

For Presentation at the Air & Waste Management Association's 90th Annual Meeting & Exhibition, June 8-13, 1997, Toronto, Ontario, Canada

97-RA94.05

Sensitivity of Ozone Predictions to Biogenic Hydrocarbon Chemistry and Emissions in Air Quality Models

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Abstract

Over the last decade, there is growing evidence that biogenic hydrocarbons play an important role in regional and urban ozone (O₃) formation in the United States. As a result, the regulatory guidelines issued by the USEPA require that biogenic emissions be included in photochemical modeling. Significant changes and improvement have also been made for estimating the emissions and chemical reaction rates of biogenic hydrocarbons in air quality models. In this paper we examine the sensitivity of ozone predictions to the changes in biogenic hydrocarbon chemistry and emissions and investigate why ozone are sensitive to these changes. We first use a Lagrangian box model, the OZIPR/EKMA model, to examine the differences of O₃ predicted using two sets of chemical mechanisms, the original CB4 mechanism and the updated CB4 mechanism with new isoprene chemistry under various emission scenarios. Our results show that in the selected urban case, the updated CB4 mechanism predicted lower O₃ than the original CB4 mechanism because of the lower isoprene incremental reactivity in the updated CB4 mechanism. However, in the selected rural case, the updated CB4 mechanism predicted higher O₃ than the original CB4, which is in contradiction to a recent OTAG study using the updated CB4 mechanism. The Eulerian grid model simulation using the MCNC's EDSS/MAQSIP system further lends support to our box model results. The grid model simulations show that the updated CB4 mechanism predicts much lower O₃ than the original CB4 mechanism over the areas where significant amount of NO_x is emitted; on the contrary, over the Southeastern United States region with high isoprene emission rates, the updated CB4 mechanism predicts much higher O₃. Our results suggest that the updated CB4 mechanism tend to predict higher O₃ than that using the original CB4 mechanism in the rural areas where isoprene is the major emitted VOC and tend to predict lower O₃ in the urban areas where there is plenty of NO_x emitted (VOC-limited). We also found that the level of temperature selected has a significant impact to the calculation of biogenic emission rates. In one case we found that the emission rates of isoprene increase significantly (up to 50%) around the Great Lakes shore areas, and the afternoon isoprene emission rates drop as much as 20% in the selected Southeastern region when the model temperature at 19 m instead of OTAG's 1.5 m is used. Our next task is to perform further detailed chemistry analysis to understand why the updated CB4 mechanism predicts differently from the original CB4 mechanism.

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Introduction

Ozone (O₃) is formed from a series of photochemical reactions among its precursors, primarily nitrogen oxides (NO_x) and volatile Organic Compounds (VOC), emitted from both anthropogenic and biogenic sources. Over the last decade, there is growing evidence that biogenic VOC, especially isoprene, play an important role in regional and urban O₃ formation in the United States (Trainer et al., 1987; Chameides et al., 1988). As a result, the regulatory guidelines issued by the USEPA require that biogenic emissions be included in photochemical modeling (EPA, 1991). Significant changes and improvement have been made for estimating the biogenic emission rates in emission inventory models (Geron et al., 1994; Jackson et al., 1995) and reaction rates of isoprene in chemistry mechanisms (Carter, 1996; Carter and Atkinson, 1996) in air quality modeling systems. For example, in 1995, EPA updated the Biogenic Inventory System (BEIS) (Pierce et al., 1990) and release the revised version (BEIS2) (EPA, 1995); in the regional modeling effort by the Ozone Transport Assessment Group (OTAG), the CB4 mechanism was updated with new isoprene chemistry developed by Carter (1996) in the Urban Airshed Model Version V (UAM-V) (Whitten et al., 1996).

Carter and Atkinson (1996) developed a detailed mechanism for the isoprene reactions in the presence of NO_x based on most recent laboratory results and understanding of the photochemical reaction system. They have found the presence of important isoprene secondary photooxidation products which is not included in the existing mechanisms. To reduce the computer impact in incorporating the new isoprene mechanism into airshed models, Carter (1996) has further developed a condensed mechanism for isoprene with either one or four isoprene's oxidation products. Based on his evaluation against smog chamber simulations and other existing chemistry mechanisms, Carter (1996) suggested that the new mechanism for isoprene be used in airshed models to improve the accuracy of ozone simulations where isoprene emissions are important. Carter's new isoprene mechanism has been first incorporated into the OTAG's regional modeling effort in which the UAM-V/CB4 mechanism is updated with one-product condensed isoprene mechanism (Whitten et al., 1996). It was shown in this study that the UAM-V with updated CB4 mechanism generally predicts less ozone than that with original CB4 because of the lower isoprene reactivity in the updated CB4 mechanism with new isoprene chemistry. However, there were

no model sensitivity analysis or simple box model simulations presented in this work. It was shown in Carter's (1996) work that the new isoprene mechanism could lead to O₃ increase as well as O₃ decrease, depending upon the level of NO_x. Several studies also shown that biogenic emission rates are very sensitive to the changes in temperature and solar radiation (Geron et al., 1993; Geron et al., 1994). In a recent emission inventory modeling effort (Houyoux et al., 1996), we have also found that the level of temperature used has significant impact to the calculation of biogenic emission rates. However, the impact of isoprene emission rates caused by temperature sensitivity and its effect on the model predictions of O₃ is not fully explored elsewhere.

