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GAS AND AEROSOL SCAVENGING

MASTER

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INTRODUCTION

The wet removal rate and wet deposition of pollutants is ultimately dependent upon the rate of pollutant attachment to the falling precipitation particles (hydrometeors) and to the precipitation flux at the ground. This attachment to the hydrometeors or collector particles is, in turn, dependent upon the physical characteristics of the pollutant. As expected, when considering wet removal, gases behave differently than aerosols. Modelers of gas scavenging (eg., Hales 1972, Adamowitz 1979) stress the importance of drop size distribution, vertical gradients of gas concentration in the atmosphere and solubility in determining gas deposition at the surface. Aerosols, on the other hand, are removed at various rates depending upon aerosol size distribution, solubility, environmental humidity and age.

Before the specifics of wet removal are dealt with, it is helpful to present some of the basic mathematical concepts used for treating problems in precipitation scavenging. By doing so, current terminology can be introduced and placed into a framework that should alleviate confusion about meaning. For example, a distinction between "scavenging coefficients" and simply "scavenging" will be made. The terminology in-cloud, below-cloud, washout, and rainout will be shown to be ambigious and will be dismissed. Other concepts, such as washout ratio, nucleation scavenging, vapor deposition versus accretion will be shown to be more appropriate or useful when considering wet removal of aerosol and gas.

To facilitate the presentation, gas and aerosol removal will be considered in general. For each, the emphasis will be upon surface deposition, and upon properties that must be known to approximate wet surface fluxes. In the final section, the suspected properties of organics and metals will be presented and related to wet removal.

WET DEPOSITION OF AEROSOL

By letting χ equal the total concentration of an aerosol per unit volume of space, the individual components contributing to χ are:

χ_a = concentration of pollutant associated with dry aerosol

χ_c = concentration of pollutant associated with cloud water (liquid)

χ_p = concentration of pollutant associated with precipitation water (liquid or ice)

where

$$\chi = \chi_a + \chi_c + \chi_p \ . \tag{1}$$

The value χ can represent either number of mass concentration.

Then by recognizing that the continuity equation forms the basis which assures conservation of mass, the local change of each of the above components can be expressed as:

$$\frac{\partial \chi_a}{\partial t} = -\nabla \cdot \chi_a \vec{V} - L_{ac} - L_{ap} \tag{2a}$$

$$\frac{\partial \chi_c}{\partial t} = -\nabla \cdot \chi_c \vec{V} + L_{ac} - L_{cp} \tag{2b}$$

$$\frac{\partial \chi_p}{\partial t} = -\nabla \cdot \chi_p \vec{V} - \frac{\partial \chi_p V_p}{\partial z} + L_{cp} + L_{ap} \tag{2c}$$

where L_{ac} is related to the attachment rate of <u>a</u>erosol to <u>c</u>loud water, L_{cp} is related to the attachment rate of <u>c</u>loud water to <u>p</u>recipitation water (coalescence, accretion, riming), and L_{ap} is related to the attachment rate of <u>a</u>erosol to <u>p</u>recipitation water.

In Equations (2), the notation $\nabla \cdot \chi_i \vec{V}$ is used to denote the flux of pollutant into or out of the volume of interest due to both the mean and turbulent wind. In (2c), the second term on the right hand side occurs because precipitation is falling, and is able to carry pollutants to lower levels in the atmosphere. The L_{ij}'s represent the rate of attachment of pollutant to the condensed ice or water. These L_{ij}s are often called "scavenging coefficients" (eg., see Slinn 1977) and define an inter-phase (air to liquid or ice, gas to liquid) transport or exchange that takes place between the pollutant and the condensed water. For a monodisperse aerosol, the familiar form for the scavenging coefficient, ψ, results:

$$\psi = \frac{L_{ac} + L_{ap}}{\chi_a} = \int_0^\infty K \, \eta\langle r\rangle dr \tag{3}$$

where $\eta\langle r\rangle$ represents the size distribution of droplets and hydrometeors in the cloud and K represents a collection kernel between the aerosol and condensed water. Here, an important aside, is that the scavenging coefficients have non-zero values even when there is no precipitation.

A further simplication is often obtained by adding Equations (2b) and (2c), assuming steady state and a horizontally uniform pollutant concentration. Then,

$$L_{ac} + L_{ap} = \frac{\partial \chi_p V_p}{\partial z} \quad (4)$$

and using Equation (3)

$$-(\chi_p V_p)_0 = \int_0^H \psi \chi_a dz . \quad (5)$$

Thus, the pollutant deposition at the ground depends upon the vertically integrated scavenging coefficient and upon the vertical distribution of pollutant above the ground.

