

Effects of using the CB05 vs. SAPRC99 vs. CB4 chemical mechanism on model predictions: Ozone and gas-phase photochemical precursor concentrations

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Abstract

A three-dimensional air quality model is used to examine the magnitude and spatial distribution of differences in predictions among three chemical mechanisms that are used for regulatory and research modeling. The Carbon Bond mechanism CB05 is compared to an earlier version, CB4, to assess how much changes due to an update might potentially affect previous model conclusions on ozone concentrations and behavior. SAPRC-99 is compared to identify differences that might be expected between two more recent mechanisms, namely CB05 and SAPRC-99. The predicted ozone concentrations are similar for most of the United States, but statistically significant differences occur over many urban areas and the central US. SAPRC-99 predicts higher concentrations than CB05 on average, and both predict higher ozone than CB4. The difference in ozone predictions depends on location, the VOC/NO_x ratio and concentrations of precursor pollutants. We highlight where the largest differences occur, give some explanation for why they occur, and discuss the effect of differences on model applications.

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1. Introduction

Air quality models (AQMs) are used to describe the transport, formation, decay, and deposition of ozone, air toxics, particulate matter and other pollutants, in order to develop strategies for decreasing their concentrations below harmful levels. An important component of AQMs is the gas-phase chemical mechanism, which describes reactions that

take place in the atmosphere and interactions among chemicals. Different methods have been developed to represent atmospheric chemistry (Dodge, 2000), ranging from simple (approximately seven species) to complex (over 4000 species). Most mechanisms draw on the same data for reaction rates and products, but vary on how they handle unmeasured product mass, pressure and temperature dependence of rate constants, poorly understood photolysis parameters and unknown reaction rates. There are also differences in methods for condensing the organic chemistry into a simplified set of species and reactions for use in AQMs.

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Given numerous uncertainties in atmospheric chemistry and differences in condensation strategies, it is not surprising that different mechanisms sometimes yield different predictions. Several previous studies have used box and trajectory models to examine how much, where, and why predictions differ. For example, Jimenez et al. (2003) summarize many earlier studies, and add a detailed study using a box model to compare seven different mechanisms, including Carbon Bond 4 (CB4) (Gery et al., 1989) and SAPRC-99 (Carter, 2000). With common model conditions and a simple scenario, they found some large variations among model predictions, especially for reactive species, such as hydroperoxy (HO_2) and nitrate (NO_3) radicals, resulting in large differences in termination species such as nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Gross and Stockwell (2003) compared the RADM2 and its update, RACM, with the EMEP mechanism, and found larger species and process differences under urban than rural conditions, due to differences in organic speciation. Luecken et al. (1999) noted that while different mechanisms may predict similar ozone, they distribute oxidized nitrogen species differently. Cycling of oxidized nitrogen among short-lived species (including nitric oxide (NO), nitrogen dioxide (NO_2); where NO and NO_2 are collectively defined as NO_x , as well as less abundant species such as nitrous acid, dinitrogen pentoxide, and peroxyxynitric acid) and longer-lived species (including HNO_3 , organic nitrates, peroxyacetyl nitrate (PAN) and PAN homologs; collectively defined as NO_z), affects ozone production. This cycling can also affect model response to NO_x emission reductions. Tonnesen and Luecken (2001) examined differences between two mechanisms; CB-IV_99 (Adelman, 1999) and SAPRC-99, and found that differences in production and propagation of HO_2 , hydroxyl radicals (OH) (together known as HO_x), and organic peroxy radicals affect ozone formation.

Few comparisons have been done with three-dimensional AQMs, which treat atmospheric processes more realistically than box models, but are more complex to interpret. Arteta et al. (2006) compared predictions from RACM and the simplified CV-MOCA2.2 mechanism in box models and in a fully coupled, three-dimensional meso-scale AQM. They found that differences in mechanism predictions for ozone and NO_x were smaller in the AQM because atmospheric dynamics play an important role, although differences in radicals

were higher in the AQM. Both Byun et al. (2006) and Faraji et al. (2008) used AQMs with versions of CB4 and SAPRC-99 over the Houston–Galveston area. Byun et al. (2006) used two different AQMs and found that SAPRC-99 often predicted more ozone than CB4, although the difference varied from day to day, between locations, and among AQMs. Faraji et al. (2008) examined ozone sensitivity to VOC and NO_x conditions. They found that an updated version of CB4 often showed similar sensitivity to emission reductions as SAPRC-99, but SAPRC-99 predicted higher concentrations than CB4, and note several mechanism features that account for some of the ozone differences.

These previous studies provide evidence that the choice of chemical mechanism in a model can potentially affect ozone predictions. The US Environmental Protection Agency has used the CB4 chemical mechanism extensively in past years to develop and analyze regulations to control ozone and particulate matter. SAPRC-99 is also widely used for both regulatory and research applications. With development of the CB05 chemical mechanism (Yarwood et al., 2005) as an update to CB4, and continued use of SAPRC-99, the question arises whether changing the chemical mechanism might change control strategies. Examining how and why ozone predictions might depend on the chemical mechanism can help us better understand the uncertainty inherent in model predictions, and assist efforts to reconcile modeling studies done by diverse research groups with dissimilar models at various locations.

In this study, we examine differences in predictions of ozone and gas-phase ozone precursors between three chemical mechanisms: CB4, CB05 and SAPRC-99, as implemented in a three-dimensional AQM, the Community Multi-Scale Air Quality (CMAQ) modeling system (Byun and Schere, 2006). This analysis differs from previous studies by examining how predictions vary over a large geographic area and an entire month. The objectives are to: (1) analyze effects of replacing a legacy version of a mechanism (CB4) with an updated version of the same mechanism (CB05); (2) determine how much difference the choice between two alternate mechanisms (CB05 and SAPRC-99) might cause, and (3) identify whether differences are due to updating versus fundamental properties, providing guidance for future mechanism updates.

2. Modeling simulation

2.1. Model and model domain

This study used the CMAQ version 4.5.1 with 14 vertical layers and 36-km horizontal grid cells covering the continental US. Additional simulations were performed with a one-way nested 12-km domain over the Eastern US, starting at approximately -100°W . Meteorological inputs were obtained from the MM5 model (<http://box.mmm.ucar.edu/mm5/>) version 3.6.1. The simulations described in this paper were performed for one month of July 2001, with a 10-day spin-up period in June. Simulations over the 36-km domain were run to calculate integrated rates of reaction and process throughputs for an episode from July 19 to 21, 2001.

We created emissions based on the 2001 National Emissions Inventory (NEI) (<http://www.epa.gov/ttn/chief/net/critsummary.html>). Model species emissions were allocated from organic emissions in the NEI according to speciation rules for each mechanism (Yarwood et al., 2005; Carter, 2000). Biogenic emissions were calculated with BEIS v3.12 (www.epa.gov/asmdnerl/biogen.html). Emissions were processed with SMOKE v.2.0 (<http://www.smoke-model.org>).

2.2. Mechanism descriptions

General characteristics of the three mechanisms used in this study are summarized in Table 1. A detailed discussion on construction of chemical mechanisms and condensation techniques can be found in Dodge (2000) and complete listings of each mechanism are available in the Supplementary material. Several versions of CB4 are available, as documented in Adelman (1999). The version in CMAQ (<http://www.cmaq-model.org>) has 14 spe-

cies and 15 reactions more than the original CB4, including additional termination reactions for peroxy radical operators, updated PAN kinetics, temperature and pressure dependence of some reaction rates, split of the singlet-D oxygen atom reaction with air, updated reactions for isoprene, production of aqueous species, and production of aerosols (Gipson and Young, 1999).

