

CONCENTRATIONS OF TOXIC AIR POLLUTANTS IN THE U.S. SIMULATED BY AN AIR QUALITY MODEL

Deborah J. Luecken and William T. Hutzell*

1. INTRODUCTION

The U.S. Environmental Protection Agency is examining the concentrations and deposition of air pollutants that are known or suspected to cause cancer or other serious health effects in humans. These "air toxics" or "hazardous air pollutants" (HAPs) include a large number of chemicals, ranging from non reactive (i.e. carbon tetrachloride) to reactive (i.e. formaldehyde), exist in gas, aqueous, and/or particle phases and are emitted from a variety of sources. Some HAPs, such as formaldehyde and xylene, also play an important role in the production of ozone and particulate. In addition, concentrations of air toxics are required over both shorter (days) as well as longer (a year) time scales in order to analyze health risks resulting from exposure to these compounds. These requirements challenge the current capabilities of numerical air quality models beyond their needs for other pollutants, such as ozone.

Most previous assessments of risks from HAPs have used Gaussian plume dispersion models to predict concentrations, while ignoring or simplifying the atmospheric chemistry that affects the concentrations of these pollutants (i.e. Rosenbaum et. al, 1999). Several HAPs, such as formaldehyde and acetaldehyde, can be produced in the atmosphere in greater quantities than they are directly emitted, so it is critical to adequately characterize this complex chemistry. A 3-D photochemical grid model is better suited to account for atmospheric chemistry, including the time-varying changes in radical concentrations that affect the ambient concentrations of HAPs.

We have modified a numerical air quality model to simulate the concentration of toxic air pollutants over large spatial and temporal scales. The application described here focuses on a subset of HAPs that exist in the gas phase. We describe the development and testing of a chemical mechanism appropriate for HAPs; the incorporation of this chemistry and physics into a chemical transport model; and analysis of the model results.

* U.S. Environmental Protection Agency, MD E243-03, Research Triangle Park, NC.
Luecken.deborah@epa.gov

2. MODEL DESCRIPTION

2.1 Model Platform, Domain and Meteorology

The Community Multi-Scale Air Quality Model (CMAQ) version 4.3 (Byun and Ching, 1999, Byun and Schere, 2004) was the base air quality model used for this application. In order to provide predictions for a domain that sufficiently covers the continental U.S., the domain extends at least 450 km beyond the US borders in all directions. This domain includes 153 horizontal east-west and 117 north-south grid cells, and 15 vertical layers from the surface to $1.0E^4$ Pa (~ 12 km.) Simulations were performed on an IBM SP2 for the full year of 2001 with a 10-day spinup period.

Meteorology for the simulation was calculated with the Penn State/NCAR Mesoscale Model (MM5) (<http://box.mmm.ucar.edu/mmm5/>), version 3.6.1. The simulation for 2001 meteorology consisted of 34 vertical layers, using ACM parameterization for the PBL, Kain-Fritsch cumulus parameterization and 4DDA nudging (Alpine Geophysis, 2003).

2.2 Modeled HAPs and Chemical Mechanism

The toxic pollutants simulated represent the gas-phase HAPs that EPA has identified, under the Urban Air Toxics Program, to pose the highest risk to the U.S. population. To calculate concentrations of HAPs, we started with a Carbon Bond 4 (CB4) mechanism (Gery et. al, 1989) with cloud chemistry and minor modifications (Gipson and Young, 1999). The new mechanism, CB4_TX1P, accounts for the additional production and decay of air toxics, while retaining the full chemistry and radical cycling of the mechanism. Toxic species were added to the mechanism either by 1) integrating species production and decay into the full mechanism, or 2) calculating chemical decay at each time step based on the current model conditions, but with no feedback to the mechanism.