The purpose of this research work is to examine the sensitivity of ozone predictions to the changes in biogenic chemistry and emissions in air quality models. In the sensitivity study, we first use a Lagrangian box model as the tool to compare the differences of O₃ simulated by two sets of chemical mechanisms; the original CB4 mechanism vs. the updated CB4 mechanism with new isoprene chemistry. Our second task is to use an Eulerian grid models to make comparisons of the differences of O₃ simulated by these two different mechanisms and different biogenic emission inputs based on various temperature scenarios. The modeling tool we use is the MCNC's Environmental Decision Support System - Multiscale Air Quality Simulation Platform (EDSS/MAQSIP) (Fine and Ambrosiano, 1996; Odman and Ingram, 1996), which is a prototype of the EPA's Models-3 system (Dennis et al., 1996). We will finally apply a diagnostic analysis tool, the Process Analysis Method (Jang et al., 1995a and 1995b), to investigate why ozone is sensitive to the changes in biogenic chemistry and emissions.

Model Description

1. Lagrangian Box Model

The Lagrangian Box Model we first use to test O₃ sensitivity to the changes in biogenic chemistry and emissions is a research version of EPA's Ozone Isopleth Plotting Package (OZIP) computer modeling program, or OZIPR (Gery and Crouse, 1996). The OZIP and OZIPR use a trajectory-based air quality simulation model, in conjunction with the Empirical Kinetic Modeling Approach (EKMA), to relate O₃ concentrations to levels of NO_x and VOC. While the OZIP has a rigid structure to be implemented in O₃ simulation, the OZIPR has an enhanced structure to provide flexible input of more parameters and expanded output of more information for detailed analysis of model performance. For example, OZIPR provides a flexible chemistry reader to allow easy changes for chemistry mechanism, which is very desirable for this study.

2. Eulerian Grid Model

The Eulerian grid model we use for this study is a state-of-the-science air quality modeling system, the MCNC's MAQSIP (Odman and Ingram, 1996) model, which is developed under the umbrella of MCNC's EDSS (Fine and Ambrosiano, 1996) and EPA's Models-3 system (Dennis et al., 1996). The MAQSIP is a flexible and complete chemistry/transport air quality modeling framework that manifests the concept of modularity, portability, and data compatibility (Jang et al., 1995c). The EDSS/MAQSIP has many enhanced features and options for representing various chemical and physical processes, such as multiscale modeling capabilities, options for various chemistry mechanism and solvers, options for

advanced advection and diffusion schemes, advanced cloud parameterizations, advanced aerosol modeling, process analysis capabilities, etc. The EDSS/MAQSIP model has been well tested and under evaluation for a number of regional and urban applications in the United States, such as the Seasonal Model for Regional Air Quality (SMRAQ) project for southeastern U.S. seasonal ozone study (Smith et al., 1996), the California's San Joaquin Valley ozone study (Odman et al., 1996), and the eastern U.S. ozone and acid deposition study. With the system's modularity and advanced sciences, the EDSS/MAQSIP provides an ideal platform for this sensitivity study.

3. Chemistry Mechanism

The Carbon Bond Mechanism IV (CB4) is used in the UAM to simulate the photochemical kinetic reactions of atmospheric species. In this sensitivity study, we compare two mechanisms, the original CB4 (Gery et al., 1989) and the updated CB4 with new isoprene chemistry (Whitten et al., 1996). A detailed description of the differences between these two mechanisms is given in Whitten et al. (1996). Briefly, the major differences are the addition of an important isoprene photooxidation product (ISPD) and a great reduction of isoprene incremental reactivity resulting from the newly formulated isoprene reactions with OH, O₃, O(³P) and NO₃. Table 1 gives a list of isoprene reactions that are different in these two mechanisms.

Results and Discussion

1. Lagrangian Box Model Simulations

For the Lagrangian box model (OZIPR) study, we selected the Atlanta area for this sensitivity test because of the abundance of biogenic emission in this southeastern U.S. region. We have selected two areas in this study : an urban area over the Atlanta metropolitan area and a rural area west of Atlanta, in which we used a similar amount of isoprene as well as NO_x and VOC emission rates to the that emitted in the Eulerian grid model simulation described later over the same areas. Other input parameters for the Atlanta base case scenario are the same as that derived by the EPA to represent 39 different O₃ non-attainment city areas around the United States (Baugues, 1990) and are available upon request.

The OZIPR model with the original and updated CB4 mechanisms were used to simulate the O₃ formation for the two urban and rural areas under various isoprene (ISOP) emission scenarios. Table 2 lists the predicted O₃ peaks for these two selected areas using the two different mechanisms under 5 different isoprene emission scenarios, ISOP x 4, ISOP x 2, ISOP x 1, ISOP / 2, and ISOP / 4. As expected, over the urban area, the updated CB4 predicted lower O₃ than the original CB4 because of the lower isoprene incremental reactivity in the updated CB4. The original CB4 with the highest isoprene emission (ISOP x 4) gives the highest O₃ prediction (187 ppb) and largest difference between the two mechanisms (-8 ppb), and the differences between O₃ predicted by the two mechanisms with highest and lowest isoprene emissions are relatively large, both indicating that this urban area is VOC-limited. On the contrary, over the rural area, the updated CB4 generally predicted higher O₃ than the original CB4, which is in contradiction to the OTAG work by Whitten et al.(1996). The updated CB4 with the highest isoprene emission (ISOP x 4) gives not-so-high O₃ prediction (90 ppb), and the differences

between O₃ predicted by the two mechanisms with highest and lowest isoprene emissions are relatively small, both showing that this rural cell is very NO_x-limited. It appears that the impact of new isoprene mechanism to the O₃ predictions are strongly dependent upon the availability of NO_x and VOC (NO_x-limited or VOC-limited conditions), which will be supported by the Eulerian grid model sensitivity study next.

