

Development and analysis of air quality modeling simulations for hazardous air pollutants

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Abstract

The concentrations of five hazardous air pollutants were simulated using the community multi-scale air quality (CMAQ) modeling system. Annual simulations were performed over the continental United States for the entire year of 2001 to support human exposure estimates. Results are shown for formaldehyde, acetaldehyde, benzene, 1,3-butadiene and acrolein. Photochemical production in the atmosphere is predicted to dominate ambient formaldehyde and acetaldehyde concentrations, and to account for a significant fraction of ambient acrolein concentrations. Spatial and temporal variations are large throughout the domain over the year. Predicted concentrations are compared with observations for formaldehyde, acetaldehyde, benzene and 1,3-butadiene. Although the modeling results indicate an overall slight tendency towards underprediction, they reproduce episodic and seasonal behavior of pollutant concentrations at many monitors with good skill.

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1. Introduction

The US Environmental Protection Agency is examining the concentrations and deposition of hazardous air pollutants (HAPs) that are known or suspected to cause cancer or other serious health effects in humans. HAPs, as specified in the 1990 US Clean Air Act, Section 112, include a large number of compounds, from non-reactive (e.g. carbon tetrachloride) to reactive (e.g. formaldehyde), which exist in all atmospheric phases and are emitted from a variety of sources. HAPs, such as formaldehyde

and xylene, also play a role in the production of ozone and fine particulate matter. Some HAPs can be both directly emitted and photochemically produced in the atmosphere. HAP concentrations are required over shorter (hours) and longer (a year or more) time scales for assessing health risks from exposure to these compounds.

For risk assessments to date, Gaussian plume dispersion models have been used to predict concentrations, ignoring or simplifying the atmospheric chemistry and long-range transport (i.e. Rosenbaum et al., 1999). While plume models might capture localized areas of high concentrations in the near field, concentrations farther away can be in error due to transport simplifications. HAPs that are photochemically produced in the atmosphere

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cannot be accurately predicted if their chemistry is not adequately characterized. A three-dimensional photochemical Eulerian grid model better accounts for atmospheric chemistry by simulating the time-varying changes in radical concentrations that affect HAP concentrations. An integrated ozone, particulate matter and HAP model can also be used to develop multi-pollutant control strategies.

Previous modeling studies of HAPs using Eulerian models have shown the utility of these models for compounds whose concentrations are affected by chemistry (Harley and Cass, 1994; Fraser et al., 2000; Environ, 2002; Seigneur et al., 2003). These studies have had some success at reproducing ambient concentrations, although only limited observations are available for comparison with model predictions. These previous studies were limited to short episodes (2–5 days) and/or small domains (Southern California, the northeastern quadrant of the US) and did not provide the information necessary for large-scale annual risk assessments.

Solberg et al. (2001) used the EMEP oxidant trajectory model for an in-depth study of formaldehyde at six rural locations in Europe over a four-year period. The model reproduced temporal trends in the monitoring values well, but often underestimated the concentrations.

In this paper, we describe the modification and application of a numerical air quality model to simulate HAP concentrations over large spatial and temporal scales. This paper focuses on five HAPs that exist in the gas phase: formaldehyde, acetaldehyde, benzene, 1,3-butadiene and acrolein. We describe the chemical mechanism used for these HAPs, the chemical transport model, analysis of the model results, and comparison of results with monitoring data.

2. Model description

2.1. Model platform and domain

Version 4.4 of the community multi-scale air quality (CMAQ) modeling system (Byun and Ching, 1999; Byun and Schere, 2006) was modified for this application. The model domain includes 153 east–west and 117 north–south, 36 km^2 grid cells, covering the contiguous US and extending about 600 km beyond the borders. It includes 15 vertical layers from the surface to $1.0\text{E}4 \text{ Pa}$ ($\sim 12 \text{ km}$). The modeling period was calendar year 2001. The

CMAQ chemical transport model (CCTM) was configured to use the piecewise parabolic method for transport processes, multiscale method for horizontal diffusion, and eddy method for vertical diffusion. Cloud processes were modeled, but aerosol formation was omitted since the HAPs considered here exist primarily in the gas-phase. A version of the Euler Backward Iterative (EBI) gas-phase chemistry solver was created for the chemical mechanism described below. The EBI solver is computationally efficient, which facilitates annual simulations.