In the first instance, the full chemical mechanism was modified by changing two existing CB4 model species (FORM and ALD2) so that they simulate only formaldehyde and acetaldehyde, and adding 7 model species, listed as having feedback in Table 1. Including primary-only species quantifies the role of atmospheric chemical production on the total concentrations, as opposed to atmospheric transport of direct emissions of these species. Reactions which originally produced ALD2 were modified to produce either acetaldehyde or higher aldehydes, depending on the reactants. Acrolein and 1,3-butadiene were added to CB4_TX1P using reaction rates from Carter (2000) and product distributions corresponding to those from mapping the species to CB4 model species ([2.0]OLE for 1,3-butadiene, [0.5]OLE+[1.0]ALD2 for acrolein), with product coefficients scaled to the reaction rates. Production of acrolein from 1,3-butadiene reactions were added based on the product yields identified in SAPRC99 (Carter, 2000).

Under the second criteria, sixteen species were added to the chemical mechanism with no feedback to the chemical mechanism (Table 1). Because these species are present in small quantities or are relatively non-reactive, they do not affect the overall radical balance and chemistry, therefore their effect on the chemistry was not included. Their concentrations were updated at each chemical time step based on the current radical and environmental conditions. By including them as decay-only, however, the computational requirements of the model were significantly reduced. These species were included in all subsequent transport, advection, and deposition calculations of CMAQ.

Table 1. Species added to CB4, with and without feedback to chemistry calculations

Species	Feedback	Reactions	Definition
Formaldehyde	Yes	Photolysis, OH, NO ₃ , O	Formaldehyde
Form-surrogate	Yes	Photolysis, OH, NO ₃ , O	Species which are not formaldehyde but are mapped in CB4 as formaldehyde
Prim. formaldehyde	Yes	Photolysis, OH, NO ₃ , O	Formaldehyde from direct emissions only
Acetaldehyde	Yes	Photolysis, OH, NO ₃ , O	Acetaldehyde plus internal olefins that react immediately to form acetaldehyde
Higher aldehydes	Yes	Photolysis, OH, NO ₃ , O	Aldehydes with more than 2 carbons
Prim. acetaldehyde	Yes	Photolysis, OH, NO ₃ , O	Acetaldehyde from direct emissions only
Acrolein	Yes	Photolysis, OH, O ₃ , NO ₃ , O	Acrolein
Prim. Acrolein	Yes	Photolysis, OH, O ₃ , NO ₃ , O	Acrolein from direct emissions only
1,3-butadiene	Yes	OH, NO ₃ , O ₃ , O	1,3-butadiene from direct emissions only
Naphthalene	No	OH, O ₃ , NO ₂ , NO ₃	
1,3-dichloropropene	No	OH, O ₃	
Quinoline	No	OH, O ₃ , NO ₂	
Vinyl chloride	No	OH, NO ₃	
Acrylonitrile	No	OH, O ₃ , NO ₃ ,	
Trichloroethylene	No	OH	
Benzene	No	OH	
1,2-dichloropropane	No	OH	
Ethylene oxide	No	OH	
1,2-dibromoethane	No	OH	
1,2-dichloroethane	No	OH	
Tetrachloroethylene	No	OH	
Carbon tetrachloride	No	OH	
Dichloromethane	No	OH	
1,1,2,2-tetrachloroethane	No	OH	
Chloroform	No	OH	

2.4 Emissions

The simulation included hourly emissions of all relevant organic and inorganic species. Emissions of HAPs in Table 1 were from the 1999 National Emission Inventory (NEI) v3 (www.epa.gov/ttn/chief/net/index.html.) Other emissions were from the 1999 NEI v2. The 1999 inventory was chosen because it was the best inventory available at the time of simulation, and the differences between 1999 and 2001 were not large. Biogenic VOC emissions were from BEIS v3.11 (www.epa.gov/asmdnerl/biogen.html). Emissions were integrated and processed using the SMOKE processing software.

3. RESULTS AND DISCUSSION

3.1 Concentration Distributions

The resulting annual concentrations of formaldehyde at the surface are displayed in Figure 1. One noticeable characteristic of this figure is the area of higher concentrations in the Southeast. Formaldehyde is emitted directly as well as produced in the atmosphere

