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Chapter 10

AEROSOLS IN MODELS-3 CMAQ

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ABSTRACT

The aerosol module of the CMAQ is designed to be an efficient and economical depiction of aerosol dynamics in the atmosphere. The approach taken represents the particle size distribution as the superposition of three lognormal subdistributions, called modes. The processes of coagulation, particle growth by the addition of new mass, particle formation, etc. are included. Time stepping is done with analytical solution to the differential equations for the conservation of number and species mass conservation. The module considers both $PM_{2.5}$ and PM_{10} and includes estimates of the primary emissions of elemental and organic carbon, dust and other species not further specified. Secondary species considered are sulfate, nitrate, ammonium, water and organic from precursors of anthropogenic and biogenic origin. Extinction of visible light by aerosols represented by two methods, a parametric approximation to Mie extinction and an empirical approach based upon field data. The algorithms describing cloud interactions are also included in this chapter.

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10.0 THE AEROSOL PORTION OF MODELS-3 CMAQ

Inclusion of aerosol particles in an air quality model presents several challenges. Among these are the differences between the physical characteristics of gases and particles. In treating gases in an air quality model, the size of the gas molecules is not usually of primary importance. In contrast, particle size is of primary importance. The interaction between condensing vapors and the target particle depends in an important way on the particle size in relation to the mean free path in the atmosphere. For gases, once the concentration is known, the corresponding number of molecules is known. This is not the case for particles. Thus, including aerosol particles in an air quality model means choosing how the total number, total mass, and size distribution of the particles is represented. Once this choice is made, then important physical and chemical processes involving particles must be represented. Particles may be emitted into the air by natural processes such as wind blowing dust from a desert. Human activities may disturb the soil to allow wind to blow soil particles off the ground. Sea salt particles come into the atmosphere by wind driven waves on the sea surface. Volcanic activity is another source of particles for both the troposphere and the stratosphere. Particles can be made in the atmosphere directly from chemical reaction. The most important example of this is the transformation of sulfur dioxide, a by-product of fossil fuel combustion, into sulfate particles. Hydroxyl radicals attack the sulfur dioxide and make sulfuric acid that then may nucleate in the presence of water vapor and ammonia to produce new particles. If there are particles already present in the atmosphere, the new sulfate may condense on the existing particles or nucleate to form new particles depending upon conditions which are only recently beginning to be understood. Reactions of organic precursors such as natural monoterpenes and anthropogenic organic species with ozone and other oxidants or radicals make new species that condense on existing particles or make new particles depending upon conditions. Combustion sources emit particles composed of mixtures of organic carbon and elemental carbon. The exact mixture of organic and elemental carbon is a strong function of the conditions of combustion. Once these particles are in the air, they may grow by condensing of species upon them as has already been mentioned. For a large group of particles made in the air, i.e., secondary particles, growth may be related to relative humidity because of water condensing on the particles. Another gas-particle interaction is the chemical equilibration of species within or on the surface of a particle with gases and vapors within the air. Unlike gases, particles coagulate, e.g., collide and form a particle whose mass and volume are the sums of the masses and volumes of the colliding particles. Thus, adding particles to an air quality model means adding a new set of physical processes.

In designing the aerosol component of CMAQ the following assumptions were made. Any representation of particles had to be consistent with observations of particles. The representation had to be mathematically and numerically efficient to minimize computer time. And finally the representation had to be usable for regional to urban simulations. These assumptions led to a choice of two methods. The first method would be to model particle behavior in set of bins of increasing size. This approach is quite popular and is described originally by Gelbard et. al. (1980) and more recently by Jacobson (1997). The second approach, the one chosen for implementation in CMAQ, is to follow Whitby (1978) and model the particles as a superposition of lognormal subdistributions called modes. The sectional method using the discrete size bins requires a large number of bins to capture the size distribution. If one wishes to model several chemical components then the number of components is multiplied by the number of bins. This leads to a very large number of variables that must be added to an air quality model to capture particle behavior. In the modal approach, using the three modes suggested by Whitby(1978), only three integral properties of the distribution, the total particle number concentration, the total surface area concentration, and the total mass concentration of the individual chemical components in each of the three mode. The current approach differs from that taken by Binkowski and Shankar (1995) where the sixth moment was chosen as a third in integral property in place of the second moment. That moment as chosen because of a mathematical simplification (see Whitby and McMurry, 1997). The mathematical simplifications of the modal method allow analytical solutions to be used for the aerosol dynamics. The current approach uses numerical quadratures to calculate all of the coagulation terms. The numerical quadratures were compared with the analytical expressions exhibited in Whitby et al. (1991) and are accurate to six decimal places. The choice of using numerical quadratures was made to reduce the memory requirements associated with a variable geometric standard deviation and because the second moment unlike the sixth moment does not have an analytical form.

The aerosol component of the CMAQ is derived from the Regional Particulate Model (RPM) (Binkowski and Shankar, 1995) which in, turn, is based upon the paradigm of the Regional Acid Deposition Model (RADM), an Eulerian framework model (Chang et al., 1990). The particles are divided into two groups, which are fine particles and coarse particles. These groups generally have separate source mechanisms and chemical characteristics. The fine particles result from combustion processes and chemical production of material that then condenses upon existing particles or forms new particles by nucleation. The coarse group is composed of material such as wind-blown dust and marine particles (sea salt). The anthropogenic component of the coarse particles is most often identified with industrial processes. The common EPA nomenclature used in air quality refers to $PM_{2.5}$ (particles with diameters less than 2.5 μm) and PM_{10} (particles with diameters less than 10μm). Note that PM_{10} includes $PM_{2.5}$. Thus, in the present context, coarse particles are those with diameters between 2.5 and 10 μm. Then, the mass of the coarse particles is the difference between the masses in PM_{10} and $PM_{2.5}$.