CB05 is an updated version of CB4, but retains the lumped-structure approach. In CB05, reaction rate constants were updated, additional inorganic reactions were included, and 10 organic species were added to better represent stable organic species and radicals in the atmosphere (Yarwood et al., 2005).

SAPRC-99 is of intermediate age between the other two mechanisms, uses a different scheme for condensing the organic chemistry and has more detailed organic chemistry than the Carbon Bond mechanisms. The version of SAPRC-99 in CMAQ was modified to include aerosol production and reactions of organic acids. Updated reaction rates in CB05 are an area of difference between CB05 and SAPRC-99, but there are substantial differences between the two more recent mechanisms (SAPRC-99, CB05) and CB4. The most important of these include better description of NO_x and NO_z cycling, representation of secondary products and their reactions in lower- NO_x environments, differentiation of aldehydes, representation of internal alkenes, and updated cross section and quantum yields for photolysis.

3. Results

We first present results for ozone, followed by NO_z and other species that affect ozone. We discuss differences between CB4 and CB05 followed by those between CB05 and SAPRC-99.

Table 1

Comparison of species, reactions, and approximate simulation time for each of the three mechanisms examined in this study

	CB4	CB05	SAPRC-99
Date of last major update	1989	2005	1999
Type of representation	Lumped structure	Lumped structure	Lumped molecule
Total number of reactions	96	156	214
Number of inorganic reactions	45	63	45
Total number of species	46	59	80
Number of organic species	30	41	64
Approximate run time relative to CB4 (12 km domain)	1	1.14	1.39
Approximate run time relative to CB4 (36 km domain)	1	1.23	1.51

3.1. Ozone

Fig. 1 displays ozone concentrations from each of the three chemical mechanisms and differences between mechanisms; these are monthly averages of daily maximum 8-h ozone concentrations. There are many ways to analyze ozone, and while comparisons can differ slightly from day-to-day, the general spatial patterns do not change much. Overall, SAPRC-99 predicts the highest ozone, CB05 predicts next highest and CB4 predicts the

least. Differences between CB4 and CB05 are not large in the Northeastern part of the country (averaging <5%), but can be much larger in the Southern Plains (Oklahoma, northern Texas, and Arkansas), averaging 12%. In the Great Lakes area (Illinois, Indiana, Ohio, Michigan, Kentucky), the average difference is about 7%. In the Southeast (Georgia, North Carolina, South Carolina, Tennessee, Alabama), the average difference is 9%. Overall, SAPRC-99 is more spatially similar to CB05, with the exception of differences up to 16% in

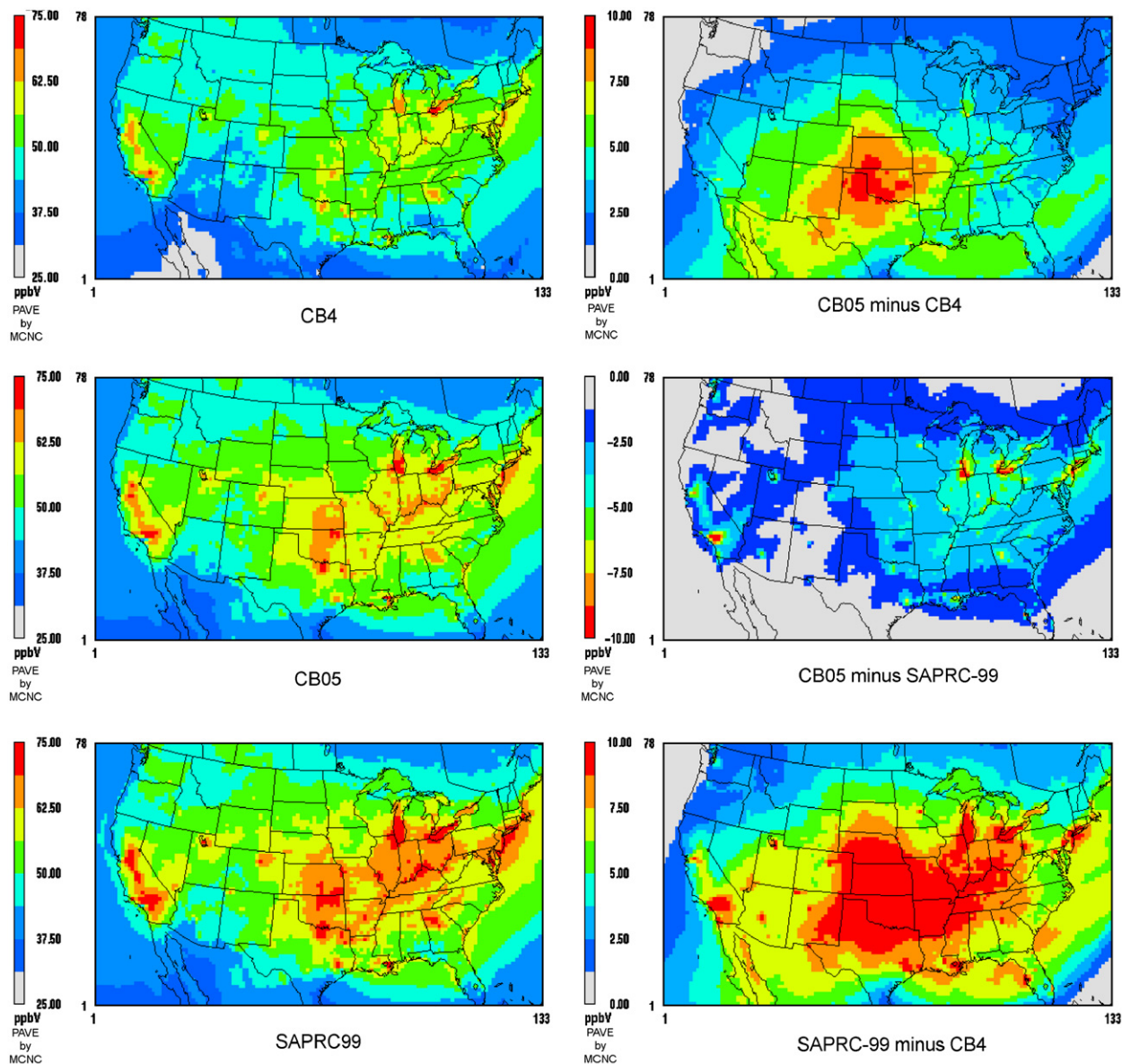


Fig. 1. Left: July 2001 surface level average 8-h maximum ozone concentrations for the three mechanisms. Right: differences between pairs of mechanisms for the 36-km simulations.

urban areas and the Ohio River valley. Like CB05, SAPRC-99 predicts large differences from CB4 in the Southern Plains.

To highlight temporal differences, we selected 11 grid cells for further examination, with locations displayed in Fig. 2, including grid cells at eight cities (at a grid cell where the ozone is high) and three non-urban areas influenced by biogenic VOCs (see Supplementary material for daily distributions). Fig. 3 presents a distribution of daily differences in 8-h maximum ozone for these 11 grid cells. While Fig. 1 showed average patterns, this figure emphasizes differences in urban areas and their large temporal variability. Predictions in Chicago and Houston, for example, range from only slightly different (less than 2 ppb) on some days to substantially different (up to 23 ppb). Open circles on Fig. 3 indicate days when CB05 predicts higher than 8-h averaged 75 ppb ozone. Higher differences often occur at higher ozone concentrations, but are not always well correlated. One mechanism can predict ozone concentrations above the current US standard (85 ppb for 8-h average) while others do not. These occurrences are most likely to happen in urban areas including Chicago, St. Louis, Cleveland, Atlanta, and Los Angeles, and along the Ohio River Valley (see Supplementary material). The number of these occurrences is small and geogra-

phically limited, but can potentially affect ozone characterization and control strategies.

