

Draft Version 1.5

The Effect of the Updated Isoprene Chemistry on Ozone Concentrations in OTAG

Brian Timin, Jay Lawrimore, North Carolina Division of Air Quality
Carey Jang, MCNC
Harvey Jeffries, University of North Carolina- Chapel Hill

Summary

Overpredictions of ozone in the OTAG base case model runs led to the implementation of updated isoprene chemistry in the Carbon Bond IV chemical mechanism. SAI adapted new isoprene reactions developed by Carter (1996), for use in CB-IV and updated the mechanism to account for this new information. It was hypothesized that the updated mechanism would produce less ozone due to its lower incremental activity compared with the old mechanism. All four modeling centers tested the updated mechanism and found that the new mechanism lowered ozone peaks across most of the OTAG domain by ~5-15 ppb or more.

Closer examination revealed numerous errors in the OTAG isoprene chemistry results (June, 1996). The OTAG comparison of the original and updated chemistry contained other unreported changes to the UAM-V "chemparam" input file. Several errors in the file were fixed at the same time that the updated chemistry code was delivered to the Modeling Centers. Therefore most of the ozone reductions that were attributed to the updated isoprene chemistry were actually due to the errors that were corrected in the updated chemparam file.

In this study, sensitivity runs were conducted to assess the true impact of the updated chemistry. In much of the southern half of the domain, the updated isoprene chemistry caused the peak ozone to increase as much as 15 ppb. The ozone reductions due to the non-isoprene chemparam changes masked the increases that were seen due to the isoprene chemistry alone. In NO_x rich urban areas, peak ozone decreased by up to 15 ppb.

It appears that the updated isoprene chemistry was implemented correctly in UAM-V version 1.24 and therefore the final OTAG base case and strategy runs are correct. However, due to the simultaneous changes to the model, the impact of the updated isoprene chemistry on ozone concentrations in OTAG was misstated.

Introduction

The Carbon Bond IV (CB-IV) chemistry mechanism is used to simulate ~~the amount of~~ ozone that is photochemically produced in the troposphere as a consequence of anthropogenic and biogenic emissions of volatile organic carbon (VOC) and nitrogen oxides (NO_x). This chemistry mechanism is used in several air quality models, UAM-IV,

UAM-V, MAQSIP, SAQM, RPM-IV, and others. The Carbon Bond IV mechanism has undergone several modifications since its original version was published in 1989 (Gery et al., 1989). This report documents the versions of CB-IV that were used in the OTAG UAM-V modeling.

There are several versions of tables listing the CB-IV reactions used in UAM-V. The users manuals provided by SAI with the UAM-V code when North Carolina Division of Air Quality signed its UAM-V license agreement is dated February 1996 (the footer on the manual pages is dated April 1995). In "User's Guide To The Variable-Grid Urban Airshed Model (UAM-V)", Table 2-1 lists the chemical reactions, rate constants, and activation energies for each reaction in the mechanism. In this version there are 86 reactions listed.

Parameters which control the CB-IV used by the UAM models are furnished to the program through an input file called "chemparam." In UAM-IV the file was binary, in UAM-V the file is ASCII and is in a different format. The chemparam file supplies the reaction rate and activation energy information for each chemical reaction in the model. The original chemparam file used in OTAG was given to LADCO by SAI and then distributed by LADCO to the other 3 modeling centers. LADCO made no changes to the file before they distributed it.

History of OTAG CB-IV changes

Prior to the isoprene chemistry update, the UAM-V executable used by OTAG was version 1.23 and the chemparam file was called `chem.ng.commonfile.ai.basa`. Each modeling center used the same file with the same name.

In June of 1996, SAI undertook to update the older CB-IV isoprene chemistry to include new information produced in recent years and a study of Carter that showed that the older CB-IV isoprene exhibited twice as much incremental reactivity in NO_x rich situations such as urban areas. As a result of the new isoprene chemistry, 5 new reactions were added to the CB-IV mechanism. Four of the new reactions involved the new species ISPD which is a product of the new isoprene reactions. The fifth new reaction was $\text{ISOP} + \text{NO}_2$. When SAI provided the new isoprene chemistry update, they gave each modeling center a new chemparam file, a new photolysis rates file, and a new compiled version of the UAM-V executable:

- The new executable was called UAM-V version 1.24. The new isoprene reactions and species were updated in this version.
- The new photolysis rates file contained 6 sets of photolysis rates instead of 5. A new set of rates for acrolein photolysis was included to estimate the photolysis of the new species ISPD introduced in the new isoprene chemistry additions.
- The new chemparam file was updated to include the new isoprene product reactions and rate constants.

The Reported Effect of the New Isoprene Chemistry

SAI submitted a report dated July 22, 1996 detailing the changes to the isoprene chemistry and accounting for the changes to these reactions and their rate constants. The report contained comparisons of the new and old isoprene mechanisms tested against smog chamber data. The report also contained preliminary results of UAM-V version 1.23 (old chemistry, old photolysis rates and old chemparam file) and UAM-V version 1.24 (new chemistry, new photolysis rates, and new chemparam files) comparisons. The comparisons were done for the 1993 OTAG episode for Atlanta, for the full OTAG domain for the 1988 episode, and for the full OTAG domain for the 1993 episode. In all cases, *“maximum simulated ozone concentrations are generally lower in all parts of the domain with the use of the updated CB4 isoprene mechanism..... Although a full examination of all simulated species has not been undertaken for these simulations, the results for ozone using the updated chemistry for the 1988 (1993) episode appear reasonable.”* This conclusion was supported by the assertion that because the incremental reactivity of isoprene was lowered it would be expected that ozone would be lower.

In our own tests, the UAM-V version 1.24, with new photolysis rates file and the new chemparam file (which the SE modeling center called chem.ng.commonfile.ai.basC2UC) was used in an “updated chemistry” run to compare its ozone production with that from the UAM-V version 1.23 with the old mechanism. Difference plots showed that peak ozone levels were reduced by 10-25 ppb or more across the *entire* OTAG domain in the UAM-V version 1.24 simulations, i.e., the new isoprene chemistry resulted in *less* ozone everywhere in the domain, not just in the urban areas as expected from its lower incremental reactivity. Erroneous result

At this point SAI discovered an error in the new chemparam file they had provided. The rate constant for reaction 90 (ISPD + OH) was missing a zero, so it was an order of magnitude too low. The modeling centers were provided with a new chemparam file (chem.ng.commonfile.basD2) with the correct rate constant for reaction 90.