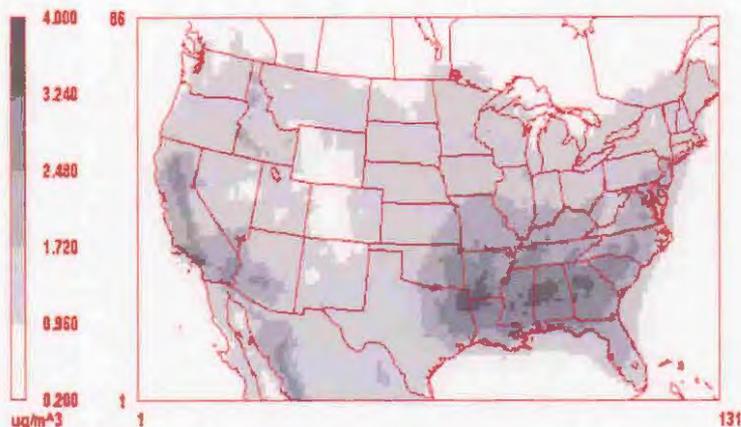


Figure 1. Concentration of total formaldehyde. Annual average, $\mu\text{g}/\text{m}^3$

via chemical reaction with almost every other VOC in the atmosphere. Formaldehyde is higher in summer than in winter, but the summer to winter ratio varies across the U.S., with highest values in the Midwest (7-10), slightly lower values in the Northeast (5-7) and lowest values in the West (< 4).

Figures 2 and 3 display the fraction of total formaldehyde resulting from atmospheric production during winter (Dec., Jan., Feb.) and summer (June, July, Aug.). In both seasons, over half the total formaldehyde is due to production in the atmosphere, but the fraction is higher in summer than in winter. The importance of atmospheric production varies across the domain and by season. In summer, higher photolysis rates, temperatures and biogenic emissions contribute to the observed high formaldehyde concentrations. Acetaldehyde concentrations show similar patterns and behavior to formaldehyde.

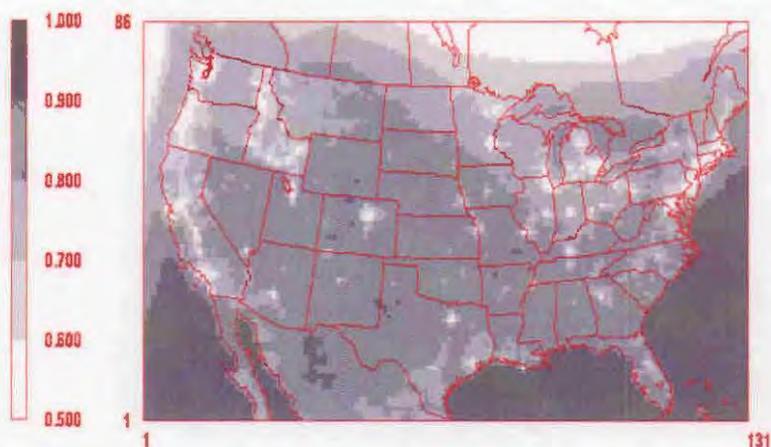


Figure 2. Fraction of total formaldehyde due to atmospheric formation in winter. Three-month averages.

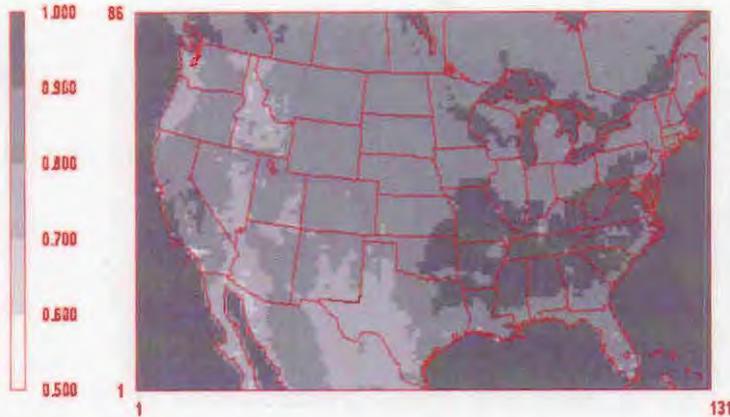


Figure 3. Fraction of total formaldehyde due to atmospheric formation in summer. Three-month averages.

