

5. DEPOSITION PROCESSES

5.1 Dry deposition

Dry deposition describes the uptake of atmospheric species (gases or aerosol particles) at the surface of the Earth. It provides a surface boundary condition for atmospheric chemistry models. When describing dry deposition, we can either view the uptake by the surface as an irreversible loss for the species (one-way deposition), or as a reversible process where the surface provides a reservoir for the species and allows re-emission to the atmosphere (two-way exchange). We will discuss both in order.

5.1.1 One-way deposition

In one-way deposition, the irreversible uptake of a species at the surface is characterized by the *dry deposition flux* F_d (molecules $\text{cm}^{-2} \text{s}^{-1}$), to be applied to the model gridpoint closest to the surface. The dry deposition flux is dependent on the species *surface concentration* and on the reactivity of the surface. However, the lowest model gridpoint is at finite altitude z_I above the surface. Vertical transport to the surface is determined by turbulent motions (section 2.2), for which parameterization is necessary. To construct this parameterization, we consider an altitude z_s below which the vertical flux can be assumed uniform and equal to F_d , that is, $F_z(z_s) \approx F_d$ to within a certain error tolerance (10% is typical). In meteorological applications concerned with the deposition of sensible heat and momentum, this column $[0, z_s]$ defines the *surface layer* and is typically 50-100 m deep. Vertical flux conservation in this surface layer is a good assumption for depositing species with relatively long lifetimes (of the order of one hour or more). For highly reactive species there may be a significant vertical flux divergence within the surface layer, but we are generally not concerned with the deposition of these species since chemical loss tends then to dominate over deposition.

Let us assume for now that our lowest model gridpoint is within the surface layer ($z_I < z_s$); we will discuss later the case where this is not satisfied. Since the vertical flux is conserved between z_I and the surface, we can express F_d solely as a function of the number density $n(z_I)$ at altitude z_I , the rate of turbulent transfer from altitude z_I to the surface, and the reactivity at the surface. If the loss at the surface is a linear function of the local number density $n(0)$ (as is generally the case), then the deposition flux is linearly dependent on $n(0)$, which in turn is linearly dependent on $n(z_I)$:

$$F_d = -V_d(z_I)n(z_I) \quad (5.1)$$

where $V_d(z_I)$ is the *dry deposition velocity* (cm s^{-1}) at altitude z_I . It is called a ‘velocity’ because of its units, and it could be viewed as an equivalent sedimentation velocity applied at z_I , but in fact the processes involved are turbulent transport and chemical reaction as analyzed below.

In the standard “big-leaf” parameterization of dry deposition we view the surface as uniform (that is, as a big leaf). We can then decompose the deposition process

as involving the turbulent transfer from z_l to the surface, followed by reaction at the surface. Invoking the eddy diffusion parameterization (section 2.2) to describe the turbulent transfer, we write

$$F_d = -K_z(z)n_a \frac{dC(z)}{dz} \approx -K_z(z) \frac{dn(z)}{dz} \quad (5.2)$$

where we have neglected the small variation of the air density n_a with altitude. Equation (5.2) can be integrated to express F_d in terms of the concentration difference between z_l and the surface:

$$F_d = -\frac{n(z_l) - n(0)}{\int_0^{z_l} \frac{dz}{K(z)}} = -\frac{n(z_l) - n(0)}{R_a} \quad (5.3)$$

where $R_a = \int_0^{z_l} \frac{dz}{K(z)}$ (s cm^{-1}) is the *aerodynamic resistance* to deposition. The term “resistance” reflects the analogy with electrical circuits: $n(z_l) - n(0)$ is the analog of a difference in potential and F_d is the analog of an intensity. We can express the reaction at the surface in a similar way, where the difference of potential analogy applies to the difference in concentrations $n(0) - n_s$ between the surface air and those inside the ‘big leaf’ (n_s), taking $n_s = 0$ for our assumption of irreversible uptake:

$$F_d = -\frac{n(0) - n_s}{R_c} = -\frac{n(0)}{R_c} \quad (5.4)$$

where R_c (s cm^{-1}) is the *surface resistance* to deposition and is a measure of the chemical reactivity of the surface. Combining equations (5.1), (5.3), and (5.4) we obtain

$$V_d = \frac{1}{R} = \frac{1}{R_a + R_c} \quad (5.5)$$

where R is the *overall resistance* to deposition. We see that the resistances add in series, consistent with our electrical analogy.

