seem to be important in dispersion of the GCOS emissions in that measured snow flux contours are elongate in the north-south direction only (Mann 1978).

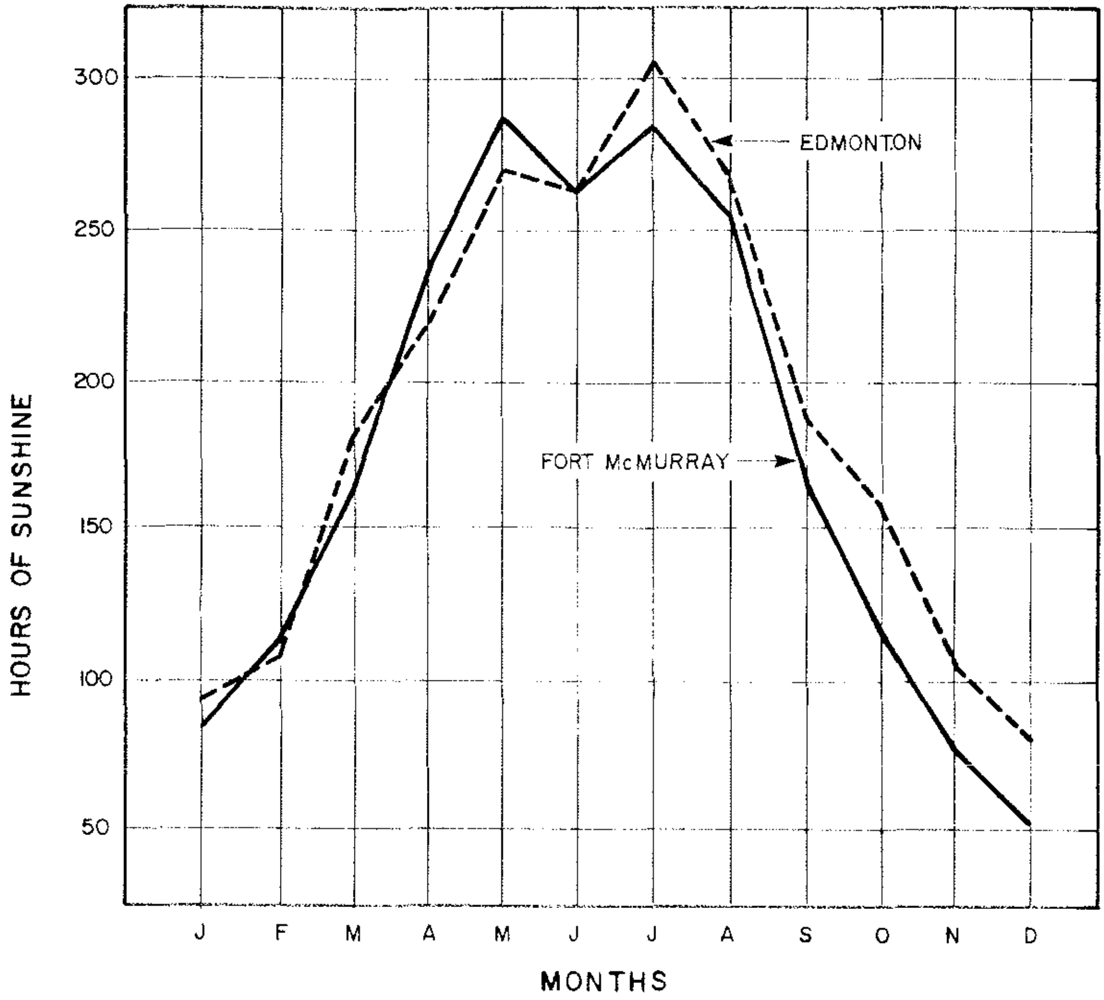


Figure 25. Hours of bright sunshine--Fort McMurray and Edmonton.

Analysis of upper level winds for dry and wet periods by season of the year can be obtained from the work of Denison (1976). Table 25 summarizes this information. There are two major upper level wind components: WNW and S. In the winter during precipitation, a source region from SW to NW prevails. During dry periods, wind is predominantly from the west with a small southerly source component, suggesting field programs might be located in the east or north study areas. In the winter months, a plume trapping situation should prevail a reasonable amount of time. The mixing depth is established by solar heating and, during the winter season, sampling should be considered only for 3 to 4 hours during the afternoon for dry deposition. Surface winds may be more important and result in dry depositions in snow sampling more in northern and southern areas.

There is a greater variability in source wind directions during wet periods. Both S and WNW components prevail during winter, spring, and fall, and a continuous SW to NW source prevails in the fall. The W to NW components may be modified into N and W components of surface winds, and the S and SW components may be modified into S and W components of surface winds. Hence, sampling in the north, south, and east of the study area might be advisable.

Snow flux measurements (Mann 1978) do not indicate the W component for sampling in the eastern portion of the study area.

3.3 PARAMETERS TO BE MEASURED

3.3.1 Introduction

The purpose of this section is twofold:

1. To review field methods for the wet/dry deposition of various constituents to compare with model estimates, and

Table 25. Wind source direction for dry and wet seasons of the year. Source headings are given.

Season	Dry Periods	Approximate Mixing Heights	Wet Periods	Rainfall Intensity	Approximate Mixing Heights
<u>Upper Level Winds</u>					
Dec., Jan., Feb.	290°	see text	290, 170	-	limited, 500 m
Mar., Apr., May	170, 250	500, 750 m	300, 190	light-moderate (300) moderate (190)	1,000 m 2,000 m
Jun., Jul., Aug.	270	1,200	280	light-occasionally heavy	3,000 m
Sept., Oct., Nov.	290, 190	1,200, 750	245, 325°	light (NW) moderate (SW)	1,500 m 3,000 m
<u>Surface Winds</u>					
Dec., Jan., Feb.	190, 325		290, 350		
Mar., Apr., May	210, 170		160, 350		
Jun., Jul., Aug.	260		320, 130		
Sept., Oct., Nov.	270		190, 290		

2. To review field measurements required for input into algorithms of Section 2 to compare with the above.

Taking into consideration that there are many levels of sophistication of analysis, the two purposes become intertwined. Hence, each experiment may be conceived of as testing more than one deposition model with emphasis on different parameters. For example, an experiment might compare dry deposition velocities for a simple constant V_p model and, at the same time, accumulate information on particle size distributions as input to a more sophisticated model. It is felt that the best test or confirmation of a deposition model is obtained when the model is in "good agreement" under a wide range of conditions. "Good agreement" is defined by Dana et al. (1973) for SO_2 concentration measurements to be within a factor of 2 with model predictions.

There are many different methods of estimating deposition parameters. Direct methods determine the flux and are dependent upon the precision of emission, transport, and chemical reactivity data and algorithms, in addition to the deposition algorithm. Indirect measurements compare atmospheric measurements to fluxes and/or deposition velocities, and are mostly independent of the other portions of the model.

All techniques of field measurement can have large inaccuracies in design and can lead to erroneous conclusions. Therefore, the best approach to design of a field program is to build in as many levels of redundant checking as are reasonably possible, and to carry out all of the measurements simultaneously. Hence, a few in-depth studies with internal checks are better than many uncontrolled analyses.

In this section, basic concepts and equipment are discussed for a ground program. These ideas are extended to an aircraft study in Section 3.4, and a review of previous ground, aircraft, and ground-plus-aircraft studies of a similar scale is given as background in Section 3.5 to a series of proposed field studies (Section 3.6).

The parameters discussed relate to deposition parameters: V_p, V_g, V_w as deposition velocities; Λ, scavenging coefficient, and W, scavenging ratio; meteorological measurements of wind, temperature, and gas and particle concentrations; particle size analysis of given parameters; gas analysis of SO_2 and NO_x; plume depth measurements, measurements during snow conditions; precipitation intensity and raindrop size analysis; measurements pertinent to lake and forest cover and instrument siting; and other effects.

3.3.2 Gradient Analysis, Deposition Velocity, Scavenging Coefficient, and Scavenging Ratio

Deposition velocity of a gas V_g, a particle V_p during non-precipitation periods is given by

$$F = V\chi$$

where F is the flux in mass-area^{-1}-time^{-1}.

V is the appropriate deposition velocity in length/time

χ is the atmospheric concentration adjacent to the ground in mass-volume^{-1}.

It is possible to measure both F and χ and obtain V directly. It is also possible to estimate F by the concentration gradient and obtain V. V varies mainly with the particle size, whether solid or gas; and, due to the large impact term, with the nature of the interface (water, forest, grass, etc.) and the near-surface wind velocity. Indirectly, mesoscale meteorology can affect the particle size distribution, thermal stability and wind velocity and affect the average deposition velocity, $\bar{V}$.

Λ, the scavenging coefficient, is used for wet deposition and is defined by

$$d\chi = -\Lambda\chi dt$$

W, the scavenging ratio, is the ratio of precipitation concentrations to air concentrations, and is (Gatz 1976)

$$W = \frac{\chi_w \rho}{\chi_a}$$

where χ_w is the concentration in precipitation (μg/g),

χ_a is the concentration of unwashed air (μg/m^3),

ρ is the density of air defined at 20 degrees, 760 mm Hg as 1 200 g/m^3, and

W is dimensionless using the above units.

Flux rate during precipitation is obtained by multiplying χ_w by precipitation intensity. Λ and W depend upon rainfall intensity, J, and raindrop size spectra, N(R) (for example, Slinn 1977); Krey and Tonkel 1977; Gatz Section 2, 1977). Rainfall concentrations and air concentrations can be measured to obtain W, and similarly a gradient and/or time technique can be used to obtain values of Λ. Variations in atmospheric concentration, meteorological factors affecting particle distributions, and rainfall intensity can change during the experiment, affecting Λ and W in a manner analogous to V.

Wet deposition poses an additional problem in that dry deposition can be significant during a period of wet deposition. Hence field measurements would include both wet and dry deposition during precipitation.

Dana and Hales (1977) explain that the definition of the scavenging coefficient, Λ, can vary depending upon the definition of amount for a polydisperse aerosol. Imagine a bimodal particle distribution with different efficiencies for each size and for varying raindrop sizes. Hence, Λ is a function of the raindrop size spectrum, particle size spectrum and the collection efficiency. Since the mass is defined almost entirely by the larger sizes, this portion and associated Λ would define the conventionally used "mass-Λ", but number, length, and area would be defined by different parts of the particle spectrum and associated scavenging, and would give different values for Λ.

The variability of Λ can be extended to chemical considerations also, to add an additional variable. For example, imagine that the fraction of "soluble" trace metal is a function of pH, then Λ would vary for variable pH's in addition to variation with fixed particle spectrum, raindrop spectrum, and associated collection efficiencies.

These considerations have great ecological impact as the final assessment is to determine the quantitative ecological effect of atmospheric fluxes. If the reactions in the environment represent a "limiting chemical reactant", then mass is important; however, if the environmental reactions are limited by "surface adsorbtion", then Λ's for area are important.

It is obvious that the mass definition of Λ is used since mass is more easily measured. But it is not clear whether mass fluxes are the most significant for environmental considerations.

W and Λ can be related in the following way: using Λ, the wet flux, F_w is

$$F_w = \bar{\chi}\Lambda H \tag{3.1}$$

where $\bar{\chi}$ is the average concentration of rain during the precipitation period,

Λ is the scavenging coefficient, and

H is the height scavenged.

Similarly, using W

$$F_w = \chi_w J = W\chi_A \; J/\rho \tag{3.2}$$

where J is the precipitation rate, χ_w is the concentration of parameter in precipitation,

χ_A is the concentration of the air before scavenging, and

ρ is the density of air.

Hence, rearranging (3.1) and (3.2) for wet deposition

$$\frac{\Lambda}{W} = \frac{\chi_A J}{\bar{\chi} H \rho} \tag{3.3}$$

This function is operationally defined and varies from a theoretical approach (Section 2, and especially Slinn 1977). It assumes a uniform and constant scavenging and must include in-cloud and under-cloud scavenging to obtain Equation (3.1). The latter would be incorporated in the definition of Λ. However, Equation (3.3) represents a function that can be measured in the field. Gatz (1976) has used this approach successfully on event rainfall samples, and this approach has been used for monthly bulk samples. W appears to increase from about 100 for 0.5 μm particles. For bulk samples measured on a monthly basis, W increases from about 100 for 0.5 μm to approximately constant 1,000 for 1 μm and greater particles. The filtered component of trace metals of monthly samples gives results for W quite similar to W for event samples. Relationships of W and Λ to average particle size D (μm) and rainfall intensity J (min/h) are

$$\mathrm{Log}_{10} W = 2.31 - 0.5 \log_{10} D \tag{3.4}$$

$$\mathrm{Log}_{10} \Lambda = -4.96 + 2.05 \log_{10} D \tag{3.5}$$

$$\mathrm{Log}_{10} \Lambda = -3.8 + 0.8 \log_{10} J \tag{3.6}$$

The interdependence of J and D on Λ or W has not been determined in field measurements.

The procedure for measuring scavenging coefficients, Λ, and scavenging ratios, W, is as follows:

1. Obtain the atmospheric concentration of the air parcel at reference height, z, that is to be scavenged by rain. At the time the air concentration is measured, particle sizing (Sections 2.6 and 3.3.5) may be carried out.
2. During precipitation, collect sample(s) for analysis. If only W is desired, one sample is collected. Note rainfall intensity, as W is a function of J. To calculate Λ, collect sequential volumes in a logarithmic time interval. From the basic definition of Λ, $\chi t = \chi_0 e^{-\Lambda t}$, where t is time after commencement of rainfall for initial precipitation concentration, χ_0, and χt after time, t, plot a curve of Log χ against time and determine the slope, Λ. Sampling may be carried out manually during the rainstorm or else various sensing devices and automatic samplers can be devised. In addition for certain chemical parameters, either continuous analysis using specific ion electrodes (H^+, NH_3, possibly NO_3^-) or an autoanalyzer system (i.e., NH_3, NH_4^+, Cl^-, SO_4^{-2}, PO_4^{-2}) connected to the sampling unit can be employed. It is important here as with dry deposition measurements to separate filtered (soluble) from particulate matter during or immediately after sampling.