All four modeling centers ran UAM-V version 1.24 (with new photolysis rates and the fixed version of the chemparam file) and produced difference plots against the UAM-V version 1.23 (with the old mechanism, old photolysis rates and old chemparam file). Results from all four modeling centers showed that **ozone went down by about 5-20 ppb or more in the UAM-V version 1.24 simulations compared to the UAM-V version 1.23 simulations.** Ozone reductions occurred across all grid cells. Although incremental reactivities mostly effect NO_x rich conditions, the modeling groups concluded that ozone went down across the domain because of the decrease in incremental reactivity of the new isoprene mechanism. There was, however, also a small emissions change embedded in these tests, so it was unclear if all of the change was due to the change in chemistry. The SE modeling center ran two three day simulations using

version 1.23 and version 1.24 with exactly the same emissions files. These V1.24 results were almost identical to those from version 1.24 with the emissions changes. That is, when compared to the version 1.23 results, peak ozone went down by 5-20 ppb throughout most of the domain, with reductions of as much as 40 ppb in Atlanta.

Contradictory Modeling Results with Other Models

As part of the Seasonal Model for Regional Air Quality (SMRAQ) study being conducted at MCNC for the southern states, Carey Jang implemented the CB-IV mechanism with both the new and old isoprene chemistries in the MCNC MAQSIP model system. Jang found that on switching from old to new isoprene chemistry with everything else the same, the MAQSIP model showed *ozone increases in the rural areas and ozone decreases in the urban* when the old chemistry was replaced with the new chemistry, which is quite *different* from the UAM-V, version 1.23 change to version 1.24 results reported above (Jang et al. 1997). To confirm these results, Jang also did the same tests in OZIPR, a one-cell trajectory model, using Atlanta urban conditions and Georgia rural conditions. The latter results were also consistent with MAQSIP's results and inconsistent with the UAM-V version 1.23 to version 1.24 changes.

In an effort to understand the UAM-V results better, Brian Timin at the NC Division of Air Quality (DAQ) undertook an investigation of the UAM-V version 1.23 and 1.24 simulations that had been the basis of the SE modeling center's original findings. In this investigation, Timin found undocumented changes in the UAM-V version 1.24 chemparam file that had been used in their comparisons (i. e. , chem.ng.commonfile.basD2) and that presumably was used by all the OTAG modeling centers for all UAM-V simulations performed since SAI fixed the error in Reaction 90 that was described above.

Undocumented chemparam file Changes

The chemparam file supplied by SAI to the modeling centers for use with UAM-V, version 1.24 (i. e. , chem.ng.commonfile.basD2) which was thought to reflect only the changes due to the new isoprene chemistry changes has other *very important and undocumented changes*. OTAG participants were not aware of any other changes to the file except for the isoprene chemistry updates. Some of the differences are due to corrections of rate constant *errors* that were in the chem.ng.commonfile.ai.basA chemparam file; some of the differences reflect the use of *alternative rate constants and activation energies* to the non-isoprene portion of CB4 that were not in UAM-V, version 1.23; *both* files contain *zero* rates for reactions that are part of the base CB4 chemistry effectively removing them from the mechanism. None of these changes were documented to OTAG. Table 2-1 in the latest version of the UAM-V User's Guide dated October 1996 (the file uamvman.exe at <http://134.67.104.12/html/scram/uamv.htm>) has been updated to include the

additional reactions and rate constant changes, but the text in the manual still reads the same as the 1995 version.

Upon examination, Timin found that the rate constants in the `chem.ng.commonfile.ai.basA` file were consistent with the user's manual dated February 1996 (April 1995) with one exception; the rate constant for reaction 14 was incorrect.

The rate constant for the non-photolysis reactions must be multiplied by 60 to convert the units of the User's Guide Table 2-1 ($\text{ppm}^{-n}/\text{minute}$) to the units of the chemparam file ($\text{ppm}^{-n}/\text{hour}$). Photolysis rates are provided in the `rates` file for 6 reactions (reactions 1,9,38,39,45, and 93.) There are 6 additional photolysis reactions whose rates are based on the photolysis rates of NO_2 and Formaldehyde (reaction 8,14,18,23,34,69 and 74.) The rate constants for the 6 photolysis reactions which have data in the `rates` file should be multiplied by 60 to convert table 2-1 to the chemparam file. The other 6 reactions **should not** be multiplied by 60 in order to avoid multiplying twice. In the chemparam file `basA`, reaction number 14, NO_3 photolysis ($\text{NO}_3 \rightarrow 0.89\text{NO}_2 + 0.89\text{O} + 0.11\text{NO}$), had been multiplied by 60. According to the user's manual, the rate constant should be $33.9 \times K_1$ (K_1 is the photolysis rate for NO_2 calculated in a separate lookup table). The chemparam file contained the value $2034 \times K_1$ which is 60 times the correct rate.

A second rate constant error in the file `chem.ng.commonfile.ai.basA` was discovered after further investigation. The rate constant for reaction 81 ($\text{XO}_2\text{N} + \text{NO} \rightarrow$) was set to $1,000 \text{ ppm}^{-1} \text{ minute}^{-1}$ in UAM-V 1.23. The correct rate for UAM-V versions 1.23 and 1.24 should be $12,000 \text{ ppm}^{-1} \text{ minute}^{-1}$. Further details of this correction are provided in the next section. [Note: some chemical reactions are represented as having no formation products. The actual products are inert species whose concentrations are not calculated in order to save computer time. The main inert species product referenced in this memo is organic nitrates (NTR)]

The new chemparam file supplied by SAI for UAM-V, version 1.24 had both of these errors corrected. The simulations performed by the modeling centers to compare the effects of the isoprene chemistry changes also compared the effects of fixing these rate constant errors.