To derive R_a we assume similarity between the deposition of the species and deposition of momentum, which has been extensively studied in the micrometeorological literature. Observations show that under neutral buoyancy conditions the wind speed u increases logarithmically with altitude:

$$u(z) = \frac{u^*}{k} \ln \frac{z - d}{z_o} \quad (5.6)$$

where $u^* = [-\langle u'w' \rangle]^{1/2}$ (m s^{-1}) is the *friction velocity* defined as the square root of the absolute value of the wind velocity deposition flux $F_u = \langle u'w' \rangle$, $k = 0.35$ is the von

Karman constant, d is the *displacement height* which represents the altitude above ground of the “big leaf”, and z_o is the *roughness height*. As a rule of thumb, if z_c is the canopy height, then $d \approx 2z_c/3$, $z_o \approx z_c/30$, and $u^* \approx u/10$. Note from (5.6) that u decreases to zero at $z = d + z_o$, so that the roughness height represents the altitude above the big leaf where the wind dies out. Applying now the eddy diffusion parameterization to the transport of momentum (i.e., wind velocity), we obtain an expression for the eddy diffusion coefficient $K_z(z)$:

$$K_z(z) = -\frac{F_u}{du/dz} = \frac{u^{*2}}{u^*} = ku^*(z-d) \quad (5.7)$$

Replacing into the definition for R_a we obtain

$$R_a = \int_{d+z_o}^{z_1} \frac{dz}{K(z)} = \frac{1}{ku^*} \ln \frac{z_1 - d}{z_o} \quad (5.8)$$

Data are generally available for u^* , enabling calculation of R_a .

The neutral buoyancy conditions assumed in (5.6) and used to derive (5.8) apply to the lowest part of the atmosphere where turbulence is largely driven by mechanical forcing. At higher altitudes, turbulence is largely driven by heating gradients (buoyancy). The *Monin-Obukhov height* L defines the altitude where the mechanical and buoyant contributions to turbulence are equal, and is given by

$$L = -\frac{\rho C_p T u^{*3}}{kgF_\theta} \quad (5.9)$$

where ρ is the air density, $C_p = 1.00 \text{ J g}^{-1} \text{ K}^{-1}$ is the specific heat of air, T is the surface temperature, g is the acceleration of gravity, and $F_\theta = \rho C_p \langle \theta' w' \rangle$ is the surface flux of sensible heat (θ is the potential temperature). Under unstable conditions where the surface is a source of sensible heat to the atmosphere ($F_\theta > 0$), we see that L is negative; conversely under stable conditions L is positive. Under strictly neutral conditions ($F_\theta = 0$), L goes to infinity. As z_1 approaches $|L|$, one must apply *stability correction functions* to the calculation of R_a given in (5.8); see section 19.2.1 of Seinfeld and Pandis [1998]. One often takes $|L|$ as the top of the surface layer.

Notice that the aerodynamic resistance as calculated in (5.8) extends only down to $d+z_o$ (zero point for momentum). Below that point the wind is taken to be zero and further transport to the surface is controlled by molecular diffusion. One defines an additional *boundary resistance* $R_b = f(D)$ to characterize transport between $d+z_o$ and the surface, such that

$$V_d = \frac{1}{R_a + R_b + R_c} \quad (5.10)$$

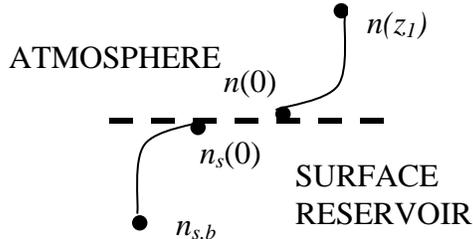
In all conditions $R_b \ll R_a$, so the specification of R_b is of little importance.