2. Eulerian Grid Model Simulations

For the photochemical grid model sensitivity study, we select an on-going EDSS/MAQSIP project, the Seasonal Model for Regional Air Quality (SMRAQ) project, which is an modeling effort to simulate the ozone formation and transport from May to September for the eastern U.S. with a focus on the southeastern U.S. seasonal ozone distribution (Smith et al., 1996). The modeling domain which is similar to the OTAG domain has 48 x 50 grid cells at a 54 kilometer resolution and 22 vertical layers (first layer at about 20 m) with denser grids at lower level to better resolve the boundary layer. The models used for the project is the EDSS/MAQSIP for ozone chemistry and transport, Mesoscale Model Version 5 (MM5) for meteorology, and the Sparse Matrix Operator Kernel Emissions (SMOKE) (Houyoux, 1996) system for emissions. The emission inventory was derived from the 1995 OTAG inventory which use the updated BEIS2 emission model to account for the biogenic emissions of VOC and NO_x. In this study, we have also applied a diagnostic analysis tool, the Process Analysis method (Jang et al., 1995a and 1995b), on the MAQSIP system to investigate why ozone are sensitive to the changes in biogenic chemistry and emissions.

The simulation period selected for this sensitivity study is a 5-day model simulation starting at 1300 GMT (0900 EDT) on July 7, 1995. The modeling domain, covering eastern two thirds of the continental U.S., is shown in Figure 1. As a part of modeling effort in the SMRAQ project, we have first focused the O₃ sensitivity study on the Southeastern U.S in which there is abundance of biogenic VOC emitted. The selected southeastern U.S. subdomain is also highlighted in Figure 1.

Figure 1 Shows the O₃ concentrations simulated by the model using the original CB4 mechanism at 2100 GMT (1700 EDT) on July 11, 1995, the fourth day of the simulation period that has the maximum O₃ prediction (179 ppb) located in the Atlanta area. There are also high O₃ levels observed in other metropolitan areas such as Washington D.C. and Houston, but no obvious O₃ highs observed in the conventional high O₃ areas such as New York and Chicago because of the prevailing meteorological conditions at this selected simulation day. Figure 2 shows the differences of O₃ concentrations simulated by the model using the original CB4 and the updated CB4 (updated CB4 - original CB4). There are major O₃ decreases (up to 20 ppb) in several spatially-limited areas such as the Ohio river power plant area, Chicago, New York city, and Nashville areas, where significant amount of ~~VOC~~^{NO_x} is emitted. On the contrary, in the southeastern U.S., the majority of the region has a significant amount of O₃ increases predicted by the model using the updated CB4 mechanism. Figure 3 shows the time series of the differences of 5-day O₃ simulated by the model using the two different mechanisms for the selected Southeastern subdomain and the grid cell with maximum predicted O₃ over the Atlanta area. There is a consistent O₃ increase in average over the simulation period for the selected Southeastern subdomain, while in the maximum grid cell, O₃ generally decreased in the afternoon. It seems that the

effects of new isoprene mechanism on the O₃ predictions are strongly dependent on the distribution of NO_x and VOC emissions. This is supported by Figure 4, 5, and 6 which show the emission rates of isoprene, the ratio of isoprene and total VOC, and the ratio of NO_x and VOC, respectively, in the first layer at 2100 GMT (1700 EDT) on July 11, 1995. As shown in the Figure 4, there are obviously major isoprene emitted in the Southeastern U.S. In fact, the amount of emitted isoprene is so overwhelming that it account for more than two thirds of the total VOC emissions in the most of Southeastern U.S. and more than 83 % in most regions over the states of Missouri and Kansas, as shown in Figure 5. It appears that the pattern of regions with significant O₃ increase using the updated CB4 mechanism matches very well with the pattern of regions in which isoprene is the major emitted VOC. This is in contradiction to the study by Whitten et al. (1996) in which the southeastern U.S. has significant decrease of O₃ using the updated CB4 mechanism. On the other hand, by examining the areas that have significant O₃ decrease using the updated CB4 mechanism, we found that these areas also match well with the areas with high NO_x/VOC ratio as shown in Figure 6. This can be explained by the lower isoprene incremental reactivity in the updated CB4 mechanism causing lower O₃ prediction over the areas that are VOC-limited. Our results suggest that the model using the updated CB4 mechanism with new isoprene chemistry tends to predict higher O₃ than that using the original CB4 mechanism in the rural areas where isoprene is the major emitted VOC and predict lower O₃ in the urban areas where there is plenty of NO_x emitted (VOC-limited).

Figure 7 shows the time series of the differences of O₃ process contributions using the original CB4 and updated CB4 mechanisms (updated CB4 - Original CB4) for the selected Southeastern subdomain and the Atlanta grid cell with predicted O₃ maximum. In Figure 7(a) for the Southeastern subdomain, it is obvious that the increase of O₃ predicted by the model using the updated CB4 mechanism is caused by the significant increase of chemistry process contribution; in fact, some of the chemistry process contribution (O₃ Chem) is compensated by the vertical transport process (O₃ V_Trans) to produce otherwise higher O₃ increase. Similarly, decrease of O₃ using the updated CB4 mechanism is caused by the decrease of chemistry process contribution, and again some of the chemistry process contribution is compensated by the vertical transport process to cause otherwise higher O₃ decrease.

In the emission modeling effort for this SMRAQ project, we have found that biogenic emission rates are very sensitive to the changes in temperature and solar radiation. In one case we found that the level of temperature selected has significant impact to the calculation of biogenic emission rates.

