SOME APPROXIMATIONS FOR THE WET AND DRY REMOVAL OF PARTICLES AND GASES FROM THE ATMOSPHERE

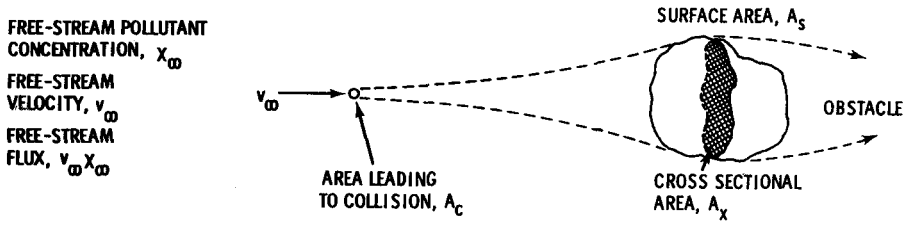
W. G. N. SLINN, Atmospheric Sciences Department, Battelle, Pacific Northwest Laboratories, Richland, Washington 99352, USA.

ABSTRACT

Semi-empirical formulae are presented which can be used to estimate precipitation scavenging and dry deposition of particles and gases. The precipitation scavenging formulae are appropriate both for in- and below-cloud scavenging and comparisons with data indicate the importance of accounting for aerosol particle growth by water vapor condensation and attachment of the pollutant to plume or cloud particles. It is suggested that both wet and dry removal of gases is usually dictated by other than atmospheric processes. Dry deposition of particles to a canopy is shown to depend on canopy height, biomass, vegetative type and mean wind. Two large-scale practical problems are addressed dealing with the relative importance of wet and dry deposition and with the sources which contribute to deposition in a specific location.

Essentially all air pollution is eventually cleansed from the atmosphere by the natural processes generally referred to as precipitation scavenging and dry deposition. The purpose of this report is to present formulae which can be used to approximately describe these cleansing processes. Within the details of the development of these formulae, some unifying features may not be apparent and it may be worthwhile to mention them here. One is that in all cases, whether the removal is by rain, snow, grass, leaves, water surfaces or whatever, the efficiency with which the pollutant is removed from an air stream by an obstacle must be considered. This collection efficiency is usually written as the product of a collision efficiency, defined in Figure 1, multiplied by a retention efficiency. In most cases, out of ignorance, the retention efficiency will be taken to be unity although some comments will be made about the retention of aerosol particles by vegetation and the desorption of gases from liquids. A second unifying feature is that after a collection efficiency has been obtained, it is necessary to sum over all collecting elements to obtain an overall removal rate and usually these integrals must be rather severely

DEFINITIONS



EFFICIENCIES: COLLISION, $E = A_C/A_X$

RETENTION, ϵ

COLLECTION $= \epsilon E$

COLLECTION RATE $= \epsilon E A_X v_\infty X_\infty$

COLLECTION FLUX $= \epsilon E v_\infty X_\infty A_X/A_S$

NORMALIZED COLLECTION FLUX $= \epsilon E A_X/A_S$

Figure 1. Some definitions. In the sequel the retention efficiency will be taken to be unity.

approximated. A third feature, one that is only beginning to become apparent, is that with further study into the removal processes (accounting for effects such as aerosol particle growth, foliage density within canopies, etc.) the removal rates tend toward simple and rather obvious results, in a sense frustrating the substantial effort devoted to unraveling the complexities. In the closing section of this report some practical applications will be discussed for a few problems which are of current interest. A list of symbols is included as an appendix.

A. PRECIPITATION SCAVENGING OF AEROSOL PARTICLES

By precipitation scavenging or washout is meant the removal of a pollutant from the atmosphere by various types of precipitation such as rain, snow, etc. The obvious abbreviations, rainout, snowout, etc., are also used.* Sometimes it is convenient to distinguish below-cloud scavenging from in-cloud scavenging if the elevation of the pollutant is clearly below or above, respectively, the cloud base. The formulae to be developed are applicable to both cases. The focus in this section will be on washout of particles; then some of the complications associated with gas washout will be mentioned.

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*Readers familiar with earlier precipitation scavenging literature might notice the change in terminology here, recommended at the 1974 International Precipitation Scavenging Meeting. For further details see Slinn (1975a).

1. GENERAL FORMULATION

To describe aerosol particle washout it is convenient to start from a general formulation. Let χda be the amount of contaminant per unit volume associated with particles of radii a to a + da (viz., "a-particles"). Then the evolution of this contaminant is governed by a continuity equation:

$$\frac{D\chi}{Dt} = \nabla\cdot(K\cdot\nabla\chi) - \psi\chi + G\chi - L(\chi) \tag{1}$$

where $D/Dt = \partial/\partial t + \vec{v}\cdot\nabla$ is the usual total time derivative; $\vec{v}$ is the wind field of the air, assumed incompressible; K is the turbulent diffusivity (or, more generally, $K\cdot\nabla\chi$ symbolizes the turbulent flux); ψ is the precipitation scavenging (or washout) rate coefficient; and G and L symbolize gain and loss of contaminant associated with a-particles because of condensation, evaporation, coagulation, etc. Dry deposition could also enter here but it is more convenient to, and later we will, treat it as a boundary condition.

One way to temporarily avoid the many complications in (1) is to take various averages or moments. Thus, if (1) is averaged over all particle sizes it becomes

$$\frac{D\chi_t}{Dt} = \nabla\cdot(K\cdot\nabla\chi_t) - \bar{\psi}(\vec{r},t)\chi_t \tag{2}$$

where the total contaminant density is

$$\chi_t = \int_0^\infty da\chi(\vec{r},t;a) \tag{3}$$

and the particle-average removal rate is

$$\bar{\psi}(\vec{r},t) = \int_0^\infty da\psi(\vec{r},t;a)\chi/\chi_t. \tag{4}$$

To obtain (2) from (1) it has been assumed that turbulence acts on all particles similarly and use has been made of the observation that in all processes contributing to G and L, the contaminant is not lost from the space volume. In turn, if (2) is integrated over a large enough volume of space so that no contaminant is convected from the volume by the wind, then use of the divergence theorem (and $\nabla\cdot\vec{v} = 0$) leads to

$$\frac{\partial Q_t}{\partial t} = -\langle\bar{\psi}(t)\rangle Q_t \tag{5}$$

where the total amount of contaminant present is

$$Q_t = \int d\vec{r}\chi_t(\vec{r},t) \tag{6}$$

and the space- and particle-average removal rate is

$$\langle \bar{\psi}(t) \rangle = \int d\vec{r} \bar{\psi}(\vec{r},t) \chi_t(\vec{r},t)/Q_t. \tag{7}$$

For the case that $\langle \bar{\psi} \rangle$ is time independent then the solution to (5) is

$$Q_t = Q_{t_0} \exp\{-\langle \bar{\psi} \rangle t\} \tag{8}$$

which is a familiar expression used in precipitation scavenging studies.

That the above formalism only temporarily avoids the complexities of (1) is seen when one attempts to evaluate analytically the average removal rates $\bar{\psi}$ or $\langle \bar{\psi} \rangle$; clearly $\psi(\vec{r},a,t)$ and $\chi(\vec{r},a,t)$ must be known. Presumably ψ can be specified (see below) but to obtain χ, apparently (1) must be solved. But if (1) could be solved, there would be no need for the development from (2) to (8). To extricate us from this circuitous development and yet to utilize these coarser descriptions of scavenging, a number of approximations for χ will be introduced. First, though, it is useful to see the accuracy to which ψ can be specified.

2. REMOVAL RATES FOR PARTICLES BY RAIN AND SNOW

Consider first rain scavenging (viz., rainout) of particles. Let the number of a-particles per unit volume be $n(a;\vec{r},t)da$. Then the number of these particles removed per unit volume during dt by drops of radii R to R + dR is

$$N(R)dR\pi R^2 E(a,R) v_t(R) dt \; n(a)da \tag{9}$$

where $N(R)$ is the number distribution function for the raindrops, $v_t(R)$ is their terminal velocity and $E(a,R)$ is the collection efficiency (the collision efficiency multiplied by retention efficiency which herein will be taken to be unity). A suggested semi-empirical expression for the collection efficiency, which accounts for particle diffusion, interception, and inertial impaction, is (Slinn, 1975b)

$$E(a,R) = \frac{4}{Pe}\left[1 + 0.4\, Re^{1/2} Sc^{1/3}\right] + 4K\left[K + \frac{(1 + 2VK)}{(1 + VRe^{-1/2})}\right] + \left[\frac{s - s_*}{s + c}\right]^{3/2} \tag{10}$$

where the symbols are defined in the appendix. Figure 2 shows a plot of (10) with some experimental data.

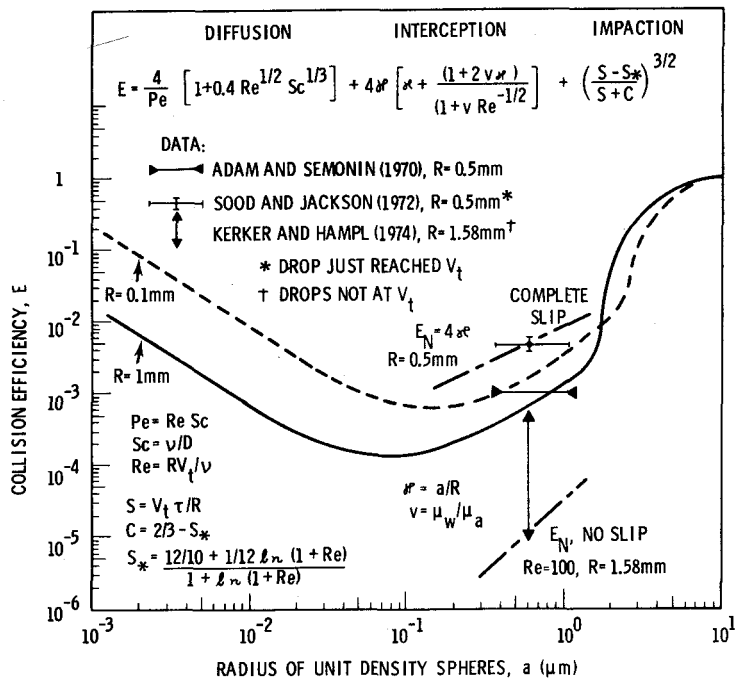

Figure 2. The proposed semi-empirical expression (10) for the collision efficiency between drops and particles as a function of particle size and accounting for diffusion, interception and inertial impaction. See Slinn (1974b) for a possible explanation of the scatter in the data for particles of radii ∿0.5 μm. The diffusion and impaction portions of the curves have sufficient experimental support to consider the corresponding expressions reliable to within a factor of 2 or 3.

