

# MODELLING WET DEPOSITION

National Power (D D Apsley) and CERC

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*In this document 'ADMS' refers to ADMS 5.2, ADMS-Roads 4.1, ADMS-Urban 4.1 and ADMS-Airport 4.1. Where information refers to a subset of the listed models, the model name is given in full.*

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## 1. Introduction

ADMS models three plume depletion processes: dry deposition, wet deposition and radioactive decay. This paper describes the Wet Deposition Module. All three processes lead to a variation with downwind distance, or travel time, of the plume strength  $Q$ :

$$Q(x) = \int_{-\infty}^{\infty} dy \int_0^{\infty} C(x, y, z) U_m dz \quad (1.1)$$

where  $U_m$  is the wind speed at mean plume height and  $C$  is the concentration.

The type of wet deposition that can be modelled in ADMS depends on the source and pollutant type:

1. Wet deposition of all pollutants from all source types can be modelled using a washout coefficient (Sections 2 and 3).
2. In ADMS 5 only, wet deposition of SO<sub>2</sub> and CO<sub>2</sub> from all source types calculated using a washout coefficient is pH-limited (Section 4).
3. In ADMS 5 only, wet deposition of SO<sub>2</sub> and HCl from point sources can be modelled using the ‘falling drop’ method [4] (Section 5).

The washout coefficient method is linear and simple to implement. The pH-limited method goes some way to representing the effect of the reduced uptake of acidic pollutants when the concentrations of these pollutants become high in the raindrops. The final ‘falling drop’ method is complex and non-linear, and attempts to model the kinetic and thermodynamic processes that occur at the surface of and within the raindrop; this method consequently requires significant computation time. Only point sources can be modelled with this ‘falling drop’ method. Table 1 summarises the wet deposition algorithms implemented in ADMS 5.

	Algorithms implemented in code							
	Point sources				Non-point sources			
	SO <sub>2</sub>	HCl	CO <sub>2</sub>	Other	SO <sub>2</sub>	HCl	CO <sub>2</sub>	Other
Wet deposition	pH-limited WC	WC	pH-limited WC	WC	pH-limited WC	WC	pH-limited WC	WC
Wet deposition with falling drop method	FD	FD						

Table 1 - Summary of wet deposition model options in ADMS 5 for the different source types and pollutants (WC means washout coefficient, and FD means falling drop)

### 1.1 Plume-plume interaction

In order to model the chemistry involved in the wet deposition calculations correctly, total concentrations are required. Therefore, wet deposition should be modelled after the concentrations from all sources have been calculated. This is computationally intensive, however, so has been neglected in the current implementation i.e. wet deposition is calculated for each plume separately, and plume-plume interaction is neglected.

When a washout coefficient is used to represent wet deposition, the deposition values vary linearly with concentration. Therefore, wet deposition results are the same whether or not the plumes are modelled separately, or all together, i.e. neglecting plume-plume interaction does not affect results. For the pH-limited and falling drop methods however (Sections 4 and 5), results would be different if plume-plume interaction was included in the model.

## ***1.2 Near-calm conditions***

As described in technical specification paper P10/01&P12/01, in ADMS 5, in near-calm conditions, concentrations are calculated using a weighted average of a 'radial' plume and a Gaussian plume. The same approach is adopted for the wet deposition, i.e. the total wet deposition is taken to be a weighted average of that from the 'radial' and Gaussian plumes.

## **2. Modelling Wet Deposition using a Washout Coefficient**

Modelling wet deposition using a washout coefficient means that all the physical and chemical processes involved in the removal of pollutant from the plume are represented by simple proportionality between removal rates and the local airborne concentration of material.

It is assumed that:

- (i) removal processes act independently;
- (ii) removal processes are irreversible.

The first assumption implies that plume strength can be written as a product of source strength and depletion factors corresponding to each removal process. Where species with significantly different deposition parameters are present in the release a separate calculation must be performed for each. Variation of deposition parameters with the formation of new isotopes following radioactive decay cannot, however, be modelled and the values of dry deposition velocity and washout coefficient should reflect the contents of the initial isotope inventory. Assumption (ii) precludes gases dissolving in raindrops only to come out of solution close to the ground; this 'out-gassing' is modelled correctly in the falling drop method described in Section 5.

### ***2.1 Washout Coefficient Concentration Profile***

Removal processes are integrated into the dispersion model as follows. Let  $C_1(x, y, z)$  be the mean concentration *per unit source strength* in the absence of deposition and assume that it can be factorised as:

$$C_1 = \chi_1(x, z)C_y(y) \quad (2.1)$$

in terms of the crosswind-integrated concentration  $\chi_1$  and normalised crosswind profile  $C_y(y)$ . Let  $Q_s$  be the source strength of the species under consideration in [mass units]  $s^{-1}$ .

Given the mean wind speed over the depth of the plume, the Wet Deposition Module, Section 2.2, calculates a depletion factor  $q_w(x)$  and crosswind-integrated wet deposition flux  $f_w(x)$ .