Fig. 4 shows the effect of grid size by presenting results from the more resolved 12-km simulations. This figure shows daily differences in the 8-h maximum ozone for each of the nine, 12-km cells that make up the 36-km Chicago grid. The mechanisms are more variable at smaller grid cells, with differences from CB05 ranging from -0.3 to 22.5 for CB4 and -1.2 to -38.6 for SAPRC-99, versus differences on the 36-km grid of -0.2 to 15.2 for CB4 and -2.6 to -22.6 for SAPRC-99. Larger grid cells smooth out spatial variations in emissions and concentrations, resulting in less variability.

Differences among mechanisms also occur at higher levels above the surface. Fig. 5 displays the same information as Fig. 3, but at model layer 6, approximately 660 m. Ozone concentrations are higher at this level (more circles indicating concentrations greater than 75 ppb), but the differences are not substantially larger than at the surface. The version of CB4 used in CMAQ has reaction rate temperature and pressure dependencies that should allow it to represent conditions at higher levels, contributing to the similar magnitude of differences between CB4, CB05 and SAPRC-99 at both the surface and elevated levels.

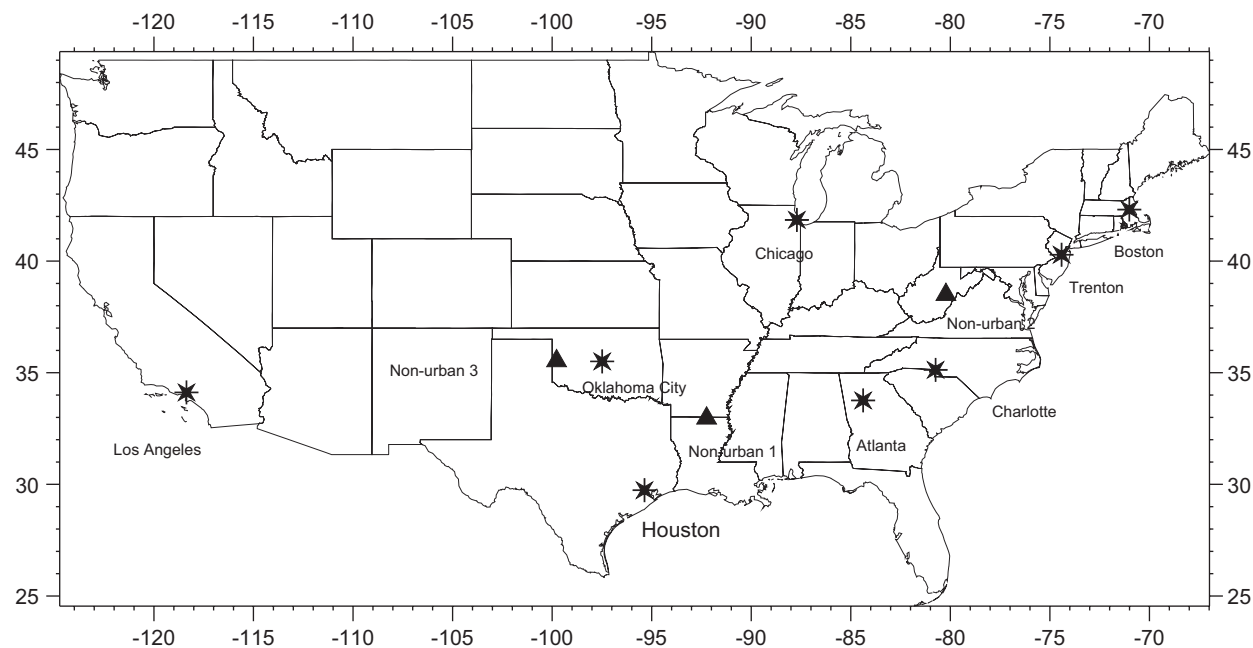


Fig. 2. Location of grids for individual analysis. Stars indicate predominantly urban areas and triangles indicate predominantly rural grids.

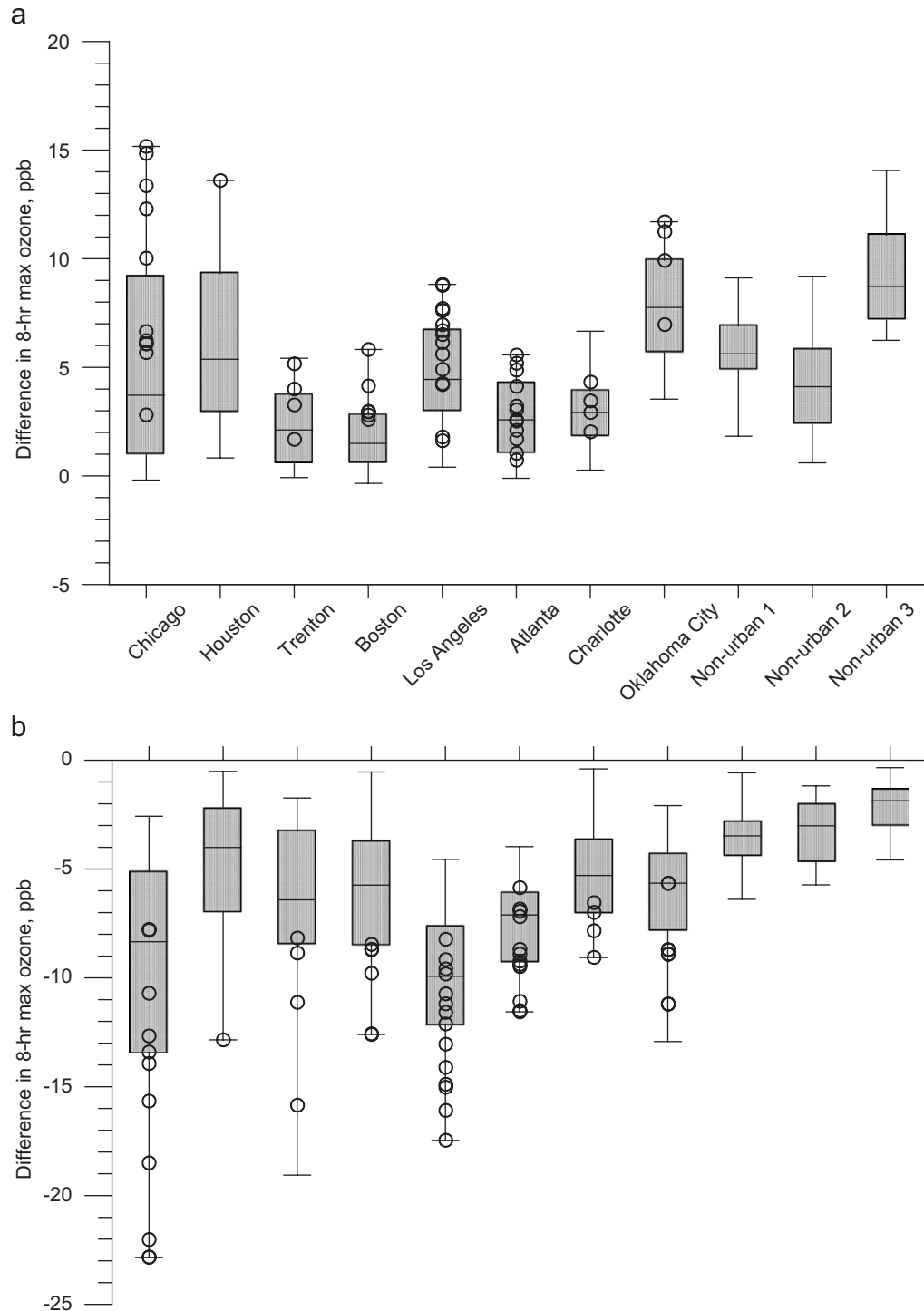


Fig. 3. Box-and-whisker plot of differences in 8-h maximum ozone concentrations in the surface layer between: (a) CB05 and CB4 and (b) CB05 and SAPRC-99. Differences are shown for each day in July 2001 in the 36-km simulations. End caps mark minimum and maximum differences, box bottom and tops mark first and third quartiles, and the middle line indicates median. Open circles represent days when CB05 predicts ozone concentrations greater than 75 ppb.