The OTAG biogenic emissions inventory use a default level of temperature at 1.5 m to calculate the biogenic emission rates. It is believed that the leaf temperature should be used for calculating the emission rates and the level of temperature used should be more than 1.5 m. As a sensitivity test, we use the model temperature which is calculated at about 19 m to see the changes of isoprene emissions in these two cases. Figure 8 shows the differences of isoprene emissions (ratio of [ISOPa-ISOPb]/ISOPb) caused by using the temperature at 19 m (ISOPa) and at 1.5 m (ISOPb) in the first layer at 2100 GMT (1700 EDT) on July 11, 1995. It is interesting to find that the emission rates of isoprene increase significantly (up to 50%) around the Great Lakes shore areas and generally decrease elsewhere when the temperature at 19 m is used. With a coarse resolution of 54 km, it is reasonable that shore areas are not be well resolved so the temperature in the cooler lake/shore areas tend to increase, which results in a higher isoprene emissions in these lake/shore areas when we use temperature at 19 m instead of 1.5 m at the surface. The time series (not shown here) of the average differences of isoprene emissions resulting

from using the temperature at 19 m and at 1.5 m in the first layer over the selected southeastern U.S. subdomain shows that that daytime isoprene emission rates drop as much as 20% because of the lower temperature at 19 m used. Figure 9 shows the differences of O₃ concentrations (ISOP at 19m - ISOP at 1.5m) caused by the different isoprene emission rates calculated using the temperature at 19 m and at 1.5 m in the first layer at 2100 GMT (1700 EDT) on July 11, 1995. As expected, there are significant O₃ decreases in the areas with major NO_x emission (VOC-limited) using temperature at 19 m instead of 1.5 m because of the lower isoprene emitted using temperature at 19 m. There is no significant change in the southeastern rural areas since there is already plenty of isoprene emitted in these areas.

Conclusions

In this paper we study the sensitivity of ozone predictions to the changes in biogenic chemistry and emissions in air quality models. In this sensitivity study, we first use a Lagrangian box model, the OZIPR model, as the tool to examine the differences of O₃ simulated by two sets of chemical mechanisms; the original CB4 mechanism vs. the updated CB4 mechanism with Carter's (1996) new isoprene chemistry. We then use an Eulerian grid models, the EDSS/MAQSIP, to examine the differences of O₃ simulated by these two different mechanisms as well as using different biogenic emission inputs based on various temperature scenarios.

The Lagrangian box (OZIPR) model was used to simulate the O₃ formation for the two selected urban and rural areas under various isoprene (ISOP) emission scenarios. As expected, over the urban area, the updated CB4 predicted lower O₃ than the original CB4 mechanism because of the lower isoprene incremental reactivity in the updated CB4 mechanism. However, over the rural area, the updated CB4 generally predicted higher O₃ than the original CB4, which is in contradiction to the OTAG work by Whitten et al.(1996). It appears that the impact of new isoprene mechanism to the O₃ predictions are strongly dependent upon the availability of NO_x and VOC (NO_x-limited or VOC-limited conditions). The Eulerian grid model (EDSS/MAQSIP) simulation further lends support to this finding. We also found that the level of temperature selected has significant impact to the calculation of biogenic emission rates. We found that the emission rates of isoprene increase significantly (up to 50%) around the Great Lakes shore areas and daytime isoprene emission rates drop as much as 20% in the selected Southeastern region when the temperature at 19 m is used. The model simulation uses different isoprene emission rates show that there are significant O₃ decreases in the areas with major NO_x emission (VOC-limited) using temperature at 19 m instead of 1.5 m because of the lower isoprene emitted using temperature at 19 m. There is no significant change in the Southeastern rural areas since there is already plenty of isoprene emitted in these areas. Our next task is to perform further detailed chemistry analysis to understand why the updated CB4 mechanism predicts differently from the original CB4 mechanism.

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Table 1. List of isoprene reactions that are different between the original CB4 mechanism and the updated CB4 mechanism with new isoprene chemistry.

Original CB4 (Gery et al., 1989)	Updated CB4 (Whitten, et al., 1996)
ISOP + O --> 0.55 OLE + 0.8 ALD2 + 0.5 XO2 + 0.6 HO2 + 0.5 CO + 0.9 PAR + 0.45 ETH [K ₂₉₈ = 27000 (ppm ⁻¹ min ⁻¹ at 298 K), E/R = 0]	ISOP + O --> 0.75 ISPD + 0.5 FORM + 0.25 XO2 + 0.25 HO2 + 0.25 C2O3 + 0.25 PAR [K ₂₉₈ = 53200 (ppm ⁻¹ min ⁻¹ at 298 K), E/R = 0]
ISOP + OH --> 1.0 ETH + 1.0 FORM + 1.0 XO2 + 0.67 HO2 + 0.13 XO2N + 0.4 MGLY + 0.2 ALD2 + 0.2 C2O3 [K ₂₉₈ = 142000, E/R = 0]	ISOP + OH --> 0.912 ISPD + 0.629 FORM + 0.991 XO2 + 0.912 HO2 + 0.088 XO2N [K ₂₉₈ = 147600, E/R = -407.6]
ISOP + O3 --> 0.55 ETH + 1.0 FORM + 0.2 MGLY + 0.44 HO2 + 0.1 OH + 0.4 ALD2 + 0.1 PAR + 0.06 CO [K ₂₉₈ = 0.018, E/R = 0]	ISOP + O3 --> 0.65 ISPD + 0.6 FORM + 0.2 XO2 + 0.066 HO2 + 0.266 OH + 0.2 C2O3 + 0.15 ALD2 + 0.35 PAR + 0.066 CO [K ₂₉₈ = 0.019, E/R = 1912]
ISOP + NO3 --> XNO2 X O2 + [K ₂₉₈ = 470, E/R = 0]	ISOP + NO3 --> 0.2 ISPD + 0.8 NTR + 1.0 XO2 + 0.8 HO2 + 0.2 NO2 + 0.8 ALD2 + 2.4 PAR [K ₂₉₈ = 996, E/R = 448]
	ISPD + OH --> 1.565 PAR + 0.167 FORM + 0.713 XO2 + 0.503 HO2 + 0.334 CO + 0.168 MGLY + 0.273 ALD2 + 0.498 C2O3 [K ₂₉₈ = 49660, E/R = 0]
	ISPD + O3 --> 0.114 C2O3 + 0.15 FORM + 0.85 MGLY + 0.154 HO2 + 0.268 OH + 0.064 XO2 + 0.02 ALD2 + 0.36 PAR + 0.225 CO [K ₂₉₈ = 0.0105, E/R = 0]
	ISPD + NO3 --> 0.357 ALD2 + 0.282 FORM + 1.282 PAR + 0.925 HO2 + 0.634 CO + 0.85 NTR + 0.075 C2O3 + 0.075 XO2 + 0.075 HNO3 [K ₂₉₈ = 1.478, E/R = 0]
	ISPD + hν --> 0.067 ALD2 + 0.90 FORM + 0.832 PAR + 1.033 HO2 + 0.333 CO + 0.70 XO2 + 0.967 C2O3 [J : Scaled to acrolein photolysis, QY = 0.0036]
	ISOP + NO2 --> 0.2 ISPD + 0.8 NTR + 1.0 XO2 + 0.8 HO2 + 0.2 NO2 + 0.8 ALD2 + 2.4 PAR [K ₂₉₈ = 0.00022, E/R = 0]