2.2. Initial and boundary conditions

The initial and boundary concentrations represent clean air concentrations (Gipson, 1999). The influence of the initial conditions was minimized by a 10-day spin-up period. Boundary conditions of benzene, 1,3-butadiene and acrolein were set to zero because continental emissions are assumed to dominate trans-oceanic transport. McCarthy et al. (2006) estimate background concentrations ranging from 0.047 to $0.27 \mu\text{g m}^{-3}$ for benzene from measurements made at remote North American sites, and concentrations $< 0.02 \mu\text{g m}^{-3}$ for 1,3-butadiene and acrolein, based on tetrachloroethylene measurements at remote sites. Nowak et al. (2004) measured benzene concentrations from 0.1 to $0.3 \mu\text{g m}^{-3}$ over the Pacific, and Milne et al. (2000) measured similar concentrations over the Atlantic, although values in both cases were highly variable, depending on the air mass. Given the short lifetimes of 1,3-butadiene and acrolein, the zero boundary condition assumption is reasonable across the oceanic boundaries, although emissions from Mexico and Canada may affect border concentrations. Boundary conditions, including transport across US boundaries, could be important for benzene, but seasonally and spatially accurate boundary concentrations are not established. We plan to explore improvements in future analyses. We note that zero concentration boundary conditions could be a problem for other toxic compounds which are long-lived in the atmosphere, such as halocarbons, or those with significant contributions from sources across model boundaries.

2.3. Meteorology

Simulations were driven by 2001 meteorology from the Penn State/NCAR Mesoscale Model

(MM5) (<http://box.mmm.ucar.edu/mm5/>), version 3.6.1. The MM5 simulation meteorology had 34 vertical layers and is described in more detail in McNally (2003) and in Gilliam et al. (2006). The meteorological files were processed for model-ready input using the CMAQ Meteorology-Chemical Interface Processor (MCIP), version 2.2.

2.4. Chemical mechanism

To calculate HAP concentrations, we modified a condensed version of the SAPRC-99 mechanism used in the CMAQ system (Carter, 2000a). The modified mechanism accounts for additional production and decay of HAPs, while retaining the chemistry and radical cycling of the original mechanism. HAPs were added either by (1) integration into the full mechanism, or (2) calculation of chemical decay at each chemical integration step using current model conditions.

In the first case, formaldehyde, acetaldehyde, acrolein and 1,3-butadiene are represented explicitly in the mechanism. Formaldehyde in SAPRC-99 is an explicit species, but the species CCHO represents both acetaldehyde and glycoaldehyde. We added a model species to represent glycoaldehyde and modeled it separately, using CCHO to represent acetaldehyde. Reactions of acrolein and 1,3-butadiene were added to the condensed mechanism, from Carter (2000b), and include reactions with OH, O₃, NO₃, and O(³P), as well as photolysis for acrolein. The SAPRC-99 product METHACRO was replaced with acrolein for explicit representation in our modified mechanism. We added reactive tracer species to the mechanism to assess contributions of direct formaldehyde, acetaldehyde and acrolein emissions to total concentrations. The total chemical mechanism integrated by the

CCTM included 234 reactions and 82 chemical species.

In the second case, HAPs were added to the model and their concentrations were updated at the end of each chemical integration step based on the solution of the first case, without altering the former solution. These species are present in small quantities or are relatively non-reactive, so they do not affect the overall radical balance and chemistry. We tested all HAPs added this way to ensure the accuracy of this treatment. In the application described here, only benzene was modeled in this manner, using the reaction rate with OH from Carter (2000b). These species are included in all transport, advection and deposition calculations of CMAQ.

2.5. Emissions

The model simulations used hourly emissions of HAPs, other VOCs and inorganic compounds from the 1999 National Emission Inventory (NEI), v.3 (<http://www.epa.gov/ttn/chieff/net/1999inventory.html#final3haps>). This was the best inventory available and differences between 1999 and 2001 emissions are small. Biogenic emissions were calculated with BEIS v3.12 (<http://www.epa.gov/asmdnerl/biogen.html>). Emissions were merged and processed with SMOKE v.2.0 software (<http://cf.unc.edu/cep/empd/products/smoke/index.cfm>).

3. Results

3.1. Concentration patterns

Annual concentrations of formaldehyde and acetaldehyde at the surface are presented in Fig. 1. They have similar spatial structure, although

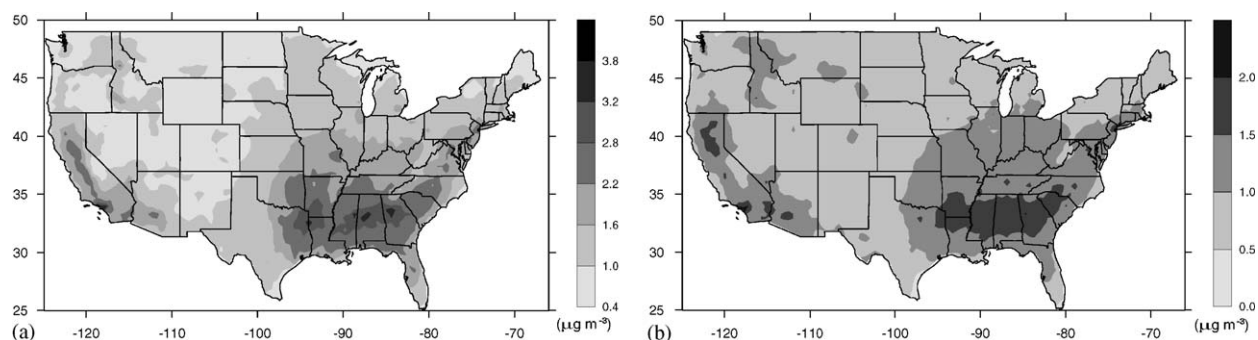


Fig. 1. Modeled annual concentrations of (a) formaldehyde and (b) acetaldehyde ($\mu\text{g m}^{-3}$).

acetaldehyde concentrations tend to be lower with a smaller range of values. The maps indicate an area of higher concentrations in the Southeast that cannot be explained solely by direct emissions. This area is significantly influenced by atmospheric reactions that both reduce (via oxidation and photolytic decay) and produce aldehydes (via oxidation and decomposition of other VOCs).

