PREDICTING AEROSOL NUMBER AND SIZE DISTRIBUTION WITH CMAQ: HOMOGENEOUS NUCLEATION ALGORITHMS AND PROCESS ANALYSIS

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1. INTRODUCTION

Accurately simulating number concentration and size distribution of particulate matter (PM), in particular, PM with an aerodynamic diameter up to 2.5 μm ($PM_{2.5}$), is a challenge in PM modeling. Emissions and homogeneous nucleation are the two major processes to generate new particles; they thus play an important role in determining the number and mass concentrations and the shape of the size distributions of $PM_{2.5}$. Large uncertainty exists in the homogeneous nucleation parameterizations that are derived either empirically from laboratory experiments or from kinetic models that are based on classical binary and ternary nucleation theories (Zhang et al., 1999; Zhang and Jacobson, 2005). A comparative study of seven binary and one ternary homogeneous nucleation parameterizations has been recently conducted in a box model (Zhang and Jacobson, 2005). Significant differences are found among the binary nucleation rates calculated with different parameterizations and between the binary and ternary nucleation rates (e.g., by up to 3-7 orders of magnitude under specific conditions). In this study, four homogeneous nucleation parameterizations, three for binary nucleation (i.e., Pandis et al. (1994), Fitzgerald et al. (1998), and Vehkamäki et al. (2002)) and one for ternary nucleation (i.e., Napari et al. (2002)), have been implemented into the U.S. EPA Models-3/Community Multiscale Air Quality (CMAQ) modeling system and compared with two existing parameterizations in CMAQ (i.e., Kulmala et al. (1998) in CMAQ v4.4 and Harrington and Kreidenweis (1998) in all versions prior to v4.4). The 12-28 June 1999 Southern Oxidants Study (SOS) episode is selected as a testbed to evaluate the PM number and size predictions of CMAQ with the six different nucleation parameterizations. The predicted number concentrations and size distributions of PM are evaluated against measurements from the Aerosol Research and Inhalation Epidemiology Study (ARIES) (McMurry et al., 2000; Woo et al., 2001; Woo, 2003). The statistical measures are calculated and analyzed for the total number, volume, and surface areas of $PM_{2.5}$ as a sum of the Aitken- and accumulation-mode PM and those of PM in individual segregated size sections over the diameter range of 0.00306 to 2 μm that was used in the ARIES measurements for PM_2.

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2. SUMMARY OF THE SIMULATION RESULTS

The simulation results show that all nucleation parameterizations overpredict (by a factor of 1.35 to 2.07) the total number concentrations of accumulation-mode PM; all but that of Harrington and Kreidenweis (1998) significantly underpredict (by a factor of 1.95 to 55.57) the total number concentrations of Aitken-mode PM. The Harrington and Kreidenweis (1998) parameterization overpredicts the total Aitken-mode PM number by a factor of 13.24. The PM number predictions with different nucleation parameterizations can differ by 4 and 1.5 orders of magnitude for Aitken- and accumulation-mode PM, respectively, with the lowest by Kulmala et al. (1998) and the highest by Harrington and Kreidenweis (1998). The ternary nucleation parameterization of Napari et al. (2002) gives the best overall performance in predicting PM number and size distributions in terms of both temporal variations and performance statistics.

Major atmospheric processes and their relative impact on model predictions of PM number and size distribution are analyzed through the Integrated Process Rate (IPR) analysis and sensitivity studies. These processes include horizontal transport, vertical transport, emissions, dry deposition, PM processes, aqueous processes, and mass balance adjustment. PM processes represent the net effect of PM thermodynamics, new particle formation due to homogeneous nucleation, gas-to-particle mass transfer, condensation of sulfuric acid and organic compounds on preexisting particles, and coagulation in and between Aitken and accumulation modes. Aqueous processes represent the net effect of aqueous-phase chemistry, cloud scavenging, and wet deposition. At Jefferson Street (JST), Atlanta, GA where the ARIES measurement data are available, the production of Aitken-mode number is dominated by PM processes and vertical transport (49.88% and 49.33%, respectively); its loss is dominated by dry deposition (96.5%). Emissions contribute to 0.79% of Aitken-mode number production; and aqueous processes, horizontal transport, and mass balance adjustment contribute to 2.9%, 0.53%, and 0.07%, respectively, of its loss. Production of new particles through homogeneous nucleation is greater than the loss due to intra- and inter-mode coagulation, resulting in a net production due to PM processes. The controlling processes for accumulation-mode PM number are quite different. Emissions dominate its production (~100%), and vertical transport, aqueous processes, and horizontal transport (65.55%, 15.87%, and 10.23%, respectively) dominate its loss. The controlling processes for PM number, volume, and surface areas are being contrasted at different locations representative of remote, rural, coastal, and urban conditions. The causes for underestimation in Aitken-mode number and overestimation in accumulation-mode number are being identified through sensitivity studies.

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