

Wet Removal of Pollutants from Gaussian Plumes: Basic Linear Equations and Computational Approaches

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ABSTRACT

Over the past several years, a number of Gaussian plume-based computer codes have been produced. These codes describe transport, transformation, and deposition of air pollutants under a variety of atmospheric conditions. For a number of reasons, there is increasing interest in simulating wet-deposition processes in such codes, and several approaches have been applied to this end. Some of these approaches involve elaborate solubility and chemistry characterizations, but many of them resort to a diversity of approximate techniques. This paper presents a procedure that can be used as a practical guide to improve many of these formulations, especially for the case of pollutant gases. The approach takes the form of a set of analytical equations that correspond to five kinds of Gaussian plume formulations: standard bivariate-normal point-source plumes, line-source plumes, unrestricted instantaneous puffs, and point-source plumes and puffs that experience reflection from inversion layers aloft. These equations represent the concentration of scavenged pollutants in falling raindrops and are similar in complexity to their associated gas-phase plume equations. They are strictly linear, thus allowing superposition of wet-deposition contributions by multiple plumes.

1. Introduction

Over the past several years, a number of Gaussian plume-based computer codes have been produced. These codes describe transport, transformation, and deposition of air pollutants under a variety of atmospheric conditions (e.g., EPA 1995; Scire et al. 2000). Such codes are based on numerous idealizations of physical behavior, and caution is mandatory in their application to real-world situations. Despite this caveat, however, they are often useful as assessment tools and continue to be applied extensively for regulatory purposes. Moreover, there is an increasing emphasis on simulating wet-deposition processes in such codes, and several approaches—many resorting to a diversity of approximate and often uncertain techniques—have been applied to this end. In response to an obvious need for improvement in this particular area, the goal of this paper is to present a consistent, computationally tractable procedure for wet-removal calculation. Such a procedure can be used as a practical guide to improve many of these formulations, especially for the case of pollutant gases.

Although more exact than many of its predecessors, the approach presented here involves several important assumptions. Most significant, it preserves linearity by assuming that pollutant-gas solubility and mass-transport parameters are concentration independent—a con-

venient feature for multisource Lagrangian models, which usually rely on superposition to compute collective plume behavior. This assumption is reasonably well justified for gaseous pollutants whose water solubility obeys Henry's law, and it can be extended to moderately deviant systems by linearization of the associated equations, although it can produce radically incorrect results for strongly nonlinear systems (e.g., Dana et al. 1975).

Moreover, the approach assumes negligible vertical redistribution of the plume by "washdown" caused by absorption and subsequent desorption of pollutant from the falling rain. This assumption is justified under most practical conditions because vertical transport by atmospheric mixing largely obscures washdown effects (Slinn 1974). The approach also assumes vertical rainfall and no aqueous-phase reaction, a constraint that can be removed for simple, linear reacting systems by appropriate adaptation of the associated equations. The procedure also assumes that interactions between the plume and clouds are negligible—a situation that often can be justified in the case of gas scavenging but can become problematic for suspended particulate matter, where in-cloud capture mechanisms tend to dominate (see section 8).

The approach presented here takes the form of a set of analytical equations that correspond to five kinds of Gaussian plume formulations: standard bivariate-normal point-source plumes, line-source plumes, unrestricted instantaneous puffs, and point-source plumes and puffs that experience reflection from inversion layers aloft. As a starting point, this paper applies an equation for

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gaseous pollutant scavenging from point-source plumes (Hales 1972b) that was field tested several years ago for gases such as sulfur dioxide (SO₂) (Hales et al. 1973) and tritiated water vapor (Dana et al. 1978). Using the nomenclature applied in these earlier publications (see appendix B for definitions of all parameters used in this paper), the change of mixed-average pollutant concentration c (mol cm⁻³) with respect to height in a raindrop falling through a plume is simply

$$\frac{dc(a, z)}{dz} = \frac{3K_y(a)}{v_z(a)a} [y_{Ab} - H'c(a, z)], \quad (1)$$

where a (cm) is the raindrop's radius, H' (cm³ mol⁻¹) is a solubility parameter, v_z (cm s⁻¹) is the raindrop's vertical velocity, y_{Ab} is the (spatially varying) mixing ratio of pollutant in air expressed as moles of pollutant per mole of air, and z (cm) is the raindrop's vertical position. As described later in this paper, K_y (mol cm⁻² s⁻¹) is an overall mass-transfer coefficient and can be estimated on the basis of physical properties. Note here that with this usage *increasing* H' corresponds to *decreasing* solubility. The particular definition of the solubility coefficient applied is immaterial as long as consistency of usage is maintained in the equations.

Equation (1) reflects the reversible nature of gas scavenging, which allows pollutant gas to either sorb into or desorb from the falling drop, depending on ambient conditions. For highly soluble gases (as well as suspended particles), H' is effectively zero, and the scavenging process is essentially irreversible. Integration of (1) over all drop sizes under such circumstances leads to the scavenging-coefficient approach, familiar in the aerosol-washout literature (e.g., Slade 1968; see sections 5 and 7).

The pollutant concentration in bulk rain collected at any given height z is given by the deposition-weighted average over the raindrop size spectrum:

$$c_{\text{bulk}}(z) = \frac{4\pi n_0}{3J} \int_0^\infty a^3 n(a) v_z(a) c(a, z) da \quad (\text{mol cm}^{-3}), \quad (2)$$

where n_0 is the total number of raindrops existing in a cubic centimeter of space, $n(a)$ (cm⁻¹) is the associated probability density function for raindrops of size a , and J (cm s⁻¹) is the rain flux. It follows directly that the

$$c(a, z) = -\frac{\alpha}{2\sqrt{2\pi H'}} \exp\left(\frac{-y^2}{2\sigma_y^2}\right) \left\langle \exp\left(\frac{\sigma_z^2 \zeta^2}{2}\right) \left\{ \exp[-\zeta(z-h)] \operatorname{erfc}(\beta_1) + \exp[-\zeta(z+h)] \operatorname{erfc}(\beta_2) \right\} \right\rangle + \frac{y_{Ab|bkg}}{H'}, \quad (6)$$

where $\alpha = (QF\zeta)/(\sigma_y u)$ (dimensionless), $\beta_1 = (-\zeta\sigma_z^2 + z - h)/(\sqrt{2}\sigma_z)$ (dimensionless), $\beta_2 = (-\zeta\sigma_z^2 + z + h)/(\sqrt{2}\sigma_z)$ (dimensionless), and $\zeta = [3K_y(a)H']/[v_z(a)a]$ (cm⁻¹). The form of (6) usually employed for practical

wet-deposition flux of pollutant approaching the surface at $z = s$, Flux_s , is simply

$$\text{Flux}_s = Jc_{\text{bulk}}(s) \quad (\text{mol cm}^{-2} \text{ s}^{-1}). \quad (3)$$

Note here that J , v_z , and Flux_s are negative downward under this convention.

2. Standard bivariate-normal plumes

a. Basic equations

If the vertical distribution of gas-phase pollutant is known, (1) can be integrated in a straightforward manner. For the particular case of a standard bivariate-normal plume embedded in a uniform background, this distribution is (Slade 1968)

$$y_{Ab} = \frac{QF}{2\pi\sigma_y\sigma_z u} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \times \left\{ \exp\left[-\frac{(z-h)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+h)^2}{2\sigma_z^2}\right] \right\} + y_{Ab|bkg}, \quad (4)$$

where σ_y and σ_z (cm) are, respectively, the horizontal and vertical plume-spread parameters, u (cm s⁻¹) is the mean wind velocity, h (cm) is the emission height, y and z (cm) denote vertical and crosswind positions, respectively, and $y_{Ab|bkg}$ denotes a spatially invariant background mixing ratio. The dimensionless variable F , which varies between 1 and 0, is a factor that accounts for plume depletion by upwind washout. For consistency of units, the emission rate Q is expressed here as the volume of pollutant gas, at local temperature and pressure, emitted per unit time (cm³ s⁻¹). This quantity may be related to the more conventional emission rate \hat{Q} (moles of pollutant released per second) by the relationship

$$\hat{Q} = c_{\text{air}} Q, \quad (5)$$

where c_{air} (moles of air per centimeter cubed) is the molar density of air at ambient temperature and pressure.

