10 DRY AND WET DEPOSITION

Deposition phenomena are the way in which the atmosphere cleans itself. The process is efficient as only a few gases (most notably CO_2) show signs of global increase in spite of the large emission of pollutants from both natural and anthropogenic sources. There are two types of deposition mechanisms: dry deposition, i.e., the uptake at the earth's surface (soil, water, or vegetation), and wet deposition, i.e., absorption into droplets followed by droplet precipitation (e.g., by rain) or impaction on the earth's surface (e.g., fog droplets).

This section describes and discusses deposition phenomena and their mathematical treatment (see also Yamartino, in Houghton, 1985). Recently, deposition processes have received much attention. The development of long-range transport (LRT) studies and experiments has required a better understanding of these phenomena, whose importance is proportional to the length scale of the investigation -- the larger the space and time scales, the better deposition phenomena need to be understood and simulated, in order to predict correctly concentration impacts. Moreover, acidic deposition has become an important environmental issue (e.g., see the review by Schwartz, 1989, for a general discussion of acid deposition phenomena), which has required a correct representation of deposition phenomena, not just to forecast *concentration* impacts, but to assess *deposition* rates and their adverse effects.

The deposition modules of air quality models possess large uncertainties and much work seems still to be required to provide an accurate parameterization of the complex deposition phenomena. Performance evaluation studies of deposition modules have been performed by several authors (e.g., Doran et al., 1984; Doran and Horst, 1985).

10.1 DRY DEPOSITION

Dry deposition is commonly measured by the deposition velocity V_d, which was defined by Equation 6-10 as the ratio between the pollutant deposition flux F (g m^{-2} s^{-1}) and the pollutant concentration c (g m^{-3}), i.e.,

$$V_d = F/c \qquad (10\text{-}1)$$

V_d is not a real velocity but an "effective" one. (It has been called a velocity mostly because of its units.) In fact, as discussed below, only large particles possess a deposition velocity dominated by gravitational effects and, therefore, interpretable as an actual velocity.

As far as gases are concerned, dry deposition is strongly affected by their chemical interactions with the surface. See, for example, Figure 6–4, where SO_2 deposition velocities for different surfaces are presented.

For particles, deposition velocities have been computed from wind tunnel experiments, as for example shown in Figure 10–1. As discussed by Nicholson (1988a), for very small particles (i.e., with a diameter less than 0.1 μm), Brownian motion allows rapid movements across the viscous air layers just above

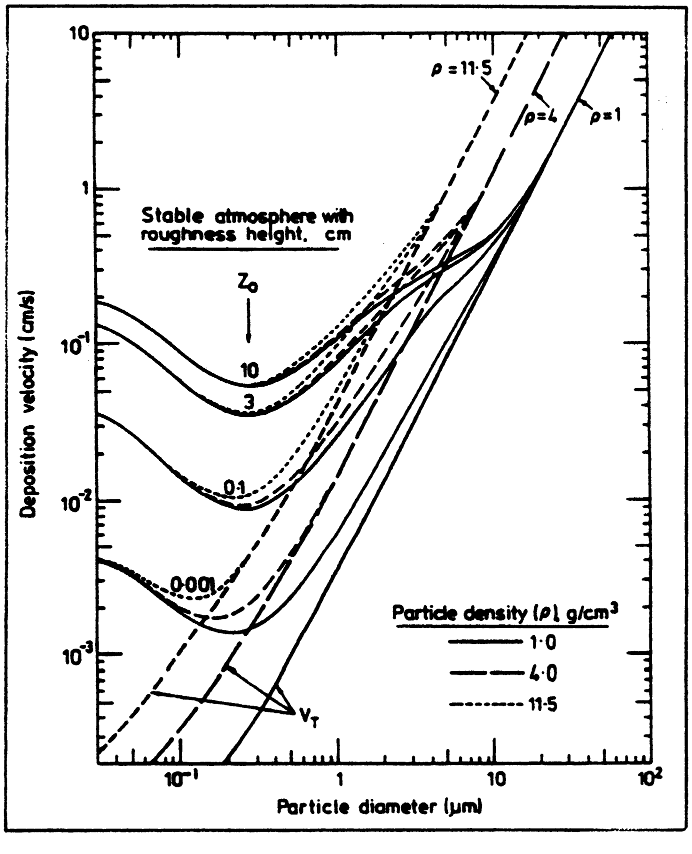

Figure 10–1. Extrapolations from correlations of wind–tunnel measured deposition velocities for z = 1 m, densities of 1, 4 and 11.5 g cm^{-3}. V_T *represents terminal settling velocity (from Sehmel, 1980, as presented by Nicholson, 1988a). [Reprinted with permission from Permagon Press.]*