Another equally trivial result comes from summing Equation (2): (Implicit in these summations is that turbulance acts upon aerosol and condensed water particles in the same way)

$$\frac{\partial \chi}{\partial t} = \nabla \cdot \chi \vec{V} + \frac{\partial \chi_p V_p}{\partial z} \quad (6)$$

Here the change in total aerosol concentration in a volume occurs because of fluxes associated with the wind and with falling precipitation. This is scavenging in its true sense. That is, there is no net change in aerosol concentration unless there is precipitation. For a horizontally uniform pollutant distribution, the surface deposition represents the change in total pollutant concentration above the collector; ie.,

$$(\chi_p V_p)_0 = \int^H \frac{\partial \chi}{\partial t} \, dz \; . \tag{7}$$

In either Equations (5) or (7) it is important to note that the wet surface deposition of aerosol is determined by an integral of events occurring above the surface. Pollutant is collected and carried to the surface by "collector particles" such as raindrops or snow flakes. As long as pollutant is available it makes little difference to the collector particle whether or not it is in the cloud or below the cloud.

If one recognizes that vertical motions within storms can distribute surface level pollutants to heights of several km, then one can readily see that since the cloud thickness is generally ten times or more greater than the distance from the ground to cloud base, the aerosol mass scavenged from within the cloud is considerably greater than aerosol mass scavenged below cloud. Indeed, there is no need to consider separately the in-cloud and below-cloud contributions for aerosol scavenging. The removal mechanisms are the same regardless of location. Similarily, the ambigious terms rainout and washout have no place when considering wet removal of aerosols.

RATE LIMITING PROCESSES

Regardless of the form used to describe wet removal of aerosol from the atmosphere, it is necessary to describe the term χ_p, the concentration of pollutant associated with precipitation water. Because the bulk of the aerosol pollutant mass associated with a precipitation particle is obtained by accretion of the tiny cloud droplets, both the precipitation growth mechanisms and the chemistry of the tiny cloud droplets captured by the falling precipitation must be considered in deriving χ_p. In addition, the aerosol not associated directly with the cloud water is able to attach directly to the falling precipitation particles (cf., Equation 2a).

What is being considered here is therefore a system which is determined by two classes of rate limiting processes. First, the aerosol must attach to the condensed water, and second, the condensed water must fall out. The slower of the two rates determines the rate of deposition upon the surface. Table 1 lists a few of the processes which must be evaluated when considering wet removal of aerosol.

Attachment Mechanisms

The collection and collision efficiency is probably the most important and the most difficult attachment process to estimate. Figure 1 from Slinn (1977) provides an illustration of the extreme sensitivity of collection to the size of the collected and collector particles. As to the size of the aerosol, solubility plays a major role. Figure 2, from

Tang and Munkelwitz (1977) illustrates the relationship between size and humidity for a variety of soluble materials. At typical sub-cloud humudities of 90 to 100 percent, during precipitation, soluble aerosol can increase its dimensions by a factor of four or more over its dry dimensions.

How long does it take soluble aerosol to grow to cloud droplet size? It depends upon the fraction of the particle that is composed of soluble material and upon various cloud microphysical properties such as updraft velocity, temperature, number of aerosol competing for available water. Figure 3 illustrates conditions thought to be representative for many storm systems. Here, aerosol composed of 50 percent ammonium sulfate and at equilibrium in an environment at 80 percent humidity is drawn into a cloud with water supersaturation of 0.1 percent. Aerosol that was initially 0.2 and 0.5 μm in diameter can grow to cloud droplet size in an interval of a minute or less.

The above numbers are important to consider because they illustrate a likely pathway for removal of insoluble, submicron material from the atmosphere. The 50 percent insoluble material in the above example could well be something like lead which is thought to have a diameter (mmd) of ~0.5 μm. The tiny Pb aerosol by itself would be very difficult to remove (see Figure 1) because of its size. However, if the Pb was attached to a soluble aerosol and drawn into a cloud environment it would almost instantaneously be incorporated within cloud water. Within minutes it would achieve a maximum collision efficiency of 1. Often this rapid growth of aerosol to cloud droplet size is called "nucleation scavenging".

Thus, age of the aerosol is also an important feature to consider. The older the aerosol, the larger the mean diameter because of coagulation, but equally important is the likelihood of attachment to some soluble aerosol. Figure 4, from Gatz (1976) lends some weak support to these ideas. The farther away from the source the greater the washout ratio. Other equally important features could, however, produce the same trend.