At any downwind distance the plume strength  $Q(x)$  in [mass units]  $s^{-1}$  is then given by:

$$Q = q_w(x)Q_s \quad (2.2)$$

The mean concentration  $C$  in [mass units]  $m^{-3}$  is given by:

$$C = Q(x)\chi_1(x, z)C_y(y) \quad (2.3)$$

and the wet deposition flux at a point in [mass units]  $m^{-2} s^{-1}$  is:

$$F_{wet} = Q(x)f_w(x)C_y(y) \quad (2.4)$$

Washout is assumed to occur in proportion to the local concentration throughout the depth of the plume and the wet deposition is modelled in terms of a washout coefficient  $\Lambda$ . Washout coefficients are assumed to be uniform throughout the domain, except (in ADMS 5) where limited by high concentrations of  $SO_2$  or  $CO_2$ . Algorithms for estimating their values are given in Sections 3 and 4.

## 2.2 Evaluation of the Wet Deposition Flux and Plume Depletion Coefficient

When wet deposition is modelled using a *washout coefficient*  $\Lambda$ , this means that the mass of pollutant incorporated into rainfall is

$$\Lambda C \quad (2.5)$$

per unit volume per unit time, where  $C$  is the local airborne concentration.  $\Lambda$  is dependent on a large number of parameters, including the rainfall rate, raindrop and aerosol size distributions and concentrations in air and raindrops. In ADMS,  $\Lambda$  may be input directly by the user or estimated by the system from other data such as rainfall rate. The choice of parameter values is discussed in Section 3.

Assuming irreversible uptake, the total wet deposition rate per unit horizontal area per unit time,  $F_{wet}$ , is found by integrating through a vertical column of air:

$$F_{wet} = \int_0^{\infty} \Lambda C dz \quad (2.6)$$

The result is that the plume strength diminishes with distance:

$$\frac{dQ}{dx} \Big|_{wet} = - \int_{-\infty}^{\infty} F_{wet} dy \quad (2.7)$$

The following assumptions are made:

- (1) All plume material lies in or below rain cloud; no distinction is made between in-cloud scavenging (*rainout*) or below-cloud scavenging (*washout*).
- (2) Uptake of pollutants is irreversible; precipitation scavenging does not lead to a *redistribution* of material in the plume.
- (3) Solution in raindrops does not lead to saturation, except for the cases described in §4
- (4) The rainfall rate is uniform over the domain.

The rate at which pollutant is washed out of the plume per unit horizontal area per unit time  $F_{wet}$  is given by equation (2.4) and the crosswind-integrated deposition flux per unit plume strength is:

$$f_w = \frac{\Lambda}{U_m(x)} \quad (2.8)$$

The amount of pollutant remaining in the plume decays exponentially:

$$q_w = e^{-\Lambda t_r(x)} \quad (2.9)$$

$Q_s$  is the initial source strength (possibly depleted by dry deposition),  $U_m$  the wind speed at mean plume height and  $t_r$  the travel time in rain.

### **3. Calculation of Washout Coefficient**

The washout coefficient  $\Lambda$  may be specified as a constant value by the user, in which case the wet deposition calculated will be independent of the precipitation rate and, indeed, wet deposition will be predicted in the absence of precipitation. The default value of washout coefficient  $\Lambda$  is  $1.0 \times 10^{-4} \text{s}^{-1}$ .

Alternatively the washout coefficient can be modelled as a function of pollutant species and rainfall rate only. The latter implies a fixed spectrum of raindrop sizes and makes no distinction between different types of rain (frontal, convective, orographic, etc). The following expression is then used to calculate the washout co-efficient:

$$\Lambda = aJ^b \quad (3.1)$$

$J$  is the rainfall rate in  $\text{mm hr}^{-1}$  and  $a$  and  $b$  are parameters depending on the type of pollutant. Constants  $a$  and  $b$  are supplied by the user and take the default values  $a = 1.0 \times 10^{-4}$ ,  $b = 0.64$ , see reference [1].

#### **4. Limit on Washout Coefficient**

The uptake of acidic pollutants is, in practice, limited at high concentrations by the limiting effect of the raindrop pH. The simplest way of modelling this is by defining a set of solubility coefficients to calculate the effective solubility of pollutants and, hence, the acidity within the raindrops. The scheme is only applied to SO<sub>2</sub> and CO<sub>2</sub>, and is only implemented in ADMS 5.

The scheme calculates the aqueous concentration of source material (SO<sub>2</sub> or CO<sub>2</sub>) in the rainfall that has passed through the plume,  $M_1$ , without considering the limiting effect of pH. This concentration  $M_1$  is compared with the maximum aqueous concentration that would be permitted by considering the pH of the raindrop,  $M_2$ . If  $M_2 < M_1$ ,  $\Lambda$  in equation (2.6) is replaced by  $\Lambda M_2/M_1$  which limits the wet deposition. Sections 4.1 and 4.2 describe how  $M_1$  and  $M_2$  are calculated.

