JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 115, D03203, doi:10.1029/2009JD012313, 2010

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Simulation of in situ ultrafine particle formation in the eastern United States using PMCAMx-UF

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Received 24 April 2009; revised 22 August 2009; accepted 18 September 2009; published 5 February 2010.

[1] A three-dimensional chemical transport model has been developed incorporating the Dynamic Model for Aerosol Nucleation for the simulation of aerosol dynamics into the regional model PMCAMx. Using a scaled version of the ternary H_2SO_4-NH_3-H_2O nucleation theory and the Two Moment Aerosol Sectional algorithm, the new model (PMCAMx-UF) is used to simulate a summertime period in the eastern United States. The model predicts, in agreement with observations, frequent nucleation events that take place over hundreds to thousands of kilometers, especially in the northeastern United States. Detailed comparison with the observations of the Pittsburgh Air Quality Study suggests that the model reproduces reasonably well the details of the events in this sulfur rich area but has a tendency to overpredict the frequency of the events. Regional nucleation is predicted to increase the total number concentrations by roughly a factor of 2.5 over the whole domain. The corresponding increases for particles larger than 10 nm (N_{10}) and 100 nm (N_{100}) were 75% and 15%, respectively. In the Ohio River Valley the increases are as much as a factor of 10 for total particle number and 40% for N_{100}. Contrary to the total particle concentration, increases of N_{100} take place often in areas different than those of the nucleation events. Nucleation is predicted to decrease the N_{100} in some areas even if it increases the total number concentration. The sensitivity of the model to the nucleation rate scaling parameter and the ammonia levels is discussed.

Citation: Jung, J., C. Fountoukis, P. J. Adams, and S. N. Pandis (2010), Simulation of in situ ultrafine particle formation in the eastern United States using PMCAMx-UF, *J. Geophys. Res.*, *115*, D03203, doi:10.1029/2009JD012313.

1. Introduction

[2] Direct emissions and nucleation are the two major processes responsible for injecting new particles into the atmosphere. Ultrafine particles can grow to cloud condensation nuclei (CCN) through condensation and coagulation. Cloud droplets are formed on the CCN, and the resulting clouds play a significant role in the energy balance of our planet through their interactions with solar radiation [*Charlson et al.*, 1992; *Penner et al.*, 1992]. These particles, with diameters below 100 nm, can be more harmful to human health than larger particles [*Donaldson et al.*, 1998, 2002]; several reasons have been hypothesized for these effects [*Oberdörster et al.*, 2005] including their high surface area per unit mass which allows them to carry efficiently toxic compounds into the human body [*Delfino et al.*, 2005].

[3] Investigation of the interactions between the sources of ultrafine particles, atmospheric transport, growth, and removal processes requires the development of comprehensive chemical transport models (CTMs) that can simulate ultrafine, fine, and coarse particle dynamics and chemistry on regional scales. Aerosol CTM studies in the United States initially focused on California [*Russell and Cass*, 1986; *Pilinis and Seinfeld*, 1988; *Lurmann et al.*, 1997; *Sun and Wexler*, 1998; *Meng et al.*, 1998] and more recently on the eastern United States [*Mebust et al.*, 2003; *Pinder et al.*, 2006; *Gaydos et al.*, 2007; *Lane et al.*, 2007; *Dawson et al.*, 2007; *Karydis et al.*, 2007]. The models used in the above studies generally tracked only mass concentrations for regulation purposes, neglecting or oversimplifying the treatment of number concentrations.

[4] Owing to the important role of ultrafine particles in atmospheric chemistry and physics, a number of studies related to these smaller particles has been performed recently [*Tolocka et al.*, 2005; *Sardar et al.*, 2005; *Sioutas et al.*, 2005; *Wang et al.*, 2006; *Vana et al.*, 2006]. Although there have been a number of significant efforts [*Jacobson*, 2001a, 2001b; *Trivitayanurak et al.*, 2007; *Mebust et al.*, 2003; *Spracklen et al.*, 2006], nucleation modeling studies in three-dimensional regional CTMs are in an early stage. Both nucleation and growth mechanisms and rates remain highly uncertain [*Kulmala et al.*, 2004]. Furthermore, the smallest detectable particle size is still too large to determine unambiguously the nucleation mechanism [*Stanier et al.*, 2004b].

[5] As nucleation, along with direct emission, is an important source of ultrafine particles, both an accurate

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0148-0227/10/2009JD012313$09.00

nucleation theory and its computationally efficient parameterization are required. While binary nucleation of water and sulfuric acid reproduces observations in the upper troposphere and lower stratosphere [*Adams and Seinfeld*, 2002], it almost always underpredicts observed nucleation rates in the lower troposphere [*Kulmala et al.*, 2004]. A substantial amount of work has been devoted to the identification of the dominant nucleation mechanisms in the boundary layer [*Vehkamäki et al.*, 2004; *Lovejoy et al.*, 2004; *Kulmala et al.*, 2006; *Yu*, 2006a, 2006b; *Eisele et al.*, 2006], the results, however, are still inconclusive for most regions (e.g., boreal forest). Condensation of organic species [*Kerminen et al.*, 2000; *Anttila and Kerminen*, 2003] or ion-enhanced condensation [*Laakso et al.*, 2002] has also been proposed as possible nucleation mechanisms. By analyzing two European measurement campaigns, *Sihto et al.* [2006] and *Riipinen et al.* [2007] have proposed a simple power law relationship between observed particle formation rates and sulfuric acid vapor concentration where the sulfuric acid exponent varies between one and two. *Kuang et al.* [2008] also analyzed nucleation measurements in diverse continental and marine atmospheric environments and concluded that the observed nucleation rates were proportional to the square of the sulfuric acid concentration.

[6] Ammonia has also been considered as a species that may participate in the formation of nuclei [*Russell et al.*, 1994, and references therein] stabilizing clusters by reducing their free energy of formation [*Coffman and Hegg*, 1995; *Napari et al.*, 2002]. Several nucleation measurement and modeling studies have supported the potential participation of ammonia in the nucleation process in boreal forest regions [*Kulmala et al.*, 2001] and in polluted regions including Pittsburgh, Pennsylvania [*Stanier et al.*, 2004b; *Gaydos et al.*, 2005], and Atlanta, Georgia [*Smith et al.*, 2005; *Sakurai et al.*, 2005]. More recent studies [*Ortega et al.*, 2008; *Torpo et al.*, 2007] support the significance of ammonia in the nucleation mechanism while others question it [*Kurtén et al.*, 2007; *Riipinen et al.*, 2007].

[7] *Gaydos et al.* [2005] successfully simulated nucleation events in the Pittsburgh area using a box model and the ternary (H_2O-H_2SO_4-NH_3) nucleation parameterization of *Napari et al.* [2002]. Recent work [*Vehkamäki et al.*, 2004; *Merikanto et al.*, 2007] has however questioned the assumption of *Napari et al.* [2002] that the critical cluster consists of stable ammonium sulfate with a diameter of about 1 nm. These more recent studies have predicted significantly lower ternary nucleation rates. *Jung et al.* [2008] tested six different nucleation parameterizations using measurements from the Pittsburgh Air Quality Study and found that only the ternary expression of *Napari et al.* [2002] reproduced observations on all days studied. Even if this ternary parameterization reproduced the occurrence of the events it clearly overpredicted the observed nucleation rates. *Merikanto et al.* [2007] proposed a new ternary H_2O-H_2SO_4-NH_3 nucleation parameterization based on the work of *Anttila et al.* [2005], which takes into account that sulfuric acid and ammonia may produce hydrate-like ammonium bisulfate in the vapor phase. The predicted nucleation rates by the new model are much lower, sometimes even tens of orders of magnitude, than the rates calculated by the ternary parameterization of *Napari et al.* [2002].