Table 2. Predicted O₃ peaks by the Lagrangian box model (OZIPR/EKMA) using the original and updated CB4 mechanism for two selected urban and rural areas under various isoprene emission scenarios.

Urban Area (Atlanta)				Rural Area (Atlanta)		
	Original CB4	Updated CB4	Difference (Upd. - Ori.)	Original CB4	Updated CB4	Difference (Upd. - Ori.)
ISOP x 4	187	179	-8	86	90	+4
ISOP x 2	172	166	-6	86	88	+2
ISOP x 1	162	158	-4	85	85	0
ISOP / 2	155	153	-2	83	83	0
ISOP / 4	152	151	-1	82	81	-1

Figure 1. The modeling domain and the O₃ concentrations simulated by the MAQSIP model at 2100 GMT (1700 EDT) on July 11, 1995. The highlighted subdomain is the selected Southeastern subdomain for the O₃ sensitivity study.

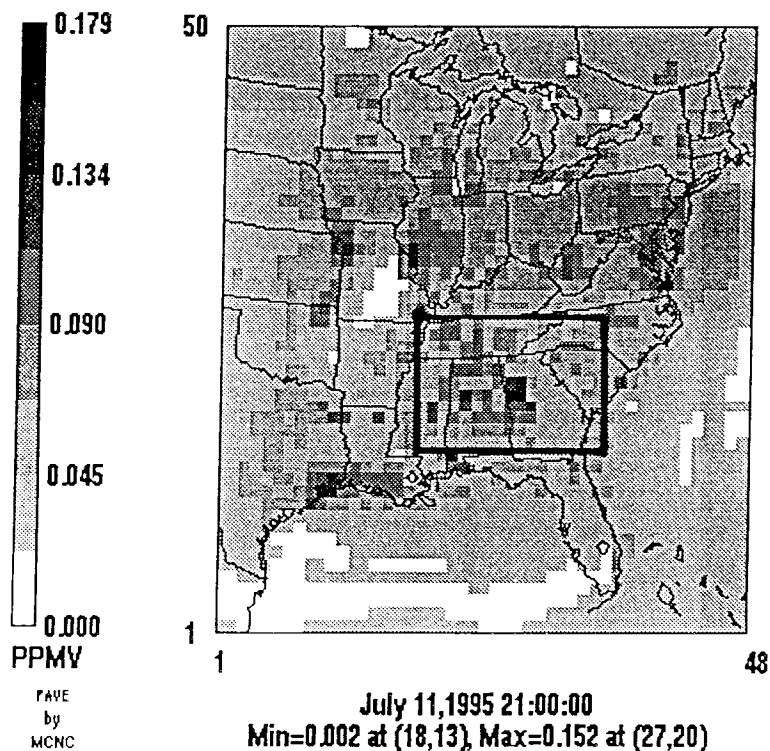


Figure 2. The differences of O₃ concentrations (O₃b-O₃a) simulated by the MAQSIP model using the original CB4 (O₃a) and updated CB4 (O₃b) at 2100 GMT (1700 EDT) on July 11, 1995.

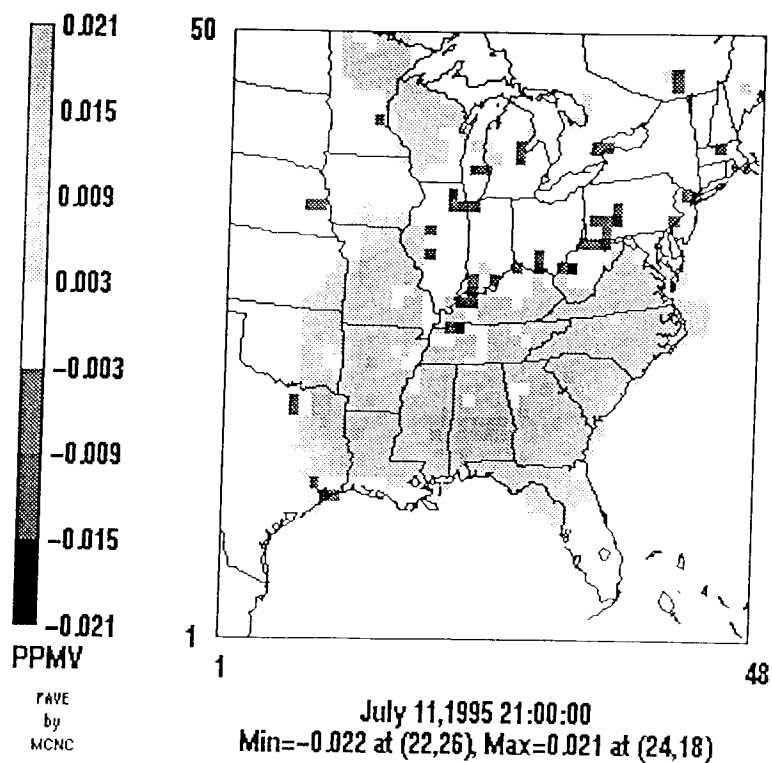


Figure 3. Time series of the differences ($O3b-O3a$) of 5-day O_3 simulated by the MAQSIP model using the original CB4 ($O3a$) and updated CB4 ($O3b$) for (a) the selected Southeastern subdomain and (b) the Atlanta grid cell with maximum predicted O_3 .