##### ***4.1 Calculation of non-limited aqueous concentration $M_1$***

The rate of loss with downstream distance of source material from the plume is given by:

$$\frac{dQ_w}{dx} = -\frac{\Lambda Q_w}{U_m} \quad (4.1)$$

where  $Q_w$  (g/s) is the total mass flux of source material in the plume at a given downwind distance. This loss of source material from the plume must be balanced by deposition of material by the raindrops. If  $M_p(x)$  (kg/m<sup>3</sup>) is a wake averaged value for the concentration of source material in the raindrops, then the deposition of source material in the raindrops is given by

$$M_p (J/3.6 \times 10^6) \Delta y \quad (4.2)$$

where

- $J$  = precipitation rate in mm/hr
- $3.6 \times 10^6$  is used to convert from mm/hr to m/s
- $\Delta y$  = a lateral plume scale in metres, here taken to be  $\sqrt{2\pi}\sigma_y$

Equating (4.1) and (4.2) allows the aqueous concentration,  $M_1$  of source material in the raindrops in (moles/litre), to be derived. It is given by:

$$M_1 = \frac{Q(x)\Lambda}{MW_{SO_2}(J/3.6 \times 10^6)U\sqrt{2\pi}\sigma_y} \times 10^{-3} \quad (4.3)$$

where  $MW_{SO_2}$  = the molar mass of the pollutant, here SO<sub>2</sub>, in g/mole  
 $10^{-3}$  is used to convert from moles/m<sup>3</sup> to moles/litre

Note that  $M_1$  is a plume averaged value whereas  $M_2$ , described in §4.2 refers to plume centreline values.

## 4.2 Calculation of pH-limited aqueous concentration $M_2$

The maximum permitted concentration of pollutant in the raindrops,  $M_2$ , is calculated by iteration and depends on:

- (i) the partial pressure of the pollutant in the plume, so for  $\text{SO}_2$ ,  $p_{\text{SO}_2}$
- (ii) the acidity of the raindrops

The solubility of  $\text{SO}_2$  and  $\text{CO}_2$  in cloud water drops is determined by the Henry's Law solubility coefficients  $H_{\text{SO}_2}$  and  $H_{\text{CO}_2}$  (given in Table 2 in Section 7). The subsequent dissociation reactions of the aqueous gases  $\text{SO}_2$  and  $\text{CO}_2$  are shown in Table 2 with  $K_{\text{SO}_2}$  and  $K_{1\text{CO}_2}$  the respective equilibrium constants and  $K_w$  the ionic product of water.

The effective solubility of a species is determined from the reaction constants. For  $\text{SO}_2$ , the effective solubility  $X_{\text{SO}_2}$  (mole litre<sup>-1</sup> atm<sup>-1</sup>) is calculated as follows:

$$X_{\text{SO}_2} = H_{\text{SO}_2} \left\{ 1 + \frac{K_{\text{SO}_2}}{[\text{H}^+]} \right\} \quad (4.4)$$

The acidity of the raindrops is in turn given by the concentration of hydrogen ions,  $[\text{H}^+]$  (mol dm<sup>-3</sup>) in the raindrops,

$$\text{pH} = -\log_{10}[\text{H}^+] \quad (4.5)$$

and the partial pressure of the pollutant e.g.  $\text{SO}_2$ , is given by:

$$\frac{p_{\text{SO}_2}}{p_{cl}} = \frac{N_{\text{SO}_2}}{\left( \frac{L_w X_{\text{SO}_2} p_{cl} F_2}{\rho_w F_1} + \frac{p_{cl}}{RT_{cl}} \right)} \quad (4.6)$$

- where
- $p_{\text{SO}_2}$  = the partial pressure  $\text{SO}_2$  (Pascals)
  - $N_{\text{SO}_2}$  = total number of moles of  $\text{SO}_2$  in 1m<sup>3</sup> of atmosphere  
= (concentration of pollutant on plume centreline/ $MW_{\text{SO}_2}$ )
  - $L_w$  = the liquid water content of raindrops in the atmosphere (kg/m<sup>3</sup> of atmosphere)
  - $F_1$  = 1.01325x10<sup>5</sup>, the conversion factor from atmospheres to Pascals
  - $F_2$  = 1000, the conversion factor from m<sup>3</sup> to litres
  - $p_{cl}$  = the atmospheric pressure on the plume centreline (Pascals)
  - $T_{cl}$  = the temperature on the plume centreline (K)
  - $R$  = molar gas constant, 8.3143 kJ/(kmole K)
  - $\left( \frac{L_w F_2}{\rho_w} \right)$  = number of litres of water per m<sup>3</sup> of atmosphere

$L_w$  (kg/m<sup>3</sup>) the liquid water content of raindrops in the atmosphere is calculated from

$$L_w = \frac{\rho_w (J/3.6 \times 10^6)}{w_t} \quad (4.7)$$



$w_t$  (m/s) is a terminal velocity of droplets which is calculated using one radius to represent a distribution of droplet sizes based on the Marshal-Palmer distribution [3].

The electro-neutrality equation may be written as:

$$[H^+]^3 - (K_w + H_{SO_2}K_{SO_2}p_{SO_2})[H^+] = 0 \quad (4.8)$$

where  $K_w$  is the ionic product of water.