[8] Many recent studies (see *Kulmala et al.* [2004] for a review) have suggested that nucleation events often occur on regional scales. *Vana et al.* [2004] reported that new particle formation events happened simultaneously in three monitoring sites in northern Europe that were separated by more than 1000 km. *Stanier et al.* [2004b] suggested that nucleation events take place over an extended area in the northeastern United States by measuring aerosol size distributions simultaneously at two sites approximately 50 km apart. One of the sites was urban and the other was a continental background site located upwind of the urban area. Nucleation took place almost always at both locations during the same days and practically at the same time. There were days when nucleation events were observed in Philadelphia, Pennsylvania; Pittsburgh, Pennsylvania; and St. Louis, Illinois at the same time [*Stanier et al.*, 2004a, 2004b; *Qian et al.*, 2007]. Extensive measurements showed that these regional nucleation events occur throughout the year in the central and eastern United States and, depending on the location and season, are observed on 5% to 50% of the days [*Woo et al.*, 2001; *Stanier et al.*, 2004a, 2004b; *Qian et al.*, 2007]. The resulting local increase in number concentrations ranges from two to ten times during the events, while the rate of growth of the freshly nucleated particles can range between 1 and 20 nm hr^{-1} to sizes between 10 and 100 nm throughout a day [*Kulmala et al.*, 2004]. The effects of these events on the number concentrations over larger scales are yet to be elucidated.

[9] This paper describes the incorporation of the Dynamic Model for Aerosol Nucleation (DMAN) (discussed in the work of *Jung et al.* [2006, 2008]) in a three-dimensional chemical transport model, PMCAMx [*Karydis et al.*, 2007; *Gaydos et al.*, 2007], to investigate the spatial scale and frequency of the regional nucleation events in the eastern United States. The resulting new model, PMCAMx-UF, is evaluated by comparing its predictions against the Pittsburgh Air Quality Study (PAQS) measurements. Its results are used to estimate the contribution of these nucleation events to total particle number concentrations but also to Cloud Condensation Nuclei (CCN) levels defined for the purposes of this study as particles larger than 100 nm.

2. Model Description

[10] A new three-dimensional CTM, PMCAMx-UF, has been developed extending PMCAMx to simulate accurately and efficiently the number size distribution together with the aerosol mass/composition size distribution. The framework of CAMx [*Environ*, 2003] is used in PMCAMx (and PMCAMx-UF), describing the processes of horizontal and vertical advection, horizontal and vertical dispersion, wet and dry deposition, and gas-phase chemistry. Aqueous-phase chemistry is simulated using the approach of *Fahey and Pandis* [2001]. The main difference between PMCAMx-UF and PMCAMx is in the simulation of aerosol microphysics. PMCAMx-UF uses the DMAN model of *Jung et al.* [2006] to track both aerosol mass and number size distribution. The mass emission inventory used is based on the Midwest Regional Planning Organization's BaseE inventory [*Lake Michigan Air Directors Consortium*, 2003] with updated ammonia [*Pinder et al.*, 2006] and carbonaceous aerosol emissions [*Lane et al.*, 2007].

[11] Details about the methods used for the simulation of PMCAMx advection, dispersion, gas-phase chemistry, emissions, and wet/dry deposition are provided by *Gaydos et al.* [2007]. For the aerosol processes (coagulation, condensation/evaporation, emissions, and nucleation) the DMAN model is used assuming that the aerosol is internally mixed. DMAN uses the Two-Moment Aerosol Sectional (TOMAS) algorithm of *Adams and Seinfeld* [2002] to simulate both the aerosol number and mass distributions. The relatively low CPU time requirements of DMAN make it a good choice as an aerosol module for three-dimensional chemical transport models focusing on ultrafine particles.

2.1. Size Resolution

[12] The accurate simulation of nucleation, growth, coagulation, and removal of multicomponent nanoparticles usually demands considerable computational resources [*Koo et al.*, 2003]. Tracking both mass and number size distributions is required to obtain the required accuracy for both the ultrafine particles (dominating the aerosol number concentrations) and the particles in the accumulation and coarse modes (dominating the aerosol surface and mass concentrations). We use a sectional approach to track aerosol number and mass, although modal approaches can also be used to track both moments under certain conditions [*Mebust et al.*, 2003].

[13] The TOMAS algorithm explicitly tracks both mass and number concentrations in each size section simultaneously. The aerosol size distribution is discretized in 41 sections covering the diameter range from 0.8 nm to 10 μm. The lowest boundary is at 3.75×10^{-25} kg of dry aerosol mass per particle that corresponds to 0.8 nm dry diameter assuming a density of 1.4 g cm^{-3}. Each successive boundary has twice the mass of the previous one for these 41 size sections. From 10 μm to 40 μm, two additional size sections are used for the description of cloud chemistry.

2.2. Aerosol Composition

[14] PMCAMx-UF tracks 13 aerosol species including four secondary organic aerosol components, primary organic aerosol, elementary carbon, crustal material, water, chloride, sodium, ammonium, nitrate, and sulfate. DMAN tracks for the ultrafine particles explicitly sulfate, ammonia, and water while the rest of the species are currently lumped into one surrogate species that is assumed to be inert. In the future DMAN will be extended to include explicitly all relevant species.

2.3. Nucleation

[15] On the basis of the results of *Gaydos et al.* [2005] and *Jung et al.* [2006], the *Napari et al.* [2002] ternary nucleation parameterization overpredicts ultrafine number concentrations during nucleation events. Similar overpredictions have also been reported by *Yu* [2006a, 2006b] and *Merikanto et al.* [2007]. As a zeroth-order correction we have scaled the nucleation rate using a nucleation tuner equal to 10^{-5}. This value was chosen based on several simulations comparing the peak concentration in the 10–100 nm size range predicted by the box model of *Jung et al.* [2008] with the measurements during the Pittsburgh Air Quality Study during nucleation days. The resulting nucleation rate expression should be viewed as a semiempirical ternary rate expression trying to correct for some of the weaknesses of the *Napari et al.* [2002] rate as discussed by *Merikanto et al.* [2007]. The sensitivity of the PMCAMx-UF results to this choice of nucleation tuner is investigated in section 3.

[16] The sensitivity of the DMAN predictions to other nucleation mechanisms was examined by *Jung et al.* [2008], who tested six different nucleation parameterizations against the PAQS measurements. The evaluation was conducted for (1) the ternary NH_3-H_2SO_4-H_2O nucleation parameterization of *Napari et al.* [2002], (2) the binary H_2SO_4-H_2O parameterization of *Vehkamäki et al.* [2002], (3) the binary H_2SO_4-H_2O parameterization of the *Jaecker-Voirol and Mirabel* [1989] theory by *Russell et al.* [1994], (4) the semiempirical first order in sulfuric acid concentration expression proposed by *Spracklen et al.* [2006], (5) the ion-induced nucleation parameterization of *Modgil et al.* [2005], and (6) the barrierless rate expression of *Clement and Ford* [1999]. *Jung et al.* [2008] reported that the only parameterization that reproduced the observations on all days examined was the ternary expression of *Napari et al.* [2002]. The barrierless expression of *Clement and Ford* [1999] predicted nucleation events on most of the days, while the ion-induced nucleation expression and the binary H_2SO_4-H_2O parameterization of *Vehkamäki et al.* [2002] predicted no nucleation events. The semiempirical expression of *Spracklen et al.* [2006], based on measurements from the boreal forest, performed well on 70% of the days in the sulfur-rich environment of Pittsburgh.

