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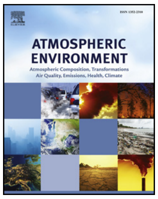

# Overprediction of aerosol nitrate by chemical transport models: The role of grid resolution

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## ABSTRACT

This study examines the role of grid resolution on particulate nitrate predictions over the Eastern US during the summer using the three-dimensional chemical transport model (CTM) PMCAMx. The Base Case simulation with coarse resolution (36 × 36 km) often predicts high nighttime nitrate production rates thus leading to overprediction of aerosol nitrate levels. This overprediction is due to the artificial mixing of $NO_x$-rich plumes from major point and area sources with the background atmosphere. Three different horizontal grid resolutions were tested (12 × 12 km, 4 × 4 km and telescoping 12x12/4 × 4 km) for parts of the northeastern US. The bias for $PM_{2.5}$ nitrate decreased by 65% when the grid resolution was increased to 4 × 4 km. However, the remaining discrepancies between nitrate predictions and measurements indicate the need for additional improvements including better simulation of the total emissions of ammonia and their temporal evolution, improved description of nighttime chemistry and mixing etc.

## 1. Introduction

Inorganic particulate nitrate can be a significant fraction of the total aerosol mass mostly in polluted regions (Adams and Seinfeld, 2002; Hueglin et al., 2005; Jaffe et al., 2005; Park et al., 2004; Pathak et al., 2009; Pringle et al., 2010). Nitrates have been found to be at least as important as sulfates in some regions of Europe and US (Zhang et al., 2007; Xu and Penner, 2012; Malm et al., 2004). Particulate nitrate levels are in most cases higher in urban than in remote areas (Tolocka et al., 2001; Malm et al., 2004; Putaud et al., 2004) and show significant seasonal variation (Malm et al., 2004; Hueglin et al., 2005; Galindo et al., 2008; Cao et al., 2012). The large reduction of $SO_2$ emissions over Europe and US and thus sulfate aerosols over Europe and US has increased nitrate levels in various areas (West et al., 1999; Myhre et al., 2006; Bauer et al., 2007; Pinder et al., 2008; Pye et al., 2009; Bellouin et al., 2011; Hand et al., 2012).

Aerosol nitrate is formed mostly through gas-to-particle conversion processes of nitric acid. Nitric acid is produced during daytime by the reaction of $NO_2$ with the hydroxyl radical (OH) (Seinfeld and Pandis, 2006):

$$NO_2 + OH \rightarrow HNO_3 \quad \text{(R1)}$$

The nighttime pathway forming $HNO_3$ requires the availability of both $NO_x$ and $O_3$ and includes the following reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R2)}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R3)}$$

$$NO_2 + NO_3 \leftrightarrow N_2O_5 \quad \text{(R4)}$$

$N_2O_5$ acts as a nighttime reservoir species for reactive nitrogen (McLaren et al., 2004) and can react with water vapor to produce nitric acid:

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad \text{(R5)}$$

The same reaction with liquid water can take place on an aerosol surface (Joyce et al., 2014):

$$N_2O_5 + H_2O_{(aq)} \rightarrow 2HNO_3 \quad \text{(R6)}$$

The produced nitric acid from reactions (R5) and (R6) can then be transferred to the particulate phase by reacting with $CaCO_3$, $NH_3$, NaCl, etc.

A number of studies have indicated that aerosol nitrate concentrations are often overpredicted by chemical transport models (CTMs). Yu et al. (2005) examined the ability of a three-dimensional air quality model to predict aerosol nitrate in three sites in the US and reported an overprediction of the mean nitrate levels by a factor 1.6 to 4 in all sites.

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Pye et al. (2009) used the chemical transport model GEOS-Chem over the US for 1999–2001 and found that nitrate is typically overpredicted in the Eastern US. Fountoukis et al. (2011) found that aerosol nitrate levels were overpredicted (mean bias ranged from 0.8 to 2.4 μg m$^{-3}$) by PMCAMx in almost all the European measurement stations during May 2008. The WRF/Chem model overpredicted nitrate levels over Europe for 2007 by a factor of 2 (Tuccella et al., 2012). The simulations of Heald et al. (2012) indicated that nitrate concentrations were overestimated in most areas of the US for 2004 and especially in the Eastern US. Walker et al. (2012) also found that nitrate was overpredicted especially in the Eastern and Midwestern US with mean bias of 176% for the whole domain. Im et al. (2015) concluded during the second phase of the Air Quality Model Evaluation International Initiative (AQMEII) that nitrate levels were overestimated by the majority of models used. The simulations of Ciarelli et al. (2016) led to nitrate overprediction in all the examined European sites for February–March 2009, with the mean bias ranging between 0.8 and 4.5 μg m$^{-3}$.

As aerosol nitrate is semi-volatile, its partitioning between the gas and aerosol phases determines to a large extent its concentration in the particulate phase. Errors in the simulation of this gas-to-particle partitioning have been assumed to be one of the causes of the CTM difficulties in reproducing aerosol nitrate levels. However, a number of studies using field measurements suggest that the corresponding thermodynamic models used in CTMs do a reasonable job. Nenes et al. (1999) used three thermodynamic models to predict the physical state and composition of inorganic aerosol and found that all three predicted nitrate concentrations that were in good agreement with observations as the mean error ranged from 3 to 17%. Takahama et al. (2004) used the GFEMN model to simulate the partitioning of $PM_{2.5}$ nitrate and nitric acid using highly time-resolved measurements collected at the Pittsburgh Air Quality study during summer and winter. The model reproduced observed aerosol nitrate concentrations reasonably well and errors in predictions were about 0.5 μg m$^{-3}$ on average, which could be explained by experimental uncertainties. Similar results were reported by Fountoukis et al. (2009) who used ISORROPIA-II in Mexico City.