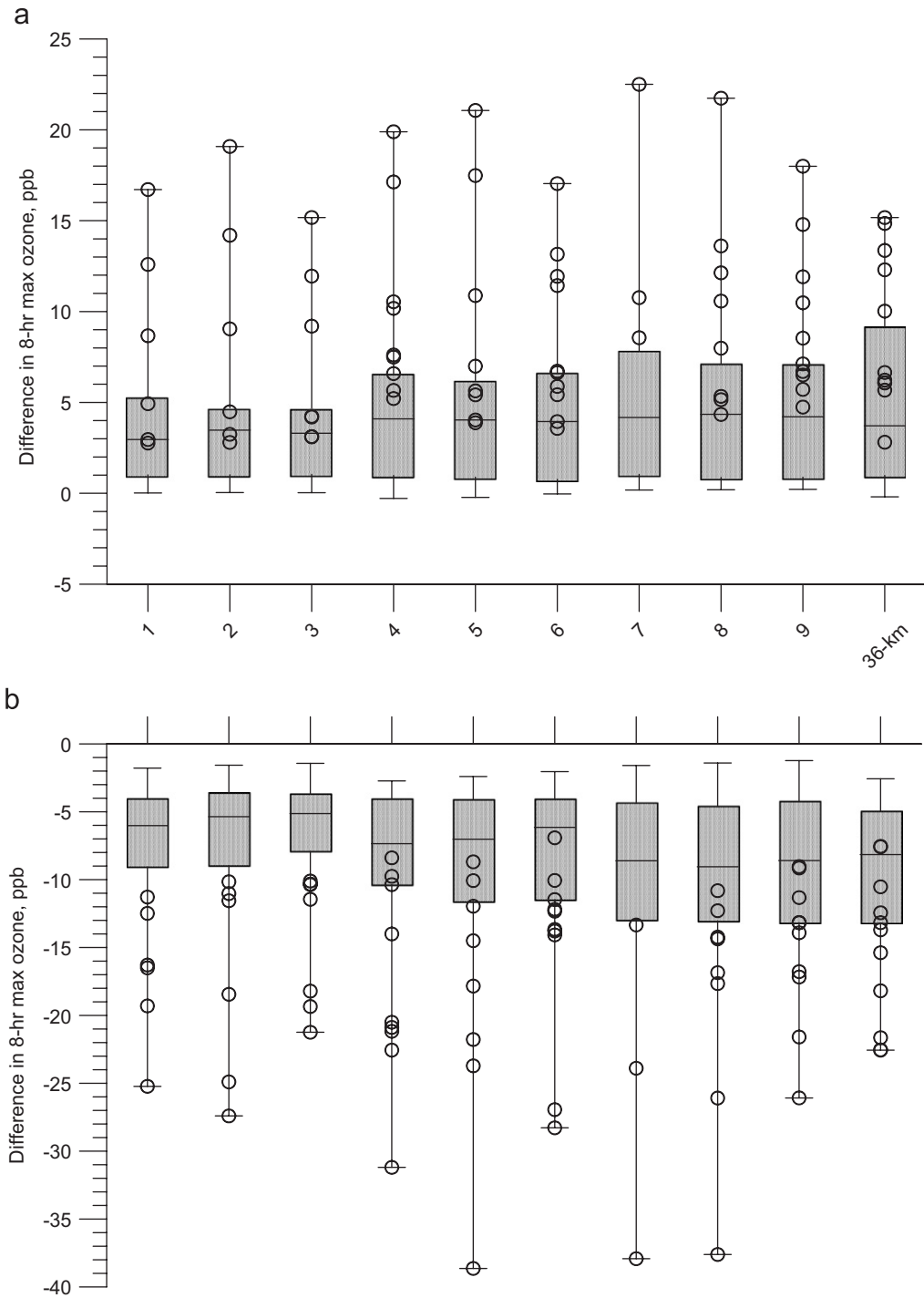


Fig. 4. Differences in 8-h maximum ozone concentrations in the surface layer between: (a) CB05 and CB4 and (b) CB05 and SAPRC-99, for the nine grid cells encompassed by the 36-km Chicago grid in Fig. 3. The last plot shows the 36-km Chicago values from Fig. 3. Differences are shown for each day in July 2001 for the 12-km Eastern US simulations. Open circles represent days when CB05 predicts ozone concentration greater than 75 ppb.