Equations (4.4)-(4.8) are solved by iteration for the partial pressure of  $SO_2$  with the initial pH being that of water with  $CO_2$  dissolved (pH=5.6) to account for absorption by the rainfall of  $CO_2$  from the atmosphere. When the solution has converged the number of moles of  $SO_2$  in aqueous phase per litre of water is then given by:

$$M_2 = K_{SO_2}p_{SO_2} \quad (4.9)$$

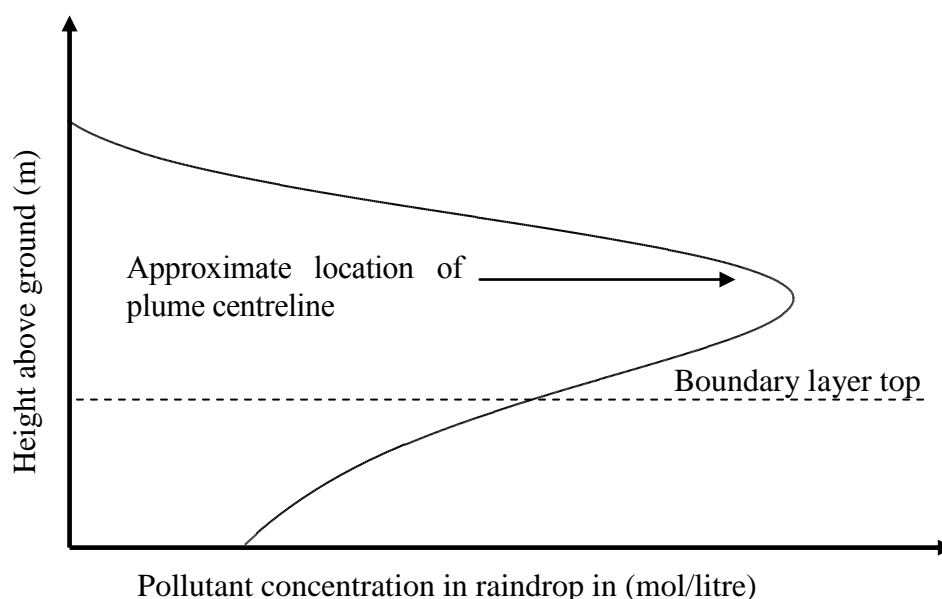
If  $M_2$ , the pH-limited aqueous concentration, is less than  $M_1$ , the non-limited concentration, the calculation of wet deposition uses a modified wet washout co-efficient,  $\Lambda M_2/M_1$ . This limiting effect is applied near to the source. If  $M_2 > M_1$  is satisfied at a distance from the source,  $\Lambda$  is not pH-limited downstream of that point. In particular, if  $M_2 > M_1$  at the first calculation point  $\Lambda$  will not be pH-limited. The test is applied to centreline concentrations and, therefore, no account is taken of the variation in  $M_1$  across the plume.

## **5. Modelling Wet Deposition using the Falling Drop Method**

This modelling option is only available in ADMS 5.

As mentioned in the Introduction, the uptake of gases in clouds and rain, and their subsequent deposition at the ground in solution, is a complex kinetic process that must be simplified for application in practical models of wet deposition. The methods described in Sections 2 to 4 above are significant simplifications of the processes involved, but the predicted values of wet deposition are relatively accurate when the uptake of pollutants is irreversible. However, after passing through the plume centreline, raindrops often fall through some relatively 'clean' air before reaching the ground. If the pollutant in question undergoes out-gassing (i.e. where the concentration gradient between the drop and the air causes the pollutant to pass back into gaseous form), the pollutant concentration within the drop at the ground will be reduced relative to the maximum concentration that was achieved at, or in fact often just below, the plume centreline. The gas of most interest that undergoes significant out-gassing before the drop reaches the ground is SO<sub>2</sub>.

Figure 1 gives an example vertical concentration profile as the raindrop travels vertically through the plume.



**Figure 1** – Pollutant concentration of a raindrop falling vertically through the plume, when significant out-gassing occurs below the plume centreline

The major features of this process may be examined by using a simple model of a rain drop falling through a vertical profile of gas with the assumption of kinetically controlled gas uptake and rapid solution equilibration.

As described in Section 4 above, the uptake of acidic pollutants such as SO<sub>2</sub> is limited at high concentrations by the limiting effect of the raindrop pH. In practice, the pollutant that affects SO<sub>2</sub> concentrations most significantly is HCl. In addition, any dissolved CO<sub>2</sub> and other pollutants in the 'clean' rain entering the top of plume affects the initial pH, and consequently the initial uptake of both SO<sub>2</sub> and HCl. Therefore, the 'falling drop' method has been implemented in the following way:

- The kinetic and thermodynamic processes of SO<sub>2</sub> and HCl are modelled as a coupled system.
- The user-entered pH of the rain entering the top of the plume is used to calculate a constant

value of  $[H^+]$  in solution that represents the dissolved  $CO_2$  and other pollutants in ‘clean’ rain.