Kinds of sampling containers are important to the measurements. Common ions such as K^+, Na^+, Ca^{+2}, Mg^{+2}, Cl^-, and SO_4^{-2}, may be collected in clean polyethylene or similar containers; but soluble phosphates may be partially adsorbed along with soluble trace metals. Preservation in about pH 1 acid inhibits adsorbtion, but modifies the soluble/particulate ratio. NO_3 and NH_3, if stored for any length of time, can be altered by biological action.

Three separate sampling containers fractionated from a vertical sided container will satisfy most requirements. Fraction 1 can be collected in a clean polyethylene container and analyzed immediately for pH and later for Ca^{+2}, Mg^{+2}, Na^+, K^+, Cl^-, NH_3, unfiltered. A portion of fraction 1 can be filtered during collection, or immediately after sampling, filtered and acidified, and analyzed for filtered trace metals and other soluble parameters.

Fraction 2 is collected in pH 1, high purity HNO_3 and analyzed for total trace metals, and fraction 3 is collected in an acidified $Hg\ Cl_2$ preservative and analyzed for NH_4^+ and NO_3^-. Alternativelyfraction 3 can be eliminated if the fraction 1 is frozen, or better yet if NO_3^- and NH_4^+ are analyzed immediately after collection.

The cross-section of the collector is usually about 1,000 cm^2 to obtain a representative sample. The top of the collector is generally at 1-m elevation with about 0.5-m depth to reduce splash. Collector walls should be vertical, and baffling, to fractionate the sample, should be placed only in the bottom of the collector. Separate precipitation collectors are preferable to separation of fractions of one sample. Square cross-section collection containers are available and are readily adaptable to stanchion configurations and addition of other instrumentation.

The parallel treatment of the air sample required to determine W is to portion the sample in two parts, analyze one portion for total particulates, and dissolve the second portion in (hot) water for about 10 minutes and analyze the soluble fraction. In addition, for size fractionation directly by instrumentation, a third portion of the paper can be analyzed for particle size distribution by scanning electron microscope or by an optical enlargement device. See also, analysis as a function of raindrop size in Section 3.3.9.

In the above procedure, Λ and W can be measured and compared with one another along with particle distribution and precipitation intensity.

3.3.3 Gradient Analysis

The gradient method and/or resistance method (Section 2.4.6) is used to determine the flux, F; the deposition velocity is obtained by dividing the flux by the atmospheric concentration. As pointed out in Section 2.4, the deposition velocity, V_p, or V_g, is a function of height above the interface, z. z is often 1 m for grass and soil surfaces, and 10 m for forest canopies.

The details of development of the "three-box" model are given in Section 2.4. Garland (1977) gives details of field measurements and analysis for SO_2 over grass, soil, water, and forest. The flux is obtained from

$$F = K\frac{d\chi}{dz} \tag{3.7}$$

where K is the eddy diffusivity.

The diffusivities of heat, K_H, and of momentum K_M, are assumed to be similar to the diffusivity for the substance in question, K. Assuming a 1-m reference height $K_H > K_M$ by about 50 percent, for unstable conditions, but is similar for neutral and stable conditions (see Figure 7).

Wind speed, temperature, and concentration gradients are obtained for the reference height (1 m) from measurements at many heights. Typically, five detection devices arranged in approximate logarithmic spacing are used. Details for flat land and forest cover are given in Table 26. Garland (1977) used platinum resistance thermometers enclosed in polished metal radiation shields and

Table 26. Measurement requirements for obtaining deposition velocities using the gradient method of analysis of wind speed, temperature, and parameter concentration.[a]

	Instrument		
	Vertical Height and Interface		Scale of Constant Interface Required Upwind
Terrain	Minimum	Maximum	
Level - grass, soil, water	20 cm	4 m	100 + m
Forest - n m high	n + 2 m	(n+10 m)+	>(100)(n+10 m)
Example: 15-m forest stand	17 m	∿30 m	>3 000 m x 3 000 m

[a] Reference level for gradient is 1 m. Five gauges are assumed in each vertical array.

ventilated by a small fan. Temperature differences of 0.02°C can be obtained. Five anemometers pointed into the wind were mounted on a separate parallel stand. The sampling ports were mounted on a third stand; the SO_2 was drawn through a bubbler tube at 30 L/min and was adsorbed in 40 mL of H_2O_2. The SO_2 was determined by the automated Thorin method (see Section 3.3.6 for other methods of analysis). Maximum error in estimating the deposition velocity due to concentration variation during the sampling time (not constant flux) is given as

$$\Delta V\ (z) < \frac{\Delta\chi z}{\chi\Delta t} \tag{3.8}$$

where $\Delta\chi$ represents the sample concentration variation during sampling time Δt at reference height, z. For z = 1 m, $\Delta V \sim 0.03$ cm/s, but for z $\sim$20 m (forest), ΔV may be as high as 0.5 cm/s.

Details of the calculations are as follows:

the flux, F, is obtained from

$$F = \frac{k^2 \dfrac{du}{d[\ln (z - D)]} \; \dfrac{d\chi}{d[\ln (z - D)]}}{\phi_M \; \phi_H} \tag{3.9}$$

where u is the velocity,

k = 0.41 (von Kārmān constant),

z is height above the interface,

D is the displacement height, and

Φ_M and Φ_H are dimensionless gradients of momentum and heat.

u_*, the friction velocity, z_o, the roughness length, and d were obtained by fitting wind speed data for low temperature gradient conditions to

$$u = \frac{u_*}{k} \ln \left[\frac{z - D}{z_o}\right] \tag{3.10}$$

Empirical formulae are used to obtain Φ_M and Φ_H using the Richardson number

$$R_i = \frac{g\left(\frac{dT}{dz}\right)}{T\left(\frac{du}{dz}\right)^2} \tag{3.11}$$

where g is the acceleration of gravity,

$\left(\frac{dT}{dz}\right)$ is the thermal gradient, T is the absolute temperature, and

$\left(\frac{du}{dz}\right)$ is the wind speed gradient.

If $R_i \leq 0$,

$$\Phi_M = (1-16\ z/L)^{-\frac{1}{4}} \tag{3.12}$$

$$\Phi_H = (1-16\ z/L)^{-\frac{1}{2}} \tag{3.13}$$

If $R_i > \Phi$, $\Phi_H = \Phi_M = (1+5.2\ z/L)$ (3.14)

where L is the Obukhov length

$$L = \frac{u_*^3 \rho C_p T}{kgH}$$

where ρ is the density of air, C_p is the heat capacity of air at 1 atm, and H is the vertical flux of sensible heat. u_* is obtained from the value of Φ_M from (3.12) or (3.14) substituted into the definition of Φ_M

$$\Phi_M = \frac{k(z-D)}{u_*} \frac{du}{dz}$$

For initial solutions of (3.12), (3.13), or (3.14) (u_* is unknown), L is obtained from

$R_i \leq 0 \quad z/L \sim R_i$

and $R_i \geq 0 \quad z/L = R_i/(1 - 5.2\ R_i)$.

Although the above discussion is for SO_2, there is an analogous approach for other gases and particulates, found in Section 2.4.6 using Figure 7, Equations (2.23), (2.24), (2.21) and (2.22) after z_o and u_* are characterized for the terrain. As pointed out, however, the validity of Equation (2.22) for the scale of a forest height has not been confirmed in the field.

The following summarizes the field requirements for the measurement of deposition velocity for gases and particulates:

1. Vertical measurement of wind velocity, temperature, and concentration are required. Table 26 summarizes the horizontal and vertical scales for flat terrain and forests.
2. The terrain must be initially characterized so as to obtain u_*, z_o and d, Equation (3.10).
3. Instruments for measuring concentrations and particle sizes must not consume so much volume as to modify the natural gradients or to interfere with one another. Therefore, sampling position is important relative to each sampler and sample volume must be kept as small as possible.
4. It is desirable to have a common data acquisition system in order to synchronize all of the measurements.

3.3.4 Precipitation, Dry Deposition, and Bulk Flux Measurements

Bulk and precipitation samplers can be and often are used to determine wet and dry fluxes. These measurements in combination with other measurements such as precipitation amount and atmospheric gas and particulate concentration are used to determine scavenging coefficients, scavenging ratios, and dry deposition velocity. There have been no redundant tests to show whether direct loading estimates are better than calculated estimates such as the gradient method. Certainly siting of samplers is extremely important, as well as sample preservation; Granat (1977) suggests that these two factors with occasional sample contamination (2 percent) are much more important than analytical errors for monthly bulk collectors.

Samplers are generally 1 m in height off the interface, have a constriction to reduce or eliminate evaporation during rain periods, and have a minimum cross-section so as to have minimum effect on wind pattern and scavenging efficiency. Some samplers are heated for below $0^{\circ}C$ weather, but the effect of bulk container against wind and vertical thermal gradient due to heating probably has a large effect upon deposition. A typical bulk rain sampler consists of a 300 - 1,000 cm^2 funnel which fits directly into a 5-L sample bottle, or alternatively a square or round vertical funnel with a short length of tubing into a sample bottle. Funnels are generally equipped with spokes or "bird-offs" to eliminate obvious contamination.

Single event samplers consist of wet/dry collectors that are actuated by a resistance type sensor or a capacitor type sensor. The sensor activates a lid which opens for collection of rain sample and is covered during dry periods. Both line voltage and storage battery models are available. It has been found that multiple sensors, electrically active in parallel, mounted on horizontal arms up to 1 m from the collector in different directions are more likely to detect the initial rainfall and open the collector. In addition, the sensor should be adjustable for different raindrop sizes (Section 3.3.9). These collectors can be equipped with heaters on the sensor for snow sampling, but the response or efficiency for sampling is not well known (Section 3.3.8).

It is quite common to study individual events by manually removing lids from precleaned collectors. Alternatively, collection can be carried out using mechanically spring-operated lids activated for each event manually or by a sensor.

Krey and Toonkel (1977) estimated an average dry deposition velocity for monthly bulk samples for Sr^{90} by plotting flux/concentration versus precipitation. Extrapolation of precipitation to 0 gives the average dry deposition velocity. This technique also permits calculation of an average scavenging ratio. Estimates of deposition velocities and scavenging coefficients and ratios can be criticized in that there are variations in other key parameters such as particle size spectrum, raindrop size spectrum, and wind velocity which affect the parameters by 1 to 2 orders of magnitude. On the other hand, if one dry deposition velocity for a parameter and one wet scavenging value is deemed sufficient, measurements of bulk deposition, atmospheric concentration, and rainfall and using the method of Krey and Toonkel (1977) are the most straightforward and probably the most representative of the real situation. In this case, multiple samplers would be worth considering, and the error analysis approach of Granat (1977) could be followed to ascertain siting and sampling errors. These results could then be directly compared with model estimates, or be compared with other measures of deposition.

It is often more desirable to determine deposition parameters on a short-term basis where particle size spectrum, wind velocity regime, and rain intensity and raindrop spectrum are relatively constant and can be measured. For this situation, dry deposition velocity can be estimated using the gradient technique (Section 3.3.3), or literature values as a function of particle size, surface roughness, and wind velocity can be used (Section 2.4). Similarly, wet deposition scavenging can be ascertained on an event basis using closely spaced sequential sampling or air concentration measurement prior to the precipitation event and measurement of precipitation concentration (Section 3.3.2). Both techniques assume a constant medium flux during all measurements which may not often be valid.

3.3.5 Particle Size Analysis and Parameter Analysis in a Size Class

As pointed out in Sections 3.3.2 and 3.3.3, particle size is an important parameter in the determination of all wet and dry scavenging coefficients. Therefore, the particle size distribution should be measured for each chemical variable concurrently with the determination of fluxes and scavenging coefficients.

Particle size spectra are often bimodal with the maximum of the larger sizes >1 μm and the maxima of the smaller distributionfrom 0.01- 0.1 μm. There is often a minimum of particles of 1 μm, but mass median diameters for many distributions are about 1 μm. The smaller distribution often consists of authigenic and anthropogenic particles, whereas the coarser sizes often consist of soil-entrained material.

Particle sizing by itself is not too difficult for a wide range of sizes (0.002 to >100 μm), but it is much more difficult to quantify the distribution for a specific substance in a polydisperse aerosol. As a preliminary procedure, often only the larger sizes (primary, >1 μm) and the smaller sizes (secondary, <1 μm) are separated for chemical analysis.

The particle sizing problem involves both the difficulties of physical separation and retention, and the fact that the amount of material obtained in the smaller sizes is often too little for chemical analysis.

The term "particle size" in the following discussion may vary from one measuring technique to another. In general, density and shape are the key factors that define the aerodynamic size. One may expect large variations for sizes of spheres and fibres that are optically measured compared with measurement using an aerodynamic technique. A more detailed discussion on definitions and effects on instrumental design is found in Peterson (1972).

If a distribution is log normal and the geometric standard deviation (diameter 84 percent/diameter 50 percent) is known, the relationship between mass and count distribution is

$$\log d\ (NO) = \log d\ (W) - 6.9078 \log^2 \sigma$$

where d (NO) and d (W) are in μm, and are number and weight diameter respectively, and
σ = the geometric standard deviation
= diameter 84 percent/diameter 50 percent

Particle sizing is obtained by direct optical and electron optical measuring, spectrometric, and electrostatic-depositional and/or inertial-centrifugal techniques. Not all methods are designed to collect enough material for chemical analysis. The optical techniques have a resolution of about 1 μm; electron optical techniques, about 0.01 μm (0.5 for elemental analysis); electrical aerosol analyzers 0.01 - 0.5 μm (Liu et al, 1967); optical particle counters 0.5 - 15 μm (Zinky 1962); axial scattering laser spectrometer 0.1 - 30 μm; and impactors 0.08 - 20μ.

