# AEROSOL SIZE DISTRIBUTION PERFORMANCE BASED ON CHANGES TO PARTICLE EMISSIONS AND NUCLEATION

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## 1. INTRODUCTION

Epidemiological studies suggest that the health effects of air pollution are concentrated in the ultrafine particles, those having an aerodynamic diameter less than 100 nm (Oberdorster et al., 2005). Although some modelers have looked at performance for ultrafine particles (e.g., Zhang et al., 2006), most of our air quality modeling capabilities have focused on the current regulations for $PM_{10}$ and $PM_{2.5}$. This paper examines the entire size distributions from Community Multiscale Air Quality model (CMAQ) version 4.4 for the Pacific Northwest (Byun and Schere, 2006). It updates the model science for ultrafine particles and tests the updates against aircraft and surface measurements.

## 2. CMAQ MODELING STRATEGY AND OBSERVATIONAL DATASETS

CMAQ version 4.4 at 4 km resolution simulated a period of August 2001 when extensive chemical and aerosol observations were available from Pacific Northwest 2001 (PNW2001) near Seattle, Washington and from its larger sister field campaign, Pacific 2001, in metropolitan Vancouver, British Columbia. The CMAQ domain covers the entire region that would significantly impact the Puget Sound / Lower Fraser Valley (Figure 1). The aerosol size distribution is represented as three, overlapping lognormal modes in the Aitken, accumulation, and coarse regimes (Binkowski and Roselle, 2003).

Local and national government agencies in the USA and Canada provided emissions estimates for all major sources in the domain. Boundary conditions for most species come from the GEOS-CHEM global chemistry model valid for August 2001, and others are from typical coastal observations. MM5 with the MRF boundary layer and 5-layer soil model provided 4 km meteorological input.

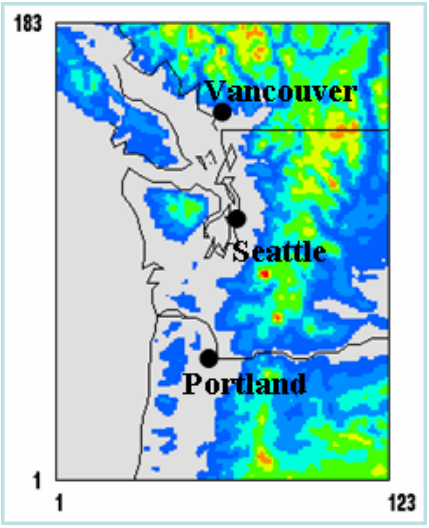


Figure 1. CMAQ 4-km modeling domain. Colors represent elevation.

## 3. BINARY NUCLEATION

CMAQ version 4.4 uses the Kulmala et al. (1998) nucleation algorithm to produce new particles from gaseous sulfuric acid and water vapor. As implemented in CMAQ, new particles are assumed to be 2-nm diameter spheres comprised exclusively of sulfuric acid. The new number, surface area, volume, and sulfate mass are immediately added to the Aitken mode.

Previously presented results showed that this algorithm underpredicts aerosol number by typically a factor of 10 to 100. Surface $PM_{2.5}$ measurements demonstrate that the number underprediction occurs in spite of mass performance similar to other published CMAQ results. The underprediction persists at all hours and is greater for smaller size ranges. Size-resolved, speciated aerosol measurements reveal that the number underprediction is consistent for sulfate, organics, and nitrate species. The Kulmala binary algorithm produces few new particles for this simulation despite regional nucleation being fairly common in this environment.

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The binary nucleation algorithm does not represent the current understanding of particle nucleation. Measured gas-phase sulfuric acid concentrations are not high enough to produce the observed nucleation rates (Kulmala et al., 2000). Although possible additions to the theory are ion-induced nucleation, iodine, and aromatic acids, ammonia is the most widely recognized addition to the nucleation process (Korhonen et al., 1999).

## 4. TERNARY NUCLEATION

Ternary $NH_3$-$H_2SO_4$-$H_2O$ nucleation was implemented into CMAQ to improve the model science and in hope of improving CMAQ model performance for ultrafine particles. The ternary Napari et al. (2002) parameterization was substituted for the binary Kulmala algorithm. All other aspects of the implementation, such as the size of nucleated particles and their introduction to the Aitken mode, remained the same.

The addition of ammonia to the nucleation process dramatically increased the number of predicted particles. Ternary nucleation produced daytime urban number concentrations in the millions $cm^{-3}$. This compares to observed concentrations of 5000-25,000 $cm^{-3}$ and represents an overprediction by 2-4 orders of magnitude. However, the instruments had lower limits of detection between 6 and 9 nm, and most of the particles in CMAQ were below these detection limits. When the number of CMAQ particles is restricted to observable size ranges, the model still overpredicts the number concentrations but instead by 1-2 orders of magnitude.

