DIAGNOSTIC STUDY ON FINE PARTICULATE MATTER PREDICTIONS OF CMAQ IN THE SOUTHEASTERN U.S.

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1. INTRODUCTION

Fine particulate matter ($PM_{2.5}$) is a significant pollutant due to its impacts on human health, visibility degradation, and climate change. The complex physical and chemical processes associated with $PM_{2.5}$ formation, transport, and fate make the accurate representation of $PM_{2.5}$ difficult in air quality models. An operational evaluation of the U.S. EPA Models-3/Community Multiscale Air Quality (CMAQ, v4.4) modeling system was conducted previously for the 1999 Southern Oxidants Study episode for the period of 12-28 June 1999. The results show that the CMAQ model significantly underpredicts nitrate (NO_3^-), organic carbon (OC), and black carbon (BC), and moderately overpredicts sulfate (SO_4^{2-}) during this episode (Liu et al., 2005).

Process analysis (PA) is an approach that tracks the contribution of a process to the species conservation equation (Jeffries and Tonnesen, 1994). It has been applied to study ozone (O_3) chemistry and transport (Jeffries and Tonnesen, 1994; Jang et al., 1995; Jiang et al., 2003; O'Neill and Lamb, 2005), impacts of climate change on O_3 and particles (Hogrefe et al., 2005), and particle number concentration and size distribution (Zhang et al., 2005). PA consists of the Integrated Process Rates (IPRs) analyses and Integrated Reaction Rates (IRRs) analyses. IPRs quantify the contributions of different physical and chemical processes to the ambient concentrations of the species of interest; IRRs quantify the chemical evolution of gaseous species (Byun and Ching, 1999). In this study, we use the PA tool embedded in CMAQ to examine major processes that govern the fate of key pollutants, identify the most influential processes that contribute to model errors, and guide the diagnostic and sensitivity studies aimed at improving model predictions of inorganic $PM_{2.5}$. IPRs and IRRs are first calculated and analyzed for $PM_{2.5}$ mass, $PM_{2.5}$ composition, and gaseous precursors of secondary $PM_{2.5}$ at surface layer to identify dominant processes. Eight sites in the Southeastern Aerosol Research and Characterization (SEARCH) network in the southeastern U.S. are selected for IPRs analyses. The IPRs are calculated as an average of the hourly values over a 15-day period for a block of grid cells that contains each site, where the block is defined as the grid cell in which the site is located and its eight surrounding grid cells. The correlation of the large model errors and the individual process contributions are then analyzed for SO_4^{2-} and NO_3^- at SEARCH urban and rural sites (where the large model error refers to a value of > 20% for the absolute difference between predictions and observations). If a particular process is highly correlated with the large errors, this process may contribute to the error. The IRRs of 214 reactions in the Statewide Air Pollution Research Center Mechanism (SAPRC99) are also analyzed, especially those reactions related to HNO_3 production and depletion. Finally, several sensitivity simulations are conducted to analyze the model responses to changes in key processes identified via IPRs and those that are correlated with model errors. Specific uncertainties examined through sensitivity studies include the dry deposition velocities of $PM_{2.5}$ precursors (e.g., HNO_3, NH_3, and SO_2), the emissions of NH_3, and the in-cloud SO_4^{2-} formation (e.g., the aqueous-phase oxidation of SO_2 in the presence of H_2O_2 and cloud).

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2. SUMMARY

Major physical and chemical processes (≥ 10% of total production or loss in a block of cells) contributing to the changes of surface $PM_{2.5}$, NO_3^-, NH_4^+, SO_4^{2-}, and their precursors, HNO_3, NH_3, and SO_2, are identified in both urban and rural areas. Emissions and aerosol processes are two major contributors to the increase of $PM_{2.5}$, while vertical transport, dry deposition, and cloud processes contribute to the loss of $PM_{2.5}$ in most areas. The dominant processes may

be different for different $PM_{2.5}$ components and their gaseous precursors. Column IPRs will be further analyzed to understand the effects of different processes in the boundary layer. The correlation between major atmospheric processes in the surface layer and model biases shows that the largest model errors at urban sites correlate with vertical transport and emissions for both SO_4^{2-} and NO_3^- and with aerosol processes for NO_3^-. At rural sites, the positively-correlated processes include aerosol processes, vertical transport, cloud processes for SO_4^{2-}, and horizontal and vertical transport for NO_3^-. The strongest anti-correlation is found for dry deposition and mass balance adjustment at both urban and rural sites. Large contrasts between urban and rural sites exist for the correlations of model biases with some processes such as aerosol processes and emissions for SO_4^{2-} and NO_3^-.

The sensitivity studies show that decreased dry deposition velocities of HNO_3 and NH_3 and increased NH_3 emissions can increase NO_3^- and NH_4^+ formation, therefore appreciably improving NO_3^- and NH_4^+ predictions when they are both underpredicted. A 10% reduction of dissolved H_2O_2 concentration cannot significantly affect the SO_4^{2-} formation during this episode. More sensitivity simulations can be conducted to investigate other possible reasons that affect SO_4^{2-}, NO_3^-, and NH_4^+, including the emissions of SO_2 and primary SO_4^{2-}, the rate constant for the gas-phase SO_2 oxidation reaction (i.e., with OH), dinitrogen pentoxide (N_2O_5) hydrolysis, and PM processes such as gas-to-particle conversion via thermodynamic equilibrium and condensation. For example, the rate constant of gas-phase SO_2 oxidation by OH used in SAPRC99 is up to 15% higher than that of the Carbon Bond Mechanism IV (CBM-IV) under some particular conditions (i.e., relatively low temperature and relatively high pressure), since this oxidation reaction is both temperature and pressure dependent. This may contribute partly to the overpredictions in SO_4^{2-}. As indicated in Bhave et al. (2006), the heterogeneous reaction probability of N_2O_5 is a function of not only SO_4^{2-} and NO_3^- concentrations, but also temperature and relative humidity. Uncertainties in the rate of N_2O_5 hydrolysis may likely contribute to the model bias in simulating $PM_{2.5}$ and its composition.

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