Implementation of State-of-Science PM Modules into the PMCAMx Photochemical Grid Model

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ABSTRACT

The Comprehensive Air-quality Model with extensions (CAMx) is a photochemical grid model developed in the late 1990s to treat urban and regional scale ozone issues. Since the first CAMx applications performed as part of the Ozone Transport Assessment Group (OTAG), the model has undergone continuous development and refinement. Because CAMx consists of all new computer coding in a modular framework, it is ideally suited for extension to other air quality issues beyond ozone. This paper discusses the extension of the CAMx to treat particulate matter (PM) and visibility issues through the inclusion of state-of-science aerosol modules. A sectional approach has been adopted in PMCAMx to treat size resolved PM. Aerosol thermodynamics are treated using either a full dynamic module or the ISORROPIA equilibrium module. A multi-sectional aqueous-phase chemistry algorithm has also been implemented. Secondary organic aerosol is being treated using a reversible semi-volatile scheme. New dry and wet deposition schemes have been developed. A PM Source Apportionment Technology (PSAT) is also being developed and implemented into PMCAMx that allows source attribution of primary and secondary PM to user selected geographic source regions and source categories. This paper presents the technical formulation of the PMCAMx treatment of aerosols and the application and evaluation of the model to Southern California.

INTRODUCTION

The Comprehensive Air-quality Model with Extensions (CAMx) is a three-dimensional multi-scale photochemical grid model[1] that is publicly available without fees or restrictions on model application. CAMx was developed with all new code during the late 1990s using modern and modular coding practices. This has made the model an ideal platform for extension to treat a variety of air quality issues including ozone, particulate matter (PM), visibility, acid deposition and air toxics. The flexible CAMx framework has also made it a convenient and robust host model for the implementation of "probing tool" techniques such as Process Analysis, the Decoupled Direct Method (DDM) and the Ozone Source Apportionment Technology (OSAT). The Coordinating Research Council (CRC) have sponsored ENVIRON, together with Sonoma Technology, Inc. (STI) and Carnegie Mellon University (CMU), to add state-of-the-science algorithms for aerosol modeling to CAMx to create a new particulate matter model called PMCAMx (version 3.01).

The development of PMCAMx was based on version 3.01 of CAMx as distributed from http://www.camx.com. The extension to treat PM involved the addition of science modules to represent important physical processes for aerosols:

- Size distribution is represented using the Multi-component Aerosol Dynamics Model (MADM), which uses a sectional approach to represent the aerosol particle size distribution[2]. MADM treats the effects of condensation/evaporation, coagulation and nucleation upon the particle size distribution.

- Inorganic aerosol thermodynamics are represented using ISORROPIA[3,4] within MADM.

- Secondary organic aerosol thermodynamics are represented using the semi-volatile scheme of Strader and co-workers[5].

- Aqueous-phase chemical reactions are modeled using the Variable Size-Resolution Model (VRSM) of Fahey and Pandis[6], which automatically determine whether water droplets can be represented by a single 'bulk' droplet-size mode or whether it is necessary to use fine and coarse droplet-size modes to account for the different pH effects on sulfate formation.

- The CAMx deposition algorithms were improved for particle deposition. Dry deposition is represented for the size-resolved particle distribution[1]. A new wet deposition algorithm has been developed but was not implemented in PMCAMx version 3.01 discussed in this paper.

The new PMCAMx model was evaluated for a Los Angeles PM episode. The episode selected was October 17-19, 1995 from the PM_{10} Technical Enhancement Program (PTEP) because this period had previously been modeled using the UAM-AERO and therefore important components of the modeling database were already available and tested.

PMCAMx TECHNICAL FORMULATION

PMCAMx represents particulate matter using a sectional approach that tracks the mass of aerosol constituents in a number of fixed size sections. PMCAMx was developed from version 3.01 of the CAMx air quality model[1] by adding or modifying science modules to represent the following processes:

- Aerosol Size Distributions And Chemical Species
- Gas-Phase Chemistry
- Secondary Organic Aerosol Formation
- Inorganic Aerosol Chemistry
- Particle Size Distribution
- Aqueous-Phase Chemistry
- Deposition

This section describes the technical formulation for each of these processes.

Aerosol Size Distribution And Chemical Species

The dynamic behavior of a spatially homogeneous aerosol is described by the so-called aerosol General Dynamic Equation (GDE)[7]:

$$\frac{dn(m,t)}{dt} = -\frac{\partial}{\partial m}\left[I(m,t)\cdot n(m,t)\right] + \frac{1}{2}\int_0^m K(m,m-m')\cdot n(m',t)\cdot n(m-m',t)dm'$$
$$-n(m,t)\int_0^\infty K(m,m')\cdot n(m',t)dm' + E(m,t) + N(m,t) - D(m,t)$$

Where m is the particle mass, $n(m,t)$ is the size distribution function at time t, such that $n(m,t)dm$ is the number concentration of particles having masses in the range $[m,m+dm]$, $K(m,m')$ is the coagulation coefficient for particles with mass m and m', $I(m,t)$ is the rate of change of particle mass resulting from condensation and evaporation, $E(m,t)$ is the emission rate of particles, $N(m,t)$ is the rate of production by homogeneous nucleation[8], and $D(m,t)$ is the rate of removal due to dry deposition. Although the composition of particles of the same mass m can vary from particle to particle due to external mixing. Due to our lack of understanding of these variations and for mathematical simplicity, PMCAMx assumes that all particles of the same size have the same chemical composition (internal mixture assumption).

PMCAMx tracks thirteen chemical components of aerosols as shown in Table 1. These components account for all of the major primary and secondary aerosol constituents. Each component is represented in every size section. The number of size sections and their size ranges can be defined by the user for each PMCAMx simulation. The size distribution developed for the Los Angeles test case are shown in Table 2. This size distribution contains 10 sections defined according to a lognormal distribution and with cut-points at both 2.5 µm and 10 µm. The mass of $PM_{2.5}$ can be calculated by summing over section 1-6 and the mass of PM_{10} can be calculated by summing over sections 1-8. Thirteen components in ten size sections lead to a total of 130 aerosol species in PMCAMx.

Table 1. Aerosol constituents in PMCAMx.

PMCAMx Name	Description	Primary	Secondary	Molecular Weight*
SOA1	Secondary organic aerosol 1		X	n/a
SOA2	Secondary organic aerosol 2		X	n/a
SOA3	Secondary organic aerosol 3		X	n/a
SOA4	Secondary organic aerosol 4		X	n/a
POC	Primary organic carbon (matter)	X		n/a
PEC	Primary elemental carbon	X		n/a
CRST	Crustal material (dust)	X		n/a
PH2O	Water in aerosol phase		X	18
PCL	Chloride ion	X		36.5
NA	Sodium ion	X		23
PNH4	Ammonium ion		X	18
PNO3	Nitrate ion		X	62
PSO4	Sulfate ion	X	X	96

* Molecular weight is not applicable (N/A) for several species. Nominal values are used on the PMCAMx chemistry parameters file[9].

Table 2. Aerosol size sections for PMCAMx version 3.01 application to the Los Angeles region.

Section	Lower Cut-point (µm)	Upper Cut-point (µm)
1	0.039063	0.078125
2	0.078125	0.15625
3	0.15625	0.3125
4	0.3125	0.625
5	0.625	1.25
6	1.25	2.5
7	2.5	5
8	5	10
9	10	20
10	20	40

PMCAMx Species Names

The aerosol species simulated by PMCAMx are named according to chemical constituent (see Table 1) and size section (see Table 2). The naming convention is "constituent_section" and some examples are given as follows:

- PSO4_7 is sulfate in size section 7; and
- PNH4_4 is ammonium in size section 4.