Combining (4) and (1) and integrating with respect to z results in the form

scavenging calculations corresponds to $z = s$, resulting in concentration values in rain approaching the surface, that is, $c(a, s)$.

Application of (6) requires some caution for two rea-

sons. First, the term $\exp[-\zeta(z + h)] \operatorname{erfc}(\beta_2)$ becomes computationally intractable for large, positive values of

β_2 , and under such conditions the following asymptotic approximation¹ to (6) may be applied:

$$c(a, z) = -\frac{\alpha}{2\sqrt{2\pi}H'} \exp\left(\frac{-y^2}{2\sigma_y^2}\right) \left\{ \exp\left(\frac{\sigma_z^2 \zeta^2}{2}\right) \exp[-\zeta(z - h)] \operatorname{erfc}(\beta_1) + \frac{1}{2\sqrt{\pi}} \exp\left[\frac{-(z + h)^2}{2\sigma_z^2}\right] \frac{1}{\beta_2} \left[2 - \left(\frac{1}{\beta_2}\right)^2\right] \right\} + \frac{y_{\text{Ab|bkg}}}{H'}. \tag{6a}$$

For computers using single-precision arithmetic, it is appropriate to make a transition from (6) to (6a) whenever β_2 exceeds about 3.5.

The second cautionary note pertains to the term

$\exp[(\sigma_z^2 \zeta^2)/2]$, which can become unmanageably large for situations that involve large plume spreads and rapid mass-transfer rates. Under such conditions, the following additional asymptotic expression can be employed:

$$c(a, z) = -\frac{\alpha}{2\sqrt{2\pi}H'} \exp\left(\frac{-y^2}{2\sigma_y^2}\right) \left\{ \frac{1}{2\sqrt{\pi}} \exp\left[\frac{-(z - h)^2}{2\sigma_z^2}\right] \frac{1}{\beta_1} \left(2 - \frac{1}{\beta_1^2}\right) + \frac{1}{2\sqrt{\pi}} \exp\left[\frac{-(z + h)^2}{2\sigma_z^2}\right] \frac{1}{\beta_2} \left(2 - \frac{1}{\beta_2^2}\right) \right\} + \frac{y_{\text{Ab|bkg}}}{H'}. \tag{6b}$$

Again based on single-precision arithmetic, (6b) should be applied whenever the absolute value of β_1 exceeds about 3.5. Equations (6), (6a), and (6b) are somewhat similar to those given by Hales et al. (1973) but are more general and more computationally robust.

Values of β_1 and β_2 increase with σ_z and, thus, with distance downwind from the source; as such, one should normally expect progressive transitions of use from (6) to (6a) and then to (6b) as downwind distance becomes long. At even longer downwind distances, (6), (6a), and (6b) predict that the falling raindrops should approach diffusional equilibrium with respect to the local pollutant concentration and that the pollutant concentration in raindrops approaching the surface should be given simply by

$$c(a, s) = \frac{y_{\text{Ab}}(x, y, s)}{H'}, \tag{7}$$

avoiding the need for the more complex forms (6), (6a), and (6b) when such conditions prevail. This “equilibrium scavenging” condition is favored by small raindrop sizes, low solubilities, and large vertical plume spread. For rain approaching ground level, this condition can be expressed by the following dimensionless criterion (Hales 1972a):

$$N_{\text{es}} = \frac{-3e^{1/2} K_y(a) H' \sigma_z}{v_z(a) a \exp(h^2/2\sigma_z^2)} \gg 1. \tag{8}$$

Equilibrium scavenging conditions can conservatively be expected to prevail whenever N_{es} exceeds about 50.

Based on the above discussion, an appropriate computational approach could begin with inspection of (8), with direct application of (7) whenever N_{es} exceeds 50. In cases for which this condition is not met, the computation should test to see if both β_2 and β_1 exceed 3.5 and apply (6b) if this is the case. Failing this, a test should be performed for exceedance of 3.5 by β_2 only, with application of (6a) under this condition. If none of the preceding conditions are met, (6) should be applied directly.

Figure 1 shows example plots of solutions to (6) for unit emission rate and a variety of plume heights and drop sizes. As indicated by these figures, vertical position of the plume can have a considerable influence on pollutant concentrations in rain approaching ground level, especially for small drop sizes and for gases having lower solubility in water. In referring to Figs. 1a–c, it can be observed that, although highly soluble gases are scavenged more efficiently, raindrops scavenging lower-solubility gases follow equilibrium behavior more closely.

b. Plume depletion: Bivariate-normal plumes

The plume-depletion factor F is unity at the emission point and decreases toward zero as the pollutant is removed from the plume. From simple material-balance

¹ Equation (7.2.14) from Abramowitz and Stegun (1965) was used as a starting point for derivation of (6a) and (6b).

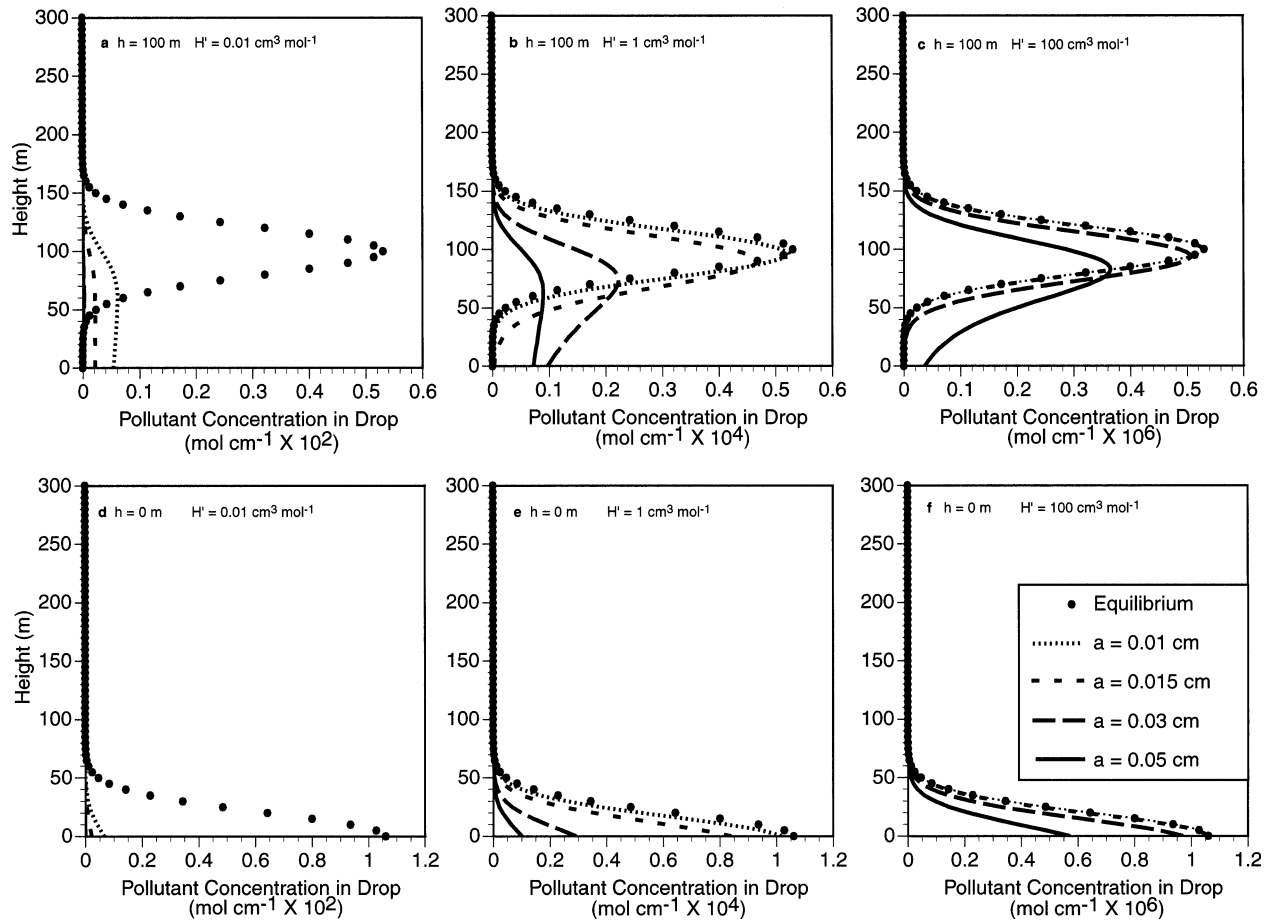


FIG. 1. Vertical profiles of pollutant concentrations in raindrops at plume centerline as functions of plume height, solubility, and raindrop size as calculated from (6) for a bivariate-normal plume of unit source strength emitted into a constant wind of 5 m s^{-1} , having plume-spread parameters σ_y and σ_z of 30 and 20 m, respectively. The liquid-phase mass-transfer coefficient is augmented by 2.5 for these calculations (see text). Note changes of scales on abscissas of the graphs.