Annual benzene concentrations are presented in Figure 4. Benzene behaves differently from formaldehyde because it is less reactive (half life of about 6 days in summer, vs. 2 hours for formaldehyde) and is not produced in the atmosphere. The concentration patterns reflect the distribution of emissions. Benzene in summer is less than half of its winter concentrations over most of the U.S. The major loss process for atmospheric benzene is reaction with the OH radical, which is lower in winter. Other factors, such as increased emissions, may also increase winter benzene concentrations.

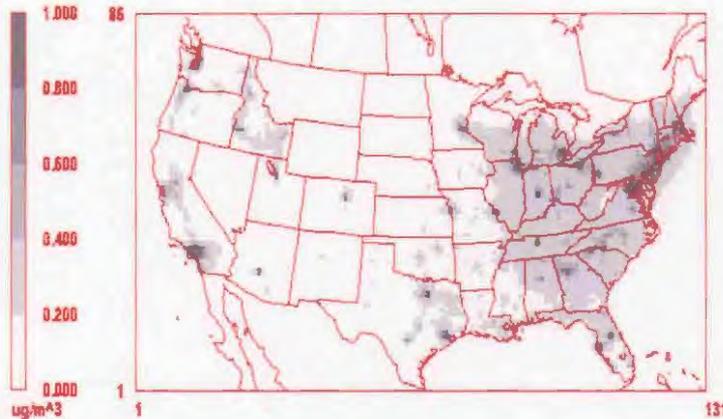


Figure 4. Concentration of total benzene. Annual average, $\mu\text{g}/\text{m}^3$

Acrolein distributions are similar to benzene, but acrolein has slightly different sources as well as competition between atmospheric production (from 1,3-butadiene) and decay. Figure 5 shows that atmospheric production accounts for about 30-40% of the total acrolein concentrations, although this varies spatially and temporally.

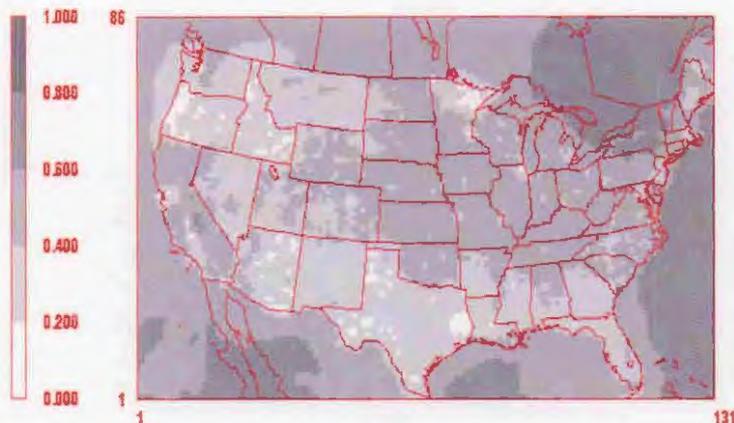


Figure 5. Fraction of total acrolein due to atmospheric formation. Annual averages.

3.2 Comparison of Modeled to Observed Concentrations

We compared model results with HAP concentrations measured in the U.S. in 2001. Our primary source of observational data was 35 monitors at 8 cities from the Air Toxics Pilot Study (Battelle, 2003), supplemented with 11 monitors from the Urban Air Toxics Monitoring Program (Eastern Research Group, 2002). Comparisons between point measurements made by monitors and volume-average concentrations from grid models such as CMAQ are difficult to interpret because there is a high degree of environmental variability within the 1296 km² area represented by one model cell. To compensate for short-term variability, we focus on monthly-averaged values. Figure 6 displays scatter plots of observed vs. modeled concentrations for formaldehyde and benzene.

