Vapor Scavenging Coefficient Estimation

Vapor scavenging coefficients are used to estimate the rate of removal of a soluble species that exists below the cloud line based on rain event characteristics, such as intensity and droplet size. This section explains the technical basis for the estimation of the scavenging coefficient of C-8 out of the vapor phase. The basis for this estimation is provided in "Atmospheric Chemistry and Physics" by J.H. Seinfeld and S.M. Pandis (1998, Wiley & Sons).

Two key assumptions have been made for the purposes of this estimation. First, we have assumed C-8 is irreversibly absorbed into the rain droplet. This is a reasonable assumption in this case, since the C-8 concentration in the droplet would be low and the C-8 would almost certainly be dissociated and therefore non-volatile. Second, while Seinfeld steps through a derivation for scavenging coefficients for a specified droplet size, it is much more accurate a determination to include a more representative spectrum of droplet sizes. This assumption will be discussed in more detail below.

The scavenging coefficient for an irreversibly soluble gas by definition is

$$\Lambda = \int_0^\infty \left(\pi * D_p^2 * K_c * n\right) dD_p$$

where D_p is the diameter of the raindrop (cm), K_c is the mass transfer coefficient of a gaseous molecule to a sphere and n represents some raindrop size distribution relationship.

The mass transfer coefficient, K_c, can be calculated by empirical correlations (Bird, R.B., Steward, W.E., and Lightfoot, E.N., "Transport Phenomena", Wiley & Sons (1960)) , such as

$$K_c = \frac{D_g}{D_p}\left[2 + 0.6 * \left(\frac{\rho_{air} * U_t * D_p}{\mu_{air}}\right)^{1/2} * \left(\frac{\mu_{air}}{\rho_{air} * D_g}\right)^{1/3}\right]$$

where D_g is the gas phase diffusivity of the species (cm^2/sec), U_t is the droplet velocity (cm/sec), ρ_{air} is the density of air (g/cm^3) and μ_{air} is the viscosity of air (g/cm-sec). The gas phase diffusivity of the C-8 molecule was estimated to be 0.0423 cm^2/sec by the method of Fuller et al (Fuller E.N., Giddings J.C., *J. Gas Chromatogr.* Vol.3, 222 (1965); Fuller E.N., Schettler P.D., Giddings J.C., *Ind.Eng.Chem.* Vol.58(5), 18 (1966); Fuller E.N., Ensley K., Giddings J.C., *J.Phys.Chem.* Vol.73., 3679(1969).). Droplet velocity is a function of raindrop particle diameter, D_p, and for the purposes of this estimation, was estimated by a curve-fit of data from Table 20.1 (page 1006) of Seinfeld's book, and expressed as

$$U_t = 1041.7 * \sqrt{D_p}$$

The raindrop size distribution, n, as described by Marshall and Palmer (Marshall, J.S., and Palmer, M.W.M., *J. Meteorol.*, V 5, pg 165-166 (1948)) is commonly used in estimating scavenging coefficients. According to the authors, this relationship may overestimate by as much as 50% the number of small droplets in the 0.02 to 0.12 cm size range, thus causing a conservative estimate of the scavenging coefficient. The relationship is expressed as

$$n = 0.08 * \exp\{-4.1 * D_p * p_o^{-0.21}\}$$

where p_o is the rain intensity (mm/hr). (There is a typographical error in Seinfeld's book on page 1007. Above relationship comes from page 831)

Substitution of the expressions for K_c, U_t, and n into the scavenging coefficient equation yields an integral expression that is difficult to integrate explicitly. For the purposes of this estimation, the final expression was numerically integrated between raindrop particle sizes of 0 and 1 cm. An upper limit of 1 cm was chosen because it represents a reasonable maximum raindrop size, as can be seen from extrapolation of the raindrop spectra data presented in Seinfeld's book, page 832. The number distribution at drop diameter equal to 1 cm is approximately 1.0E-09 and integration beyond that point adds no value to the final scavenging coefficient.

Results of the numerical integration are shown below in tabular and graphical form. The maximum intensity value used was 30 mm/hr, which exceeded the maximum observed intensity of 27.9 mm/hr recorded at the Washington Works site during 1996. (This is the year of on-site meteorological data that has been processed for use in the ISC model.)

p_o mm/hr	Scavenging Coefficient 1/hr
0	4.408E-05
1	2.311E-02
2	3.106E-02
4	4.067E-02
6	4.705E-02
8	5.190E-02
10	5.583E-02
12	5.915E-02
14	6.203E-02
16	6.457E-02
18	6.685E-02
20	6.892E-02
22	7.082E-02
24	7.256E-02
26	7.418E-02
28	7.570E-02
30	7.711E-02