

REGIONAL MODELING OF THE ATMOSPHERIC FATE AND TRANSPORT OF BENZENE AND DIESEL PARTICLES WITH CMAQ

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1. INTRODUCTION

Hazardous air pollutants (HAPs), also known as air toxics, are regulated under the Clean Air Act (Section 112). Mobile sources emit a variety of air toxics including gaseous compounds (e.g., benzene, formaldehyde and 1,3-butadiene) and particulate compounds (e.g., diesel particles). Those air toxics are also emitted by other sources. The impacts at urban scales are currently being investigated by EPA under the integrated urban air toxics strategy and by some states (e.g., the Arizona Department of Environmental Quality study) and local agencies (e.g., the South Coast Air Quality Management District's MATES-II study in the Los Angeles basin). However, regional scale impacts have not yet been investigated although they may be significant for those air toxics that have a long atmospheric lifetime. We present here a case study for two air toxics that have a long atmospheric lifetime and are emitted by motor vehicles among other sources. These two air toxics are benzene and particles from diesel combustion sources (hereafter referred to as diesel particles).

2.0 DESCRIPTION OF THE EPISODE AND MODELING DOMAIN

We simulated the July 11-15, 1995 period of the NARSTO/Northeast program. The first two days of the period were used as spin-up to clear the majority of the initial conditions from the modeling domain. Therefore, results from the last three simulation days were analyzed. All times listed hereafter in the figures are for Eastern Standard Time (EST).

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The meteorological inputs were obtained from an MM5 simulation conducted by Seaman and

Michelson (2000). During the July 11 to 15 period, there was a synoptic scale mid-tropospheric flow with a westerly component across the Appalachian Mountains. In the leeward side of the mountains, air sank and warmed, creating the mesoscale Appalachian lee trough. Winds ahead of the trough turned cyclonically and flowed in a south-southwesterly direction up the urban corridor. Having a marine origin, this air remained slightly cooler than the air to the west of the Appalachian mountains. The result was a shallow boundary layer capped by hot midwestern air mass at middle levels. Nocturnal jets may have also played a role in long-range transport of pollution up the coast.

The modeling domain consists of two nested grids. The outer domain has 150 x 129 grid cells with a horizontal resolution of 12 km and the inner domain has 99 x 135 grid cells with a horizontal resolution of 4 km. The vertical resolution consists of 13 layers with finer resolution near the ground.

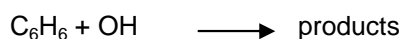
3.0 EMISSIONS

The 1996 EPA National Toxics Inventory (NTI) was used as the basis for the development of the gridded emission files for benzene. PM_{2.5} emissions from the 1996 EPA National Emission Trends (NET) were used to generate diesel particle emissions. All PM_{2.5} emitted from sources that burn diesel fuel were defined to constitute diesel PM emissions. Canadian emissions were not included. The year 1996 was the year closest to 1995 for which emission inventories were available for air toxics. NTI and NET are annual inventories with a county-based spatial resolution. To develop gridded emission files with 12 km and 4 km spatial resolution and a 1-hour temporal resolution, we used the Sparse Matrix Operator Kernel Emissions model (SMOKE), version 1.3.

4.0 MODIFICATIONS TO CMAQ

Modifications were made to CMAQ since benzene and diesel particles are not included explicitly in the original model formulation. The August 2000 version of CMAQ was used.

Benzene (C₆H₆) is included in VOC emission inventories developed for O₃ formation but its chemistry is not explicitly treated in the CBM-IV and RADM2 gas-phase chemical mechanisms available in CMAQ. Benzene reacts with OH radicals and has an atmospheric lifetime of about one week for a typical OH concentration of 10⁶ radicals cm⁻³.



The chemical kinetic rate parameter is as follows: $k = 2.5 \times 10^{-12} \exp(-0.397/RT) \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$, where R equals 0.0019872 kcal/mol-K and T is the temperature in Kelvin (Carter, 1990). This reaction was added to the CBM-IV chemical kinetic mechanism used in the simulation conducted here.

Dry deposition was assumed to be negligible for benzene, akin to other aromatic species simulated in CMAQ. Wet deposition was not simulated because there was only limited precipitation in localized areas during this summer period.

