APPENDIX 6C: Differential Mass Balance Model

Overview

Differential Mass Balance (DMB) model is a receptor model combined with elements of a deterministic model which is designed to calculate the fraction of an ambient species contributed by an emissions source. This model has been shown to be a special case of the GMB model. In this approach, the concentration of the given species contributed by the source is calculated by scaling the ambient concentration of tracer by the ratio of the emission rates of the species of interest to the tracer, multiplied by a factor which accounts for deposition and conversion of the species of interest. The name "Differential Mass Balance" refers to the fact that conversion and deposition of a species of interest may differ from that for a tracer. Thus, the difference in mass resulting from deposition and conversion during the time from emission to measurement at receptor site must be determined. In the current application, the species of interest are sulfur dioxide (SO2) and Sulfate (SO4) and the tracer is deuterated methane (CD4).

Model Equations

Consider the basic equation for ambient concentration C_{ik} of species i resulting from many regional sources j, during sampling period k.

$$C_{ik} = \sum_{j=1}^{n} (c_{ijk} r_{ijk} d_{jk} + c_{i^*jk} r^*_{ijk} d_{jk}) \tag{1}$$

The quantity r_{ijk} is a factor that accounts for deposition and conversion of species, the quantity r^*_{ijk} is a factor that accounts for the formation of the species i from a parent species i^* (if species i is a primary species then this factor is zero), and d_{jk} is a dispersion factor resulting from winds and atmospheric mixing over transport time t from source j to the receptor.

Our objective in the DMB model application is to determine the concentration of species i resulting from the source from which tracer was released, which we will define as source 1, and to compare this concentration C_{i1k} to the total concentration C_{ik} resulting from all n of the regional sources. Thus we are interested in the first term of equation (1):

$$C_{i1k} = c_{i1k} r_{i1k} d_{1k} + c_{i^*1k} r^*_{i1k} d_{1k} \tag{2}$$

Since the tracer is only released from one source (j=1) and since the tracer does not deposit or convert, the ambient tracer concentration $C_{CD4,k}$ is simply the product of the tracer concentration at the source and the dispersion factor d_{1k},

$$C_{CD4,k} = c_{CD4,1,k} d_{1k} \tag{3}$$

Substituting this relation in equation (2) above we obtain the fundamental equation for DMB as

$$C_{i1k} = (c_{i1k} r_{i1k} + c_{i^*1k} r^*_{i1k}) \frac{C_{CD4,k}}{c_{CD4,1,k}}$$

or equivalently,

$$C_{i1k} = (\frac{c_{i1k}}{c_{CD4,1,k}} r_{i1k} + \frac{c_{i^*1k}}{c_{CD4,1,k}} r^*_{i1k}) C_{CD4,k} \tag{4}$$

It may be remarked that the dilution ratio d_{1k} is simply the χ/Q of dispersion models:

$$\chi/Q = 1/(2\pi\sigma_y\sigma_z u)$$

for a Gaussian plume, and

$$\chi/Q = 1/[(2\pi)^{1/2}\sigma_y H_m u]$$

for a Gaussian plume uniformly mixed in the vertical to height H_m. However, it should be noted that the theoretical values of the dilution factor are not needed for the DMB. Only the empirically determined ratios $c_{i1k}/c_{CD4,1,k}$ and $c_{i^*1k}/c_{CD4,1,k}$ are needed.

For a species that is directly emitted, and is deposited and/or converted, the fundamental equation for the DMB reduces to

$$C_{i1k} = \frac{c_{i1k}}{c_{CD4,1,k}} r_{i1k} C_{CD4,k}. \tag{5}$$

The ratio $c_{i1k}/c_{CD4,1,k}$ is assumed known and the form of r_{i1k} in this case is

$$r_{i1k} = exp(-(K_c(i,1,k) + K_d(i,1,k))t_{1k}).$$

For a species that is not directly emitted, but is a secondary species which is absent at the source, the fundamental equation for the DMB reduces to

$$C_{i1k} = \frac{c_{i^*1k}}{c_{CD4,1,k}} r^*_{i1k} C_{CD4,k}. \tag{6}$$

The ratio $c_{i^*1k}/c_{CD4,1,k}$ is assumed known and the form of r^*_{i1k} in this case is

$$r^*_{i1k} = \frac{K_c(i^*,1,k)}{K_c(i^*,1,k) + K_d(i^*,1,k) - K_d(i,1,k)} \times$$
$$\{exp(-K_d(i,1,k)t_{1k}) - exp(-[K_c(i^*,1,k) + K_d(i^*,1,k)]t_{1k})\}$$

where

$K_c(i,1,k)$ = conversion rate of species i from source 1 to its secondary form, during sampling period k.
$K_d(i,1,k)$ = deposition rate of species i from source 1 during sampling period k.