The rain scavenging rate is found by integrating (9) with (10) over all drop sizes:

$$\psi_r(a) = \int_0^\infty dR\ N(R) v_t(R) \pi R^2 E(a,R). \tag{11}$$

By comparing (11) with the expression for the rainfall rate

$$p = \int_0^\infty dR\ N(R) v_t(R)\ \frac{4}{3}\pi R^3 \tag{12}$$

and appreciating some of the many uncertainties in the rain scavenging problem (Slinn, 1975b), the author suggests the approximation to (11):

$$\psi_r(a) \simeq \frac{p(\vec{r},t)}{2R_m} E(a,R_m) \qquad (13)$$

where the possible dependence of rainfall rate on position (especially on height within clouds) and on time has been made explicit. In (13), R_m is the volume-mean drop diameter which usually is related to rainfall rate, e.g., for steady frontal rain

$$R_m = 0.35\text{mm}(p/1\text{mm hr}^{-1})^{1/4}. \qquad (14)$$

There is little field data available to evaluate the particle size dependence of ψ_r as given by (13). What data there is, shown in Figure 3, obtained in a plume, 10^3 seconds downwind from a Kraft-process

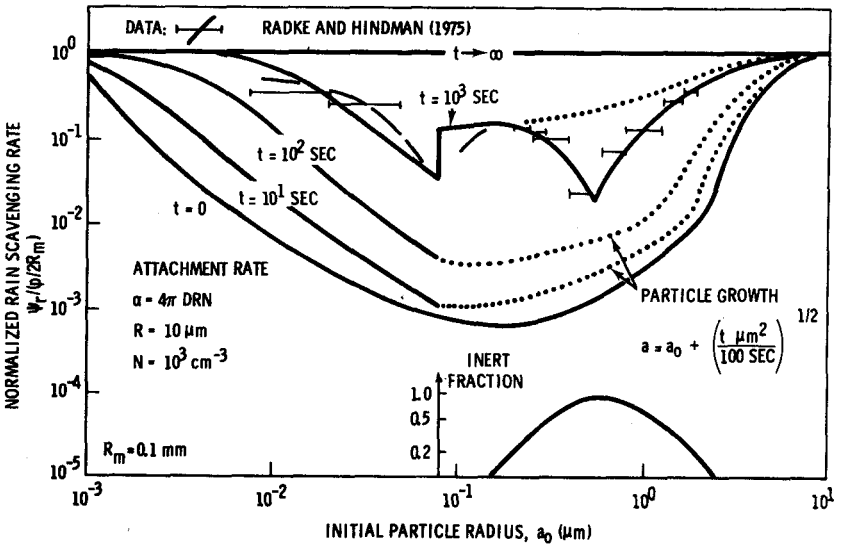

Figure 3. A comparison of the predictions from Equation (13) with experimental data obtained by Radke et al. (1975). Particles smaller than 0.16 μm are assumed to attach to plume droplets (E = 1) at the rate shown. The dotted curve (••••) is obtained assuming that all particles larger than 0.16 μm diameter grow by water vapor condensation, at the rate shown. The solid curve (——) for t = 10^3 seconds is obtained assuming that only some of the particles larger than 0.16 μm grow by water vapor condensation. The inert (non growing) fraction is shown in the inset.

paper mill by Radke et al. (1975) seems to demonstrate the importance of accounting for changes in particle size because of attachment of the particles to plume droplets (and similarly to cloud particles, Slinn, 1974a) and because of water vapor condensation.

In the case of scavenging by ice crystals (viz., snow scavenging or snowout) then the approximations for the removal rate must at the present time be even cruder than those introduced above for rain scavenging. Elsewhere (Slinn, 1975b) the author has suggested

$$\psi_s(\vec{r},t;a) \simeq (10^6 \text{cm/sec}^2)\, \frac{p(\vec{r},t)}{\langle v_t^2 \rangle}\, \mathcal{E}(a,\ell) \qquad (15)$$

where p is the precipitation rate (in rainwater equivalent); $\langle v_t \rangle$ is the average settling speed of the snowflakes; and $\mathcal{E}(a,\ell)$ is the particle/ice crystal collection efficiency in which ℓ is a characteristic dimension of the collecting element in the ice crystal, not necessarily related to the overall size of the ice crystal. A suggestion for $\mathcal{E}$ along with essentially all available data is shown in Figure 4. Calculations based

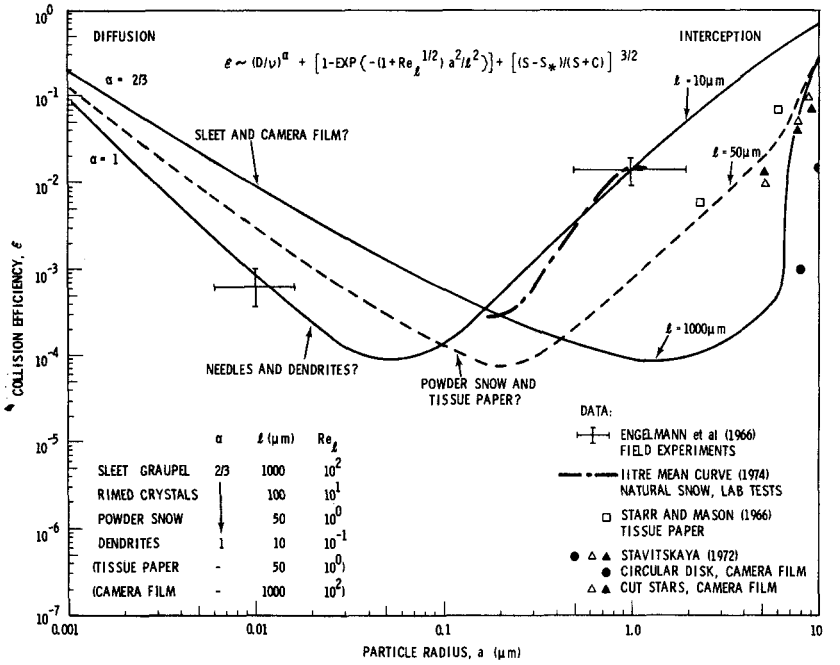

Figure 4. A tentative suggestion for the collision efficiency for particles by snow.

on (15) with data for v_t from Mason (1971) and with $\mathcal{E} = 1$ are shown in Figure 5, as well as some fits to data.

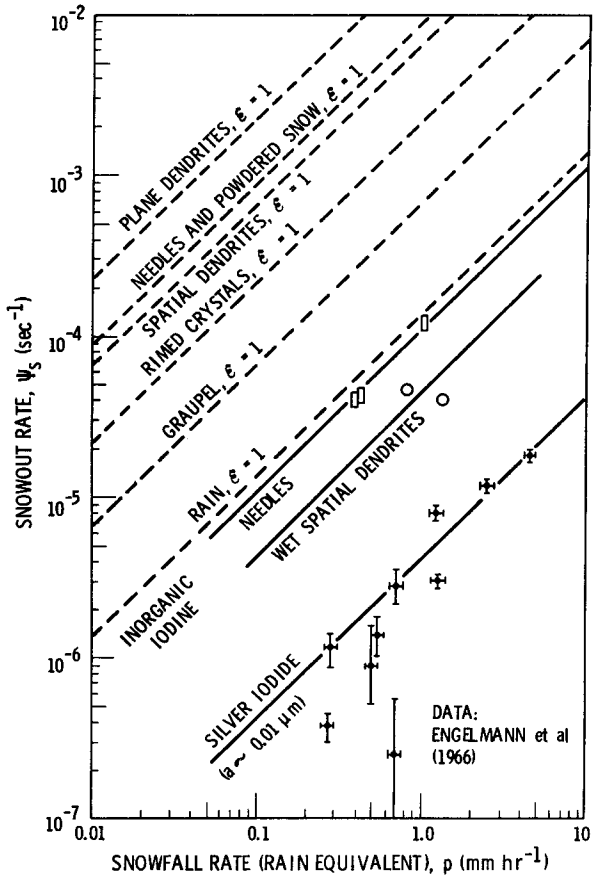

Figure 5. The snowout rate as a function of precipitation intensity as given by (15). The top curves, with $\mathcal{E} = 1$, show the influence of crystal type. The $\mathcal{E}$ values chosen to fit Engelmann et al's. (1966) data were: $\mathcal{E} = 1.3 \times 10^{-2}$ for process-plant iodine scavenged by needles and $\mathcal{E} = 6 \times 10^{-4}$ for AgI particles scavenged by various crystal types, usually powdered snow or spatial dendrites.

3. APPROXIMATIONS FOR PARTICLE- AND SPACE-AVERAGE REMOVAL RATES

Returning now to expressions (4) and (7) for the particle- and space-average removal rates, respectively, it is seen that fairly crude approximations to the air concentration χ would be consistent with the crudeness to which the removal rates, (13) and (15), are known. It should also be mentioned that usually the turbulent diffusion of the contaminant is not known very precisely, rarely to within a factor of two. Here the following approximations are introduced:

• For each chemical species of aerosol present, three portions of the size spectrum are identified, qualitatively as shown in Figure 6 and labelled χ_f (free), χ_g (growing) and χ_h (hosted). Thus

$$\chi = \chi_f + \chi_g + \chi_h \tag{16}$$

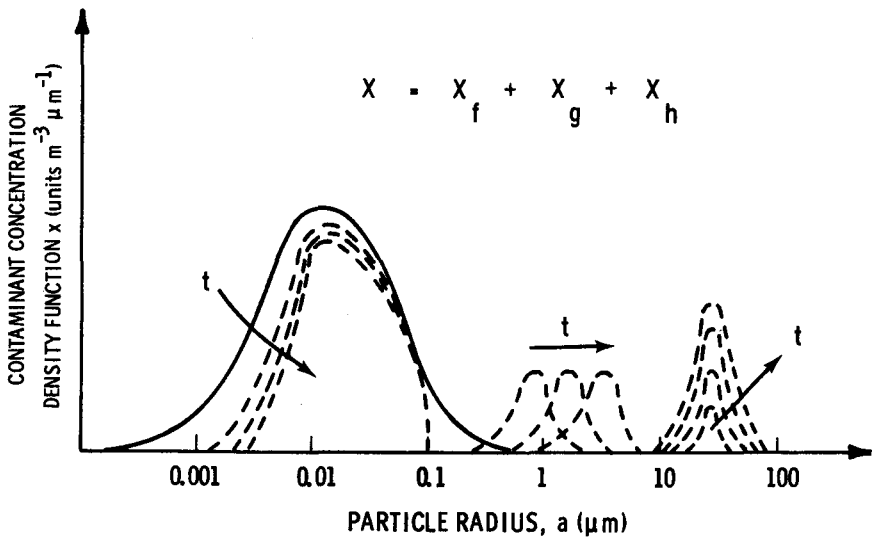

Figure 6. A schematic illustration of the contaminant's assumed distribution among the three particle classes (free, growing and hosted) and their time evolution.