Particles are treated in CMAQ; however, the speciation of primary particles was limited to elemental carbon (EC), organic compounds (OC) and other particulate material in the 2000 version. Diesel particles consist of EC, OC and some sulfate and nitrate. To avoid double-counting particulate species such as EC and OC, it was necessary to modify CMAQ to treat diesel particles explicitly. We added a new "species" representing diesel particles.

A fixed bimodal distribution of diesel particles was assumed for the emitted and ambient diesel particles, with modes centering around 0.055 and 0.5 μm (Shi and Harrison, 1999; Kittelson et al., 2002). Dry deposition characteristics were calculated based on this bimodal distribution using the approach of Venkatram and Pleim (1999). Sedimentation was not treated because it is negligible for fine particles. Wet deposition was not simulated as discussed above.

5.0 BENZENE SIMULATION

Initial and boundary concentrations of benzene were set to zero for the 12-km simulation. The use of zero boundary concentrations as well as no Canadian emissions implies that we are analyzing solely the effect of U.S. benzene emissions within the modeling domain. As shown

below, the rapid decrease of benzene concentrations away from emission source areas justifies this approach.

The simulated benzene concentrations are presented for the entire modeling domain in Figure 1 for July 14 (Friday). The concentrations are presented for 6 a.m., which corresponds to a period when benzene concentrations tend to be high because the low mixing height minimizes dilution of the primary emissions. Results are presented for both the outer and inner domains. High concentrations are typically simulated around cities and major source areas. In the spatial plots of the 12 km domain, plumes of benzene are visible along the northeast corridor connecting major urban areas and from urban areas in the Midwest and southern United States. The plume of benzene along the northeast coast is the dominant feature of the spatial plots for the 4 km domain. Outside of source areas, the concentrations of benzene drop quite rapidly to rural background concentrations that may be lower than the urban concentrations by as much as a factor of 10.

The model performance statistics for 24-hour average benzene concentrations were calculated using data from the Photochemical Assessment Monitoring Stations (PAMS). Within the 4 km resolution domain, the coefficient of determination (r^2) between the simulated and observed 24-hour average benzene concentrations is 0.25. The normalized gross error and bias are 61% and 39%, respectively.

6.0 DIESEL PARTICLE SIMULATION

A similar modeling approach was used for diesel particles as was used for benzene. Initial and boundary concentrations were set to zero for the 12 km simulation.

The simulated concentrations of diesel particles are presented in Figure 2 for July 14. As for benzene, results are presented at 6 a.m. for both the outer and inner modeling domains. As is the case for benzene, diesel concentrations are highest around source areas such as Chicago, Atlanta, and New York. The concentrations decrease rapidly outside source areas to relatively low background concentrations. In the 4 km domain, a discernable plume of diesel particles is simulated along the Mid-Atlantic coast. Superimposed on the regional plume are individual urban plumes corresponding to emissions from individual cities, such as Washington, D.C., Philadelphia, and New York. Outside the regional diesel particle plume,

simulated concentrations are below $0.5 \mu\text{g m}^{-3}$ in rural areas.

Diesel particles lose their identity rapidly as they coagulate with other particles and act as condensation sites for secondary aerosol species. Consequently, diesel particles per se are not measured in the ambient atmosphere and a formal model performance evaluation is not feasible. We assumed that diesel particles contain on average about 50% "elemental" carbon (EC) (e.g., Kittelson et al., 2002; Moosmüller et al., 2001; Shi et al., 2000). Therefore, an approximate evaluation of the model simulation results can be conducted using EC (a chemically inert tracer) as a surrogate for diesel particles. This is an approximate evaluation because there are other sources of EC, such as biomass burning and exhaust from gasoline-powered vehicles.

A comparison of EC simulated values (assuming that diesel particles are 50% EC) was done with measurements for 15 July 1995 at two IMPROVE sites, Brigantine Wilderness Area in New Jersey and Washington, D.C. Because EC may not be a good surrogate for diesel particles (see below), no performance statistics were calculated. The comparison of simulated and observed concentrations in the 4 km resolution domain shows the simulated value being lower than the observed value by 70% at Brigantine Wilderness Area, but by only 10% in Washington D.C. These results are consistent with the fact that diesel particles are expected to contribute more to EC concentrations in an urban area such as Washington D.C. than in remote areas, such as Brigantine Wilderness Area and other Class I areas. These limited results further suggest that, since other sources (e.g., biomass burning) beside diesel fuel engines contribute significantly to atmospheric EC concentrations, EC may not be a good surrogate for diesel particles.