considerations, this is related to the emission strength and deposition flux, as follows:

$$F(X) = 1 - \frac{c_{\text{air}} Q}{\int_{x=0}^{x=X} I_y dx} \quad (\text{for } X \text{ and } I_y > 0), \quad (9)$$

where X (cm) is the current downwind position and

$$\begin{aligned} I_y &= - \int_{-\infty}^{\infty} \text{Flux}_s|_{\text{plume}} dy = - \int_{-\infty}^{\infty} J c_{\text{bulk}}(s)|_{\text{plume}} dy \\ &= \frac{-4\pi n_0}{3} \int_{y=-\infty}^{y=\infty} \int_{a=0}^{a=\infty} a^3 n(a) v_z(a) c(a, s)|_{\text{plume}} da dy, \end{aligned}$$

with $\text{Flux}_s|_{\text{plume}}$ being the deposition flux of plume material, exclusive of the background. Note again here that, by the convention used in this paper, J and Flux_s are negative downward. Note also that F occurs implicitly on the right-hand side of (9), rendering the total equation implicit and necessitating stepwise calculations in the down-plume direction.

Equation (9) is impossible to integrate analytically in the x (downwind) direction without prior knowledge of the plume-spread parameters as functions of downwind distance. On the other hand, for (6), (6a), and (6b), the y integral corresponding to raindrops of size a can be obtained in closed form:

$$I_{y,a} = \frac{2\pi n_0 \alpha \sigma_y a^3 n(a) v_z(a)}{3H'} \Gamma \quad (\text{mol cm}^{-2} \text{ s}^{-1}), \quad (10)$$

where $I_y = \int_0^\infty I_{y,a} da$, and Γ denotes the factors enclosed within angle brackets ($\langle \rangle$) in (6) or braces ($\{ \}$) in (6a) and (6b), depending on which of these equations is being applied. If, as suggested in section 4, the raindrop spectrum is approximated by lumping into a single drop size having the mass-mean radius, integration over a can be avoided, and (10) becomes simply

$$I_y = \frac{J \alpha \sigma_y}{2H'} \Gamma \quad (\text{mol cm}^{-1} \text{ s}^{-1}). \quad (11)$$

The counterpart equation for equilibrium scavenging is

$$I_y = \frac{-JQF}{\sqrt{2\pi}\sigma_z u H'} \Gamma \quad (\text{mol m}^{-1} \text{ s}), \quad (12)$$

where Γ now denotes the factors within braces in (4).

Given this, (9) can be used to compute plume depletion in a relatively straightforward fashion. One simply applies (10), (11), or (12) as appropriate to compute values of I_y as a function of downwind distance, performs a finite-difference approximation to obtain the x integral, and computes the plume-depletion factor (as a function of downwind distance) from (9).

3. Other Gaussian plume types: Line sources, puffs, and reflection aloft

a. Basic equations

Several variations of Gaussian plume models are used in practical modeling codes and thus are of interest in a gas-scavenging context. In particular, line-source dispersion models, puff models, and models that involve reflection from an inversion layer aloft are employed frequently in such calculations. The equations for gas-phase pollutant mixing ratios for these cases are (Slade 1968; Seinfeld and Pandis 1998; Nagendra and Khare 2002)

$$y_{Ab} = \frac{Q_L B F}{\sqrt{2\pi}\sigma_z u} \left\{ \exp\left[-\frac{(z-h)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+h)^2}{2\sigma_z^2}\right] \right\} + y_{Ab|bkg} \quad (13)$$

[line-source emission of magnitude Q_L ($\text{cm}^3 \text{ cm}^{-1} \text{ s}^{-1}$) and length L (cm), where

$$B = 0.5 \left[\text{erf} \left| \frac{(L/2 - y) \sin\theta - x \cos\theta}{\sqrt{2}\sigma_y} \right| + \text{erf} \left| \frac{(L/2 + y) \sin\theta + x \cos\theta}{\sqrt{2}\sigma_y} \right| \right]$$

$$c(a, z) = -\frac{Q_L B F \zeta}{2uH'} \left\{ \exp\left(\frac{\sigma_z^2 \zeta^2}{2}\right) \left\{ \exp[-\zeta(z-h)] \text{erfc}(\beta_1) + \exp[-\zeta(z+h)] \text{erfc}(\beta_2) \right\} \right\} + \frac{y_{Ab|bkg}}{H'}, \quad (17)$$

$$c(a, z) = -\frac{Q_L B F \zeta}{2uH'} \left\{ \exp\left(\frac{\sigma_z^2 \zeta^2}{2}\right) \exp[-\zeta(z-h)] \text{erfc}(\beta_1) + \frac{1}{2\sqrt{\pi}} \exp\left[-\frac{(z+h)^2}{2\sigma_z^2}\right] \frac{1}{\beta_2} \left[2 - \left(\frac{1}{\beta_2}\right)^2 \right] \right\} + \frac{y_{Ab|bkg}}{H'}, \quad (17a)$$

$$c(a, z) = -\frac{Q_L B F \zeta}{2uH'} \left\{ \frac{1}{2\sqrt{\pi}} \exp\left[-\frac{(z-h)^2}{2\sigma_z^2}\right] \frac{1}{\beta_1} \left[2 - \left(\frac{1}{\beta_1}\right)^2 \right] + \frac{1}{2\sqrt{\pi}} \exp\left[-\frac{(z+h)^2}{2\sigma_z^2}\right] \frac{1}{\beta_2} \left[2 - \left(\frac{1}{\beta_2}\right)^2 \right] \right\} + \frac{y_{Ab|bkg}}{H'} \quad (17b)$$

[line-source emission of magnitude Q_L ($\text{cm}^3 \text{ cm}^{-1} \text{ s}^{-1}$) and length L (cm)];

$$c(a, z) = -\frac{Q' F \zeta}{4\pi\sigma_x\sigma_y H'} \exp\left(-\frac{x'^2}{2\sigma_x^2} - \frac{y'^2}{2\sigma_y^2}\right) \left\{ \exp\left(\frac{\sigma_z^2 \zeta^2}{2}\right) \left\{ \exp[-\zeta(z-h)] \text{erfc}(\beta_1) + \exp[-\zeta(z+h)] \text{erfc}(\beta_2) \right\} \right\}$$

θ is the wind angle with respect to the source line, and x and y are coordinate locations with respect to the line-source center],

$$y_{Ab} = \frac{Q' F}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \exp\left(-\frac{x'^2}{2\sigma_x^2} - \frac{y'^2}{2\sigma_y^2}\right) \times \left\{ \exp\left[-\frac{(z-h)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+h)^2}{2\sigma_z^2}\right] \right\} + y_{Ab|bkg} \quad (14)$$

[instantaneous puff of magnitude Q' (cm^3)],

$$y_{Ab} = \sqrt{\frac{2}{\pi}} \frac{Q F}{u\sigma_y H_{inv}} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \times \left\{ \frac{1}{2} + \sum_{n=1}^{\infty} \cos\left(\frac{n\pi z}{H_{inv}}\right) \cos\left(\frac{n\pi h}{H_{inv}}\right) \times \exp\left[-\frac{1}{2}\left(\frac{n\pi\sigma_z}{H_{inv}}\right)^2\right] \right\} + y_{Ab|bkg} \quad (15)$$

[continuous point source with reflection from an inversion layer of height H_{inv} (cm)], and

$$y_{Ab} = \frac{Q' F}{\pi H_{inv} \sigma_x \sigma_y} \exp\left(-\frac{x'^2}{2\sigma_x^2} - \frac{y'^2}{2\sigma_y^2}\right) \times \left\{ \frac{1}{2} + \sum_{n=1}^{\infty} \cos\left(\frac{n\pi z}{H_{inv}}\right) \cos\left(\frac{n\pi h}{H_{inv}}\right) \times \exp\left[-\frac{1}{2}\left(\frac{n\pi\sigma_z}{H_{inv}}\right)^2\right] \right\} + y_{Ab|bkg} \quad (16)$$

[instantaneous puff of magnitude Q' (cm^3) with reflection from an inversion layer of height H_{inv} (cm)], where x' and y' in (14) and (16) represent respective distances from the puff's x and y centroids.