• The evolution of the free particles is approximately governed by

$$\frac{D\chi_f}{Dt} = \nabla\cdot(K\cdot\nabla\chi_f) - \alpha\chi_f - \psi_f\chi_f \qquad (17)$$

where α is the attachment rate, and it is assumed that an adequate approximation to the solution of (17) is

$$\chi_f = \dot{q}_f(a)P(\vec{r},t;K,\vec{v})\ \exp\{-\int_0^s(\alpha + \psi_f)d\tau\} \qquad (18)$$

where $\dot{q}_f(a)da$ is the number of free a-particles released per second, P is some plume model and s is either t or $x/\bar{u}$. Similar approximate solutions are assumed for χ_g and χ_h.

• The radius of the growing particles is assumed known and the host particles (e.g., plume or cloud drops) are assumed to possess the same radius, λ.

• The particle size distribution of χ_f, χ_g and χ_h are assumed to be log normal and integrals over particle sizes are approximated by evaluating the integrands at their mean value.

• It is assumed that the contaminant is distributed among the particles according to

$$\chi(a) = ca^j n(a) \qquad (19)$$

where c is an obvious normalization constant and, for example, j = 3 if the contaminant is just the mass of the particles.

If these approximations and assumptions are used in (4) then the particle-average rainout rate becomes, approximately,

$$\bar{\psi}_r = \frac{P}{2R_m}\left[F_{fo}\exp\{-\int_0^s(\bar{\alpha}+\bar{\psi}_f-\bar{\psi}_r)ds\}\,E(a_{fj},R_m)\right.$$

$$+F_{go}\exp\{-\int_0^s(\bar{\psi}_g-\bar{\psi}_r)ds\}\,E(a_{gj},R_m)+\frac{\bar{\alpha}}{(\bar{\alpha}+\bar{\psi}_f-\bar{\psi}_h)}F_{fo}$$

$$\left.\cdot[\exp\{-\int_0^s(\bar{\psi}_h-\bar{\psi}_r)ds\}-\exp\{-\int_0^s(\bar{\alpha}+\bar{\psi}_f-\bar{\psi}_r)ds\}]\,E(\lambda,R_m)\right] \tag{20}$$

where F_{fo} and $F_{go} = 1 - F_{fo}$ are the initial fractions of the contaminant associated with free and growing particles, respectively, and where

$$a_j = \bar{a}\exp\{(j+\tfrac{1}{2})\sigma^2\} \tag{21}$$

in which $\bar{a}$ is the geometric mean (number) radius and $\sigma = \ell n\bar{\sigma}$ where $\bar{\sigma}$ is the geometric standard deviation, each for the specific class of aerosol. For small time (i.e., for $\bar{\psi}_r t << 1$) or if the difference between any ψ_i and ψ_r is small, for a time independent attachment rate and for j = 3, then (20) with s = t simplifies to the transparent expression for the mass rainout rate

$$\bar{\psi}_r = \frac{P}{2R_m}\left[F_{fo}\exp\{-\bar{\alpha}t\}\,E\{\bar{a}_f\exp(\tfrac{7}{2}\sigma_f^2),R_m\}\right.$$

$$+F_{go}E\{\bar{a}_{go}\exp(\tfrac{7}{2}\sigma_g^2)+(\frac{t\ \mu m^2}{100\ sec})^{1/2},R_m\}$$

$$\left.+F_{fo}\{1-\exp(-\bar{\alpha}t)\}E(\lambda,R_m)\right] \tag{22}$$

in which a specific, particle growth rate has been assumed. Equation (22) is plotted in Figure 7 for the case of the parameters shown and demonstrates the rapid increase in the mass rainout rate both with time and with an increase in the polydispersity of the aerosol (viz $\bar{\sigma}$). For further details on this latter point see Dana and Hales (1975). Expressions similar to (20) and (22) are suggested for snow scavenging; the differences being only in the term outside the braces, [ ], see (15), and with E replaced by $\mathcal{E}$.

There is not yet available sufficient data to test this formulation. Figure 8 shows that data obtained by Burtsev et al. (1970) for the

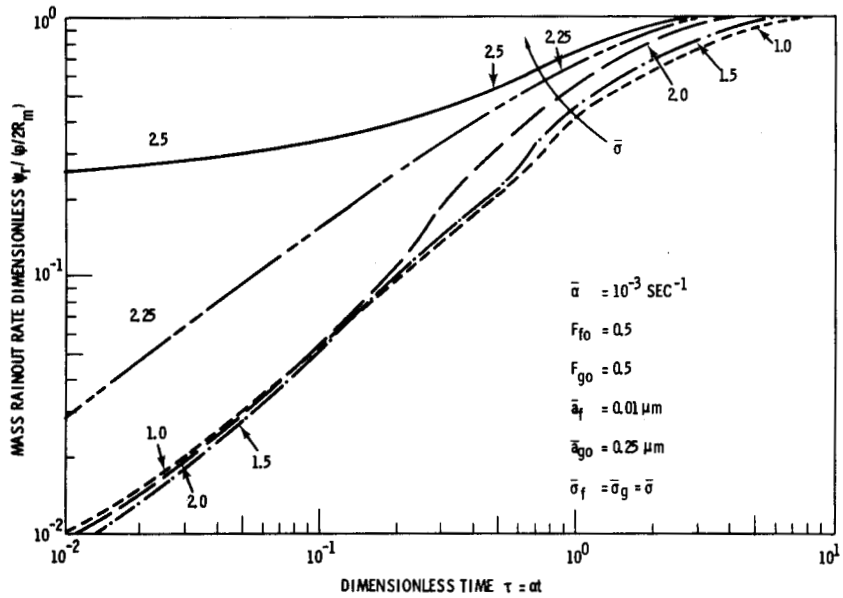

Figure 7. An illustrative example of Equation (22) for the choice of the parameters shown, which illustrates the strong dependence of the mass average removal rate on the polydispersity of the aerosol (reflected in $\bar{\sigma}$) and on the time for attachment and condensational growth.

incloud (convective storm) scavenging of a radioactively tagged aerosol with $\bar{a}$ near 0.1 μm, can be approximately fit ignoring attachment, assuming all particles acted as condensation nuclei and in the available time, grew to about 10 μm diameter drops. The data obtained by Dana and Wolf (1968, 1969, 1970), Figure 9, for removal of total aerosol mass downwind of an 8m tower release, suggests that the soluble tracer did not possess its dry-size when scavenged ($\bar{\sigma}$ is not given) and that a significant portion of the tracer dry deposited in the samplers (Dana, 1972; Slinn, 1974b, 1975b).

To obtain the particle- and space-average removal rates obviously some information is needed about the spatial distribution of the pollutant. Thus for rain scavenging (and similarly for snow scavenging) (7) becomes

$$\langle \bar{\psi} \rangle = \frac{1}{Q_t} \int d\vec{r} \, \frac{p(\vec{r},t)}{2R_m} \, [E] \chi_t(\vec{r},t) \tag{23}$$

where [E] represents the term in braces, [ ], in (20), and similarly for snow. If there is some desire to identify the separate contributions from below-cloud (b.c.) and from in-cloud (i.c.) scavenging, then obviously (23) becomes

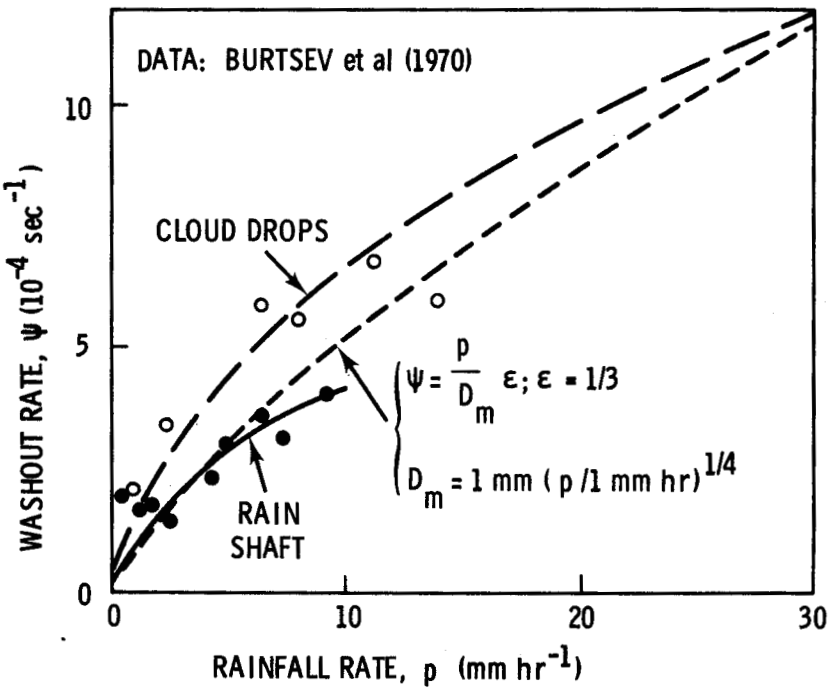

Figure 8. A comparison of theory with experimental data obtained by Burtsev et al. (1970) for the in-cloud scavenging of tracer released into the top of the rain shaft (solid curve) and into the region of "cloud drops" (dashed curve) of a cumulonimbus cloud. The "cloud drops" case probably corresponds to the region of maximum radar reflectivity and it is noted that Burtsev et al.'s description seems to imply that they released AgI seeding material, simultaneously with the release of their radioactively tagged aerosol.

$$\langle\bar{\psi}\rangle = \left(\frac{p}{2R_m}\right)_0 [E]f_{b.c.} + \left\langle\frac{p(z)}{2R_m(z)}\ [E]f\right\rangle_{i.c.} \qquad (24)$$

where f represents the fraction of the contaminant in each location and where it is assumed to be adequate to set the below-cloud values of p and R_m equal to their ground-level values, subscript zero.