Removal Mechanisms

Discussion of removal processes once cloud and precipitation water have formed should focus on the distinction between ice growth and water growth. Ice-growth processes are thought to be responsible for the initiation of most precipitation in our latitudes. However, during warm seasons, and for intervals with high freezing levels ($\sim$3 km), the coalesence process involving water-water collisions is the dominant growth mechanism (ie., not condensation). A 1 mm raindrop is the product of about a million collisions with cloud droplets. Rather than a dilution of pollutant that will occur if the drop is growing by condensation, one finds either an increase or decrease in pollutant concentration depending upon the pollutant concentration in the collected droplets. Indeed, the raindrop can be thought of as a concentrating agent by taking 10^6 cloud droplets with a mean spacing of $\sim$1 mm between droplets and placing them all into a volume of about 1 mm^3. This is the physical basis behind the "washout ratio".

When the washout ratio is expressed as a volume weighted ratio (mass of pollutant per volume of rain water divided by mass of pollutant per volume of air) the values are typically near 10^6. The implication here is that the aerosol has been readily incorporated into the cloud water and is likely to be soluble. Also implied is that the air concentration of pollutant measured near the ground is representative of the air concentration averaged over about 3 km height in the cloud.

For washout ratios below 10^6 considerable caution must be used in the interpretation - particularly when the precipitation is snow or is falling from a cold cloud with low freezing levels. The precipitation from those cold clouds was most likely in the form of snow for the bulk of its growth.

It is a mistake to assume that if the precipitation is snow, then there is no liquid water present. Cold clouds frequently contain abundant quantities of supercooled liquid water with average concentrations near ~ 0.1 g/m^3. Precipitation growth in those cold clouds is the result of a combination of vapor growth (the ice analogy of liquid phase condensation) and collection of supercooled cloud droplets. The collection or accretion process is called riming. This riming process is the dominant mechanism whereby soluble aerosol is removed from cold clouds.

In cold clouds, however, the vapor deposition component of growth is much more important than in warm clouds. As much as one-half or more of the precipitation mass can arise from vapor deposition (in the extreme limit with no riming - all of the mass). Thus, in the above example only 10^5 or fewer drops need be collected to produce the 1 mm raindrop at the ground. In the cold cloud, therefore, one would expect the washout ratios for soluble aerosols to drop to 10^5 or less.

This difference in precipitation growth mechanisms has an implication for trying to use storm water efficiencies to predict the removal efficiencies of aerosols. Here the storm water efficiency is defined as the quotient of condensed water falling out as precipitation divided by the amount of water condensed by a storm. One can argue that if the pollutant is contained within the cloud water then it must be removed at the same rate as cloud water (Slinn 1974). This is true, but the precipitation rate on the ground is not necessarily a good measure of removal of cloud liquid water because of the contribution of depositional growth to the precipitation rate.

Thus, washout ratios of the order of 10^5 or less can be an indicator of efficient ice phase mechanisms operating in the clouds. Equally likely however, is that the aerosol is not efficiently attached to cloud water. Aerosols that are insoluble, relatively young or with dimensions between 0.1 to 1.0 μm would fall into this latter category. The data presented by Gatz (1975) in Figure 4 seems to fall into the category of inefficiently removed aerosols. Table 2 also presents measured values of size and washout ratio for some metals. The more toxic metals (Ni, Cd, Pb) have large fractions of their mass less than 0.7 μm diameter.

Dependencies Upon Air Concentration

Before leaving the discussion of washout ratios and aerosol scavenging, it is important to make one more point. First, it is necessary to relate the washout ratio to the mathematical discussion at the beginning of the paper. The ultimate desire is to relate the surface deposition $\chi_p V_p$ (see Equations 5 or 7) to the washout ratio. Recognizing that $\chi_p V_p$ represents a flux of pollutant, we have

$$\chi_p V_p = CJ = \text{Flux} \quad , \tag{8}$$

where C equals the pollutant concentration in precipitation, J equals the precipitation rate, and the surface deposition D is given by

$$D = (JC)_0 = \text{Surface Deposition} , \tag{9}$$

Then, by definition, the washout ratio W is given by

$$W = \frac{C}{(\chi_a)_0} . \tag{10}$$

Subsitution of Equation 10 into Equation 9 provides the desired relationship between washout ratio and surface deposition:

$$D = W(J\chi_a)_0 . \tag{11}$$

Implicit in all deposition expressions is an assumed ability to describe the sub-cloud air concentration of pollutants during precipitation events. Naturally this depends upon the previous scavenging history of air arriving over the receptor and requires some means of constructing air trajectories. This trajectory construction problem is extraordinarily difficult, and discussion of it is beyond the scope of this talk. Suffice it to say, constant level trajectories based upon average winds are totally inadequate for describing source regions and travel times to a receptor during periods of precipitation. Vertical air motions, pollutant convergence and scavenging along the path of the trajectory must be considered.