Counterpart equations for pollutant capture by a falling raindrop are

$$+ \frac{y_{Ab|bkg}}{H'}, \tag{18}$$

$$c(a, z) = -\frac{Q'F\zeta}{4\pi\sigma_x\sigma_yH'} \exp\left(-\frac{x'^2}{2\sigma_x^2} - \frac{y'^2}{2\sigma_y^2}\right) \left\{ \exp\left(\frac{\sigma_z^2\zeta^2}{2}\right) \exp[-\zeta(z-h)] \operatorname{erfc}(\beta_1) + \frac{1}{2\sqrt{\pi}} \exp\left[\frac{-(z+h)^2}{2\sigma_z^2}\right] \frac{1}{\beta_2} \left[2 - \left(\frac{1}{\beta_2}\right)^2\right] \right\} + \frac{y_{Ab|bkg}}{H'}, \tag{18a}$$

$$c(a, z) = -\frac{Q'F\zeta}{4\pi\sigma_x\sigma_yH'} \exp\left(-\frac{x'^2}{2\sigma_x^2} - \frac{y'^2}{2\sigma_y^2}\right) \left\{ \frac{1}{2\sqrt{\pi}} \exp\left[\frac{-(z-h)^2}{2\sigma_z^2}\right] \frac{1}{\beta_1} \left[2 - \left(\frac{1}{\beta_1}\right)^2\right] + \frac{1}{2\sqrt{\pi}} \exp\left[\frac{-(z+h)^2}{2\sigma_z^2}\right] \frac{1}{\beta_2} \left[2 - \left(\frac{1}{\beta_2}\right)^2\right] \right\} + \frac{y_{Ab|bkg}}{H'} \tag{18b}$$

[instantaneous puff of magnitude Q' (cm^3)];

$$c(a, z) = \frac{Q'F}{\sqrt{2\pi}u\sigma_yH_{inv}H'} \exp\left(\frac{-y^2}{2\sigma_y^2}\right) \left\{ 1 - \exp[-\zeta(z - H_{inv})] + \frac{y_{Ab|bkg}}{H'} + 2\zeta \sum_{n=1}^{\infty} \cos\left(\frac{n\pi h}{H_{inv}}\right) \exp\left[-0.5\left(\frac{n\pi\sigma_z}{H_{inv}}\right)^2\right] \right. \\ \left. \times \frac{\zeta \cos\left(\frac{n\pi z}{H_{inv}}\right) + \frac{n\pi}{H_{inv}} \sin\left(\frac{n\pi z}{H_{inv}}\right) - (-1)^n \zeta \exp[-\zeta(z - H_{inv})]}{\zeta^2 + \left(\frac{n\pi}{H_{inv}}\right)^2} \right\} \tag{19}$$

[continuous point source with reflection from an inversion layer of height H_{inv} (cm)]; and

$$c(a, z) = \frac{Q'F}{2\pi\sigma_x\sigma_yH_{inv}H'} \exp\left(-\frac{x'^2}{2\sigma_x^2} - \frac{y'^2}{2\sigma_y^2}\right) \\ \times \left\{ 1 - \exp[-\zeta(z - H_{inv})] + \frac{y_{Ab|bkg}}{H'} + 2\zeta \sum_{n=1}^{\infty} \cos\left(\frac{n\pi h}{H_{inv}}\right) \exp\left[-0.5\left(\frac{n\pi\sigma_z}{H_{inv}}\right)^2\right] \right. \\ \left. \times \frac{\zeta \cos\left(\frac{n\pi z}{H_{inv}}\right) + \frac{n\pi}{H_{inv}} \sin\left(\frac{n\pi z}{H_{inv}}\right) - (-1)^n \zeta \exp[-\zeta(z - H_{inv})]}{\zeta^2 + \left(\frac{n\pi}{H_{inv}}\right)^2} \right\} \tag{20}$$

[instantaneous puff of magnitude Q' (cm^3) with reflection from an inversion layer of height H_{inv} (cm)].

Equations (17), (17a), and (17b) for line-source plumes, and (18), (18a), and (18b) for instantaneous puffs correspond to (6) and its asymptotic counterparts for the bivariate-normal point-source situation and should be selected using the same criteria for β_1 and β_2 . Equations

(19) and (20) pertain to the inversion-layer situation. Although these two equations are relatively robust for all situations, they and their gas-phase counterparts are comparatively demanding computationally; as a consequence, they should be applied in preference to (4) and (6) [or

(14) and (18)] only when presence of the inversion layer significantly influences plume behavior.

b. Plume depletion: Other plume types

Depletion factors associated with line-source plumes are obtained by applying (9) in conjunction with (17), (17a), or (17b). Cases involving infinite line sources with winds normal to the source line do not require cross-plume integration and are given simply by the form

$$F(X) = 1 + \frac{c_{\text{air}} Q_L}{\int_0^X \text{Flux}_s|_{\text{plume}} dx} \quad (21)$$

Depletion factors for the continuous point-source, inversion-layer situation are obtained in a manner similar to that for bivariate-normal plumes, applying (9) in conjunction with the crosswind integral. Counterparts to (10) and (11) for the crosswind integral are

$$I_{y,a} = \frac{-4\pi Q F n_0 a^3 v_z(a) n(a) \Gamma}{3u H_{\text{inv}} H'} \quad (\text{mol cm}^{-2} \text{ s}^{-2}) \quad (22)$$

and

$$I_y = \frac{-J Q F}{H' H_{\text{inv}} u} \Gamma \quad (\text{mol cm}^{-1} \text{ s}^{-1}), \quad (23)$$

where Γ now refers to the braced terms in (19).

Depletion factors associated with puffs are treated most conveniently by considering the time history of the puff's x - y deposition "footprint"; that is,

$$F(T) = 1 - \frac{c_{\text{air}} Q'}{\int_{t=t_0}^{t=T} I_{xy} dt} \quad (24)$$

where t is time, T is cumulative time, and t_0 is the puff's release time. Counterparts to (10) and (11) for the x - y integral are

$$I_{x,y,a} = \frac{2\pi Q' F n_0 a^3 v_z(a) n(a) \zeta \Gamma}{3H'} \quad (\text{mol cm}^{-2} \text{ s}^{-1}), \quad (25)$$

$$I_{x,y} = \frac{J Q' F \zeta}{2H'} \Gamma \quad (\text{mol cm}^{-1} \text{ s}^{-1}) \quad (26)$$

[instantaneous puff of magnitude Q' (cm^3)] and

$$I_{x,y,a} = \frac{-4\pi Q' F n_0 a^3 v_z(a) n(a) \Gamma}{3H_{\text{inv}} H'} \quad (\text{mol cm}^{-2} \text{ s}^{-1}), \quad (27)$$

$$I_{x,y} = \frac{-J Q' F}{H' H_{\text{inv}}} \Gamma \quad (\text{mol cm}^{-1} \text{ s}^{-1}) \quad (28)$$

[instantaneous puff of magnitude Q' (cm^3) with reflection from an inversion layer of height H_{inv} (cm)].

Equation (24) can be applied either with (18) or (20) upon substitution of the appropriate expression for Γ .

4. Aggregation

Equations in the preceding text describing aqueous-phase pollutant concentrations correspond mainly to single raindrop sizes. To compute concentrations in bulk-deposited rainwater and associated fluxes, one must somehow aggregate over the total drop size spectrum or else make some suitable approximation to this aggregate. Aggregation can be performed in a straightforward manner by computing z -level concentrations for a range of drop sizes and integrating the results over the appropriate raindrop size spectrum, as was indicated by (2).