A Summary of All changes in the chemparam file from OTAG UAM-V version 1.23 to 1.24

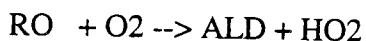
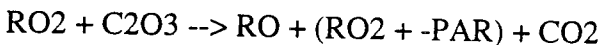
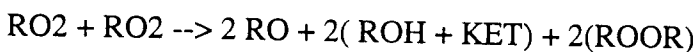
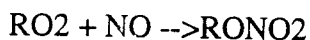
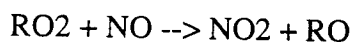
NOTE: SAI uses a non standard method for reporting reaction rate constants. The typical Arrhenius rate form is $k = A \exp(-E_a/RT)$. It has become common to report E_a/R values as the "activation energy" in units of Kelvin degrees. The A-factor has the appropriate units that match the reaction order and the concentration and time units being used. In the

case of mixing ratios, the “concentration” units are ppm and the time is generally in minutes. Thus, first order reactions have rate constant units of min^{-1} , second order reactions have units of $\text{ppm}^{-1}\text{-min}^{-1}$ and third order reactions have $\text{ppm}^{-2}\text{-min}^{-1}$. Rather than reporting the A-factor and the E_a/R value, the SAI style is to report the reaction rate at a temperature of 298 K and then give the E_a/R value assuming that the negative sign is “built-in” to the Arrhenius form. To be clear, these values should always be reported as $k_{298} = 1.6\text{E-}12 \text{ ppm}^{-1}\text{-min}^{-1}$, and $E_a/R = 6342 \text{ K}$. To compare to the standard literature, one has to convert the k_{298} to A by dividing it by $\exp(-(E_a/R)/298)$.

1. All reactions between number 1 and number 13 were the same.
2. In the updated chemparam file `basD2`, the rate constant for reaction number 14 ($\text{NO}_3 \rightarrow .89 \text{NO}_2 + .89 \text{O} + .11 \text{NO}$) was fixed. It is now $33.9 \times K_1$ instead of $2034 \times K_1$.
3. All reactions between number 15 and number 20 were the same.
4. The rate constant at 298K for reaction 21 ($\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HONO}$) was changed from $1.6 \text{E-}11 \text{ ppm}^{-2} \text{ min}^{-1}$ with no activation energy (the value assigned by Gery et al, 1989) to $3.0\text{E-}8 \text{ ppm}^{-2} \text{ min}^{-1}$ and the activation energy was changed from 0 to 6342K. This is a heterogeneously dominated reaction and has no well established rate constant. The change, however, represents an increase by 1875 times at 298 K, with an extremely high temperature dependence. This has increased the radical source strength of the model in the areas of high NO_x emissions.
5. All reactions between number 22 and number 73 were the same. It should be noted that the rate constants for reactions 29 ($\text{NO}_2 + \text{HO}_2 \rightarrow \text{PNA}$), 30 ($\text{PNA} \rightarrow \text{HO}_2 + \text{NO}_2$) and 31 ($\text{PNA} + \text{OH} \rightarrow \text{NO}_2$) were the same in all runs, but were always set to zero, effectively removing them from the mechanism. There are documented non-zero rate constants for these reactions in the UAM-V user’s guide. It is not clear why these rates were set to zero, and the effect of these reactions was not addressed in this study.
6. The rate constant for reaction 74 ($\text{MGLY} \rightarrow \text{C}_2\text{O}_3 + \text{HO}_2 + \text{CO}$) was changed from $9.64 \times K_{38}$ to $0.022 \times K_1$. K_{38} is the photolysis rate for formaldehyde which is computed from the data in the *rates* file, and K_1 is the photolysis rate for NO_2 , which is also computed from data in the *rates* file. The 9.64 ratio was determined by Gery for the UNC smog chamber in the evaluation and tuning of CB4 and is in the 1989 paper and EPA report on the evaluation and testing of CB4. At the time of this testing, however, the kinetics data for formaldehyde that was used to compute formaldehyde’s photolysis rate were based on Bass’s data which was shown to be about 30% too low after the publishing of CB4 and its adoption in regulatory use at EPA. Dodge at EPA investigated the effects of changing the formaldehyde photolysis rates in OZIPM simulations. Using the ratio of old formaldehyde to new formaldehyde rates suggested that the ratio of photolysis rates of MGLY and OPEN (another photolytic product species in the aromatics chemistry of CB4 which was also scaled to formaldehyde) to the rates of the new formaldehyde should be adjusted downward by 0.78. Thus the ratios that are consistent with the original testing and tuning of CB4 and the subsequent use of newer and better known formaldehyde data

would be $k_{hv}(\text{MGLY})/k_{hv}(\text{HCHO}) = 0.78 * 9.64 = 7.52$ and $k_{hv}(\text{OPEN})/k_{hv}(\text{HCHO}) = 0.78 * 9.04 = 7.05$. The "official numbers" are those that were implemented in ROM at this time. The change of the basis of the scale factor also makes a difference. The shape of the NO_2 photolysis curve and formaldehyde's photolysis curve is not the same, NO_2 is higher early to mid-morning and higher late afternoon than is formaldehyde.

7. Reactions 75-78 are the ISOP reactions. These were changed correctly to account for the new rate constants and product yields of the new isoprene mechanism. It appears that the rate constants and activation energies are correct for these reactions.
8. The rate constant for reaction 81 ($\text{XO2N} + \text{NO} \rightarrow$) was increased by a factor of 12. It was changed from $1,000 \text{ ppm}^{-1} \text{ min}^{-1}$ to $12,000 \text{ ppm}^{-1} \text{ min}^{-1}$. The old rate was chosen to be "fast enough" when $\text{XO2N} + \text{NO}$ was the *only* reaction of XO2N . The new rate is derived from $\text{CH3O2} + \text{NO}$ and is the same as $\text{XO2} + \text{NO}$. The two operators XO2 and XO2N are directly related: $\text{XO2}/(\text{XO2} + \text{XO2N})$ is the fraction of RO2 radicals that propagate and $\text{XO2N}/(\text{XO2} + \text{XO2N})$ is the fraction that terminate via organic nitrates formation. The "operator" approach requires that the operator species act like RO2 's. Each RO2 would



Thus three more reactions 87, 88, and 89 ($\text{XO2N} + \text{HO2} \rightarrow$), ($\text{XO2N} + \text{XO2N} \rightarrow$), and ($\text{XO2N} + \text{XO2} \rightarrow$) were added to CB4. These reactions consume XO2N , which would have formed organic nitrates if XO2N had reacted with NO . These 3 additional reactions plus the rate constant change of reaction 81 were added to CB-IV circa 1994, and were included in versions 1.23 and 1.24 of UAM-V. These reactions were not in the regulatory version of UAM-IV.

