SIMULATING URBAN AIR TOXICS OVER CONTINENTAL AND URBAN SCALES.

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1.0 Introduction

The US EPA is seeking to improve its National Air Toxics Assessment (NATA, http://www.epa.gov/ttn/atw/nata/index.html). The work computes risks to human health from Hazardous Air Pollutants (HAPs) listed in the Clean Air Act. An essential step is predicting air concentrations of the HAPs. Currently, a Gaussian plume model makes the predictions. The model may be accurate for local scale effects on ambient concentrations from emitted HAPs that have short atmospheric lifetimes, slow loss rates and no photochemical production. For HAPs such as formaldehyde, acetaldehyde and benzene, several of the assumptions fail. These compounds contribute a large component of the calculated risk based on previous results from the NATA. EPA can then improve its risk assessments by using a model that better simulates the transport and fate of these compounds. The Community Multi-scale Air Quality model (CMAQ) is one candidate. This abstract describes evaluating a version of CMAQ to support future risk assessments.

2.0 Model

Our research adapted the September 2003 release of CMAQ by expanding its version of the CB-IV mechanism that did not include atmospheric aerosols (Gipson and Young 1999). The expansion added twenty-five species to the chemical mechanism (Table 1). Each new species is assumed to exist totally as a gas based on its physical properties. Three new species do not represent a unique compound but reactive tracers that track atmospheric emissions of formaldehyde, acetaldehyde or acrolein. Six of the new species change reactions within the original chemical mechanism (Gery *et. al*, 1989). Changes separate CB-IV species representing formaldehyde-like and acetaldehyde-like compounds into explicit and surrogate representations for each compound. Surrogates represent Volatile Organic Compounds (VOCs) other than the explicit species that have aldehyde-like properties. Other changes add reactions for the destruction of 1, 3-butadiene (Liu *et. al*, 1999). Additional reactions also describe the loss and production of acrolein (Grosjean *et. al*, 1994). The remaining compounds in Table 1 undergo an exponential decay based on loss rates from first order chemical reactions. Rates use concentrations of model species determined by an Euler Backward Iterative (EBI) solver (Hertel *et. al.*, 1993) based on the 2003 release of CMAQ.

In addition to their photochemistry, new species undergo transport and deposition. All species are removed through wet deposition based on the precipitation rate and their Henry's Law constant. Both representations of formaldehyde and acetaldehyde undergo dry deposition. Remaining new species have zero dry deposition velocities based on analogies to similar hydrocarbon species in the CB-IV mechanism.

3.0 Simulations

Our application simulated a period covering the year 2001 plus ten days that initialized calculations. The spatial domain covered the continental US and included parts of Canada and Mexico. Grid cells had horizontal dimensions equal to 36X36 km^2. Vertical scale of the domain went from the surface to approximately 100 mbar and was divided into 15 layers in a sigma pressure coordinate system. The horizontal coordinate frame used a Lambert Conformal frame based on MM5 simulations that supported the photochemical modeling. Two later sets of meteorological and photochemical simulations nested within the continental domain. They focused on the Philadelphia metropolitan area. Nested simulations used grid cells with horizontal dimensions equal to 12X12 or 4X4 km^2.

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All simulations used emission rates based on the merged criteria and air toxics databases in the 1999 National Emissions Inventory (NEI). They have a discrepancy between the calendar years for the meteorological and emissions data because we did not alter the NEI to reflect emissions during 2001. To produce emission files for photochemical simulations, the Sparse Matrix Operator Kernel Emissions model processed source data in the NEI and emission rates predicted by the Biogenic Emissions Inventory System Version 3.11. Processing used the air toxics portion in the NEI only for emissions rates of HAPs. Calculations used the criteria portion for the emission rates of the remaining species in our version of CB-IV.

4.0 Evaluation Method

Our evaluations compared model predictions to observations that fell within the domain of 4X4 km^2 simulations. Based on the criteria, we obtained observations at sites in New Jersey for formaldehyde, acetaldehyde, 1, 3-butadiene, benzene, perchloroethylene and chloroform. The Air Quality System database (AQS, http://www.epa.gov/air/data/aqsdb.html) provided the observations. Observations had three averaging periods: twenty-four, three, and one hour. All six HAPs have observations at the longest averaging period. Only formaldehyde and acetaldehyde have observations at the intermediate period while only benzene has observations at the shortest averaging period. Note that each averaging period has its own sampling method and uncertainty so disagreements are found when comparing observations for the same pollutant between the different averaging periods. To investigate effects from extremes in grid cell size, we compare observations to model predictions only between the largest and smallest dimensions for grid cells.