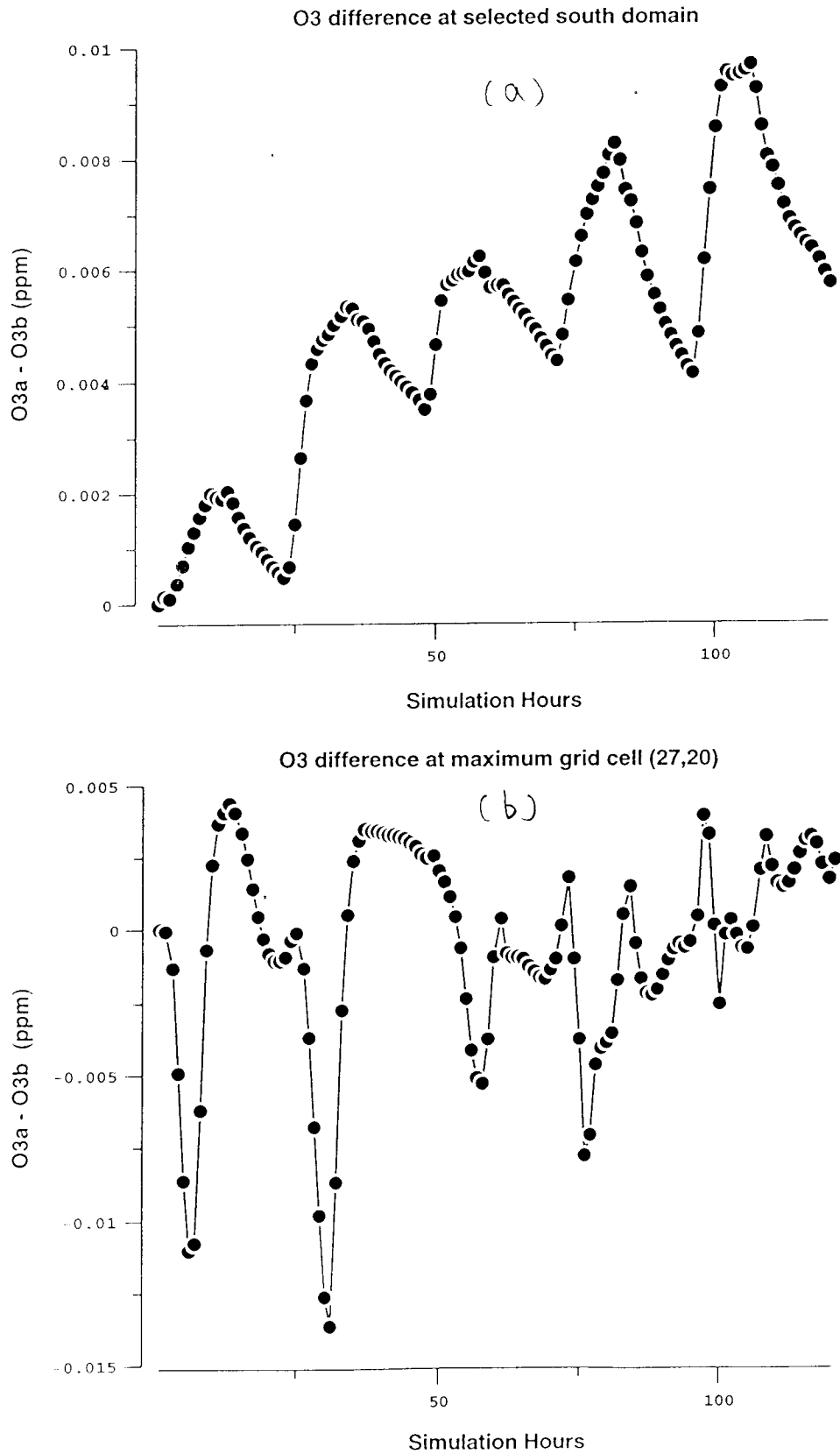


Figure 4. The emission rates of isoprene (ISOP) in the first layer at 2100 GMT (1700 EDT) on July 11, 1995.