Fig. 2 shows the annually averaged fractions of total formaldehyde and acetaldehyde concentrations produced by atmospheric reactions of other VOCs in the atmosphere. Over half of the total aldehydes is due to photochemical production, but the magnitude varies across the domain. Atmospheric production also varies by season: summer-to-winter ratios of predicted formaldehyde and acetaldehyde concentrations range from 2–6 in most areas, although they are considerably smaller in urban and more temperate areas. Higher photolysis rates, temperatures and biogenic emissions contribute to higher summer concentrations.

Annual average predicted benzene and 1,3-butadiene concentrations are displayed in Fig. 3. Benzene behaves differently from the aldehydes because it is less reactive (summer half life of 6 days

versus 2 h for formaldehyde) and is not produced in the atmosphere. Its concentration reflects emissions and long-range transport. Summer concentrations are much less than winter values because benzene decays through reaction with OH radical, which is approximately 10 times lower in winter. Higher emissions and/or lower boundary layer heights can also increase winter benzene concentrations.

Concentration patterns of 1,3-butadiene are similar to benzene, but with less transport from source areas because it is more reactive (half-life of approximately 2 h in summer). We note that large concentrations of 1,3-butadiene are predicted in Idaho, due to high emissions of 1,3-butadiene in the NEIv.3, which we suspect to be an error. Factors that are used to develop emissions from wildfires are currently being investigated as a possible cause.

Predicted acrolein concentrations are shown in Fig. 4a and the fraction of acrolein produced from photochemistry in the atmosphere is shown in Fig. 4b. The acrolein distribution is similar to benzene and 1,3-butadiene. High values in Idaho are also evident in the acrolein concentrations and have the same suspected causes as 1,3-butadiene. Acrolein concentrations are affected by atmospheric

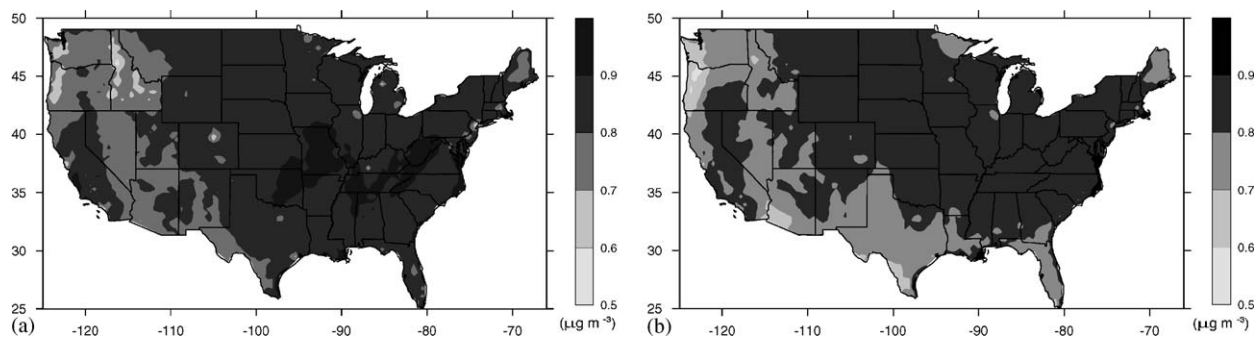


Fig. 2. Fraction of total concentrations due to atmospheric formation for (a) formaldehyde and (b) acetaldehyde.

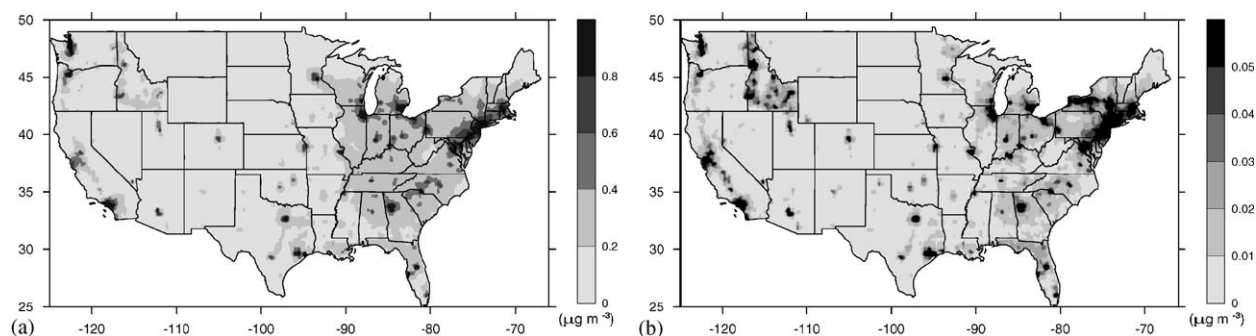


Fig. 3. Modeled annual concentrations of (a) benzene and (b) 1,3-butadiene ($\mu\text{g m}^{-3}$).