Several measures are used to compare observations to model predictions. They include the mean bias normalized by the observed mean (NMB), the root mean squared error normalized by the observed mean (NRMS) and the correlation coefficient (r). These statistics measure model predictions' accuracy, precision and representation of the observations, respectively. An additional measure determines whether predictions match the relative range of observations. It is the Coefficient of the Variation (CV) and equals the standard deviation normalized by its mean. Our evaluation presents results for the fractional difference between the predicted and observed CV.

5.0 Results

Figure 1 illustrates the results from the comparison to the twenty-four hour averages. The NMB values show that both resolutions tend to under predict concentrations but agree within a factor of two ($1 \geq \text{NMB} \geq -0.5$). Except for 1,3-butadiene, the 4X4 km^2 results show better NMB values. The NRMS error and r values do not show the same behavior because neither resolution definitively better predicts observations. Like the NMB, 1,3-butadiene has the highest values for the NRMS error. However, chloroform has the lowest correlation. A possible cause is our using zero boundary conditions in the simulations. Chloroform is a global pollutant based on its long atmospheric lifetime (0.6 years). The assumption may have introduced the error into predictions but the error may have resulted from an inaccurate emissions inventory. The highest correlations occur for benzene. The high values may occur because the pollutant has a relatively long lifetime (12 days) and accurately represented emissions as well as no photochemical production. The 4X4 km^2 results have CV values that better match observation. Our evaluation measures imply that the 4X4 km^2 simulation has a better accuracy but not precision. The CV results explain the implication if the finer resolution, 4X4 km^2, better resolves forcing on observed concentrations at a monitor such as local effects from emissions and meteorological variables. The exception of 1,3-butadiene may be explained if the finer resolution inaccurately represented emissions or meteorological forcing within a grid cell such as timing or magnitude of the forcing.

For the three hour averages, comparing predictions and observations show similar patterns (Figure 2) but there are differences. Formaldehyde predictions improve in NMB and correlations but degrade in the RMS error. Acetaldehyde predictions only improve in RMS error. These improvements correspond to better matching observed values of the CV. The finer model resolution gives moderately better predictions based on its values of the CV.

One hour averages for benzene show a poorer agreement to observations (Figure 2). The fractional differences between the CV show a smaller variability than observations. Values of the NMB show a tendency to over predict. The behavior may have arisen if the simulations included a forcing that was incorrect in timing or magnitude. The 4X4 km^2 results support the explanation because their NMB and RMS error increase.

6.0 Summary

Our evaluation shows that this CMAQ model has success at predicting the magnitude but not the timing of observed concentrations of several HAPs. The comparison using the twenty four hour averages supports the former point based on the values of the NMB and the latter point based on the RMS errors and correlation coefficients. The finer model resolution improves the accuracy of predictions usually when the smaller grid cell better reproduces the observed values of the CV. The finer model resolution fails to improve accuracy of predictions if the smaller grid cell does not contain the correct forcing on observed concentrations. The point is illustrated by comparing to observations that describe the twenty four averages of 1, 3-butadiene and one hour averages of benzene.

Disclaimer *- This paper has been reviewed in accordance with the United States Environmental Protection Agency's peer and administrative review polices and approved for presentation and publication. Although it has been reviewed by EPA, the paper does not necessarily reflect EPA policies or views.*

7.0 References

Gery, M. W., G. Z. Whitten, J. P. Killus and M. C. Dodge (1989). A photochemical kinetics mechanism for urban and regional scale computer modeling. J. Geophys. Res. 94, 12,925-12,956.

Gipson, G. L., and J. O. Young (1999). Science Algorithms in Models-3 Community Multi-scale Air Quality Modeling System (CMAQ), Byun, D. W and J. K. S. Ching (eds). EPA-600/R-99/030, US EPA, Research Triangle Park, 8-1 to 8-99.

Grosjean, E., E. L. Williams, D. Grosjean (1994) Atmospheric chemistry of acrolein. Sci. Tot. Environ., Vol. 153 (3), 195-202.

Hertel, O., R. Berkowicz and J. C. Hov (1993). Test of two numerical schemes for use in atmospheric transport-chemistry models. Atmos. Environ., Vol. 27 (16), 2591-2611.

Liu, X., H. E. Jeffries, K. G. Sexton (1999). Hydroxyl radical and ozone initiated photochemical reactions of 1,3-butadiene. Atmos. Environ., Vol. 33 (18), 3005-3022.

Table 1. Compounds added to CB-IV.