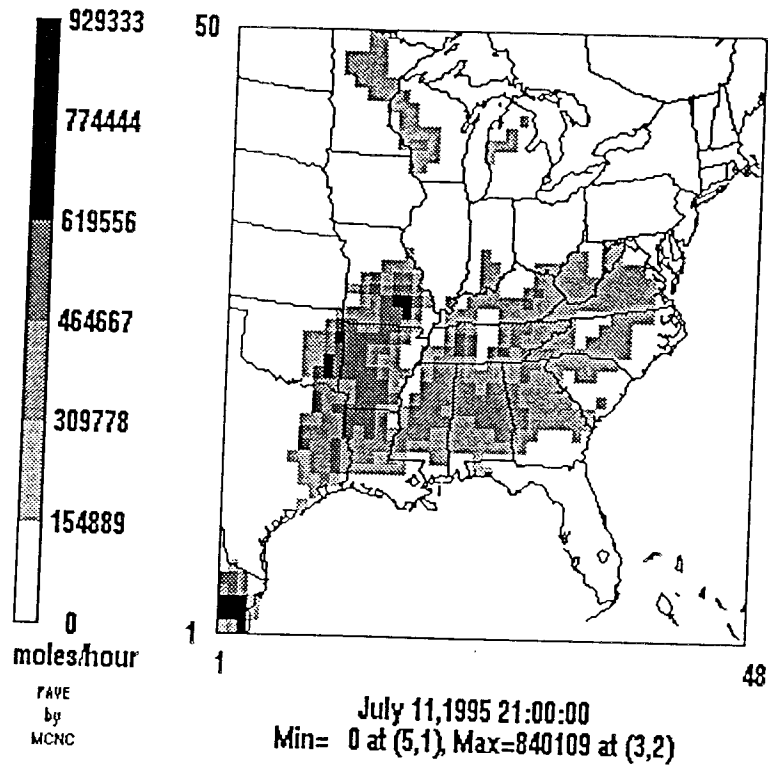


Figure 5. The ratio of isoprene and total VOC emissions in the first layer at 2100 GMT (1700 EDT) on July 11, 1995.

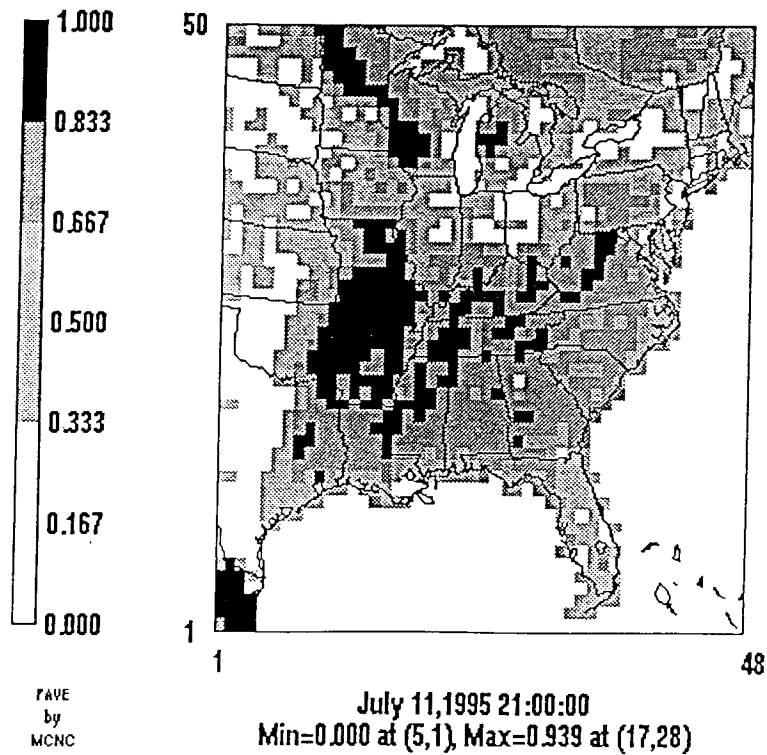


Figure 6. The ratio of NOx and VOC emissions in the first layer at 2100 GMT (1700 EDT) on July 11, 1995.

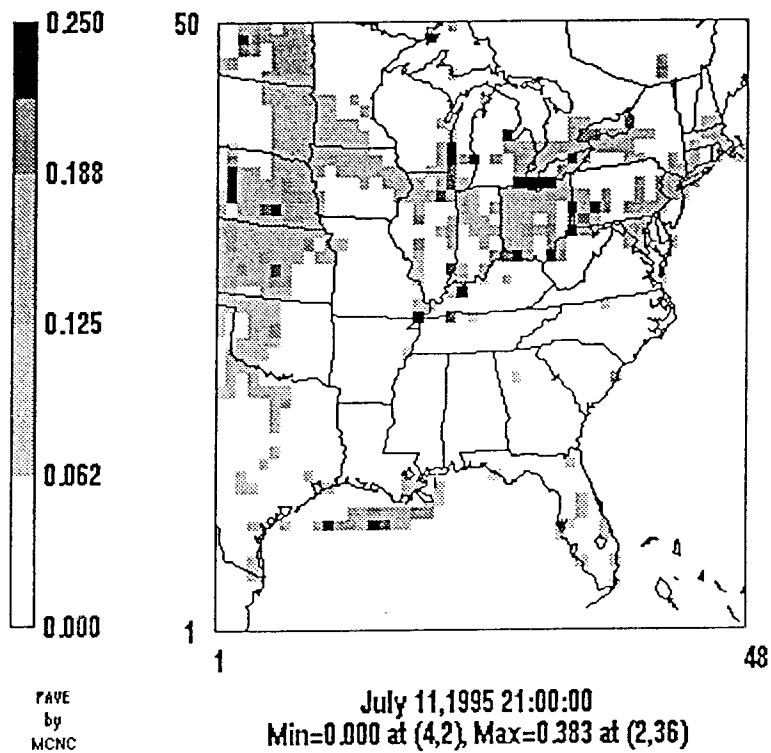


Figure 7. Time series of the O₃ differences (O₃b-O₃a) of the process contributions using the original CB4 (O₃a) and updated CB4 (O₃b) for (a) the selected Southeastern subdomain and (b) the Atlanta grid cell with maximum predicted O₃ (Chem : chemistry process; V_Trans : vertical transport process; H_Trans : horizontal transport process)