Details are given in the following sections. The majority of the science presented here is taken from papers [4] and [5].

Note that this method is equally applicable to  $SO_2$  in the absence of HCl, and vice versa.

### 5.1. Kinetics of the uptake of gases in droplets

The flux of gases to a drop depends on the drop size, diffusion coefficient of gas in the air, the diffusion of the soluble components in the drop, the vapour pressure at the surface of the drop and the fall speed of the drop, and is given by equation (5.1) [5]:

$$Flux = \frac{4\pi r D}{RT} \frac{Sh}{2} (P_g - P_s) \quad (5.1)$$

Here, the units of flux are mol/s,  $r$  is the drop radius,  $D$  is the gas phase diffusion coefficient,  $R$  is the universal gas constant,  $T$  is the temperature,  $Sh$  is the Sherwood number and  $(P_g - P_s)$  the difference between the partial pressure of pollutant in the free atmosphere,  $P_g$ , and at the surface of the drop,  $P_s$ .

The Sherwood number is proportional to the mass diffusivity divided by the molecular diffusivity. It is a non-dimensional number that represents the mass transfer rate. In still air the Sherwood number is 2. At Reynolds numbers greater than 250, the Sherwood number can be described by equation (5.2a) [8]:

$$Sh = 0.94 Re^{0.5} Sc^{0.33} \quad (5.2a)$$

An alternative formulation, which may be applicable at lower Reynolds numbers, is given by equation (5.2b):

$$Sh = 0.94 Re^{0.5} Sc^{0.33} \quad (5.2b)$$

The Reynolds number,  $Re$ , is proportional to the inertial force divided by the viscous force:

$$Re = \frac{ur}{\nu} \quad (5.3)$$

where  $u$  is the terminal velocity of the drop,  $r$  is the drop radius and  $\nu$  is the temperature-dependent kinematic viscosity of air, given by the following expression:

$$\nu = \frac{\mu}{\rho} \quad (5.4)$$

Here,  $\mu$  is the dynamic viscosity given by equation (5.5), and  $\rho$  is the density, derived from a form of the Ideal Gas equation (5.6):

$$\mu = 1.7354 \times 10^{-5} \left( \frac{390}{T + 117} \right) \left( \frac{T}{273} \right)^{1.5} \quad (5.5)$$

$$\rho = \frac{T}{T_{273}} \rho_{273} \quad (5.6)$$

where  $T$  is the temperature in Kelvin,  $T_{273} = 273$  and  $\rho_{273}$  is the density of air at 273 K.

The Schmidt number,  $Sc$ , is proportional to the kinematic viscosity  $\nu$ , divided by the molecular diffusivity:

$$Sc = \frac{\nu}{D} \quad (5.7)$$

The average terminal velocity of a drop can be approximated by an empirical relationship based on its radius,  $r$  [6]:

$$u = 1620r^{0.8} \quad (5.8)$$

## 5.2. Thermodynamics of the dissolution of gases in raindrops

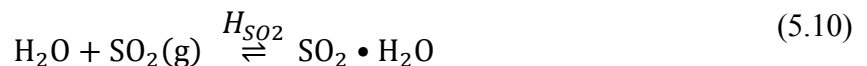
Gases in the air surrounding a raindrop will dissolve at a rate determined by the equations given in Section 5.1. As mentioned in Section 4.2, at equilibrium, the concentration of solute,  $C_s$ , in the saturated solution is given by Henry's Law:

$$C_s = Hp_g \quad (5.9)$$

where  $p_g$  is the partial pressure of the gas, and  $H$  is the Henry's Law constant, which is temperature dependent. Values of  $H$  for  $\text{SO}_2$ ,  $\text{HCl}$  and  $\text{CO}_2$  are given in Table 2 in Section 7. Henry's Law only accounts for the physical solubility of a gas in its non-dissociated form; if a dissolved gas is involved in chemical reactions, this will change the relationship. The chemical reactions of  $\text{SO}_2$ ,  $\text{HCl}$  and  $\text{CO}_2$  are described below. Note that for  $\text{CO}_2$ , both of the acid dissociation reactions are considered, whereas in Section 4.2, only the first, faster reaction is taken into account.

### 5.2.1 Chemical reactions of $\text{SO}_2$

When  $\text{SO}_2$  dissolves in water, the dominant chemical processes can be described by the following two equations:



Here,  $\text{SO}_2(\text{g})$  is the gas phase concentration of  $\text{SO}_2$  i.e. the partial pressure of  $\text{SO}_2$  at the drop surface, measured in atm. For equation (5.10), the reaction coefficient is the

Henry's Law constant  $H_{SO_2}$ , and for equation (5.11), the reaction coefficient is the acid disassociation constant  $K_{SO_2}$ ; values for  $H_{SO_2}$  and  $K_{SO_2}$  are given in Table 2.