Heald et al. (2012) investigated other possible causes for the overestimation of nitric acid concentrations, including uncertainties in the formation of $HNO_3$ arising from uncertainties in $NO_x$ emissions and uncertainties in the dry deposition rates of nitric acid. Errors in the simulation of nitrate nighttime chemistry have also been proposed to be one of the reasons for this overprediction (Gaydos et al., 2007; Karydis et al., 2007; Zhang et al., 2012; Stone et al., 2014). Recent studies have suggested that several models tend to use too high values of the $N_2O_5$ hydrolysis uptake coefficient leading to overestimation of particulate nitrate levels (Chang et al., 2016; Chen et al., 2018). Zhu et al. (2017) proposed that organic compounds may react with gas-phase $NH_3$, reducing the free ammonia levels and thus leading to reduction of ammonium nitrate concentration. This process, missing from past studies, could be another explanation for the overprediction of nitrate.

Backes et al. (2016) suggested that uncertainties in the temporal profiles of ammonia emissions in Europe may contribute to the overprediction of ammonium nitrate during summer. The sensitivity of the predicted $PM_{2.5}$ nitrate to emission changes of ammonia in the Eastern US during July 2001 (the same period is used in this study) has been quantified by Tsimpidi et al. (2007). A 50% reduction of ammonia emissions was predicted to lead to a 26% average reduction of nitrate in the domain. The predicted nitrate was reduced by 36% in the Midwest and by 21% in the Northeast and South US during the simulation period.

Another potential cause of error in the predictions of regional-scale CTMs may be the coarse grid resolution used. However, a number of studies have found only small to modest improvements in the ability of regional CTMs to reproduce the concentration fields of secondary pollutants, like ozone (Kumar et al., 1994; Russell and Kumar, 1996; Arunachalam et al., 2006) and secondary organic aerosol (Stroud et al., 2011; Fountoukis et al., 2013), when their resolution was increased.

In this study we explore the hypothesis that in areas with major $NO_x$ sources the coarse resolution cannot capture the gradients in $NO_x$ and $O_3$ in the corresponding plumes, especially during the night. To test this hypothesis, we use the Particulate Matter Comprehensive Air quality Model with extensions (PMCAMx) over the Eastern US during July 2001. This area is characterized by tens of major power plants and has a relatively dense aerosol measurement network reporting $PM_{2.5}$ nitrate levels. The aim of this work is to study the impact of grid resolution (36 × 36 km, 12 × 12 km, and 4 × 4 km are tested) on $PM_{2.5}$ nitrate production, especially during the nighttime.

## 2. Model description

PMCAMx (Tsimpidi et al., 2010; Karydis et al., 2010) uses the framework of the CAMx air quality model (Environ, 2003) describing the processes of horizontal and vertical advection, horizontal and vertical diffusion, wet and dry deposition, gas- and aqueous-phase chemistry. For the aerosols, a sectional approach is used to dynamically track the size evolution of the aerosol mass across 10 size sections spanning from 40 nm to 40 μm. The aerosol species modeled include sulfate, nitrate, ammonium, sodium, chloride, elemental carbon, primary and secondary organics. The PMCAMx version used in this work simulates the concentrations of mineral aerosol, but assumes that these particles are inert. This simplification will tend to decrease the predicted $PM_{10}$ nitrate concentrations. This effect could be important for areas with high levels of dust or sea-salt however this is not the case for the Northeast US and especially Pittsburgh. The measurements of Cabada et al. (2004) for the period simulated here showed that the coarse PM was on average around 15% of the $PM_{2.5}$. The effect of the corresponding low dust levels on nitrate partitioning is marginal. On the other hand, these alkaline particles can have an important effect on nitrate concentrations in other areas of the world (Trump et al., 2015). The gas-phase chemical mechanism used is based on the SAPRC mechanism (Carter, 2000; Environ, 2003). The version of SAPRC used here includes 237 reactions of 91 gases and 18 radicals. More details about the gas-phase chemistry can be found in Karydis et al. (2007). PMCAMx simulates only the homogeneous pathway of the $N_2O_5$ hydrolysis and does not simulate explicitly the heterogeneous pathway that can be much faster. The rate coefficient used is based on the work of Dimitroulopoulou and Marsh (1997). Therefore, PMCAMx for all practical purposes uses a lower limit for the $N_2O_5$ hydrolysis rate that is lower than that of Chen et al. (2018).

Three options are available in PMCAMx for the simulation of inorganic aerosol growth. The most computationally efficient approach is the bulk equilibrium approach, that is used here, which assumes equilibrium between the bulk inorganic aerosol and gas phase and implicitly a uniform particle composition with size. At a given time step the amount of each species transferred between the gas and aerosol phases is determined by applying the aerosol thermodynamic equilibrium model ISORROPIA (Nenes et al., 1998) and is then distributed over the aerosol size sections by using weighting factors for each size section based on their surface area (Pandis et al., 1993). This scheme has the potential of overpredicting the fine nitrate and underpredicting the coarse nitrate in areas with high dust (Karydis et al., 2010) or sea-salt levels (Trump et al., 2015). In these cases, explicit simulation of the mass transfer to at least the coarse particles is required. However, the concentrations of the coarse particles in the focus area of the northeastern US were quite low (less than 20% of the fine PM levels) so the use of this scheme should introduce marginal error in the corresponding simulation results in this case.

Primary organic aerosol (POA) in PMCAMx is assumed to be semivolatile (Shrivastava et al., 2008). Secondary organic aerosol (SOA) consists of organic aerosol of anthropogenic (aSOA) and biogenic