As already noted, the aerosol particle size distribution is modeled using the concepts developed by Whitby (1978). That is, $PM_{2.5}$ is treated by two interacting subdistributions or modes. The coarse particles form a third mode. Conceptually within the fine group, the smaller (nuclei or Aitken), *i*-mode represents fresh particles either from nucleation or from direct emission, while the larger (accumulation), *j*-mode represents aged particles. Primary emissions may also be distributed between these two modes. The two modes interact with each other through coagulation. Each mode may grow through condensation of gaseous precursors; each mode is subject to wet and dry deposition. Finally, the smaller mode may grow into the larger mode and partially merge with it. These processes are described in the following subsections. The chemical species treated in the aerosol component are fine species sulfates, nitrates, ammonium, water, anthropogenic and biogenic organic carbon, elemental carbon, and other unspecified material of anthropogenic origin. The coarse-mode species include sea salt, wind-blown dust, and other unspecified material of anthropogenic origin. Because atmospheric transparency or visual range is an important air quality related value, the aerosol component also calculates estimates of visual range and aerosol extinction coefficient.

10.1 Aerosol Dynamics

The particle dynamics of this aerosol distribution are described fully in Whitby et al. (1991) and Whitby and McMurry 1997); therefore, only a brief summary of the method is given here.

(Note: In the following equations repeated subscripts are not summed.)

10.1.1 Modal Definitions

Given a lognormal distribution defined as

$$n(\ln D) = \frac{N}{\sqrt{2\pi}\,\ln\sigma_g}\exp\left[-0.5\left(\frac{\ln\frac{D}{D_g}}{\ln\sigma_g}\right)^2\right], \tag{10-1}$$

where N is the particle number concentration, D the particle diameter, and D_g and σ_g the geometric mean diameter and standard deviation of the distribution, respectively. The kth moment of the distribution is defined as

$$M_k = \int_{-\infty}^{\infty} D^k n(\ln D)\,\mathrm{d}(\ln D) \tag{10-2}$$

with the result

$$M_k = N D_g^k \exp\left[\frac{k^2}{2}\ln^2\sigma_g\right]. \tag{10-3}$$

M_0 is the total number, N, of aerosol particles within the mode suspended in a unit volume of air. For $k = 2$, the moment is proportional to the total particulate surface area within the mode per unit volume of air. For $k = 3$, the moment is proportional to the total particulate volume within the mode per unit volume of air. The constant of proportionality between M_2 and surface area is π; the constant of proportionality between M_3 and volume is $\pi/6$. Note that the geometric standard deviation is the same no matter which moment is selected. M_3 is determined from the nine distinct fine aerosol species (including water) listed in Table 10-1 as follows:

$$M_{3i} = \sum_{n=1}^{n_{\max}} \frac{\varphi_i^n}{\frac{\pi}{6}\rho_n} \tag{10-4a}$$

$$M_{3j} = \sum_{n=1}^{n_{\max}} \frac{\varphi_j^n}{\frac{\pi}{6}\rho_n} \tag{10-4b}$$

where φ_i^n and φ_j^n are the species mass concentrations of the nth species in each mode in [μg m^{-3}], ρ_n is the average density of the nth species. The third moment for the coarse mode is obtained in a similar manner. Given a value of third moment concentration and number concentration, the geometric mean standard deviation and the geometric mean diameter for each mode is diagnosed from

$$\ln^2 \sigma_g = \frac{1}{3}\left(2 \ln(M_3) - 3 \ln(N) \right) - \ln(M_2) \qquad (10\text{-}5a)$$

$$D_g^3 = \frac{M_3}{N \exp\left[\frac{9}{2} \ln^2 \sigma_g\right]} \; . \qquad (10\text{-}5b)$$

The prediction equations for number, second moment and species mass are given in Section 10.1.4.

10.1.2 New Particle Production by Nucleation

The CMAQ aerosol component has a choice of two particle production mechanisms, those of Harrington and Kreidenweis (1998a,b) and Kulmala et al. (1998). Both of these methods predict the rate of increase of the number of particles, *J*, (in number per unit volume per unit time) by the nucleation from sulfuric acid vapor. In order to predict the rate of increase on new mass and new second moment an assumption about particle size is necessary. Following work by Weber et al. (1997), it is assumed that the new particles are 3.5 nm in diameter. Weber et al. reported measurements of the concentration of particles that are in the size range 2.7 to 4.nm. For simplicity we have chosen 3.5 nm as a representative diameter.

Using either of these methods, the production rate of new particle mass [μg m^{-3} s^{-1}] is then

$$\frac{d\,Mass}{dt} = \frac{\pi}{6} \rho d_{3.5}^3 \, J \qquad (10\text{-}6a)$$

and that for number [m^{-3} s^{-1}] is

$$\frac{d\,Num}{dt} = J \qquad (10\text{-}6b)$$

and that for second moment [m^2 m^{-3} s-1] is

$$\frac{d\,M_2}{dt} = d_{3.5}^2 \, J \qquad (10\text{-}6c)$$

where $d_{3.5}$ is the diameter of the 3.5 nm particle and ρ is the density of the particle (taken as sulfuric acid) at ambient relative humidity (Nair and Vohra, 1975).