Total  $SO_2$  solubility  $[S(IV)]$  is therefore given by equation (5.12):

$$[S(IV)] = H_{SO_2} \left( 1 + \frac{K_{SO_2}}{[H^+]} \right) [SO_2(g)] \quad (5.12)$$

### 5.2.2 Chemical reactions of HCl

When HCl dissolves in water, the dominant chemical processes can be described by the following two equations:



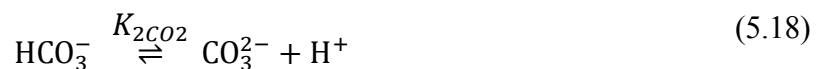
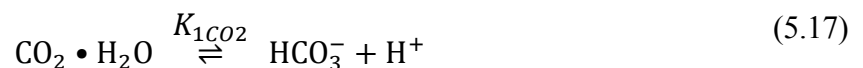
As for  $SO_2$ ,  $HCl(g)$  is the gas phase concentration of HCl i.e. the partial pressure of HCl at the drop surface, measured in atm; for equation (5.13), the reaction coefficient is the Henry's Law constant  $H_{HCl}$ , and for equation (5.14), the reaction coefficient is the acid disassociation constant  $K_{HCl}$ . However, as equations (5.13) and (5.14) occur effectively simultaneously, the reaction coefficients are never measured separately i.e. it is their product that is of interest. The value of the product of  $H_{HCl}$  and  $K_{HCl}$  is given in Table 2.

Total solubility  $[Cl^-]$  is given by the equation:

$$\frac{[H^+][Cl^-]}{[HCl(g)]} = H_{HCl}K_{HCl}. \quad (5.15)$$

### 5.2.3 Chemical reactions of $CO_2$

When  $CO_2$  dissolves in water, the dominant chemical processes can be described by the following three equations:



The reaction coefficients of equations (5.16), (5.17) and (5.18) are  $H_{CO_2}$ ,  $K_{1CO_2}$ , and  $K_{2CO_2}$  respectively; values for these coefficients are given in Table 2. These reactions can be combined to give:

$$[\text{HCO}_3^-] = \frac{[\text{CO}_2(\text{g})]H_{\text{CO}_2}K_{1\text{CO}_2}}{[\text{H}^+]} \quad (5.19)$$

and

$$[\text{CO}_3^{2-}] = \frac{[\text{CO}_2(\text{g})]H_{\text{CO}_2}K_{1\text{CO}_2}K_{2\text{CO}_2}}{[\text{H}^+]^2} \quad (5.20)$$

### 5.3 Electro-neutrality of the system

The electro-neutrality equation for the full system, taking into account  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{CO}_2$  and a constant, unknown number of dissolved cations is:

$$[\text{H}^+] = [\text{HSO}_3^-] + [\text{Cl}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{A}^-]_0 \quad (5.21)$$

where  $[\text{A}^-]_0$  equates to the concentration of the unknown pollutants.

At the top of the plume, it is assumed that  $[\text{HSO}_3^-] = [\text{Cl}^-] = 0$ . Therefore, substituting equations (5.19) and (5.20) into (5.21) gives an equation that needs to be solved to evaluate  $[\text{A}^-]_0$ :

$$[\text{A}^-]_0 = [\text{H}^+] - \frac{[\text{CO}_2(\text{g})]H_{\text{CO}_2}K_{1\text{CO}_2}}{[\text{H}^+]} - 2 \frac{[\text{CO}_2(\text{g})]H_{\text{CO}_2}K_{1\text{CO}_2}K_{2\text{CO}_2}}{[\text{H}^+]^2} \quad (5.22)$$

Here,  $[\text{CO}_2(\text{g})]$  is the partial pressure of  $\text{CO}_2$  in the atmosphere (value given in Table 2); the user enters the value of  $[\text{H}^+]$ .

In the plume, the effect of dissolved  $\text{CO}_2$  on the acidity of the raindrops is negligible with respect to the dissolved  $\text{SO}_2$  and  $\text{HCl}$ . Therefore equation (5.21) reduces to:

$$[\text{H}^+] = [\text{HSO}_3^-] + [\text{Cl}^-] + [\text{A}^-]_0 \quad (5.23)$$

### 5.4 Evaluation of wet deposition flux

The transfer of  $\text{SO}_2$  and  $\text{HCl}$  to droplets described by equation (5.1) leads to an increase in droplet concentration given by the equations:

$$\frac{d[S(\text{IV})]}{dt} = \frac{3D_{\text{SO}_2}Sh(\text{SO}_2(\text{g}) - P_{\text{SO}_2})}{2RT r^2} \quad (5.24)$$

$$\frac{d[\text{Cl}^-]}{dt} = \frac{3D_{\text{HCl}}Sh(\text{HCl}(\text{g}) - P_{\text{HCl}})}{2RT r^2} \quad (5.25)$$

Here,  $t$  is time through the plume, which can be evaluated in terms of vertical distance from the top of the plume using the terminal velocity of the drop given by equation (5.5).  $P_{\text{SO}_2}$  and  $P_{\text{HCl}}$  are the partial pressures of  $\text{SO}_2$  and  $\text{HCl}$  at the surface of the drop respectively i.e.  $[\text{SO}_2(\text{g})]$  and  $[\text{HCl}(\text{g})]$  given in equations (5.12) and (5.15). The values of the gas diffusivity constants  $D_{\text{SO}_2}$  and  $D_{\text{HCl}}$  for  $\text{SO}_2$  and  $\text{HCl}$  respectively are given in Table 2; these have been

evaluated using the Fuller relation (given by equation 3-133 in [7]). As in Section 4, the radius of the drop is calculated from the precipitation rate and the Marshall-Palmer drop size distribution [3]. Finally, note that the value of the universal gas constant,  $R$ , required by these equations (and given in Table 2) is in units of  $\text{atm dm}^3/(\text{K Mol})$ .