Liu et al. (1972) describes a composite system of optical, electrical, and condensation counters for particle size definition from 0.001 to 10 µm; samples were obtained for analysis using an impactor.

Cyclonic centripeters, centrifuges, and impactors might be more suitable to this study as they combine size analyses with sampling for chemical analysis. Although other sizing techniques can be modified to collect material, they are either in experimental stages or represent large investments. Balzer (1972) discusses the basic theory for these collectors and lists the more common instruments and commercial sources.

Cyclonic centripeters are useful in that various kinds of collection media can be used. However, their fine size resolution is often poor and is about 1.5 µm. A centripeter consists of various sized orifices and conical collectors. When an air stream passes through a central orifice, the flow lines approach radially, and emerge as a jet outward. The divergence of the flow lines carries the finer particles outward from the collector after being concentrated in the centre, but the coarser materials are collected. This instrument is straightforward, and would be convenient for separation of primary and secondary aerosols using the finest collector stage (∿ 1 µm) and a back-up filter.

Rotating centrifuge devices have also been used for sizing. Laminar flow is maintained and the particles are deposited in a spread-out pattern according to size. This kind of instrument (Sawyer and Walton 1950) could be used to plate out particles on a substrate, which could be analyzed by automated X-ray fluorescence or emission techniques (i.e., Johansson et al. 1975).

A spiral centrifuge has been designed and tested for size separation (Stöber et al. 1972). This instrument has a range of capture from 0.08 - 6 µm diameter, and the particles are spread out on a collector foil 180 cm long. Sampling rate is ≲3L/min. As above, the instrumental size separation could be used with continuous and automated analytical techniques for a quite complete separation and analysis. However, long sampling times may be required.

Cascade impactors represent another kind of collector for size analysis and analytical collection capabilities. Most conventional collectors do not permit collection of enough material for analysis but the Lundgren impactor (Lundgren 1967, 1971) allows fractionation of 4 stages on rotating drums. The Lundgren collector operates at about 5 cfm (0.14 m^3/min). This impactor allows the use of various kinds of collection media from standard filter paper to aluminum foil. The 50 percent cutoff points of the 4 stages of the impactor, for $\rho = 2$ g/cm^2 are at 10, 3, 1, and 0.3 μm when the flow rate is 4 cfm (0.11 m^3/min).

There are other impactors suitable for sizing and analysis of particulates. A 5-stage Anderson cascade impactor (Lee 1974) with size range 0.5 - 3 μm, a slit impactor marketed by BGI, Waltham, Massachusetts, with a 30-cfm (0.85 m^3/min) flow, and a 10-stage Celesco QCM system for 25 - 0.05 μm sizes at a 7.1-cfm (0.2 m^3/min) flow rate are but a few examples of other instruments available.

A recently developed active scattering aerosol spectrometer (ASAS) is marketed by Particle Measuring Systems of Boulder, Colorado. This laser beam unit is capable of measuring 60 particle size units from 0.1 - 10 μm. It is readily usable in field operations. This unit in conjunction with a multi-stage cascade impactor would be suitable for particle size analysis of most chemical constitutents.

3.3.6 Gas Analysis: SO_x and NO_x

Analysis of SO_x is fundamentally for SO_2 and aerosol of $H\text{-}SO_4\text{-}N$. General methods of analysis consist of removal of particulate SO_4's (and sulphides) on a S-free filter paper, and collection of SO_2 gas on an impregnated back-up filter (Tucker 1969; Lusis et al. 1977) or by impingement into a basic H_2O_2 solution and analysis for sulphate or directly into a detector. In addition, indirect *in situ* measurements using correlation spectrometers (Millan et al. 1976) and other long path absorption techniques (Haust 1971) have been used.

The basic measuring principles for SO_2 are conductivity, coulometry, colorimetry, and flame photometry. Conductimetric methods have had wide application, good sensitivity and response, but detect many non-SO_2 gases, such as NO_2, NH_3, Cl_2, and HCl. Due to this fact, they are no longer recommended. Coulometric techniques measure the current required to maintain a low concentration of halogen in equilibrium. SO_2 electrodes based on this principle are available for use with pH meters. They have good sensitivity and simple operation. The major disadvantage is interfering ions, especially H_2S, NO, O_3, NO_2, and Cl_2. Therefore, selective filters must be used. They are not recommended for general use.

Flame photometric analyses measure the emission energy of sulphur compounds introduced into an H_2 flame. This instrument design has high sensitivity, fast response, and excellent selectivity for sulphur compounds. Filters can remove H_2S and methyl mercaptans. The only drawback for field operation is the requirement of a compressed H_2 source.

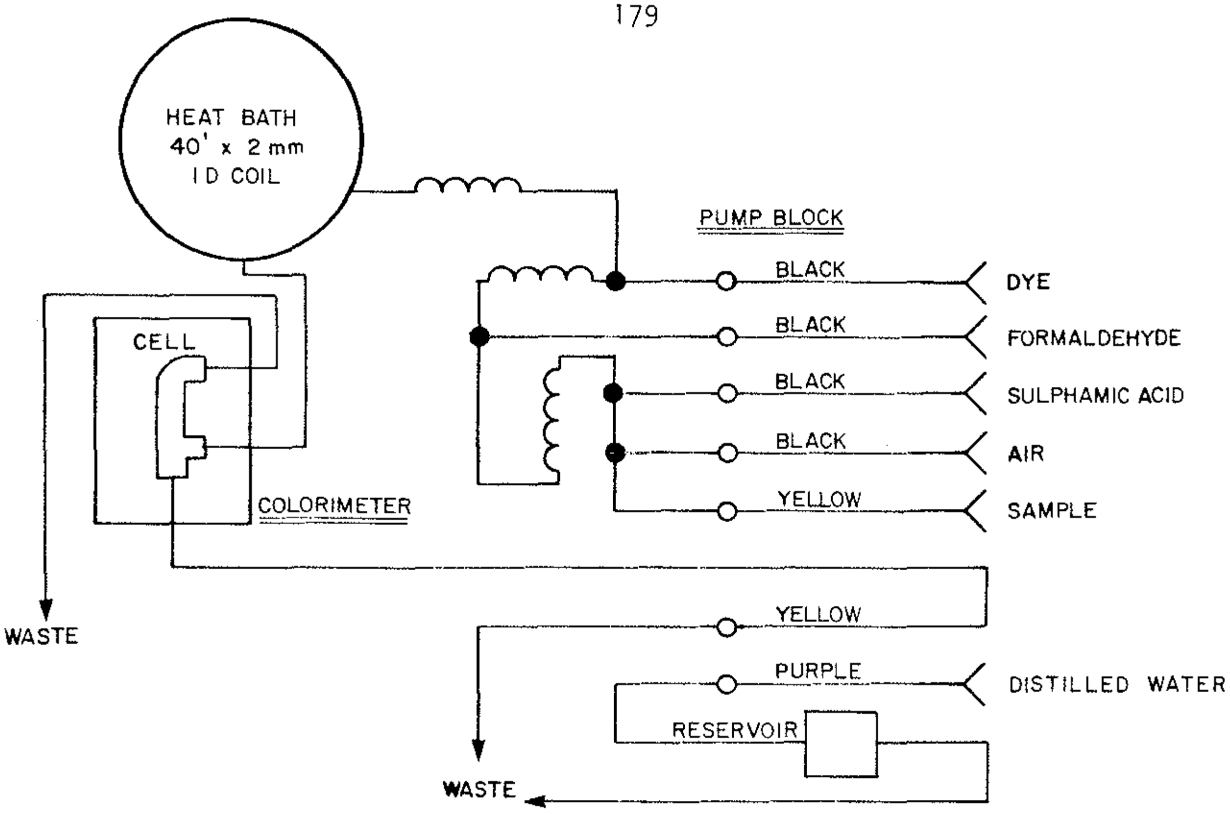
Similarly, there are more sophisticated gas chromatograph flame detector analyzers. These units are very specific to SO_2, etc., and have excellent sensitivity. The basic drawback is the sophistication of operation required.

The colorimetric method with various modifications after West and Gaeke (1956) probably is the most common technique now used. This method is based upon absorption of SO_2 (using a filter and impinger) in potassium or sodium tetrachloromercurate. A dichlorosulphitomercurate reaction with pararosanile and formaldehyde forms intensely coloured methyl sulphonic acid, which is measured spectrophotometrically. Figure 26 shows a schematic with notes for automation using an autoanalyzer pump.

Das and Kortsch (1977) give a good review of sampling and analysis of sulphur compounds. Nader (1972) can be consulted for descriptions of various instrumentation available.

Particulates containing N-H-SO_4's can be analyzed for sulphate by isotope dilution, colorimetric techniques (Ba-thorin, methyl thymol blue, or Ba-chloranilate), flame photometry, and X-ray fluorescence (XRF). A comparison study of colorimetric methods and XRF (Appel et al. 1977) suggests that the Ba-thorin method is the most consistent, but XRF methyl thymol blue, and Ba-thorin agreed within ± 10 percent. The chloranilate method is not recommended. Although the XRF technique may be slightly less sensitive than the colorimetric methods, the technique is non-destructive and may be used directly on filter papers, and many other elements can be measured simultaneously.

Some filter papers contain high metal and S blanks and are suspected of oxidizing SO_2 to SO_4. The study of Appel et al. (1977) compared Gelman AE glass fibre filters to fluoropore. The fluoropore consistently gave lower results, pointing to oxidation of SO_2 on a glass fibre filter. Byers and Davis (1970), using SO_2 in a laboratory experiment (no other particulates), showed uptake of SO_2 reached saturation on all filters, increased with humidity, and was the worst for glass fibre (compared with Nucleopore and cellulose ester membranes). Teflon and tenite filter holders took up little SO_2. Stainless steel, aluminum, copper holders, and tygon lines took up very large amounts of SO_2. Peirson (1977) concluded that teflon(fluoropore) membrane filters have the



DYE:

STOCK 0.2 g PARAROSANALINE IN 100 ml H_2O, LET STAND 48 h.
FILTER THROUGH No. 42 WHATMAN.
TAKE 20 ml OF STOCK, ADD 50 ml OF CONCENTRATED HCl, LET STAND 5 MINUTES AFTER MIXING AND DILUTE TO 1000 ml WITH D. H_2O.

FORMALDEHYDE:

DILUTE 5 ml OF 37% FORMALDEHYDE TO 1000 ml WITH DISTILLED WATER.

SULPHAMIC ACID:

MIX AND DILUTE 1.725 g IN 1000 ml D. H_2O. FORMALDEHYDE AND SULPHAMIC ACID MAY BE KEPT FOR 7 - 10 DAYS. STORE ALL DYE SOLUTIONS IN DARK, PREFERABLY COLD. WORKING SOLUTION IS GOOD FOR 3 DAYS IF KEPT IN THE DARK. STOCK SOLUTION IS GOOD FOR SEVERAL MONTHS STORED IN A REFRIGERATOR.

ABSORBING REAGENT:

2.34 g NaCl AND 5.44 g (S - FREE) $HgCl_2$ TO 1000 ml AND MIX WELL.

STANDARD ADDITIONS TECHNIQUE (ADDITION OF KNOWN $Na_2S_2O_5$) SHOULD BE CARRIED OUT IF VARIABLE AMOUNTS OF ABSORBING REAGENT ARE USED. FILTER AT $560 \mu m$. USE PLAIN, SOLVOFLEX, AND ACIDOFLEX TUBING.

Figure 26. Schematic of an auto-analyzer procedure for SO_2, using the West-Gaeke procedure.

smallest effect (0.04 μg SO_4^{-2}/cm^2 of filter), followed by cellulose ester membranes (0.8 ± 0.4 μg SO_4^{-2}/cm^2 of filter), followed by glass fibre filters (0.8 μg SO_4/cm^2). In addition, glass fibre filters show gross amounts of spurious sulphate. Teflon filters are therefore recommended, especially where low SO_2 or SO_4^{-2} concentrations are encountered.

The speciation of N-H-SO_4 aerosols is desirable. Tanner et al. (1977), expanding upon the method of Leahy et al. (1975), developed a solvent extraction scheme specific to sulphuric acid and bisulphate. The technique is to extract one filter portion with benzaldehyde to remove sulphuric acid, and a second portion is extracted with isopropanol to remove both bisulphate and sulphuric acid. Bisulphate is determined by difference. The solutions are re-extracted into an aqueous solution and are analyzed by flash volatilization-flame photometry (Husar et al. 1975).

Further characterization of the H-N-SO_4 aerosol can be accomplished by an acidity titration using the Gran technique (Seymour et al. 1977). A solution of about pH∿4, consisting of Na^+, K^+, NH_4^+, H^+, OH^-, SO_4^{-2}, HCO_3^-, CO_3^{-2}, and Cl^- is titrated at constant ionic strength of 0.1 KMCl with KOH, and the components of H_2SO_4, H_2CO_3, NH_4^+, and HCO_3^-, and the conditional stability constants are found. This analysis in combination with the above and other techniques such as X-ray diffraction and infrared analysis (Cunningham et al. 1974) should characterize the N-H-SO_4 aerosol quite well.

In summary, either flame photometry, co-spectral or second derivative spectroscopy (see Section 3.3.7), West-Gaeke colorimetry, or flame photometry are recommended SO_2 measurement techniques. Pre-filters for aerosols should be teflon. Solution and Gran analysis of acidity titration along with chemical analysis, and H_2SO_4-bisulphate via solvent extraction should be carried out on selected samples. These analyses would give a comprehensive definition to the sulphur species.