10.1.3 Primary Emissions

The EPA emission inventory for $PM_{2.5}$ and PM_{10} does not currently contain information about neither size distribution nor chemical speciation. In the CMAQ work, the assumption is that the major part of $PM_{2.5}$ particulate mass emissions are in the accumulation mode with a small fraction in the Aitken mode; i.e. a fraction of 0.999 of $PM_{2.5}$ is assumed to be in the accumulation mode and the remaining fraction, 0.001, is assigned to the Aitken mode. Sensitivity studies will be conducted to evaluate this assumption. In order to estimate the emissions rate for number and second moment from the mass emissions rate an assumed mass size distribution is required. It is convenient to express the emission rate for number, E_0, and that for second moment E_2 in terms of a total emissions rate for third moment. This is shown schematically as follows where E_n is the mass emissions rate for species n and ρ_n is the density for that species

$$E_{3n} = \left(\frac{6}{p}\right)\left(\frac{E_n}{\rho_n}\right) \tag{10-7a}$$

$$E_0 = \frac{\sum_n E_{3n}}{D_{\mathrm{gv}}^3 \exp\left(-\frac{9}{2}\ln^2\sigma_{\mathrm{g}}\right)} \tag{10-7b}$$

$$E_2 = \frac{\sum_n E_{3n}}{D_{\mathrm{gv}} \exp\left(-\frac{1}{2}\ln^2\sigma_{\mathrm{g}}\right)} \tag{10-7c}$$

where the sum is taken over all emitted species.

In Equation 10-7b,c, E_0 and E_2 schematically represent the emissions rates for the various modes. In Section 10.1.4, the nomenclature used to represent the emissions rate for number for each of the three modes will be respectively E_{0i}, E_{0j}, and E_{0cor}.

We have chosen values of 0.3 µm for the geometric mean diameter for mass, D_{gv}, and 2.0 for the geometric standard deviation, σ_{g} for the accumulation mode. The corresponding values for the Aitken mode are 0.03 µm and 1.7, and those for the coarse mode are 6 µm and 2.2.

The current emissions inventory estimates that 90% of PM_{10} is fugitive dust, and that 70% of this dust consists of $PM_{2.5}$ particles. The paradigm adopted for the CMAQ is that fugitive dust is a coarse mode phenomenon with a tail that overlaps the $PM_{2.5}$ range. Therefore, 90% of PM_{10} emissions are assigned entirely to the coarse mode species ASOIL. Sulfate emissions are treated differently in CMAQ than in RPM. In RPM sulfate emissions were treated as particles and distributed between the Aitken and accumulation modes. In CMAQ, the photochemical module has sulfate emissions incorporated into the chemical solver. Thus, the production rate for sulfuric acid will include direct emissions of sulfate. This rate is passed from the photochemical module to the aerosol module. Assigning fractional amounts of emitted $PM_{2.5}$ and PM_{10} to the specific species in Table 10-1 is a matter of ongoing discussions with those responsible for preparing the national emissions inventory.

10.1.4 Numerical Solvers

The numerical solvers for the two fine particle modes in the Models-3 aerosol component have been modified from those in RPM, which followed from Whitby et al. (1991). The major difference is that the RPM solvers linearized the quadratic term for intramodal coagulation in the equation for modal number concentration. The new solvers in CMAQ retain this quadratic term.

The number concentrations for the Aitken and accumulation modes are denoted as N_i and N_j respectively. Intramodal coagulation coefficients are functions only of the geometric mean diameters and geometric standard deviations for each mode and are denoted as F_{0ii} and F_{0jj}.

Similarly, the intermodal coagulation coefficient for coagulation between the Aitken and accumulation modes is F_{0ij}. For simplicity the following coefficients are defined.

For the Aitken mode:

$a_i = F_{0ii}$, $b_i = N_j F_{0ij}$, and

$$c_i = \frac{d\,Num}{dt} + E_{0i}, \text{ with } \frac{d\,Num}{dt} \text{ from (10-6b);}$$

and for the accumulation mode:

$a_j = F_{0jj}$, and $c_j = E_{0j}$

The emissions rates for number concentration are E_{0i} and E_{0j} and are set to values determined for each mode from Equation 10-7b.

We may now write for the particle number concentrations

$$\frac{\partial N_i}{\partial t} = c_i - a_i N_i^2 - b_i N_i \text{ ; and} \qquad (10\text{-}8a)$$

$$\frac{\partial N_j}{\partial t} = c_j - a_j N_j^2 . \qquad (10\text{-}8b)$$

Equation 10-8a, a Riccati type equation and Equation 10-8b, a logistics type equation, have different analytical solutions depending upon whether c_i and c_j are zero or nonzero. These analytic solutions are used in the CMAQ solver with the coefficients being held constant over one model time step. In discussing the analytical solutions to Equations 10-8a and b, subscripts will be omitted for simplicity

The solution to Equation 10-8a for $c_i \neq 0$ is of the form

$$N(t) = \frac{r_1 + r_2 P \exp\left(\hat{D} t\right)}{a\left[1 + P \exp\left(\hat{D} t\right)\right]}$$

where

$$\hat{D} = \left(b^2 + 4ac\right)^{\frac{1}{2}},\ r_1 = \frac{2ac}{b + \hat{D}},\ r_2 = -\frac{b + \hat{D}}{2},\ P = -\left(\frac{r_1 - a\ N(t_0)}{r_2 - a\ N(t_0)}\right).$$