Gas-Phase Chemistry

The PMCAMx gas-phase chemistry was modified to simulate the formation of secondary aerosol precursors. The changes were as follows:

- Track production of four condensable gasses (CG1 – CG4) formed in the oxidation of VOCs that are secondary organic aerosol (SOA) precursors. The selection and properties of these four SOA precursors is described in more detail elsewhere[9].
- Add a new olefin species, called OLE2, to the CB4 mechanism to represent biogenic olefins so that high SOA-yield biogenic olefins (monoterpenes) can be distinguished from low SOA-yield anthropogenic olefins.
- Track ammonia as a precursor to ammonium aerosols.
- Track SO_2 and gaseous sulfuric acid as precursors to sulfate aerosols.
- Track HCl as a precursor to and vaporization product of sea salt (sodium chloride) aerosols.

These changes were implemented in the most current version of the CB4 mechanism in CAMx, called mechanism 3, which already includes updated isoprene chemistry and radical-radical termination reactions. Similar modifications are made for the SAPRC99 mechanism introduced in CAMx version 3.1. The enhanced CB4 mechanism is called mechanism 8 in PMCAMx and is implemented for the CMC fast chemistry solver.

Secondary Organic Aerosol Formation

The partitioning of the condensable organic gases between the gas and aerosol phases is simulated using the methods developed by Strader and co-workers[5]. The secondary organic aerosol (SOA) module was designed to accommodate varying levels of chemical detail in the condensable organic components. In PMCAMx, the SOA module is implemented with four classes of semi-volatile organics that have different volatility properties (defined by saturation concentration and heat of vaporization as shown in Table 3). The four condensable gasses are called CG1 – CG4 and the corresponding secondary organic aerosols are called SOA1 – SOA4, as shown in Tables 1 and 3. The SOA module calculates the equilibrium distribution between the gas and aerosol phase for each CG/SOA pair (i.e., the amount in the gas and aerosol phases). Secondary organic material may condense to the aerosol phase or evaporate to the gas phase depending upon the CG/SOA equilibrium distribution. Evaporation and condensation change the aerosol size distribution, which is accounted for using the same algorithms as for the inorganic aerosol, described below.

The volatility properties of the condensable gases (CG1 – CG4) are shown in Table 3 along with the aerosol yields (μg m^{-3} of aerosol precursor per ppm of gas reacted) from different VOC precursors. The CG species are the only gas species in CAMx that are not in ppm units; they are in μg m^{-3} units because the aerosol yields are conventionally defined this way. The yields of the condensable gases (CG1 – CG4) are included in the listing of the gas-phase chemical mechanism[9].

Table 3. Properties of condensable gas precursors (CG1 – CG4) to secondary organic aerosols.

CB4 VOC Precursor	Condensable Gas Species	Aerosol Yield (μg m^{-3} ppm^{-1})	Saturation Concentration (μg m^{-3} at 281.5 K)	Heat of vaporization ΔH_{vap}	Molecular Weight
PAR	CG3	53.6	0.007	0	150
OLE	CG3	14.6	0.007	0	150
TOL	CG1	430	0.023	156,250	150
TOL	CG2	836	0.674	156,250	150
XYL	CG1	268	0.023	156,250	150
XYL	CG3	1178	0.007	0	150
CRES	CG1	221	0.023	156,250	150
OLE2	CG4	999	0.008	0	180

Inorganic Aerosol Chemistry

The chemical composition of the inorganic aerosol phase is calculated using the ISORROPIA model[3,4]. ISORROPIA was selected over alternative algorithms (e.g., SCAPE, SEQUILIB, MARS) because it provides good performance for accuracy, speed and stability[10]. Solid, liquid and gas phase chemistry is modeled for the sulfate, nitrate, ammonium, chloride aerosol system using the internally mixed assumption. The chemical species that are possible in each phase are listed in Table 4.

Table 4. Species considered by ISSOROPIA for gas, liquid and solid phases.

Phase	Possible Species
Gas	NH_3, HNO_3, HCl, H_2O
Liquid	H^+, NH_4^+, Na^+, NO_3^-, Cl^-, SO_4^{2-}, HSO_4^-, H_2O
Solid	NH_4HSO_4, NH_4NO_3, $(NH_4)_2SO_4$, NaCl, NH_4Cl, $NaNO_3$, $NaHSO_4$, Na_2SO_4, $(NH_4)_3H(SO_4)_2$

ISSOROPIA can solve the composition of the aerosol system in either partitioning mode or equilibrium concentration mode. The latter feature is essential for compatibility with the hybrid and dynamic mass-transfer options for size-distribution, described below. In the partitioning mode, ISSOROPIA calculates the aerosol and gas-phase concentrations of semi-volatile components from known gas/aerosol total concentrations. In the equilibrium concentration mode, the ISSOROPIA calculates the equilibrium vapor pressure of the semi-volatile components from the known aerosol composition.

Particle Size Distribution

The size distribution of aerosols is solved using the algorithms described by Pilinis and co-workers[2] for the Multicomponent Aerosol Dynamics Model (MADM). The aerosol size distribution can be modified by the following physical processes that are represented in PMCAMx:

- Condensation/evaporation of inorganic and organic aerosol constituents
- Coagulation
- Nucleation of sulfuric acid
- Aqueous-phase chemistry
- Deposition

Coagulation is modeled assuming Brownian diffusion and the formulas of Fuchs. To improve the accuracy of the coagulation calculation, the PMCAMx size distribution is over-resolved to finer distribution, coagulation is modeled, and the modified size distribution is placed back onto the PMCAMx size sections. In PMCAMx version 3.01, the coagulation size distribution is three times finer than the PMCAMx size distribution. The degree of over-resolution is determined by a model parameter that may need to be changed if PMCAMx is used with different size sections in the future.

Nucleation is modeled based on the parameterization of Russell and co-workers[11] and the work of Jaecker-Voirol and Mirabel[12]. The nucleation rate depends upon the gaseous sulfuric acid concentration, which in PMCAMx is from the gas-phase OH + SO_2 reaction. This approach is appropriate for estimating the effect of nucleation on the particle mass distribution but not the number distribution. The inclusion of a nucleation process should ensure some particle population in the finest size sections to provide a surface area onto which condensation can occur.

MADM simulates the complete atmospheric aerosol size/composition distribution by solving the condensation-evaporation equation. MADM includes three methods for solving the particle size distribution called the equilibrium, hybrid and dynamic methods. The equilibrium algorithm is

the fastest and most stable approach but may introduce errors under certain conditions[13]. Meng and Seinfeld[14] suggested that while the sub-micron aerosol may reach equilibrium in a few minutes, it may take hours or days for the coarse particles to attain this state. Laboratory measurements of Dassios and Pandis[15] showed that the mass transport of ammonium nitrate is significantly faster than the above theoretical studies had assumed, and that the time scale for equilibration of the accumulation mode probably is less than 20 minutes.

PMCAMx version 3.01 always uses the equilibrium assumption within MADM to solve the particle size distribution. The hybrid and dynamic options are retained within the MADM code and have been activated in future versions of PMCAMx based on more experience with the model and on the results of ongoing improvements in algorithm efficiency in MADM.