NO_x and NH_3 gases and aerosols may consist of NO, NO_2, NO_3, N_2O, NO_3^-, NH_4^+, NH_4^+-NO_3^--H^+-SO_4 aerosols, and organic aerosols. N_2, NH_3, NH_4, and organic N are considered to be derived from biological activity in soil and water and therefore show spring maxima. N_2O, NO, NO_2, NO_3^-, and NH_4^+ are due to natural and man-made emissions. Man-made emissions of nitrogen oxides are mostly a by-product of internal combustion engines and natural gas burning furnaces, whereas NH_3 emissions are associated with the burning of coal (Soderlund and Svensson 1976).

Monitoring of NO_x (NO and NO_2, basically) can be carried out by field sampling using a bubbler and subsequent laboratory analysis, ambient monitoring instruments, or *in situ* measurements with optical instruments.

Ambient measurements are based upon wet colorimetric, chemiluminescent, polarographic, and optical measurements (IR, UV, correlation spectrometry, second derivative spectrometry, Goldgraben 1974). The major limitation for many measuring devices is their lack of sensitivity. Because NO_2 rarely exceeds 200 $\mu g/m^3$ in air, a detection limit of ≤ 10 $\mu g/m^3$ is desirable (Stevens et al. 1974). The traditional colorimetric method is affected by O_3. The chemiluminescent method has good sensitivity (1 $\mu g/m^3$) and is specific to NO. For determination of NO_x, conversion to NO must be carried out. Conversion steps can have interference from NH_3 if carried out at 600°C, but lower temperature (240°C) conversion on gold mesh eliminates this problem. Practically, carbon conversion is used in ambient monitoring. When pumping is 0.1 L/min, the sensitivity of the chemiluminescent monitor is 2 $\mu g/m^3$.

The electrochemical technique is a membrane polarographic measurement of the reduction of NO_2 to NO. Unfortunately, sensitivity is high (30 $\mu g/m^3$) and other gases, especially H_2S, interfere.

Optical instruments consist of IR analyzers for NO (NO_2 would have to be reduced to NO for NO_x), UV analysis for NO_2, second derivative spectroscopy for NO and NO_2, and correlation spectrometry for NO and NO_2. Of the optical instruments, the IR technique is the simplest, the second derivative spectrometric the more sensitive and precise, and the correlation spectrometric method offer the greatest potential for information as it is an *in situ* instrument.

In summary, ambient monitoring is best achieved with a chemiluminescent instrument. If field sampling and later analysis is proposed, adsorption, often in NaOH, followed by colorimetric analysis for NO_2, or followed by oxidation of NO to NO_2, and colorimetric analysis of NO_x is recommended. Colorimetric analysis built into an ambient monitor is not recommended.

As with sulphates, a pre-filter (preferably teflon) should be used. Nitrate-nitrite aerosols would be very soluble and could be removed in water and measured as NO_2^- by a method analogous to the Saltzman azo-dye procedure. Alternatively, the specific ion NO_3 electrode using standard addition could be used if sufficient NO_3^- is present.

The estimated worldwide concentration of atmospheric NH_3 is about 8 $\mu g/m^3$; hence a sensitivity of measurement of about 0.3 $\mu g/m^3$ is required. Chemiluminescence techniques, colorimetric optoacoustic, electrochemical, and light scattering from specific reactants are used.

The chemiluminescence method consists of reduction of NH_3, and NO_2 to NO at 1,000^oC over a platinum catalyst; therefore, NO + NH_3 + NO_2 are measured; NO + NO_2 are measured after conversion to NO at lower temperature (240^oC). The difference of the measurements gives NH_3 (McClenny et al. 1977). Alternatively NH_3 can be scrubbed from solution using H_2SO_4 acid.

The optical scattering method consists of coating quartz wands with NH_3 active reagent (ninhydrin) and measuring the change in transmission due to the reaction (David et al. 1977).

In colorimetric analysis, NH_3 is adsorbed on glass fibre filters (generally GFC) impregnated with H_2SO_4 (Okita and Kanamori 1971). The NH_3 is then dissolved and measured using ninhydrin or indophenol complex.

The opto-acoustic method (McClenny et al. 1977) is based upon measuring acoustic disturbances upon the absorption of IR radiation. This method is still being developed.

NH_4 is important to analyze for in aerosols, as it forms NH_4-H-SO_4 compounds. Techniques for analysis and filter types to use have previously been discussed with reference to SO_2-SO_4. These compounds are very soluble in water and either colorimetry using the indophenol complex or specific ion electrode measurements are desirable. The use of the NH_3 specific ion electrode (Fagan and Dubois 1974) (sensitivity 0.02 mg/L) in combination with pH, Cl electrodes, and making measurements via standard addition has merit.

3.3.7 Plume Depth Measurements

Plume depth measurements are required for models described in Sections 2.6.3, 2.6.9, and 2.7.2. In reality, the plume depth is a scavenging height or mixing height. Therefore, vertical concentration is generally assumed in some manner in estimating this height. During precipitation, cloud base might be assumed. Other estimates of this vertical height might be obtained from model estimates, from indirect measurements using either LIDAR (Byers 1975), aircraft measurements (Section 3.5.4), or estimates from correlation spectrometer measurements. The spectrometer measurements actually give a concentration-depth product which could be directly used in the sub-models. In addition to the above, estimates of mixing height from relationships between synoptic weather and atmospheric sounding may be used to evaluate the scavenging height (McMahon et al. 1976).

3.3.8 Snow Conditions

Slinn (1976b), in his comprehensive review on scavenging, suggests that there is little or no understanding of the phenomena involved. Section 2.9 is a preliminary model for snow. In addition to the previous parameters that affect dry and wet scavenging, the kind of snow is important. A sixfold classification of graupel, rimed crystals, spatial dendrites, powder snow, needles, and plane dendrites is used.

Collector efficiency is a serious problem when considering snow. Heated collectors develop thermal gradients, and collectors with any amount of cross-section influence the wind field. Collectors with Alter Shields are more efficient than collectors without, but there is still considerable inefficiency in collection. Electrical sensor-operated collectors that must be heated will not activate in light snowfalls, as the rate of evaporation equals the rate of precipitation. Moreover, snowfalls associated with low wind velocities will not actuate the sensors without a collecting grid mounted on the sensor. The sensor gap must be adjusted to a very small length ($\lesssim 0.05$ cm) so that any drop may activate the collector lid; it is also a good idea to introduce a time delay of 10 - 30 min. (that is continuously zeroed) on the closing mechanism.

Bulk collectors with Alter Shields have been used with reasonable success for measuring snow. The design of the collector must be accommodated to problems associated with freezing and thawing as well as ablation. Even these collectors are very inefficient when there is any amount of wind at collection level.

The most practical collection device is to use a large bed or the ground itself to accumulate a snow sample or sections of a snow sample. The ground is the most practical collector if there is little wind and little chance of contamination due to entrainment of contaminants. In this operation, an area approximately 2 m by 2 m is covered with about 0.02 cm (6 mil) linear polyethylene sheeting and the snow is collected. Portions of the snow event can be sampled by placing consecutive layers of plastic sheet on top of the previously sampled snow. It is best to carry out this sampling at two or three places within the test site.

Sampling using a bed is carried out in a similar manner. This technique is used when there is concern regarding contamination. In place of a bed, a raised platform can be used. In all cases, the elevation of the bed or platform should be as close to the ground as possible.

Sampling of sequential layers of snow can be carried out in a slightly different manner. The procedure is to determine the number of snow samples desired; lay down, or fasten to a bed, the requisite number of sheets plus a cover sheet. On commencement of precipitation, the top sheet is removed, and in sequence each additional sheet is removed with sample. Weights should be used to hold the sheets in place; these can be made by sealing stones, etc., inside a plastic envelope.

Knutson and Stockham (1977) have carried out careful studies on the scavenging of snow. They found that Λ varies with kind of snow, precipitation rate, particle size, circumscribed snowflake diameter, and effective scavenging cross-section of the flake. Table 27 is taken from their work and lists Λ for four snowflake types. Looking at the equations in the table, it is possible to estimate Λ, if type of snowflake, precipitation rate, and temperature are known. This value of Λ, along with measured concentration and scavenging height can be compared with ground

Table 27. Equations for Λ for different types of snow.[a]

$$f(T,D_p) = \text{antilog}\ (-3.17 - 0.0178T + 3.41 \log D_p - 0.973 \log^2 D_p - 7.20 \log^3 D_p)$$

where T = temperature, °F

S = effective cross-section of snowflake, cm^2

D_p = particle diameter, μm

R = rainfall rate mm/h

Λ = scavenging coefficient, s^{-1}

Precipitation Particle Type	Λ	S
Lump graupel	$0.21R^{0.188}f(T,D_p)$	$[675f(T,D_p)]/R^{1.0}$
Dense rimed dendrites	$0.40R^{0.266}f(T,D_p)$	$[1309f(T,D_p)]/R^{0.834}$
Dense rimed radiating dendrite assemblages	$0.32R^{0.305}f(T,D_p)$	$[1044f(T,D_p)]/R^{0.895}$
Aggregates of unrimed radiating assemblages of dendrites	$0.41R^{0.57}f(T,D_p)$	$[1336f(T,D_p)]/R^{0.623}$

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[a] From Knutson and Stockham 1977.

flux measurements. Alternatively, sequential sampling can be used to obtain Λ.

Snow introduces another important depositional process: horizontal interception or canopy filtration. This mechanism is the ability of vertical surfaces, such as trees, to intercept and concentrate contaminants. Reiners et al.(1977) used two bucket collection systems for collection of rime in the White Mountains. In one bucket (about 25 cm) an artificial foliage was positioned 25 cm above the bucket. This collector had concentrations 8 - 50 percent greater than an adjacent bucket without artificial foliage. The extension of this study into real terrain appears to be to conduct parallel sampling in open terrain and in an adjacent forest. Practical examples of collector layouts in a pine forest are found in Richter and Granat (1978).

3.3.9 Rainfall Intensity and Raindrop Sizing

Rainfall intensity (J) is important to most scavenging functions. It can be measured nearly continuously, using a tipping bucket device, a capacitor sensor device, or at intervals by measuring units of water falling in a given area. For snow measurements, the continuous devices are not recommended because evaporation losses during heating are very large. For sensitive measurements, a resolution of 0.025 cm and a recorder time resolution of 5 cm/h or better is needed. All devices have a delay time of wetting, due to coagulation and adsorption of drops on the collector surface. Reported wetting amounts are 0.025 cm, but practically, 0.08 cm is common. Surfaces can be treated to decrease this effect using teflon or silicones, but pre-wetting appears to be the best method.

Tipping bucket collectors can be modified to be used as sequential samplers. The parts that come in contact with precipitation are coated with teflon or other suitable material. The precipitation is collected in a fraction collector under the tipping bucket. The pulse of the tipping bucket advances the collector train or, with a stepping device, the collector train can be advanced every "n" pulses of the tipping bucket. Therefore, equal volume samples can be obtained for analysis.

Raindrop sizing is carried out by measuring the soiling area on filter paper. Typically, the filter papers are tinted with dyes, and the wetting area is measured, generally with an optical particle counter (Vali 1977; Magono 1954; Dingle and Hardy 1962; Mason and Andrews 1960). Kind of filter paper does not affect the calibration. Continuous raindrop size spectra can be obtained by using moving strips of tinted filter paper. A very approximate estimate of the ion concentration variation in drops can be obtained by using chemically sensitive dyes. Hence, the H^+ ion concentration can be estimated by using H^+ ion sensitive paper. Vali (1977) carried out sequential analyses of High Plains storms in Alberta, and found the raindrop size spectra shifted with time. The shifts can be qualitatively related to rainfall intensity.

Marshall and Palmer (1948) were the first to demonstrate that the raindrop distribution is exponential. Hence,

$$n\ (R) = n_o e^{-\Lambda R}$$

where $n(R)$ is the number concentration of drops per volume and size interval of drop diameter R,

$n_o = 0.08\ \text{cm}^{-4}$, and

$\Lambda = 41\ J^{-0.21}\text{cm}^{-1}$, where J is the rainfall rate in mm/h.

Hence, by substitution

$$n\ (R) = 0.08e^{-41J^{-0.21}R} \qquad (3.15)$$

Thus, the raindrop distribution can be calculated if the rainfall rate is known. However, Slinn (1977) cautions against the use of this function, since different measurements suggest a variation of N_o of from 0.01 - 0.5 cm^{-4} and the exponential term of Equation (3.15) of 0.01 - 0.5 cm^{-1}.

3.3.10 Effects of the Surface Interface

Surface effects to the roughness parameters have been discussed in Section 2.4.6, and field methods using the gradient method are discussed in Section 3.3.3. In addition, horizontal interception and the increased surface area available for deposition must be considered. Slinn (1976a) outlined a new theory for forest canopy scavenging (Section 2.4.4). This theory has not been tested. The best approach, therefore, appears to be to measure fluxes outside, below and above the forest canopy, bearing in mind the more important parameters of the canopy theory. The pertinent variables are

$\bar{u}_c$ = average wind speed in the canopy

B = biomass per unit volume of space

γ = canopy infiltration effect

$$= \frac{HB}{\gamma\bar{\rho}}$$

where H = thickness of the canopy layer,

γ = average (typical) length scale of individual collecting fibres, and

$\bar{\rho}$ = average mass density of the foliage.

Therefore, different varieties of growth, denseness of growth, height of growth, and average wind speed seem to be key factors in in-forest scavenging. It is worth remembering that in-forest scavenging is always greater than that occurring on adjacent flat terrain by up to 2+ orders of magnitude. Therefore, forest scavenging may be as significant or more significant in depositional fluxes in the study area than are all other parameters which have been considered in scavenging.

Richter and Granat (1978) have developed a good plan for sampling. Using sequential samplers (fraction collectors or as with automatic analyzers), different fractions of a throughfall event can be collected. The scale of sampling that is used is the dimension of the horizontal projected tree canopy. Both under canopy and open, but within forest, collections were made. In all cases, analogous collections were made in adjacent areas outside the forest area.

In siting collectors, the γ effect may be estimated in a forest by measuring solar extinction values. Similarly, comparison of concentrations to rainfall amount may be helpful in defining γ.