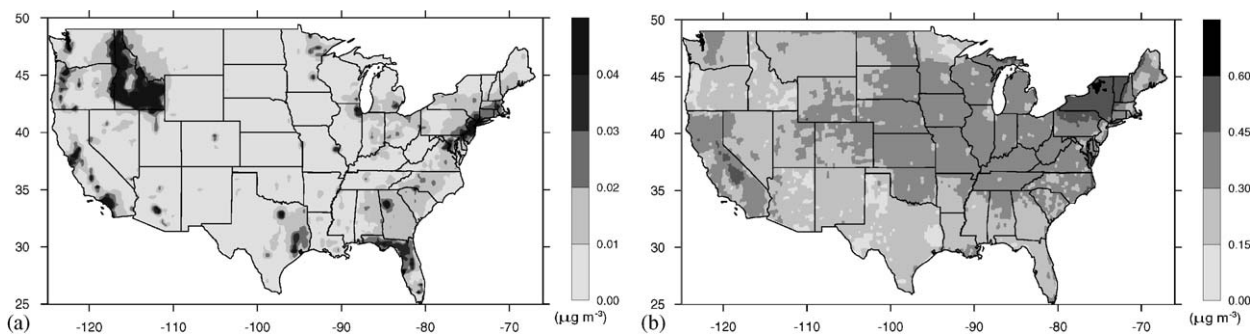


Fig. 4. Modeled annual average concentrations of (a) acrolein ($\mu\text{g m}^{-3}$) and (b) the fraction of acrolein due to atmospheric production.

production (from 1,3-dienes, of which 1,3-butadiene is the most common and only one modeled here) and destruction (largely by reaction with OH). Atmospheric production of acrolein, on an annual basis, accounts for about 30–50% of total acrolein concentrations, with a slightly higher fraction in summer than in winter.

3.2. Comparison of modeled and observed concentrations

We compared model results with HAP concentrations from 35 monitors in eight cities (San Jacinto, CA; Grand Junction, CO; Tampa, FL; Cedar Rapids, IA; Detroit, MI; Rio Rancho, NM; Providence, RI; and Seattle, WA), taken during the 2001–2002 Air Toxics Pilot Study (Battelle, 2003). This data set has been extensively analyzed and quality-assured. Data were taken at 1, 3, or 6 day intervals, with most monitors collecting data starting in the spring of 2001. We focus on 24-hour and monthly averaged values collected from May to December 2001. Our comparisons exclude acrolein because monitoring data is not available for 2001 for this network, due to measurement difficulties. There are no standard statistics or performance goals for evaluating HAP models. Different statistical formulations are available for quantifying comparisons between models and measurements, providing different insights on model performance (Yu et al., 2006). We present several metrics for comparison to previous studies, but focus mainly on normalized mean bias (NMB) and normalized mean error (NME).

It should be noted that comparisons between observations, which reflect point measurements, and model predictions, which represent volume averages, are difficult to interpret because environ-

mental variability at a scale smaller than the grid cell is not represented in the model. Individual monitors may be influenced by nearby large sources and local meteorology. Monitoring networks are usually not dense enough to reliably estimate volume averages for comparison with model predictions.

Fig. 5 displays scatter plots of monthly averaged observed and modeled formaldehyde and acetaldehyde concentrations. Points are identified by season (spring and summer versus fall and winter). The Grand Junction, CO sites are indicated separately because measured values are consistently higher than predicted and generally higher than at other measurement sites. Overall statistics and definitions of the measures are summarized in Table 1.

Overall, the model tends to underpredict formaldehyde measurements, especially at the highest measured values. Fifty-five percent of modeled values are within a factor of two of observations. Agreement is better in spring and summer, with 72% and 71% of predictions within a factor of 2, versus 44% and 46% in fall and winter. The model tends to underestimate acetaldehyde. Sixty-five percent of predicted acetaldehyde values fall within a factor of two of measured values, with larger percentages in spring and summer (72% and 84%) than fall and winter (61% and 31%). If the Grand Junction, CO monitors are removed from analyses, the statistics improve slightly.