Detailed parameterizations of R_c are available in the literature as a function of canopy structure (leaf area index), environmental conditions (solar radiation, temperature), chemical properties of the depositing gas, and so on; see Wesely [Atmos. Environ., 1989]. Application of (5.10) often produces limiting cases $R_a \ll R_c$ (weakly reactive gas, or strongly turbulent conditions) or $R_a \gg R_c$ (highly reactive gas, or strongly stratified conditions).

What should we do in our model if $z_I > |L|$, that is, the lowest model gridpoint is not within the surface layer and vertical flux conservation from z_I to the surface cannot be assumed? This happens under conditions that are either very unstable or very stable. Under very unstable conditions, transport between the top of the surface layer ($-L$) and z_I is very fast and the corresponding aerodynamic resistance is negligible; we can then assume $V_d(z_I) = V_d(-L)$ and calculate the deposition velocity at altitude $-L$. Under very stable conditions, we have a more difficult problem in that the stratification of the atmosphere below z_I is such that the deposition flux at the surface may in fact not be related to the concentration at z_I . Since the part of the atmosphere contributing to deposition is then restricted to a very shallow layer near the surface, it is best to simply neglect deposition under these conditions.

5.1.2 Two-way exchange

The deposition velocity formulation (5.1) assumes a one-way flux of the depositing species to the surface. In fact, the species may also be emitted or re-emitted from the surface reservoir (s), resulting in a *two-way exchange*. To describe this two-way exchange we extend the resistance-in-series formulation to a bulk surface reservoir, as drawn below.



Let us assume uniformity in the vertical flux between altitude z_I and the bulk surface reservoir, where the concentration is taken to be $n_{s,b}$. As we saw in section (5.1.1), we can always find an altitude z_I for which this assumption is satisfied on the atmospheric side. The same holds for the surface reservoir side. The concentration field $n_{s,b}$ may be provided as a boundary condition for the atmospheric model, or it may be coupled to the atmospheric model and solved with its own continuity equation.

We could relate the two-way exchange flux to the concentration gradient by defining resistances to turbulent transport in the atmosphere and in the surface reservoir phases, as we did to model one-way deposition in section 5.1.1. It is however customary to define *conductances* or *transfer velocities* k_a and k_s (cm s^{-1}) as the inverse of the resistances, so that

$$F_d = -k(n(z_1) - n(0)) = -k_s(n_s(0) - n_{s,b}) \quad (5.11)$$

At the surface, the concentrations in the two phases are in equilibrium, which we express by an equilibrium constant H :

$$H = \frac{n(0)}{n_s(0)} \quad (5.12)$$

Rearranging yields an expression for the deposition flux in terms of the bulk concentrations in each phase:

$$F_d = -K(n(z_1) - Hn_{s,b}) \quad (5.13)$$

where

$$\frac{1}{K} = \frac{1}{k} + \frac{H}{k_s} \quad (5.14)$$

The rate of exchange may be limited either by transfer in the gas phase ($k \ll k_s/H$) or by transfer in the surface reservoir (if $k \gg k_s/H$).

A common application of the two-way exchange formulation (5.13) is to describe exchange of atmospheric gases with the ocean. Here $n_{s,b}$ is usually specified from ship observations, H is the Henry's law constant describing equilibrium between the gas and seawater phases, and empirical formulations for k and k_s are available as a function of surface wind speed. For highly soluble gases such as HNO_3 and SO_2 , the rate of exchange is limited by transfer in the gas phase; for weakly soluble gases such as CO_2 or DMS, transfer in the aqueous phase is limiting.

5.2 Wet deposition

Wet deposition describes the scavenging of soluble gases and aerosol particles from the atmosphere by precipitation. Meteorological models generally distinguish between two types of precipitation: (1) convective precipitation resulting from convective updrafts (chapter 2) that are not resolved on the grid scale, and (2) large-scale precipitation resulting from frontal systems or other meteorological processes that are resolved on the grid scale. Different scavenging parameterizations are appropriate in each case.