Aqueous-Phase Chemistry

Aqueous-phase chemistry is important for modeling the production of sulfate from the oxidation of sulfur dioxide in cloud and/or fog water droplets. The rate of sulfate production is a non-linear function of aqueous concentrations, cloud water pH and the size of the water droplets. For simplicity and/or efficiency, many aqueous-phase chemistry algorithms assume that all the cloud droplets are the same size, which may be called a "bulk approximation" because it leads to the simplifying assumption that the concentrations in all cloud droplets can be represented by bulk average values. The bulk approximation is faster but tends to under-predict sulfate production if the coarse aerosol mode is alkaline and the accumulation mode is acidic[16]. In these cases, improved accuracy can be obtained by using a more computationally demanding size-resolved algorithm that explicitly represents cloud droplets of several different sizes[6,16]. The aqueous-phase chemistry in PMCAMx uses either bulk or size-resolved droplet models depending upon ambient conditions.

Variable Size-Resolution Model

In PMCAMx, aqueous-phase chemistry is simulated using the method described using the Variable Size-Resolution Model (VSRM)[6]. The VSRM allows both bulk and size-resolved (two sections) aqueous-phase chemistry. Selection of either the bulk algorithm or the two-section algorithm is made automatically using heuristic rules[6] every time the aqueous-phase chemistry module is called (i.e., for each grid cell at each timestep). Both algorithms simulate the dissolution of gaseous and aerosol material into cloud water droplets, partitioning of species between the aqueous and gas phases, and chemical reactions within the aqueous phase. The aqueous-phase chemistry module also modifies the size distribution of the inorganic aerosol constituents.

Selection of the Bulk or Size-Resolved Droplet Models

Differences between bulk and size-resolved model predictions can be linked to the pH differences across the droplet size spectrum and the pH-dependent reactions forming S(VI) (i.e. aqueous-phase sulfate). There are many circumstances under which the difference in sulfate production between bulk and size-resolved droplet models is small[6]. The VSRM uses the more efficient bulk method when the error is expected to be small and the more expensive two-section size-resolved method when necessary. In general, longer cloud processing time and low concentrations of alkaline dust lead to smaller differences between the bulk and size-resolved models. A set of heuristic rules can determine whether the bulk or size-resolved calculations are used. The "decisions" are based on six input conditions: liquid water content, aerosol alkaline

dust content and the initial gas-phase concentrations of SO_2, H_2O_2, NH_3, and HNO_3. These variables were chosen because aqueous-phase sulfate production is particularly sensitive to changes in these parameters.

Deposition

Removal of particles and gases by dry deposition processes are modeled as a lower boundary condition in the solution of the vertical diffusion process in PMCAMx. This means that the removal of pollutants from each column of grid cells is governed both by the deposition velocity at the surface layer and the diffusive coupling of layers moving up the column from the surface.

Dry deposition of gases is modeled based on an improved version of the Wesely[17] resistance model which is described in Section 2 of the CAMx User's Guide[1]. Deposition velocities are derived from models that account for the reactivity, solubility, and diffusivity of gases, local meteorological conditions and surface characteristics.

Wet deposition is an important removal process for particles. Particles act as cloud condensation nuclei; the cloud droplets grow and collect into sufficiently large sizes to fall as precipitation. A fraction of particles that are subsequently entrained into the cloud, and that exist within sub-cloud layers, are scavenged by liquid precipitation via impaction. The rates of nucleation and impaction depend upon cloud type (e.g., prolonged stratiform vs. vigorous convective development), rainfall rate and particle size distribution.

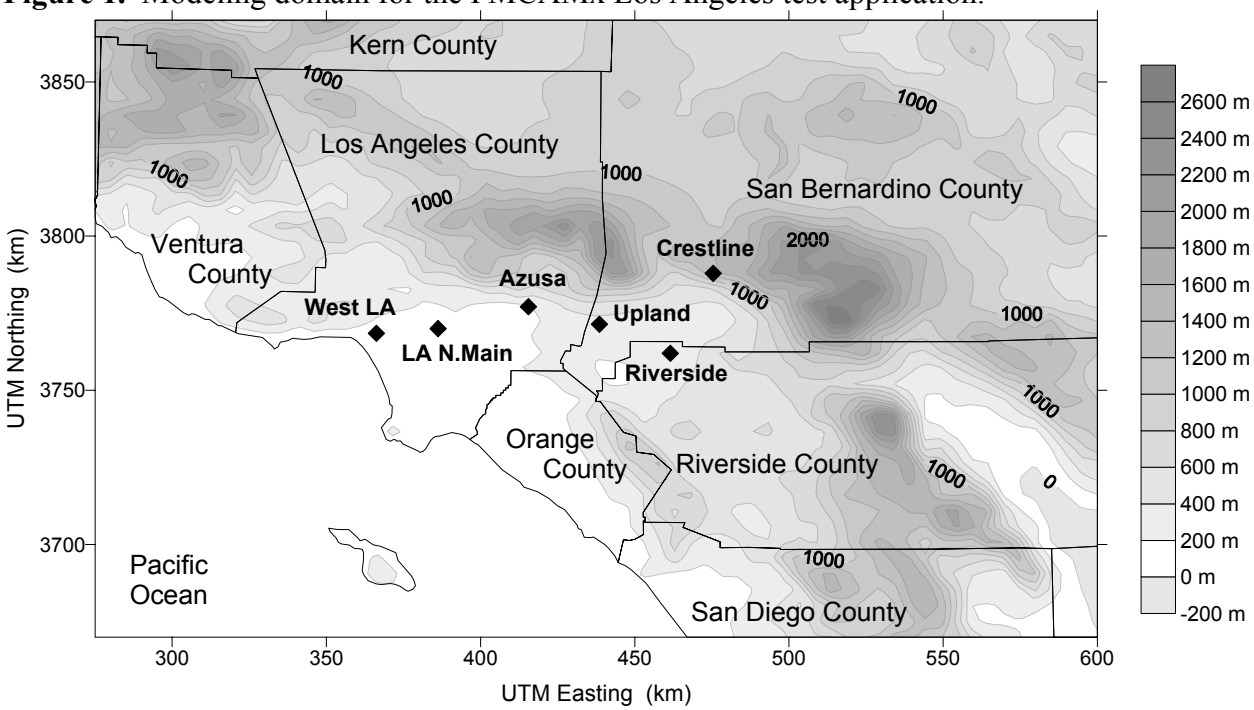
Wet deposition is currently treated in PMCAMx using a simple scavenging coefficient approach. An improved wet deposition algorithm has been developed for gases and particles that is suitable for aerosol modeling. This algorithm is currently under going testing and evaluation in PMCAMx. However, it was not available at the time the test runs were made for this paper.

PMCAMx TEST APPLICATION FOR LOS ANGELES

PMCAMx was tested for an October 17-19, 1995 episode in the Los Angeles area. This episode has the advantage of having been modeled previously with the UAM-AERO and UAM-AERO/LT. The model inputs for PMCAMx were developed using methods similar to the UAM-AERO application, that is diagnostic wind modeling rather than prognostic meteorological modeling. The objective was to develop a reasonable test case for an episode that had been previously modeled, however we do not generally recommend using diagnostic wind models to drive PMCAMx. PMCAMx performance was evaluated against the ambient data collected in the PM_{10} Technical Enhancement Program (PTEP) and compared to the previous model performance with the UAM-AERO models. Emissions sensitivity studies were conducted to characterize responses to reductions in ammonium, NOx and VOC emissions.