Raindrop size distributions vary widely between precipitation situations. In the absence of more specific information, it is acceptable to use the well-known Marshall-Palmer distribution (Pruppacher and Klett 1997), which, for the units used in this paper, can be expressed as

$$n_0 n(a) = N_0 \exp(-\lambda a), \quad (29)$$

where [as in (2)] $n(a)$ is the probability density function (cm^{-1}) for raindrops existing in a unit volume of space, and $n_0 = N_0/\lambda$ is the total number of drops existing in a given volume of air. The empirical constants N_0 and λ are set equal to 0.16 cm^{-4} and $9.06|J|^{-0.21} \text{ cm}^{-1}$, respectively, where J is the rainfall flux expressed in centimeters per second.

Dingle and Lee (1972) provide the following empirical fits to raindrop fall-velocity data:

$$\begin{aligned} v_z &= 17.8951 - 448.9498D - 16.371D^2 \\ &\quad + 45.9516D^3 \quad (D < 1.4) \quad \text{and} \\ v_z &= -24.1660 - 448.8336D + 75.6265D^2 \\ &\quad - 4.2659D^3 \quad (D > 1.4), \end{aligned} \quad (30)$$

where $D = 20a$ is the raindrop diameter in millimeters.

Thus, to aggregate an ensemble of $c(a, 0)$ values for a given rain rate, one can insert (29) and (30) into (2) and integrate numerically. Similar aggregation approaches can be taken for rain spectra not expressed by the Marshall-Palmer parameterization.

As noted in the earlier work cited above (e.g., Hales et al. 1973), many situations justify approximating the aggregated concentrations using a single, intermediate drop size deemed representative of the total raindrop population, thus eliminating the need for detailed aggregation. The mass-mean collected drop size is a reasonable first choice as a candidate for this approach, and can be expressed by the form

$$\begin{aligned} a_{\text{mass mean}} &= \frac{\frac{4\pi n_0}{3} \int_0^\infty a^4 n(a) v_z(a) da}{\frac{4\pi n_0}{3} \int_0^\infty a^3 n(a) v_z(a) da} \\ &= \frac{\int_0^\infty a^4 \exp(-9.06|J|^{-0.21} a) v_z(a) da}{\int_0^\infty a^3 \exp(-9.06|J|^{-0.21} a) v_z(a) da}. \end{aligned} \quad (31)$$

Equation (32) is an empirical fit to solutions of (31), which is useful for estimating the mass-mean drop size as a function of rainfall rate in the range $10^{-5} < |J| < 3 \times 10^{-3} \text{ cm s}^{-1}$:

$$a_{\text{mass mean}} = 0.162 + 0.00972 \ln|J| \quad (\text{cm}). \quad (32)$$

5. Scavenging of suspended particulate matter

Scavenging equations for particulate matter corresponding to their gas-phase counterparts (6) and (17)–(20) presume irreversible uptake of particles by falling raindrops. These are relatively trivial to derive and are presented here mainly for completeness. First, it should be noted that the scavenging coefficient Λ (s^{-1}) is usually taken to represent an aggregate over all raindrop sizes and is defined in terms of the equation

$$w = \Lambda c_{\text{air}} y_{\text{Ab}} = 4\pi n_0 \int_0^\infty a^2 K_y(a) y_{\text{Ab}} n(a) da \quad (33)$$

(cf. Hales 1972a), where w (in mass or moles per cubic centimeter per second) represents the local rate of removal from the gaseous medium by scavenging. Performing a material balance of rainborne pollutant over an incremental volume of atmosphere, one can combine (1) and (33) to obtain

$$\frac{dc_{\text{bulk}}(z)}{dz} = \frac{\Lambda c_{\text{air}}}{J} y_{\text{Ab}}. \quad (34)$$

Integrating this expression in the vertical for the plume types (4) and (13)–(16) results, respectively, in

$$c_{\text{bulk}}(z) = \frac{-\hat{Q}F\Lambda}{2\sqrt{2\pi}\sigma_y u J} \times \exp\left(\frac{-y^2}{2\sigma_y^2}\right) \left[\text{erfc}\left(\frac{z-h}{\sqrt{2}\sigma_z}\right) + \text{erfc}\left(\frac{z+h}{\sqrt{2}\sigma_z}\right) \right] \quad (35)$$

[bivariate-normal, with emission of magnitude \hat{Q} (mol s^{-1})],

$$c_{\text{bulk}}(z) = \frac{-\hat{Q}_L B F \Lambda}{2uJ} \left[\text{erfc}\left(\frac{z-h}{\sqrt{2}\sigma_z}\right) + \text{erfc}\left(\frac{z+h}{\sqrt{2}\sigma_z}\right) \right] \quad (36)$$

[continuous line-source emission of magnitude \hat{Q}_L ($\text{mol cm}^{-1} \text{ s}^{-1}$)],

$$c_{\text{bulk}}(z) = \frac{-\hat{Q}'F\Lambda}{4\pi\sigma_y\sigma_x J} \exp\left(-\frac{x'^2}{2\sigma_x^2} - \frac{y'^2}{2\sigma_y^2}\right) \times \left[\text{erfc}\left(\frac{z-h}{\sqrt{2}\sigma_z}\right) + \text{erfc}\left(\frac{z+h}{\sqrt{2}\sigma_z}\right) \right] \quad (37)$$

[instantaneous puff of magnitude \hat{Q}' (mol)],

$$c_{\text{bulk}}(z) = \sqrt{\frac{2}{\pi} \frac{\hat{Q}F\Lambda}{u\sigma_y H_{\text{inv}} J}} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \times \left\{ \frac{1}{2}(z - H_{\text{inv}}) + \sum_{n=1}^\infty \frac{H_{\text{inv}}}{n\pi} \sin\left(\frac{n\pi z}{H_{\text{inv}}}\right) \times \cos\left(\frac{n\pi h}{H_{\text{inv}}}\right) \exp\left[-0.5\left(\frac{n\pi\sigma_z}{H_{\text{inv}}}\right)^2\right] \right\} \quad (38)$$

[continuous point source of magnitude \hat{Q} (mol s^{-1}) with reflection from an inversion layer of height H_{inv}], and

$$c_{\text{bulk}}(z) = \frac{\hat{Q}'F\Lambda}{\pi\sigma_x\sigma_y H_{\text{inv}} J} \exp\left(-\frac{x'^2}{2\sigma_x^2} - \frac{y'^2}{2\sigma_y^2}\right) \times \left\{ \frac{1}{2}(z - H_{\text{inv}}) + \sum_{n=1}^\infty \frac{H_{\text{inv}}}{n\pi} \sin\left(\frac{n\pi z}{H_{\text{inv}}}\right) \times \cos\left(\frac{n\pi h}{H_{\text{inv}}}\right) \exp\left[-0.5\left(\frac{n\pi\sigma_z}{H_{\text{inv}}}\right)^2\right] \right\} \quad (39)$$

[instantaneous puff of magnitude \hat{Q}' (mol) with reflection from an inversion layer of height H_{inv}].

In performing these integrations, Λ and J are both presumed to be invariant with height. Because one cannot presume equilibrium with background for particle scavenging, these equations do not include background contributions.

Plume-depletion factors for particulate-matter scavenging are also relatively easy to estimate. Assuming that Λ is invariant with time, these are given by

$$F = \exp\left(\frac{-\Lambda x}{u}\right) = \exp(-\Lambda t), \quad (40)$$

where x (cm) is the distance downwind from the source. In cases in which Λ is time-variant, one may compute the associated depletion factors by downwind numerical integration in a manner similar to that described above for gas-scavenging calculations.