The `basD2` chemparam file contained these 3 new reactions with the correct rate constants for 87,88,89 and 81. The `basA` chemparam file contained only 86 reactions and had the rate constant of reaction 81 set to the original CB-IV value of 1,000 ppm/minute.

It was at first assumed that UAM-V version 1.23 did not contain reactions 87.88.89 and therefore the rate constant for reaction 81 would have been correct. This was found not to be true. An exchange of e-mail with Gary Whitten of SAI (July, 1997) revealed that even though the chemparam file and documentation supplied with UAM-V 1.23 contained 86 reactions, the model actually used 89 reactions including the 3 additional radical-radical reactions. **The rate constants of reactions 87, 88, and 89 are not controlled by the chemparam file. They are hard-coded into the chemistry solver.**

Therefore it is not necessary to have values for these 3 reactions in the chemparam file. The rate constants for reactions 87, 88, and 89 in the basD2 chemparam file are there as place holders only and changing the values has no effect on modeled concentrations.

Because the 3 radical-radical reactions were present in UAM-V 1.23, the rate constant for reaction 81 should have been set to 12,000 ppm⁻¹ minute⁻¹. In basA it was set to 1,000 ppm⁻¹ minute⁻¹ and is therefore an error. This error was corrected in the basD2 chemparam file. The correct updated rate constant for reaction 81 and the addition of reactions 87,88,and 89 are contained in the revised Table 2.1 (October 1996), but are not discussed in the text portion of the Users Guide or in the comparison report.

9. The rate constants and activation energies were changed for reactions 84 and 85 (MEOH+ OH ---> FORM +HO2) and (ETOH + OH ---> HO2 + ALD2). The rate constant for reaction 84 was changed from 1600 ppm⁻¹ minute⁻¹ to 1363 ppm⁻¹ minute⁻¹. The activation energy for reaction 84 was changed from 0K to 380K. The rate constant for reaction 85 was changed from 4300 ppm⁻¹ minute⁻¹ to 4791 ppm⁻¹ minute⁻¹. And the activation energy for reaction 85 was changed from -176K to 70K. (There are errors in table 2-1 of the October 1996 user's guide for the rates and energies of reactions 84-86. There are several numbers omitted and several numbers misplaced.)
10. Reactions 90-93 are the new ISPD reactions. ISPD is the new isoprene product species created from the new isoprene reactions (75-78,94). The rate constants and activation energies for reactions 90-93 are correct.
11. Reaction 94 is a new ISOP reaction (ISOP+ NO2). It is implemented correctly.

There are many differences in the chemparam files used in OTAG for the old isoprene chemistry (1.23) compared to the new isoprene chemistry (1.24). The changes to the isoprene reactions and the addition of the ISPD reactions were expected. These are reactions 75-78 and 90-94. The changes to the rate constants and activation energies in the new chemparam file are correct for those reactions.

What was unexpected were the numerous other undocumented changes to the chemparam file that were unrelated to the isoprene chemistry. These other changes involved reactions 14, 21, 74, 81, 84, 85, 87, 88, and 89. OTAG members are not aware of any of the changes except those documented in the July 22, 1996 memo.

Ozone reductions of 5-20 ppb or more were attributed to the new isoprene chemistry. There were many simultaneous changes, so that attributing the change in ozone to any one process would be impossible. Further sensitivity runs were needed in order to determine the effects of the changes to the chemparam file. **A true test of the effect of the new isoprene chemistry in UAM-V was not done.**

Sensitivity Runs to Determine the Impact of Chemparam Changes

The next step was to complete the necessary sensitivity runs in order to determine the separate impacts of both the isoprene and non-isoprene chemistry changes. Seven sensitivity runs were conducted using UAM-V to assess the impacts of these changes.

The 1993 OTAG episode was chosen as the test bed for the sensitivities because the input files for this episode were readily available. The UAM-V runs used the 1993 base case files (93basD2) with SAIMM meteorology. Each sensitivity was run for the first three days of the episode, July 20th, 21st, and 22nd. In the OTAG modeling, the first 2 days of the episode were considered startup days. The third episode day, July 22nd was the first day for which statistics were calculated and difference plots were produced. The sensitivity runs will focus on results from July 22nd only. Figure 1 shows the peak daily ozone maximum for the OTAG domain for July 22, 1993. Further modeling of additional days from the 1993 episode and other OTAG episodes would provide additional confirmation of the results presented here.

The 7 sensitivity runs are listed in table 1. Three runs used the original isoprene chemistry of UAM-V version 1.23 and 4 runs used the updated isoprene chemistry of UAM-V version 1.24. The sensitivity runs were performed by making changes to the chemparam input file. No other changes were made to the emissions, meteorology, other input files, or the UAM-V source code.

There were several CB-IV reactions that were impacted by changes from 1.23 to 1.24 but were not tested due to limitations in knowledge of and access to the model code. Reactions 87-89 cannot be tested by changing the chemparam file because the rate constants for these reactions are hardwired into the chemistry solver. It was not possible to determine the impact of adding or subtracting these reactions.

It was also not possible to test the impact of reaction 74 ($\text{MGLY} \rightarrow \text{C}_2\text{O}_3 + \text{HO}_2 + \text{CO}$). In UAM-V version 1.23, the rate constant for this reaction is a function of the photolysis rate of NO_2 . In version 1.24 it was changed to be a function of the photolysis rate of formaldehyde. This change is partially implemented in the chemparam file and partially implemented in the code. It was not possible to change the code. As a result of the change to reaction 74, some assumptions must be made. When directly comparing results from version 1.23 to version 1.24, it is assumed that the change to reaction 74 is insignificant and all of the change in ozone is due to the isoprene chemistry updates.

The first set of sensitivities were designed to replicate the OTAG base case before and after the isoprene chemistry was updated. Run 1 represented base case 93basD2. UAM-V version 1.24 was run with OTAG basD2 emissions, SAIMM meteorology, and chemparam 1.24 (basD2). The same emissions and meteorological files were then run with UAM-V version 1.23 and chemparam 1.23 (basA) (run 2). The difference between these two runs was

represented in OTAG as the impact of the updated isoprene chemistry. Figure 2 shows that ozone was reduced across the entire OTAG domain with the largest reductions of 6-20 ppb or more in the South. The maximum reduction of 32 ppb occurred in Atlanta. (All difference plots show the daily difference of ozone maximums for each grid cell.) Figure 2 is similar to the isoprene chemistry difference plots produced by the other 3 OTAG modeling centers in June of 1996.