Figure 1 displays the Los Angeles area modeling domain that consists of a 65 by 40 array of 5-km grid cells defined in UTM coordinates. The PMCAMx vertical layer structure was chosen to have the same model top as UAM-AERO but with finer vertical resolution. PMCAMx was configured with 10 layers with layer tops at 20, 50, 100, 250, 500, 750, 1000, 1500, 2000 and 2300 meters (as compared to 5 layers for UAM-AERO).

Figure 1. Modeling domain for the PMCAMx Los Angeles test application.



Enhanced monitoring was collected at the six PTEP sites in the LA area, namely, Downtown Los Angeles, Anaheim, Diamond Bar, Rubidoux, Fontana and San Nicolas Island. Daily sampling was conducted during the October 17-19, 1995 episode period. The October 17-19, 1995 period was a typical fall PM episode in the Los Angeles area with stagnant winds, extensive fog near the coast and inland, cool nighttime temperatures and high moisture availability. Ozone levels were lower than during summer stagnation periods and the federal ozone standard was exceeded only on October 19th. PM_{10} concentrations were very high with a maximum level of 218 $\mu g/m^3$at the Rubidoux monitoring site in Riverside.

PMCAMx Performance Evaluation

The first element in the evaluation of PMCAMx involved examining the spatial tile maps of hourly concentrations using the PAVE software. The spatial maps shows results that were comparable to those from other model simulations for the important chemical species. There are some primary species for which unusually high concentrations are estimated in the Long Beach area. Long Beach is a coastal area with high emission rates due to the nearby port operations and some of the model estimates are probably unrealistically high for this area. The second element of the review involved examining the minimum and maximum concentrations on the grid on an hourly basis. The minimum and maximum estimated concentrations were plausible.

In the third step, we compared the estimated concentrations of NO, NO_2 and ozone with the observed values at the PTEP stations (Anaheim, downtown Los Angeles, Diamond Bar, Fontana, and Riverside-Rubidoux). The NO and NO_2 estimates do not agree particularly well with the observations at the three sites that have data, but this is not uncommon for urban-scale model applications for Los Angeles. The ozone performance is more consistent across stations. The estimated ozone concentrations are 40% to 70% lower than the observed values at the five

stations. The underestimation of ozone concentrations suggests a bias in the general level of photochemical reactivity in the simulation. The simulated photo-oxidation rates of NO_x, SO_2, and VOCs are probably underestimated, which is likely to reduce the estimated concentrations of secondary aerosols (nitrate, sulfate, and SOA).

The fourth step involved comparing the estimated and measured daily chemical components of PM at the PTEP stations. Some of these results are displayed in Figures 2 through 6. The specific components considered are nitrate, sulfate, ammonium, elemental carbon, organic material, and crustal material in $PM_{2.5}$, $PM_{2.5\text{-}10}$ and PM_{10} modes. The results show a mixture of positive and negative bias for nitrate, sulfate, ammonium and organic material (OM). They also show consistent underestimation of elemental carbon (EC) concentrations and a tendency to underestimate crustal material. Note, the crustal observations are suspect because they are calculated by subtracting the other measured chemical components from the measured mass, which is uncertain because of mass measurement artifacts and volatilization losses. The performance evaluation and statistics are not sufficient to meaningfully evaluate the model performance. There are too few days simulated, too few stations with data and too little high time-resolution PM data to evaluate the model comprehensively.

The fifth step in the process was to compare the PMCAMx model estimates with those from other models for this same episode. The UAM-AERO and UAMAERO-LT models had been run for the same episode with the same emissions but slightly different meteorological inputs. Figure 7 through 11 show comparisons of daily $PM_{2.5}$ component estimates from the three different models at the five PTEP stations. The model results are quite different at times. Notable differences are evident in all of the species, but especially sulfate and organic material. PMCAMx uses more advanced modules to simulate both sulfate formation in fogs and clouds and secondary organic aerosol formation, so it is not surprising that some of the larger differences in concentrations and concentration profiles are evident for these species. Differences in the meteorological inputs as well as model formulations are expected to account for significant differences in the results.

In reviewing the PMCAMx simulation results, we looked for evidence that might suggest the model was seriously flawed or broken. Anomalously high or low concentrations, chemically unrealistic relationships between species, or unphysical spatial or diurnal patterns might suggest a serious flaw. Despite the high primary concentrations in Long Beach noted above, our overall review of the model outputs did not detect any serious flaws. More details on the PMCAMx model evaluation are available in the project's final report[9].

Figure 2. Comparison of 24-hr PM_{10} nitrate at PTEP monitoring sites on October 17th, 18th and 19th, 1995.

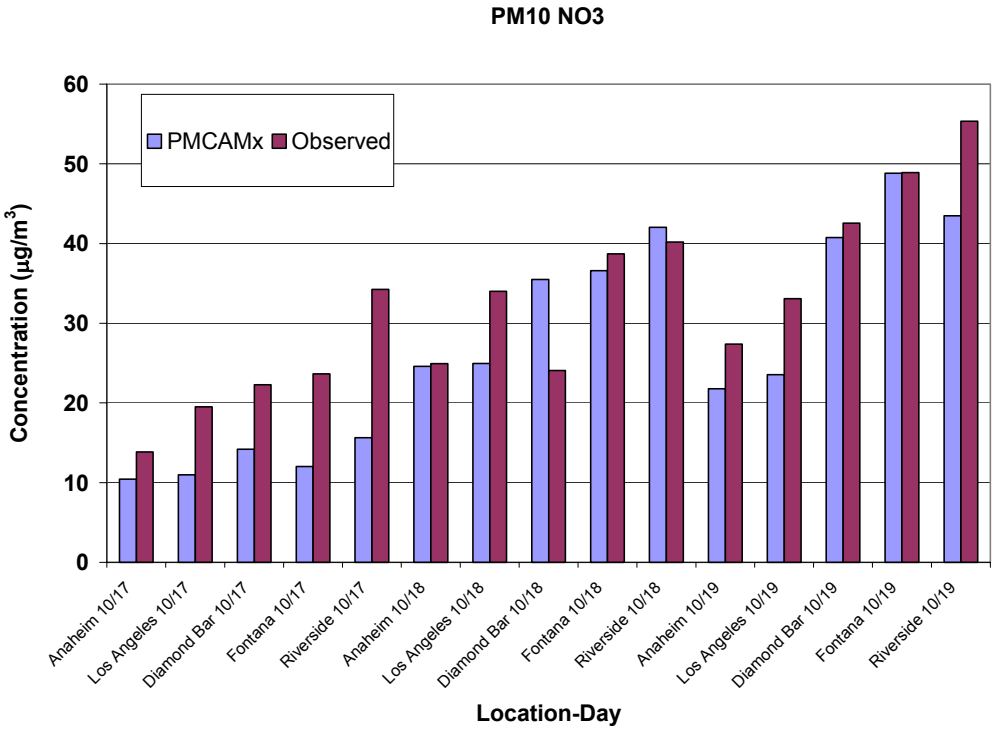


Figure 3. Comparison of 24-hr $PM_{2.5}$ sulfate at PTEP monitoring sites on October 17th, 18th and 19th, 1995.