Whereas the error for the binary nucleation case was uniform in space and time, the errors for ternary nucleation vary more from day to day and from urban to rural regions. The most concerning part of the results is that adding a large number of new particles directly to the Aitken mode has eliminated the Aitken mode and replaced it with a nucleation mode. CMAQ's three-mode structure and existing aerosol processes are not designed to accommodate the addition of an extra mode below 10 nm.

## 5. NUCLEATION MODE PROCESSING

To properly model the ultrafine particles, it is necessary to incorporate the nucleation mode (particles with diameters <10nm) separately from the Aitken mode. Given that these tiny particles tend not to form a lognormal mode and are rapidly processed, one solution is to represent them with a moving sectional model. Although the most accurate method, its downside is that it adds significant computational time. Another solution that retains the goal of an efficient air quality model is to parameterize the nucleation mode process within the existing Aitken, accumulation, and coarse mode paradigm.

Kerminen and Kulmala (2002) provide a parameterization for determining the fraction of critical clusters that reach observable sizes or the Aitken mode. The most important processes governing nucleation mode particles are growth by condensation to the Aitken mode and loss by coagulation to the accumulation mode. The new particles are highly subject to coagulation and must grow quickly if they are to survive to point of being observed. This competition between coagulation and growth rate is parameterized by:

$$\eta = \frac{\gamma * CS}{GR} \qquad (1)$$

where $\gamma$ is a constant of proportionality, CS is the pre-existing condensation sink, and GR is the nucleation mode particle growth rate. The gaseous condensation sink is used for condensation because the two processes are conceptually very similar for particles <10 nm. In reality, it is likely various condensable organics play a large role in growing nucleation mode particles (Kerminen et al., 2004). However, the identity and saturation vapor pressure of these species have yet to be identified. In their absence and using the fact that 10-20 nm particles may still be dominated by sulfate condensation in urban areas (McMurry and Eisele, 2006), the sulfate growth rate is used. For a typical $\eta$ value in urban areas, less than 1 in 1000 nucleated particles survives to be observed and included in the Aitken mode.

Figure 2 shows the observable number concentration performance of four nucleation options during one flight of PNW2001. Binary nucleation and no nucleation ("None") produce nearly identical performance. Substituting ternary nucleation of 2 nm particles for binary nucleation dramatically increases the number of particles when the aircraft is in urban areas. Addition of nucleation mode processing to ternary nucleation reduces the number of particles to within one order of magnitude of observed for this flight. For other flights and for ground data, most of the particles from ternary nucleation quickly coagulate

to the accumulation mode and do not survive to be distinct Aitken mode particles. Overall, the size distributions best represent the observed Aitken and accumulation mode when both ternary nucleation and nucleation mode processing are used (Figure 3).

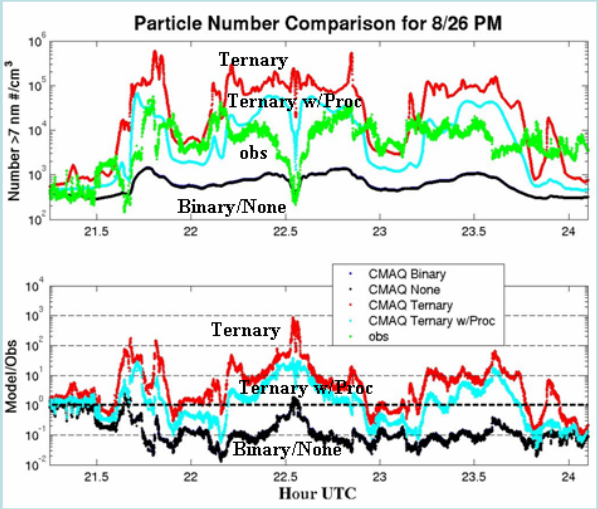


Figure 2. Particle number concentrations as a function of time for the afternoon of 26 August. The top panel shows the concentrations as observed by aircraft (green) and modeled by CMAQ (binary and no nucleation = indistinguishable dark blue and black lines; ternary = red; and ternary with nanomode processing = cyan). The bottom panel shows the modeled concentrations divided by the observed.