7.0 CONCLUSION

We presented the application of a modified version of CMAQ to the simulation of two air toxics, benzene and diesel particles.

The comparison of both benzene and diesel particle simulated concentrations in an urban area (New York City) and a remote area (Brigantine Wilderness Area) shows that, at a spatial resolution of 4 km, the regional background may contribute from 10 to 20% to the peak concentrations in urban areas. These results suggest that the regional background may not be

negligible and should be taken into account in urban air toxics studies.

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Acknowledgements

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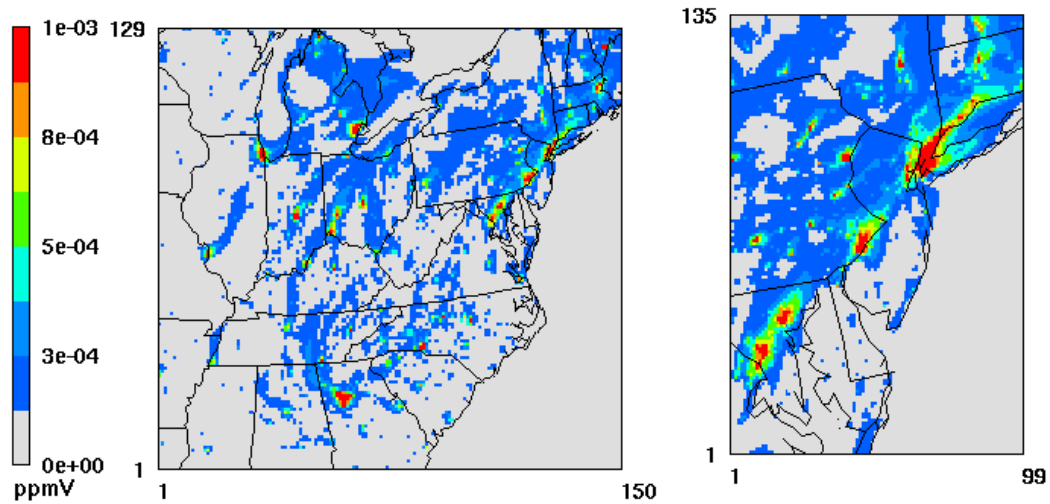


Fig. 1 Simulated benzene concentrations on July 14, 1995 at 6 a.m.

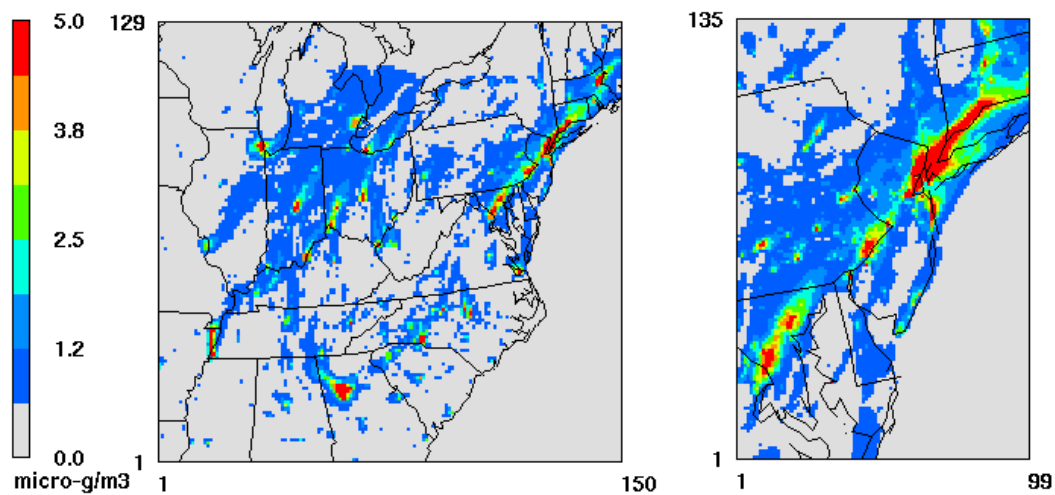


Fig. 2 Simulated diesel particle concentrations on July 14, 1995 at 6 a.m..