Model Species	CAS Number	Comment
Acrylonitrile	107-13-1	HAP
Carbon Tetrachloride	56-23-5	HAP
Propylene Dichloride	78-87-5	HAP
1,3-Dichloride Propene	542-75-6	HAP
1122-Tetrachloride Ethane	79-34-5	HAP
Benzene	71-41-2	HAP
Chloroform	67-66-3	HAP
1,2-Dibromomethane	106-93-4	HAP
1,2-Dichloromethane	107-06-2	HAP
Ethylene Oxide	75-21-8	HAP
Methylene Chloride	75-09-2	HAP
Perchloroethylene	127-18-4	HAP
Trichloroethylene	79-01-6	HAP
Vinyl Chloride	7501-4	HAP
Naphthalene	91-20-3	HAP
Quinoline	91-22-5	HAP
Formaldehyde	50-00-0	HAP
Acetaldehyde	75-07-0	HAP
Acrolein	107-02-8	HAP
1, 3-Butadiene	106-99-0	HAP
Primary Formaldehyde	50-00-0	Reactive Emissions Tracer
Primary Acetaldehyde	75-07-0	Reactive Emissions Tracer
Primary Acrolein	107-02-8	Reactive Emissions Tracer
Surrogate Formaldehyde	None	Analogous VOCs
Surrogate Acetaldehyde	None	Analogous VOCs

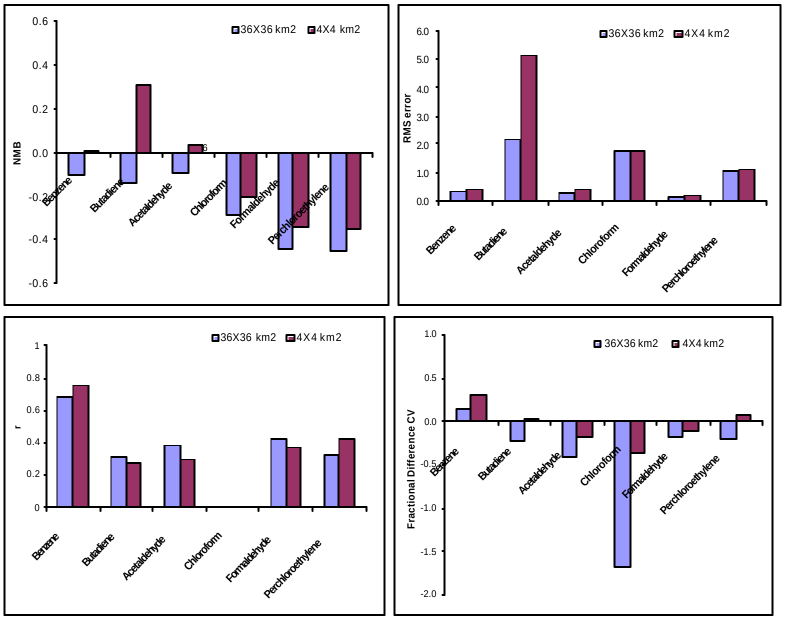

Figure 1. Evaluation measures illustrated for the comparison to twenty-four hour averages. Chloroform has missing values for r because the values are less than zero.

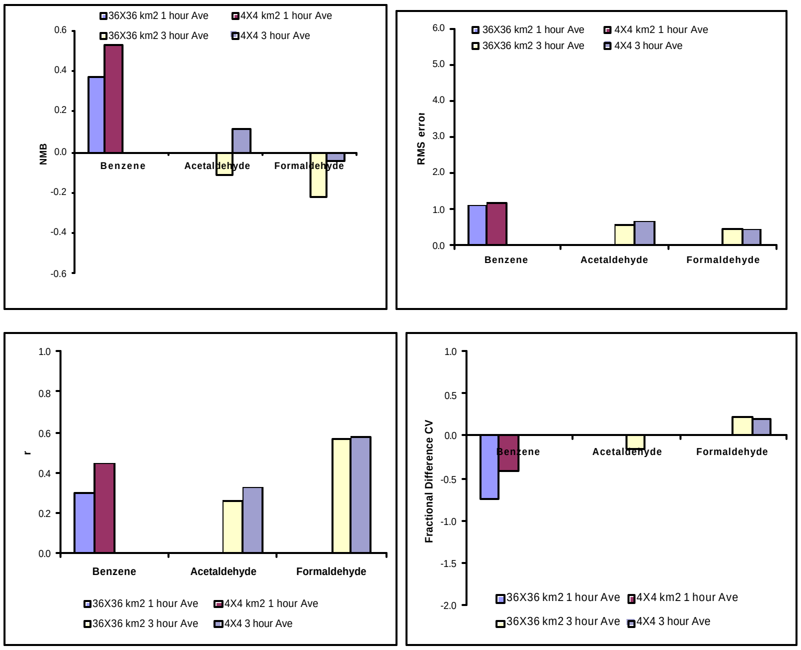

Figure 2. Evaluation measures illustrated for the comparison to three and one hour averages. For acetaldehyde from 4X4 km^2, the fractional difference between the predicted and observed CV is almost zero.