Previous discussion on horizontal penetration of forests for snow periods must be re-emphasized for dry periods. Hence, a canopy infiltration study must consider edge effects of forests with respect to sources and prevailing wind.

3.3.11 Other: Ambient Surface Temperature, Atmospheric Stability, Stack Parameters, and Gas in Water Concentration

Other measurements required in the recommended deposition models are ambient surface temperature, stack emission parameters, atmospheric stability, and concentrations in water.

Ambient surface temperature can be measured on a continuous basis at the reference elevation using various kinds of readily available equipment. Instrument sensitivity should be $\pm 0.02^{\circ}C$ or less.

Atmospheric stability is required to calculate the "reaction height" of SO_2-SO_4 in the EPAEC model. The Briggs or similar equation is used to define plume lofting and σ_z, given stack characteristics and velocity. Pasquill stability classes A-F can be used to obtain the velocity at elevation, z, compared with a measured reference level (Roth et al. 1975). Atmospheric stability is obtained from the vertical temperature gradient, and the gradient is measured by atmospheric sounding. Barrie and Whelpdale (1977) outline a fairly intensive study on atmospheric stability, ventilation coefficients, and mobile minisonde measurements in the lower atmosphere. This information should be sufficient to relate synoptic weather conditions in order to estimate atmospheric stability in addition to direct measurement. Barrie and Whelpdale (1977) note that plume rise during March 1976 could not be predicted by the Briggs equation. However, there exists sufficient information to estimate mixing heights to compare with measured and estimated plume rise height. Channelling of winds due to the topography will probably have to be considered when obtaining "reaction heights" for the EPAEC model for the GCOS case. Either relationships different from the Briggs loft equations, modifications of these equations, or additional criteria regarding mixing heights due to channelling and stratification of lower winds will have to be added to thermal plume rise estimates.

Stack emission parameters are also required in the EPAEC model for lofting. Physical parameters for plume rise calculations are stack height, stack diameter, stack exit velocity, and stack exit temperature in addition to the temperature lapse rate. Emission characteristics for gases and particulates are summarized in Section 2 of this report. Only data on NH_3 appear to be lacking for the gases. Although particulates have not been analyzed, Barrie and Whelpdale (1977) note that samples have been obtained, and metal analysis of filters is being carried out. It is not clear whether sized particulate analysis is being carried out. In addition, reference to analysis of fly ash for 28 elements is made. Measurements have also been made to indicate that 0.7 - 1.5 percent of the emitted S is as SO_4. No comment as to the form of the emitted SO_4 is made.

Water concentration data are required for the Liss air-lake gas diffusion model (Section 2.5.6). Presumably this model would relate to SO_2 and possibly methyl sulphides. For SO_2 sampling above and below the air-water interface, analysis by the West-Gaeke (Section 3.3.6) method would seem most appropriate.

3.4 AIRCRAFT MEASUREMENTS

3.4.1 Principle of Approach

Utilization of aircraft allows a more precise three-dimensional analysis of a field experiment, access to remote areas to give a better spatial distribution, and atmospheric tracking of plumes to obtain approximately instantaneous information at various locations to determine time-dependent factors such as oxidation rates, scavenging and dispersion. Aircraft utilization brings a powerful yet expensive tool to field studies. A basic requirement of aircraft studies is to carry on ground experiments simultaneously and tie the two together. In the final analysis, ground information will be used in estimating fluxes, and therefore the combined study is of utmost importance.

Additional mobility would be gained by having instrumented land vehicles in communication with aircraft, with both linked to fixed ground stations. Although this study area has relatively poor ground access, the possible use of helicopters as ground vehicles should be considered. In this way, continuous analysis of vertical columns can be achieved.

A common requirement for all field operations occupying more than one site is communication, a common clock to synchronize measurements, an automated navigational system for mobile units, and, with multiple analyses, an automated data accumulation system.

3.4.2 Parameters and Instrumentation

There are many aircraft research facilities available. Aircraft are generally multi-engine and suitable to operate at slow speeds and under adverse conditions. NCAR uses Beechcraft Queen aircraft, and the University of Washington uses a Douglas B-23. A separate and regulated power supply for research equipment is required--115 VAC, 60 Hz of about a 1-kW capacity. Sampling ports must be carefully positioned relative to the aircraft's air stream to avoid interception and contamination. Table 28 lists typical equipment required for a relatively complete survey.

Typically, gas samples are taken in front of the plane's nose and other samplers are placed at appropriate locations on the hull.

In addition to automatic recording of data on computer-processible tape, voice commentary and photography should be available.

3.5 REVIEW OF SIMILAR PROGRAMS

In this section, four programs carried out elsewhere to estimate atmospheric deposition are reviewed. These programs consist of ground, aircraft, and ground-plus-aircraft measurements. These programs, in increasing complexity, are scavenging ratio measurements HASL and ISWS, the EPAEC studies, the University of Washington aircraft study, and the University of Michigan ground-plus-aircraft-plus-mobile-ground monitor studies.

Table 28. Some equipment, range, accuracy, and resolution for research aircraft.[a]

Measurement	Range	Accuracy	Resolution
Stagnation air temperature	-70 + 30°C	±0.2°	1 s
Moisture content	-50 - 50°C	0.5 - 1°C	
Pressure, altitude	300 - 1 035 mb	±1 mb	0.025 s
Airspeed	0 - 140 m/s	±0.14 m/s	0.025 s
Cloud liquid water	0 - 6 g/m^3		1.5 s
Hydrometeor liquid water content	0.2 - 4.5 g/m^3	±10%	0.02 s
Radiometric surface temperature	-50 + 50°C	±0.5°C	
Visible radiation	0 - 2.5 ly/min		1.0 s
Isokinetic rainwater scoop			
Filter holder sampler			
Impactor			
Gas analyzers, SO_2			
Particle analysis Aerosol analyzer Spectrometer probe Nephelometer	from isokinetic inlet		
Photography, side and nose			

[a] Composite NCAR and University of Washington.

3.5.1 HASL and ISWS Studies

The Health and Safety Laboratories (HASL) and the Illinois State Water Survey (ISWS) carried out atmospheric and precipitation monitoring to obtain scavenging ratios and deposition velocities (Krey and Tonkel 1977; Gatz 1977).

The HASL study was carried out in Seattle and New York, using bulk collectors. Measurements were taken for trace metals and Sr^{90}, and samples were collected on a monthly basis. In addition, a HASL wet-dry collector was used to collect samples in New York. Atmospheric concentrations of the parameters were obtained on a 20-cm Microsorban filter at 1 ft^3/min flow rate. Individual wet samples were analyzed. In addition, for multiple precipitation events, monthly precipitation was obtained. In this study, wet plus dry deposition fluxes were obtained by analysis of the bulk sample. Only total metals were estimated, and analysis involved digestion in hot acid. Average dry deposition velocity is obtained for multiple monthly samples by extrapolation to zero precipitation, the plot of total flux/air concentration versus monthly precipitation. Wet deposition is obtained by difference. The wet-dry sampler was used to obtain independent measurements of wet and dry flux. No other parameters were obtained. This instrumentation set-up would be similar to measurements required for the "simple deposition models" recommended in Section 2.

The ISWS study was designed to measure scavenging ratios for precipitation only at about 10 locations in a 90-km radius near St. Louis, Missouri, on a daily basis. Collectors consisted of open polyethylene funnels attached to polyethylene collection bottles mounted 1.5 m above the ground. These "bulk" samplers were changed daily, and the funnel was cleaned with distilled water. On occasion, "dry" samples were also collected. Aerosol samples were collected daily, on 15-cm Whatman 41 filter paper at a flow rate of 40 m^3/h. Precipitation samples were filtered to separate soluble and insoluble fractions. Particle sizing was not actually carried out in conjunction with the sampling, but was obtained from a previous study. Rainfall amount (intensity) and synoptic rain type were two additional variables measured. Differences in the measured scavenging coefficient were obtained for different sampling locations for some parameters. Other meteorological parameters were measured from cognate studies, and statistics (i.e., student "t" test to compare means) were used to ascertain the relative degree of correlation.

3.5.2 EPAEC Study

Field measurements for this program (Dana et al. 1973) were oriented to SO_2, the reversible solubility of SO_2 in rain, and oxidation to H_2SO_4, and the testing of the EPAEC model for precipitation conditions. These field studies were carried out for tower releases ($\leq$30 m) of pure SO_2 in rain with low background SO_2, and the study of coal-fired power plants where emission data were available. Single rainfall events at various locations were studied in some detail ($\sim$200 sample sites) in an approximate 15-km diameter. Reaction transport times of about 10 minutes for these studies is typical. Rain collectors consisted of ground-level 20-cm plastic funnels draining into a 500-mL bottle. SO_2 analysis bottles contained a stabilizing solution of tetrachloromercurate. $SO_2 + SO_4^{-2}$ bottles contained H_2O_2, and a separate bottle for H^+, NO_2^-, NO_3^-, SO_4^{-2}, and trace metal was used. In addition, a simple impinger bubbler was used to measure atmospheric SO_2. The West-Gaeke automated method of analysis for SO_2 (Figure 26) was used. Supporting instrumentation consisted of a raindrop spectrometer (water-sensitive paper measured in optical imager), a fast response rain gauge, a Gill 3-component anemometer, pilot balloons for mean wind direction and speed prior to the study (to lay out sampling network), and a portable rawinsonde unit for wind, temperature, and dew point during the study. The anemometer was mounted atop a 30-m portable tower and at ground level. Correlation of oxidation and scavenging of SO_2 were found to be a function of rainfall intensity, particle size, raindrop size, and pH. SO_2 solubility is reversible in raindrops, and dry deposition can occur. Model field comparisons were considered good; that is, they were within a multiple of two of each other.

3.5.3 Aircraft Study

Various aircraft experiments have been carried out, but the study of Radke et al. (1977) is one of the better examples relating to plume scavenging. The University of Washington B-23 aircraft was used to study rainshower scavenging in a paper mill plume. Besides navigational instrumentation, sophisticated equipment for particle size and hydrometeor size was included:

1. Whitby electrical aerosol analyzer for 0.01 - 0.5 μm particles;
2. Knollenberg axial scattering spectrometer for 2 - 30 μm sizes;
3. Rapid expansion chamber for particle concentrations >0.002 μm;
4. Direct impactors of silicone-coated slides for scanning electron microscope and elemental analysis for 5 - 100 μm particles;
5. Automatic cloud condensation nuclei counter for cloud droplet concentration; and
6. Integrating nephelometry for light scattering coefficient.

The rapid expansion chamber, Whitby aerosol analyzer, optical particle counter, and nephelometer were connected to an isokinetic intake. The impactor and axial scatter spectrometer are located in the free airstream of the aircraft. Particle size from 0.002 - 100 μm, concentrations from 10^{-6} - 10^{7} cm^{-3}, along with hydrometeor size spectra were measured in the plume before and during rainshower scavenging. Rainshower scavenging as a function of particle size was ascertained. Experimental times were of the order of 10+ minutes. Λ was shown to approach zero for aerosol sizes of 1 - 0.1-μm diameter.

3.5.4 Aircraft Ground Studies

Dingle (1977) used aircraft to release Indium tracer in the updraft of a moderate convective storm, associated with a squall line. The material was analyzed in five successive storms using fixed ISWS stations and three mobile monitors. Tracking was carried on for 2 h over 50 km. Samplers consisted of wide-mouth 50-cm buckets. There were six sequential samples out of the 100-odd sample stations. Sounding maps from nearby stations were used for general scavenging lengths. Radar echoes were used to track the storm relative to release and sampling sites. Rain gauges were set out at most of the sampling locations, and sequential sampling at 10-minute intervals allowed estimations of rainfall intensity. The scavenging coefficient can be estimated from the slope of the deposition flux with distance and time. This result can be compared with the difference in concentration of sequential samplers.

3.6 AVAILABLE INFORMATION AND INSTRUMENTATION

Barrie and Whelpdale (1977) have summarized ongoing projects in AOSERP. Brief comments are made here relevant to use of information from these projects. More specific recommendations are made in Section 3.8. The *Air System Data Directory, February 1978*, (Milgate 1978) lists data obtained for the overall program. These data sets are commented upon relative to their use in estimating atmospheric deposition.

The key parameters required to estimate atmospheric deposition have been summarized in Table 22. From the data inventory, three sampling sites--Birch Mountain, Bitumount (Fort Hills), and Fort McMurray--collect all information required to estimate precipitation. Only at these stations, plus Mannix, is particulate chemistry, sized particulates, as well as event precipitation chemistry measured. In addition, gas analysis for SO_2 and NO-NO_x are carried out; continuous recording rain gauges are operated, and the frequency of analysis of noncontinuous measurements is very good from 0.5 - 1 h. Table 29 summarizes data accumulated at these three stations. The following outlines how the data may be reduced to obtain scavenging parameters:

1. Obtain scavenging ratio, W, using particulate analysis prior to rainfall and concentrations in event samplers. Compare results to those obtained by Gatz as a function of particle size and precipitation intensity. Compare results for different stations, wind velocity, and mixing height.
2. Use literature data for Λ as a function of particle size and compare calculated wet flux ($F = \Lambda\chi$) to measured wet deposition flux.

More detailed knowledge of the kind and extent of data will suggest limitations to the above calculations as well as possible additional calculations. Two possible drawbacks come to mind:

1. It is not clear that the same parameters in the same phase were measured in each case. For example, Barrie and Whelpdale (1977) note that Na^+, K^+, Ca^{+2}, Mg^{+2}, NH_4^+, SO_4^{-2}, NO_3^-, and Cl^- are analyzed in precipitation samples. Although SO_2 and NO-NO_x were

Table 29. Measurements at Birch Mountain, Bitumount and Fort McMurray for estimation of atmospheric deposition.