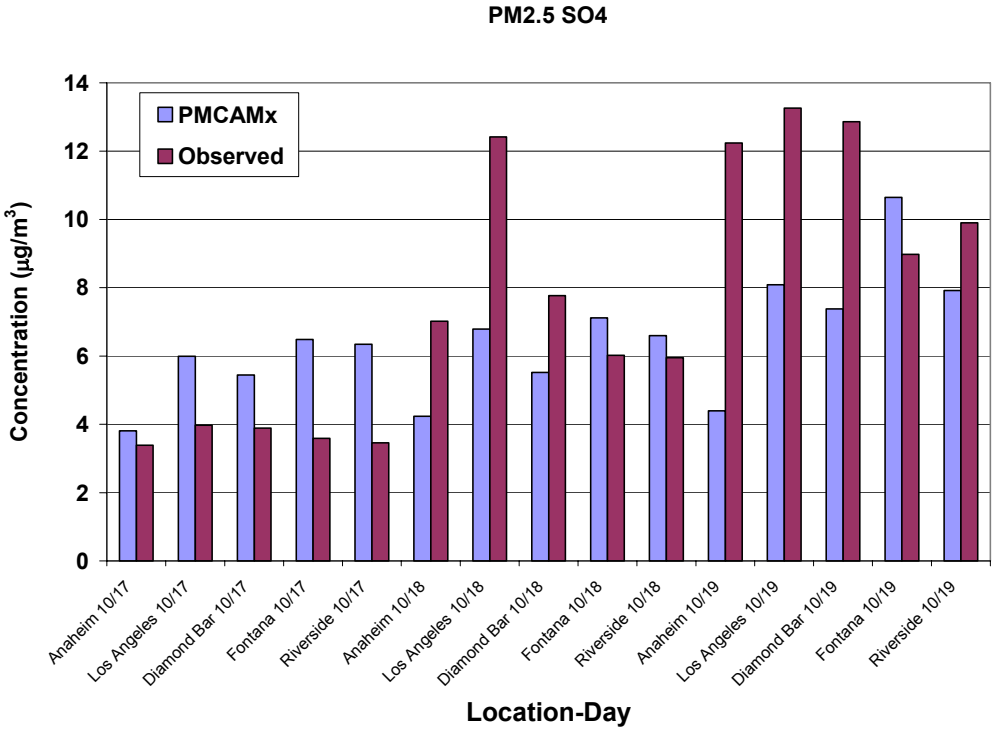


Figure 4. Comparison of 24-hr $PM_{2.5}$ organic matter (primary + secondary) at PTEP monitoring sites on October 17th, 18th and 19th, 1995.

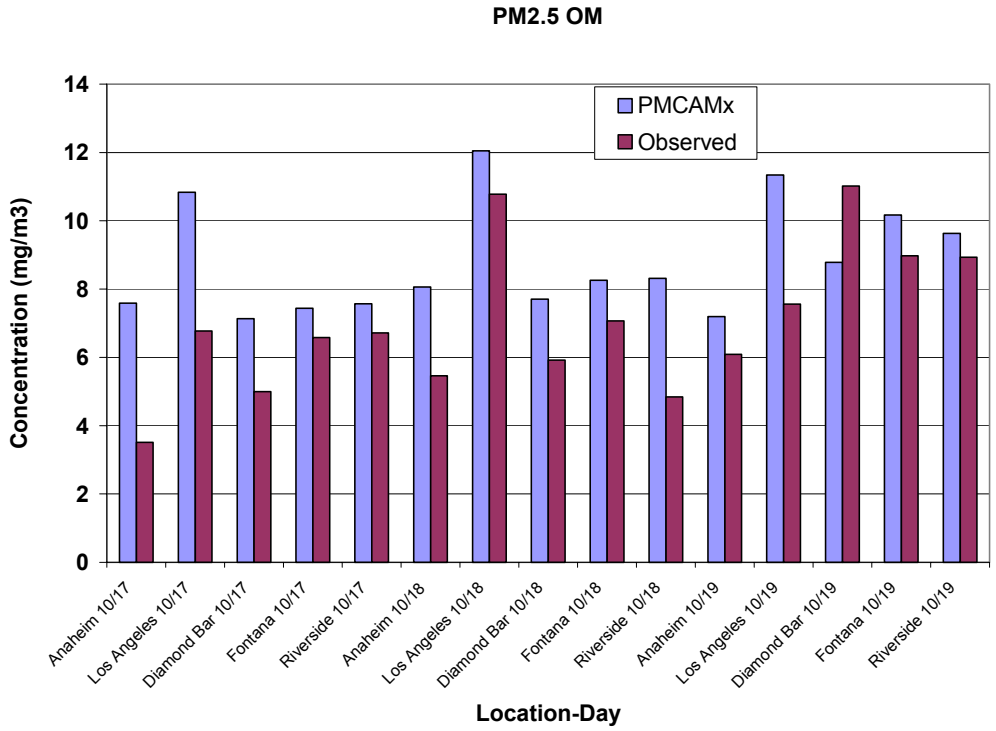


Figure 5. Comparison of 24-hr $PM_{2.5}$ elemental carbon at PTEP monitoring sites on October 17th, 18th and 19th, 1995.

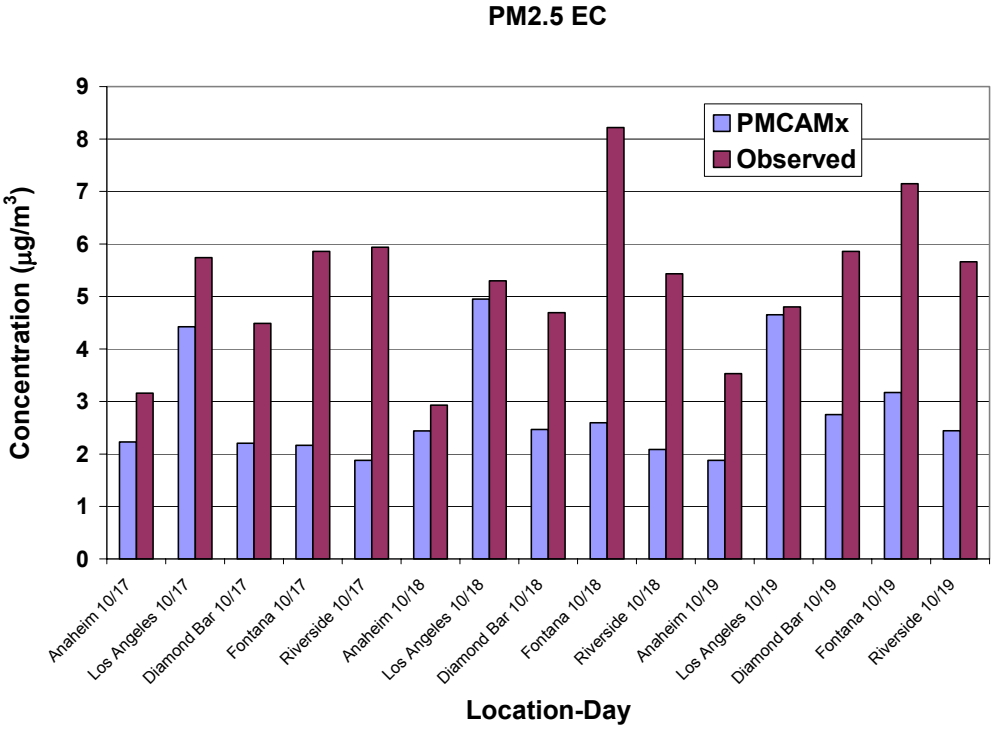


Figure 6. Comparison of 24-hr PM_{10} crustal material at PTEP monitoring sites on October 17th, 18th and 19th, 1995.