As is now known, the difference between these two runs represents more than just the update to the isoprene chemistry. Sensitivity runs were conducted to test the impacts of changing the rate constants of reactions 14,21,81,84, and 85. The rate constants used were those found in chemparam basA and chemparam basD2. Reactions 14 and 81 were tested individually with both UAM-V versions 1.23 and 1.24. Reactions 21,84 and 85 were tested simultaneously with UAM-V version 1.24.

Run 3 tested the impact of the reaction 14 rate constant mistake in UAM-V version 1.23. In sensitivity run 3 the rate constant of reaction 14 was changed in chemparam file basA from $2034 \times K_1$ to $33.9 \times K_1$. The OTAG base case A,B, and C runs were run with a rate constant value of $2034 \times K_1$. This was a mistake that was later corrected in chemparam basD2. The correct rate constant should be $33.9 \times K_1$. The difference between run 3 and run 2 represents the impact of this mistake in UAM-V version 1.23. Ozone peaks were reduced by 2 to 6 ppb across most of the domain when the mistake was corrected. The peak reduction of 18 ppb occurred in Atlanta.

The effect of the reaction 14 rate constant mistake was also tested in UAM-V version 1.24. Sensitivity run 4 uses chemparam basD2 but changes the rate constant for reaction 14 back to what it was in chemparam basA (2034). The difference between run 1 and 4 represents the impact of the reaction 14 rate constant correction in UAM-V version 1.24. Figure 3 shows the ozone reduction due to the correction of reaction 14 ($2034 \times K_1 \rightarrow 33.9 \times K_1$) in UAM-V version 1.24. The results were almost identical to the same test with UAM-V version 1.23. Ozone was reduced by 2 to 6 ppb across most of the domain with a peak reduction in Atlanta of 16 ppb. This confirms that a portion of the ozone reduction attributed to the isoprene chemistry was actually due to the change in the reaction 14 rate constant.

Several sensitivities were designed to test the impact of the reaction 81 rate constant. In chemparam basA, the rate constant was set to $1,000 \text{ ppm}^{-1} \text{ minute}^{-1}$. This would be a correct value for the original CB-IV reaction set. But the rate constant should have been multiplied by 12 since three additional radical-radical reactions (87-89) were included in UAM-V versions 1.23 and 1.24. Sensitivity run 5 corrects the rate constants for both reactions 14 and 81 using chemparam basA and UAM-V 1.23. The impact of the reaction 81 rate constant correction with UAM-V 1.23 can be found by subtracting run 5 from run 3. Figure 4 shows the ozone reduction due to the correction of reaction 81 ($1,000 \rightarrow 12,000$) in UAM-V 1.23. Ozone is reduced by 5-15 ppb over most of the Southern half of the domain with a peak reduction of 18 ppb in Atlanta.

The reaction 81 rate constant correction was also tested in UAM-V version 1.24. Sensitivity runs 6 and 7 both have the new isoprene reactions and the corrected reaction 14 rate constant. Run 6 has the corrected rate constant for reaction 81 ($12,000 \text{ ppm}^{-1} \text{ minute}^{-1}$) and run 7 has the incorrect value of $1,00 \text{ ppm}^{-1} \text{ minute}^{-1}$. Subtracting run 6 from run 7 (figure 5) gives the impact of the reaction 81 rate constant correction with the updated isoprene chemistry (UAM-V 1.24). Again, the results are almost identical to the same test with version 1.23. Ozone was decreased by 5-15 ppb across the South with a peak reduction of 18 ppb in Atlanta. This shows that in most of the domain, the majority of the reduction thought to be due to the isoprene chemistry update, was due to the reaction 81 rate constant change.

It is possible to derive the impact of the changes between the basA and basD2 rate constants for reactions 21, 84 and 85 by subtracting run 6 from run 1. This represents the impact of these 3 changes with UAM-V 1.24. Figure 6 shows that these 3 changes together result in less than a 1 ppb change in peak ozone concentrations anywhere in the OTAG domain.

The true test of the impact of the updated isoprene chemistry can be seen by subtracting run 6 from run 5. Run 5 was run with UAM-V 1.23 with both the reaction 14 and 81 rate constant corrections. Run 6 was run with UAM-V 1.24 and the same corrections to reaction 14 and 81. The only non-isoprene chemistry difference between the two runs is the rate constant of reaction 74 which was explained earlier. **Figure 7 shows that after the new isoprene chemistry is implemented, ozone increases in NOx limited, isoprene rich areas and decreases in NOx rich urban areas.** Consequently, ozone increases by 2-15 ppb across most of the South and decreases by 2-15 ppb in several NOx rich areas in the northern half of the domain.

Small decreases of 1-5 ppb also occur in the core urban areas in the South such as Atlanta, Charlotte, Birmingham, and Nashville. The largest decrease in the domain (29 ppb) occurred in downtown Memphis. The ozone values in Memphis were consistently over predicted in OTAG and are most likely due to an overestimation of NOx emissions in the Memphis area. The high concentration of NOx in Memphis would explain the large decrease due to the isoprene chemistry update.

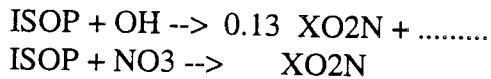
The small ozone decreases in urban areas in the South are confined to the immediate urban area. Ozone begins to increase only a couple of grid cells outside of the downtown areas. Figure 8 shows this effect in Atlanta. The maximum decrease in downtown Atlanta is 1ppb, but the rest of the Atlanta area shows large increases in ozone only 1 or 2 grid cells in each direction from downtown.

Figure 9 shows the peak isoprene concentration across the domain on July 22nd. The area of ozone increases in figure 7 corresponds fairly closely to the areas with the highest isoprene concentrations.

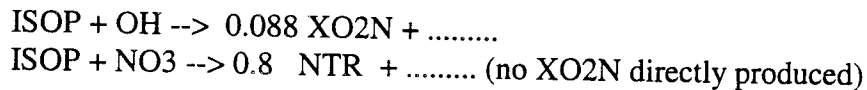
The unexpected increase in ozone in NOx limited, high isoprene areas is due to the XO2N chemistry. The updated isoprene mechanism (in UAM-V 1.24) reduces the fractional yield of

XO2N in reactions 76 (ISOP+ OH) and 78 (ISOP+NO3). This can be very important in NOx limited, high isoprene areas.