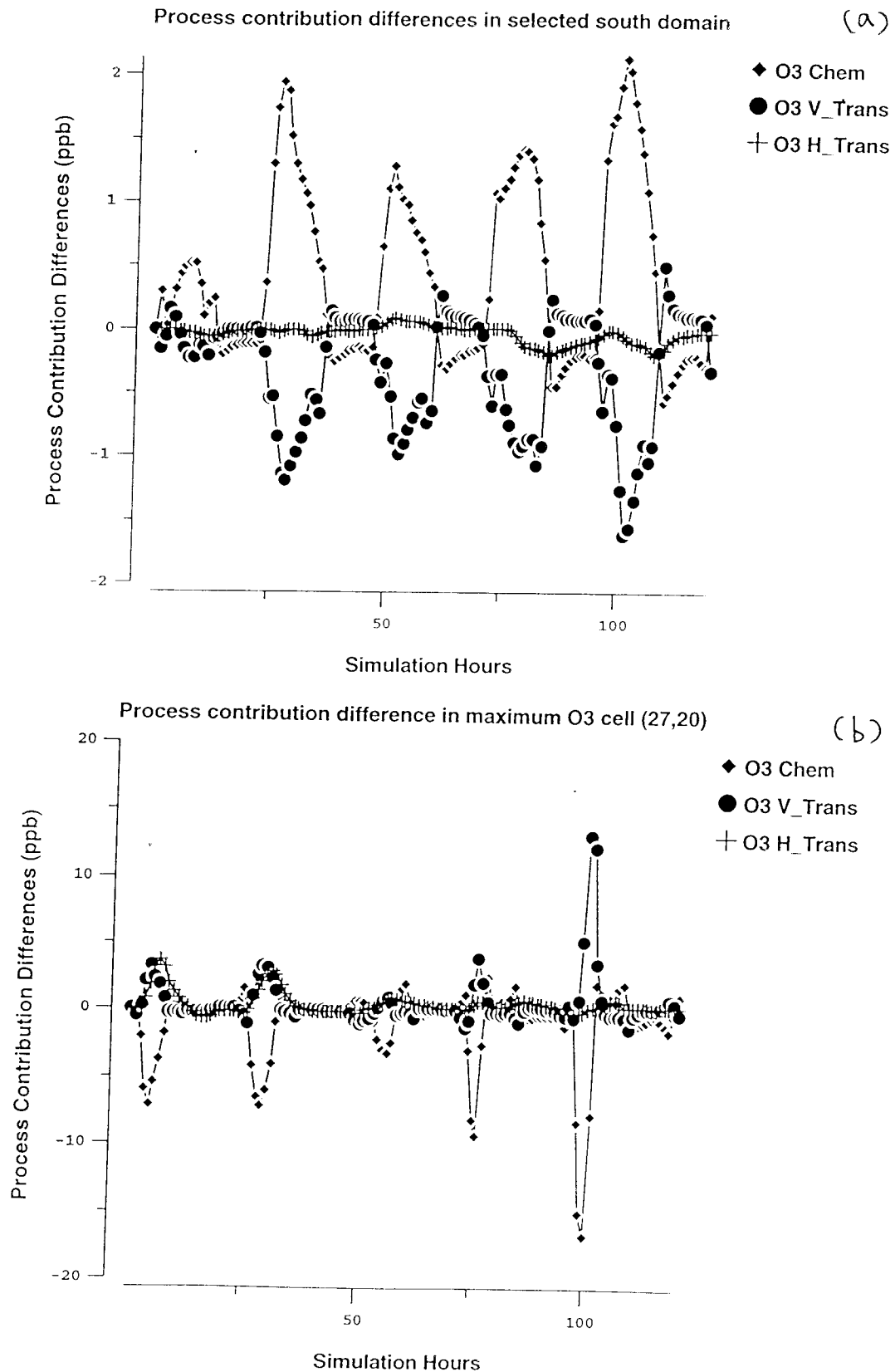


Figure 8. The differences of isoprene emissions (ratio of [ISOPa-ISOPb]/ISOPb) caused by using the temperature at 19 m (ISOPa) and at 1.5 m (ISOPb) in the first layer at 2100 GMT (1700 EDT) on July 11, 1995.

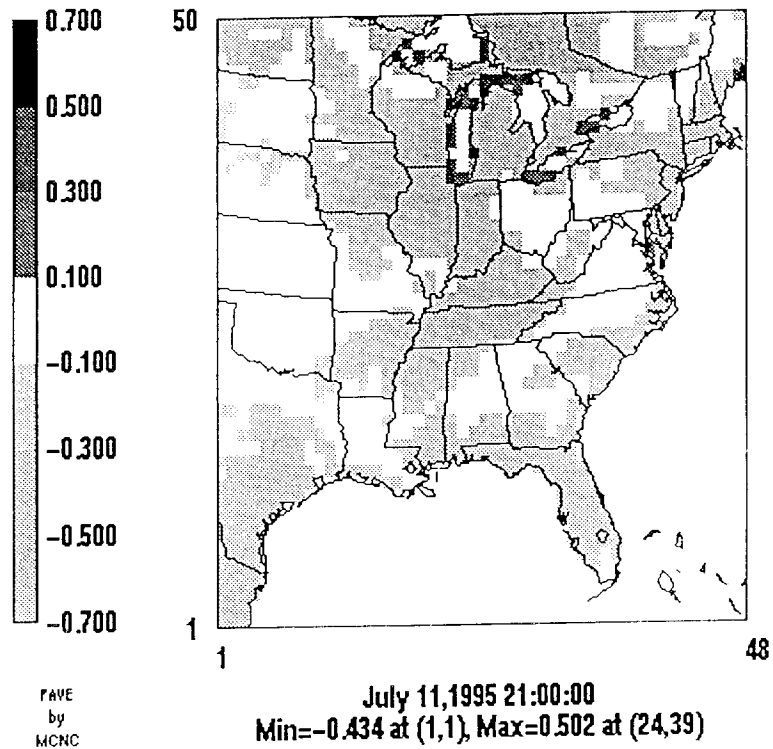


Figure 9. The differences of O₃ concentrations (O3b-O3a) caused by different isoprene emission rates calculated using the temperature at 19 m (ISOPa) and at 1.5 m (ISOPb) in the first layer at 2100 GMT (1700 EDT) on July 11, 1995.