It is more useful to obtain estimates for washout ratios, defined as the ratio of the contaminant's concentration in surface level precipitation, κ_0, to its concentration in surface level air, χ_{to}. To obtain this ratio it is noted that the rate of contaminant removal per unit volume is $\bar{\psi}\chi_t$. If the contaminant is distributed fairly uniformly horizontally, then the flux of contaminant to the earth's surface is

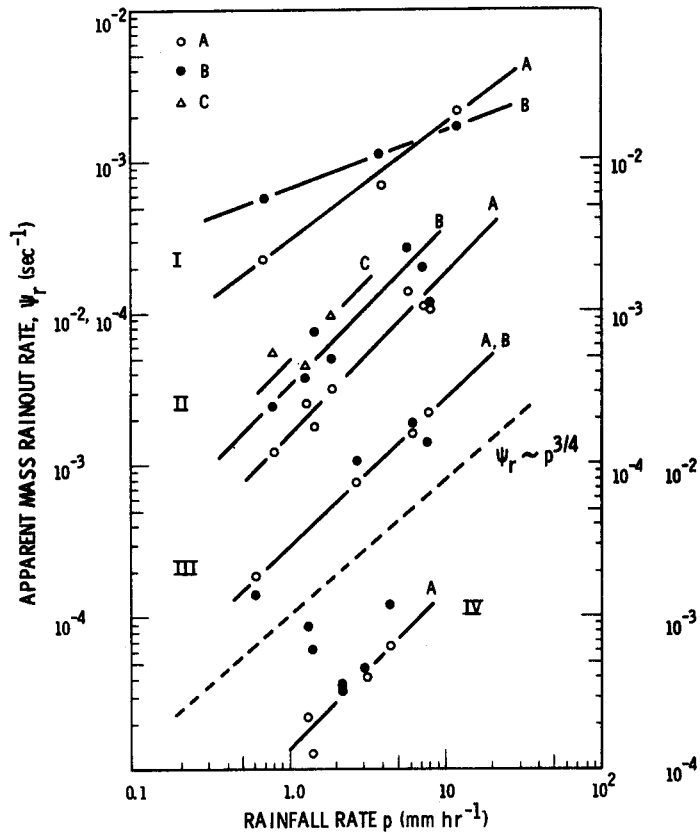

Figure 9. The apparent mass rainout measured during fairly steady rain by Dana and Wolf (1968, 69, 70). A, B and C are arc locations 50, 100 and 150 feet downwind from the release from a 26-foot tower. I: (left-hand ordinate) rhodamine particles, mmd = 11.2 μm; II: (right-hand ordinate) fluorescein particles, mean $a^2\rho_p$ = 35 μm^2 g cm^{-3}; III: (left-hand ordinate) rhodamine particles, mmd = 12. μm; IV: (right-hand ordinate) rhodamine particles, mmd = 4.8 μm.

$\int \bar{\psi}\chi_t dz$. The flux of precipitation to the surface is p_0. Therefore the washout ratio is

$$\frac{\kappa_0}{\chi_{to}} = \frac{1}{p_0 \chi_{to}} \int_{H_1}^{H_2} \bar{\psi}\chi_t dz \qquad (25)$$

where $H_2 - H_1$ spans the heights from which the contaminant is removed.

As with (23), the vertical distribution of χ_t is needed before (25) can be evaluated.

For some special cases, approximations to (25) should be fairly reliable. For example, if the pollutant's concentration is reasonably uniform and essentially constrained within the atmosphere's mixed layer, beneath the cloud base, then for this case of sub-cloud scavenging (25) with (20) or (22), and similarly for snow, leads to

$$\left(\frac{\kappa}{\chi_t}\right)_0 = \frac{[E]\ h}{2R_m} \tag{26}$$

where h is the height of the mixed layer and it is assumed that the mean drop size is invariant beneath the cloud. Another case of interest is if the pollutant is "vacuumed" from the mixed layer by a convective cloud; then one also obtains (26), but in this case, h represents the poorly known height interval $H_2 - H_1$ from which the pollutant is effectively removed. In this case, usually below-cloud scavenging could be ignored, but it would be essential to account for particle growth with E[a(t)].

Although a limited quantity of field data is available, some comparisons with theory are possible. It is seen from (26) that $(\kappa/\chi_t)_o$ is essentially independent of rainfall rate except for R_m's dependence on p. This result is well substantiated by field data (Mahkon'ko et al, 1970; Engelmann, 1970; Gatz, 1975). Figure 10 shows that the magnitude and the particle size dependence of the washout ratios for convective storms as found by Gatz (1975) are reasonably well described by (26), given that neither $\bar{\sigma}$ nor duration of condensational growth is known. For frontal storms, with the typically longer growth times available, one would expect to see less dependence on particle size and indeed one would expect $[E] \to 1$ for most particles (Slinn, 1974a). In this case $(h/2R_m)$ would reflect solely the efficiency with which cloud water is removed from the storm, which usually is the range from 10 to 90%.

B. WET AND DRY REMOVAL OF GASES

In the above, the focus was on wet removal of particles. Here it will be on gases, and it will be seen that there are common simplifying features for both wet and dry removal of gases. In addition, though, there are common features that make predictions extremely difficult, requiring the analysis of a host of interacting chemical reactions. This is generally beyond the present capabilities of the author and therefore will be avoided. The emphasis here will be on the simple aspects of the problem.

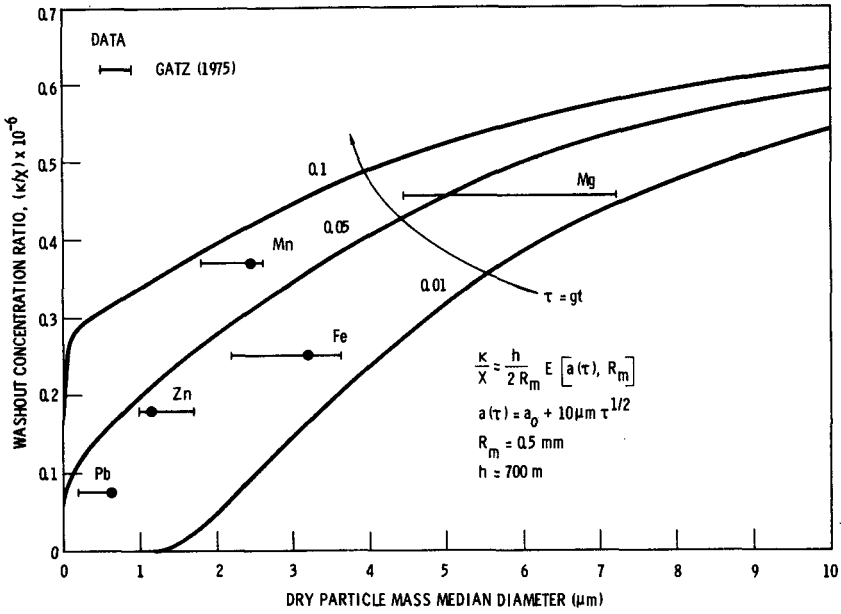

Figure 10. A comparison of predictions of Eq. (26) with the average washout ratios measured by Gatz (1975). The horizontal bars on the data reflect the different mass median diameters (mmd's) found in different cities; the dot on the bar is the mmd measured in the city (St. Louis) near which the washout ratios were measured. τ is nondimensionalized time; g is the unknown particle growth rate; a_o is the dry particle mass median radius, i.e., 1/2 the mmd as given on the abscissa. The choice of the depth of the scavenged volume $h = H_2 - H_1$, was made solely to improve the fit to the data.

Rain scavenging of gases will be considered first. Snow scavenging of gases can generally be ignored unless the gas is dissolved in plume or cloud drops, as appears to be the case for the iodine data shown in Figure 5, or unless the snow is partially melted. Here an impoverished version of the general theory of gas washout (Hales, 1972) will be considered; nevertheless the results obtained are sufficient, with guidance from the general theory, to illustrate the features considered most significant. After these have been presented, a few features of dry deposition of gases will be illustrated.

1. RAIN SCAVENGING OF GASES

For scavenging of gases by rain an expression similar to (1) for each drop size could be written and then integrated over all drop sizes to obtain a total removal rate (Slinn, 1974c); however in most cases

this much detail is not needed as will now be demonstrated. It is assumed here that gas captured by a drop is quickly, well mixed throughout the drop, either because of internal circulation within a large ($\gtrsim$ 1 mm) drop, or because of the relatively small volume-to-surface ratio of a small drop. Let the concentration of the pollutant gas in the drop be c (e.g., in moles ℓ^{-1}). If irreversible chemical reactions during the short raindrop-flight time are ignored, then the gas concentration changes according to

$$v_t \frac{d}{dz}\left(\frac{4}{3}\pi R^3 c\right) = \frac{D}{R}\left[1 + 0.4\ Re^{1/2}Sc^{1/3}\right] 4\pi R^2 (c_{eq} - c) \qquad (27)$$

where the ventilation term (in the [ ] braces) is as in (10) and c_{eq} is the equilibrium concentration of the gas in the drop for the existing air concentration, χ. For some gases, $c_{eq} = H\chi$, where H is Henry's law constant. It is noted in (27) that the driving force is the difference between c_{eq} and the actual concentration, c. For $c > c_{eq}$ the gas can be desorbed from the drop which can lead to some interesting phenomena when drops fall through a distinct plume (Hales, 1972; Slinn, 1974c).

But of more interest here is for the case of a gas fairly uniformly distributed in the atmospheric mixed layer. From (27) it is seen that the e-fold equilibration length is

$$\lambda = \frac{R}{3} \frac{Re}{\left[1 + 0.4\ Re^{1/2}Sc^{1/3}\right]} \qquad (28)$$

Supplying reasonable numerical values in (28) shows that typically, $\lambda = O(1m)$; that is, typically the concentration of the gas in the drop relatively rapidly attains its equilibrium concentration, c_{eq}. This equilibration length scale is of course longer for the unrealistic assumption of a stagnant drop, but even then the time is typically less than 10 seconds (Postma, 1970; Hales, 1972). Consequently, and especially for gases well-mixed in an atmospheric mixed layer whose depth is usually 100 to 1000m, it is reasonable to assume $c = c_{eq}$. This is the simplification alluded to earlier.

The complication is to specify c_{eq}, usually for gases at low air concentrations and usually in drops containing many other impurities. This is the chemistry problem mentioned earlier. Useful discussions and calculations for SO_2, I_2, CO_2 and NH_3 in relatively pure water are given in Junge, 1963; Postma, 1970; and Hales, 1972. However, considering the complications caused by other contaminants, it appears that the best procedure is to measure c_{eq} found in collected rainwater. Here, too, there are problems especially because of simultaneous dry deposition of gases in the rainwater collector and because of the possible desorption of the gas from the water. The latter problem can be and has been overcome in field studies by adding various fixing agents, but then it quickly becomes apparent that to assess the true deposition of gases, the addition of chemical fixing agents is

undesirable since desorption of gases from runoff water may be quite typical. Thus it can be seen that the study of wet removal of gases must give consideration to simultaneous dry deposition and chemical reactions within the ground water. This is considered now and later a few comments will be made attempting to unify the discussion of both wet and dry removal of gases.