The three equations (5.23), (5.24) and (5.25) reduce to a system of coupled equations:

$$\frac{d[S(IV)]}{dt} = \frac{3D_{SO_2}Sh(SO_2(g) - \frac{[S(IV)]}{H_{SO_2}(1 + K_{SO_2}/[H^+])})}{2RT r^2} \quad (5.26)$$

$$\frac{d[Cl^-]}{dt} = \frac{3D_{HCl}Sh(HCl(g) - \frac{[H^+][Cl^-]}{H_{HCl}K_{HCl}})}{2RT r^2} \quad (5.27)$$

$$[H^+]^2 + (K_{SO_2} - [A^-]_0 - [Cl^-])[H^+] - K_{SO_2}([A^-]_0 + [S(IV)] + [Cl^-]) = 0 \quad (5.28)$$

Equations (5.26) and (5.27) can be solved by applying an adaptive time stepping integration routine (for example, the Cash-Karp Runge-Kutta method). The positive root to equation (5.28) is evaluated at each step to give values of  $[H^+]$ .

The concentration of pollutant in solution at the ground ( $[W]_{z=0}$ , mol/litre) can be converted into a mass deposition rate,  $F_{wet}$ , in units of  $\text{g/m}^2\text{s}$  using the precipitation rate ( $J$ , mm/hr) and the molecular weight ( $M$ , g) of the pollutant in question:

$$F_{wet} = \frac{MJ[W]_{z=0}}{3600} \quad (5.29)$$

In ADMS 5, molecular weights of 64 and 36.5 are used in equation (5.29) to give wet deposition fluxes of  $\text{SO}_2$  and  $\text{HCl}$  respectively, in spite of the fact that the dissolved  $\text{SO}_2$  is mostly present as  $\text{HSO}_3^-$ , and the dissolved  $\text{HCl}$  is mostly present as  $\text{Cl}^-$ .

### 5.5 Evaluation of plume depletion coefficient

Solving equations (5.26) – (5.28) above results in a vertical profile of concentration of  $[S(IV)]$  and  $[Cl^-]$ . If the concentration of  $S(IV)$  or  $Cl^-$  in solution at the ground is non-zero, then there is a net loss of pollutant from the plume into the raindrops and this must be represented in terms of a reduction in plume strength downstream.

Using the notation that was introduced in Section 2.2, taking  $Q$  to be the plume strength in units of  $\text{g/s}$ , the plume strength diminishes with distance:

$$\left. \frac{dQ}{dx} \right|_{wet} = - \int_{-\infty}^{\infty} F_{wet} dy \quad (5.30)$$

where  $x$  and  $y$  are the downwind and crosswind distance variables as usual. Unlike the case where the wet deposition was represented by a washout coefficient, it is no longer possible to

evaluate an explicit expression for the plume depletion factor,  $q_w$ . Instead, this equation must be solved at each downstream location using a basic finite difference scheme:

$$q_w(x_{new}) = q_w(x_{old}) - \frac{x_{new} - x_{old}}{2Q_s} \left( \int_{-\infty}^{\infty} F_{wet} dy \Big|_{old} + \int_{-\infty}^{\infty} F_{wet} dy \Big|_{new} \right) \quad (5.31)$$

Here,  $x_{old}$  and  $x_{new}$  are the old and new locations at which the falling drop calculations have been evaluated;  $Q_s$  is the plume strength in the absence of depletion by wet deposition.

### 5.5.1 Comment on plume depletion above and below the boundary layer top

In convective and neutral conditions, if plume rise causes the plume to travel above the boundary layer, then the boundary layer top is represented as a ‘lid’; one part of the plume is modelled above the boundary layer, and the remaining part is trapped below the boundary layer. In this case, a plume ‘depletion’ factor must be calculated for both plumes.

However, referring to

Figure 1, it is clear that for some meteorological conditions, the concentration of pollutant in solution at the boundary layer top is greater than at the ground, due to out-gassing. The result of this is that the plume ‘depletion’ coefficient for the below boundary layer plume, as calculated by equation (5.31), is greater than 1.