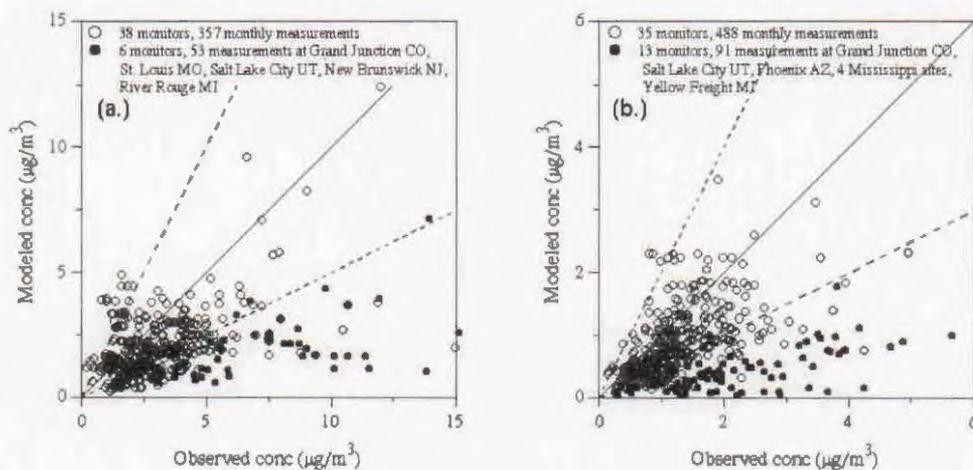


Figure 6. Comparison of observations with model predictions of (a.) formaldehyde and (b.) benzene. Monthly averaged concentrations ($\mu\text{g}/\text{m}^3$) for all months reporting data. The 1:1, 1:2 and 2:1 lines are also shown.

The model tends to slightly underpredict the formaldehyde measurements, especially at the highest measured values. Overall, about 56% of the modeled values are within a factor of two of the observations. However, the model does a much better job in the spring and summer, with 72% and 62% of the predictions matching within a factor of 2, versus 43% and 47% in the fall and winter. Greater dependence of formaldehyde concentrations on atmospheric production in the spring and summer may be a factor for the better model performance in the warmer months. Differences in meteorological model performance in the warmer months may also play a role. The majority of monitors that are severely underpredicted by the model are located at the St. Louis, MO, Salt Lake City, UT, and Grand Junction, CO sites. There can be large differences in measurements between multiple monitors sited in the same city, and the model predicts some of these monitors well and others poorly (such as the River Rouge monitor in Detroit). Overall, the relative bias is -0.47, although this varies among the states, from +0.48 to -0.82, with the larger biases at the UT and CO sites.

CMAQ also tends to underpredict benzene concentrations, with the greatest differences occurring at the monitors in Salt Lake City, UT and Grand Junction, CO, at all four Mississippi sites and at the Yellow Freight monitor in Detroit. Overall, 60% of the model predictions fall within a factor of 2, with slightly better prediction in spring and summer (67% and 62%) versus fall and winter (54% and 48%). The overall relative bias is -0.54, with individual state bias ranging from +0.48 to -0.95.

4. SUMMARY

The CMAQ model has been adapted to model concentrations of air toxics across the continental U.S. for the year of 2001. A large portion of the modeled values are within a factor of 2 of the observations.

Formaldehyde concentrations across the continental U.S. are largely due to production in the atmosphere from other VOCs. While direct emissions of formaldehyde play a role, especially in urban areas in winter, their influence is generally smaller than atmospheric production. This has implications for the development of strategies to control toxic concentrations of formaldehyde – control efforts must identify the contributing VOCs, whether toxic or not. Isoprene emitted from biogenic sources can be a major source of formaldehyde, which complicates control efforts. Formaldehyde is approximately 5 times larger in summer than winter months, due to enhanced formation rates, increased emissions of biogenic VOCs and increased volatilization of organics.

Benzene concentration distributions are influenced primarily by direct emissions of benzene, because there is no gas phase production. It is critical to obtain accurate and complete emission inventories in order to predict benzene concentrations and test the results of control strategies. High density source areas of benzene, which result in “hot spots” of concentration, are not predicted well by the model, which distributes emissions uniformly within a grid cell. The role of OH in benzene decay, and the substantial diurnal and seasonal variation in OH concentrations indicate that accurately accounting for atmospheric OH is essential for benzene predictions. Concentrations are larger in winter than summer largely due to increased OH in summer.

Acrolein concentrations have a significant secondary contribution, but the majority of acrolein is from direct emissions. Acrolein is modulated by OH concentrations in two

ways: it is lost through chemical reaction, but it is produced through reaction of OH with 1,3-butadiene. A complete description of OH radical concentrations is also necessary in order to accurately predict atmospheric acrolein concentrations.

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