[17] The ternary nucleation parameterization proposed by *Merikanto et al.* [2007] predicts no boundary layer nucleation events for the summertime conditions in Pittsburgh. According to this nucleation parameterization, for the conditions during our simulation period in Pittsburgh (average temperature = 297.3 ± 4.2 K, 0.75 ± 1.1 ppt H_2SO_4, and 1.3 ± 1.2 ppb NH_3) the nucleation rate is negligible [*Merikanto et al.*, 2007, Figure 5]. This nucleation parameterization predicts significant nucleation rates at the lower troposphere only under extremely high concentrations of sulfuric acid and ammonia that are not encountered in the area.

2.4. Pseudo Steady State Approximation

[18] The previous implementation of DMAN used a fourth-order Runge-Kutta algorithm and an adaptive time step [*Press et al.*, 1992] for the integration of the corresponding differential equations during nucleation. This numerical approach, although accurate, requires a significant amount of CPU time. To increase the computational speed, the Pseudo Steady State Approximation (PSSA) for sulfuric acid proposed by *Pierce and Adams* [2009] is used instead. Sulfuric acid vapor is produced by the reaction of SO_2 and OH, and is consumed by nucleation and condensation onto existing particles. The PSSA assumes that sulfuric acid concentration reaches steady state instantaneously during a time step or equivalently

$$0 = P_{H2SO4} - CS \cdot [H_2SO_4]_{ss} - J_{nuc} \cdot M_{nuc} \qquad (1)$$

where P_{H2SO4} is the chemical production rate of sulfuric acid vapor, CS is the condensation sink (first-order condensational loss rate constant) for sulfuric acid vapor, $[H_2SO_4]_{ss}$ is the steady state concentration for sulfuric acid vapor, J_{nuc} is the nucleation rate, and M_{nuc} is the amount of sulfuric acid in

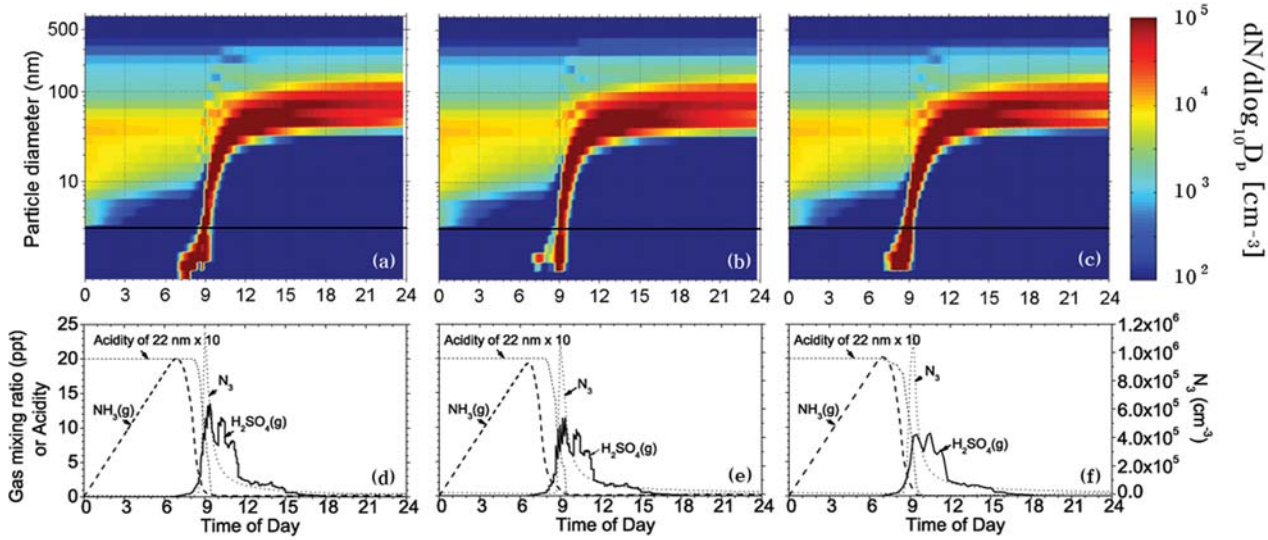

Figure 1. Predicted aerosol size distribution and gas-phase concentrations for a test case assuming an ammonia emission rate of 3 ppt h^{-1}: dry size particle distribution as a function of time with (a) the original Runge Kutta based scheme with adaptive time step, (b) pseudo steady state approximation (PSSA) with a constant 15 s time step, and (c) PSSA with a 900 s time step. Also shown is the acidity of 22 nm particles, NH_3(g), N_3 (total number concentration above 3 nm), and H_2SO_4(g) of (d) Runge Kutta adaptive time step and (e) PSSA 15 s and (f) PSSA 900 s step.

each nucleating particle. The steady state sulfuric acid concentration is calculated by solving equation (1). *Pierce and Adams* [2009] tested the PSSA method for a variety of conditions ranging from highly polluted to extremely clean conditions and found very good agreement between the PSSA method and the "benchmark model" in predicting the sulfuric acid vapor concentration (within 10%) and the number of new particles formed (within 4%) during the time scale of a typical atmospheric nucleation event.

[19] The performance of the PSSA for H_2SO_4 was evaluated by comparing the corresponding solution to that of the Runge-Kutta adaptive time step strategy in DMAN. As an initial test we assumed a constant ammonia emission rate of 3 ppt h^{-1} while the rest of the conditions were that of 12 September 2002 in Pittsburgh. This test has been used by *Jung et al.* [2006]. In the first case the PSSA was used with a time step of 15 s. For both algorithms, the simulation results are quite similar (Figure 1). The beginning and end of nucleation and the growth patterns are practically identical for particles above 3 nm. Total number concentrations above 3 nm, N_3, agree well with each other. Peak number concentrations occur at 0900 LT for both the Runge-Kutta and the PSSA algorithms, and the values were 1.15×10^6 and 1.05×10^6 cm^{-3}, respectively. The PSSA was also tested for the same period with the time step increased to 900 s, which corresponds to the master time step of PMCAMx-UF. The performance of the algorithm remains very good even if the peak of N_3 is reached 15 min later. The maximum N_3 concentration is 1.13×10^6 cm^{-3}, in good agreement with the benchmark solution. After a number of similar tests the PSSA with a time step of 900 s was chosen for the simulations.

2.5. Condensation

[20] Although the TOMAS algorithm is used for the simulation of condensation/evaporation of both sulfuric acid and ammonia, the two species are treated independently. As sulfuric acid is assumed to be in pseudo steady state, amounts of sulfuric acid mass added to each section are calculated as well as its total concentration. The mass distributed in each section is used to decide the driving force, t, of the sulfuric acid condensation using the following equation [*Adams and Seinfeld*, 2002]:

$$m_{fj} = \left(m_{ij}^{2/3} + \frac{2}{3}\tau_j \right)^{3/2} \tag{2}$$

where m_{ij} is the average mass of a single particle in size section j before the process of aqueous phase chemistry and m_{fj} is the average mass of a particle in size section j after the aqueous phase chemistry part.

[21] Condensation of ammonia is simulated numerically following the approach described by *Jung et al.* [2006]. An accommodation coefficient of 0.08 is used while its vapor pressure on the surface of the acidic particles is assumed to be zero. We limit the ammonia condensation amount in each time step to prevent condensing more than what is available. The maximum amount of ammonia that can condense to size bin k, $M_{k,NH_4^+}^{max}$, for a sulfate "rich" case is calculated by:

$$M_{k,NH_4^+}^{max} = M_{k,NH_4^+} + f_k \cdot M_{NH_3} \tag{3}$$

where M_{k,NH_4^+} is the concentration of ammonium in size bin k and M_{NH_3} is the ammonia gas-phase mass concentration. Here f_k is the fraction of the condensational driving force of ammonia in the kth size section over the total condensational driving force.