GAS SCAVENGING

Gas scavenging is in many respects quite different than aerosol scavenging because the process is often reversible in comparison to the irreversible nature of aerosol collection. Not only can gases be absorbed and desorbed in condensed water, but chemical conversions frequently occur within the water. As for aerosols, though, the phase of the condensed cloud water and of the collector particles play an important role in determining the deposition at the surface.

In general, the flux of a gas into or out of a single water drop can be related to the diffusivity of the gas, D, and to the gradient of gas concentration, C, within the vicinity of the drop:

$$\text{Flux} = D \frac{\partial C}{\partial r} \quad . \tag{12}$$

The change of pollutant mass within a drop of radius r_0 is then given by

$$V_t \frac{d}{dz} (C \tfrac{4}{3} \pi r_0{}^3) = 4 \pi r_0 D \, (C_{eq} - C)(1+F), \tag{13}$$

where V_t is the drop fall speed, C_{eq} is the equilibrium concentration of the gas in the water at an air concentration of χ_a, and C is the actual concentration of the gas in the water. The term (1+F) is a semi-empirical correction and results from the ventilation of the drop as it falls through the environment. From Equation 13, an ℓ-fold equilibrium distance can be computed (ie., the fall distance required to reach ∿63 percent of the equilibrium value):

$$Z \sim \frac{R_0{}^2 V_t}{3D(1+F)} \; . \tag{14}$$

Thus, we see that the bigger the drop and the smaller the diffusivity, the longer it takes for the drop to come into equilibrium with the environment. However, using reasonable values for the parameters in Equation 14 establishes

$$\left.\begin{array}{l} Z \; < \; o(1\ \text{m}) \\ \text{The equilibrium time } t \text{ is} \\ t \; \sim \; o(1\ \text{s}) \; . \end{array}\right\} \tag{15}$$

Therefore, it appears that the gas concentration in liquid water should be very close to the equilibrium value determined by the gas concentration in the environment, ie.,

$$\left.\begin{array}{l} C \; \simeq \; C_{eq} \\ \text{where} \\ C_{eq} = \dfrac{X_a}{H} \end{array}\right\} \tag{16}$$

where H is the Henry's Law constant.

For snow, this equilibrium concentration is determined at the altitude of impaction between a supercooled cloud droplet and a collecting snowflake. The collision rapidly freezes the cloud droplet and prevents any readjustment to near-equilibrium values at lower altitudes. For liquid precipitation, this equilibrium concentration is determined from surface air concentrations.

For gas scavenging by snow there is then the added difficulty of estimating the amount of riming on the snowflakes (which measures the mass contribution by supercooled cloud droplets), and of estimating the air concentrations within the clouds. For materials being considered here (ie., organics) the wet removal rates are generally quite low and atmospheric residence times are long. Thus, away from sources, the materials should be uniformly distributed through the troposphere.

Recalling the definition of washout ratio (Equation 10), for gases we have

$$W = \frac{1}{H} \quad . \tag{17}$$

The surface deposition (see Equation 11) is then given by

$$D = \frac{J\chi_a}{H} \quad .$$

Junge (1977) has compiled a table of washout ratios for various pesticides, PCB's and Hg by assuming these materials are present in the vapor form. These values are presented in Table 3 and can be compared with the values for metals in Table 2. In general, the wet deposition rate of the gases of Table 3 can be expected to be considerably less than aerosol metals presented in Table 2.

SCAVENGING OF ORGANICS AND METALS

If we limit the discussion to the gases and metals presented in Tables 2 and 3 or to similar materials, it is clear that the deposition rates depend strongly upon whether the material is in gaseous form or is attached to aerosol.

Figure 5 presents estimates by Junge (1977) of the fraction of gaseous material absorbed on aerosols. The fraction, ϕ, is strongly dependent upon the aerosol concentration (available surface area) and inversely related to the saturation vapor pressure. In general, large fractions of the pesticides are expected to be associated with aerosols in continental atmospheres. Other organics such as PCBs, chloroflouro-methanes (CFM) and metals such as Hg are expected to be in the vapor form regardless of the aerosol concentration. These latter materials are therefore expected to be scavenged with very low efficiency.

Some experimental evidence exists to support Junge's estimates. Atkins and Eggleton (1970) conclude from their data that DDT was removed like an aerosol in urbanized areas but like a gas in cleaner rural areas.

To summarize the discussion of previous sections, if the organics or metals are present in or attached to aerosol forms, then removal rates will depend strongly upon:

- solubility of aerosol,
- size of aerosol,
- air concentration of the aerosol.

Washout ratios for these aerosols will range over:

$$o(10^5) < W < o(10^6)$$

for rain or warm clouds and

$$W \sim o(10^5)$$

for snow or cold clouds.

If the organics or metals are present as vapors, wet removal will depend upon:

- solubility (Henry's Law),
- air concentration of the gas.