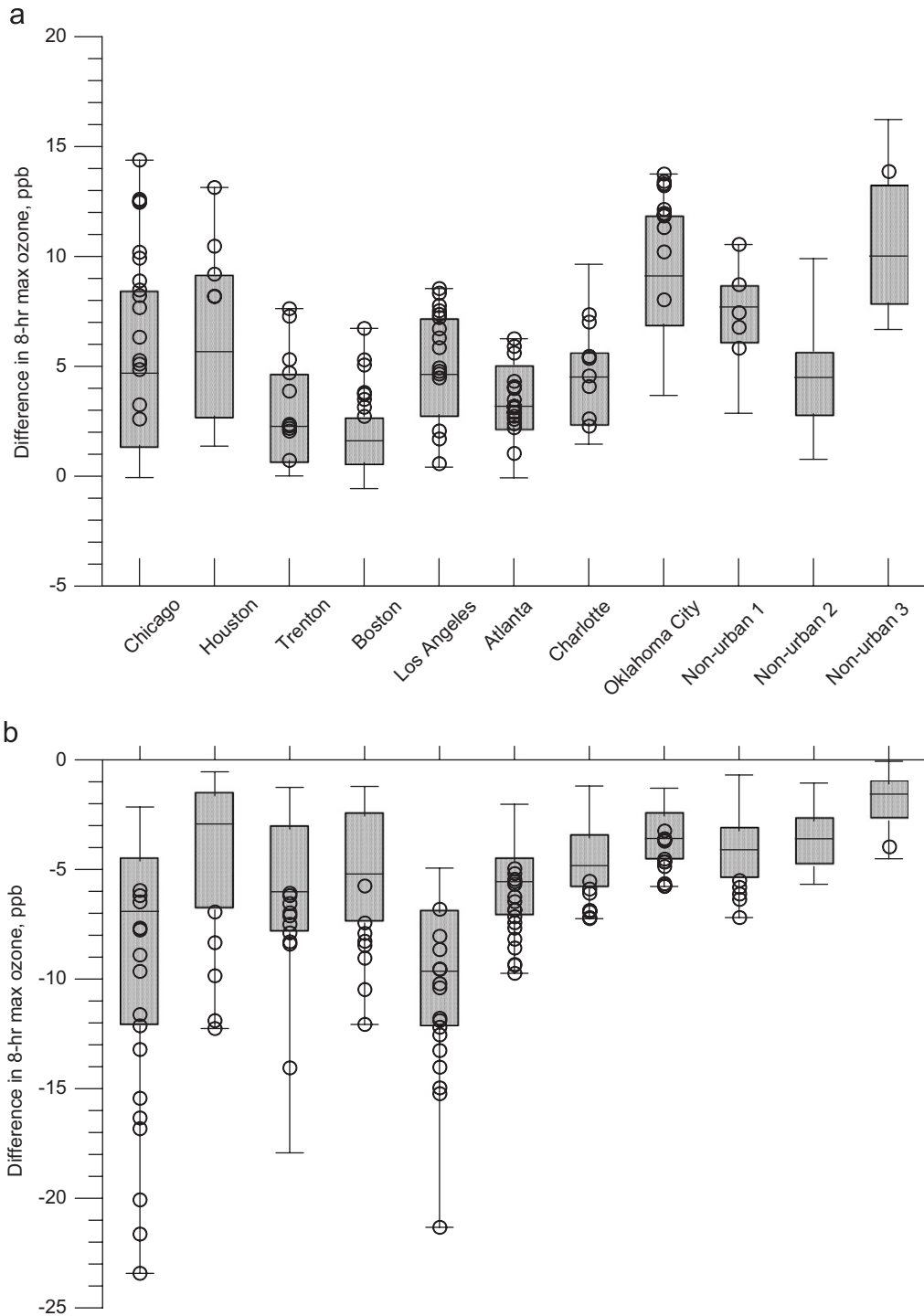


Fig. 5. Differences in 8-h maximum ozone concentrations in elevated layer 6 between: (a) CB05 and CB4 and (b) CB05 and SAPRC-99. Differences are shown for each day in July 2001 for the 36-km simulations. Open circles represent days when CB05 predicts ozone concentration greater than 75 ppb.

While many differences exist between CB4 and CB05, one of the most important for ozone is the separation of acetaldehyde (represented in CB05 by ALD2) and aldehydes having more than two carbons (ALDX). The ALDX species can produce about 50% more conversions of NO to NO₂ than ALD2; therefore reactions where the ALD2 in CB4 is now represented by part ALD2 and part ALDX have increased ozone formation. Fig. 6 shows how CB4 and CB05 differ in production of new HO_x from all aldehyde species. There are large areas of the country with average differences between 0.01 and 0.03 ppbh⁻¹, about a 25–45% difference, and the largest differences occur both in urban areas and in the Southern Plains, where the largest ozone differences are found. Production of HO_x from aldehydes depends on both production of aldehydes, which is larger in CB05 than CB4, and the photolysis of aldehydes, which is also larger in CB05 due to updated photolysis parameters and the higher photolysis rate of ALDX compared to ALD2 (see Supplementary material). Production of HO₂ via aldehydes is similar between CB05 and SAPRC, but CB05 is from 14% lower to 4% higher than SAPRC-99, depending on the location. Both CB05 and SAPRC-99 use the same photolysis parameters for aldehydes; differences result from different product coefficients of secondary aldehydes.

Differences in ozone also result from the representation of peroxy radical species. The CB4 species representing all acyl peroxy radicals (C2O3) is now

split up into two CB05 species: acetyl peroxy radical (C2O3) and other acyl peroxy radicals (CXO3). The CXO3 can convert 50% more NO to NO₂ than C2O3, and this effect is apparent in the reactions of alkenes, including isoprene, with ozone and NO₃. CB05 also replaces the alkyl peroxy radical operator (XO2) in some reactions with methyl peroxy radical (MEO2) to better represent reactions under low NO_x conditions, including peroxy radical cross and self-reaction and peroxide production.

Another difference between CB4 and CB05 was the inclusion of a model species representing internal alkenes. These species were represented by two molecules of species ALD2 in CB4, which allowed the chemicals to photolyze (which does not happen with alkenes) but not react with ozone (an important reaction for alkenes). While the net effect on ozone might be similar, this can change the temporal production of ozone.

The newer mechanisms (CB05 and SAPRC-99) have a better characterization of radical recycling than CB4. With inclusion of these recycling reactions, compounds that were previously considered termination products can re-form reactive species. In the newer mechanisms, both HNO₃ and organic nitrate photolyze, providing a source of HO_x and NO₂. Organic peroxides photolyze in CB05 and SAPRC, but not in CB4, providing additional organic radicals. In the Southern Plains, VOC concentrations are not as large as in the Southeast, and transported PANs and organic nitrate that decay are not as likely to re-form. HNO₃ and

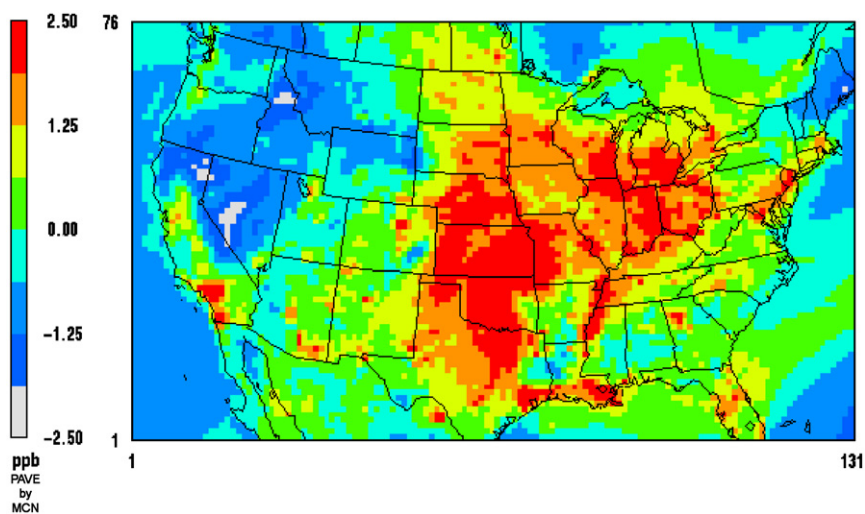


Fig. 6. Differences in total new HO_x production from all aldehydes (CB05 minus CB4 value) summed over July 19–21, 2001 for the 36-km simulations.

organic nitrate are less likely to be removed due to less precipitation in this area.

SAPRC-99 gives slightly higher ozone than CB05 overall and the largest differences occur in urban and other areas where NO_x emissions are high relative to VOC emissions (see Supplementary material). Fig. 7 shows an example of the correspondence between the average difference in 8-h maximum ozone at each grid and the VOC/ NO_x ratio in emissions. While there is no simple correlation, the low ratios tend to have larger differences and the high ratios have smaller differences. Where VOC/ NO_x is high, CB05 has slightly more (2–3% higher) reaction of OH with VOC. Where it is low (such as urban areas), SAPRC-99 has higher (up to 6%) reaction rates. The emissions are speciated differently, and while the total emitted carbon is the same, the VOC emissions are larger in SAPRC-99, especially in urban areas, because of differences in the condensation of the organic chemistry. Parameterizations of reaction rates and products should compensate for

differences in reactive VOC emissions, but these parameterizations cannot fully represent all places and all times. Some of the differences might be minimized by more harmonization of the independently developed speciation rules for each mechanism, but it is not possible to completely compare emissions of model species.

Tonnesen and Luecken (2001) found that in box model simulations, CB-IV_99 produced more ozone under low VOC/ NO_x conditions and SAPRC-99 predicted higher ozone under high VOC/ NO_x conditions—a different result. While CB-IV_99 and CB05 are both updated versions of CB4, they were developed independently and differ in their detail of organic species and in rate constants. The box model also used relatively simple VOC emissions.