When daily averages are computed, some individual monitors correlate well with predictions. Correlations range from 0.05 (the DNFL monitor in Tampa) to 0.88 (the VERI monitor in Providence) for formaldehyde, and from -0.01 (the CRIA monitor in Cedar Rapids) to 0.75 (the VERI monitor in Providence) for acetaldehyde. Poor correlations may occur when monitors located close

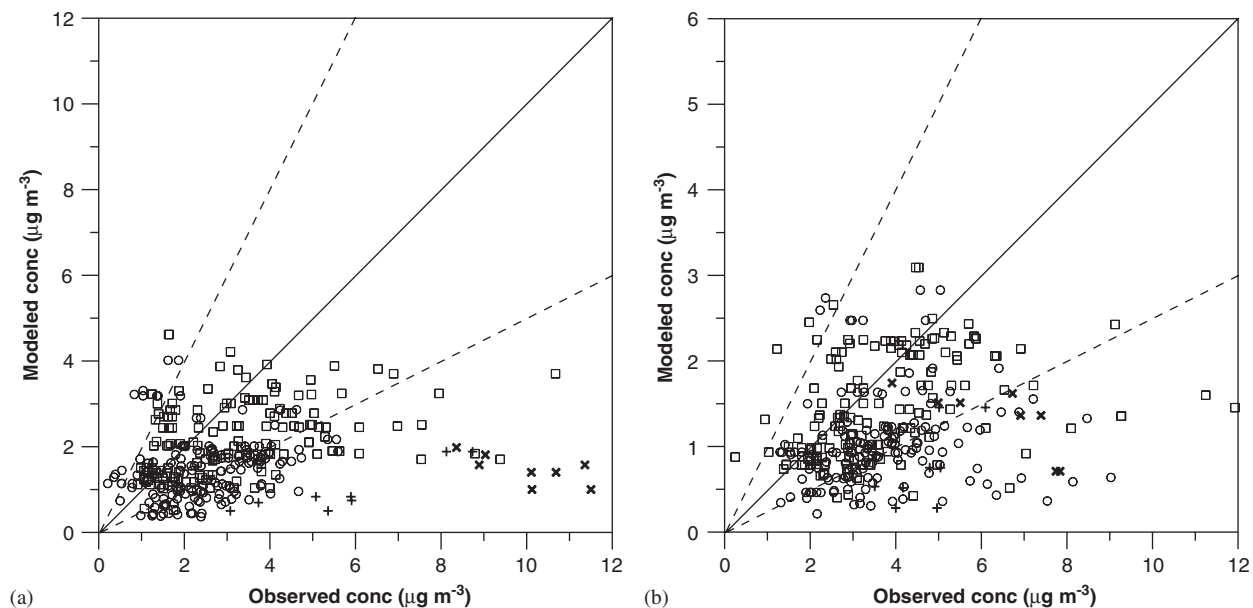


Fig. 5. Comparison of observed, monthly concentrations with model predictions for (a) formaldehyde and (b) acetaldehyde. Data points include (□) spring and summer values, (○) fall and winter values, (×) spring and summer values for CO sites, and (+) fall and winter values for CO sites. The lines corresponding to a 1:1, 1:2 and 2:1 comparison are shown.

Table 1

Summary of statistical measures comparing observations to model predictions, for 30-day average concentrations

Sites used	<i>N</i>	Model median conc.	Obs. median conc.	Model minimum/maximum conc.	Obs. minimum/maximum conc.	Fraction within factor of 2	MB	%MNB	%MNE	%NMB	%NME
<i>Formaldehyde</i>											
All	320	1.72	2.68	0.38/4.62	0.21/32.96	0.55	−1.54	−21.22	54.90	−45.81	57.28
All except CO	304	1.74	2.60	0.38/4.62	0.21/32.96	0.58	−1.27	−17.90	53.36	−40.68	53.67
All, winter	59	0.87	2.12	0.38/1.86	0.50/5.36	0.46	−1.16	−46.72	54.46	−52.00	55.00
All, summer	95	2.70	3.96	1.40/4.62	0.98/32.96	0.71	−2.15	−9.35	51.99	−38.96	54.86
<i>Acetaldehyde</i>											
All	320	1.04	1.72	0.21/3.09	0.12/10.37	0.65	−0.70	−25.01	44.27	−36.27	45.62
All except CO	312	1.04	1.67	0.21/3.09	0.12/10.37	0.67	−0.64	−23.13	43.38	−34.27	44.33
All, winter	61	0.65	1.48	0.21/1.20	0.66/4.07	0.31	−0.96	−54.21	54.21	−59.14	59.14
All, summer	95	1.87	2.05	0.61/3.09	0.12/5.96	0.84	−0.31	7.49	41.49	−14.67	34.57
<i>Benzene</i>											
All	337	0.67	1.12	0.08/2.33	0.16/64.20	0.60	−1.13	−32.83	45.43	−59.37	64.27
All except CO, NM, YFMI	300	0.71	1.07	0.08/2.33	0.16/4.95	0.67	−0.39	−26.52	40.67	−32.55	41.22
All, winter	63	0.73	1.41	0.20/2.33	0.52/4.95	0.54	−0.64	−30.89	49.36	−39.09	50.21
All, summer	99	0.53	0.96	0.08/1.34	0.16/64.20	0.61	−1.40	−36.64	45.53	−69.80	71.06
<i>1,3-Butadiene</i>											
All	281	0.06	0.11	0.01/0.19	0.01/0.60	0.46	−0.07	−38.43	54.26	−53.12	59.78
All except CO, NM, YFMI	256	0.06	0.10	0.01/0.19	0.01/0.60	0.50	−0.06	−34.51	51.88	−48.63	56.41
All, winter	56	0.06	0.15	0.01/0.17	0.03/0.60	0.41	−0.11	−35.23	57.85	−56.37	64.86
All, summer	79	0.04	0.08	0.01/0.14	0.01/0.33	0.49	−0.06	−42.31	53.68	−55.85	58.43