For $c_i = 0$, the solution to Equation 10-8a is of the form

$$N(t) = \frac{bN(t_0)\exp\left(-bt\right)}{b + aN(t_0)\left[1 - \exp\left(-bt\right)\right]}.$$

The solution to Equation 10-8b when $c_j \neq 0$ is of the same form as that to Equation 10-8a except $b = 0$. The solution when $c_j = 0$, known as Smoluchowski's solution, is:

$$N(t) = \frac{N(t_0)}{1 + aN(t_0)t}.$$

The equations for the prediction of second moment, M_2, in the Aitken and accumulation modes are both of the form

$$\frac{\partial M_2}{\partial t} = P_2 - L_2 M_2;$$

with solutions of the form

$$M_2(t) = \frac{P_2}{L_2} + \left[M_2(t_0) - \frac{P_2}{L_2}\right]\exp\left(-L_2 t\right).$$

In these equations, production of second moment is denoted by P_2 and loss by L_2 .For the Aitken mode, the production term includes the rate of second moment increase by new particle formation from Equation 10-6c, condensational growth (Equation 7a of Binkowski and Shankar, 1995) and by primary emissions from Equation 10-7c. The loss term accounts for the loss of second moment by intramodal coagulation, as well as including the transfer of second moment to the accumulation mode by intermodal coagulation. For the accumulation mode, the production term includes the transfer of second moment by intermodal coagulation, condensational growth (Equation 7b of Binkowski and Shankar, 1995) and the contribution of primary emissions from Equation 10-7c. The loss term accounts for intramodal coagulation.

It is important to note that the history variable in CMAQ is the modal surface area, which, as already noted, is π time the second moment. For convenience, however, within the internal aerosol subroutines, the second moment is the treated. Before returning to the main CMAQ routines, the second moment is multiplied by π. That is why species number 23 and 24 in Table 10-1 are identified as modal surface areas. It is also important to note that the surface area predicted by CMAQ is the surface area for *spherical* particles and may not represent the true surface area available in nonspherical particles or in porous particles such as carbon soot.

Empirical correction factors may be needed for use of CMAQ surface area predictions in certain applications.

The equations for mass concentration of species *n* may be written as:

$$\frac{\partial \varphi_i^n}{\partial t} = P_i^n - L_i \varphi_i^n; \text{ and} \qquad (10\text{-}9a)$$

$$\frac{\partial \varphi_j^n}{\partial t} = P_j^n, \qquad (10\text{-}9b)$$

where $P_i^n = \varphi_i^n + E_i^n + R^n \Omega_i$ and $L_i = N_i N_j F_{3ij} / M_{3i}$

with $\varphi_i^n = \dfrac{d\,Mass}{dt}$ from Equation 10-6a, when *n* denotes sulfate, and where $\boldsymbol{E}_i^n$ and $\boldsymbol{E}_j^n$ are the emission rates and R^n is the gas-phase production rate for species *n*. The factors Ω_i and Ω_j, defined by Equations A17 and A18 of Binkowski and Shankar (1995) represent the fractional apportionment of condensing species. F_{3ij} is the coagulation coefficient for the third moment.

Note that the loss of mass in Equation 10-9a is a gain of mass in Equation 10-9b. This represents the transfer of mass by intermodal coagulation. There is no such transfer of number in Equations 10-8a,b because of the convention that when a smaller particle coagulates with a larger particle there is a loss of number from the population of smaller particles, but no gain of number in the population of larger particles. There is, however, a transfer of mass. Equations 10-9a and b have an analytic solution holding the coefficients constant for the time step of the form:

$$\varphi(t) = \frac{P}{L} + \left[\varphi(t_0) - \frac{P}{L}\right] \exp\left(-Lt\right).$$

The solution to Equation 10-9b are by an Euler forward step once again holding the production terms constant over that time step.

The equation for the prediction of coarse mode mass is

$$\frac{\partial \varphi_{cor}^n}{\partial t} = E_{cor}^n,$$

The solution is by an Euler forward step. The equation for coarse mode number is similar because coagulation is ignored for the coarse mode, and is also solved by an Euler forward step.

10.1.5 Mode Merging by Renaming

In Binkowski and Shankar (1995), the Aitken mode diameters grew over the simulation period to become as large as those in the accumulation mode. While this is probably true in nature, it violates the modeling paradigm that two modes of distinct size ranges always exist. This phenomenon can be modeled by mode merging as follows. The Aitken mode approaches the accumulation mode by small increments over any model time step when particle growth and nucleation are occurring. Thus, an algorithm is needed that transfers number and mass concentration from the Aitken mode to the accumulation mode when the Aitken mode forcing exceeds the accumulation mode forcing and the number of particles in the accumulation mode is no larger than that in the Aitken mode.

This algorithm is formulated as follows (Binkowski et al., 1996). When Equation 10-10 is satisfied, the diameter of overlap, $\tilde{d}$, for the modal number distributions can be calculated exactly. Given this diameter, the fraction of the total number of Aitken mode particles greater than this diameter is easily calculated from the complementary error function

$$F_{num} = 0.5\left[1 + \mathrm{erfc}\,(x_{num})\right] \text{ , where} \tag{10-10a}$$

$$x_{num} = \frac{\ln\left(\tilde{d}/d_{gni}\right)}{\sqrt{2}\,\ln\left(\sigma_{gi}\right)}$$

and d_{gni} is the geometric mean diameter for the Aitken mode number distribution.