6. Estimation of gaseous mass-transfer coefficients

Fundamental mass-transfer theory maintains that the transfer of pollutant between the gas phase and the aqueous phase within a droplet follows this relationship: flux passing through gas-liquid interface in the positive radial direction

$$= -K_y(a)(y_{\text{Ab}} - H'c_{\text{Ab}}) \quad (\text{mol cm}^{-2} \text{ s}^{-1}). \quad (41)$$

The reciprocal of the overall mass-transfer coefficient K_y is considered as a “resistance” to mass transfer, which can be expressed as the sum of individual resistances occurring in the gas phase, the liquid phase, and the interface between the two:

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{H'c_{\text{water}}}{k_x} + \frac{1}{k_i} \quad (\text{s cm}^2 \text{ mol}^{-1}), \quad (42)$$

where c_{water} (mol cm^{-3}) is the molar density of water, and k_y , k_x , and k_i represent respective individual mass-transfer coefficients for the gas phase, the liquid phase, and the interface.

a. Gas-phase mass-transfer coefficient

The gas-phase mass-transfer coefficient associated with a falling drop can be estimated easily and reliably using the mass-transfer analog of the Froessling equation (Bird et al. 1960):

$$\frac{2ak_y}{D_{\text{Ay}}c_{\text{air}}} = 2 + 0.6\left(\frac{-2av_z}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{\text{Ay}}}\right)^{1/3}, \quad (43)$$

where D_{Ay} ($\text{cm}^2 \text{s}^{-1}$) and ν ($\text{cm}^2 \text{s}^{-1}$) are the pollutant's diffusivity in air and the kinematic viscosity of air, respectively.

b. Liquid-phase mass-transfer coefficient

Because of relatively slow mixing processes within liquid drops, the liquid-phase mass-transfer coefficient tends to be exposure dependent and thus changes in magnitude as the raindrop interacts with the plume. In addition to complicating the issue appreciably, such behavior adds a component of nonlinearity to the mathematical system, which inhibits application of plume superposition in multisource models.

Several previous authors [e.g., Hadamard and Rybczynski (see discussion thereof in Levich 1962); Kronig and Brink 1950; Garner and Lane 1959; Pritchard and Biswas 1967; Baboolal et al. 1981; Walcek and Pruppacher 1984; Mitra and Hannemann 1993] have performed detailed fluid mechanics analyses, as well as measurements of liquid-phase mass transfer in falling drops. These usually have involved step-function exposures in which initially clean water falls into environments with a constant concentration of pollutant and/or pollutant-saturated drops fall into clean air. Although experiment and theory are in general agreement for these conditions, the influence of real-world exposure history renders these results of limited value for general applications. As a consequence, the approach recommended for current purposes is to linearize the liquid-phase characterization and to consider behavior to be limited by two asymptotic situations.

The first limiting situation occurs for relatively clean drops that experience rapid increases or for previously saturated drops that experience decreases in ambient gas-phase concentration with time, and it is favored by rapid internal mixing and high-solubility (low H') conditions. Under such circumstances, the gas-phase resistance dominates, and the liquid-phase mass-transfer coefficient is essentially negligible; that is,

$$1/k_x = 0. \quad (44)$$

The opposing limiting situation is favored for low solubilities and for drops having no internal circulation,

that is, "stagnant drops," thus making molecular diffusion the sole mechanism for internal mass transfer. This situation is normally exposure dependent. However, for conditions in which the ambient forcing of the gas-phase concentration is a constant upward or downward ramp function, the mass-transfer coefficient reverts to the exposure-independent form (Hales 1972a)

$$k_x = \frac{5D_{\text{Ax}}c_{\text{water}}}{a} \quad (\text{mol cm}^{-2} \text{s}^{-1}), \quad (45)$$

where D_{Ax} ($\text{cm}^2 \text{s}^{-1}$) is the diffusivity of the pollutant in water.

Some previous authors (e.g., Mitra and Hannemann 1993) have suggested adding empirical attenuation factors to the gas-phase coefficient to reflect liquid-phase influences, and others (e.g., Kronig and Brink 1950) discuss amplification factors for stagnant-drop formulations to compensate for within-drop circulation. Kronig and Brink's modeling results suggest that multiplying (45) by 2.5 should approximately compensate for internal circulation processes in falling raindrops, a simple approach that—while admittedly approximate—appears to be somewhat consistent with later studies. Nonidealities associated with drop deformation, turbulence, and impurities (particularly surfactants), however, contribute a large degree of uncertainty to such adjustments.

It is obvious that the degree of detail to be applied to liquid-phase mass-transfer coefficient estimation is largely up to the model practitioner. In practice, just knowing the envelope between the two limiting cases may be sufficient for the issue at hand, whereas more refined calculations may be required in other situations. The plots in Fig. 2 provide some initial insight in this context. Dotted lines in these plots denote assumption of negligible liquid-phase influence on the mass-transfer coefficient (i.e., "well-mixed" drops: $K_y = k_y$). Solid lines denote assumption of combined gas and liquid mass-transfer resistance, where the liquid mass-transfer coefficient is given by the stagnant-drop relationship of (45). Dashed lines denote application of (45) multiplied by a factor of 2.5, as suggested by Kronig and Brink (1950).

The reader should note changes of scales on ordinates of the graphs and also that results for the three mass-transfer assumptions nearly coincide for high-solubility cases (Figs. 2a,d), whereas they deviate markedly for Fig. 2c. Here results for the stagnant-drop case lie well above the equilibrium curve, whereas the others are much lower, visually coinciding with the equilibrium points lying close to the abscissa. One should note that points lying near the abscissa do not imply zero concentrations; rather, they correspond to finite concentrations that are much smaller than the vertical scales of the plots (centerline concentrations in Fig. 2c corresponding to stagnant-drop, augmented stagnant-drop, gas-phase limited, and equilibrium conditions are 0.627

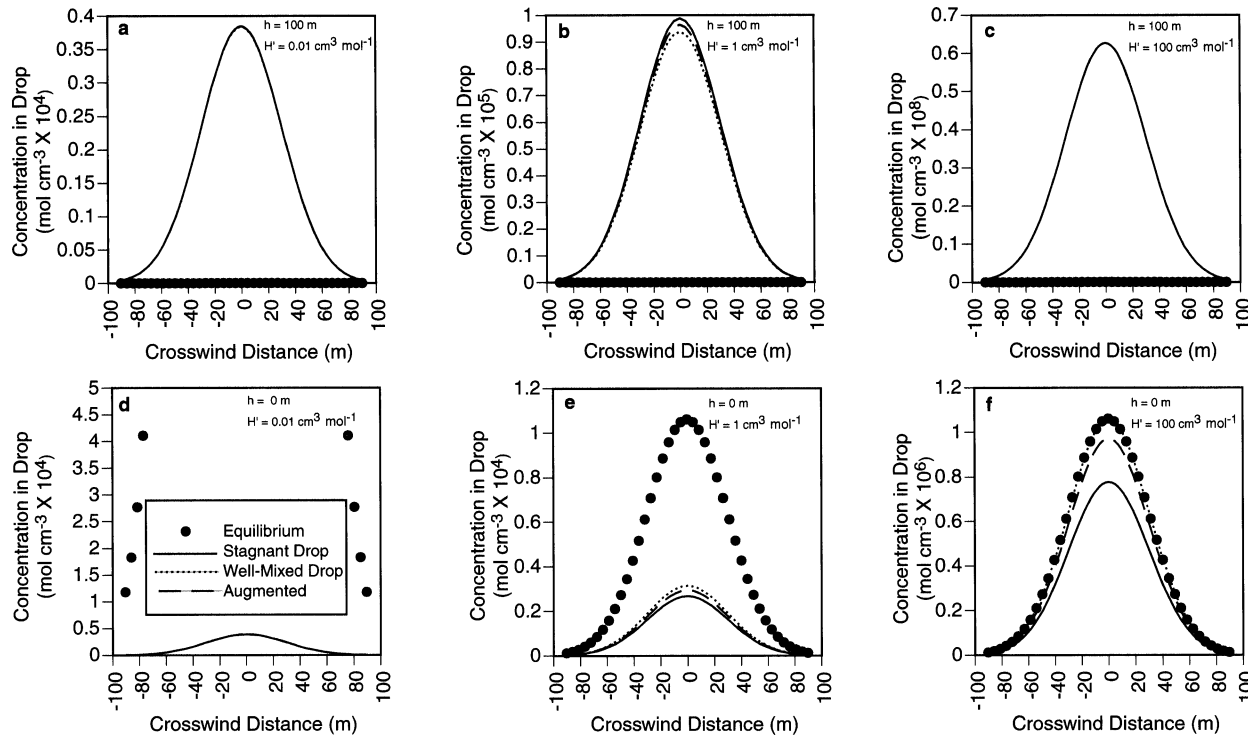


FIG. 2. Ground-level concentrations of pollutant in 0.03-cm-radius raindrops as functions of crosswind position, plume height, solubility, and calculated mass-transfer coefficients as calculated from (6) for a bivariate-normal plume of unit source strength emitted into a constant wind of 5 m s⁻¹, having plume-spread parameters σ_y and σ_z of 30 and 20 m, respectively.