5.2.1 Scavenging in wet convective updrafts

This scavenging must be applied within the convective mass transport algorithm in order to prevent soluble species from being transported to the top of the

convective updraft and then dispersed on the grid scale without experiencing scavenging. The transport model provides wet convective air mass fluxes through each gridbox in the updraft. As air is lifted a distance Δz from one gridpoint to the next, it loses a fraction F_i of soluble tracer i to scavenging. This fraction depends on (1) the rate constant k (s^{-1}) for conversion of cloud condensate (including liquid and ice) to precipitation; (2) the fraction $f_{i,L}$ of species present in the liquid cloud condensate; (3) the fraction $f_{i,I}$ of tracer present in the ice cloud condensate; and (4) the retention efficiency R_i of tracer in the liquid cloud condensate as it is converted to precipitation ($R_i < 1$ accounts for volatilization during riming). Thus the rate constant k_i (s^{-1}) for loss of species from the updraft is given by

$$k_i = (R_i f_{i,L} + f_{i,I})k \quad (5.15)$$

and the fraction F_i of tracer scavenged as the air is lifted by Δz is

$$F_i = 1 - \exp\left[-\frac{k_i \Delta z}{w}\right] \quad (5.16)$$

where w is the updraft velocity, which may be provided by the meteorological model or else needs to be estimated. Appropriate estimates are $k = 5 \times 10^{-3} \text{ s}^{-1}$ and $w = 10 \text{ m s}^{-1}$ (continents) or 5 m s^{-1} (oceans) [Mari et al., J. Geophys. Res., 2000].

Aerosols and HNO_3 are 100% in the cloud condensate phase ($f_{i,L} + f_{i,I} = 1$), and we assume $R_i = 1$, therefore $k_i = k$. For gases other than HNO_3 a significant fraction may be in the gas phase so that $k_i < k$. The phase partitioning depends on the cloud liquid water content L (cm^3 water cm^{-3} air) and the cloud ice water content W (cm^3 ice cm^{-3} air). Typical values for L and W are:

$$\begin{aligned} L &= 2 \times 10^{-6} & T &\geq 268 \text{ K} \\ L &= 2 \times 10^{-6} \frac{T - 248}{20} & 248 &< T < 268 \text{ K} \\ L &= 0 & T &\leq 248 \text{ K} \\ W &= 2 \times 10^{-6} - L \end{aligned}$$

The partitioning between the gas phase and the liquid phase is given by the temperature-dependent Henry's law constant [Jacob, Atmos. Environ., 2000]. The partitioning between the gas phase and the ice phase can be obtained from a co-condensation model [Mari et al., J. Geophys. Res., 2000]

5.2.2 Scavenging by large-scale precipitation

Scavenging by large-scale precipitation is generally parameterized as first-order losses from rainout and washout. *Rainout* refers to in-cloud scavenging by

precipitation of cloud droplets or ice crystals. *Washout* refers to below-cloud scavenging by precipitation. The model must provide information on precipitation rates P_k through the bottom of each gridbox. Rainout takes place in gridboxes where new precipitation forms ($P_k > P_{k+1}$) and washout takes place in gridboxes where precipitation evaporates ($P_k < P_{k+1}$). Evaporation results in fractional or total release of species in the evaporating gridbox. One starts the scavenging calculation at the top of each precipitating column and progresses downward gridpoint by gridpoint, applying rainout or washout/reevaporation as appropriate. Formulations used to compute scavenging efficiencies in the precipitating column are similar to the ones used for convective precipitation (section 5.2.1). Because scavenging of soluble gases and aerosols by precipitation is highly efficient, a critical variable for quantifying the loss from wet deposition is the areal fraction of the grid square actually experiencing precipitation. This fraction is usually very small, of the order of 10%, and its parameterization is the largest uncertainty in the computation of scavenging from large-scale precipitation.