The number concentration corresponding to these particles is transferred to the accumulation mode, a processes denoted here as renaming the particles. A similar process is used to transfer mass (third moment) concentration and surface area (second moment) concentration from the Aitken to the accumulation mode using the complementary error function corresponding to the third moment.

$$F_k = 0.5\left[1 + \mathrm{erfc}\,(x_k)\right] , \tag{10-10b}$$

where $x_k = x_{num} - \dfrac{k \ln\left(\sigma_{gi}\right)}{\sqrt{2}}$.

For numerical stability, the transfer of number and mass is limited so that no more than one half of the Aitken mode mass may be transferred at any given time step.

This is accomplished by requiring that $\dfrac{3\ln\left(\sigma_{gi}\right)}{\sqrt{2}} \le x_{num}$.

The fraction of the total number and surface area (k= 2) and mass (k=3) remaining in the Aitken mode is calculated from the error function of the overlap diameters as:

$$\Phi_{num} = 0.5\left[1 + \mathrm{erf}\,(x_{num})\right] \tag{10-10c}$$

$$\Phi_k = 0.5\left[1 + \mathrm{erf}(x_k)\right] \tag{10-10d}$$

Using these fractions, Aitken and accumulation mode number and mass concentrations are updated as

$$N_j = N_j + F_{num} N_i \tag{10-11a}$$

$$\varphi_j^n = \varphi_j^n + F_3\varphi_i^n \tag{10-11b}$$

$$M_{2\,j} = M_{2\,j} + F_2 M_{2i} \tag{10-11c}$$

$$N_i = \Phi_{num} N_i \tag{10-11d}$$

$$\varphi_i^n = \Phi_3 \varphi_i^n \tag{10-11e}$$

$$M_{2\mathrm{i}} = \Phi_2 M_{2i} \tag{10-11f}$$

This method of particle renaming is analogous to the procedure discussed by Jacobson (1997) where particles are reassigned in the moving center concept of a bin model. When the particles grow beyond the boundaries of their size bin, they are reassigned to a larger bin and averaged with the new bin.

10.2 Aerosol Dry Deposition

The rate of dry deposition of particle zeroth and third moment to the earth's surface provides the lower boundary condition for the vertical diffusion of aerosol number and species mass, respectively. The method of doing this follows the RPM approach with the following exceptions. In RPM total fine mass was deposited. In CMAQ the species mass in each mode is deposited separately using the dry deposition velocity for the third moment. The impaction term is omitted for the coarse mode particles in both the zeroth and third moment dry deposition velocities. See Binkowski and Shankar (1995) Equations A25 through A34 for details.

10.3 Cloud Processing of Aerosols

Clouds are formed when the relative humidity reaches a value at which existing aerosol particles are activated. That is, they pass through a potential barrier and grow rapidly from a few micrometers to several micrometers to become cloud droplets (cloud nucleation). Soluble gases are then dissolved into the cloud droplets where aqueous-phase chemical equilibria and reactions occur. The attack on dissolved sulfur dioxide by hydrogen peroxide produces a dissolved sulfate species (oxidation of Sulfur (IV) to Sulfur (VI)). Because these processes are very complex in detail and occur at subgrid scale, most cloud modeling in mesoscale meteorological models and in air quality models uses simplified parametric approaches to model the effect of clouds rather than modeling the clouds directly. This approach was used in RADM and RPM and is applied in the first version of CMAQ.

The assumptions for aerosol behavior in clouds are:

- The Aitken (i) mode forms interstitial aerosol which is scavenged by the cloud droplets. All three integral properties of the Aitken mode respond to in-cloud scavenging.

- The accumulation (*j*) mode forms cloud condensation nuclei and thus is distributed as aerosol within the cloud water. Mass and number in this mode may be lost through precipitation. Mass but not number is increased by in-cloud scavenging of the Aitken mode.

- All new sulfate mass produced by aqueous production is added to the accumulation mode, but the number of accumulation mode particles is unchanged as is the geometric standard deviation, σ_g, of the accumulation mode processes (cf Leaitch, 1996 for cumulus clouds).

- The assumption about the accumulation mode geometric standard deviation means that the surface area of the accumulation mode is reconstucted from the new mass and new number in the accumulation mode at the end of the cloud lifetime.

- The aerosol is mixed vertically by the same mechanisms mixing other species. The wet removal of aerosol is proportional to wet removal of sulfate (See Chapter 11).

The limitations are:

- The cloud process modules are similar to those of RPM and RADM with cloud droplet number concentrations being modeled by an empirical fit to data from Bower and Choularton (1992).

- Cloud droplet size distributions are lognormal with σ_g set to 1.2. Using the cloud liquid water content and the cloud droplet number concentration, the geometric mean cloud droplet diameter, d_g, can be calculated.

The mathematical approach begins with an extension (Binkowski and Shankar, 1994; Shankar and Binkowski, 1994) of Slinn's (1974) two-step model as used by Chaumerliac (1984).

The in-cloud scavenging of interstitial Aitken mode number, surface area and mass concentration, y_{ak}, may be represented by:

$$\frac{dy_{ak}}{dt} = -\alpha_k y_{ak} \tag{10-12}$$

with solution (10-13)

$$y_{ak}\left(t + \tau_{cld}\right) = y_{ak}(0) \exp\left(-\alpha_k \tau_{cld}\right)$$

where α_k (k = 0,2,3) is the attachment rate for interstitial aerosol concentration. The attachment rate is assumed to be held constant over the cloud lifetime τ_{cld}. The initial values $y_{ak}(0)$ are determined after cloud mixing (see Equations 11-4 and 11-5).