MB = $1/N \sum (\text{Model} - \text{Obs})$; MNB = $1/N \sum ((\text{Model} - \text{Obs}) / \text{Obs})$; MNE = $1/N \sum (|(\text{Model} - \text{Obs}) / \text{Obs}|)$; NMB = $\sum (\text{Model} - \text{Obs}) / \sum \text{Obs}$; NME = $\sum |(\text{Model} - \text{Obs})| / \sum \text{Obs}$.

to roadways or industrial areas report localized high concentrations which are not comparable to volume-averaged values simulated by the model.

There can also be large differences in measurements between multiple monitors located in close proximity to one another. Fig. 6 shows an example from the Providence, RI site, where five monitors fall within a single CCTM grid. The difference in concentration among sites can be a factor of 2 or more. At other sites, such as Detroit, MI, the difference among monitors within a single CCTM grid can be a factor of 3. The model generally does a better job at predicting the average of multiple

monitors within one grid than individual monitors ($r = 0.89$ for Providence, $r = 0.64$ for Detroit, $r = 0.93$ for Cedar Rapids). While the CCTM tends to underpredict the magnitude of concentrations, it reproduces temporal behavior, as seen in Fig. 6.

Comparisons between monthly-averaged model predictions and observations for benzene and 1,3-butadiene are shown in Fig. 7. Again, the model tends to underpredict both HAPs, especially at higher observed concentrations. Sixty per cent of benzene predictions fall within a factor of 2 of observations, with no significant difference between spring and summer (66% and 61%) versus fall and

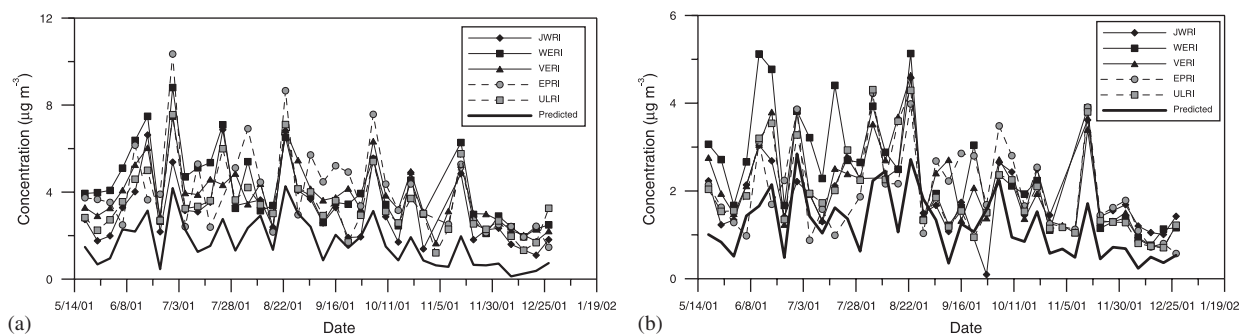


Fig. 6. Time series of 24-hour averaged concentrations at the Providence, RI site for all monitors falling within model grid (135,72), and model predictions for (a) formaldehyde and (b) acetaldehyde.