Measurement	Parameter Calculated
Aerosol metal analysis, particle size, special analysis, total concentration	W dry deposition using literature v_d Λ,W = f (particle size)
Gas analysis	
SO_2	Λ - SO_2
NO + NO_x	Λ - NO_2
Rainfall intensity: weighing, tipping bucket	Λ, W = f (J)
Precipitation chemistry	
event	W, Λ, flux maps
bulk, event	dry deposition, deposition velocity
Wind velocity	W, Λ = f (u)

measured at the three sites, details of parameters measured or phase (soluble or total) for air particulates are lacking.

2. There could be contamination at all sites due to local sources which may not characterize the atmospheric deposition of constituents from the oil sands operations. Both Birch Mountain and Bitumount have diesel generators within 70 - 130 m of the sampling sites. In fact, Birch Mountain has generators both north and south of the site. Fort McMurray may be influenced by activities of the airport and townsite. A scheme must be developed to test how significant this local contamination is.

Bitumount offers added attraction in that it has a 17-m instrument tower adjacent to a dense 15-m forest. Deposition using gradient methods of analysis might be carried out using existing concentration data and vertical wind and temperature gradients.

Finally, it is worthwhile to note that:

1. All three sites lie outside the immediate deposition area for snow as determined by Barrie and Whelpdale (1977), and therefore are more indicative of long (∿100-km) transport.
2. The three stations lie in an approximate N-S direction, which is parallel to surface winds and the snow deposition gradient. Furthermore, Bitumount and Fort McMurray are about equidistant from source and at about the same elevation (265 and 369 m), whereas Birch Mountain is at 853 m. Comparison of deposition effects due to elevation should be interesting relative to plume trapping.

A second set of analyses would be to prepare contour maps for precipitation flux (χ_w.J) for events from the 13 stations in the area. Variations from map to map can be compared with synoptic meteorological conditions for the period of time. These maps also can be used in a postdiction sense to compare to model results once the model is operative.

The AOSERP Mildred Lake Research Facility is perhaps unique in that bulk sampling and event samples are both measured. An estimate of dry deposition can be obtained from the difference in the bulk fluxes and cumulative event measurements. Furthermore, results from the Finnish automatic samplers can be compared with the event samples.

There are also 19 other dry deposition collectors within 25 km of GCOS. These stations could be used to give first estimates of dry deposition; using particle size distributions and atmospheric concentrations, dry deposition velocities could be estimated.

Finally, the data set itself should be analyzed for consistency. Chemical analysis of aerosols should be compared with soil analysis via enrichment factors, and the composition of aerosols should be compared with source emissions in context to particle size. The precipitation chemistry should be tested for electroneutrality, and, if specific conductance were measured, the measured value should be compared with the estimated value in order to flag inconsistencies (Section 4).

Figure 3 shows the locations of the precipitation monitoring sites that have data that can be used to calculate important deposition parameters. As can be seen, there is good areal spread. The only gap in the data is the limited number of stations at lower elevations, particularly 50 - 100 km north of the GCOS.

3.7 SITING AND LOGISTIC ASPECTS

Siting and logistic aspects of field measurements consider terrain characteristic (elevation, relief, vegetative cover, or extent of water surface), access, and location relative to wind characteristics.

The following conclusions are based primarily upon one fly-over of the area, inspection of 1:50,000 topographic maps, and the project summary of Barrie and Whelpdale (1977).

Due to difficulties in access to the area, sites that are already manned and instrumented appear logical choices for initial studies of deposition. Some detailed sampling could be carried out in the vicinity of these sites. The following are suggested from a logistical point of view.

1. Mildred Lake AOSERP facility has the manpower and laboratory facilities and access to carry out the most sophisticated study. The site is at low elevation and within 10 km of the emissions. At a minimum, all experiments should be "dry run" at this location.
2. Bitumount is within 50 km of the emission, at low level (360 m), and is well instrumented. Access is available by air and water, and bush roads exist for deployment of secondary instrumentation. There is a dense forest adjacent to the site for studies of forest scavenging. The diesel power plant is sited 130 m north of the instrument site. Emissions from this generator should not interfere with GCOS emissions. McClelland Lake, approximately 4 km by 6 km in size, and approximately 15 km NE of Bitumount would be a companion site for a study of deposition on a water surface. The lake is at a slightly lower elevation of 299 m. Access appears to be available by bush roads in many parts of the region.
3. The Birch Mountain Tower site is well manned and instrumented, and represents a site for deposition measurements at higher elevation (800 m). However,

there may be excess traffic and enough contamination from diesel generators to necessitate avoiding this site. Experiments should be carried out when interference from generators and other activities will be nil.

4. A detailed survey of other instrumented sites (Figure 27) should be carried out relative to type of terrain, access to the site, access in the vicinity for secondary instrumentation, and possible interferences from local sources and activities. Initial emphasis might be placed on sites in the eastern portion of the area, because of the prevailing wind patterns.

Previous discussion focussed on the importance of the forest canopy in atmospheric scavenging. A map showing forest distribution as to height of canopy, canopy density, and homogeneity of types would be valuable logistically in picking locations for deposition studies.

Barrie and Whelpdale (1977) have emphasized that the coupling of atmospheric deposition to terrain effects is a major purpose in the program. A soils map showing or indicating soil pH, base saturation, and composition would be desirable for picking areas to carry out depositional experiments. Initially, this mapping and analysis might be carried out near the instrumented stations.

Bog and swamp cover a large portion of the area, especially in the north. Very little information is available regarding deposition characteristics across this "water/land" interface. Furthermore, Gorham (1978) has proposed intensive study of highland bogs as they may represent the area most susceptible to change due to atmospheric deposition. These areas, however, are not well covered by present instrumentation, nor are they readily accessible. Studies concentrating on deposition in swamps at Richardson and in elevated bogs in the Birch Mountains might be considered.

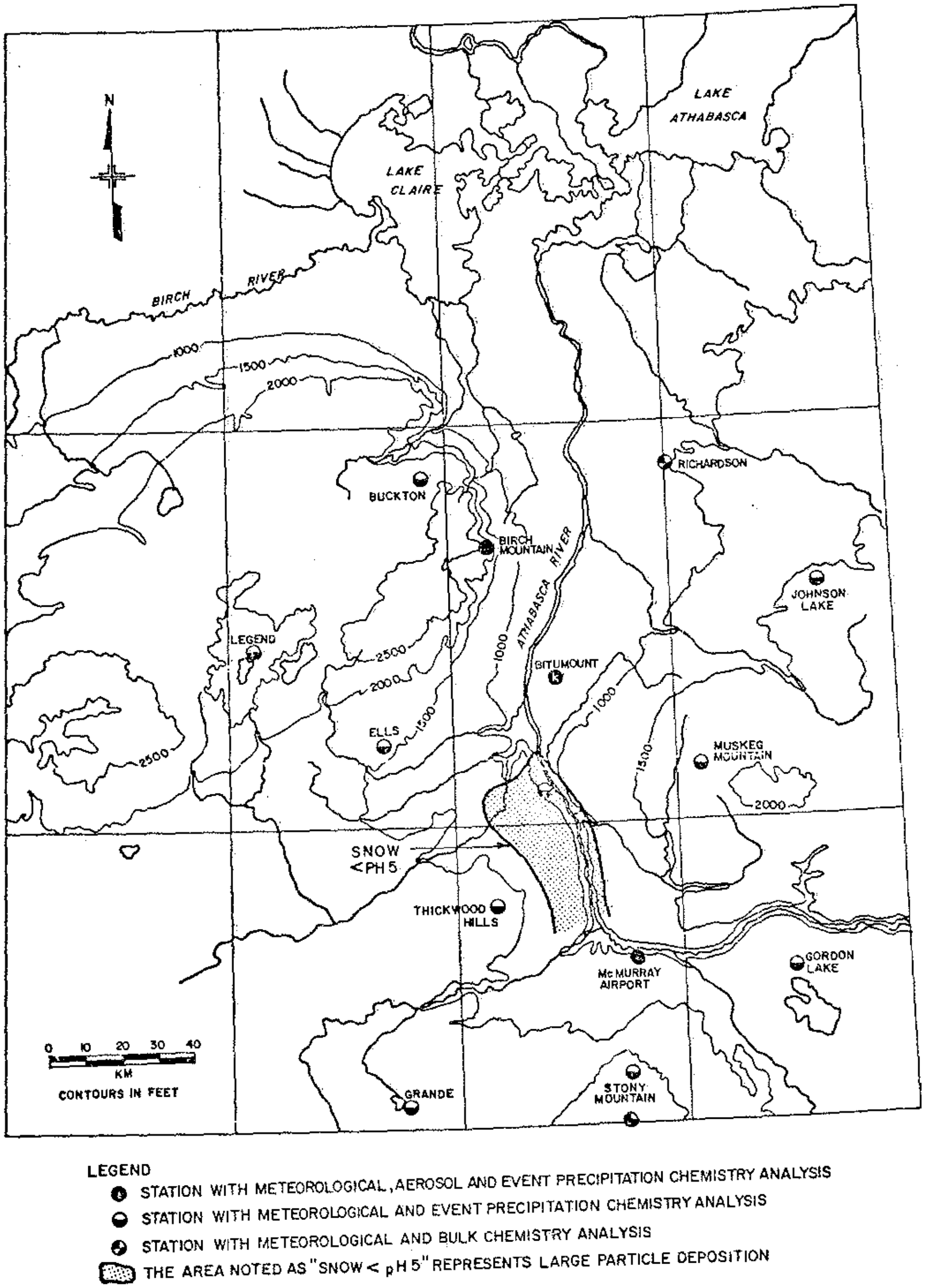

Figure 27. Location of monitoring sites.

Fort Chipewyan represents an accessible base for studies of more distant deposition (∿200 km) on a large lake surface.

3.8 PROPOSED FIELD PROGRAMS

3.8.1 Rationale of Approach

The fundamental approach is to design each new experiment from information and hypotheses obtained from previous studies. Secondly, there should be a few coherent and complete studies rather than large data gathering exercises. Thirdly, experiments should be designed whenever possible with redundancy built in; that is, there should be more than one method of obtaining key depositional parameters. Fourthly, careful attention must be paid to sampling and analytical control at the field and laboratory level; and fifthly, in the list of parameters, emphasis should be placed on SO_2-SO_4^{-2}-H^+ deposition, but not to the point of excluding other parameters.

The following recommendations are made without synthesis of information already obtained. In theory, the field experiments should be designed in detail only after the analysis of previous data, as suggested in Section 3.6, is carried out. In practice, perhaps parallel analysis of previous information and field experimentation would be useful.

Mention has already been made of concern regarding equivalent definition of chemical parameters.

The following outlines coherent sampling and analysis for gas, particulate, and precipitation phases:

1. Gas: SO_2 after filtration, using teflon filters to remove particulate SO_4, analysis by instrumentation or sampling by impinger with preservative and analysis by West-Gaeke method.

NO, NO_2, NO_x after filtration, using teflon filters to remove particulates, instrumental chemiluminescent analysis is carried out.

NH_3 after filtration, ammonia may be collected by scrubbing with dilute H_2SO_4.

2. Particulate: Water soluble and total particulate should be separated and analyzed. Although hot or boiling water extraction is used, extraction using room temperature water (buffered to pH of adjacent water bodies) is of value.

   NH_4^+, SO_4^{-2}, NO_3^-, H^+, Cl^- particulates are usually quite soluble.

   Na^+, K^+, Mg^+, Ca_2^+ have variable fractional solubilities depending upon the portion of silicate minerals.

   Trace metals, fraction soluble is usually small, at the µg/L to ng/L level, except for low pH and small particle size.

   Organics occur at the ng/L to µg/L level and may occur in gaseous, particulates, and particulate water soluble phases.

   Total particulates are determined by instrumental techniques such as X-ray fluorescence and neutron activation, or by acid digestion and atomic absorption (after chelation/extraction or ion-exchange concentration) and polarographic techniques (see Section 4).

3. Liquid Phase: Both soluble (filtered) and total concentrations should be measured. Acid preservatives generally change the proportion of soluble components. Therefore, multiple sampling is required.

> Acidity titrations using the Gran technique on soluble fractions (Section 3.3.6) should be used on occasion to characterize the soluble fraction and confirm individual analyses.

Glass fibre filters are not suitable for the above analyses as they are contaminated with S and metals, and accelerate SO_2 oxidation. Certain cellulose membrane filters are free of contamination but enhance the SO_2 oxidation. Teflon filters have a very small effect on SO_2 oxidation and are generally free of contamination.

In summary, equivalent analyses of gas, particulate, and precipitation must be carried out to obtain proper deposition parameters. In general, the soluble fraction should be characterized in addition to total concentrations.

Redundancy in obtaining depositional parameters varies from multiple sampling at one site for simple experiments to multiple experiments for more sophisticated studies.

It is proposed that a field study similar to the EPAEC power plant study be conducted for SO_2-SO_4.

The following proposals are discussed under the subheadings: locations, instrumentation, meteorological conditions, and results. The "simple field program" might better be construed as "first measurements".

3.8.2 Simple Field Program

This study is designed to interpret wet and dry deposition as a function of particle sizes and rainfall intensity. W and Λ are measured. The dry deposition portion may be the weakest part of the program.

3.8.2.1 Locations. AOSERP Mildred Lake Research Facility initially, then Bitumount and Birch Mountain. Other studies possibly at precipitation event localities (Figure 27).

3.8.2.2 Instrumentation. Every precipitation study:

1. 1 - 3 precipitation collectors at 1-m elevation,
2. Weekly/monthly bulk collectors,
3. High-volume sampling prior to rainfall sampling,
4. Precipitation intensity, wind velocity, synoptic weather, and
5. Measure pH, SO_2, $NO-NO_x$ at the site on a continuous basis.

Occasional basis (1 or more times):

1. Lundgren (or similar) particle size sampling analysis prior to precipitation,
2. Sequential sampling using tipping bucket technique or manually,
3. High-volume sampling after precipitation,
4. Multiple sampling within 100 m in same terrain,
5. Forest canopy sampling adjacent to open terrain (average wind velocity in forest should be estimated), and
6. Simultaneous study at multiple stations.