In UAM-V version 1.23, ISOP reacts with OH and NO3 as follows :



In the updated chemistry of UAM-V 1.24, ISOP reacts with OH and NO3 as follows :



Where isoprene is abundant, less XO2N is produced with the updated isoprene chemistry. In reaction 81 ($\text{XO2N} + \text{NO} \rightarrow$), XO2N consumes NO and forms inert organic nitrates. This reaction takes NO out of the system leaving less NOx available to form ozone. In the updated isoprene chemistry, reactions 76 and 78 produce less XO2N therefore less NO is terminated, more NO is oxidized to NO2 and more ozone is produced in NOx limited areas. In NOx rich areas, the XO2N yields are not important because there is already excess NOx in the system. Ozone formation is limited by the availability of radicals.

The results from this study are very similar to those found by Jang (Jang, 1997) with the MAQSIP model using the July 1995 episode. In that study, ozone increased in the high isoprene areas of the South and decreased somewhat in NOx rich areas in the North when the isoprene chemistry was updated. Figure 10 shows an example of the change in ozone on July 11, 1995 at 4:00 PM EST (2100 GMT) using the MAQSIP air quality model.

Both of these results are consistent with Carter's (Carter, 1996) findings. With the new treatment of the isoprene chemistry, Carter found that the incremental reactivity of isoprene was reduced in NOx rich urban mixtures. Carter's new mechanism was tested with smog chamber data and found to perform better than the old mechanism. The smog chamber data used by both Carter and SAI never tested the mechanisms under NOx limited, high isoprene conditions. The OTAG UAM-V runs were the first real test of the new isoprene mechanism under these conditions.

Conclusions

In the June 1996 tests, the true response of the chemical mechanism in UAM-V was masked by other corrections made to the chemparam file. Almost all of the ozone reductions in rural, high isoprene areas in the 1996 comparison were due to the rate constant corrections of reactions 14 and 81. In many areas, the ozone reduction due to these two reactions overwhelmed the ozone increase due to the isoprene chemistry update. This led to an incorrect conclusion regarding the impact of the isoprene update. The results presented in this

Jang et al. (1997)

study and those found by Jang are believed to be the correct response of photochemical grid models (UAM-V and MAQSIP) to the updated CB-IV isoprene mechanism.

Future Work

Additional studies should be completed to verify the results presented here and to learn more about the reactions in the current CB-IV mechanism. The updated isoprene chemistry should be tested with additional ozone episodes using UAM-V. Replication of this work should also be completed with the CAM-X and SAQM models.

Further study of the 3 additional XO₂N reactions (86, 87 and 88) is needed. MCNC has found large changes in ozone, particularly in the South, due to the addition of these 3 reactions (Kasibhatla, 1997). The impact of the XO₂N reactions has not been studied on a regional basis using UAM-V. Due to the hard coding of these reactions, it was not possible to determine their impact in this study.

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Table 1.

Sensitivity Tests of CB-IV Chemistry vs. Updated Isoprene CB-IV Chemistry in OTAG

B-IV Reaction No.	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
14	New	old	New	old	New	New	New
21	New	old	old	New	old	old	old
74	New	old	old	New	old	New	New
75-78	New	old	old	New	old	New	New
81	New	old	old	New	New	New	old
84	New	old	old	New	old	old	old
85	New	old	old	New	old	old	old
90-94	New	N/A	N/A	New	N/A	New	New

	Rate Constants in Chemparam	
	OLD (UAM-V 1.23)	New (UAM-V 1.24)
4= NO3---> .89NO2+.89O+.11NO	2034 x K1	33.9 x K1
1= NO+NO2+H2O---> 2 HONO	1.6E-11	3E-08
4= MGLY---> C2O3+HO2+CO	9.64 x K38	0.022 x K1
5-78=Isoprene reactions	old	new
1= XO2N+NO--->	1,000	12,000
4= MEOH+OH---> FORM+HO2	1600	1363
5= ETOH +OH---> HO2+ALD2	4300	4791
90-94= ISPD reactions (94=ISOP+NO2)	N/A	new

Old= UAM-V 1.23 (basA)
 New=UAM-V 1.24 (basD2)

Rate Constants are in ppm -n /minute

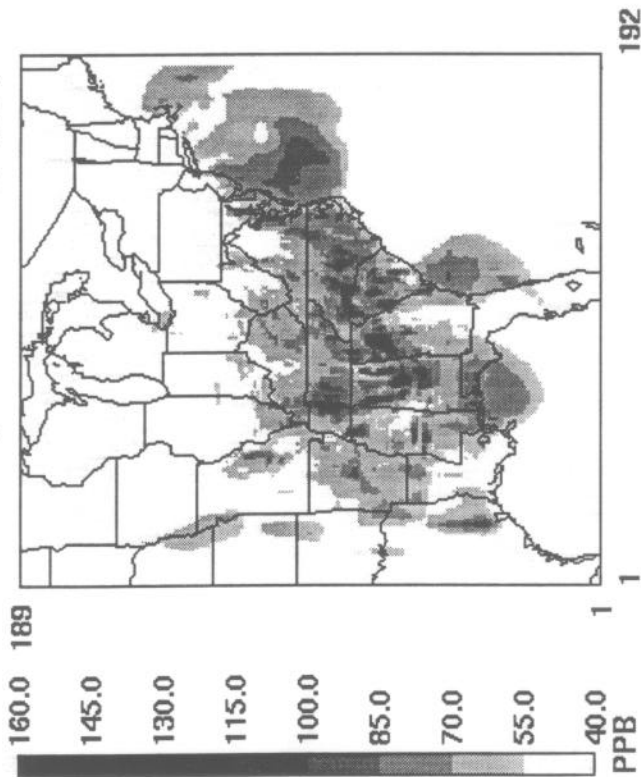
Activation energies of Rx 21, 84 and 85 were also changed

All runs were done with the final OTAG 93basD2 emissions and meteorological (SAIMM) fields