the surface, while the motion of large particles (i.e., with a diameter greater than 1 μm) is dominated by sedimentation (gravitational) effects, as shown in Figure 10–1 where the "terminal" velocity V_T (or gravitational settling velocity V_G) increases with particle size. Intermediate size particles are strongly affected by impaction and interception phenomena, which are difficult to quantify correctly. In particular, particles in the size range 0.1 to 1 μm have low predicted deposition velocities due to the relative weakness of Brownian motion and gravitational settling effects, even though field measurements indicate high deposition rates. Surface roughness, as illustrated in Figure 10–1 seems to play an important role in a stable atmosphere, as it significantly influences the near-surface turbulence and, in turn, the rate of pollutant transfer to the surface.

A literature review of dry deposition velocities of oxides of sulfur and nitrogen, based on long-range transport modeling studies in North America, is provided by Voldner et al. (1986).

Dry deposition phenomena are often parameterized using Equation 10–1, which requires the knowledge of the deposition velocity V_d for both primary and secondary pollutants, a velocity whose evaluation (as illustrated in Figure 6–4 for the SO_2) is uncertain. The theory of gaseous and particle dry deposition is complex: it is governed both by transfer in the gas phase and by sorption at the surface, which is generally assumed to be an irreversible process.

Following the description of Garland (1978), when the concentration $c(0)$ at the surface is not too high, the rate of sorption is expected to be proportional to $c(0)$. In this case, the concentration flux at the surface is

$$F = \frac{c(0)}{r_s} \tag{10–2}$$

where r_s is the surface resistance s (m^{-1}) which, in ideal conditions, depends only on the affinity of the surface for the particular pollutant under examination. The flux can be related to a vertical dispersion coefficient K_z; i.e.,

$$F = K_z(z)\frac{\partial c}{\partial z} \tag{10–3}$$

which, by integration, gives

$$F = \frac{c(z) - c(0)}{r_g(z)} \tag{10–4}$$

where

$$r_g(z) = \int_0^z \frac{dz'}{K_z(z')} \tag{10-5}$$

is the gas-phase resistance.

From Equations 10-2 and 10-4, we obtain

$$F = \frac{c(z)}{r_s + r_g(z)} \tag{10-6}$$

indicating that the total resistance *r(z)* to deposition is simply the additive sum of the resistances sequentially encountered by the pollutant in its journey to its final sink. This total resistance

$$r(z) = r_s + r_g(z) \tag{10-7}$$

can then be expressed in terms of deposition velocity by

$$V_d(z) = \frac{1}{r(z)} = \frac{F}{c(z)} \tag{10-8}$$

The surface resistance r_s is a function of the physical and chemical properties of the surface and the pollutant and is difficult to evaluate. The gas-phase resistance is easier to evaluate in a turbulent flow, where eddy diffusion dominates and the transport characteristics are expected to be the same for all gases, vapors and small particles (e.g., not greater than a few μm). Similarity theory considerations allow, for example, the estimates presented in Table 10-1, in which r_g is computed as a function of surface type, z_o, wind speed, L, u_*, and elevation.

Most long-range transport models use the above formulation, together with some empirical evaluation of V_d either as a constant or as a function of surface type and hour of the day. LRT models are sensitive to dry deposition computations (Doran, 1979; Smith, 1981), and the reliability of their outputs is affected by the lack of direct evaluation and verification studies of dry deposition phenomena.