Washout ratios for those gases will range over:

$$o(10^0) < W < o(10^4)$$

A further difficulty encountered when considering wet removal of gases is the very real possibility of re-emission to the atmosphere once the gas has been placed on the ground. Many of the pesticides and PCBs can evaporate quite readily (Junge, 1977 ; Spenser and Cliath, 1969). Hogstrom, et al., (1979) also present evidence that Hg can be re-emitted at locations where previous deposition has occurred. Finally, the drying of the wet surface layer can result in re-emission caused by increased concentrations in the aqueous phase.

Table 1. Rate Limiting Processes

1. Attachment
    - A. Collection Efficiency
    - B. Solubility
    - C. Size
    - D. Condensation, evaporation
    - E. Age

2. Removal
    - A. Precipitation Growth Processes (Riming, Accretion, etc.)
    - B. Storm Efficiency
    - C. Seasonal Variations

Table 2. Some Measured Values for Size and Washout Ratio of Metals

Element	MMD (μm)*	Washout Ratio** ($x10^6$)
Mg	- , 5.7	0.38
K	- , -	0.46
Ca	- , -	0.29
Al	2.1, -	-
Cu	2.0, -	-
Fe	1.7, 3.0	0.21
Cr	1.4, -	-
Mn	1.4, 2.0	0.31
Zn	0.8, 1.0	0.15
Cd	0.6, -	-
Ni	0.6, -	-
Pb	0.5, 0.5	0.06

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*First value is from McDonald and Duncan (1979), second value is from Gatz (1975).

**Values from Gatz (1975).

Table 3. Estimates of Washout Ratios, W, and Saturation Vapor Pressure, P_s, For Various Gases*

Compound	$W(x10^6)$	P_s(mm Hg)
Pesticides		
Lindane	$5x10^{-2}$	$9x10^{-6}$
DDT	$6x10^{-4}$	$1x10^{-7}$
Aldrin	$2x10^{-3}$	$6x10^{-6}$
Dieldrin	$1x10^{-1}$	$1x10^{-7}$
PCBs		
Aroclor 1254	$9x10^{-6}$	$8x10^{-5}$
Aroclor 1242	$4x10^{-5}$	$4x10^{-4}$
Aroclor 1248	$7x10^{-6}$	$5x10^{-4}$
Aroclor 1260	$3x10^{-6}$	$4x10^{-5}$
Hg	$2x10^{-6}$	$1x10^{-3}$

*From Junge (1977).