Other studies (Faraji et al., 2008; Tonnesen and Luecken, 2001) identified aromatic reactions as an important source of differences in ozone formation between Carbon Bond mechanisms and SAPRC-99. The treatment of aromatics in CB05 is identical to

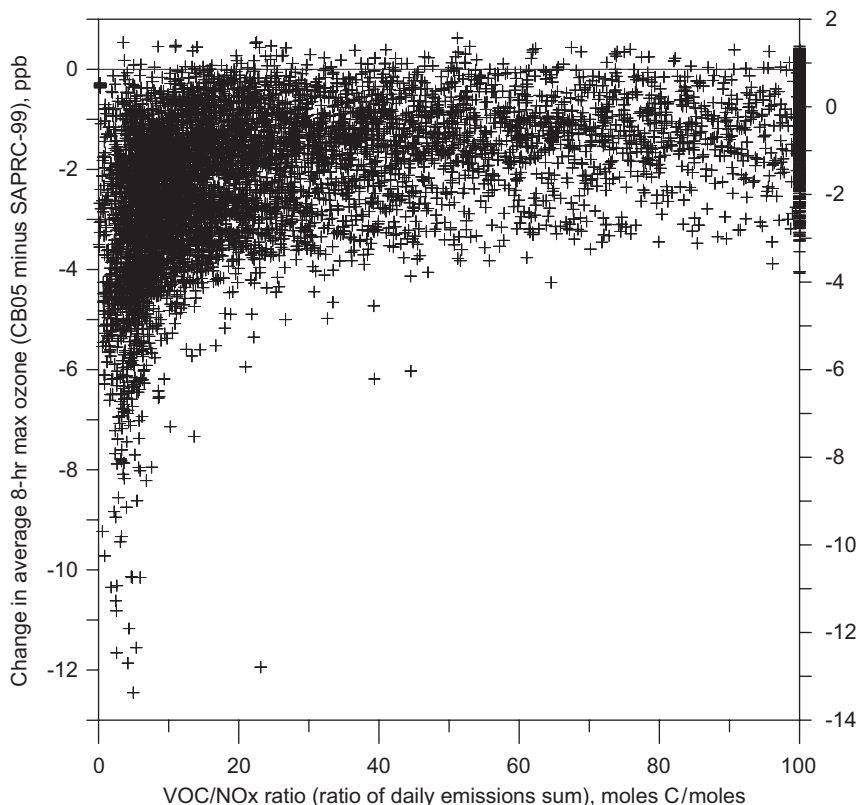


Fig. 7. Correspondence between differences in average 8-h maximum ozone concentrations and VOC/ NO_x emission ratios at each grid cell in the 36-km domain. Ozone is averaged during July 2001. Emissions ratios are calculated from a daily sum of VOC and NO_x emissions at each grid cell on July 19, 2001, and all ratios greater than 100 are plotted at a value of 100.

that of CB4. Faraji et al. (2008) show that aromatic fragments in SAPRC-99 are more reactive than those in CB05.

3.2. NO_z

The inorganic chemistry in CB05 has been significantly updated and enhanced, which affects the concentrations, spatial distributions and cycling of oxidized nitrogen species. The amount of oxidized nitrogen that is present as NO_2 , which leads to ozone production, versus that in NO_z , affects the rate and magnitude of ozone production. Differences in NO_z show similar spatial patterns as the ozone differences and the VOC/ NO_x ratios. Fig. 8 shows monthly average concentrations of

total NO_z and three NO_z species at the 11 selected grid cells.

Fig. 8a illustrates that HNO_3 in CB4 is generally within 10% of the concentration predicted by CB05, despite the higher termination reaction rate in CB4 (about 8% higher), lower reaction rate for loss with OH (5% less) and no loss from photolysis. SAPRC-99 has a higher HNO_3 concentration than CB05 in urban areas but is similar to CB05 elsewhere. CB05 uses the rate for NO_2 reaction with OH from Sander et al. (2003), which is 13% larger than that in SAPRC-99, based on a 1998 version of the same reference. Counterbalancing the lower rate, SAPRC-99 has higher OH concentrations on average in many urban areas, such as Chicago, where the OH concentration is 25% higher in

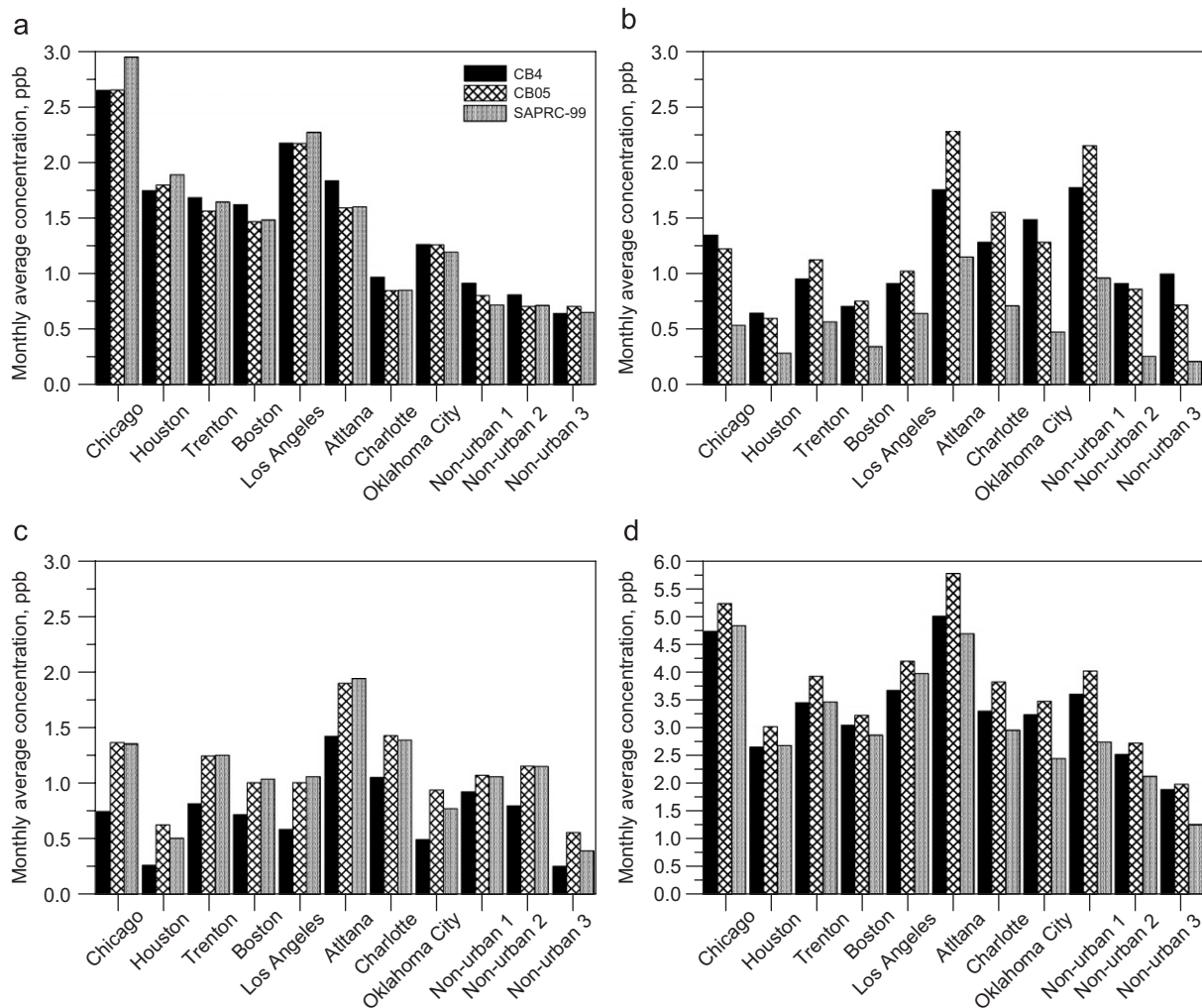


Fig. 8. Example of spatial variation of concentration of: (a) nitric acid, (b) organic nitrate, (c) peroxyacetyl nitrates, and (d) total NO_z , averaged over July for the 36-km simulations.