Several LRT models, however, do not use Equation 10-7 in a direct way, but decrease the pollutant mass by a certain fraction *df* during the time *dt*, where

$$df = \frac{V_d}{\Delta z_e} dt \tag{10-9}$$

Surface and z_0 (m)	Wind speed at 100 m (m s^{-1})	Monin–Obukhov length. L* (m)	u_* (m s^{-1})	$r_g(1)$ (s cm^{-1})	$r_g(100)$ (s cm^{-1})
Grass	3	∞	0.13	1.25	2.1
(0.01)		−11	0.18	0.89	1.21
	10	∞	0.45	0.41	0.67
		−215	0.49	0.38	0.57
		+630	0.41	0.44	0.77
Cereal crop	3	∞	0.18	0.87	1.5
(0.1)		−27	0.25	0.66	0.93
	10	∞	0.59	0.32	0.50
		−480	0.64	0.30	0.45
		+1700	0.57	0.33	0.54
				$r_g(5)$	
Forest	3	∞	0.27	0.26	0.54
(1.0)		−85	0.36	0.20	0.43
	10	∞	0.89	0.11	0.24
		−1500	0.93	0.10	0.22
		+6100	0.88	0.11	0.24

*** Unstable conditions (L negative) assume a heat flux of 50 W m^{-2} and stable conditions (L positive) assume a downward heat flux of 10 W m^{-2}. $L = \infty$ when conditions are neutral. In stable conditions at the lower wind speed, the surface is isolated from the 100 m level, preventing diffusion from this height and making resistances from 1 m unpredictable.**

Table 10–1. Examples of calculated values of the gas–phase resistance (from Garland, 1978). [Reprinted with permission from Pergamon Press.]

and Δz_e is the vertical thickness of the plume. The fractional reduction can then be integrated and dynamically computed at each time step Δt by the exponential mass reduction

$$M^{(new)} = M^{(old)} \exp\left(-\frac{\Delta t}{T_d}\right) \qquad (10\text{–}10)$$

where $M^{(old)}$ and $M^{(new)}$ are the old and new masses, respectively, of the plume element under consideration, and $T_d = \Delta z_e / V_d$ is the time scale of the dry deposition process.

Zannetti and Al–Madani (1983) proposed a probabilistic approach for a parameterization of dry deposition, resuspension and permanent absorption phenomena using Lagrangian particle methods (discussed in Section 8.3). According to this method, if a plume is represented by the dynamics of, say, n_p active particles, at the end of each time step Δt, all active particle locations need to be tested to single out those particles (say n_b) that, because of semirandom fluctuations, have been moved below terrain. Some of these n_b particles will be reflected and the rest will be deposited on the ground. If T_d is the time scale of this partial deposition process, each of the n_b particles below the terrain has a probability

$$p_d = 1 - \exp\left(\frac{-\Delta t}{T_d}\right) \tag{10-11}$$

of being deposited. Therefore, $p_d n_b$ randomly selected particles (among the previously identified n_b) will be deposited, and the rest of them $(n_b - p_d n_b)$ will be reflected.

Particles deposited on the ground can be resuspended back to the computational domain or permanently absorbed by the ground. If n_d is the current number of deposited particles and T_s is the time scale of the resuspension process, each of these n_d particles has a probability

$$p_s = 1 - \exp\left(\frac{-\Delta t}{T_s}\right) \tag{10-12}$$

of being resuspended. Therefore, at each time step, $p_s n_d$ particles will be resuspended; but if a particle remains deposited on the ground for longer than a critical value T_{dmax}, the particle will be permanently absorbed.

T_d, T_s, and T_{dmax} are functions of the meteorology (especially the surface wind speed) and of the characteristics of both the pollutant and the ground surface. The proper inference of these values is a challenging task.

Alternatively, the same probabilistic method described by Equations 10–11 and 10–12 can be used in a way in which, instead of deleting randomly selected particles from a certain group, an appropriate reduction of mass is applied to all particles of the group. For example, in applying Equation 10–11, instead of deleting $p_d n_b$ randomly selected particles from the previously identified group of n_b particles, a reduction of the mass M of each of the n_b particles can be applied, such as

$$M^{(new)} = (1 - p_d)\, M^{(old)} \tag{10-13}$$

and all particles will be reflected. This second way of applying the probabilistic approach for deposition simulations may be easier to handle computationally, even though it requires the attribution of a time-varying mass to each particle.

Dry deposition of small particles has been reviewed recently by Nicholson (1988). Also, Noll and Fang (1989) have proposed a dry deposition model for coarse particles, while Nicholson (1988b) has reviewed particle resuspension phenomena.