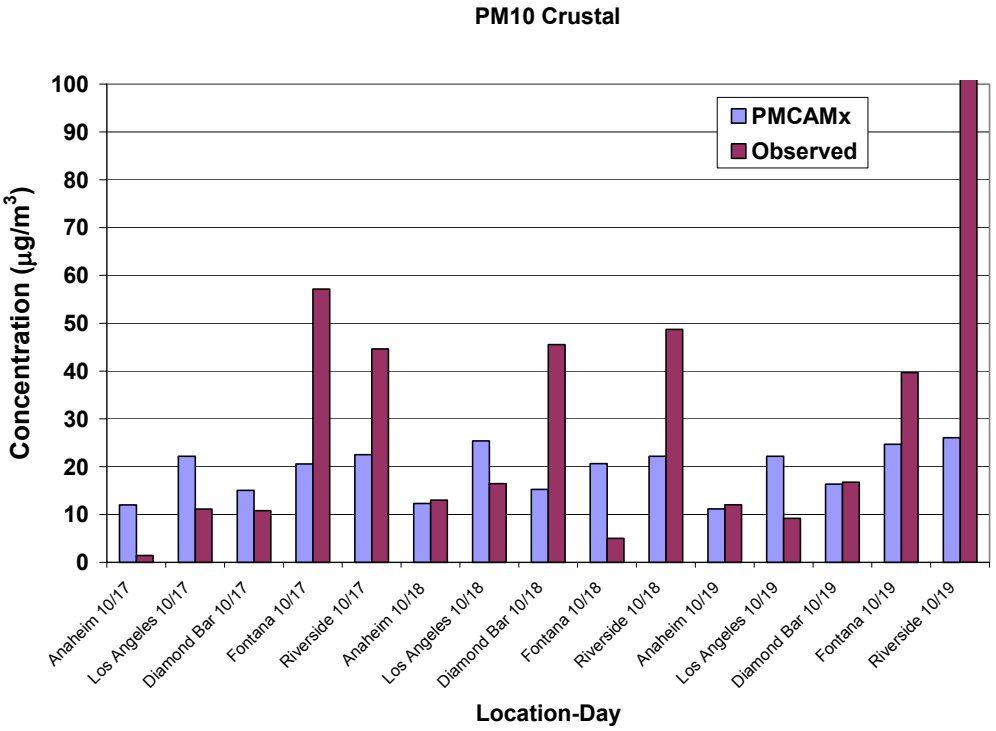


Figure 7. Comparison of 24-hr $PM_{2.5}$ at Anaheim between PMCAMx, UAM-AERO and UAM-AERO/LT (October 17-19, 1995).

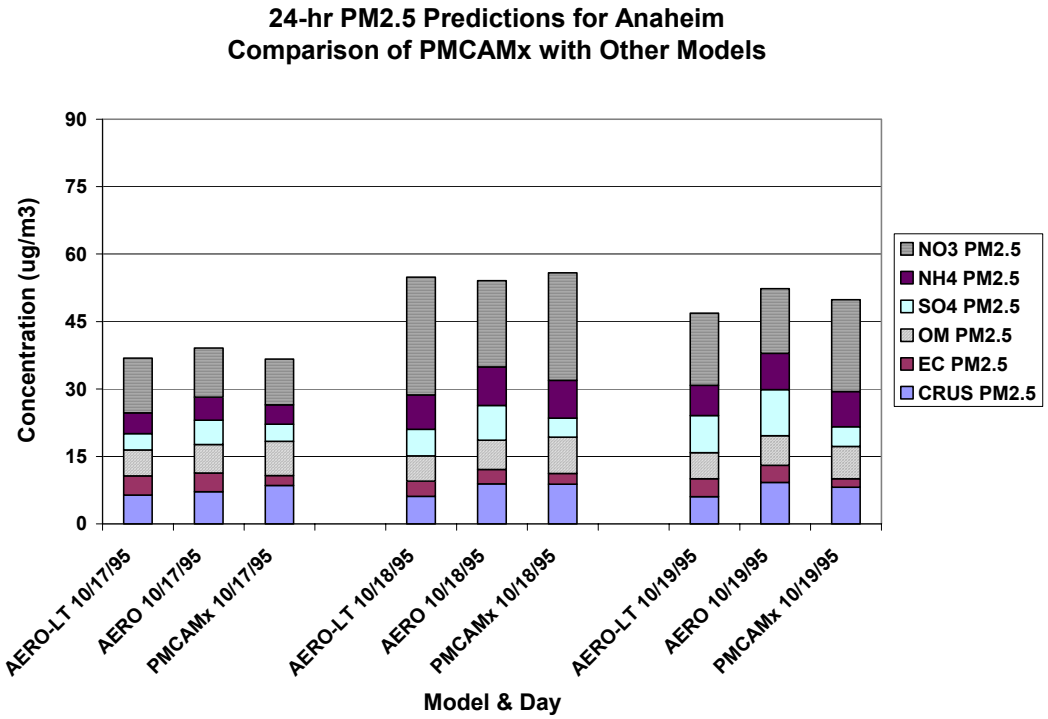


Figure 8. Comparison of 24-hr $PM_{2.5}$ at Diamond Bar between PMCAMx, UAM-AERO and UAM-AERO/LT (October 17-19, 1995).

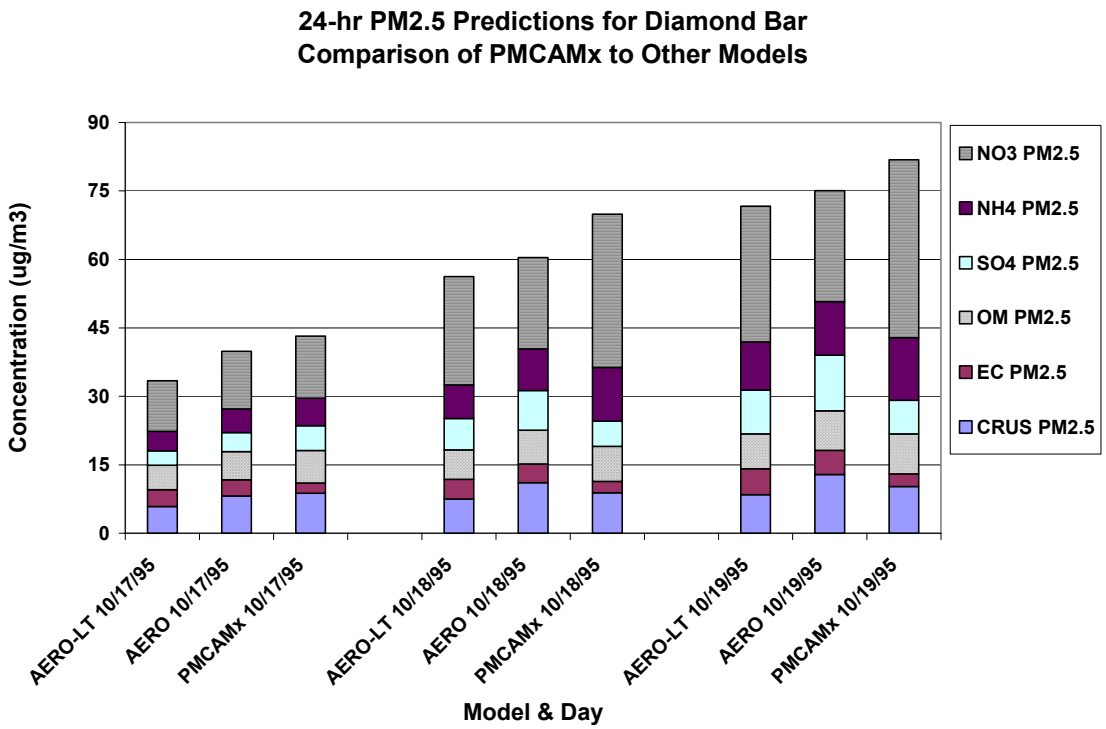


Figure 9. Comparison of 24-hr $PM_{2.5}$ at Riverside between PMCAMx, UAM-AERO and UAM-AERO/LT (October 17-19, 1995).