SAPRC-99. Updates to SAPRC-99 (Carter, 2007) will include a higher termination rate, equivalent to that in CB05, but the net effects on ozone will depend on other changes, including a slightly higher NO_2 photolysis rate.

In Fig. 8b, CB4 predicts higher organic nitrate in the Southern Plains (Oklahoma City and Non-urban 3), where ozone differences are highest, but less in most other areas. In both CB05 and SAPRC-99, organic nitrate can react back to NO_2 , but not in CB4. There are large differences between SAPRC-99 and CB05 everywhere, with the largest percentage differences occurring where isoprene is high. Reactions of NO_3 and isoprene (and isoprene products) produce more organic nitrate in CB05 than SAPRC-99, and none in CB4.

Fig. 8c shows that CB4 apportions peroxyacetyl nitrate (PAN) and homologs (peroxypropionyl nitrate and larger compounds) differently than the other two mechanisms. In CB4, the species PAN represents all peroxyacetyl nitrates, whereas in the other mechanisms, PAN is separate from other homologs. CB4 has a lower PAN formation rate and higher decomposition rate than CB05, contributing to lower concentrations of total PANs. Despite differences in description of PANs (SAPRC-99 has 4 PAN homologs), decomposition rates and production pathways of higher peroxyacylnitrates, both CB05 and SAPRC-99 predict similar concentrations of total PANs.

Fig. 8d shows that total average NO_2 concentrations in CB05 are higher than in the other mechanisms. Some relationships between ozone and total NO_2 concentrations are shown in Fig. 9 for the period July 19–21, for the hours of 1000–1700 CST. As a surrogate for ozone production efficiency, the slope of this line is indicative of the net ozone production for each NO_x that is terminated to NO_2 , as described in Trainer et al. (2000). For cities examined in this study, CB05 has higher rates of both ozone production and termination than CB4, but a similar slope. SAPRC-99 consistently has a higher slope than CB05 and CB4. SAPRC-99 produces more ozone, and has a slightly higher NO_x termination than CB05, but ozone loss plays a relatively larger role earlier in the afternoon in CB05, resulting in a lower net ozone production in CB05. In the Southern Plains sites (Fig. 8d), the slope is indeterminate, but ozone in SAPRC-99 is higher than CB05, and the NO_2 concentration is lower.

3.3. Aldehydes

Fig. 10a shows differences between CB05 and CB4 in predicted concentrations of formaldehyde. CB4 produces more formaldehyde than either CB05 or SAPRC-99 everywhere, much more in the Southeast and Southern Plains. CB4 produces more formaldehyde directly from $\text{VOC} + \text{OH}$ reactions and from acetaldehyde photolysis. This direct production was removed from CB05 by adding the methyl peroxy radical, which does not force production of formaldehyde from VOCs and OH under low NO_x conditions. In addition to higher production, CB4 also has a formaldehyde photolysis rate that is about 25% less via the radical channel and 40% less through the molecular channel. In CB4 and CB05, emissions of some non-formaldehyde VOCs are apportioned partially to formaldehyde.

CB4 also predicts higher concentrations of aldehydes with two or more carbons (acetaldehyde and larger) than CB05 or SAPRC-99 in the Southeast and Pacific Northwest. The comparison is complicated because internal alkenes in CB4 were allocated to aldehydes and biogenic sources emit large amounts of internal alkenes in the Southeast and Pacific Northwest. CB05 predicts twice as much acetaldehyde as SAPRC-99, with approximately 60% of the difference due to product coefficients in alkene (other than isoprene and ethene) reactions, mostly through alkene reactions with ozone.

3.4. Hydrogen peroxide

Differences in predicted H_2O_2 concentrations between CB05 and CB4 are shown in Fig. 10b. All mechanisms show similar spatial distributions of H_2O_2 but differ in absolute concentrations. CB4 has the highest concentration because its formation rate is 62% higher than CB05 (from Sander et al., 2003) or SAPRC-99 (from Atkinson et al., 1997). While both CB05 and SAPRC-99 have similar rate constants for H_2O_2 formation and photolysis, concentrations are 30% larger in CB05 than SAPRC-99 because CB05 produces more new HO_2 , enhancing formation of H_2O_2 . Large differences occur in the Southern Mississippi valley, where isoprene and terpene emissions are large.

4. Discussion

Ozone formation in ambient atmospheres is complex, and differences in mechanism predictions are not