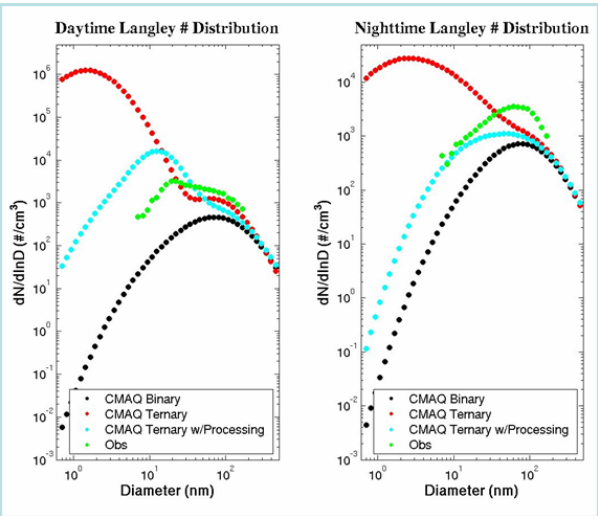


Figure 3. Average daytime and nighttime size distributions as observed at Langley 26-29 August, 2001 (green), as modeled by CMAQ (base version 4.4 = black; ternary = red; and both ternary nucleation and nanomode processing = cyan).

## 6. EMISSION SIZE DISTRIBUTION

The size distribution of emitted particles in CMAQ must be appropriate for the grid resolution used. A model emission process is by definition combustion at the source and everything that happens to the by-products before they reach the smallest scale resolved in the model. This includes particle coagulation, nucleation, dilution with ambient air, and mixing with other nearby sources. For large point sources the subgrid scale processes are accomplished with the plume-in-grid model within CMAQ, although there are still issues of what distribution to use for the stack emissions. Plume-in-grid is not realistic for the thousands of small mobile, area, and point sources within an urban region.

It is possible to parameterize the subgrid scale processes as part of emissions by using measured aerosol size distributions which represent the mesoscale grid. For this project, 40 published datasets that represent urban sources 5-15 km in scale were merged to determine a new emissions size distribution. The major change from CMAQ version 4.4 is to apportion a larger fraction of the emitted $PM_{2.5}$ mass into the Aitken mode. CMAQ's standard distributions are from observations with older instruments that were not able to capture the entire Aitken mode and from observations that represent a regional scale. A focus on newer observations and on observations that represent the model emissions scale increases the importance of the Aitken mode. As a best guess estimate, 10% of the emitted mass is apportioned to the Aitken mode. This increases the number of emitted particles by a factor of 4. To constrain the effect of the emission size distribution, an upper bound of 20% was used, which increases the number of emitted particles by a factor of 14.

When the best guess and upper bound emissions size distributions are used in CMAQ, the resulting particle concentrations increase by a factor 2.4 and 6.4 respectively. In other words, 50-60% of the increase in emitted particles is preserved in the final modeled number concentrations. The increase is spatially and temporally uniform within the urban areas. With number underpredictions from CMAQ v4.4 by a factor of 10-100, an increase in the number of particles by at most a factor of 6 does not solve

the model's weak performance. However, the best guess emission size distribution improves the shape of the modeled Aitken and accumulation modes by emphasizing the Aitken mode and shifting its median diameter to a smaller size (Figure 4).

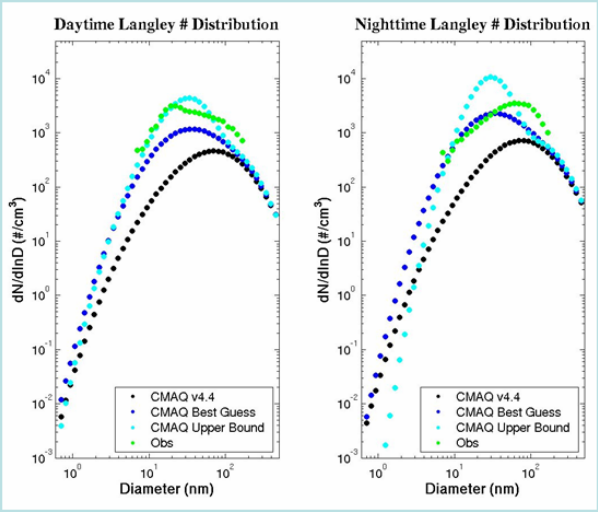


Figure 4. Average daytime and nighttime size distributions as observed at Langley 26-29 August, 2001 (green) and as modeled by CMAQ (version 4.4 = black; best guess emission size distribution = blue; and the upper bound emission size distribution = cyan).

## 7. CONCLUSION

CMAQ version 4.4 underpredicts number concentrations, especially in the ultrafine range, despite average $PM_{2.5}$ performance. Improvements to the chemistry and physics of the particle nucleation process increase the number of particles by a factor of 5 on average but performance is inconsistent. Updates to the emission size distributions also increase number concentrations by a factor of 5. Although the combination of these two changes do not entirely compensate for the model errors, they produce size distributions that more adequately represent the Aitken mode in prominence and median size. These changes apply to CMAQ for the Pacific NW region but could be incorporated into any regional air quality model.

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