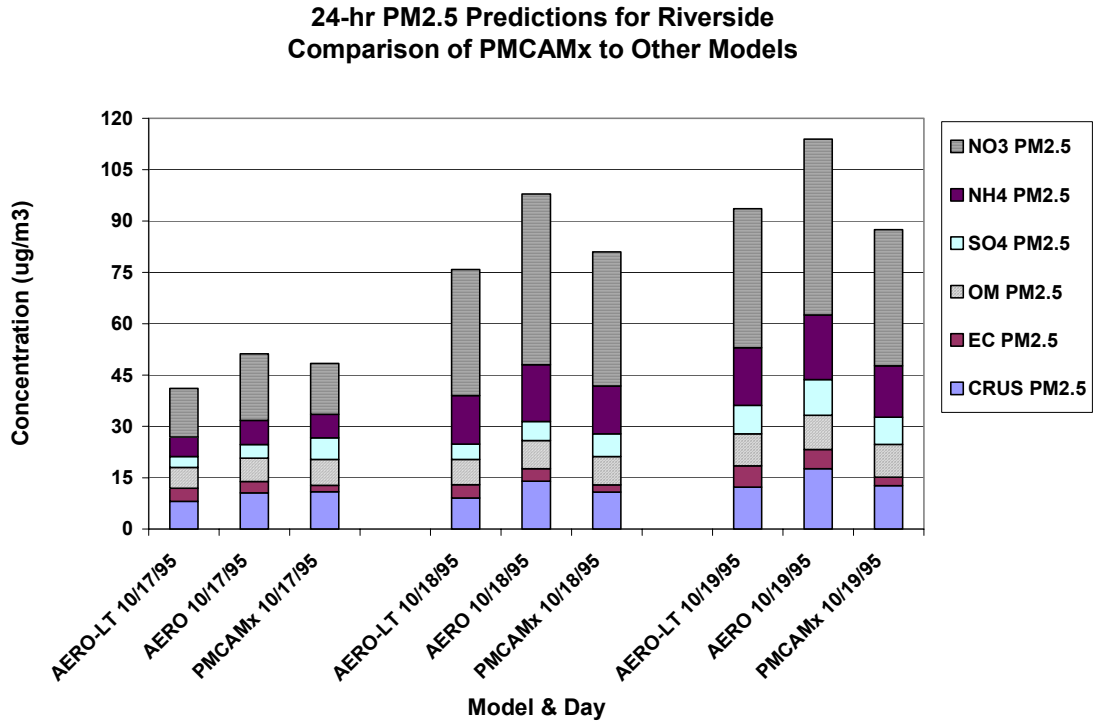


Figure 10. Comparison of 24-hr $PM_{2.5}$ at Fontana between PMCAMx, UAM-AERO and UAM-AERO/LT (October 17-19, 1995).

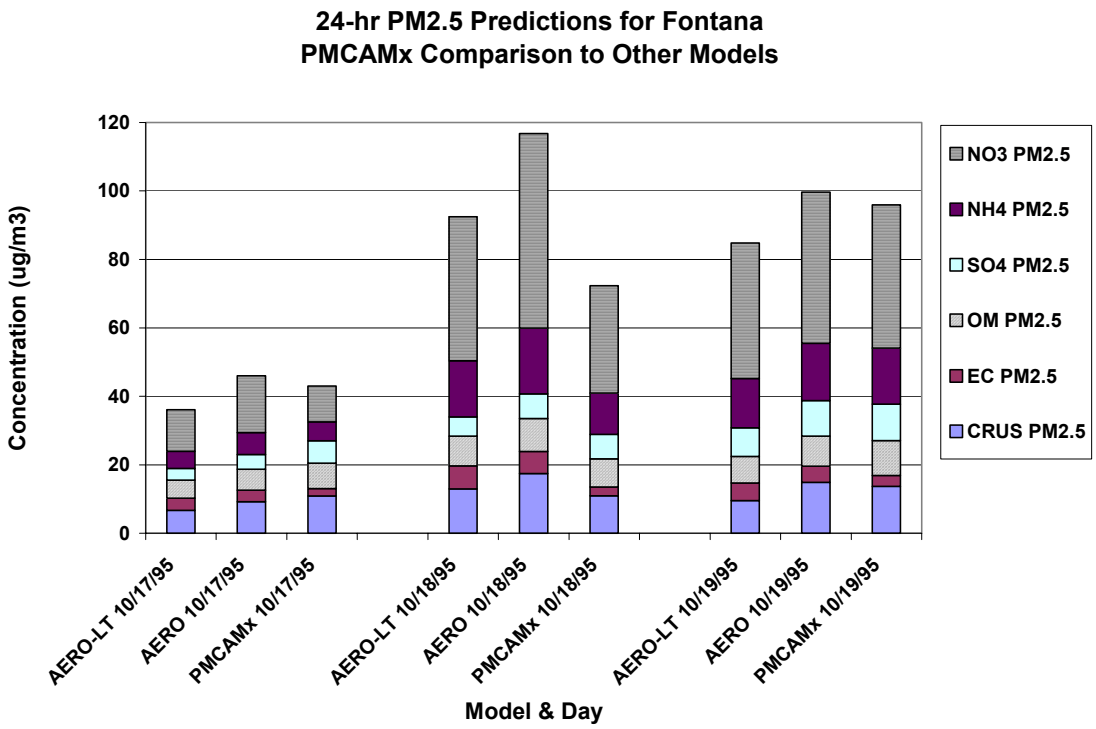
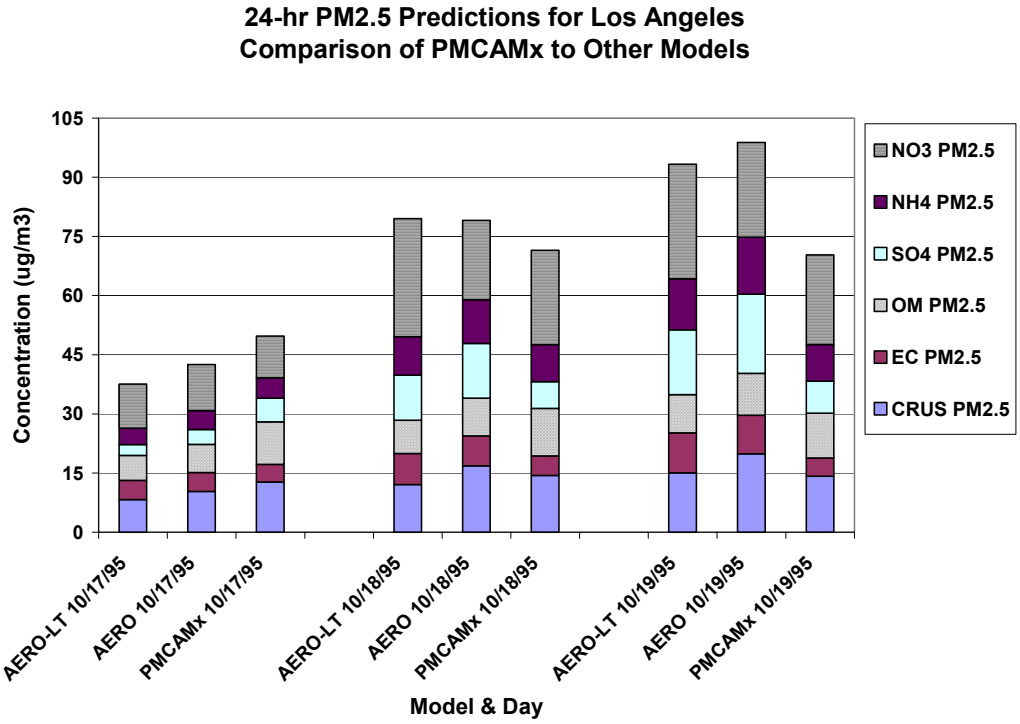


Figure 11. Comparison of 24-hr $PM_{2.5}$ at Los Angeles North Main between PMCAMx, UAM-AERO and UAM-AERO/LT (October 17-19, 1995).



