Introduction

Atmospheric models must be fast in order to be useful on urban, regional, and global scales. However, the speed of atmospheric models often comes at the expense of accuracy. Many of today’s models use methods to condense a large system of chemical reactions down to a few reactions to make the model faster. Since organic species are combined into groups, their individual characteristics are lost. This negatively impacts the accuracy of the gas-phase chemistry because even similar species may react very differently in the atmosphere. It also reduces the ability to model aerosol formation because the vapor pressures of species in the same group can differ greatly. These limitations can be overcome by using an explicit mechanism, but it is important that the speed of the model does not suffer. Here, we examined the speed and accuracy of using the Master Chemical Mechanism (MCM) version 3.1 in SMVGEAR II (Jacobson 1994, 1995, 1998b) by measuring the speed and comparing the results to smog chamber data. An earlier version of MCM was previously investigated using SMVGEAR (Liang et al. 2000).

Chemical Mechanism

The Master Chemical Mechanism (MCM) is a near-explicit chemical mechanism describing the tropospheric degradation of 135 commonly-emitted volatile organic chemicals (VOCs). It was developed at LEEDS University (http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmemprev.html) and is being continuously updated with the latest scientific information. The current version (3.1) incorporates over 13,500 chemical reactions and over 4,600 species. The aromatics in particular have been updated since the earlier versions, but their true mechanisms are still under investigation.

Gear Solver

SMVGEAR II is a sparse-matrix ordinary differential equation (ODE) solver. It was chosen for two main reasons – it uses a Gear solution mechanism, which is considered accurate, and it uses a sparse-matrix technique during matrix decomposition and backsubstitution that dramatically decreases the run times.

Accuracy

To test the accuracy of MCM v. 3.1 in the SMVGEAR II solver, it is important to compare the model results with smog chamber data. Here, we compared the results for four different species: two alkenes (1-butene and propene) and two aromatics (toluene and m-xylene).

Outdoor Smog Chamber:

The toluene and m-xylene data was from the University of North Carolina’s large outdoor smog chamber. The temperature profile was unknown – only the initial and the final temperatures were reported – so three different temperature profile scenarios were chosen to model the smog chamber, as shown in Figure 1. Differences between data and model results may have been due to sample loss, lighting inaccuracies or mechanism inaccuracies – the toluene mechanism in particular is the subject of current research by MCM developers.

- MCM v3.1 model over-predicted ozone formation by almost double, although the timing was good - much better than MCM v2 (not shown), which had a late peak
- Temperature had a big impact on formaldehyde (HCHO) results

Indoor Smog Chamber:

- Nitric Oxide (NO), Formaldehyde (HCHO) and 1-Butene (1-C₄H₈) - model matched observed data very well
- Ozone (O₃) - model captured 98% of the peak, timing was good

Propene

- NO, HCHO and Propene (C₃H₆) - model matched observed data well, formaldehyde model results were only slightly high
- Ozone - captured 94% of peak, model ozone increase was slightly early (~20 minutes)

Speed

SMVGEAR II dramatically decreased the required run times for solving chemical mechanisms through sparse matrix decomposition and backsubstitution (Figure 6). In this case, the order of matrix equaled the number of species in the model (for MCM v3.1, there are approximately 4,600 species).

- SMVGEAR II reduced the number of necessary multiplications by over 99% (Figure 7)
- The percent reduction increased with increasing number of species - it got more efficient with bigger mechanisms!
- A 3-D model with 50,000 grid cells (e.g., 50 x 50 x 20 layers) would only take about 7.7hrs to run one day of simulation.

Ethanol (E85) vs Gasoline

To test the impact of ambient temperature on the ozone production from the emissions of vehicles using E85 versus gasoline, an initial model run was done using an Adjusted Carbon Bond Mechanism (ACBM) in a box model approximately the size of the LA Air Basin. All emissions occurred at 6 am and the model was run for 12 hours. The emissions were based on vehicle emission rates in Los Angeles. Emission rates were the same for each different ambient temperature and based on Jacobson (2007).

- Ozone, formaldehyde, and acetate concentrations were higher for E85 than gasoline, and increased more rapidly with increases in ambient temperatures
- The ambient temperature had a bigger impact on the difference in ozone concentrations for the high NOx case

Conclusions and Next Steps

- MCM v.3.1 in SMVGEAR II is very fast and is accurate enough to use in modeling air pollution
- MCM v3.1 is a huge improvement over v2 for modeling the degradation of toluene and m-xylene, but work needs to continue on toluene
- Propene and 1-Butene model results are excellent
- SMVGEAR II dramatically reduces computer run times, which is important for large scale grids and long simulations
- Increases in ambient temperatures increase ozone production from vehicles using E85 more than vehicles using gasoline
- NEXT – the impact of ambient temperatures on air pollution from E85 vehicles versus gasoline vehicles will be examined in more detail using MCM v3.1 and SMVGEAR II
- NEXT – the model will be expanded to include aerosol formation

Acknowledgements

Thank you to NASA and EPA for sponsoring this research.