2. DRY TRANSPORT OF GASES THROUGH THE ATMOSPHERE

In the case of wet deposition, one usually ignores the transport of the pollution through the atmosphere since obviously the pollution is transported by the precipitation. Further comments on this will be made later in the section dealing with macroscale processes. However, in the case of dry deposition it is essential to evaluate transport through the atmosphere by diffusion since sometimes this can be the rate-limiting stage of the entire dry deposition process. For example, for pollution released from a tall stack on a very stable day, the pollution may not reach the earth's surface for more than 100 km. As interesting as this aspect of the problem is, here it will be ignored. It will be assumed that through the use of some diffusion formula (e.g., Slade, 1968) the near-surface-level air concentration of the pollution (gas or particles) is known. We now address the question: given the pollutant's concentration near the surface collectors (i.e., in the usually, well-mixed, turbulent boundary layer) what is the dry flux to the collectors?

As in the case of wet deposition of gases, the dry deposition flux of gases is usually dictated by the chemistry of dissolution rather than by physical processes in the atmosphere. To see this we review here Chamberlain's (1966) estimate of the flux which the atmosphere can deliver to the surface. It is convenient to write this flux as proportional to the ground-level (or 2 m) air concentration χ_o; the proportionality constant is known as the deposition velocity, v_d. An upper bound (maximum possible value) for v_d is found from an analogy with the momentum flux to the surface, i.e., τ, also written as ρu_*^2 where u_* is known as the friction velocity. The "concentration" of momentum at the 2m height is $\rho\bar{u}_{2m}$. Then a "deposition velocity" for momentum can be written as $\rho u_*^2/(\rho\bar{u}_{2m}) = u_*^2/\bar{u}_{2m}$. Invoking Reynold's analogy, which is strictly appropriate only for smooth surfaces since there is no mass transfer analogy to form (or pressure) drag, we obtain an upper bound for the deposition velocity for a completely-absorbed gas,

$$v_d = u_*^2/\bar{u}_{2m} \tag{29}$$

Typically, with $u_* = 25$ cm sec^{-1} and $\bar{u}_{2m} = 1$ m sec^{-1}, then $u_*^2/\bar{u}_{2m} = 5$ cm sec^{-1}. Actually, since $\bar{u}$ depends linearly on u_* (or v.v.) and both u_* and the roughness height are not nearly so convenient parameters as $\bar{u}$, it is more convenient and may be sufficiently accurate to approximate (29) by

$$v_d = 5 \text{ cm sec}^{-1} \; [\bar{u}_{2m}/1 \text{ m sec}^{-1}]. \tag{30}$$

3. RATE LIMITING PROCESSES FOR BOTH DRY AND WET DEPOSITION OF GASES

Experimental results indicate that the above deposition velocity is rarely attained except for very reactive gases such as I_2. 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 the ground water or the ground water's motion, or by passage of the gas through plant membranes. An extreme example of non-atmospheric rate limitation is for the noble gases whose deposition velocity is essentially zero. In the case of gas deposition to lakes or oceans then for reasonably reactive gases, the atmosphere may be rate-limiting since mixing in the water body may promote transfer in the sink. Liss and Slater's (1975) estimates lead them to conclude that the transport to the ocean of SO_2, NH_3, NO_2, SO_3, HCl are limited by atmospheric transport, whereas even to the ocean, the transport of gases such as N_2O, CO, CH_4, CCl_4, CCl_3F, MeI and $(Me)_2S$ are rate-limited by transport in the ocean.

A simple model for dry deposition of gases to a stationary water body (a simulation for soil moisture) may assist toward quantifying the above qualitative comments. With obvious approximations and assumptions, the problem is to solve

$$\frac{\partial \chi}{\partial t} = K \frac{\partial^2 \chi}{\partial z^2} \quad , \qquad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - kc \; ,$$

$$K \left.\frac{\partial \chi}{\partial z}\right|_{z=0} = D \left.\frac{\partial c}{\partial z}\right|_{z=0} \quad , \qquad c(0,t) = H_0 \chi(0,t) \tag{31}$$

where k is the rate at which the dissolved gas is irreversibly converted to a nonvolatile product and H_o is the overall partion coefficient, the ratio of the total gas in solution (including any ionized component) to the equilibrium air concentration (Postma, 1970). If the initial conditions are $\chi(z,o) = \chi_o$, $c(z,o) = o$ then the solution to the set of equations (31) can be easily found using Laplace transform techniques and yields

$$\frac{v_d}{(K/\pi t)^{1/2}} = \frac{\beta^{1/2} e^{-\kappa} - 1}{\beta - 1} + \frac{\beta(\pi\kappa)^{1/2}}{(\beta - 1)^{3/2}} \exp\{\kappa/(\beta - 1)\}$$

$$\cdot [\mathrm{erf}(\frac{\beta\kappa}{\beta - 1})^{1/2} - \mathrm{erf}(\frac{\kappa}{\beta - 1})^{1/2}] \qquad (32)$$

where $\kappa = kt$ and $\beta = K/(H_o^2 D)$. For $\beta = 1$ the rhs of (32) reduces to $[1 - \{1 - \exp(-\kappa)\}/(2\kappa)]$. For $\beta < 1$, (32) can be written in terms of Dawson's integral. Equation (32) is plotted in Figure 11 and

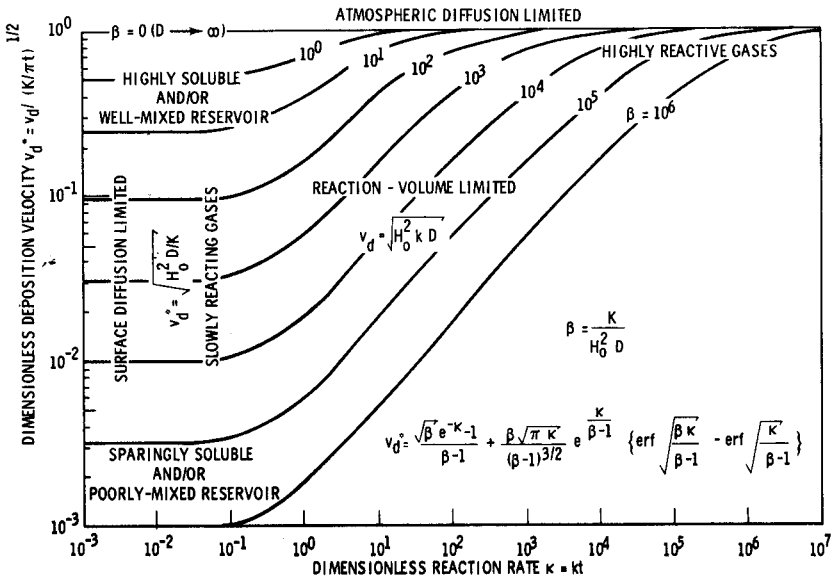

Figure 11. A plot of Eq. (32) which demonstrates that the dry deposition velocity for gases is frequently dictated by other than atmospheric phenomena.

demonstrates that dry deposition can be rate-limited by slow mixing in the ground water, low solubility, or slow reaction rate. The plot of (32) shown in Figure 12 suggests that the model may have some merit for the interpretation of dry deposition to vegetation.

In summary then, both for dry and wet deposition of gases, atmospheric considerations are usually of secondary importance. The atmosphere can deliver a flux of pollutant gas of about (5 cm sec^{-1}) ($\bar{u}$/1m sec^{-1}) χ_o, dry, and a flux of about $H_o \chi_o p$, wet, where p is the precipitation rate. If the sink will not accept this flux then the

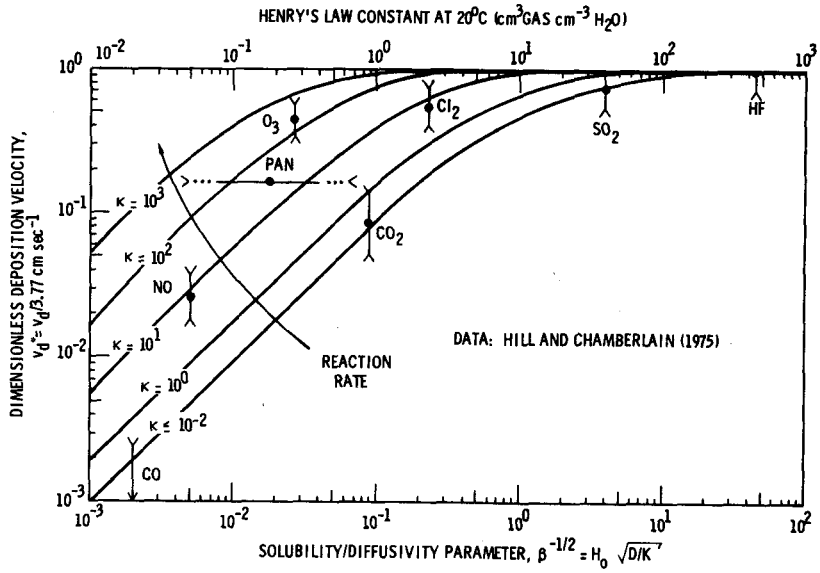

Figure 12. A second plot of Eq. (32), in this case with $\beta^{-1/2}$ on the lower abscissa and the reaction rate as a parameter. For a given diffusivity in the sink, D, and atmospheric diffusivity, K, then $\beta^{-1/2}$ is a constant multiplied by the overall partion coefficient, H_o, which in turn is proportional to the Henry's law constant. Consequently, by conveniently shifting the upper abscissa and normalizing the deposition velocities as measured by Hill and Chamberlain (1975) by their measured value for HF, it can be seen that the theory is capable of reflecting the measured data for the dry deposition of gases to alfalfa. The error bars on the data are subjectively estimated by the author.

process is rate-limited elsewhere than in the atmosphere, and it is therefore not an atmospheric problem. In this case the author must acknowledge his incompetence and leave the problem to soil scientists, biologists, etc., to unravel the complicated chemistry.

C. DRY DEPOSITION OF PARTICLES

Dry deposition of particles is somewhat simpler than gases because atmospheric transport is almost always rate-limiting. In addition, it is usually correct to assume that particles are not re-entrained into the atmosphere, unless the wind speeds are high as in a dust storm (Slinn, 1975c). Nevertheless the problem is complicated. Here results

will first be given for dry deposition of particles to a smooth surface, not because it is very significant to the practical problems of interest at this meeting, but because it is simpler and introduces fundamental concepts. Then a model for dry deposition to a canopy will be presented.