Table 1. Boundary Conditions for July 2001 in PMCAMx-UF

Species	Boundary Concentration (μg m^{-3})
Organic aerosol	0.8
Primary elemental carbon	0.1
Ammonium	0.37
Nitrate	0.1
Sulfate	0.9

2.6. Emission Size Distributions and Boundary Conditions

[22] The size distribution of primary carbonaceous aerosol from transportation was calculated based on the ambient measurements of *Stanier et al.* [2004a] during the Pittsburgh Air Quality Study. For sulfate and the rest of the primary species the size distributions recommended by AEROCOM are used [*Dentener et al.*, 2006]. Assumed boundary conditions of aerosol species for July 2001 are shown in Table 1 [*Karydis et al.*, 2007].

3. Nucleation in the Eastern United States

3.1. Model Predictions Over the United States Domain

[23] PMCAMx-UF is used to simulate a period of 17 days from 12 July to 28 July 2001 in the eastern United States. Nucleation starts in general in the east and moves toward the west following the evolution of photochemical activity. Figure 2 shows the average predicted total number concentration of particles above 0.8 nm ($N_{0.8}$), 3 nm (N_3), 10 nm, (N_{10}), and 100 nm (N_{100}) for the ground level for the full simulation period. The major nucleation areas are the Ohio River Valley and the northeastern coast. Areas where frequent nucleation events are predicted to take place also include the midwestern states, eastern Texas, and upstate New York. Fewer and weaker nucleation events are predicted in the southeastern United States. Strong nucleation events are predicted as well in the areas around St. Louis, Baton Rouge, and New Orleans. Finally, there are some areas with more localized new particle formation events including western North Dakota and northeastern Colorado. The maps of average $N_{0.8}$, N_3, and N_{10} concentration fields have in general similar features, while the spatial distribution of N_{100} is quite different (Figure 2). The average ground concentrations over the whole modeling domain are predicted to be 15900, 8700, 6700, and 710 cm^{-3} for $N_{0.8}$, N_3, N_{10}, and N_{100}, respectively.

[24] An additional simulation was performed for the same period with nucleation turned off. Figure 3 shows the fractional increase of particle number concentrations due to nucleation (i.e., $(N_n - N_o)/N_o$, where N_n and N_o are the particle number concentrations with nucleation turned on and off, respectively). Nucleation is predicted to increase the ground-level $N_{0.8}$ by a factor of 10 or more over wide areas and the N_3 by a factor of 4. The increase in N_{10} is smaller, up to a factor of 3 in the Ohio River Valley area. The patterns of these fractional increases are quite similar to those of the corresponding average concentrations. Significant fractional increases are also predicted for the cleaner oceanic regions next to the eastern coast as well as in the Gulf of Mexico. No nucleation events are predicted for these regions, but some of the fresh particles are transported to these cleaner areas causing significant increases in particle number concentrations. The increase in N_{100} concentrations varies from 20 to

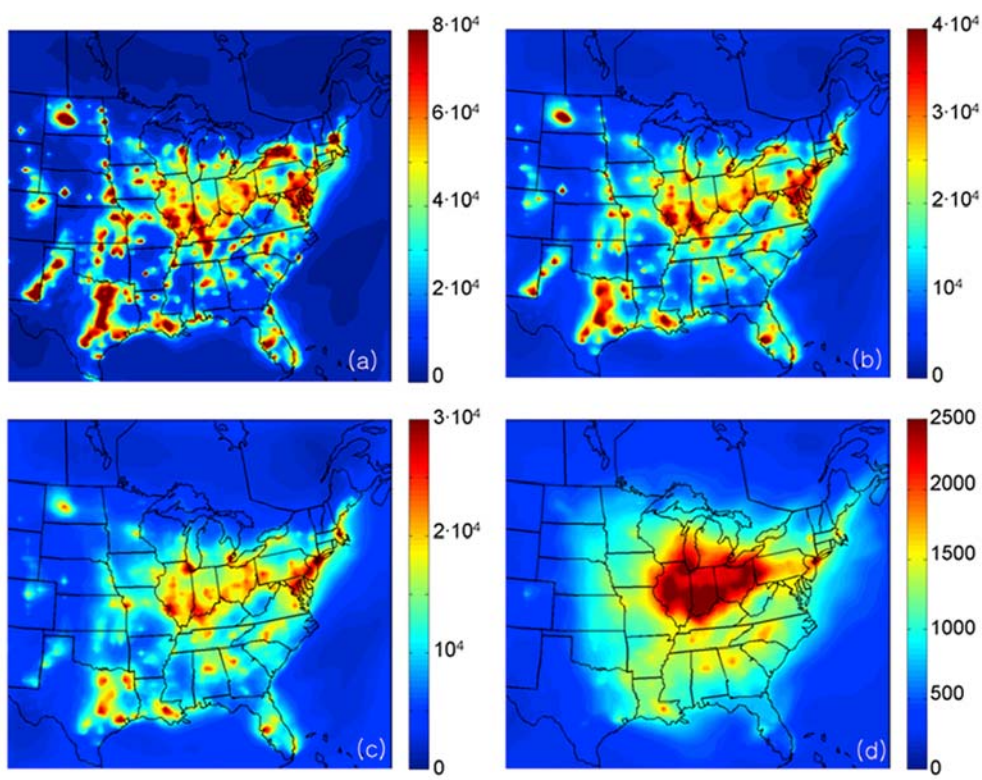

Figure 2. Predicted average number concentrations (cm^{-3}) at the ground level above (a) 0.8 nm, (b) 3 nm, (c) 10 nm, and (d) 100 nm for the 12–28 July 2001 base case simulation.

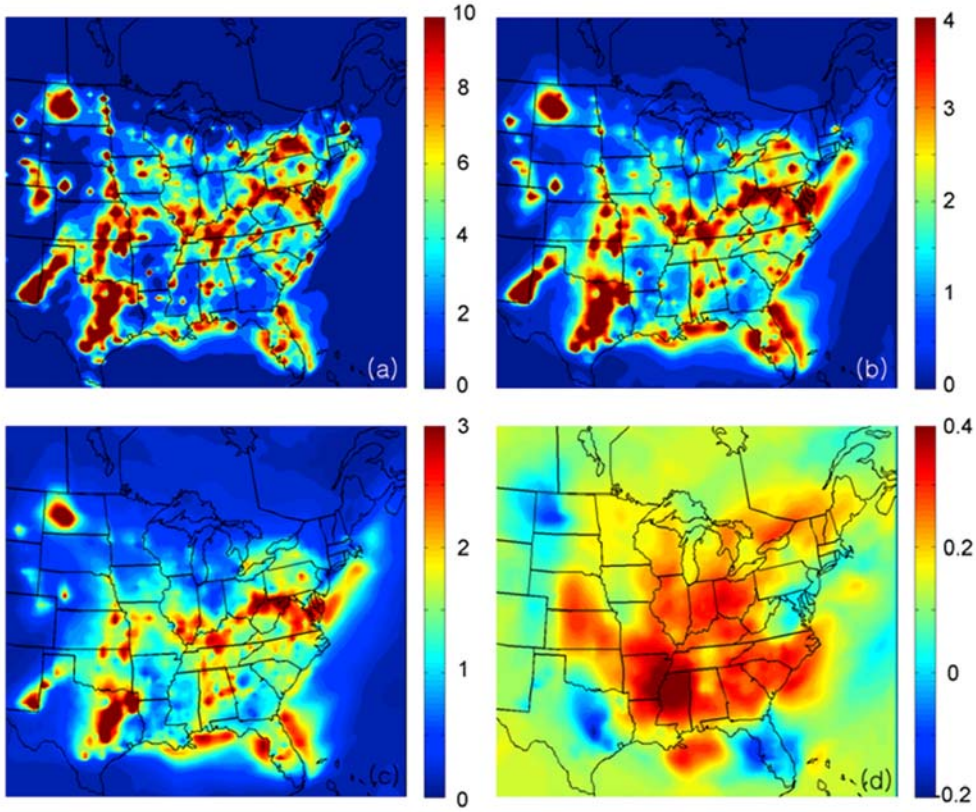

Figure 3. Predicted fractional increase of the corresponding ground level number concentration due to nucleation for particles with diameters above (a) 0.8 nm, (b) 3 nm, (c) 10 nm, and (d) 100 nm for the 12–28 July 2001 simulation.