- **A More Refined Simulation of Dry Deposition**

A few new models, e.g., CALGRID (Yamartino et al., 1989), incorporate more refined mechanisms for simulating dry deposition of gases and particles, such as those suggested by Sehmel (1980) and Hicks (1982). New parameterizations have also been proposed by Wesely (1989). The mechanisms of the CALGRID model are summarized below.

Deposition velocity, as anticipated in Equation 10-8, is expressed as the inverse of a sum of "resistances" in three sequential layers:

1. The surface layer, i.e., the layer in which atmospheric fluxes are constant (typically 20 m above the ground). In this layer, pollutant transfer is characterized by atmospheric turbulence properties.
2. The deposition layer, i.e., a thin layer just above the surface characterized by intermittent turbulence. In this layer, gases are affected by molecular diffusion and particles by Brownian diffusion and inertial impaction.
3. The vegetation layer, which is a major sink for many pollutants, a pathway that, in CALGRID, includes deposition directly to the ground or water surface.

For gases, we have

$$V_d = (r_a + r_d + r_c)^{-1} \tag{10-14}$$

where r_a is the atmospheric resistance through the surface layer, r_d is the deposition layer resistance, and r_c is the canopy/vegetation resistance. All resistances are in units of s m^{-1}.

The atmospheric resistance r_a can be derived (Wesely and Hicks, 1977) by

$$r_a = \frac{1}{k\,u_*}\left[\ln(z_s/z_o) - \psi_c\right] \tag{10-15}$$

where z_s is the reference height (m), z_o is the roughness length (m), k is the von Karman constant ($\simeq 0.4$), u_* is the friction velocity (m s^{-1}), and ψ_c is a stability correction term needed to take into account the effects of buoyancy-induced changes in flux-gradient relationships. It is generally assumed that the pollutant transfer is similar to that for heat and, therefore, $\psi_c = \psi_h$, where ψ_h was discussed in Section 3.6.

The deposition layer resistance can be parameterized as a function of the Schmidt number S_c, i.e.,

$$r_d = d_1 \frac{S_c^{d_2}}{k\, u_*} \tag{10–16}$$

where

$$S_c = \nu/D \tag{10–17}$$

ν is the kinematic viscosity of the air ($m^2\, s^{-1}$), D is the molecular diffusivity of the pollutant ($m^2\, s^{-1}$), and d_1, d_2 are empirical parameters ($d_1 \simeq 1.6 - 16.7$, and $d_2 = 0.4 - 0.8$, with a suggested choice of $d_1 = 5$, $d_2 = 0.66$).

The canopy resistance r_c accounts for the main pathways for uptake/reaction of the pollutant in the vegetation surface and can be computed by

$$r_c = [LAI/r_f + LAI/r_{cut} + 1/r_g]^{-1} \tag{10–18}$$

where LAI is the leaf area index (i.e., the ratio of leaf surface area divided by ground surface area), r_f is the internal foliage resistance, r_{cut} is the cuticle resistance, and r_g is the ground or water surface resistance. Moreover, the internal foliage resistance is due to two components

$$r_f = r_s + r_m \tag{10–19}$$

where r_s is the resistance for transport through the stomatal pore and r_m is the resistance to dissolution or reaction of the pollutant in the mesophyll cells.

Values for r_s and r_m are discussed by O'Dell et al. (1977). The resistance r_{cut} is parameterized by Pleim et al. (1984). The ground resistance is discussed by Pleim et al. (1984), while liquid phase resistance is parameterized by Slinn et al. (1978).