The cloud water aerosol concentration is represented by

$$\frac{dy_{ck}}{dt} = \delta_{k3}\left(\alpha_k y_{ak} + P\right) - \beta\delta_{k0} y_{ck},\ k \neq 2 \tag{10-14}$$

where β is the precipitation removal rate, and P is the production of new sulfate mass by aqueous chemistry. The first Kronecker delta indicates that only mass (k=3) is increased for the accumulation mode by chemical production and in-cloud scavenging. The second Kronecker delta indicates that only number (k=0) is removed by the precipitation removal term in this form. Mass is removed explicitly in the cloud processor.

The attachment rates, α_k, using the form recommended by Pruppacher and Keltt (1978) and including an enhancement factor for the settling velocity of the cloud droplets, v_{dc} are given by:

$$\alpha_k = 2\pi m_{1c} \hat{D}_{pk}\left(1 + 0.5\, Pe_k^{1/3}\right),\ k = 0,2,3; \tag{10-15}$$

Where

$$m_{1c} = N_c d_{dg} \exp\left[\frac{1}{2}\ln^2\left(\sigma_{dg}\right)\right]. \tag{10-16}$$

N_c and d_d are the cloud droplet number concentration and geometric mean diameter respectively.

$$Pe_k = \frac{v_{dc} d_d}{\hat{D}_{pk}} \text{ is a Peclet number.} \tag{10-17}$$

The polydisperse diffusivity is given by

$$\hat{D}_{pk} = \left(\frac{k_b T}{3\pi\upsilon\rho_{air} D_g}\right) \times \left\{\exp\left(\frac{(-2k+1)}{2}\ln^2\sigma_g\right) + 1.246\mathrm{Kn}_g \exp\left(\frac{(-4k+4)}{2}\ln^2\sigma_g\right)\right\}$$

and is the same form as that for dry deposition algorithm (10-18)
(see Binkowski and Shankar, 1995, Equation A29).

The precipitation removal rate for number is given by

$$\beta = \frac{1}{\tau_{cld}}\left(\frac{\left[\delta SO_4\right]_{wetdep}}{\left[SO_4\right]_{init} + \left[SO_4\right]_{scav} + \left[\delta SO_4\right]_{prod}}\right) \tag{10-19}$$

where τ_{cld} is the cloud lifetime, $[\delta SO_4]_{wetdep}$ is the change in sulfate concentration due to precipitation loss, and $[SO_4]_{init}$ is the sulfate concentration at the beginning of the cloud lifetime, $[SO_4]_{scav}$ is the amount of sulfate added from in-cloud scavenging of Aitken mode sulfate; $[\delta SO_4]_{prod}$ is the amount of new sulfate produced by aqueous chemistry.

10.4 Aerosol Chemistry

The aerosol chemical species are listed in Table 10-1. The secondary species sulfate is produced by chemical reaction of hydroxyl radical on sulfur dioxide to produce sulfuric acid that may condense on existing particles or nucleate to form new particles. Emissions of fresh primary sulfate are treated in the gas-phase chemistry component, and this contributes to the total change in sulfate from the chemistry component. This is a change from RPM where primary sulfate emissions were treated as a source of new mass and new particle number. Other inorganic species such as (ammonia and nitric acid) are equilibrated with the aerosols.

An assumption of the model is that organics influence neither the water content nor the ionic strength of the system; however, this assumption may not be valid for many atmospheric aerosols. Although much progress has been made (e.g. Saxena et al., 1995; Saxena and Hildemann, 1996), sufficient basic data are not yet available to treat the system in a more complete and correct way. Over continental North America for $PM_{2.5}$, sea salt and soil particles are not considered in the equilibria. Thus, for the initial release of CMAQ, only the equilibrium of the sulfate, nitrate, ammonium and water system is considered. The equilibria and the associated constants are based upon Kim et al. (1993a) and shown in Table 10-3.

The aerosol water content is computed using the ZSR method (see Kim et al., 1993a) from:

$$W = \sum_n \frac{M_n}{m_{n0}(a_w)} \tag{10-20}$$

where W is the aerosol liquid water content [kg m^{-3}], M_n is the atmospheric concentration of the nth species [moles m^{-3}], and m_{n0} is the molality [moles kg^{-3}], of the nth species at a value of water activity (fractional relative humidity) of a_w. The values for the molality as a function of water activity are calculated from laboratory data from Giauque et al. (1960), Tang and Munkelwitz (1994), and Nair and Vohra (1975). The ZSR method is used in a somewhat different way than usual. The water content of sulfate aerosols depends strongly upon the ionic ratio of ammonium to sulfate. This ratio varies from zero for sulfuric acid to 2.0 for ammonium sulfate with intermediate values of 1.0 for ammonium bisulfate, and 1.5 for letovicite. The usual method would span this range with a single expression; however, Spann and Richardson (1985) have shown that this is not correct. They proposed a modification which resulted in a correction term. A very similar result is obtained by using the ZSR method between the ranges of the ionic ratio of sulfuric acid to ammonium bisulfate, ammonium bisulfate to letovicite, and letovicite to ammonium sulfate. The binary activity coefficients are computed using Pitzer's method and the Bromley method is used for the multicomponent activity coefficients in the aqueous solution (see Kim et al., 1993a) for details.