Recall the convention that i^* refers to the parent species corresponding to the species i. Specializing the fundamental equation for DMB for SO4 and SO2, we get,

$$C_{SO4,1,k} = \frac{c_{SO2,1,k}}{c_{CD4,1,k}} r^*_{SO4,1,k} C_{CD4,k} \tag{7}$$

and

$$C_{SO2,1,k} = \frac{c_{SO2,1,k}}{c_{CD4,1,k}} r_{SO2,1,k} C_{CD4,k} \tag{8}$$

where

$$\begin{aligned} r^*_{SO4,1,k} &= \frac{K_c(SO2,1,k)}{K_c(SO2,1,k) + K_d(SO2,1,k) - K_d(SO4,1,k)} \times \\ &\{exp(-K_d(SO4,1,k)t_{1k}) - exp(-[K_c(SO2,1,k) + K_d(SO2,1,k)]t_{1k})\} \end{aligned} \tag{9}$$

and

$$r_{SO2,1,k} = exp(-(K_c(SO2,1,k) + K_d(SO2,1,k))t_{1k}). \tag{10}$$

From now on we shall use the notation $K_c = K_c(SO2,1,k)$, $K_1 = K_d(SO2,1,k)$ and $K_2 = K_d(SO4,1,k)$. Furthermore, these parameters may be related to deposition velocities v_1 for SO2 and v_2 for SO4, and SO2 oxidation rate C by the equations

$$K_c = C * RH \tag{11}$$

$$K_1 = \frac{v_1}{H_m} \tag{12}$$

$$K_2 = \frac{v_2}{H_m} \tag{13}$$

where RH is in percent and H_m is the mixing height. The relation $K_c = C * RH$ is a consequence of our assumption that K_c is linearly related to Relative Humidity.

Model Calculations

The contribution of SO4 and SO2 by the source of interest ($j = 1$) to the receptor is calculated using equations (7) and (8). The value of $c_{SO2,1,k}/c_{CD4,1,k}$ is estimated from field measurements. The plume ages t_{1k} are derived from the plume streakline analysis (see separate appendix). $C_{CD4,1,k}$ are ambient concentrations of CD4 at the receptor and were measured during the experiment. The values of K_c, K_1 and K_2 are unknown and may be estimated based on literature values of deposition velocity for SO2 and particles and pseudo-first-order SO2 oxidation rates.

Alternatively, they may also be empirically derived from the measurements made during the experiment. To judge if a particular combination of these parameters is consistent with the field measurements the following procedure may be adopted. Using the chosen combination of values for these parameters we first calculate the SO4 contributions $C_{SO4,NGS,k}$ of source $j = 1$ (NGS) for each sampling period. It is supposed that the amount of the ambient SO4 not explained by the NGS contribution should be explainable as due to sources for which species $i_2, i_3, \cdots, i_h$, not emitted by NGS, serve as tracers. (CD4 corresponds to subscript i_1). Therefore, the regression model

$$C_{SO4,k} = \beta_0 + C_{SO4,NGS,k} + \sum_{u=2}^{h} \beta_u C_{i_u,k} + error \tag{14}$$

may be fitted and the adequacy of the fit judged by the resulting R^2 value. If the chosen parameter combination results in a high R^2 value, then it may be judged as being consistent with observed data. The best possible value of R^2 obtained, by varying the values of v_1,v_2 and C over their entire range of values suggested in the literature, may be denoted by R^2_{opt}. The values $v_1 = v_{1,opt}$, $v_2 = v_{2,opt}$, and $C = C_{opt}$ which result in the best R^2 may be used to calculate the daily NGS contributions to SO4 and SO2 at the receptor. By calculating the ratio of the total NGS contribution over the entire sampling period to total ambient concentrations over the same period we can calculate the fractional SO4 and SO2 contributions by NGS during the experimental period.

Uncertainty Calculations.

Uncertainties in the final results are primarily due to three sources.

- Uncertainties in the model parameters such as K_c, K_1 and K_2.
- Uncertainties in the measured values.
- Uncertainties in the extent to which the model assumptions are violated.

Uncertainties in the model parameters.

The model parameters in question are K_c, K_1 and K_2 which are not known. Suppose a review of the literature suggests deposition velocities v_1 for SO2 ranging from l_1 to u_1 cm/sec and v_2 for SO4 ranging from l_2 to u_2 cm/sec. In addition suppose the sulfur dioxide oxidation rates varied from $C = l_c$ to $C = u_c$ percent per hour at 100% relative humidity.