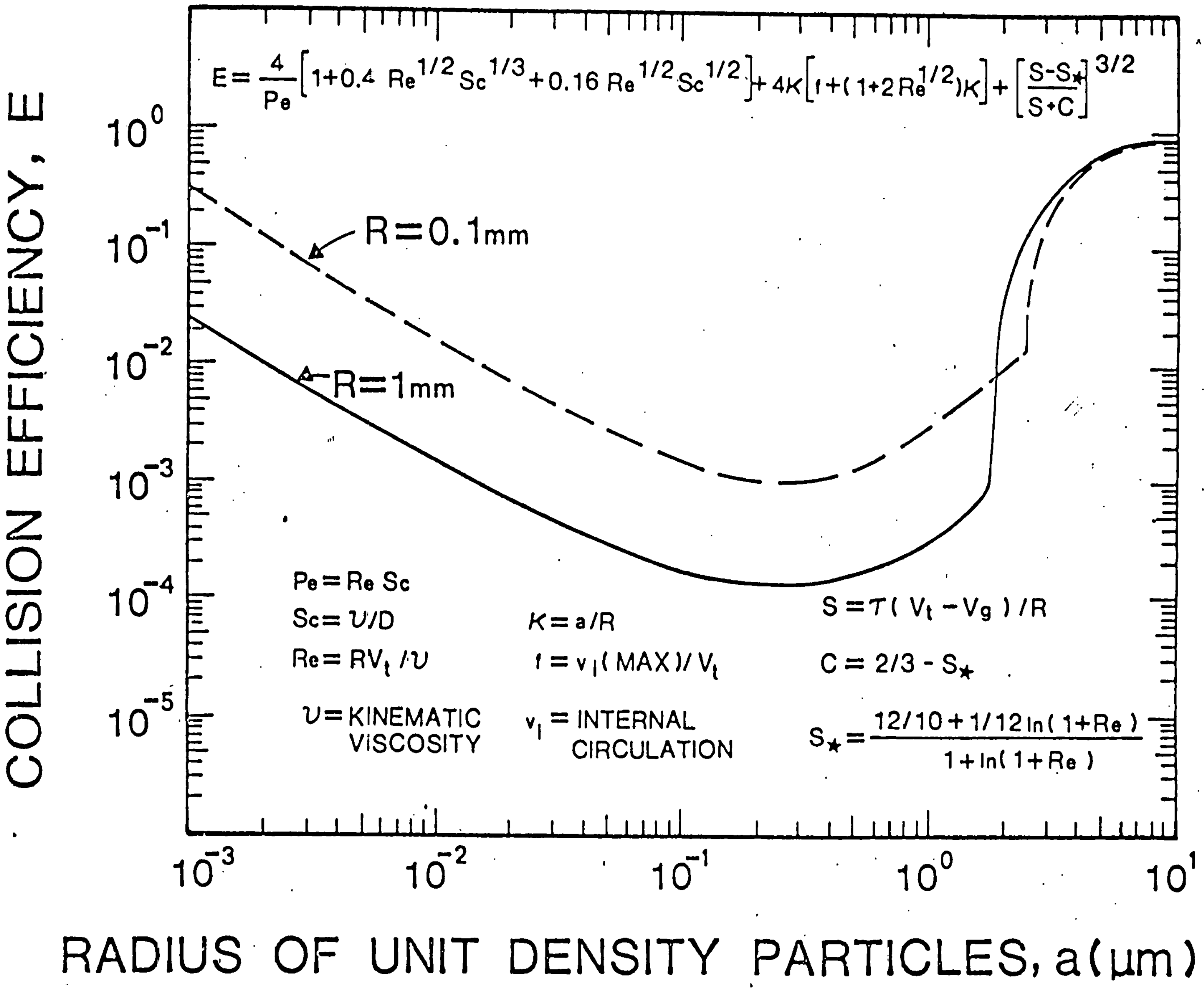


Figure 1. Stress Importance of Size Distribution of Aerosol

Figure 2. Theoretical Growth Curves for Solution Droplets of Sulfuric Acid and Other Inorganic Salts of Interest at 25°C