Dry deposition of particulate matter differs from that of gases. In fact, for particles, the resistance in the vegetation layer (r_c) is practically zero, since particles that penetrate the deposition layer stick to the surface. Also, particles are affected by the gravitational settling V_g and this represents an alternative pathway to turbulent exchange for reaching the ground. Therefore, for particles, the deposition velocity involves resistances "in parallel" and is given as

$$V_d = (r_a + r_d + r_a r_d V_g)^{-1} + V_g \qquad (10\text{–}20)$$

in which r_a is computed by Equation 10–15, and the deposition layer resistance is

$$r_d = (S_c^{-2/3} + 10^{-3/S_t})^{-1}\, u_*^{-1} \qquad (10\text{–}21)$$

where S_c is the Schmidt number given by Equation 10–17 (where D, in this case dealing with particles, is the Brownian diffusivity of the pollutant in air instead of the molecular diffusivity), and S_t is the Stokes number

$$S_t = \frac{V_g\, u_*^2}{g\, \nu} \qquad (10\text{–}22)$$

The gravitational settling V_g is a function of the particle size, shape and density (e.g., see Figure 8–6). For particles that can be approximated by spheres, the Stokes equation gives

$$V_g = [d_p^2\, g\, (\varrho_p - \varrho_a)\, C]/(18\, \mu) \qquad (10\text{–}23)$$

where d_p is the particle diameter (m), ϱ_p is the particle density (g m^{-3}), ϱ_a is density of the air (g m^{-3}) and C is the Cunningham correction factor for small particles

$$C = 1 + (2\,\lambda/d_p)\, [a_1 + a_2\, \exp(-\, a_3\, d_p/\lambda)] \qquad (10\text{–}24)$$

where λ is the mean free path of air molecules ($\lambda = 6.53\ 10^{-6}$ cm) and a_1, a_2, a_3 are constants (= 1.257, 0.40, 0.55).

10.2 WET DEPOSITION

Extensive discussion of wet deposition phenomena can be found in Seinfeld (1986), Finlayson-Pitts and Pitts (1986), and Hales (1986). Only a brief outline will be given here.

Wet deposition is caused by both precipitation scavenging and surface deposition of fog and cloud droplets. Unlike dry deposition, a phenomenon that occurs in the lower layers of the PBL, precipitation scavenging affects all volume elements aloft inside the precipitation layer. Following Seinfeld (1986), the wet flux of a pollutant to the surface is

$$W_g = \int_o^\infty \Lambda(z,t)\; c(x,y,z,t)\; dz \tag{10–25}$$

for gases and

$$W_p = \int_o^\infty \Lambda(d_p; z,t)\; c(d_p; x,y,z,t)\; dz \tag{10–26}$$

for particles, where Λ is the washout coefficient and c the concentration expressed, for particles, as a function of the particle diameter d_p. It must be noted that Λ varies spatially and temporally. Techniques are available (e.g., Scott, 1982) for calculating Λ as a function of storm type and precipitation amounts, information that can be inferred from NWS observations.

The knowledge of the wet flux W (W_g or W_p) allows the definition of the wet deposition velocity

$$V_w = \frac{W}{c(x,y,0,t)} \simeq \overline{\Lambda} H \tag{10–27}$$

where the last equality assumes that the pollutant is uniformly distributed between $z = 0$ and $z = H$. The wet deposition velocity V_w can be computed by

$$V_w = w_r\, p_o \tag{10–28}$$

where w_r is the species-specific washout ratio (i.e., the concentration of material in surface-level precipitation divided by the concentration of material in surface-level air) and p_o is the precipitation intensity (m s^{-1}). For example, if $w_r = 10^6$ and $p_o = 2.8\ 10^{-7}$ m s^{-1} (i.e., corresponding to a typical light rainfall of 1 mm h^{-1}), then $V_w = 28$ cm s^{-1}, which gives, for $H = 1000$ m, $\overline{\Lambda} = 2.8\ 10^{-4}\ s^{-1}$.

The estimate of w_r from available acid rain chemistry data collected in the monitoring networks allows, under certain conditions, a direct evaluation of wet deposition of pollutants (Slinn et al., 1978; Baker et al., 1983; Davies, 1983; Bilonick and Nichols, 1983). (See also Wisniewski and Kinsman, 1982, for an overview of acid precipitation monitoring activities in North America.) In fact, after the washout (or scavenging) coefficients $\overline{\Lambda}$ are evaluated, wet deposition can be dynamically computed by decreasing the mass of the plume elements according to Equation 10–10, where the time scale T_d is replaced by

$$T_w = 1/\overline{\Lambda} \tag{10-29}$$

the time scale of the wet deposition process.