40% over most of the domain and has a different spatial pattern. Some of the fresh nuclei grow to 100 nm and the enhancement covers a much wider area than the nucleation events themselves. There are some areas where decreases in average N_{100} concentration are predicted because of nucleation (Figure 3d). These areas include Florida, eastern Texas, western North Dakota, and West Virginia, where frequent nucleation events are predicted. The increase in number concentration of ultrafine particles in these areas creates a lot more sites for condensation of sulfuric acid. The growth of each particle is smaller (the condensate is distributed to too many particles) and thus fewer particles grow to sizes above 100 nm. The average fractional increases are 2.5, 1.1, 0.75, and 0.15 for the $N_{0.8}$, N_3, N_{10}, and N_{100}, respectively, over the whole domain.

3.2. Model Evaluation

[25] Figures 4–6 show comparisons of the PMCAMx-UF predictions in Pittsburgh with measurements from the Pittsburgh Air Quality Study (PAQS). Figure 4 depicts the mass concentrations of $PM_{2.5}$ sulfate, total ammonia ($PM_{2.5}$ ammonium + gas phase ammonia), and organic aerosol. $PM_{2.5}$ sulfate and total ammonia are underpredicted on 18 and 19 July, something also observed in the earlier PMCAMx simulations of *Gaydos et al.* [2007]. They explained this underprediction by the poor representation of precipitation during these days. PMCAMx-UF underpredicts the concentration of organic aerosol because it does not simulate the formation of secondary organic aerosol. The average predicted organic aerosol concentration is 2.1 μg m^{-3}, while the measured average is 3.22 μg m^{-3}. Most of the difference between the prediction and the measurement can be explained by SOA formation, which was not considered in this initial application.

[26] The concentration peaks in $N_{0.8}$ in Figure 5 are due to nucleation events while the concentration remains relatively flat during days without nucleation. Nucleation events are predicted for 12 out of the 17 days of the simulation in Pittsburgh, while the measurements showed the occurrence of nine nucleation events. This suggests that the model does a reasonable job in reproducing the frequency of nucleation in Pittsburgh with a tendency toward overprediction. The corresponding sulfuric acid and ammonia concentrations predicted by PMCAMx-UF are shown in Figure 6. A low concentration of gas-phase ammonia during the morning hours is the primary reason for the absence of nucleation during the nonnucleation days. Measured average values of N_3 and N_{10} in Pittsburgh during this period are 25,100 and 17,600 cm^{-3}, respectively, while the predicted average values are 30,600 and 26,200 cm^{-3}, respectively. The model overpredicts these concentrations by 22% and 49%, respectively. This overprediction could be due to the overprediction of the nucleation frequency and intensity or a possible overprediction of the primary emissions of ultrafine particles. To further explore this overprediction, we compared predicted (with nucleation "turned off") and observed values of N_3, N_{10}, and N_{100} for 5 nonnucleation days (18, 19, 20, 23, and 28 July). On average, the model slightly underpredicts N_3

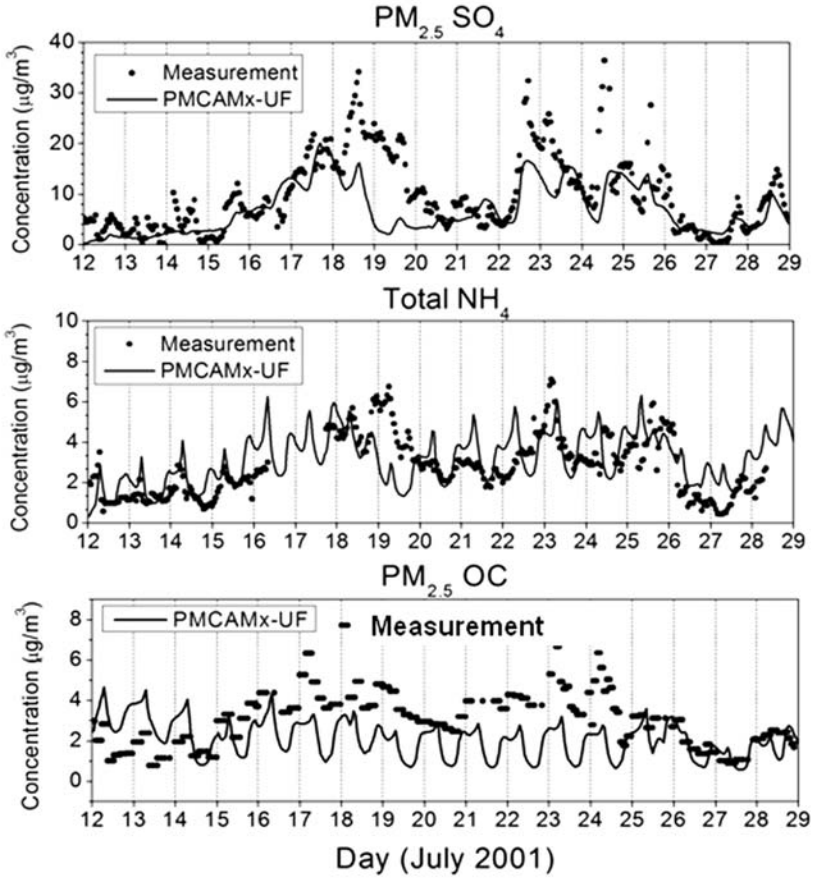

Figure 4. Comparison of PMCAMx-UF predictions with hourly measurements taken during the Pittsburgh Air Quality Study (PAQS) in July 2001.

(20,400 cm^{-3} observed versus 18,800 cm^{-3} predicted) and N_{100} (2,400 cm^{-3} observed versus 2,300 cm^{-3} predicted) but overpredicts N_{10} (by 46%) for these nonnucleation days. This indicates that the overall overprediction of N_3 is at least partially due to the overprediction of the nucleation frequency and intensity.

[27] The complete measured and predicted number concentration distributions for Pittsburgh as a function of particle size and time of day are shown in Figures 7 and 8. The model predicted correctly the occurrence of nucleation events for the first 4 days (12–15 July) as well as their onset time (Figure 7). No strong nucleation events took place according to the measurements during the next 4 days (16–19 July). The model reproduces this lack of activity during the first 3 days of the period but predicts incorrectly a nucleation event during 19 July. A comparison with the box model results [*Jung et al.*, 2008] for that day showed that PMCAMx-UF overpredicts the NH_3 concentration (Figure 6) which caused the false prediction of nucleation event for 19 July. On 16 July, according to the model, a nucleation event took place but the newly formed particles did not grow to detectable sizes. Instead they were lost by coagulation with the preexisting aerosol. During the next 4 days (20–23 July) the model predicts moderate nucleation during the first three days and no nucleation on 23 July (Figure 8). According to the measurements the nucleation event on 20 July did not take place, there are weaker and shorter events during 21 and 22 July, and indeed no nucleation event was observed during 23 July. Finally, during the last 5 days of the simulation period the model predicts four nucleation events while only three of them took place (on 24, 26, and 27 July). The potential role of ammonia in these events is investigated in the sensitivity analysis of section 3.3.