PAVE by MCNC

O3 Max - Final 1993 OTAG Base Cas

O3 Max July 22, 1993 only
NC DAQ (finl.Jul22.1993.18.grey.gif)

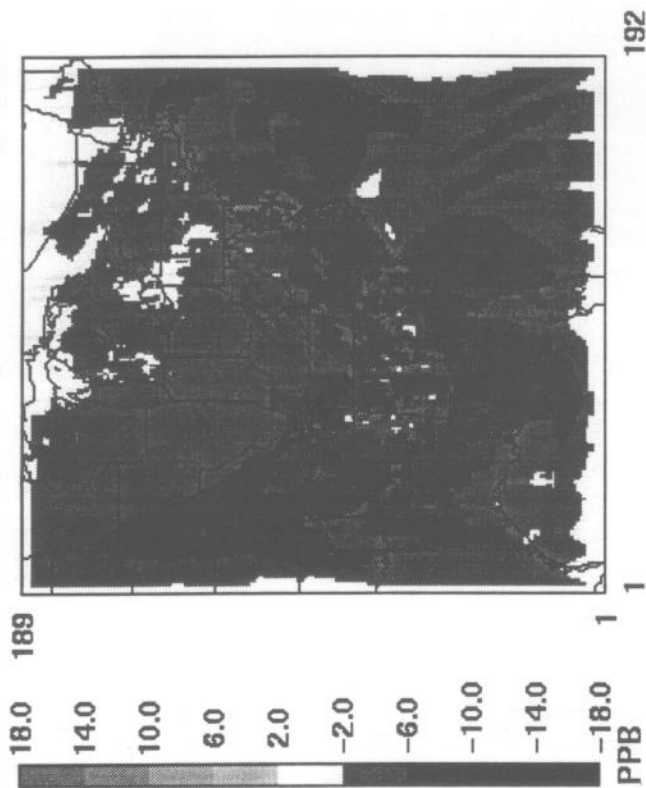


July 22, 1993 0:00:00
Min=-999.0 at (1.1), Max=279.2 at (89,71)

PAVE by MCNC

Impact of All Chem Changes

O3 Maxdif - Isoprene Update as Represented in OTAG
NC DAQ (finl-orig.Jul22.1993.18.grey.gif)



July 22, 1993 0:00:00
Min=-32.1 at (89,71), Max=0.2 at (188,41)

Figure 1. Maximum ozone predicted on July 22nd in OTAG 1993 base case

Figure 2. Maximum ozone difference between base case and OTAG updated chemistry run (UAM-V 1.24) as represented in OTAG (June, 1996).

PAVE by NCNC

Rx14 Correction w/New ISOP

O3 Maxdif- w/o other changes, Rx14 correct(2034-->33.9
NC DAQ (rx14-ispr.Jul22.1993.18.grey.gif)

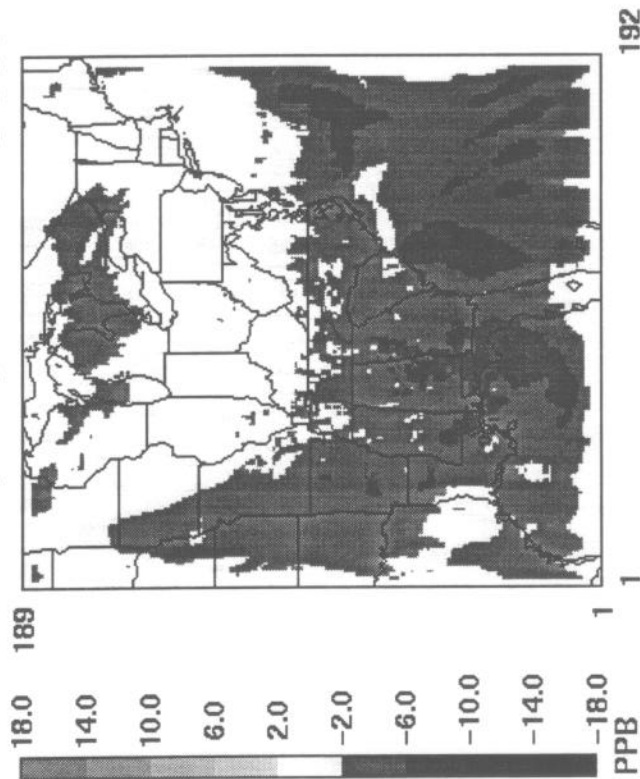


Figure 3. Maximum ozone difference on July 22nd due to reaction 14 rate constant correction using UAM-V 1.24

PAVE by NCNC

Impact of Rx 81 Rate Change

O3 Maxdif- Rx 81 rate X 12 -Old Chem
NC DAQ (or1481-or14.Jul22.1993.18.grey.gif)

