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MODELING REGIONAL HAZE IN BIG BEND NATIONAL PARK WITH CMAQ

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1. INTRODUCTION

The Big Bend Regional Aerosol and Visibility Observational (BRAVO) study was designed to investigate the probable causes of visibility degradation in Big Bend National Park (BBNP), Texas. The field study took place in 1999. Gaseous inert tracers were released from several locations and their ambient concentrations were monitored at several sites including BBNP. In addition, measurements of aerosols and precursors were conducted at 40 sites within the study area. As a key component of BRAVO, the atmospheric processes that govern the transport and transformation of the pollutants that contribute to regional haze are simulated using state-of-the-science modeling tools.

CMAQ is a state-of-the-science 3-D model that was developed by the U.S. Environmental Protection Agency (EPA)[1]. CMAQ is first applied in the BRAVO study without its treatment of chemical transformation to simulate the transport and dispersion of inert tracers [2]. With chemistry and aerosol dynamics, CMAQ is applied to simulate $PM_{2.5}$ and regional haze.

2. SIMULATION METHODS

Two regional haze episodes at BBNP were simulated: (1) August 15 to August 25 and (2) October 5 to October 15. The August period featured southerly winds. In the October episode, prevailing winds were from the northeast to southeast.

The simulation domain covers an area extending about 1500 km in the east-west direction and 900 km in the north-south direction with nested grids of 12 km and 4 km horizontal resolution. A resolution of 4 km is applied over the BBNP area [2].

Meteorological fields were obtained from a simulation conducted by the group of Professor Nelson Seaman at Pennsylvania State University using the prognostic meteorological model MM5 with four-dimensional data assimilation.

Emission inventories were compiled for U.S. and Mexican point, area, non-road, mobile, and biogenic sources for the BRAVO project [3]. The Sparse Matrix Operator Kernel Emissions (SMOKE) model was used by MCNC to generate model-ready emission input files. Sea salt emissions were generated using a separate processor and merged into the input files.

Initial conditions (IC) were generated from available measurements (e.g., BRAVO, IMPROVE, CASTNet) using spatial interpolation. Default concentrations were used for species for which no data are available. Boundary conditions (BC) for gases and particles were obtained from routine measurements at IMPROVE and CASTNet sites outside the domain.

The version of CMAQ used in this work is the August 2000 version as released by EPA. The model is enhanced with the addition of new modules, including the Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution (MADRID) [4] and the Carnegie-Mellon University (CMU) aqueous-phase chemical kinetic mechanism [5]. MADRID simulates the chemical composition of PM and the dynamics of the particle size distribution. In the BRAVO application, particulate matter is represented in two size sections: a fine section representing $PM_{2.5}$ and a coarse section representing $PM_{2.5-10}$.

MADRID 1 uses ISORROPIA [6] to simulate the thermodynamics of inorganic PM species in MADRID. ISORROPIA treats sulfate, nitrate, ammonium, sodium, chloride and water and solves the thermodynamic equilibria of the various chemical species in the gas, liquid and solid phases. Therefore, coarse nitrate particles can be

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simulated when chloride ions in sea salt are displaced by nitrate. MADRID offers a more detailed secondary organic aerosol (SOA) formation than the basic CMAQ. The formulation of MADRID 1 uses an empirical representation of SOA formation that is based on data obtained in smog chamber experiments [7, 8]. The MADRID 1 formulation for SOA includes two anthropogenic VOC precursors, which are characterized as one with low SOA yield (XYL) and one with high SOA yield (TOL). The SOA products were added to the products of the reactions of these two species with OH. We use twelve biogenic precursors of SOA. The Clausius-Clapeyron equation is used to account for the temperature dependence of the saturation vapor pressure. Values of 88 kJ/mole and 175 kJ/mole are used for the enthalpy of vaporization of condensable products from terpenes and aromatics (< C10) and sesquiterpenes, respectively [9, 10].

3. RESULTS

Figure 1 shows time series of 24-hour average fine particulate sulfate concentrations during the October episode. The maximum 24-hour average sulfate concentrations were observed at BBNP on October 12. Simulated concentrations in the 4-km resolution domain also showed a peak on that day. In general, the simulation reproduced the daily fluctuations in sulfate concentrations although with lesser amplitude. A regression between the observed and simulated data shows a coefficient of determination (R^2) of 0.69 at the BBNP site.