3.3. Sensitivity Tests

[28] An important source of uncertainty in the model predictions of aerosol number concentrations is the nucleation rate in the H_2SO_4-NH_3-H_2O system expressed here as the rate scaling parameter, f_n. The base case simulation ($f_n = 10^{-5}$) in Pittsburgh showed a tendency for overprediction of both the nucleation frequency and the number concentration of particles larger than 3 and 10 nm compared to the measurements. Therefore the July simulations were repeated with a decreased nucleation rate parameter of 10^{-7} thus decreasing further the nucleation rate by two orders of magnitude. Table 2 shows N_3 and N_{10} concentrations observed in Pittsburgh and predicted by PMCAMx-UF for the different nucleation rate parameters. Number concentration of particles decrease substantially for both N_3 and N_{10} when $f_n = 10^{-7}$ is used, while the absolute error is also decreased. The decreased nucleation rate parameter f_n, caused a general underprediction of the frequency of nucleation events as well as of their intensity. This is also shown in Figure 9 where we compare N_3 predicted and observed during PAQS. The error bar shows the effect of the scaling factor (when reduced from 10^{-5} to 10^{-7}) during high and low

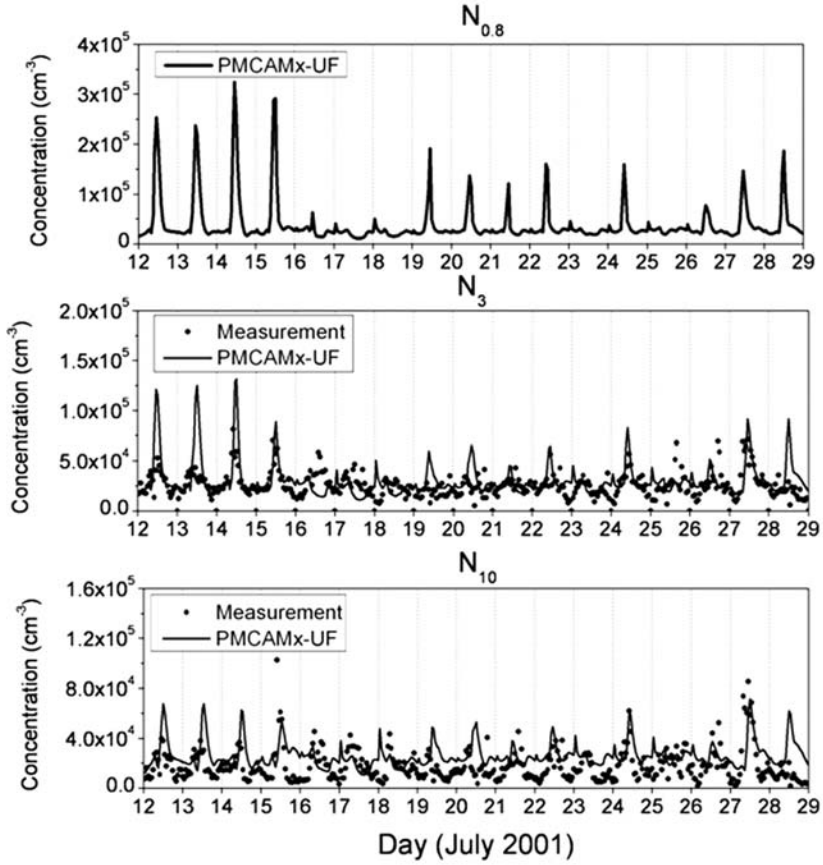

Figure 5. Comparison of model predictions with hourly measurements of number concentrations taken during the Pittsburgh Air Quality Study (PAQS) during July 2001.

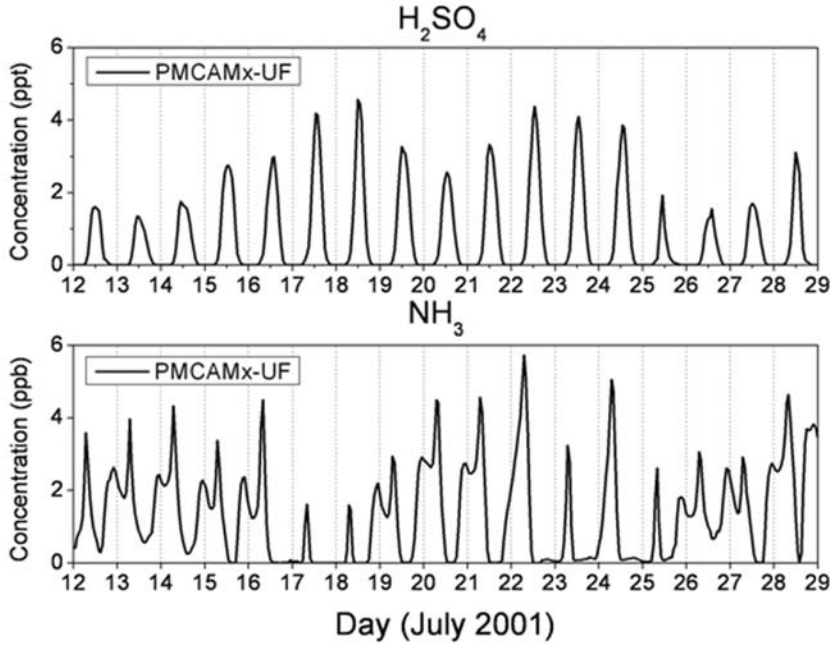

Figure 6. Sulfuric acid and ammonia concentrations predicted by the model for the July 2001 period in Pittsburgh.