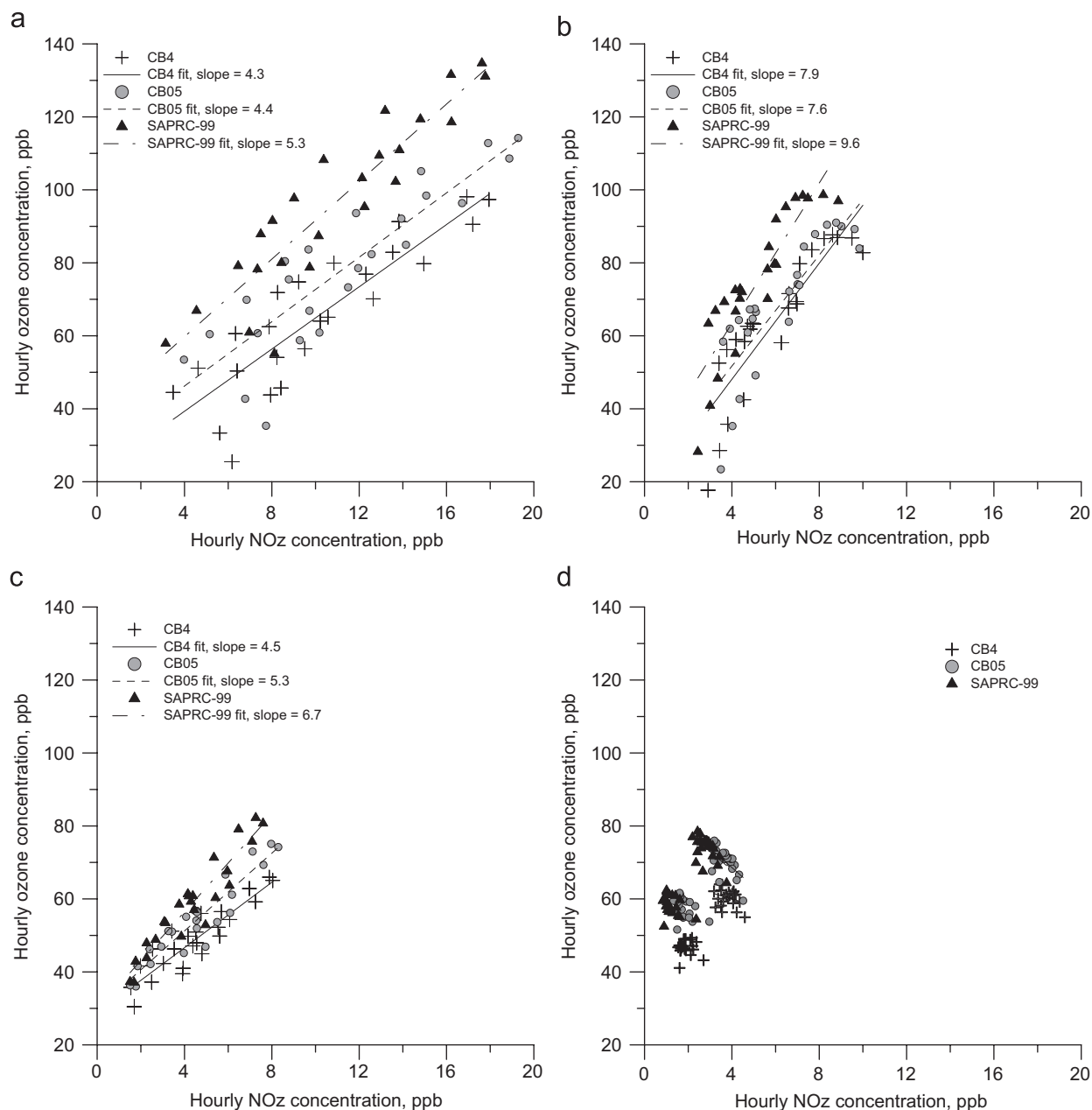


Fig. 9. Examples of correspondence between ozone and NO_2 concentrations for daytime periods 1000 through 1700 CST during July 19–21 for the 36-km simulations. Values are plotted for grids representing: (a) Chicago, (b) Atlanta, (c) Houston, and (d) Oklahoma City (higher cluster) and non-urban 3 (lower cluster).

explainable by single components of the mechanisms. Numerous factors contribute to ozone differences under different conditions and locations throughout the US. The largest differences in mechanism predictions for ozone occur in urban areas and the Southern Plains, with substantial differences for other species also seen in the Southern US.

The 36-km grid resolution used in this study allowed us to examine predicted differences across a large area. We note that the mixing occurring in these relatively large grid cells can smooth out smaller-scale variations in emissions and chemistry. Comparisons over the smaller 12-km grids show a slightly larger variation in differences from

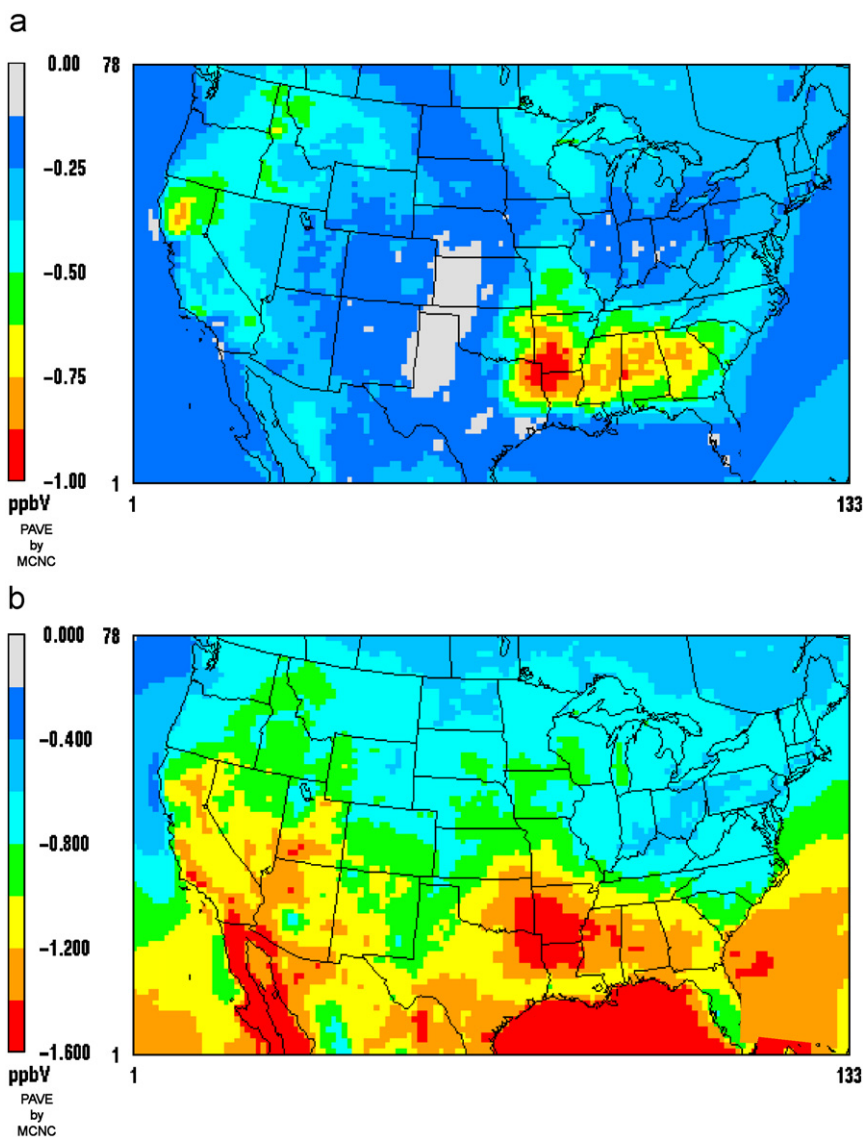


Fig. 10. Differences in concentrations (CB05 value minus CB4 value) of: (a) formaldehyde and (b) hydrogen peroxide. Concentrations are July monthly averages for the 36-km simulations.

day-to-day but the general patterns are consistent in both resolutions.

Although there is not an easily quantifiable relationship between ozone concentration and ozone differences, the largest differences often occur at higher ozone concentrations for a given location. There are some instances where one mechanism predicts concentrations above the standard and another does not. Many differences among mechanisms occur in areas with large biogenic emissions. The high reactivity of biogenic alkenes and large emissions during the summer make this a particularly important component of ozone production.

Both reaction rate constants and radical concentration differences affect the production of ozone. Predictions of the two most recent mechanisms (CB05 and SAPRC-99) are more similar in spatial patterns than either one is with the older CB4 because both the reactions and the rates are more consistent with current knowledge. Inclusion of NO_x and HO_x recycling reactions, for example, has small effects on ozone predictions in some parts of the country, especially where less precipitation occurs. It is important that older chemical mechanisms be revised periodically to be consistent with current knowledge. With the imminent update

of SAPRC-99 (Carter, 2007), comparison of predictions with CB05 might converge more closely.

Emission speciation among independently derived chemical mechanisms can affect the ozone predictions, complicating comparisons of chemistry. Simplifications made in mechanism condensation and fundamental differences in condensation techniques between CB05 and SAPRC-99 make it difficult to define equivalent emissions. The large number and diversity of emitted VOCs is also a challenge. Techniques to produce more consistent emission assignments for AQMs have been recently developed (Adelman et al., 2005) and should be considered for future studies. However, different assumptions of reaction rates and product coefficients to represent parameterized model species will complicate comparisons of VOC emissions.

Because of these differences in ozone, it is also important to study how mechanisms react to reductions of NO_x and VOC emissions, so that we understand how control strategy development might be affected. This is the focus of current work at the US Environmental Protection Agency and is necessary to give us confidence that previous control strategies developed with CB4 will be generally valid with the updated CB05. When mechanisms differ in their speciation of oxidized nitrogen and production of H₂O₂ and OH, they can also differ in production and partitioning of sulfate and nitrate aerosol, affecting particulate matter concentrations.

Given differences among mechanism predictions and difficulty in proving which one is “correct,” regulatory decisions based on model predictions should account for the uncertainty due to differences in chemical representation. The range of predictions resulting from mechanism comparison studies can be used to establish uncertainty ranges in model predictions and should be a consideration in the development of robust control strategies. Regulatory modeling should also use mechanisms that are consistent with our best knowledge of atmospheric chemistry to ensure that we are representing not just ozone concentration, but also its precursors and its sensitivity to precursors as correctly as possible.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2007.08.056.

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