1. PARTICLE DEPOSITION ON A SMOOTH SURFACE

A new theory for dry deposition of particles from a turbulent fluid to a smooth surface was recently presented by the author (Slinn, 1975c); here it will only be outlined. This model rejects the "free-flight" model of Friedlander and Johnstone (1957) and its variations (e.g., Chamberlain, 1960; Davies, 1966) and instead develops Owens' (1969) suggestion that the particles finally reach the surface, convected by bursts of turbulence. Then the collection of particles by a surface depends on a collection efficiency similar to the collection efficiency for particles in a viscous jet impactor. From this picture and the definition of the deposition velocity as the flux to the surface divided by the (assumed constant) free-stream air concentration, one obtains the deposition velocity

$$v_d = v_s + 10^3 \frac{cm}{sec}\left(\frac{\dot{m}''}{1\ g\ cm^{-2}sec^{-1}}\right) + \frac{u_*^2}{\beta \bar{u}} E_j \qquad (33)$$

where v_s is the particle's settling velocity and the author suggests for the collection efficiency

$$E_j = 10^{-3/St} + \frac{\beta}{\gamma}(Sc)^{-0.6} \qquad (34)$$

in which $St = \tau u_*^2/\nu$ is the particle's Stokes number based on the characteristic velocity u_* and the viscous length scale ν/u_*. In (33), β and γ are empirical constants. The second term on the rhs of (33) accounts for a diffusiophoretic contribution to v_d (thermophoresis is usually negligible): $\dot{m}''$ (>o for condensation) is the water vapor mass flux.

Equation (33) is plotted in Figure 13, using $\beta = \gamma = 0.4$, and compared with some experimental data. For a polydisperse aerosol and contaminant distributed among the particles according to $ca^j n(a)$, then the contaminant flux is, of course, obtained by integrating (33), weighted by $a^j n(a)$, over all particle sizes. It would almost always be consistent with the accuracy of the model to approximate the resulting integral just by evaluating (33) at the particle size a_j given in (21). It might also be useful to mention that if u_* exceeds the threshold velocity shown in Figure 14, then even if the "sandblasting effect" of other particles is ignored (Slinn, 1975c), particles can be resuspended from the surface.

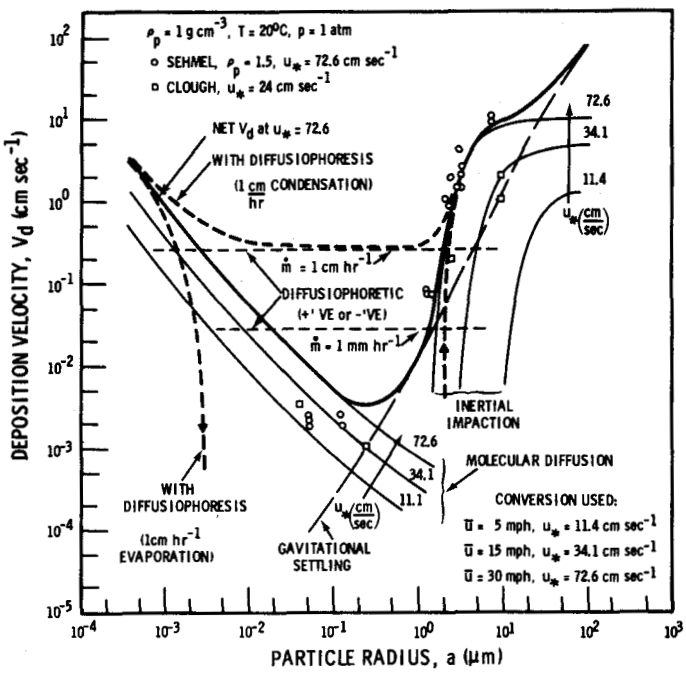

Figure 13. The deposition velocity as given by Eq. (33) with $\beta=\gamma= 0.4$ compared with experimental data. Notice that (33) is evaluated using a particle density, ρ_p = 1 g cm^{-3} whereas Sehmel's (1973) data is for particles with ρ_p = 1.5 g cm^{-3}. The water vapor mass flux $\dot{m}''$ has been divided by the density of water to give $\dot{m}$.

2. PARTICLE DEPOSITION IN A CANOPY

An outline of a new theory for dry deposition in a canopy, which emphasizes the canopy's filtration effect was given in Slinn (1975c). Here further details are developed. Figure 15 shows the assumed fluxes. From this picture there results the obvious steady-state continuity equation

$$\frac{\partial \chi_c}{\partial \chi} + \frac{(\alpha u_* + CH)}{\bar{u}_c H} \chi_c = (\alpha u_* - \frac{u_* E_j}{\bar{u}_g \beta}) \chi_B \qquad (35)$$

where C is the fraction of the a-particles filtered out per second by the canopy. If χ_B is a constant then (35) predicts an x- independent solution in a distance $O[\bar{u}H/(\alpha u_*+CH)]$ which is typically about 10 canopy heights. Then for x- independent conditions, (35) can easily be

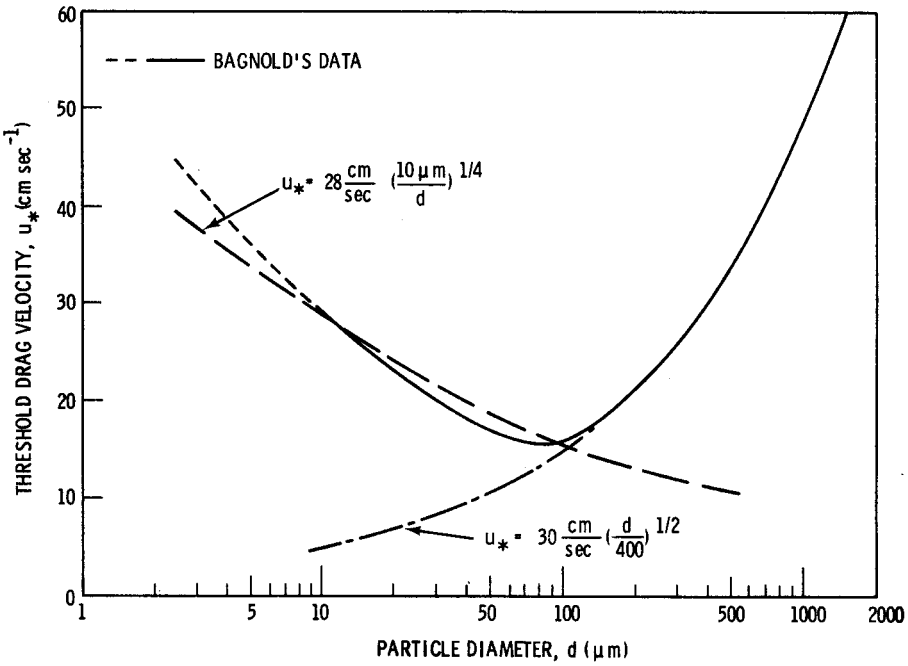

Figure 14. The critical friction velocity required to move monodisperse aerosol particles along a flat plate as measured by Bagnold (1960) and as fit with a semi-empirical theory (Slinn, 1975c). It should be noted that for a polydisperse aerosol, once some particles are set in motion then a sandblast effect occurs, moving many.

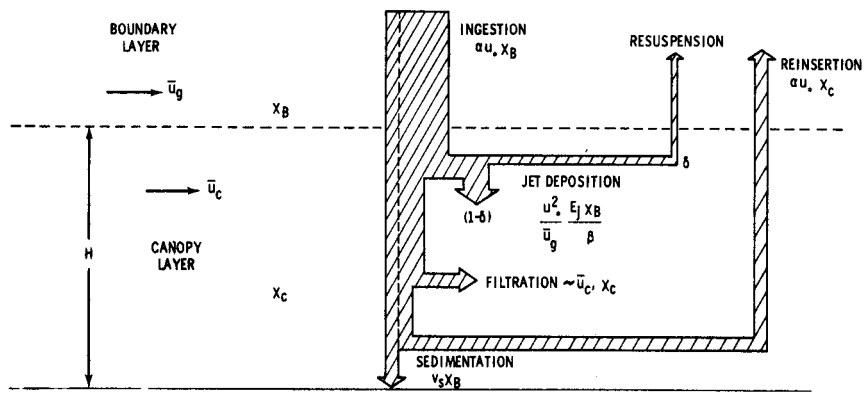

Figure 15. Assumed pollutant fluxes in a canopy.

solved to give χ_c in terms of χ_B. From this result, the deposition velocity, the net flux to the canopy divided by χ_B, becomes

$$v_d = v_s - \frac{\delta u_*^2 E_j}{\bar{u}_g \beta} + \frac{\alpha u_*}{\alpha u_* + CH}\left[CH + \frac{u_*^2 E_j}{\bar{u}_g \beta}\right] \tag{36}$$

This is essentially the same result as given in the earlier report (Slinn, 1975c).

Here some new results will be presented concerned with the canopies filtration efficiency. The amount of contaminant removed during dt by a single collector of cross-sectional area normal to the wind equal to A is $\bar{u}_c$ dt $A\mathbb{E}\chi_c$ where $\mathbb{E}$ is the collection efficiency. If the number of collectors, per unit volume, of cross-sectional area A to A+dA is N(A)dA then the total removal per unit volume during dt is

$$C\chi_c dt = \chi_c \int_{\substack{\text{all} \\ \text{collectors}}} \mathbb{E}\,\bar{u}_c dt \;\; AN(A)\; dA. \tag{37}$$

This integral would obviously be extremely difficult to evaluate for real canopies. Here it will be approximated as were the similar integrals in the precipitation scavenging problem. For vegetative canopies it is noted that the total biomass per unit volume is essentially

$$B = \bar{\rho} \int_{\substack{\text{all} \\ \text{collectors}}} \lambda AN(A)\; dA \tag{38}$$

where $\bar{\rho}$ is an average mass density of the foliage and λ is a typical length scale (e.g., radius) of individual fibers. $B/\bar{\rho}$ might be called a packing density. Upon comparing (37) and (38) it is suggested that the removal rate be approximated by

$$C = \frac{\bar{u}_c B}{\lambda \bar{\rho}}\,\mathbb{E}(a,\lambda) \tag{39}$$

which is to be used in (36).