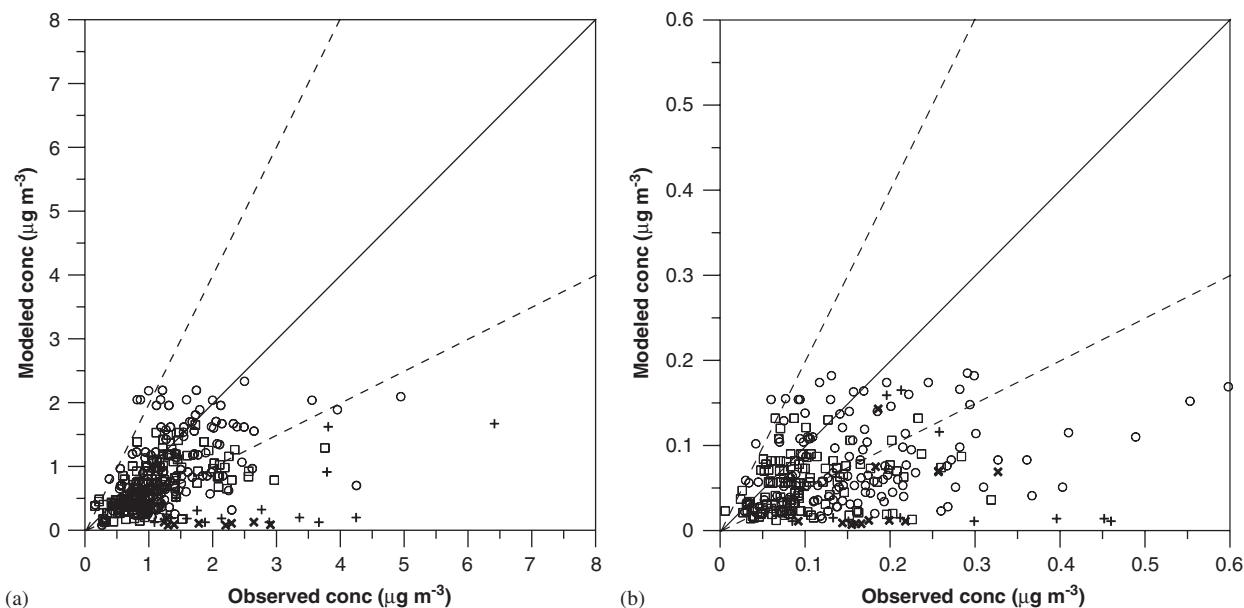


Fig. 7. Comparison of observed, monthly averaged concentrations with model predictions for (a) benzene and (b) 1,3-butadiene. Values are for (□) spring and summer, (○) fall and winter, (×) spring and summer for CO, NM, and YFMI sites, and (+) fall and winter for CO, NM and YFMI.

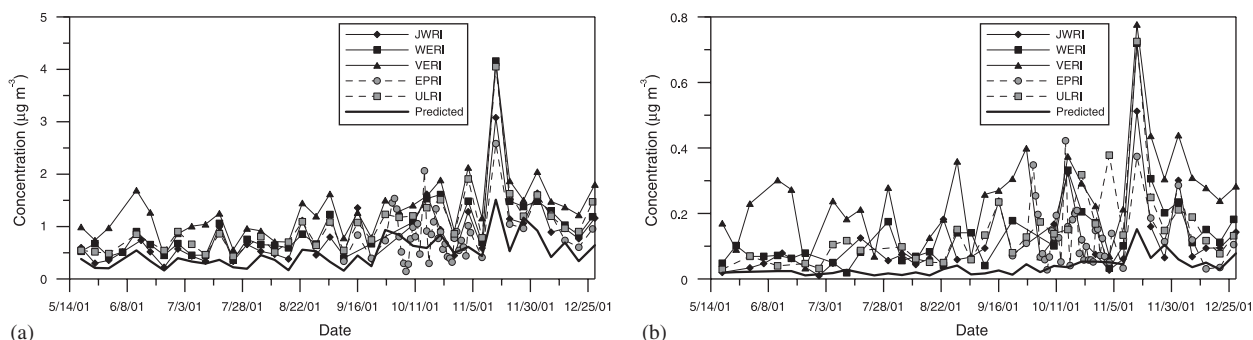


Fig. 8. Time series of 24-hour averaged concentrations at the Providence, RI site for all monitors falling within model grid (135,72), and model predictions for (a) benzene and (b) 1,3-butadiene.

winter (60% and 54%), although bias and error improve during colder months. The benzene mean normalized bias (MNB) of -32% and mean normalized error (MNE) of 45% are comparable with benzene statistics reported in [Seigneur et al. \(2003\)](#) and [Environ \(2002\)](#). The removal of extreme values at Grand Junction, CO, Rio Rancho, NM, and the YFMI monitor in Detroit improves the bias and error statistics, and increases the fraction of modeled values that are within a factor of 2. For 1,3-butadiene, 46% of model predictions fall within a factor of 2 of observations. The bias and error are also somewhat larger than for benzene, with comparable performance in winter and summer. Two factors make comparison for 1,3-butadiene difficult: low concentrations, around $0.10\text{--}0.2$ ($\mu\text{g m}^{-3}$), and potential analysis difficulties due to elution of 1,3-butadiene on the tail of acetaldehyde, both of which make the observations more uncertain.

Subgrid-scale variability in benzene and 1,3-butadiene for the Providence, RI site is shown in [Fig. 8](#). The model is biased low compared to most sites, but agreement in temporal patterns is apparent. Correlation coefficients for individual sites vary widely, with relatively good agreement indicated at some sites (such as Providence, RI) but much poorer agreement at others.

4. Discussion

The CCTM does a reasonable job at predicting episodic trends in concentrations, but has an overall tendency to underpredict the concentrations. Underpredictions may result from volume-averaging that occurs in a model grid. This averaging occurs over horizontal ($36 \times 36 \text{ km}^2$) and vertical (approx-

mately 38 m) dimensions of the grid cell. Local sources of high formaldehyde emissions and its highly-reactive precursors may impact the monitors but not be reflected in the volume-averaged model predictions. A smaller grid size would likely better represent these localized areas of high HAPs concentrations, although it is possible that some point sources of fast-reacting HAPs cannot be exactly represented in a grid model, even with a very fine resolution. Spring and summer predictions match observations better than winter predictions for aldehydes, perhaps due to the role of photochemical production in warmer months.