Clearly, not all combinations of values of v_1,v_2 and C are physically possible. To judge which combinations of these parameters are reasonable, the following procedure may be adopted. A grid of values for v_1,v_2 and C may be chosen by taking all possible combinations of these parameters resulting from

$$v_1 = l_1 \text{ to } u_1 \text{ in increments of } \delta_1.$$

$$v_2 = l_2 \text{ to } u_2 \text{ in increments of } \delta_2.$$

$$C = l_c \text{ to } u_c \text{ in increments of } \delta_c.$$

To decide whether a particular combination of values of v_1,v_2 and C are reasonable we first calculate the SO4 contributions, $C_{SO4,NGS,k}$ of source $j = 1$ (NGS) for each sampling period using these parameter values. Since the amount of the ambient SO4 not explained by the NGS contribution should be explainable as due to the remaining sources for which species i_2, i_3, $\cdots$, i_h, not emitted by NGS, serve as tracers (CD4 corresponds to subscript i_1), the regression model

$$C_{SO4,k} = \beta_0 + C_{SO4,NGS,k} + \sum_{u=2}^{h} \beta_u C_{i_u,k} + error \tag{15}$$

may be fitted and the adequacy of the fit judged by the resulting R^2 value. The best possible value of R^2 over the range of these parameters is denoted by R^2_{opt}. A value R^2_0 less than R^2_{opt} but close to it is chosen, based on subjective judgement, as a criterion value for judging the reasonablesness of various combinations of the parameter values. Parameter combinations resulting in an R^2 equal to R^2_0 or greater may be considered reasonable. The set of all such parameter combinations will be denoted by the symbol $\mathcal{A}$. NGS contributions can be calculated for each of the parameter combinations in the set $\mathcal{A}$. This will result in a whole range of values for the daily NGS contributions and the overall average NGS contributions. The mean and the standard deviation for this range of values (as well as the minimum and the maximum values) may be calculated to assess the uncertainty in the estimated NGS contributions due to imprecise knowledge of the model parameters. The measured values of concentrations of species are assumed to be exact in these calculations.

Uncertainties in the measured values.

To assess the effect of errors in measurements on the estimated NGS contributions to SO4 and SO2 at the receptor, we fix the values of v_1,v_2 and C at their optimum values obtained as explained in the previous subsection. The measured values used in the calculations are: (1) The ambient CD4 concentration, $C_{CD4,k}$, (2) The ambient SO4 concentration $C_{SO4,k}$, (3) The ambient SO2 concentration $C_{SO2,k}$, (4) Relative Humidity RH_k at the receptor, and (5) Transport time $t_{NGS,k}$ for the aerosol mixture from NGS to arrive at the receptor. Suppose each of these measurements have associated with them a standard deviation characterizing the uncertainty in the respective measurements. We generate a number of synthetic data sets (one hundred is sufficient for most purposes) on the computer by perturbing the measured values using random gaussian deviates with zero means and standard deviations associated with each of the measured values. For each synthetic data set thus generated, the daily NGS contribution to SO4 and SO2 at the receptor as well as the average contributions over the entire sampling period are calculated. The range of values thus obtained for each of these quantities gives an indication of the uncertainty that would be due to imprecise measurements alone. The results are reported in the form of means and standard deviations of each of the quantities of interest calculated from the synthetic data sets. Throughout this exercise, the model parameters, viz, the conversion and deposition parameters, were kept constant at their optimum values.

Uncertainties in the extent to which the model assumptions are violated.

Assessment of the uncertainties in reported results arising from model violations can be evaluated by conducting extensive sensitivity studies involving various perturbations in the model assumptions themselves.

Overall uncertainties.

Since the first two categories of uncertainties are expected to be "independent" , the total uncertainty due to these two sources may be characterised by the effective total standard deviation

$$\sigma_{Total} = (\sigma_1^2 + \sigma_2^2)^{1/2}$$

where σ_1 and σ_2 are the standard deviations associated with the two categories of uncertainties respectively.

Model Assumptions.

The DMB model assumes that the rates for deposition and conversion processes in the atmosphere are first-order and invariant in space and time. In particular, these rates are assumed to be constant at every point in space and time along the transport path. Deposition is dominated by dry deposition; precipitation scavenging is small by comparison. It is also assumed that the ratio of the emission rates for the species of interest (or its parent species) and the tracer is known.

Potential Deviations from Assumptions.

Rates for deposition processes may not be first-order and invariant in space and time. For example, no dry deposition will occur until the plume has been mixed to the ground. Dry deposition velocities are known to vary depending on atmospheric stability, and the type of surface (vegetation or rock, dry or wet). Wet deposition during periods of intense precipitation may deposit more material than dry processes do. The ratio of the emission rates for the species of interest (or its parent species) and the tracer may not be known precisely.

Model Inputs.

The inputs to the model are, as a function of time, the relative emission rates of SO2 and tracer, ambient concentrations of tracer,SO2, and SO4, and plume ages, deposition velocities for SO2 and particulates (v_d), Mixing height (H_m), SO2 pseudo-first-order oxidation rate (possibly entered as a constant or as a function of relative humidity).

Model Outputs.

Ambient concentrations and fractions of total ambient concentrations of SO2 and SO4 resulting from the given source.