Equation (36) with (39) is plotted in Figure 16 for the case of the parameters shown. The canopies filtration effect is governed by the parameter $\gamma = HB/\lambda\bar{\rho}$. To evaluate (39) the collection efficiency $\mathbb{E}$ was taken to be the same as for snowflakes, with the characteristic length scale λ = 1mm (see Figure 4). The rationale for the choice to use this collection efficiency is governed by two considerations. One is that the physical processes governing the collection in both cases (viz., Brownian diffusion, interception, inertial capture, etc.) are

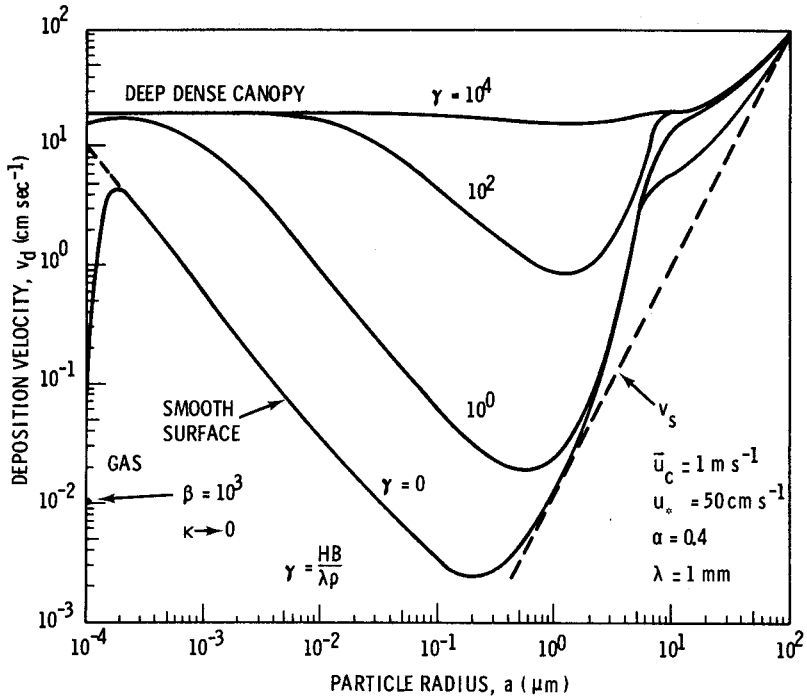

Figure 16. A plot of Eq. (36) with the removal rate given by (39), demonstrating a significant increase in deposition velocity for particles smaller than about 10 μm, with increases in canopy height, H or biomass, B. There is a similar increase of v_d with increasing wind speed within the canopy, $\bar{u}_c$. The increase in v_d with decreasing characteristic dimension of the collectors, λ, is even more dramatic because of the concomittant increase in the collection efficiency. At the left-hand side of the plot is qualitatively indicated the possible reduction in v_d for gases because of non-atmospheric effects. This reduction can be significantly less in a canopy (compare the dashed and solid portions of the $\gamma = 10^0$ curve) because of the increased collector area.

the same and therefore the collection efficiencies will be similar. The second consideration is that although the analogy almost certainly fails in detail, the general accuracy of the predictions are so crude as to tolerate inaccuracies in the specification of Ξ.

There is not yet available sufficient data to test (36) and to evaluate the parameters α, β, γ and δ. Nevertheless it can easily be

seen from (36) and (39) that the theory is consistent with the following experimental results:

- a linear increase and then saturation of v_d with $\bar{u}_c$ and H (Hill and Chamberlain, 1975).
- an increase of v_d with roughness height (Sehmel, 1975).
- an increase of v_d with biomass (Heinemann, et al., 1975).
- the reduction in v_d caused by resuspension (Chamberlain, 1967; Slinn, 1975c).

To account for the observed variations (Heinemann, et al., 1975) of v_d for gases as a function of humidity and biological activity (e.g., stomata openings), a reintroduction of the surface, rate-limiting arguments is needed. Such considerations lead to the reduction in v_d for gases, qualitatively as shown in Figure 16, using the results given in Figure 11 for the β of (32) equal to 10^3 and for $\kappa = 0$.

D. SOME APPLICATIONS

In this closing section use of the formulae given above for wet and dry deposition will be illustrated by applying them to two questions which are of current interest: What is the relative importance of wet and dry deposition? What sources contribute to pollutant deposition in a specific location? It might be noticed that these two questions generally deal with larger space and time scales then the "microphysical" scales with which this paper has so far been concerned; consequently a few remarks will be made about "macroscale" deposition processes. First, though, a few comments on philosophy of approach may be appropriate.

It is clear that the total problem of relating air pollution sources to resulting effects is extremely complex. Some links in the chain are: source characteristics, Q; pollutant transport and diffusion, P; chemical and physical transformations, T; wet and dry removal fluxes, F; resulting air concentrations, χ; fluxes to receptors, F; and details of various types of effects, E. It is noted that in this chain, Q-P-T-F-χ-F-E, wet and dry removal fluxes, F, enter in two places, and it might have been surmised from the previous sections where it was generally assumed that χ was known, that the focus here would be on the sub-chain χ-F-E. It will not be, although of course the formulae can be applied to this sub-chain. Of main concern here will be accounting for wet and dry removal processes so that sources, Q, can be related to resulting air concentrations, χ.

The reason for this emphasis follows from the practical viewpoint that the primary goal is to relate sources to effects (or damages). In most cases (the nuclear accident case may be an exception) evaluating the fluxes in the sub-chain χ-F-E is practically superfluous (although scientifically interesting) because effects can be correlated directly with air concentrations. On the other hand it at present appears to be extremely important to develop predictive formulae for the wet and dry removal link to predict the air concentration resulting from sources at large ($\gtrsim$ 100 km) distances. At shorter distances, evaluating the fluxes is of less significance because at this scale not only can effects be correlated with air concentrations, in many cases (e.g., in the neighborhood of the SO_2 sources at Sudbury) the effects can be correlated directly with the source strengths. Thus on the local scale ($\lesssim$ 100 km) it appears, from a practical viewpoint, that none of the links in the chain linking Q to E, viz. P-T-F-χ-F are of much significance. But, again, it appears to be imperative at the present time to devote substantial effort to evaluating the removal fluxes link in the long-range problem; otherwise we will not be able to respond to practical questions such as: what additional damages will be incurred, for example in New England forests, caused by the proposed 200 new coal-fired power plants to be constructed in the U. S. during the next decade?

1. SOME COMMENTS ON MACROSCALE ASPECTS OF REMOVAL PROCESSES

In the earlier sections of this report the emphasis was on microscale aspects of the removal processes. Above it was emphasized that large scale aspects appear to be more important from a practical viewpoint. Here some comments will be made about applying the formulae developed to larger space scales and it will be seen that some simplifications are possible.

Consider first precipitation scavenging. A qualitative indication of the deposition pattern for pollution from a specific source as a hypothetical stable warm front passes is shown in Figure 17. Similar sketches can be drawn for scavenging by other storm systems. Interestingly, a cold front will invert the lobes of deposition patterns, as can easily be checked from a simple sketch. From such sketches and the realization that the removal rates for most real pollutants by typical storms is $O(1\ hr^{-1})$, i.e., in a distance of less than 100 km, it can be concluded that even the scale of individual frontal storms is still too small if we are to relate sources to the effects occurring at great distances.

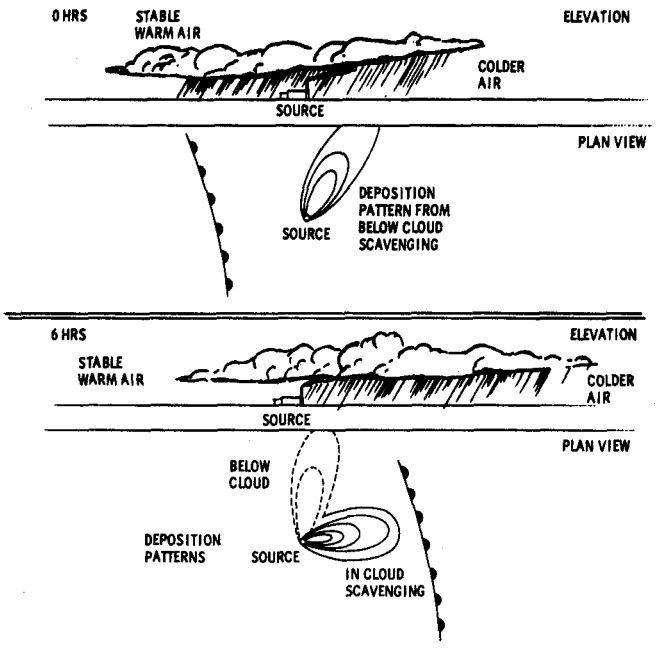

Figure 17. A qualitative plot of a pollutant's wet deposition pattern as a hypothetical, stable warm front passes a pollution source. Similar sketches can be easily made for other storm systems and lead to some interesting differences in deposition patterns. The main point to notice, however, is that the deposition pattern is typically local to the specific source (typically within ∿100 km).

The magnitudes of the time and space scales of interest in the long range wet deposition problem are derived here from the following considerations:

(a) For the large-scale problem, most wet removal of industrial pollutants occurs by in-cloud scavenging;

(b) In-cloud scavenging typically removes 10-90% of the pollutant ingested by the storm, depending on the efficiency with which the storm removes cloud water;

(c) The long range wet removal space scale is dictated by the distance over which the material is transported, between its encounters with storms which efficiently remove their precipitation.

Consequently, for the large (synoptic and greater) space scale and to a first approximation, precipitation scavenging can be viewed as a Poisson process in time: corresponding to the Poisson random selection of points in a time interval, there is the "random" occurrence of precipitation events, say with average frequency $\bar{\nu}$, each of which removes ingested pollution, say with average efficiency, $\bar{\varepsilon}$. In this way, the statistics of scavenging events reduces to a study of the statistics of rain events and the variability of ε. Some details will be given in a later subsection, but it is already clear from knowledge of the Poisson process that the average (e-fold) residence time of pollution removed with average efficiency $\bar{\varepsilon}$ is of the order of $(\overline{\varepsilon\nu})^{-1}$. The corresponding space scale is of the order of $\bar{u}(\overline{\varepsilon\nu})^{-1}$ where $\bar{u}$ is a representative wind speed between efficient storm events.

For the analysis of large space scale dry deposition, a major reorientation of concepts is not needed: The formulae developed earlier in this paper can be used although some consideration should be given to physical and chemical changes of the pollution as it is transported, and to estimating typical values for canopy heights, biomass, etc. Indeed, not only can the previous results be used with little change, but it is relatively easy to carry the analysis further and thereby estimate the ground level air concentration. This will be done later by assuming that for space scales larger than about 100 km, the pollution is well-mixed in the lowest layer of the atmosphere. We turn to some of these details now in our response to the two rhetorical questions asked earlier.

2. THE RELATIVE IMPORTANCE OF WET AND DRY DEPOSITION

Whether wet or dry deposition is more important depends sensitively on the distance from the source, the pollution type and its initial release height. For example, it is quite incorrect to generalize to all pollutants the results for stratospheric bomb debris that typically 90% is deposited wet, the remaining, dry because in this case the debris enters the troposphere from above, frequently during intense storm systems, and therefore in-cloud scavenging can be expected to be substantially more effective than dry deposition. In contrast, near a specific ground level source in an arid region it is relatively simple to demonstrate that dry deposition can predominate (Slinn, 1975b). Here some estimates are given for the relative magnitudes of pollutant wet and dry deposition from the atmosphere's mixed layer to a forest in the northeastern United States.