Seinfeld (1986) provides a detailed mathematical discussion of precipitation scavenging of particles, and the calculation of collision efficiencies and scavenging rates, and precipitation of gases, for both irreversibly soluble gases (such as nitric acid, HNO_3) and reversibly soluble gases. Also, a generalized multidimensional model for precipitation scavenging and atmospheric chemistry has been presented by Hales (1989).

In addition to precipitation phenomena, wet deposition is also caused by surface impaction of polluted droplets of fog or cloud. These phenomena, whose parameterization is still poorly understood, are outlined in Figure 10-2.

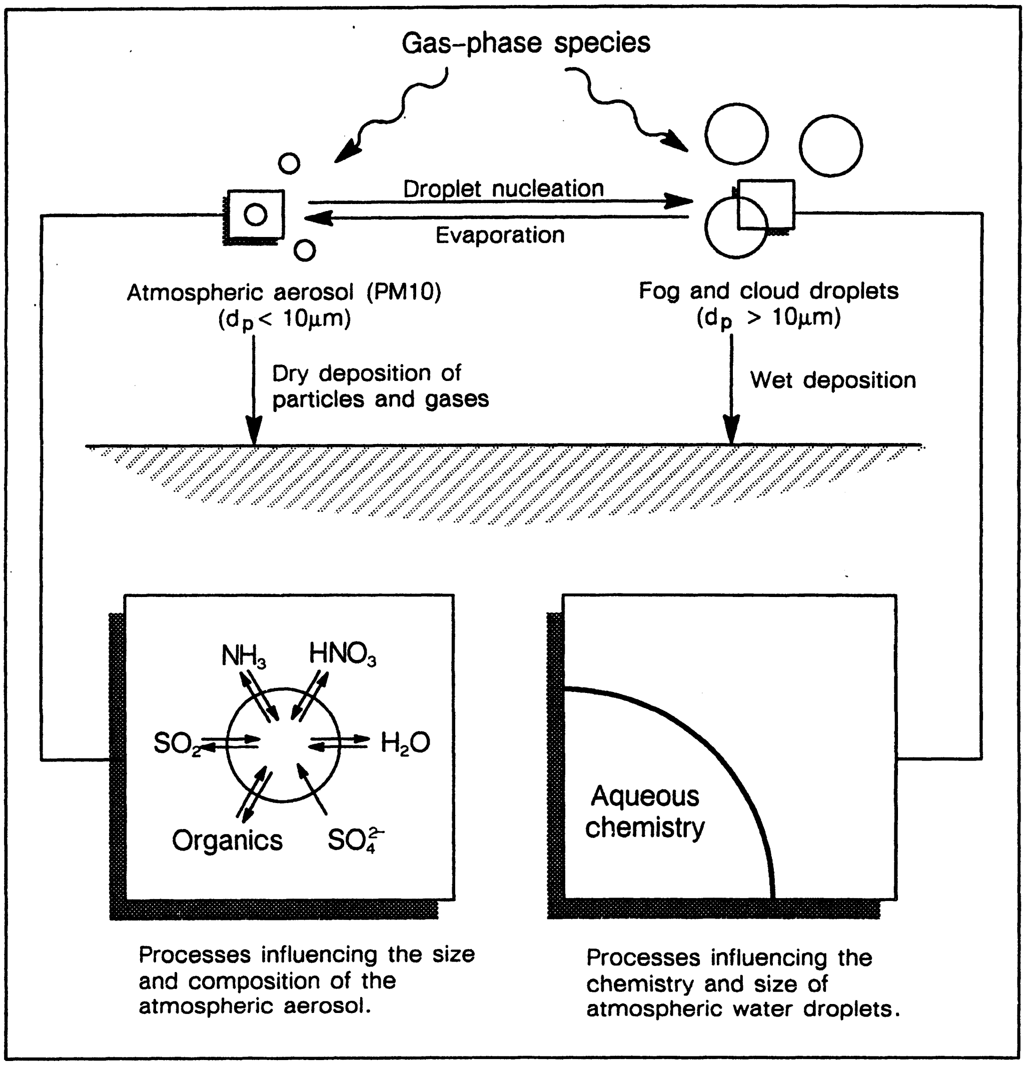

Figure 10-2. Flow chart of atmospheric processes leading to airborne and deposited acidity (from Seinfeld, personal communication).

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