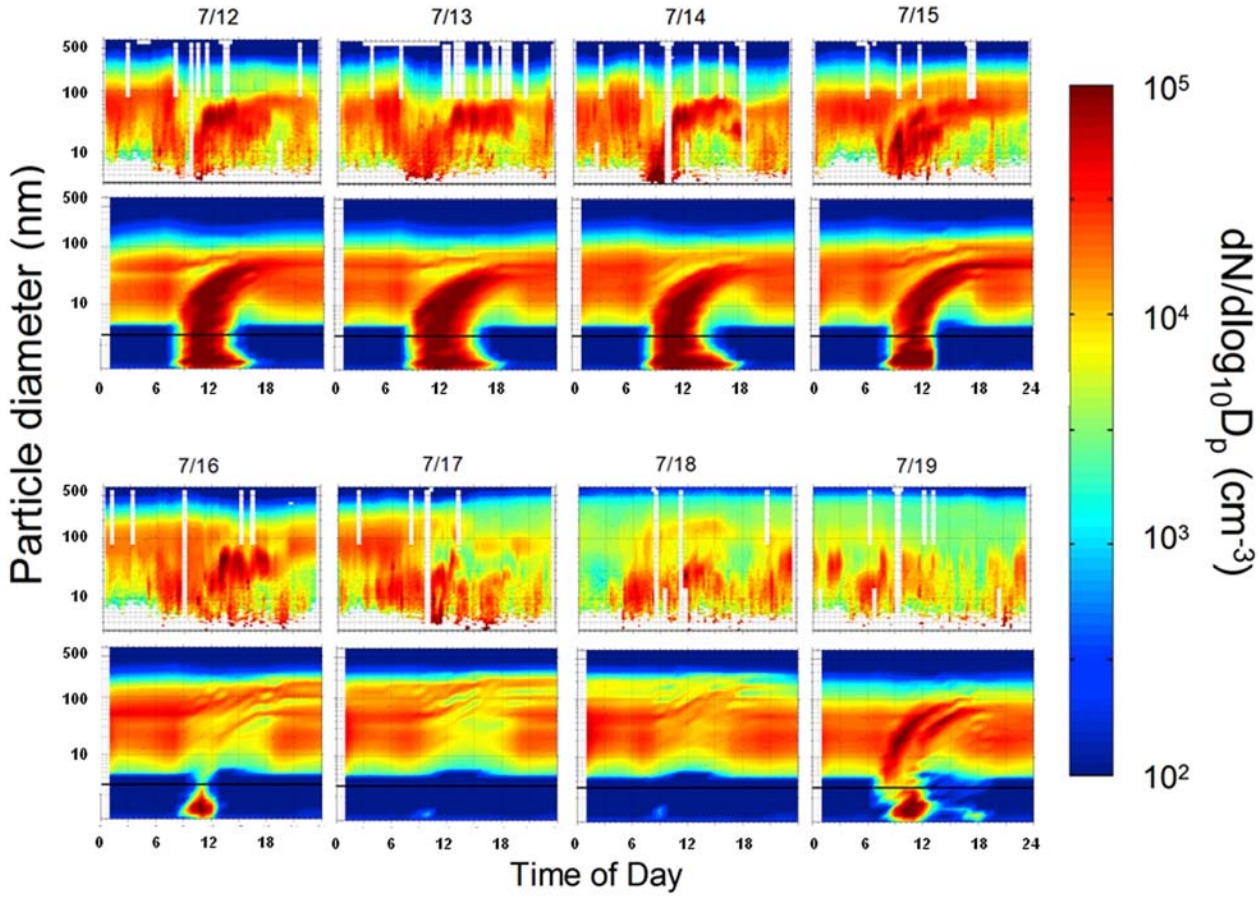

Figure 7. Comparison of (top) measured and (bottom) predicted dry size distribution in Pittsburgh, Pennsylvania, as a function of time from 12 July to 19 July 2001. The predicted diameter range extends to 0.8 nm, while the measured diameter range extends to only 3 nm. A black line in the predicted diameter range indicates the measurement threshold.

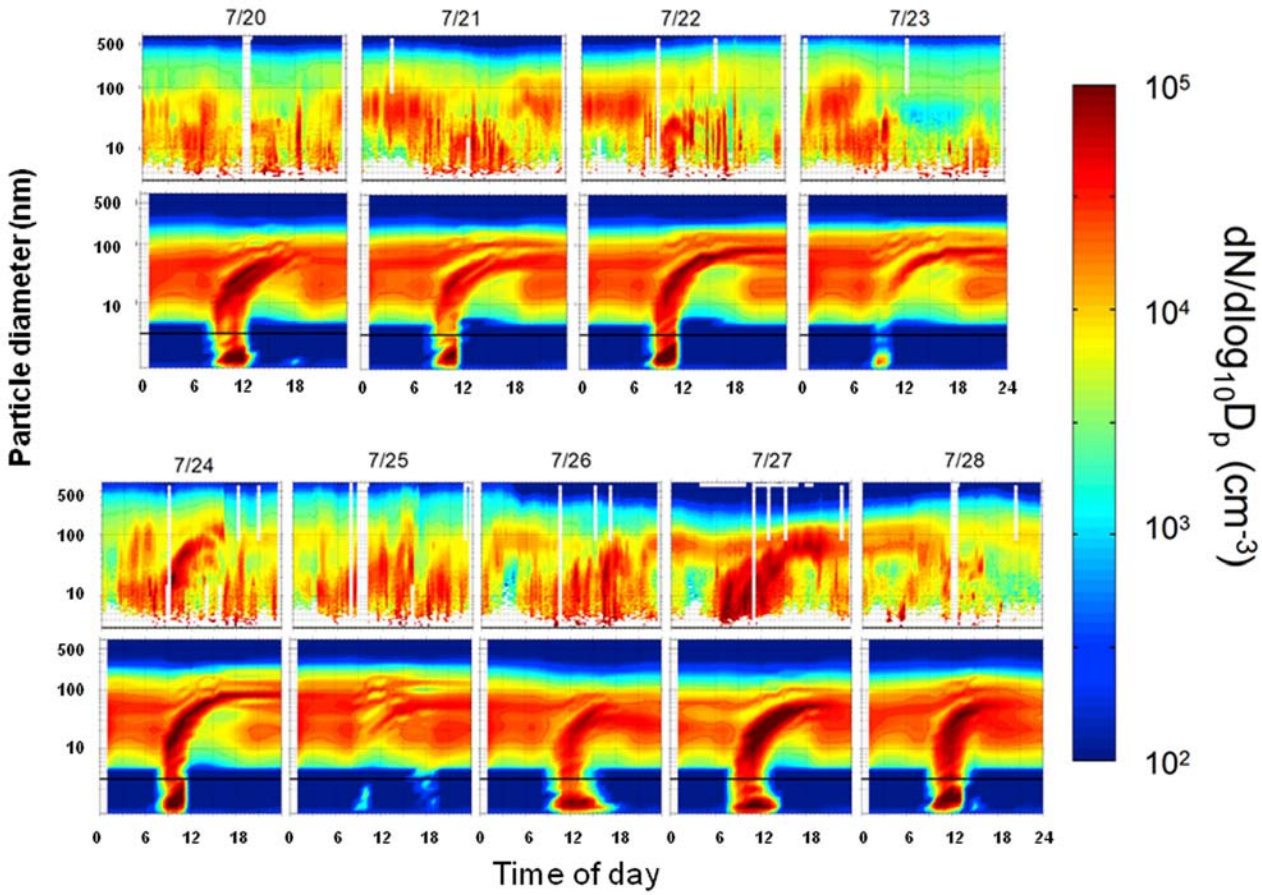

Figure 8. Comparison of (top) measured and (bottom) predicted dry size distribution in Pittsburgh, Pennsylvania, as a function of time from 20 July to 28 July 2001. The predicted diameter range extends to 0.8 nm, while the measured diameter range extends to only 3 nm. A black line in the predicted diameter range indicates the measurement threshold.

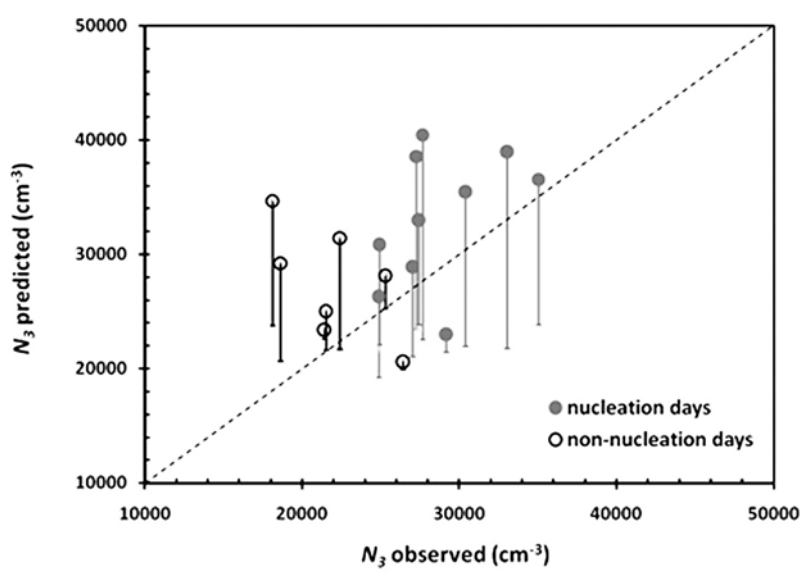

Figure 9. Comparison of measured and predicted (base case) number concentration for particles larger than 3 nm during the Pittsburgh Air Quality Study (PAQS) in July 2001. Each point represents a daily average value of N_3. The error bars show model predictions for $f_n = 10^{-7}$.