$\times 10^{-8}$, 0.103×10^{-9} , 0.406×10^{-11} , and 0.390×10^{-11} , respectively). This example underscores the fact that liquid-phase mass-transfer resistances become dominant for low-solubility gases, thus amplifying consequences of their estimation uncertainties.

c. Interfacial mass-transfer coefficient

Interfacial mass-transfer resistance occurs whenever the gas-liquid interface reflects, rather than accommodates, a significant fraction of approaching gas-phase pollutant molecules. Based on classical gas-kinetic theory (Findlayson-Pitts and Pitts 1999), the associated mass-transfer coefficient is given by

$$k_i = \frac{\alpha c_{\text{air}} u_{\text{avg}}}{4} = \frac{\alpha c_{\text{air}}}{4} 100 \sqrt{\frac{8000RT}{\pi M}} \quad (\text{mol cm}^{-2} \text{ s}^{-1}), \quad (46)$$

where α is the accommodation coefficient (1 for total accommodation, 0 for total reflection), u_{avg} (cm s⁻¹) is the average velocity of gas molecules, R (J mol⁻¹ K⁻¹) is the gas-law constant, T (K) is the local temperature, and M is the gram molecular weight of the pollutant.

Equations (43) and (46) can be combined for the case of small drops to give the following indication of the relative influences of gas-phase and interfacial resistance:

$$\frac{k_i}{k_y} \approx \frac{\alpha u_{\text{avg}} a}{4D_{Ay}}. \quad (47)$$

Measured values of α are available for a variety of compounds (Findlayson-Pitts and Pitts 1999), which typically range between 1 and about 10^{-3} . Applying these to (47) suggests that interfacial resistance can be safely ignored under the majority of conditions in the current context.

7. Estimation of scavenging coefficients

As noted in the context of (34), the below-cloud scavenging coefficient Λ is usually presumed to be a quantity that is integrated over the total spectra of both raindrop and aerosol-particle sizes. With the assumption of spherical particles, this aggregation can be described by

$$\Lambda = \frac{-n_0 \pi \int_{r=0}^{\infty} \int_{a=0}^{\infty} r^3 E(r, a) p(r) a^2 n(a) v_z(a) dr da}{\int_{r=0}^{\infty} r^3 p(r) dr}, \quad (48)$$

where $E(r, a)$ is the capture efficiency associated with particles of radius r by falling raindrops of radius a , and $p(r)$ is the number density function for aerosol particles. The magnitude of $E(r, a)$ depends strongly on both dif-

fusive and inertial capture mechanisms and thus varies markedly with particle size; as a consequence, Λ depends strongly on the particle size distribution of the aerosol being scavenged.

Although the derivations are too lengthy to be described in detail here, previous references (e.g., Dana and Hales 1976; Slinn 1977; Seinfeld and Pandis 1998) provide formal integrations of (48) that allow relatively straightforward estimation of Λ on the basis of aerosol- and raindrop-spectrum data. The reader is encouraged to consult these references for practical estimation purposes.

8. Cloud influences

As noted in section 1, the derivations given here presume that the modeled plumes experience scavenging solely by below-cloud processes: either the modeled plumes do not come into contact with clouds, or else in-cloud mechanisms are considered to be negligible when compared with their below-cloud counterparts. The absence of cloud contact may be a good assumption in many near-source situations, but it obviously deteriorates at extended downwind distances at which the plume’s vertical extent becomes large; thus, it is appropriate here to address possible influences of cloud contact on the validity of the scavenging equations presented above.

The case for nonreactive gas scavenging is relatively straightforward. Here, the primary mechanism for cloud interaction is the dissolution of pollutant within cloud droplets followed by accretion of these droplets by the falling rain. As a first-order approximation, one can assume that the droplets are saturated with pollutant in their ambient environment (equilibrium) and that accretion within the plume does not add substantially to the raindrop’s water content. Then, from basic cloud-physics theory (see appendix A), one may write

$$\left. \frac{dc}{dz} \right|_{\text{accretion mechanism}} = \frac{-3E_c m y_{Ab}}{4aH' \rho_w}, \quad (49)$$

where E_c represents the efficiency for capture of cloud drops by the falling raindrops of radius a , m (g cm^{-3}) is the mass density of suspended cloud drops, and ρ_w (g cm^{-3}) is the density of liquid water.

By assuming additivity of mechanisms, (49) may be combined with (1) to give

$$\frac{dc(a, z)}{dz} = \left[\frac{3K_y(a)}{v_z(a)a} - \frac{3E_c m}{4aH' \rho_w} \right] y_{Ab} - \frac{3K_y(a)H'}{v_z(a)a} c(a, z), \quad (50)$$

which by inspection indicates that the cloud-capture mechanism should be negligible when compared with conventional below-cloud processes whenever the first

term in brackets significantly exceeds the second; that is,

$$N_{cs} = -\frac{E_c m v_z}{4K_y H' \rho_w} \quad (\text{dimensionless}) \ll 1. \quad (51)$$

This suggests that the cloud-capture mechanism should become progressively less important for small raindrops (small v_z) and low solubilities (large H'). Conservatively high values for E_c and m are 1 and $3 \times 10^{-6} \text{ g cm}^{-3}$, respectively. Applying these numbers in conjunction with (47) leads to the values presented in Fig. 3, providing a practical guide for the modeling decision process. This guidance could be elaborated if one were to develop some kind of an ensemble N_{cs} by integrating (51) over a representative raindrop size distribution. The simple guidance given here, however, is sufficient for most practical situations.

The contours in Fig. 3 are conservative, both because of the noted choices of m and E_c and also because (50) tacitly assumes the total plume to exist in-cloud. In a majority of cases, lower portions of the plume are below-cloud, where normal absorption-desorption processes tend to erase influences of the cloud interactions experienced aloft. As a consequence, the decision to neglect cloud processes for high-solubility gases should be at the discretion of the practitioner upon determining the extent of cloud contact and other features of the system of interest. For lower solubilities (i.e., H' roughly 1 and above), cloud scavenging can be safely neglected under all conditions.

This relatively benign situation for gases is unfortunately not usually the case for aerosol scavenging. Aerosol particles typically interact extensively with cloud droplets and even participate actively in cloud formation through processes such as cloud-droplet nucleation. As such, cloud droplets act as efficient, and usually irreversible, capture agents whose influence heavily outweighs below-cloud phenomena. For this reason, the aerosol-scavenging equations given in this paper are not recommended for use whenever significant plume contact with cloudy regions occurs.

9. Conclusions

The equations presented in this paper provide a practical and computationally efficient approach to calculating wet removal from plumes in situations in which Gaussian models give accurate representations of true plume behavior. Based on this condition, the equations should be most applicable at limited (i.e., meso γ) distances from source regions and for precipitation situations that are mainly nonconvective in nature. Within limits, associated calculations for nonreactive gas scavenging are valid for plumes in both clear and cloudy environments; corresponding calculations for aerosol scavenging, however, are valid only for cloud-free situations.

