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Improvement of simulation of fine inorganic PM levels through better descriptions of coarse particle chemistry

Erica R. Trump [a], Christos Fountoukis [b], Neil M. Donahue [a], Spyros N. Pandis [a, c, *]

[a] Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA
[b] Institute of Chemical Engineering Sciences, ICEHT/FORTH, Patras, Greece
[c] Department of Chemical Engineering, University of Patras, GR 26500, Greece

HIGHLIGHTS

- Sea-salt particles in polluted areas cause reductions in submicron PM nitrate.
- Overprediction of fine nitrate due to inability to describe fine-coarse competition.
- A hybrid dynamics scheme leads to significant improvement of nitrate performance.

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ABSTRACT

Atmospheric chemical transport models (CTMs) have often serious difficulties reproducing the observed aerosol nitrate levels. We hypothesize that one of the reasons for these errors is their treatment of the competition between the accumulation and coarse-mode particles for the condensing nitric acid. The hybrid mass transfer method is used in the CTM PMCAMx to test this hypothesis. The simulation approach combines the dynamic calculation of mass transfer to coarse-mode particles while maintaining computational efficiency by assuming that the fine mode particles are in equilibrium. The resulting model is applied to Europe and evaluated for the period of May 2008 against ground-based and airborne Aerosol Mass Spectrometer measurements from the EUCAARI campaign.

PMCAMx using the default equilibrium approach to calculate the partitioning of semi-volatile PM components between the gas and particle phases seriously overpredicts PM_1 nitrate levels especially for locations in which there were relatively high coarse-mode particle concentrations (significant sea-salt or dust concentrations). This shortcoming was especially apparent for the Mace Head site in Ireland, where a large amount of nitrate was associated with sea-salt. The improved simulation of the coarse-mode particle chemistry results in significant improvement of the predictions of PM_1 nitrate and ammonium. Sea-salt emissions in areas with high nitric acid levels reduce the PM_1 nitrate concentrations.

1. Introduction

Atmospheric particulate matter (PM) has important air quality and climatic effects. Fine particulate mater in particular is associated with adverse human health effects (Peters et al., 1997; Pope et al., 2009). For this reason, many air quality studies focus on predictions of particles having diameters less than 1 μm (PM_1) or 2.5 μm ($PM_{2.5}$). Particulate nitrate is an important aerosol component influencing regional air quality, visibility and water uptake (Adams et al., 1999).

Nitrate predictions by CTMs have proven to be challenging for many reasons. First, because nitrate is a secondary species, its simulations rely on accurate gas-phase emissions inventories and accurate descriptions of gas-phase chemistry. Second, the gas-particle partitioning of nitrate is sensitive to meteorological conditions such as ambient relative humidity and temperature, as well as to aerosol pH, which is highly influenced by the presence of sulfate (another secondary species). Third, nitrate partitioning is sensitive to the presence of sea-salt. Stelson and Seinfeld (1982) developed the first models to predict ammonium-nitrate concentrations based on thermodynamic principles. In one of the early

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[*] Corresponding author. Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA
E-mail address: spyros@andrew.cmu.edu (S.N. Pandis).

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CTM studies, total nitrate (PM nitrate + HNO_3) predictions mostly agreed with measurements; however PM nitrate predictions near coastal areas were not accurate (Russell et al., 1988). Thermodynamic models were extended to represent the interaction of nitrate and sea salt (Pilinis and Seinfeld, 1987), and later models were further improved to better represent complex multi-component interactions (Nenes et al., 1998). The most recent thermodynamic models also include interactions with the crustal components calcium, magnesium, and potassium (Fountoukis and Nenes, 2007).

Nitrate interacts with both fine- and coarse-mode particles, and therefore resolving the predicted particle mass into PM_1 and coarse components poses an additional challenge. Significant portions of PM nitrate may be associated with coarse-mode cations such as sodium from sea spray. The competition between fine and coarse particles needs to be simulated accurately in order to correctly predict PM_1 nitrate concentrations.

Fountoukis et al. (2011) previously evaluated the PM_1 predictions of PMCAMx-2008 against aerosol mass spectrometry (AMS) data for Europe. Measurements from May 2008 are available from the intensive European Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) campaign (Kulmala et al., 2009). During the campaign, AMS measurements were collected from four ground-based stations across Europe: Cabauw, Netherlands; Finokalia, Greece; Mace Head, Ireland; and Melpitz, Germany. For all EUCAARI stations, the modeled results reported by Fountoukis et al. (2011) were in good agreement with hourly measurements for the organic aerosol (OA) and sulfate components of PM_1. At each location, at least 80% of OA and at least 60% of sulfate predictions were within a factor of two of the AMS measurements. However, model performance was poorer for PM_1 nitrate and ammonia. For Mace Head there was a significant over-prediction of PM_1 nitrate, with only 16% of predictions within a factor of two of the AMS measurements. PM_1 ammonium was also substantially overpredicted for Mace Head (only 20% of predictions within a factor of two of the measurements).