To make these estimates consider first the case of small (e.g., $SO_4^=$) particles. For such particles their gravitational settling speed can be ignored as, indeed, can the settling of most particles for the large scale problem. From previous sections and from data it can be assumed that a typical deposition velocity for such particles to a forest, and averaged over a long time period, is $0.3 \lesssim V_d \lesssim 3$ cm sec^{-1}.

The flux is approximated by $v_d\bar{\chi}$ where $\bar{\chi}$ is a representative value for the pollutant's air concentration. A similar crude estimate for the wet deposition flux can be found using the washout concentration ratios developed earlier. From the theory and data it can be estimated that the wet flux is 10^5 to 10^6 multiplied by $p\bar{\chi}$ where p is the precipitation rate. Using these values, multiplying by the time during which they operate, and recalling that the total rainfall in the area is about 100 cm yr^{-1}, then we have that the ratio of dry to wet deposition is

$$\frac{D}{W} \sim \frac{(0.3 - 3 \text{ cm sec}^{-1})(3 \times 10^7 \text{ sec yr}^{-1})}{(10^5 - 10^6)(100 \text{ cm yr}^{-1})} \sim O(1). \qquad (40)$$

That is, to within an order of magnitude, wet and dry deposition of $SO_4^=$ particles are of comparable importance. Similar estimates are valid for gases such as SO_2. Because of this it should be emphasized that in the title of this meeting the word "precipitation" is not restricted to what the weatherman talks about; here "precipitation" should mean "deposition", both wet and dry.

3. SOURCES CONTRIBUTING TO DEPOSITION

The other topic to be briefly addressed here is to estimate the spaces scales over which pollutants such as $SO_4^=$ are transported. For the case of dry deposition of a pollutant whose average concentration in the mixed layer (of height $\bar{h}$ and mean wind speed $\bar{u}$) is $\bar{\chi}$, the governing steady-state continuity equation (ignoring horizontal diffusion) is

$$\bar{u}\bar{h} \frac{\partial \bar{\chi}}{\partial x} = -v_d \bar{\chi} . \qquad (41)$$

Therefore the e-fold dry deposition length scale is $\lambda_d = \bar{u}\,\bar{h}/v_d$. This can predict substantially different numerical values. For example, over a forest in winter, if $\bar{u}$ = 5 m sec^{-1}, $\bar{h}$ = 200 m and v_d = 1 cm sec^{-1}, then $\lambda_d \sim 10^2$km. In contrast, say for 0.1 μm particles over water during a well-mixed summer day, with $\bar{u}$ = 5 m sec^{-1}, $\bar{h}$ = 2 km and v_d = 0.1 cm sec^{-1}, then $\lambda_d \simeq 10^4$ km. Consequently, depending on meteorological and other factors, $10^2 \lesssim \lambda_d \lesssim 10^4$ km and thus sources which are of the order of 10^4 km upwind can contribute to the dry deposition of pollution in a specific forest.

Now consider the wet removal space scale. As was indicated earlier, it is usually not profitable to pursue a washout model leading to an expression such as

$$\bar{u} \frac{\partial \chi}{\partial x} = - \langle \psi \rangle \chi \qquad (42)$$

which leads to an e-fold length of 10 to 100 km, because (42) is, at best, applicable only when there is precipitation. Instead, the appropriate large space scale for wet removal is related to the distances

over which the pollutant is transported between efficient storm events. From statistics presented by Huff (1971), it is noted that 67% of the storms in east central Illinois, during the period 1955-1964, lasted for less than 1 day, and for the 50-year period 1906 - 1955, 63% of the total precipitation occurred at a rate of 0.1 to 1 inch per day. Then roughly, if these two statistics are incorporated with a typical annual precipitation of 40 inches per year, we obtain that on the average, an efficient ($\sim$ 0.5" precipitation) storm occurs once in every 4.5 days, ignoring any seasonal variation. If this result is typical for the region, and if the average pollutant removal efficiency, $\bar{\varepsilon}$, is in the range $0.1 \lesssim \bar{\varepsilon} \lesssim 1$, then for $\bar{\nu} \gtrsim (5\ d)^{-1}$ and $\bar{u} \gtrsim 5\ m\ sec^{-1}$, the wet removal space scale, λ_w, is typically in the range $10^3 \lesssim \lambda_w = \bar{u}(\overline{\varepsilon\nu})^{-1} \lesssim 10^4$ km. Thus $\lambda_w \gtrsim \lambda_d$, which is consistent with (40); that is, wet and dry deposition are typically of comparable importance.

From these results, it is seen that both wet and dry removal length scales can be crudely estimated to be 10^2 - 10^4 km, and that more exact estimates can be made for specific pollutants and weather conditions. Incidentally, this range of length scales is suggested both for $SO_4^=$ particles and SO_2 gas. In the latter case there is the question of its rate of conversion to $SO_4^=$ but in this regard we note that few estimates of this rate would suggest the space scale is greater than 10^4 km and that the conversion can be accelerated within a storm or at the earth's surface. From these estimates arises a strong argument against the "tall-stack solution" to the pollution problem. It is a "solution" only if one lives in a small country or if, say, the 200 new coal-fired power plants to be constructed in the U.S. during the next decade are distributed, for example: 100 near Cape Cod and the other 100 near Cape Hatteras--and the load is shunted between the two centers, depending on which site has westerly winds!

CONCLUSIONS

In this report a number of semi-empirical expressions have been suggested which can be used to estimate wet and dry removal of particles and gases from the atmosphere. The formulae are semi-empirical in that their forms have theoretical bases but free parameters have been chosen to fit experimental data. By reviewing these formulae it can be seen that new data would be most helpful in the following areas:

- The collection efficiency for drops and 0.1-1.0 μm, monodisperse particles;

- The collection efficiency for snowflakes and particles of essentially all sizes;

- The rate of growth of real pollutant particles within plumes, caused by water vapor condensation;

• Rainout and snowout data unbiased by simultaneous dry deposition;

• In-cloud scavenging of particles ingested naturally into large-scale (frontal) storm systems;

• Solubility and reaction rates for gases at low concentrations in polluted rainwater and in soil water;

• The dependence of dry deposition in canopies on canopy height, biomass, wind speed, humidity and type of foliage.

The author expects that most of the formulae presented are capable of predictions to within an order of magnitude and in some instances, to within a factor of 2 or 3. It is noted for future studies, however, that pursuing accuracy to within a factor of 2 is of questionable value since rarely could the pollutant's air concentration be predicted to within this accuracy.

Many applications of the formulae presented could be described, especially for deposition in the neighborhood of specific sources. However, the author believes that the most important applications are to larger space scales and of those considered here it was concluded that wet and dry deposition of most industrial pollutants are of comparable importance and that the removal space scales for both processes are typically 10^2 - 10^4 km. At such distances it is of course true that diffusion dilutes the contribution from a specific source but as the distribution of sources becomes more diffuse and ubiquitous, diffusion becomes of no significance to the receptor.

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APPENDIX

The following is a list of frequently used symbols, their dimensions and, in case of multiple use of a single symbol, the equation number in which the symbol appears.

a = aerosol particle radius, L

B = biomass per unit volume, ML^{-3}

c = $(2/3\text{-}S_*)$, Eq. (10)

= concentration of gas in precipitation, units L^{-3}, Eq. (27)

C = canopy removal rate (fraction of a-particles filtered out per second), T^{-1}

D = molecular diffusion coefficient, L^2T^{-1}

$E(a,R)$ = particle/drop collision efficiency

$\mathcal{E}(a,\ell)$ = particle/snowflake collision efficiency

$\mathfrak{E}(a,\ell)$ = particle/canopy-fiber collision efficiency

$E_j(a)$ = jet collection efficiency

h = mixed layer height, L, Eq. (41) or $H_2 - H_1$, L, Eqs. (25) and (26)

H = canopy height, L, Eq. (35)

= Henry's law constant

H_0 = overall partition coefficient

k = reaction rate, T^{-1}

K = atmospheric diffusivity, L^2T^{-1}

$\mathbf{K}$ = second order tensor atmospheric diffusivity, L^2T^{-1}

$n(a)da$ = number of particles per unit volume of radii a to a + da, L^{-3}

$N(R)dR$ = similarly, for raindrops, L^{-3}

p = precipitation rate, LT^{-1}

Pe = RV_t/D = Péclét number

R = raindrop radius, L

R_m = volume-mean drop radius, L

Re = RV_t/ν = Reynolds number

s = $\tau V_t/R$ = Stokes number

s_* = critical Stokes number = $\dfrac{(12/10) + (1/12)\ \ln(1 + Re)}{1 + \ln(1 + Re)}$

Sc = ν/D = Schmidt number

St = $\tau u_*^2/\nu$ = Stokes number in turbulent flow

$\bar{u}$ = mean wind speed, LT^{-1}

$\bar{u}_c$ = mean wind speed in canopy, LT^{-1}

$\bar{u}_g$ = mean wind (geostrophic wind) above canopy, LT^{-1}

u_* = friction velocity, LT^{-1}

v_s = particle settling velocity, LT^{-1}

v_t = drop terminal velocity, LT^{-1}

$\langle v_t \rangle$ = average snowflake terminal velocity, LT^{-1}

V = μ_w / μ_a = ratio of dynamic viscosities, water to air

α = attachment rate, T^{-1}, Eq. (17)

= empirical constant, Eq. (35)

β = $K/(H_0^2 D)$, Eq. (32)

= empirical constant, Eq. (33)

κ = kt, nondimensional reaction rate, Eq. (32)

= concentration of contaminant in precipitation, units L^{-3}, Eq. (25)

= a/R, interception parameter, Eq. (10)

λ = radius of plume- or cloud-drops, L, Eq. (20)

= characteristic length (e.g., radius) of fibers in a canopy, L, Eq. (38)

ν = kinematic viscosity of air, L^2T^{-1}

ψ = removal rate, T^{-1}

$\langle \psi \rangle$ = space-average removal rate, T^{-1}

$\bar{\psi}$ = particle-average removal rate, T^{-1}

ψ_r, ψ_s = rain, snow removal rates, T^{-1}

$\bar{\rho}$ = average mass density of foliage, ML^{-3}

τ = particle relaxation time, T

SUBSCRIPTS

f,g,h = free, growing, hosted

2m = two meter

0 = ground level

t = total

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