The equations are fundamentally linear and thus can

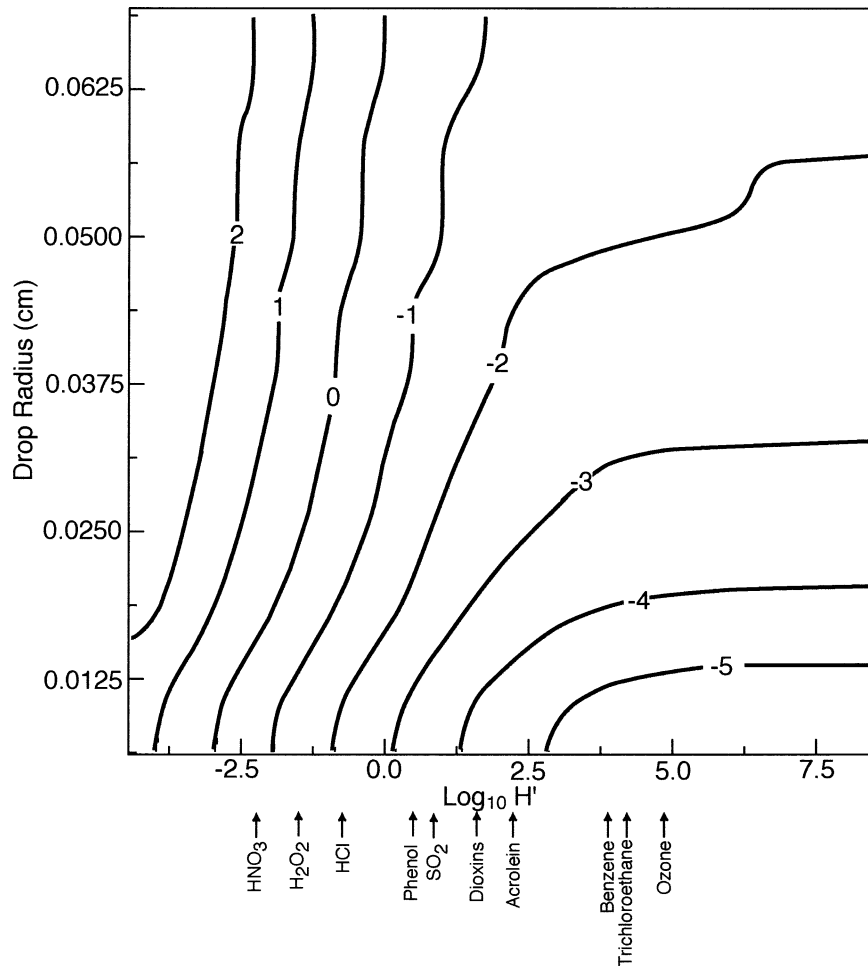


FIG. 3. Contours of \log_{10} of the cloud-scavenging number N_{cs} plotted vs raindrop radius and \log_{10} of the solubility parameter H' . Approximate solubilities of selected compounds are indicated on abscissa. Note that the solubilities indicated for compound families such as dioxins and trichloroethanes, as well as for dissociating species such as SO_2 , are intended to depict general ranges of values only. (Solubility data are from R. Sander's Henry's law constants available online at <http://www.mpch-mainz.mpg.de/~sander/res/henry.html>.)

be applied conveniently to multisource models for which superposition is required. This linear nature depends in part on the assumption of Henry's law being applicable to solubility behavior. Systems that deviate moderately from Henry's law can be treated by these equations after appropriate linearizations are performed; however, the reliability of results becomes diminished as the deviations increase.

These equations should be applied at extended source-receptor distances with considerable caution, both because Gaussian models become less valid under such circumstances and because encounters with cloud systems become more extensive and likely. Such conditions are usually best treated by Eulerian modeling techniques, which account more realistically and directly for nonlinear features and in-cloud scavenging processes.

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APPENDIX A

Derivation of Equation for Pollutant Pickup by Cloud-Water Accretion [Eq. (49)]

Consider a single raindrop falling through a cloud. The volume of space swept by this drop per second is $-\pi a^2 v_z$. The volume of cloud water accreted by this drop per second is $-\pi a^2 v_z E_c m / \rho_w$, where m (g cm^{-3}) is the cloud-water content, ρ_w is the density of water, and E_c is the capture efficiency. Assume the cloud-water-bound pollutant is at solubility equilibrium with its gas-phase surroundings. Then p , the number of moles of pollutant picked up per second by the drop via the accretion mechanism is

$$p = \frac{-\pi a^2 v_z E_c m y_{Ab}}{H' \rho_w} \quad (A1)$$

This results in an associated concentration change rate in the falling drop of

$$\left. \frac{dc}{dz} \right|_{\text{accretion mechanism}} = \frac{p}{(4/3)\pi a^3 v_z} = \frac{-3E_c m y_{Ab}}{4aH' \rho_w} \quad (\text{mol cm}^{-4}). \quad (A2)$$

APPENDIX B

Nomenclature

a	Raindrop radius (cm)
$a_{\text{mass mean}}$	Mass-mean radius of collected raindrops (cm)
c	Concentration of pollutant in drop (mol cm ⁻³)
c_{Ab}	Gas-phase concentration of pollutant (mol cm ⁻³)
c_{air}	Concentration of air molecules (mol cm ⁻³)
c_{bulk}	Bulk concentration of pollutant in collected raindrops (mol cm ⁻³)
c_{water}	Molar density of water (mol cm ⁻³)
D	Raindrop diameter, used in equations of Dingle and Lee (1972) (mm)
D_{Ax}	Diffusivity of pollutant in water (cm ² s ⁻¹)
D_{Ay}	Diffusivity of pollutant in air (cm ² s ⁻¹)
E	Capture efficiency for particles by raindrops (dimensionless)
E_c	Capture efficiency for cloud drops by raindrops (dimensionless)
F	Plume-depletion factor (dimensionless)
Flux	Rainborne pollutant flux (mol cm ⁻² s ⁻¹)
H'	Solubility coefficient (cm ³ mol ⁻¹)
H_{inv}	Height of inversion layer (cm)
h	Emission height (cm)
I_y	Cross-wind integrated deposition flux
J	Rainfall flux (cm s ⁻¹)
K_y	Overall mass-transfer coefficient (mol cm ⁻² s ⁻¹)
k_i	Interfacial mass-transfer coefficient (mol cm ⁻² s ⁻¹)
k_x	Liquid-phase mass-transfer coefficient (mol cm ⁻² s ⁻¹)
k_y	Gas-phase mass-transfer coefficient (mol cm ⁻² s ⁻¹)
L	Length of line source (cm)
M	Molecular weight (g mol ⁻¹)
m	Mass density of suspended cloud droplets (g cm ⁻³)
N_{cs}	Cloud-scavenging number (dimensionless)
N_{es}	Equilibrium-scavenging number (dimensionless)
N_0	Parameter in Marshall–Palmer distribution (raindrops per centimeter to the fourth power)
$n(a)$	Number probability density function for raindrops of size a (cm ⁻¹)

n_0	Total number of raindrops in a unit volume of atmosphere (drops per centimeter cubed)
p	Number of moles of pollutant picked up per second by drop via accretion mechanism
$p(r)$	Number probability density function for particles of size r (cm ⁻¹)
Q	Volumetric pollution emission rate (cm ³ s ⁻¹)
Q_L	Volumetric line-source pollution emission rate (cm ³ cm ⁻¹ s ⁻¹)
\hat{Q}	Emission rate (mol s ⁻¹)
Q'	Instantaneous emission puff (cm ³)
\hat{Q}'	Molar puff emission amount (mol)
\hat{Q}'_L	Molar line-source pollutant emission rate (mol cm ⁻¹ s ⁻¹)
R	Gas-law constant (J mol ⁻¹ K ⁻¹)
r	Aerosol-particle radius (cm)
s	Vertical position of surface at a particular x - y location (cm)
T	Cumulative time (s); also temperature (K)
t	Time (s)
t_0	Puff's release time
u	Wind speed (cm s ⁻¹)
u_{avg}	Average velocity of gas molecules (cm s ⁻¹)
v_z	Raindrop sedimentation velocity (cm s ⁻¹)
w	Local rate of removal from gaseous medium by scavenging (mol cm ⁻³ s ⁻¹)
X	Current downwind position (cm)
x	Downwind distance (cm)
x'	Distance from puff's x centroid (cm)
y	Crosswind distance (cm)
y'	Distance from puff's y centroid (cm)
y_{Ab}	Mixing ratio of pollutant in gas phase (mol mol ⁻¹)
$y_{Ab bkg}$	Mixing ratio of background pollutant in gas phase (mol mol ⁻¹)
z	Distance above origin (cm)
α	$QF\zeta/\sigma_y u$ (dimensionless); also accommodation coefficient (dimensionless)
β_1	$(\zeta\sigma_z^2 + z - h)/\sqrt{2\sigma_z}$ (dimensionless)
β_2	$(-\zeta\sigma_z^2 + z + h)/\sqrt{2\sigma_z}$ (dimensionless)
Γ	Factor within (4), (6), (6a), (6b), or (19)
ζ	$3K_y H'/v_z a$ (cm ⁻¹)
Λ	Scavenging coefficient (s ⁻¹)
λ	Parameter in Marshall–Palmer distribution (cm ⁻¹)
ν	Kinematic viscosity of air (cm ² s ⁻¹)
ρ_w	Mass-density of liquid water (g cm ⁻³)
σ_x	Plume-spread parameter in x direction (cm)
σ_y	Plume-spread parameter in y direction (cm)
σ_z	Plume-spread parameter in z direction (cm)
θ	Angle between wind direction and source line

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