3.8.2.3 Meteorological conditions. Studies with plume movement in direction of collector should be emphasized, with a few sampling periods when plume movement is away from collector. Periods anticipating extremes in wind velocity and precipitation intensity should be emphasized. Short and long periods between storms and varying mixing heights (scavenging) should be considered.

3.8.2.4 Analysis Procedures

1. Use precipitation concentrations (filtered total), precipitation intensity, aerosol concentration (soluble total) to calculate W.

2. Extrapolate plot of bulk collector flux, F, divided by air concentration *versus* precipitation to zero precipitation to obtain dry deposition for soluble and total parameters.
3. From sequential sampling, ascertain Λ from slope of plot of log concentration *versus* time of rainfall. Compare with particle size and rainfall intensity.
4. Compare flux measurements for multiple samplings and determine an overall "error" or accuracy.
5. Compare variations in scavenging fluxes as to mixing height, time between precipitation, air concentrations after precipitation to obtain ideas on atmospheric mixing and concentration homogeneity. Try to design some experiments based on conclusions reached from analysis of negative results.
6. Determine the forest canopy effect from ratio of forest flux to open terrain flux. Relate this ratio to wind velocity, canopy height, and density.
7. Determine variability in scavenging in canopy by measuring from multiple containers. Determine windward edge effects of forest canopy. Initially, conductivity and pH might be measured as first estimate of the variability.

3.8.3 The "EPAEC SO_2 Program"

3.8.3.1 Location. Mildred Lake and vicinity. Set out a series of samplers in a 90° arc with the plume bisecting the arc. Farthest arc should extend beyond 25 km. Closest arc might be 3 km. The AOSERP Mildred Lake Research Facility meteorological facilities could be used for the study.

3.8.3.2 Instrumentation

1. Rainfall collectors consisting of 20-cm diameter funnel attached to 500-mL funnel supported by "ring stand" and consisting of sample bottle treated with TCM for SO_2, sample bottle treated with H_2O_2 for $SO_2 + SO_4^{-2}$, untreated sample bottle for trace metals and pH.

   At every third site, a battery-operated bubbler impinger is used to sample SO_2 in the air during the experiment. About 200 sample sets are used.
2. Automated field laboratory for analysis of SO_2 and SO_4 (methyl thymol blue technique) (McSwain and Watrous 1974).
3. Correlation spectrometer study would be most desirable to run along with minisonde or rawinsonde.
4. Fast response rain gauge at central location.
5. Raindrop sizing equipment. A reel of water sensitive paper with aperture.

3.8.3.3 Meteorological conditions. Precipitation with plume from the south.

3.8.3.4 Analyses. Dispersion, oxidation, and scavenging of SO_2 and SO_4 for comparison to Gaussian plume model.

3.8.4 Sophisticated Analysis

These studies add to the simple studies. Basically, the more sophisticated studies consist of gradient method for dry deposition and short-period sequential sampling.

3.8.4.1 Location. Initially at AOSERP Mildred Lake Research Facility, then at Bitumount and Birch Mountain. Other precipitation event locations plus McClelland Lake for water deposition, forests (Bitumount), and muskeg should be considered.

3.8.4.2 Instrumentation. The following is in addition to that outlined for simple experiment.

1. Surface wind and thermal gradients. Using an approximate 3+ m tower with five temperature/wind sensors, the gradient at reference level is obtained.
2. Gas and particle concentrations at surface wind elevations. High-volume samplers at elevations and gas analyzers or impingers are used.
3. Continuous precipitation sampling using a tipping bucket and fraction sampler. Continuous measurement of pH.
4. Aerosol particle size spectra.
5. Composition of sized aerosol spectra.
6. Intensive in-forest sampling during precipitation. Up to 50 collectors to characterize throughfall, canopy interception, and stem flow are used at one location. Forest edge effects should also be studied. This program might first be carried out at Bitumount.
7. Lake water gas concentration and atmospheric gas concentration at specified heights.

3.8.4.3 Meteorological conditions. Plume should be in direction of study area. Extremes of scavenging height, wind velocity and precipitation intensity should be characterized. For forest canopy studied, varying periods between precipitation should be studied to determine the effect of washdown of dry deposition.

3.8.4.4 Results. Dry deposition from bulk collector extrapolation and from gradient method (Section 3.3.3).

1. W is characterized from precipitation and aerosol concentrations (soluble and total), Λ is obtained from sequential sampling. Λ and W can be compared.
2. Forest canopy scavenging can be empirically related to Slinn's model.
3. Diffusion model for SO_2 across a lake can be tested.
4. Variations in V_o, Λ and W on a lake surface, flat surface, and in a forest canopy can be compared.

An extension of the above may be warranted if more detail is required concerning forest canopy scavenging. The next step would involve analysis of deposition above the forest canopy compared with that within the canopy and on flat terrain. Instrumented scaffolding in the canopy with aerosol and meteorological instrumentation extending 10 m above the canopy would be required. Wind velocity, humidity, temperature, aerosol, and precipitation concentration and intensity should be monitored above and within the canopy at about 10 elevations.

The snow sampling studies of Barrie and Whelpdale (1977) should be extended to obtain ambient gas and aerosol concentrations.

A study at AOSERP Mildred Lake Research Facility initially and later at other sites should be carried out to ascertain snow scavenging relative to Sections 2.9 and 3.3.8. The temperature, particle size spectra, kind of snow, and snowfall rate are required to determine Λ. In addition, sequential sampling can be used to obtain Λ, or W can be obtained from snow flux and aerosol concentration.

Snowfall scavenging in the forest canopy may be a most important process. Snow sampling inside and outside can reveal differences compared with rain studies. The Bitumount area should be studied initially to compare with rain scavenging results.

3.8.5 Aircraft Measurements

It is difficult to propose a sensitive aircraft study without the assistance of preliminary results from ground data. A few guidelines can be given, however:

1. Aircraft studies should always be carried out in conjunction with ground studies so that calculations and conclusions are comparable; in addition, atmospheric soundings and correlation spectrometer plume analysis should be intercorrelated into a major air-ground analysis.
2. Aircraft analysis may be important in defining plume characteristics and concentrations during winter months; the snow scavenging model could be tested by flying in and out of the plume, especially at extended distances (>50 km) from source.
3. Aircraft plume studies can be used to study plume ageing and scavenging at long distances (>50 km) from source during rain periods; analysis of plume in-cloud and out-of-cloud can be used to obtain Λ to compare with ground estimates.

If ground studies do not result in predictive information comparable to literature results (Section 2), aircraft measurements may be needed to develop more sophisticated models. However, ground information should be first obtained and analyzed. At present, given the overall state of knowledge of atmospheric scavenging, winter aircraft studies might be the most beneficial since the least is known about atmospheric deposition in snow.

4. SAMPLING, ANALYSES, AND ERRORS

4.1 INTRODUCTION AND REVIEW OF INTERLABORATORY SURVEYS

Sampling, preservation of samples, and analysis are equally important in field experimentation. Each aspect can contribute a major error. In addition, anomalous results can occur on an occasional basis. A well-designed field program will be able to exclude or include these results in a rational way.

Hume (1973) reviewed results obtained for trace elements analysis among 79 professional laboratories. For synthetic samples run in triplicate (after omitting results in gross error by 10 times or more), the standard deviation about the mean ranged from 20 - 40 percent. A similar study on the analyses of subsamples of a seawater sample for trace elements showed a range from 4 - 70 percent standard deviation. Atomic absorption, neutron activation, and colorimetric methods were used. The concentrations were similar to precipitation samples ranging from tenths to tens of micrograms per litre. Sources of the variability depend upon heterogeneity of subsampling, storage container condition and length of time of storage, contamination, improper laboratory procedures, and operator efforts. Nonetheless, one should expect an overall "accuracy" for interpretation of results of about 20 percent.

Sample heterogeneity has been investigated quite thoroughly for rain collectors by Granat (1977). Any experimental site must be examined in the early stages of the study as to variability of sampling and local effects. Therefore, experiments using the same collector or analyzer at various nearby locations must be carried out to test spatial variance. Of course, the parameters measured in the test must be pertinent to the study, and have a reproducibility of measurement better or as good as the spatial variance. For precipitation samples, amount of precipitation, specific conductivity, and pH can be measured with precision and can be measured quite easily at the study site.

The sampling and processing medium is most important in field experimentation. The importance of filter media has previously been discussed in Section 3.3.6. In addition, one must assume that all collection containers react with precipitation. At the same time, if preservatives are added, some of the chemical species will be altered. For the parameters considered in this study, the following sampling media are recommended for precipitation.

1. Sample with no preservative: teflon, pyrex glass, or linear polyethylene. Containers should be aged with precipitation. In cleaning the containers between sampling, the obvious contaminants should be removed. The container should be rinsed in distilled water. Parameters to be measured are pH, Cl^-, SO_4^{-2}, K^+, Na^+, Ca^{+2}, Mg^{+2}, particulate, (NH_4^+, NO_3^{-2}), and filtered trace metals. Filtration for "soluble" components should be carried out in the field immediately after sample collection. Trace metal samples should be acidified to a pH of about 1, with high purity NHO_3 after filtration.
2. Total trace metals: the container may be linear polyethylene, well cleaned, acid and distilled water rinsed, and contain after collection pH ∿1 high-purity HNO_3.
3. NH_4^+ and NO_3^- can be and are best collected in containers with no preservative. However, if the samples are not analyzed at once, biological activity will modify the proportions of NH_4 and NO_3^-. Samples that are stored for a period of time should contain about 55 mg/L $HgCl_2$ preservative.
4. Organics should be collected in well-cleaned glass or metal containers. Stainless steel and aluminum are often used. Filtration should be carried out at field conditions.

Samples are usually stored in the dark and at cold, but not freezing, conditions. This procedure is designed to decrease biological modification of chemical species. Storage by freezing greatly reduces alteration, but the concentration process of the liquid phase associated with freezing may produce irreversible change. Overall, the storage time should be kept to a minimum.

Minimum storage time can be achieved by analyzing for most parameters in the field or at a field laboratory. In every case, the problems encountered by field analysis are outweighed by the minimum storage time, the "individual treatment" given to the project, and the rapid turnaround of results for study. Section 4.2.2 outlines a field laboratory for this project.

Most errors in chemical analysis involve either:

1. Interference in a technique by an unknown or unrecognized parameter,
2. Contamination from laboratory air and from common usage of equipment, or
3. Operator mistakes, particularly in data handling.

All three can be of equal significance when working with low concentrations. Mistakes involved in data transfer can be reduced by automation, but automation of an analytical laboratory tends to obscure control of stochastic errors and errors due to sequence of sample analysis. Since concentrations in samples for this study will be at low levels, the modern analytical laboratory must be considered a major source of contamination for any parameter under investigation. Modern buildings, facilities, and the white laboratory coat do not automatically compensate for the concentrated acids, bases, and salts on the reagent shelves. Most modern laboratories have central air circulation and filtered recirculated air. Therefore, one must anticipate a continuous low level of atmospheric contamination. This contamination is not present in the field laboratory generally.

Redundancy of sampling, spiking of samples, random insertion of blanks and controls as blind samples, and ongoing and continuous scrutiny for consistency of results are the means of finding and controlling sampling, preservation, and analytical errors. The best control is to use the standard additions method. In this procedure, known amounts of the parameter(s) to be analyzed are added to sample containers before sample collection if possible. With two or more collectors, a linear relationship between analytical signal (y-axis) exists with spike added (x-axis). The negative intercept on the x-axis gives the original amount in the sample. Least squares statistics can be carried out on results; in addition, sampling and analytical problems can be spotted by data points deviating from the straight line. In a three-sampling collection, spikes of 0, 1, and 2 times the estimated amount would be suitable.

Another method of spiking is sequential dilution of an original sample in a known ratio. The limitation to this technique is the purity of the diluting medium (generally distilled water), and the dilution must not decrease the resulting concentration to the detection limit.

In a well-controlled study, known blind samples, multiple sub-samples and standard additions or dilutions are submitted in a random basis of about one tagged sample for every five unknowns. These samples should be submitted as an ordinary sample for analysis.

It is common to use standard solutions in the laboratory and field for control and calibration. Since this study will deal with low concentration samples, it may be often more suitable to use de-ionized or distilled water along with standard solutions. Hence, standard acids and bases can be compared with a field sample of distilled water for an alkalinity or acidity titration. Similarly, samples of blank filters, distilled water samples in collection containers, and standard reagents should be considered as samples submitted for analysis. pH buffers might be submitted for laboratory pH.

Ionic solutions have two colligative properties which should always be calculated. Electroneutrality considers the difference in (+) and (-) charges. For the constituents to be measured in precipitation

$$(NH_4^+) + (H^+) + 2[(Mg^{+2}) + (Ca^{+2})] + (Na^+) + (K^+)$$
$$= 2(SO_4^{-2}) + (NO_3^-) + (Cl^-) + (HPO_4^{-2}) + (H_2PO_4^-) + (HCO_3^-)$$

where ( ) refer to molar concentrations.

Often the fractional difference in charge equivalence

$$\frac{\Sigma(+) - \Sigma(-)}{\Sigma(+)}$$

is ascertained. Deviations greater than about 0.15 suggest either an analytical error or lack of complete or proper definition of the ionic medium. Typically, this analysis pertains to filtered samples and gives no hint of conformity for total samples, particulates, etc.

Measured specific conductivity can be compared with calculated contributions from each ionic species. The Kohlrausch rule states that an infinite dilution, the equivalent conductance, Λ^o, is the sum of each ionic equivalent conductance. Hence

$$\Lambda^o = \Sigma\lambda^o_{\pm}$$

We assume this function holds at small concentrations. Hence

$$\Lambda = \Sigma\lambda_{\pm} \qquad (4.1)$$

The equivalent conductance is related to the specific conductance, k by

$$k = \frac{\Lambda\chi}{1,000} \qquad (4.2)$$

where $\Lambda = ohm^{-1}\ cm^2$,

χ is the concentration in gram equiv/L, and

$k = ohm^{-1}\ cm^{-1}$, all at specific temperature (25°C).