Many contemporary air quality models have had difficulty reproducing PM nitrate concentrations over Europe. The EUROTRAC 2 Report indicated that the models EUROS, LOTOS, REM3 and EURAD/FFA all overpredicted PM nitrate, though most models performed better for total nitrate (Hass et al., 2003). Further, the Polyphemus/Polair3D CTM significantly overestimated PM nitrate (Lecoeur and Seigneur, 2013). On the other hand, the CALIOPE CTM using the CMAQv4.5 aerosol module, which does not account for the association of nitrate with coarse-mode cations, underpredicted total PM nitrate for Europe (Basart et al., 2012).

Given the above problems our fundamental understanding of aerosol nitrate formation and removal has come into question. Our hypothesis is that at least some of the difficulties encountered in previous studies (e.g., Fountoukis et al., 2011) were caused by the simplifying assumptions used in the corresponding modeling studies. The "bulk equilibrium" method used by Fountoukis et al. (2011) assumes that the gas phase equilibrates instantaneously with the entire particulate mass without accounting for the dependence of chemical composition on size. In Mace Head, where the model predictions for PM_1 nitrate were quite problematic, there was both a significant amount of ammonia present in the gas phase and also a lot of sea salt; there was thus a competition for nitrate condensation between the fine- and coarse-mode particles. This competition is not represented by the bulk equilibrium method used in that study.

In this work we apply the three-dimensional CTM PMCAMx-2008 to model the atmosphere over Europe for May 2008. We utilize a more accurate method for describing the gas-particle partitioning of inorganic species. The earlier work of Karydis et al. (2010), which employed PMCAMx-2004 with the hybrid method, demonstrated that mineral dust in Mexico City has a substantial influence on PM_1 predictions. The employed hybrid method combines two approaches: thermodynamic bulk equilibrium is assumed for the smallest particles (<1 μm), while the mass transfer to the larger particles is calculated explicitly (Capaldo et al., 2000). Additionally, we apply the updated thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007) to describe the thermodynamics of the crustal species calcium, potassium, and magnesium. For comparison, we also simulate the atmosphere over Europe using the bulk-equilibrium method for all particle sizes; these results are comparable to the work of Fountoukis et al. (2011). We refer to particles having wet diameters greater than 1 μm but less than 10 μm as coarse-mode particles or PM_{1-10}.

2. Model description and application

2.1. PMCAMx-2008

PMCAMx uses the framework of the CAMx air quality model to simulate advection and dispersion, wet and dry deposition, and gas-phase chemistry. PMCAMx describes the size-resolved evolution of particulate matter (PM) through the inclusion of three detailed modules: inorganic aerosol formation, aqueous-phase processing, and organic aerosol formation. PMCAMx-2008 includes an improved organic aerosol module in which both primary and secondary organic species are treated as semivolatile and reactive (Lane et al., 2008; Murphy and Pandis, 2009). The approach of Fahey and Pandis (2001) is used for the simulation of aqueous-phase chemistry. The SAPRC99 chemical mechanism is used to describe the gas-phase chemistry (Carter, 2000). Particle mass and composition are resolved across 10 discrete aerosol size sections, with particle wet-diameters ranging from 40 nm to 40 μm. In this work, PMCAMx-2008 with ISORROPIA II (Fountoukis and Nenes, 2007) is applied to Europe to calculate aerosol thermodynamic equilibrium for inorganic species. Modeled aerosol species include: sulfate, nitrate, ammonium, sodium, chloride, potassium, calcium, magnesium, elemental carbon, and primary and secondary organics. Additional details regarding PMCAMx-2008 are given in Fountoukis et al. (2011).

2.2. Partitioning of semi-volatile components

The most computationally efficient method for calculating gas-to-particle mass transfer in PMCAMx is the bulk equilibrium approach (Capaldo et al., 2000); however, this method relies on a number of simplifying assumptions. First, although particle composition is size-resolved within PMCAMx, partitioning is simulated based on the bulk particle mass; this implicitly assumes a uniform composition across all particle sizes. ISORROPIA II is used to calculate the mass transfer required to bring the particle bulk into thermodynamic equilibrium with the gas phase; the condensing or evaporating mass is then distributed to the size-resolved aerosol sections in proportion to particle condensation sink (Pandis et al., 1993). An additional assumption is that this equilibration occurs instantaneously. For the smallest particles, which have equilibration timescales shorter than the 10-min simulation time step, this is a good assumption; however larger particles are not necessarily in equilibrium with the gas phase (Wexler and Seinfeld, 1990). The coarse mode particles (especially the larger ones) are often not in equilibrium with the gas phase in polluted environments in which the concentrations of semi-volatile inorganic particle components (nitric acid, hydrochloric acid, ammonia) change rapidly (Meng and Seinfeld, 1996; Pilinis et al., 2000).