Two regimes of ammonium to sulfate ionic ratio are considered. The ammonia deficient regime (in which the ionic ratio of ammonium to total sulfate ion is less than two) leads to an acidic aerosol system with very low concentrations of dissolved nitrate ion which depend very strongly on ambient relative humidity. The second regime is one in which the ammonium to sulfate ratio exceeds two, the sulfate is completely neutralized, and there is excess ammonia. If there is nitric acid vapor in the system, it will dissolve in the aqueous particles along with the excess ammonia and produce abundant nitrate.

For cases when the relative humidity is so low that the aerosol liquid water content comprises less than 20 percent of the total aerosol mass, and the ionic ratio of ammonium to sulfate is greater than two, "dry ammonium nitrate" aerosol is calculated with the following equilibrium relationship:

$$NH_4NO_3(s) \Leftrightarrow NH_3(g) + HNO_3(g) \tag{10-21}$$

The value of the equilibrium constant is taken from Mozurkewich (1993) as noted in Table 10-2.

Precursors of anthropogenic organic aerosol (such as alkanes, alkenes, and aromatics) react with hydroxyl radicals, ozone, and nitrate radicals to produce condensable material. Monoterpenes react in a similar manner to produce biogenic organic aerosol species. The rates of production of sulfuric acid and the organic species are passed from the photochemical component to the aerosol component. The formation rates of aerosol mass (in terms of the reaction rates of the precursors) are taken from Pandis et al. (1992). These factors are given in Table 10-3.

10.5 Visibility

Visibility is usually defined to mean the furthest distance one can see and identify an object in the atmosphere. For a detailed presentation on the concepts of visibility, see Malm (1979). In a perfectly clean atmosphere composed only of nonabsorbent gases, the only process restricting visibility during daylight is the scattering of solar radiation from the molecules of the gases. This is known as Rayleigh scattering. Scattering is usually represented by a scattering coefficient. If absorption is also occurring in addition to scattering, an absorption coefficient may also be defined. The sum of the scattering and absorption coefficients is called the extinction coefficient. If absorption is not occurring, the extinction coefficient is defined to be equal to the scattering coefficient. The visibility in an atmosphere in which Rayleigh scattering is the only optical process active may be taken as a reference. A useful index for quantifying the impairment of visibility by the presence of atmospheric aerosol particles is the deciview (Pitchford and Malm, 1994). The deciview index, *deciV*, is given as

$$deciV = 10 \ln \left(\frac{\beta_{ext}}{0.01} \right) \tag{10-22}$$

where the value of 0.01 [km^{-1}] is taken as a standard value for Rayleigh extinction. The aerosol extinction coefficient, β_{ext} [km^{-1}], must be calculated from ambient aerosol characteristics such as index of refraction, volume concentration and size distribution.

The extinction coefficient at a wavelength of λ for aerosol may be expressed as

$$\beta_{ext} = \frac{3\pi}{2\lambda} \int_{-\infty}^{\infty} \frac{Q_{ext}}{\alpha} \frac{dV}{d\ln\alpha} d\ln\alpha \, , \tag{10-23}$$

where the particle distribution is given in a lognormal form as

$$\frac{dV}{d\ln\alpha} = V_T\left(\frac{A}{\pi}\right)^{1/2}\exp\left[-A\ln^2\left(\frac{\alpha}{\alpha_V}\right)\right], \qquad (10\text{-}24)$$

where $\alpha = \frac{\pi D}{\lambda}$, $\alpha_V = \frac{\pi D_{gv}}{\lambda}$, $A = \frac{1}{2\ln^2\sigma_g}$.

V_T is the total particle volume concentration, Q_{ext}, the Mie extinction efficiency factor, is a function of α and the index of refraction of the particles. Willeke and Brockmann (1977) showed that the behavior of the extinction coefficient is a smooth function of the geometric mean diameter for the volume distribution D_{gv}, and the index of refraction. This smooth characteristic implies that an accurate approximation to the Mie efficiency can be used in its place to reduce a very computationally intensive task. The method of Evans and Fournier (1990), a highly accurate approximation, is used to calculate Q_{ext}.

Because routine measurements of aerosol species mass concentrations are often available, but particle size distribution information is not, an additional method of calculating extinction has also been included. This is an empirical approach known as reconstructed extinction. The method is explained by Malm et al. (1994). The formula used here is a slight modification of their Equation 12 (Sisler, 1998).

β_{ext} [1/km] = 0.003* f(rh)*{ [ammonium sulfate] + [ammonium nitrate] } (10-25)
+ 0.004 *[organic mass}
+ 0.01*[Light Absorbing Carbon] + 0.001*[fine soil]
+ 0.0006*[coarse mass]

In implementing this method, ammonium sulfate and ammonium nitrate were taken as the sum of ammonium, plus sulfate, plus nitrate. Organic mass was taken as the sum of all organic species. Light absorbing carbon was taken as elemental carbon. Fine soil was taken as the unspeciated portion of $PM_{2.5}$ emitted species, and the coarse mass term was not implemented in CMAQ at this time. The reason for not implementing coarse mass was that the uncertainty in the emissions was deemed to be too large at the present time. The relative humidity correction, f(rh), is obtained from a table of corrections with entries at one- percent intervals. The methodology for the corrections is given in Malm et al. (1994).

10.6 Summary

The CMAQ aerosol component is a major extension of the RPM. Addition of the coarse mode and primary emissions now allow both $PM_{2.5}$ and PM_{10} to be treated. Ongoing work will improve the representation of the production of secondary organic aerosol (SOA) material by including a version of the method of Pankow (1994a,b) as discussed by Odum et al. (1996). This method, based upon laboratory experiments, calculates the yield of SOA as a function of the amount of organic material already in the particle phase.