The lack of HAP monitoring data hampers our ability to make conclusive evaluations of the model predictions. Improving the density and duration of observations would help better assess the model skill for these compounds, and analyze factors controlling their concentrations.

Biases in model predictions may be due to several factors, including errors in emissions, meteorology, chemical reactions or other physical processes in the CCTM. Underestimation of direct emissions of formaldehyde and acetaldehyde may contribute to model underpredictions in urban areas, although the model predicts that these emissions are usually only a small component of aldehyde concentrations. Underprediction of VOC emissions that produce aldehydes could contribute to negative model biases. Biogenic isoprene and other olefins are precursors of formaldehyde and acetaldehyde, and uncertainties in temporal and spatial emissions of these olefins will affect predicted aldehyde concentrations. Indeed, [Solberg et al. \(2001\)](#) found that increasing the isoprene emissions by a factor of 4 improved their comparisons at some sites. [Hanna et al. \(2004\)](#) estimated an overall uncertainty factor

of two in benzene and formaldehyde emissions using a Monte Carlo simulation for Houston, TX. 1,3-butadiene and acrolein emissions are likely to be at least as uncertain as benzene. The incongruities in Idaho are one illustration of emission inaccuracies. An inaccurate accounting of benzene transport across model boundaries may also cause under-predictions of benzene concentrations.

Errors in meteorological forcing in the model, especially in describing subgrid-scale phenomena and winter conditions, may affect model predictions although it is not clear whether these errors would lead to underprediction. Inaccurate precipitation rates might alter aldehyde concentrations, but do not account for the benzene underprediction due to benzene's relative insolubility in water and low reactivity. The MM5 fields used in this application tend to have a cold bias in winter, which can affect reaction rates and pollutant concentrations. If the modeled wind fields are too low or slightly misdirected, they may be unable to capture the larger peaks in the observations (Gilliam et al., 2006). EPA is continuing to look at the link between errors in the meteorological model and air quality predictions in more detail.

Because model predictions represent volume-averaged concentrations, sharp vertical gradients in HAPs concentrations or precursors within the first model layer will not be represented by the model. In addition, any modeled physical processes that unrealistically dilute the concentrations in the vertical dimension, such as unrealistically high boundary layer or overmixing in the vertical dimension, can decrease predicted concentrations.

The chemical mechanism describing decay and photochemical production of pollutants may play a role in the model underprediction. Aldehyde production from VOCs is estimated from expected pathways of VOC oxidation and decomposition (Carter, 2000a). Production of aldehydes may be in error due to condensation and simplification of a complex chemical mechanism. The decay rate of HAPs is affected by the OH concentration, and it is difficult to determine how well the mechanism predicts OH concentrations. The SAPRC-99 mechanism has undergone extensive evaluation of its predictions for ozone and particulate matter, but most testing has been performed under summer conditions and high concentrations, so its performance over an entire year and a wide variety of conditions throughout the US is not well studied. However, the simulated chemistry for benzene

decay is relatively simple and it is unlikely that errors in the chemical mechanism alone can account for benzene underpredictions.

We are continuing to expand and update the chemical mechanism in the CMAQ system to more accurately simulate tropospheric chemistry, and to simulate additional HAPs, including aerosol-bound HAPs such as toxic metals and polycyclic aromatic hydrocarbons, as well as additional, high-risk, gas-phase HAPs.

5. Summary

The CMAQ modeling system has been adapted to model concentrations of five HAPs across the continental US for 2001. Most of the predictions are within a factor of 2 of the measured concentrations. Formaldehyde and acetaldehyde concentrations across the continental US are predicted to be largely due to photochemical production. While direct emissions play a role, especially in urban areas during winter, their influence is generally small. These results suggest that strategies to control formaldehyde and acetaldehyde must identify the contributing VOCs, whether toxic or not. Olefins emitted from biogenic sources can be a major source of aldehydes and will complicate control efforts.

Benzene and 1,3-butadiene concentrations depend on direct emissions. It is critical to obtain accurate and complete emission inventories in order to accurately predict concentrations and test control strategies. Large sources of these pollutants result in concentration hot spots which may not be reflected in the model grid-averaged predictions.

The model predicts that about 30–50% of ambient acrolein concentrations are due to photochemical production. Acrolein is modulated by OH concentrations in two ways: it is lost through chemical reaction, and is produced through reaction of OH with 1,3-butadiene. Hence, an accurate description of OH radical concentrations and 1,3-butadiene emissions is necessary to accurately predict acrolein concentrations. Source attribution of atmospheric acrolein must consider sources of 1,3-butadiene that produce acrolein.

Comparisons between modeled and observed concentrations show that the model reproduces concentrations well at some sites, but not at others. At most sites, the model reproduces temporal behavior, although it tends to underpredict concentrations. Overall, the model underpredicts, with mean biases from –9.4 to –69.8%, depending on

pollutant, season and exclusion of outliers. Despite the negative biases, correlations at 24-hour averaging times are good.

Disclaimer

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