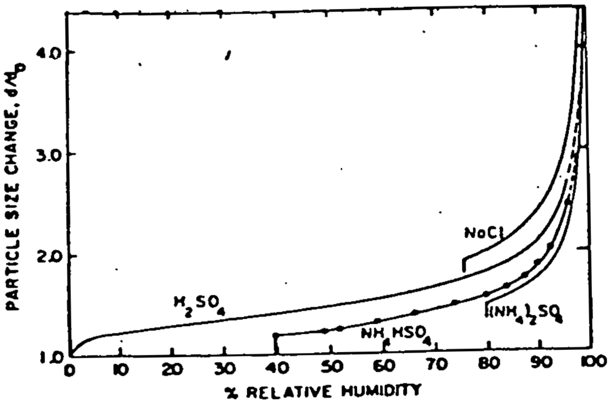


Figure 3. Growth of Aerosol Composed of 50 Percent $(NH_4)_2\ SO_4$

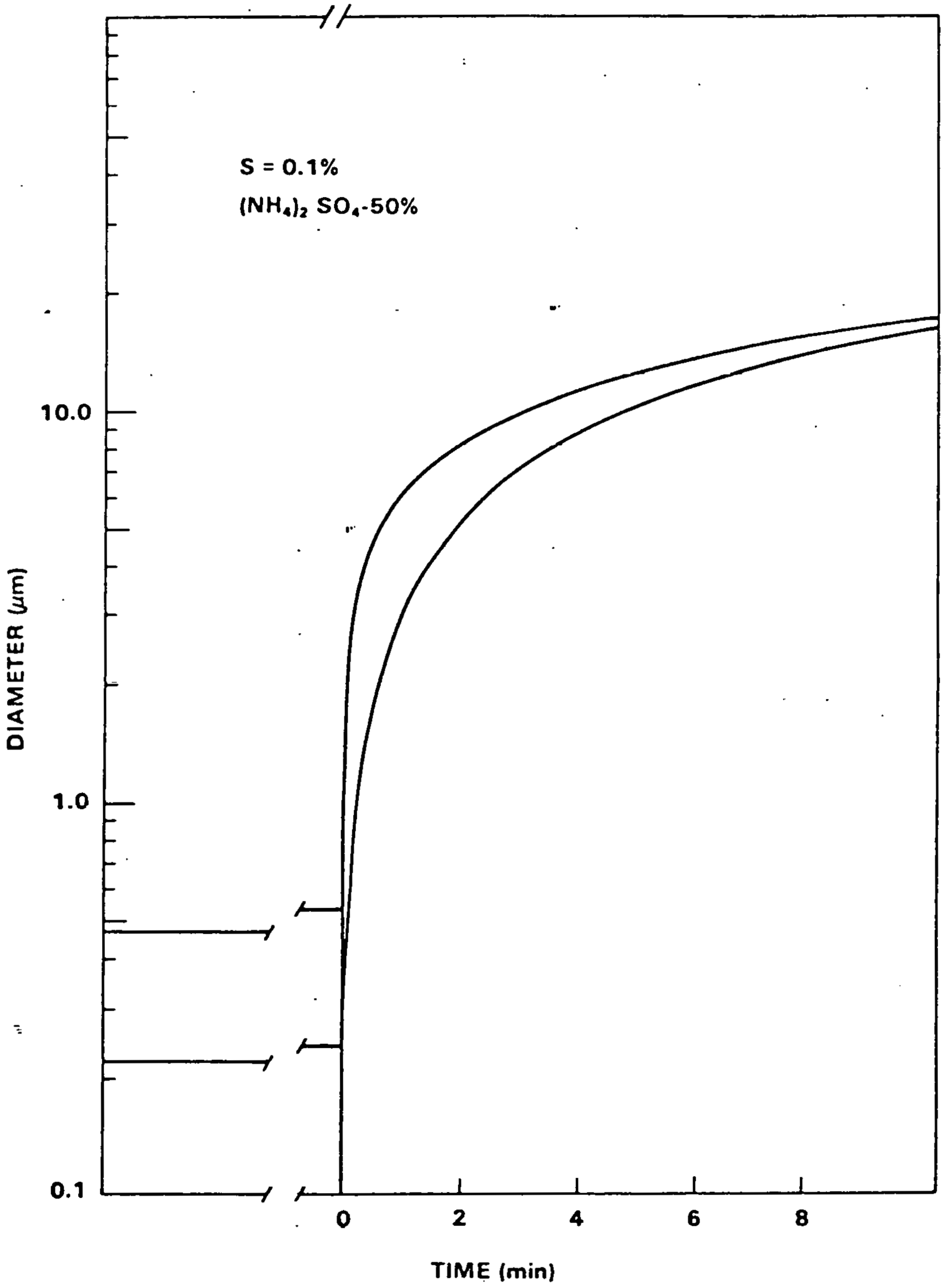


Figure 4. Variation of Scavenging Ratio, W, With Mass Median Diameter (MMD) and Distance From Urban Sources For St. Louis and Chilton, U.K.