CPU Times for PMCAMx

The CPU times for PMCAMx operating on a Linux PC (Athlon MP2000 1.67 GHz), DEC-Alpha (500 MHz) and SUN Ultra-30 (333 MHz) using a single processor are compared in Table 5. The DEC and SUN workstations gave similar performance and the Linux PC was much faster because of the higher CPU clock speed. The DEC workstation halted on the third day (October 19th) because of a floating-point math error (underflow). The DEC was able to complete the third simulation day at lower optimization level suggesting that the compiler may be partly responsible for this problem. The CPU time increased on successive days for all workstations.

Table 5. CPU Times (hours) for the Los Angeles Test Case (65 x 40 5-km grids with 10 vertical layers) on different workstations.

Day	Linux	Sun	DEC
October, 17th	1.4	7.4	7.3
October, 18th	1.9	10.5	11.9
October, 19th	2.4	11.7	15*

* The DEC workstation required a lower optimization level to complete this day.

The breakdown of CPU time between the aerosol modules and the CAMx core model was analyzed for the Linux workstation leading to the following conclusions:

- The aerosol modules dominate the PMCAMx CPU-time (55 – 81%) over the host CAMx model. This means that most of the CPU time in PMCAMx is going toward the aerosol science calculations.

- Adding 130 PM species to the CAMx host model transport and diffusion calculations adds relatively little CPU-burden relative to the science calculations within the aerosol modules.

- The Secondary Organic Aerosol Production (SOAP) module is efficient and contributes a small fraction (7-9%) of the total CPU-time.

- The MADM aerosol chemistry and the aqueous-phase chemistry are the largest contributors to the CPU-time.

- The CPU-time for the MADM and aqueous chemistry modules varies significantly between days in response to differences in chemical/environmental conditions (e.g., the amount of fog or clouds present).

EMISSION SENSITIVITY TESTS

A series of emission sensitivity tests were performed for the Los Angels October 17-19, 1995 episode to investigate the response of predicted concentrations to emission changes and check that PMCAMx was stable for a range of emission scenarios. The anthropogenic emissions of NOx, VOC and NH_3 were reduced by 50% separately and in combination for a matrix of eight emission scenarios. The runs were performed on a Linux (Athlon MP2000) workstation. The PMCAMx runs all completed without problems and the run times were all within 15% of each other. There was a small tendency for run times to decrease as the NOx and VOC emissions

were reduced. The effects of the emission reduction sensitivity simulations on changes in PM concentrations are discussed below for an upwind site in central downtown Los Angeles and a downwind site at Rubidoux-Riverside (See Figure 1).

- Reducing ammonia emissions reduces nitrate, sulfate and ammonium at both the upwind and downwind sites. Nitrate is reduced because there is less ammonia to combine with nitrate acid so less ammonium nitrate forms. Sulfate is reduced because there are more acidic water droplets due to less buffering by ammonia that inhibit aqueous sulfate production. Ammonium reductions are associated with both the nitrate and sulfate reductions.

- Reducing VOC emissions reduces organic matter (that includes secondary organic aerosols) at both the upwind and downwind sites. At the downwind site, reducing VOC emissions also reduces ammonium nitrate due to the reduced photochemical activity that lowers the production of nitric acid from NOx.

- Reducing NOx emissions <u>increases</u> ammonium nitrate at the upwind site and decreases ammonium nitrate at the downwind site. This demonstrates that fundamental differences can exist between the NOx-nitrate relationships at different sites, similar to well-known differences in ozone-NOx relationships.

    - The upwind increase in ammonium nitrate is explained by more rapid nitric acid production when NOx emissions are reduced, i.e., nitric acid production is NOx-inhibited at the upwind site in the base case.

    - The downwind decrease in ammonium nitrate is explained lower nitric acid production when NOx emissions are reduced, i.e., nitric acid is NOx-limited at the downwind site in the base case.

- Reducing NOx emissions increases organic matter (that include secondary organic aerosols) at the upwind and downwind sites. This is due to acceleration in the oxidation of VOCs to SOA when NOx emissions are reduced.

The concentration responses to reductions in combinations of precursor emissions are generally consistent with the points listed above, but do not necessarily reflect linear combinations of effects.

CONCLUSIONS AND RECOMMENDATIONS

The testing and evaluation of the new PMCAMx code demonstrated that the code was stable and produced reasonable results comparable to other aerosol models (e.g., UAM-AERO). No unusually or anomalous model estimates were seen. Because of deficiencies in the meteorological fields generated using diagnostic techniques, a more definitive assessment of the PMCAMx model estimates could not be obtained. However, the implementation of the state-of-science PM modules in PMCAMx has produced a set of recommendations as follows:

- PMCAMx should be tested for additional episodes under a variety of conditions to further probe the reliability and completeness of the model algorithms. Episodes with

extensive ambient data for model performance evaluation and reliable input data will be needed to learn more about PMCAMx model performance.

- PMCAMx should be tested for a nested-grid domain. The grid nesting algorithms have been implemented for PM but not tested and ENVIRON does not recommend that they be used yet.

- PMCAMx sensitivity tests should investigate optimum model configurations, for example:
    - Aerosol size section schemes – the number of sections and the cut-points needed for specific types of model application.
    - Secondary organic aerosol species – how many volatility groups are warranted for anthropogenic vs. biogenic emissions?
    - Adequacy of current gas-phase chemical mechanisms to support PM modeling.
- Further development of the aqueous-phase chemistry model (VSRM) would be beneficial. Issues in need of attention are efficiency/stability of the numerical integration routines (especially the VODE numerical solver) and removing assumptions that prevent the PMCAMx aerosol size distribution from being a user adjustable parameter. Also, it may be possible to improve the implementation of VSRM in PMCAMx to make better use of available information, such as remembering liquid-phase concentrations between calls to VSRM (especially when the two-droplet size algorithm is being used) and passing liquid concentrations to the deposition module for use in wet-deposition calculations.

- The PMCAMx host model should be upgraded from CAMx version 3.01 to CAMx version 3.1 (or most current). When this is done, the SAPRC99 mechanism should be interfaced to the secondary organic aerosols in PMCAMx.

- Upgrades to the CMU aerosol modules should be implemented and maintained in PMCAMx. For example, CMU enhanced the MADM aerosol size algorithms by using a trajectory-grid approach and this should be maintained in the next version of PMCAMx.

- The wet-deposition module developed by ENVIRON should be added to PMCAMx.

- The secondary organic aerosol module should be integrated with MADM to improve efficiency.

- The PMCAMx "full science" (FS) algorithms should be implemented alongside more efficient algorithms in a single model version. This would allow evaluation of FS and more efficient approaches in a common platform. There is great interest in more computational efficient algorithms for annual PM and visibility modeling.

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