On October 12, the observed 24-hour average $PM_{2.5}$ concentration was 13.5 $\mu g/m^3$ at BBNP, whereas 9.7 $\mu g/m^3$ was predicted by CMAQ-MADRID (i.e., 28% underprediction). A comparison between the observed and predicted chemical compositions of $PM_{2.5}$ in BBNP is shown in Figure 2. The largest component of $PM_{2.5}$ was sulfate in both the observed (55%) and predicted (54%) PM. The other components ranked as follows in the observation: the second most abundant component was ammonium, representing 16% of the fine PM mass, the third was the “other” component (15%), including small concentrations of sea salt, and organic compounds (12%) ranked fourth. Primary and secondary organic compounds (OC) ranked second in the simulated composition and accounted for 20% of the simulated PM mass. The contribution of SOA exceeded that of primary OC at BBNP, with biogenic SOA dominating the simulated SOA concentrations. The third most abundant component in the simulated PM was ammonium (14%). The “other” PM component constituted about 12% of the predicted PM. These components ranked second and third in the observed PM and were slightly under-represented in the model predictions. Elemental carbon (EC) and nitrate, which were minor components of $PM_{2.5}$, were under-represented by the model.

4. CONCLUSION

The initial results of the application of CMAQ-MADRID to the BRAVO show satisfactory model performance for a regional simulation. A comprehensive model evaluation will be performed for both episodes using the tracer data as well as gaseous and particulate data from all sites within the BRAVO domain. Additionally, sensitivity studies will be conducted to identify areas of source contribution.

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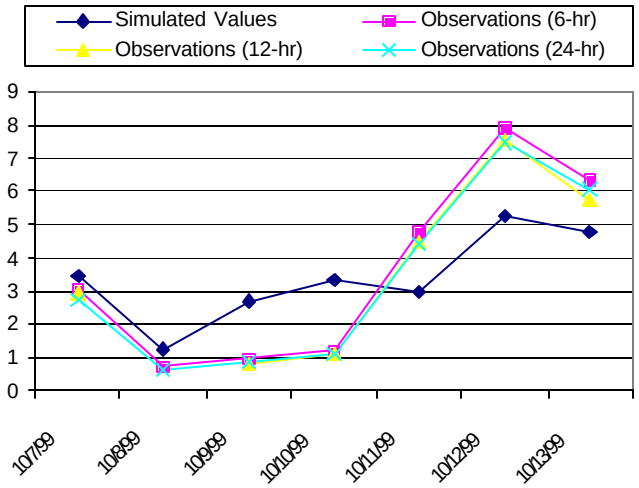

Fig. 1 Comparison of 24-hour average observed and predicted $PM_{2.5}$ time series at Big Bend National Park.

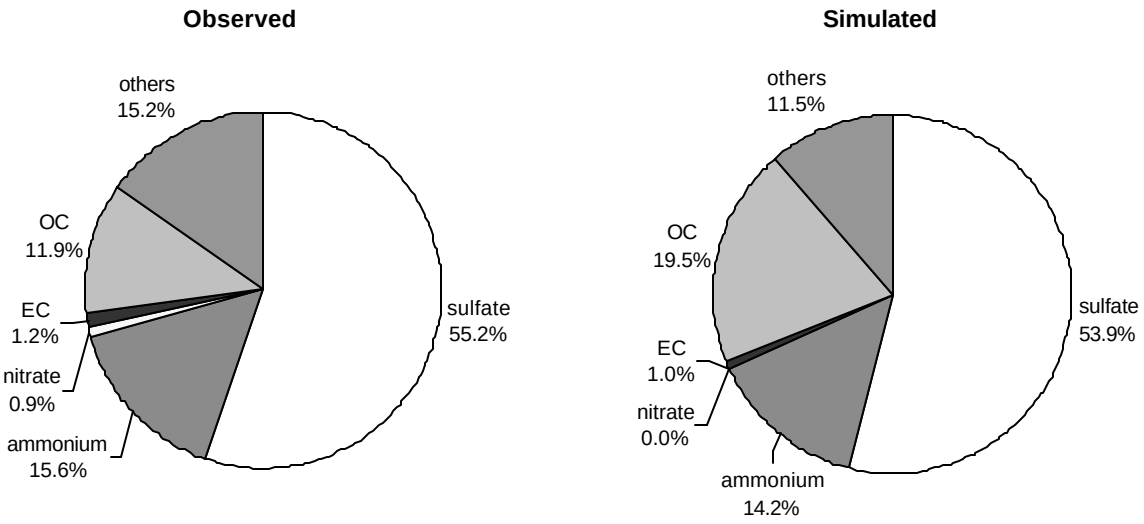

Fig. 2 Comparison of observed and predicted $PM_{2.5}$ chemical compositions at Big Bend National Park on 12 October 1999.