In fact, for some plumes of initially high temperature and/or density, the whole plume may travel above the boundary layer. In this case, the usual ADMS representation of the plume would be that ground level concentrations are zero, because the above boundary layer plume has no effect on concentrations at the ground. However, due to the fact that the falling drop method includes out-gassing of pollutant back into the atmosphere, in these cases, a limit on the fraction of the plume that passes above the boundary layer top has been imposed (99.9%). That is, a small percentage of the plume is always kept below the boundary layer in order that the plume ‘depletion’ factor may be applied to represent the increase in concentrations below the boundary layer top due to out-gassing. A better way of representing the out-gassed pollutant may be introduced in future versions of the model, for example, a shape factor similar to that used to represent the redistribution of material within the plume due to dry deposition.



## **6. Nomenclature**

$a, b$	parameters relating washout coefficient to rainfall rate
$C$	concentration
$F_{wet}$	wet deposition flux at a point
$f_w$	crosswind-integrated wet deposition flux
$J$	rainfall rate ( $\text{mm hr}^{-1}$ )
$K_i$	reaction constant, $i = 1,2$ ( $\text{moles litres}^{-1} \text{ atm}^{-1}$ )
$K_j$	reaction constant, $j = 3,4$ ( $\text{moles litres}^{-1}$ )
$K_{SO_2}$	effective solubility of $\text{SO}_2$ ( $\text{moles litres}^{-1} \text{ atm}^{-1}$ )
$L_w$	liquid water content of raindrops in the atmosphere ( $\text{kg/m}^3$ )
$M_1$	non-limited aqueous concentration of source material in raindrops ( $\text{moles litre}^{-1}$ )
$M_2$	pH-limited aqueous concentration of source material in raindrops ( $\text{moles litre}^{-1}$ )
$M_p$	concentration of source material in raindrops ( $\text{kg/m}^3$ )
$MW_{SO_2}$	molecular weight of $\text{SO}_2$ in g/mole
$N$	total number of moles of source material
$p_{cl}$	atmospheric pressure on plume centreline (Pascals)
$p_p$	partial pressure of source material (Pascals)
$q_w$	plume depletion factor for wet deposition
$Q_s$	source strength
$R$	molar gas constant ( $\text{KJ/kmole K}$ )
$T_{cl}$	temperature on plume centreline (K)
$U_m$	wind speed at mean plume height (m/s)
$w_t$	terminal velocity of water droplets (m/s)
$x, y, z$	Cartesian co-ordinate system: x along-wind, y crosswind; z vertical
$\chi$	crosswind-integrated concentration
$\Lambda$	washout coefficient ( $\text{s}^{-1}$ )
$\rho_w$	density of water ( $\text{kg/m}^3$ )

### **Subscripts**

$cl$	plume centreline
$p$	partial
$s$	source
$l$	per unit plume strength

## 7. Coefficients

A number of parameters are required for these calculations. These are summarised in Table 2 below.

Variable/ constant	Units	Description	Value
$D_{SO_2}$	m <sup>2</sup> /s	Gas diffusion coefficient of SO <sub>2</sub>	1.26 x 10 <sup>-5</sup>
$D_{HCl}$	m <sup>2</sup> /s	Gas diffusion coefficient of HCl	1.76 x 10 <sup>-5</sup>
$R$	atm dm <sup>3</sup> /(K Mol)	Universal gas constant	0.08205
$H_{SO_2}$	mol/(l atm)	Henry's Law coefficient for SO <sub>2</sub>	1.23 exp (3148 (1/T-1/298) )
$K_{SO_2}$	mol/l	Acid dissociation constant for SO <sub>2</sub>	1.30 x 10 <sup>-2</sup> exp (2095 (1/T-1/298) )
$H_{HCl}$	mol/(l atm)	Henry's Law coefficient for HCl	$H_{HCl}K_{HCl} =$ 2.0 x 10 <sup>6</sup> exp (9000 (1/T - 1/298))
$K_{HCl}$	mol/l	Acid dissociation constant for HCl	
$H_{CO_2}$	mol/(l atm)	Henry's Law coefficient for CO <sub>2</sub>	3.4 x 10 <sup>-2</sup> exp (2443 (1/T-1/298) )
$K_{1CO_2}$	mol/l	Acid dissociation constant for CO <sub>2</sub>	4.3 x 10 <sup>-7</sup> exp (-922 (1/T-1/298) )
$K_{2CO_2}$	mol/l	Acid dissociation constant for CO <sub>2</sub>	4.7 x 10 <sup>-11</sup> exp (-1788 (1/ T-1/298) )
$K_w$	(mol/l) <sup>2</sup>	Ionic product of water	1.0 x 10 <sup>-14</sup> exp (-716(1/T-1/298))
Mol <sub>air</sub>	g	Molecular weight of air	28.97 (approx)
Mol <sub>SO<sub>2</sub></sub>	g	Molecular weight of SO <sub>2</sub>	64
Mol <sub>HCl</sub>	g	Molecular weight of HCl	36.5
CO <sub>2</sub> (g)	atm	Partial pressure of CO <sub>2</sub> in the atmosphere	0.00037
$\nu$	m <sup>2</sup> /2	Kinematic viscosity of air	1.45 x 10 <sup>-5</sup>

Table 2 – Summary of constants and other parameters required for the wet deposition chemistry calculations ( $T$  is temperature in K)

## **8. References**

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