Table 2. Sensitivity of Number Concentration Predictions to the Nucleation Rate Parameter f_n and the NH_3 Emissions in Pittsburgh During July 2001[a]

		PMCAMx-UF		
Average (cm^{-3})	Measured	Base Case	$f_n = 10^{-7}$	−50% NH_3
N_3	25,100	30,600 (22)	22,100 (−12)	25,200 (0.4)
N_{10}	17,600	26,200 (49)	20,300 (15)	22,200 (26)

[a]Values in parentheses show the percent error.

number concentration conditions. Reducing f_n causes an underprediction of N_3 for the nucleation days but decreases the error during nonnucleation days. In this sensitivity test PMCAMx-UF predicts nucleation events for 6 out of the 17 days of the simulation while based on measurements 9 days were classified as nucleation days. Compared to the base case, the sensitivity test "corrected" three wrong predictions (on 19, 20, and 28 July) but at the same time resulted in three new false predictions on 21, 22, and 26 July. Overall, decreasing the nucleation rate did not change the number of days correctly predicted. This behavior is due to the fact that errors in a three-dimensional CTM are due not only to the nucleation rate but also on other parameters such as the predicted concentrations of the corresponding gas-phase species or the aerosol surface area.

[29] Another source of uncertainty in the prediction of nucleation events is the ammonia emission levels. The July 2001 simulations were repeated with ammonia emission levels reduced by 50% compared to the base case. Reducing ammonia caused an average reduction in N_3 by 18% and in N_{10} by 15%. The average error for N_3 and N_{10} concentrations decreased (Table 2) and the predicted nucleation events decreased by one (21 July). However, on that day a nucleation event did take place so the number of correct predictions was reduced to 13 (Table 3). For the remaining days the predictions of the occurrence or not of a nucleation event were the same as those of the base case run. For some days (12, 13, and 14 July), the predicted nucleation bursts become more similar to the observations (not shown); however, this sensitivity run also underpredicts the intensity of some other events (15, 16, 21 July). This insensitivity of the model predictions to the ammonia levels is rather expected since the theory of the ternary nucleation [*Napari et al.*, 2002] suggests that nucleation rates should be insensitive to ammonia mixing ratios above 0.1 ppb. During PAQS, ammonia levels ranged most of the time between 0.5 and 6 ppb (Figure 6).

3.4. Nucleation in Other United States Cities

[30] Measurements in urban east St. Louis, Illinois [*Qian et al.*, 2007], showed that nucleation events were observed on 40% of the days during July 2001. Our PMCAMx-UF simulations (base case) predicted nucleation events for 15 out of the 17 days of the simulation period in July 2001, while reducing the nucleation tuner to 10^{-7} predicts nucleation 50% of the time in St. Louis. Nucleation events in Atlanta, Georgia, occurred with around 40% frequency during August 1998 [*Woo et al.*, 2001]. Although this is a different period than our simulation run, this frequency is in agreement with PMCAMx-UF predictions for July 2001 in Atlanta (also 40%) when using the reduced nucleation rate parameter. Reducing ammonia emissions by 50% caused only a small decrease (~10%) in the predicted number of nucleation events in both cities compared to the base case. These results suggest that the 10^{-7} tuner results in predictions that are closer to observations at least in the eastern United States.

4. Conclusions

[31] PMCAMx-UF is a newly developed three-dimensional chemical transport model tracking both aerosol number and mass concentrations. The model relies on the PMCAMx modeling framework replacing its mass-based aerosol module with the Dynamic Model for Aerosol Nucleation (DMAN) [*Jung et al.*, 2006, 2008]. DMAN uses the pseudo-steady state approximation of sulfuric acid, a simplification that increases significantly its computational efficiency without deteriorating its performance. The model uses the ternary nucleation parameterization and a nucleation scaling factor.

[32] PMCAMx-UF was used to simulate 17 days from 12 July to 28 July 2001 in the central and eastern United States. The results show that nucleation events start generally from the east coast and move to the west following the photochemical activity. Nucleation events are predicted to occur over scales of hundreds to thousands of kilometers mainly in the upper Midwest and northeast United States. A much lower nucleation frequency is predicted for the southeast United States. Number concentration of particles is predicted to increase due to nucleation events by roughly a factor of 2.5 (on average) for particles larger than 0.8 nm and 15% for particles larger than 100 nm over the whole domain.

[33] The first comparison with the PAQS measurement data set is encouraging for the frequency, time of onset, and strength of the nucleation events. PMCAMx-UF correctly predicts the occurrence or lack of nucleation in Pittsburgh during 82% of the simulated days. The model has a tendency of overpredicting nucleation. Reducing the nucleation scaling factor to 10^{-7} reduces significantly the predicted frequency

Table 3. Sensitivity of Predictions of Nucleation Events to the Nucleation Rate Parameter f_n and the NH_3 Emissions in Pittsburgh During July 2001[a]

		PMCAMx-UF		
Date (July 2001)	Observed	Base Case	$f_n = 10^{-7}$	−50% NH_3
12	yes	YES	YES	YES
13	yes	YES	YES	YES
14	yes	YES	YES	YES
15	yes	YES	YES	YES
16	no	NO	NO	NO
17	no	NO	NO	NO
18	no	NO	NO	NO
19	no	yes	NO	yes
20	no	yes	NO	yes
21	yes	YES	no	no
22	yes	YES	no	YES
23	no	NO	NO	NO
24	yes	YES	YES	YES
25	no	NO	NO	NO
26	yes	YES	no	YES
27	yes	YES	YES	YES
28	no	yes	NO	yes
Correct predictions		14	14	13

[a]Days are classified as nucleation or nonnucleation days depending on the rate of change of particle number concentration between 3 and 10 nm. A nucleation event has $dN_{3-10}/dt > 2000\ cm^{-3}\ h^{-1}$. Below this value, dN_{3-10}/dt was not distinguishable from the natural variability of particle number due to local primary emissions [*Stanier et al.*, 2004].

and intensity of nucleation events, causing an underprediction in Pittsburgh, while it improves predictions of nucleation frequency in St. Louis, Illinois, and Atlanta, Georgia, during summertime. A reduction of the NH_3 emission levels by 50% caused, on average, a 10% decrease in the number of nucleation events predicted in all three cities.

[34] Although a test of six different parameterizations has been conducted [*Jung et al.*, 2008] using the box model and a modest success was achieved by applying the ternary nucleation parameterization of *Napari et al.* [2002] to the PAQS data set, it remains unclear whether the ternary nucleation theory is the best candidate since the specific parameterization has been challenged [*Merikanto et al.*, 2007; *Anttila et al.*, 2005] and the relative importance of the different nucleation pathways is still debated. Future applications of PMCAMx-UF are planned to focus on testing different nucleation parameterizations in various different environments and seasons. The new model using a series of nucleation mechanisms can be applied in urban/regional air quality and global climate modeling studies.

[35] **Acknowledgments.** This work was supported by NSF ATM-0732598 and the European Commission through the project EUCAARI. C. Fountoukis acknowledges support from a Marie Curie International Reintegration Grant. The authors thank J. R. Pierce for his help with the pseudo-steady state approximation.

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