Kleeman et al. (1997) have shown that various source types have size and species information that may be looked upon as a source signature. This assumes the availability of such source characteristics for the entire modeling domain. As noted in Section 10.1.3, there are ongoing discussions with those responsible for the national emissions inventory. As more information becomes available, identification of source signatures may be possible for a larger domain than the Los Angeles area, and an effort similar to Kleeman et al. (1997), albeit using a modal approach, might be undertaken. Other planned improvements for primary particles are the inclusion of marine aerosol as well as a better treatment of fugitive dust.

Future plans also include an intensive effort to evaluate the CMAQ aerosol component using atmospheric observations from selected field studies in which aerosol particles were observed. Comparison with routine visual range observations during the field study periods will provide an additional method of evaluation.

10.7 References

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Table 10-1 Aerosol Species Concentrations

Units: mass [μg m^{-3}], number [# m^{-3}]

{ a1}	ASO4 J	Accumulation mode sulfate mass
{ a2}	ASO4I	Aitken mode sulfate mass
{ a3}	ANH4J	Accumulation mode ammonium mass
{ a4}	ANH4I	Aitken mode ammonium mass
{ a5}	ANO3J	Accumulation mode nitrate mass
{ a6}	ANO3I	Aitken mode aerosol nitrate mass
{ a7}	AORGAJ	Accumulation mode anthropogenic secondary organic mass
{ a8}	AORGAI	Aitken mode anthropogenic secondary organic mass
{ a9}	AORGPAJ	Accumulation mode primary organic mass
{a10}	AORGPAI	Aitken mode mode primary organic mass
{a11}	AORGBJ	Accumulation mode secondary biogenic organic mass
{a12}	AORGBI	Aitken mode biogenic secondary biogenic organic mass
{a13}	AECJ	Accumulation mode elemental carbon mass
{a14}	AECI	Aitken mode elemental carbon mass
{a15}	A25J	Accumulation mode unspecified anthropogenic mass
{a16}	A25I	Aitken mode unspecified anthropogenic mass
{a17}	ACORS	Coarse mode unspecified anthropogenic mass
{a18}	ASEAS	Coarse mode marine mass
{a19}	ASOIL	Coarse mode soil-derived mass
{a20}	NUMATKN	Aitken mode number
{a21}	NUMACC	Accumulation mode number
{a22}	NUMCOR	Coarse mode number
{a23}	SRFATKN	Aitken mode surface area
{a24}	SRFACC	Accumulation mode surface area
{a25}	AH2OJ	Accumulation mode water mass
{a26}	AH2OI	Aitken mode water mass

Table 10-2. Equilibrium Relations and Constants
(Kim et al., 1993a)

Equilibrium Relation	**Constant**	**K(298.15)**	**a**	**b**	**Units**
$HSO_4^-(aq) \Leftrightarrow H^+(aq) + SO_4^{2-}(aq)$	$\frac{[H^+][SO_4^{2-}]\gamma_{H^+}\gamma_{SO_4^{2-}}}{[HSO_4^-]\gamma_{HSO_4^{2-}}}$	1.015E-02	8.85	25.14	mol / kg
$NH_3(g) \Leftrightarrow NH_3(aq)$	$\frac{[NH_3(aq)]\gamma_{NH_3}}{P_{NH_3}}$	57.639	13.79	-5.39	mol / kg atm
$NH_3(aq) + H_2O(aq) \Leftrightarrow NH_4^+(aq) + OH^-(aq)$	$\frac{[NH_4^+][OH^-]\gamma_{NH^+}\gamma_{OH^-}}{[NH_3(aq)]\gamma_{NH_3}a_w}$	1.805E-05	-1.50	26.92	mol / kg
$HNO_3(g) \Leftrightarrow H^+(aq) + NO_3^-(aq)$	$\frac{[H^+][NO_3^-]\gamma_{H^+}\gamma_{NO_3^-}}{P_{HNO_3}}$	2.511E06	29.17	16.83	mol^2 / kg^2 atm
$NH_4NO_3(s) \Leftrightarrow NH_3(g) + HNO_3(g)$	$P_{NH_3}P_{HNO_3}$	5.746E-17#	-74.38#	6.12#	atm^2
$H_2O(aq) \Leftrightarrow H^+(aq) + OH^-(aq)$	$\frac{[H^+][OH^-]\gamma_{H^+}\gamma_{OH^-}}{a_w}$	1.010E-14	-22.52	26.92	mol^2 / kg^2

The constants a and b are used in the following to adjust for ambient temperature

$$K = K(T_0)\exp\left[a\left(\frac{T_0}{T} - 1\right) + b\left(1 + \ln\left(\frac{T_0}{T}\right) - \frac{T_0}{T}\right), T_0 = 298.15\ [K]\right]$$

These values are only used by Kim et al. (1993a,b). The values used in the CMAQ are from Mozurkewich (1993):

$$K = \exp\left(118.87 - \frac{24084}{T} - 6.025\ \ln\ (T)\right)$$

where Mozurkevich reports in nanobars squared. This yields a value for the equilibrium constant of 43.11 [nb^2] at 298.15 K.

Table 10-3. Organic Aerosol Yields in Terms of Amount of Precursor Reacted (From Pandis et al. (1992) and Bowman et al. (1995))

Gas-Phase Organic Species	**Aerosol Yield [μg m^{-3} / ppm(reacted)]**
C8 and higher alkanes	380
Anthropogenic internal alkenes	247
monoterpenes	740
toluene	424
xylene	342
cresol	221