Equation (4.2) can be defined for a specific ionic species

$$k_{\pm} = \frac{\lambda_{\pm}\chi_{\pm}}{1\ 000} \qquad (4.3)$$

where the units are as above and for each ionic species.

Fitting experimental data for $\chi = 0 - .001$ eq/L for various substances to the Onsager equation relates $\lambda_{\pm}$ at $\chi_{\pm}$ to $\lambda^{o}_{\pm}$

$$\lambda_{\pm} = \lambda^{o}_{\pm} - [32z^{2} + 0.655z^{3}\lambda^{o}_{\pm}]\sqrt{\chi_{\pm}} \qquad (4.4)$$

where z is the charge on the ion in question,

$\chi_{\pm}$ is the concentration of the ion, and

$\lambda^{o}_{\pm}$ is the equivalent conductance at infinite dilution.

The equation is written for 25°C, and it is assumed that the ionic equivalent conductance is dependent upon the ionic concentration. Table 30 lists values of $\lambda^{o}_{\pm}$ for ionic substances common in precipitation. Therefore, $\lambda_{\pm}$ can be obtained for each ionic constituent using Equation (4.4) and Table 30, $k_{\pm}$ can be calculated from Equation (4.3), and the $k_{\pm}$'s can be summed to give a calculated specific conductance to compare with the measured specific conductance. For most dilute solutions (≤ 0.001 eq/L), the above procedure should produce results correct to $\pm 5 \times 10^{-6}$ ohm^{-1} cm^{-1} (25°C). It should be noted that temperature affects specific conductivity measurements by about 2 percent/°C.

4.2 SUGGESTED ANALYTICAL PROGRAM

There are two basic factors in the design of the following program; redundancy of measurement and analysis of as many parameters as possible, either *in situ* or in a field laboratory.

Table 30. Equivalent conductance of ions at infinite dilution ($\lambda^{o}_{\pm}$) common in precipitation at 25°C.[a]

Ions	Equivalent Conductance (ohm^{-1} cm^2)	Ions	Equivalent Conductance (ohm^{-1} cm^2)
H^+	349.8	OH^-	197.8
Na^+	50.11	Cl	76.35
K^+	73.52	NO_3^-	71.44
NH_4^+	73.4	HCO_3^-	44.5
½ Mg^{+2}	53.06	½ SO_4^{-2}	80.0
½ Ca^{+2}	59.5		
½ Zn	53.0		

[a] The concentration base is equivalent/L (Harned and Owen 1958). λ's in ohm^{-1} cm^2.

Field and laboratory analysis depends basically upon electrode analysis and specific parameter instrumentation automated analysis. Cl^-, pH, NH_3 and NO_3^-, and specific conductivity can be measured by direct electrode measurement and by standard addition and electrode. SO_2, SO_4^{-2}, Cl^-, NO_3^-, NH_3(g), NH_4^+, and NO_2 (gas) can be analyzed by automated wet chemical techniques; and NO, NO_x, and SO_2 can be analyzed by automated techniques. Indeed, NO, NO_x, and SO_2 are continuously monitored at the recommended prime study sites. Therefore, only Ca^{+2} Mg^{+2}, Na^+, and K^+ for precipitation need be analyzed by alternative methods such as flame emission spectroscopy; acidity and alkalinity titrations (Section 3.3.6) would be analyzed manually; trace metals would be analyzed by atomic absorption, neutron activation, or polarographic techniques.

It is suggested that a continuous recording pH meter be constructed to measure rainfall. The electrode would be a combination gel reference electrode in a flow line containing a trap. The electrode would be placed in the bottom of the trap to keep the electrode tip wetted between rainfalls. A rainfall sensor would activate both the pH meter and the recording device. The continuous electrode data would be compared to the pH of the entire sample or to the pH of segmented event samples taken using a tipping bucket or similar device.

Specific conductivity would be measured in the field laboratory or station using a constant temperature bath set at 25°C. Segmented sample analysis could also be carried out.

SO_2 should be sampled using pump impinger and analyzed using the automated West-Gaeke method. Results can then be compared with automated analyzer. SO_4 can be analyzed automatically using the methyl thymol blue technique (Lazrus et al. 1965); NO_3^- is analyzed automatically by Cd-reduction and diazotization; NO_2(g) is analyzed by the same technique after impinger sampling; NH_3 (g), after adsorption is H_2SO_4, and NH_4^+ are measured using the indophenol complex method. This method can be compared with analysis using the NH_3 electrode. Four automated units sampling from a fraction collector such as a Gilson 200 sample unit would be suitable for the above analyses.

Electrode analysis can be done separately or sequentially if a manual or automated electrode switch is available. A laboratory pH unit capable of about ≤ 0.6 mV sensitivity and stability can also be used in the field. Because solutions are of low ionic strength, gel-type Ag-AgCl reference electrodes should always be used. Alternatively, a small battery-operated pH meter with stability and sensitivity of 3 mV can be used in the field with gel reference electrode for pH measurements.

A sequence of analysis might be:

1. Precipitation
   (a) Field
      - weigh or measure volume of sample
      - measure pH and specific conductivity
      - filter and preserve samples as required.
   (b) Laboratory
      - *carry out auto-analyzer measurements for $SO_2(g)$, SO_4^{-2}, $NH_3(g)$, $NO_2(g)$, NO_3^-, NH_4^+
      - *carry out electrode analyses for pH (lab), specific conductivity, Cl^-, $NH_3(g)$, NH_4^+, and NO_3^- (optional).
2. Filter Samples
   (a) Field
      - preserve samples in desiccant.
   (b) Laboratory
      - weigh filters
      - section filters for total analysis, soluble analysis

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* May be done in field also, depending upon equipment availability and site.

- dissolve in acid for total or water for soluble fraction
- analyze for parameters using auto-analyzers and electrodes.

3. Gases
   (a) Field
      - collect gases in impingers and on impregnated filter paper.
   (b) Laboratory
      - carry out auto-analyzer and electrode analysis.

4.3 SENSITIVITY AND DETECTION LIMITS

Table 31 summarizes method reproducibility and detection limit for some of the analyses.

5. SUMMARY AND RECOMMENDATIONS

5.1 SUMMARY

1. Tables 32 and 33 summarize the atmospheric deposition models recommended for use in the AOSERP modelling program. References to specific sections of the report are mentioned.
2. A review of ongoing measurements suggests that there is enough information to make a series of preliminary estimates of many of the parameters required for the deposition formulae.
3. Bitumount, AOSERP Mildred Lake Research Facility, Birch Mountain, and Fort McMurray are three well-instrumented sites suitable for additional studies. Bitumount appears to be suited to forest canopy scavenging experiments. A second set of stations measuring event precipitation are suitable for additional experiments.

Table 31. Detection limit and estimated reproducibility for electrode and automated wet chemical methods.

Parameter	Method	Reproducibility	Detection Limit
pH	electrode	±0.02	
Cl^-	electrode-standard addition	2 percent	10 µg/L
SO_4^{-2}	methyl thymol blue, long cell	5 percent	10 µg/L
NO_2-NO_3	azo dye colorimetric	5 percent	30 µg N/L
NO_2-NO_3	electrode-standard addition		100 µg N/L
NH_3-NH_4^+	indophenol complex	5 percent	20 µg N/L
NH_3-NH_4^+	electrode-standard addition	5 percent	20 µg N/L
Acidity-Alkalinity	electrode + 0.1 m KCl Gran titration	0.1 percent	10 µg eq/L

Table 32. Simple or first approach.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Empirical deposition velocity, v_p (2.4.3)	Ground-level concentration Deposition surface Particle size	Ground-level concentration Particle size spectrum	Empirical model	Up to 1 order of magnitude	Minimal computational effort
Empirical deposition velocity, v_g (2.5.2)	Ground-level concentration Deposition surface	Ground-level concentration	Empirical model	Grass ±70% Water ±80%	Satisfactory
Empirical coefficient Λ_p (2.6.3)	Average concentration of particles in atmosphere Particle size Scavenging height Duration of rainfall	Vertical concentration profiles of particles Depth of plume Snowfall duration and rate Type of snow Temperature Particle size spectrum	Field tested	Within factor of 3	Satisfactory
Empirical scavenging coefficient Λ_g (2.7.2)	Average concentration of gas in atmosphere Scavenging height Duration of rainfall	Vertical concentration profile of gas Depth of plume Rainfall duration	Empirical model	Too little field data to estimate Λ_g	Determine field value

Table 33. Sophisticated or second approach.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Sehmel's Integral Resistance Model (2.4.6)	Ground-level concentration Particle size and density Particle settling velocity Roughness height Friction velocity Particle diffusion coefficient Air viscosity Obukhov length	Ground-level concentration Particle size spectrum Vertical surface wind profile Vertical surface temperature profile Ambient air temperature	One field test	$\pm$100%	Satisfactory
Gaseous Resistance Model (2.5.4)	Ground-level concentration Wind speed Surface friction velocity von Kārmān's constant Stomatal resistance Diabatic corrections	Ground-level concentration Vertical surface wind profile Vertical surface temperature profile	Empirical model	Same order as v_g	Satisfactory

Continued ...

Table 33. Continued.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Gaseous Air-Water Interface Model (2.5.6)	Water surface concentration Gas phase exchange rate Liquid phase exchange rate Molecular diffusivity of gas Henry's law constant Hydration rate constant Ratio of total to ionic forms of gas in solution	Water surface concentration	Some general comparisons found satisfactory	Probably similar to v_g	Satisfactory
Stratiform In-cloud Scavenging Model (2.6.13)	Intensity and duration of rain Type of cloud Temperature Raindrop size (Marshall-Palmer) Particle size Terminal velocity of raindrops Terminal velocity of particles Collision efficiency (Mason) Various constants	Rainfall intensity and duration Type of cloud Temperature Particle size spectrum	Some testing	Unknown, but may be large because of collison efficiency	Feasible procedure

Continued ...

Table 33. Continued.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
Sulphate Washout Model (2.6.14)	Source strength of SO_2 Rainfall duration and rate Source strength of particles Particle size and density Terminal velocity of raindrops Terminal velocity of particles Gas phase mass transfer coefficient Gas phase viscosity Empirical correction parameters	SO_2 stack emission Rainfall intensity and duration Particle stack emission Particle size spectrum	Not tested	Unknown, but may be large because of utilization of collision efficiencies	Complete model of transport diffusion and deposition

Continued ...

Table 33. Concluded.

Model (Section)	Data Requirement		Model Testing	Errors	Comments
	Input Data	Field Data			
EPAEC Washout Model (2.7.7)	SO_2 emission strength Dispersion coefficients Stack characteristics Wind speed Ambient temperature Rainfall rate and duration Raindrop size Gas phase mass transfer coefficient Henry's law constant Gaseous diffusion coefficient in liquid	SO_2 stack emission Atmospheric stability Ambient temperature Wind speed Rainfall intensity and duration Raindrop size spectrum	Field tested for various conditions	Within factor of 2 for greater than 100 m from stack	Satisfactory; complete model of transport, diffusion and deposition
Improved Model of Reversible SO_2 (2.7.7)	Vertical profile of SO_2 Rainfall intensity and duration Raindrop size spectrum (Best)	Vertical concentration profile of SO_2 Rainfall intensity and duration	Not tested	Expect to be little more accurate than EPAEC model	Satisfactory

4. Sampling, methods of analysis, and testing for quality control are discussed. The value of carrying out chemical analysis in the field is argued both from a quality control point and for rapid data calculations.

5.2 RECOMMENDATIONS FOR FURTHER RESEARCH

The following are listed in approximately chronological order:

1. Obtain estimates of deposition parameters for existing data from AOSERP Mildred Lake Research Facility, Bitumount, Birch Mountain, and Fort McMurray. Ascertain the compatibility of different data sets used in these estimates and attempt to assess quality control.

   Data reduction, wet and dry scavenging coefficients can be obtained in a preliminary fashion and should be related to meteorological parameters (wind speed and direction, plume and mixing heights, surface stability, rainfall intensity). These results should be compared with data from the literature, and particular attention should be paid in the following studies to situations which seem anomalous to other studies. Applicability of these results to other portions of the study area should be estimated from results of other ongoing programs. In this sense, emphasis on bog and forest interfaces is suggested.
2. Carry out wet (sequential sampling and scavenging ratio) measurements and dry deposition (gradient technique) at Mildred Lake, Bitumount, Birch Mountain, and Fort McMurray.

Preliminary forest scavenging experiments should be carried out at Bitumount.

3. Carry out snow scavenging studies at AOSERP Mildred Lake Research Facility and Bitumount. Forest canopy scavenging experiments with some emphasis on horizontal interception should be carried out. This program may precede recommendation 2 depending upon timing.
4. Carry out a field experiment similar to that of the EPAEC study for near-source deposition (≤25 km). AOSERP Mildred Lake Research Facility is suggested as the centre for this study.
5. Using forest and soil data as criteria for siting, carry out experiments in bog and forest cover.
6. Using water quality data as criteria, carry out a water interface scavenging study.

Recommendations 5 and 6 may be deleted if soil and water quality data do not suggest susceptible terrain and if Bitumount is deemed representative of forest cover in the area.

7. Set up and maintain a separate and coherent data file for the deposition studies. Pertinent data from other studies should be stored in the file. The file should be annotated, and internal checking of the data file should be carried out automatically. This aspect of the study could be initiated with the review of existing data (recommendation 1.).
8. Using updated emission data, reassess the parameters considered in the study.
9. Special chemical characterization studies should be carried out on an occasional basis in order to ascertain the chemical speciation.

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