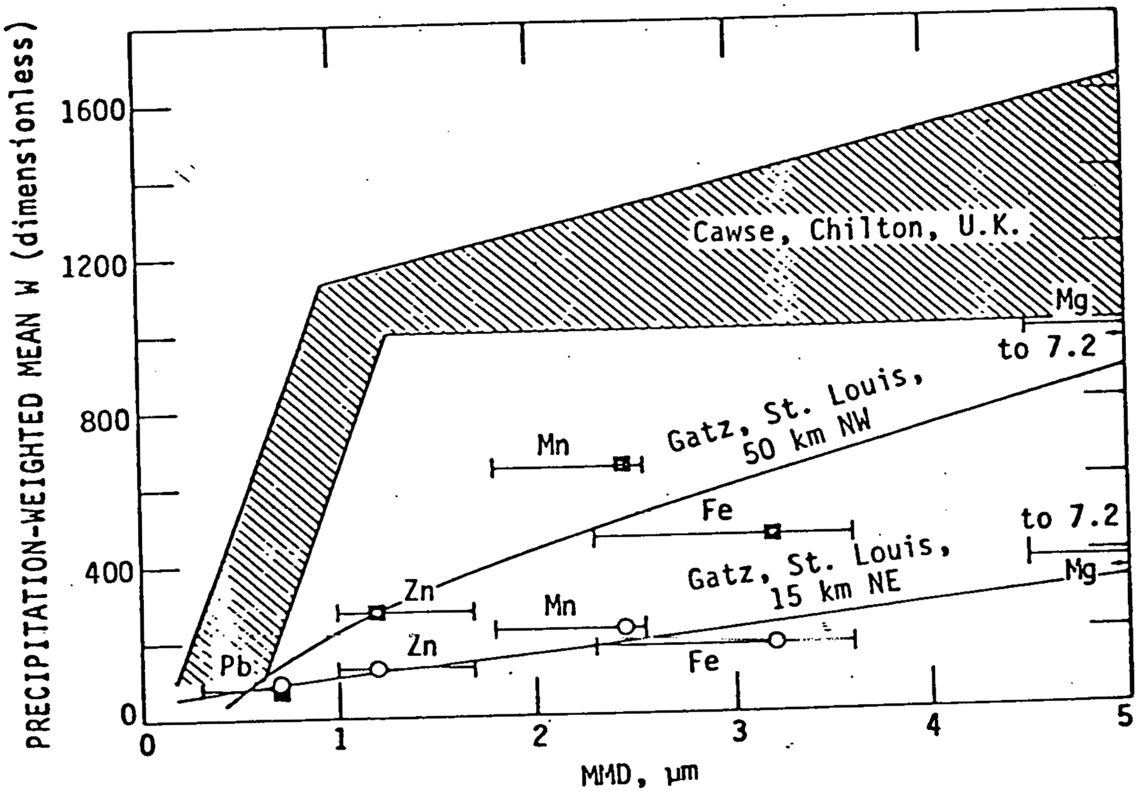
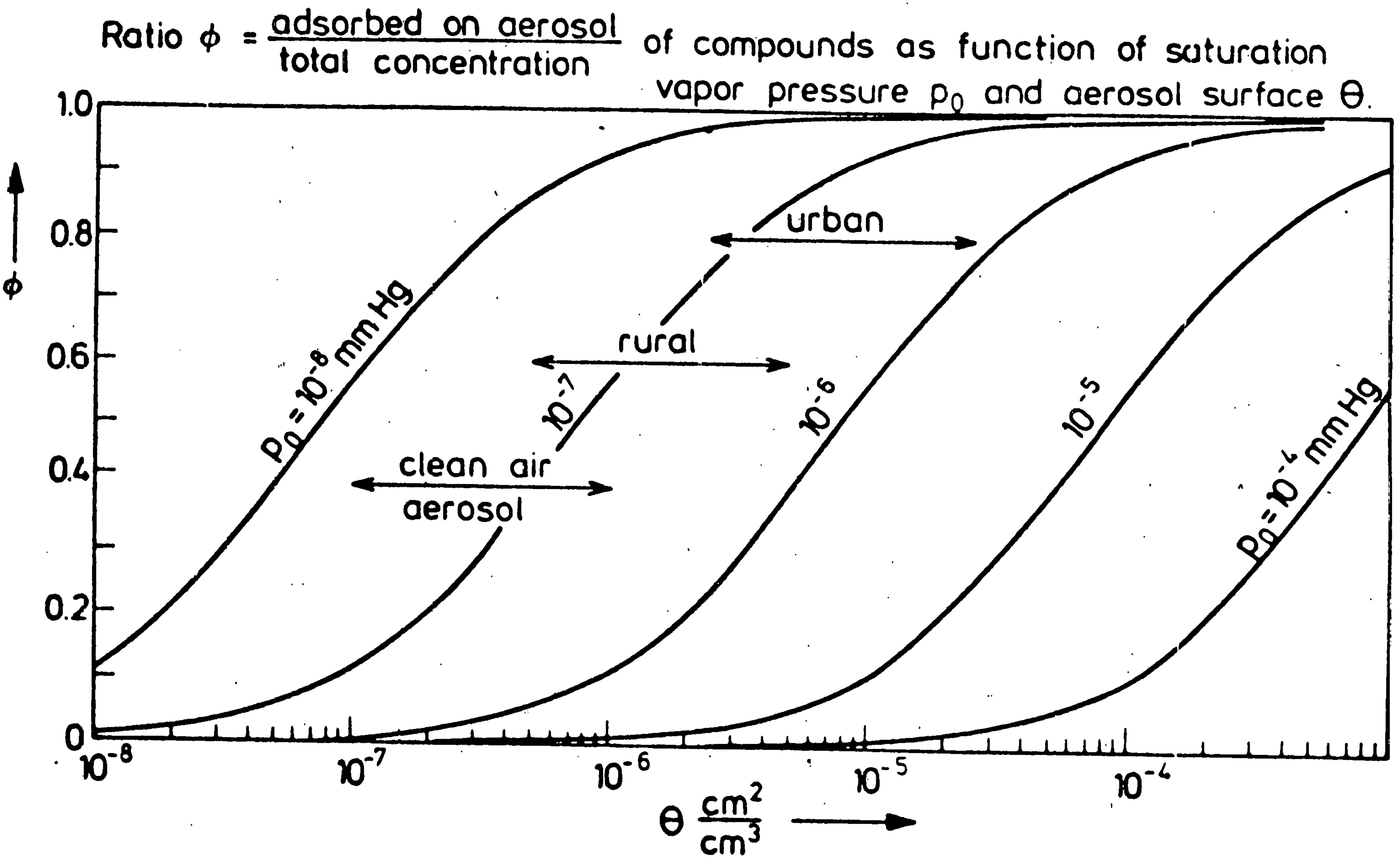


Figure 5. Expected Values of ϕ = (Amount of Substance Absorbed in Aerosols)/(Total Concentration) As a Function of Saturation Vapor Pressure (mm Hg) and Surface Area of Aerosols (cm²/cm³ air). The Calculations are Based on Adsorption Theory and Can Only be Indicative of the Order of Magnitude. (Junge 1977).



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