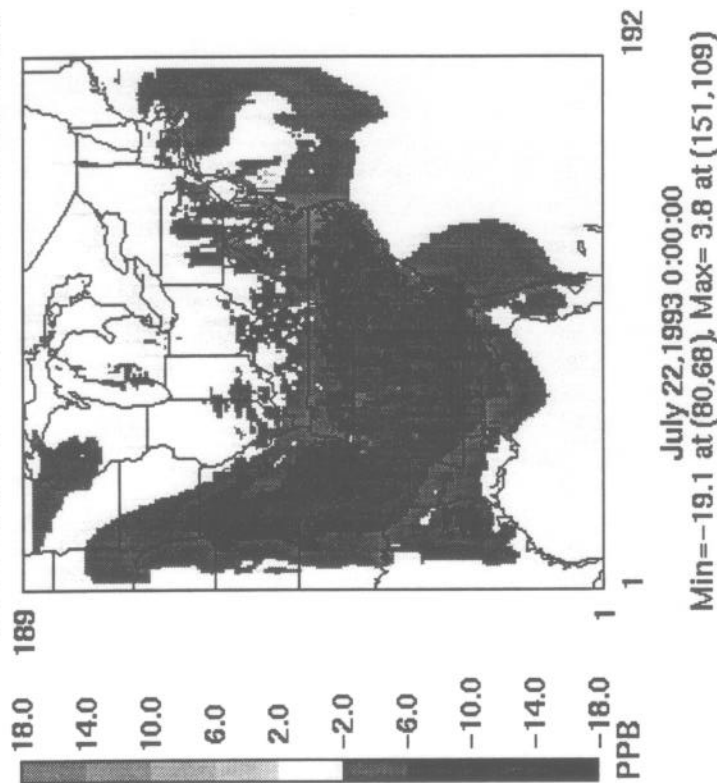
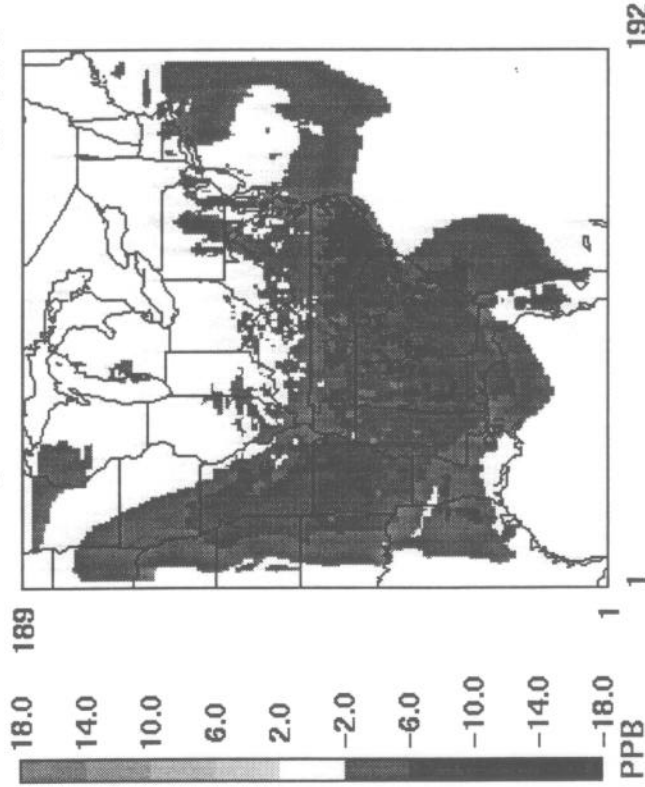


Figure 4. Maximum ozone difference on July 22nd due to reaction 81 rate constant correction using UAM-V 1.23

PAVE by MCNC

Impact of Rx 81 Rate Change

O3 Maxdif- Rx 81 rate X 12 -New Chem
NC DAQ (rad-finl.Jul22.1993.18.grey.gif)



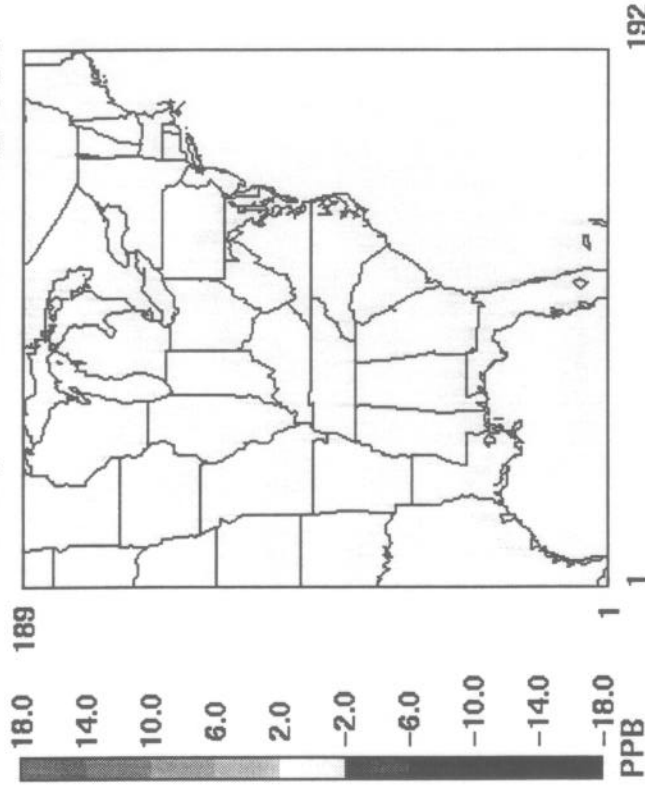
July 22, 1993 0:00:00
Min=-17.8 at (82,65), Max= 1.8 at (98,143)

Figure 5. Maximum ozone difference on July 22nd due to reaction 81 rate constant correction using UAM-V 1.24

PAVE by MCNC

Impact of New Rates - Rx 21,84,85

O3 Maxdif- New rates for Rx 21,84,85 w/new ISOP
NC DAQ (rad-finl.Jul22.1993.18.grey.gif)



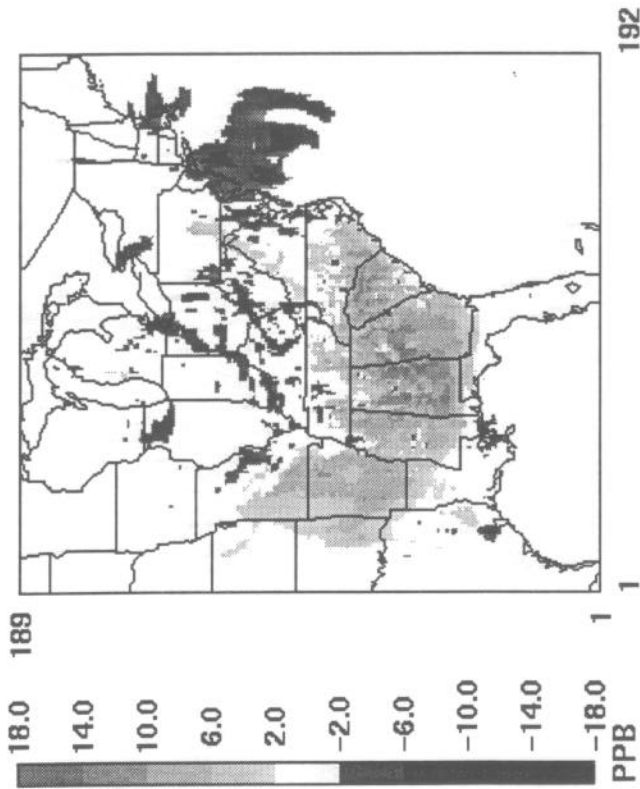
July 22, 1993 0:00:00
Min=-0.9 at (148,109), Max= 0.8 at (60,97)

Figure 6. Maximum ozone difference on July 22nd due to change in reaction 21, 84 and 85 rate constants using UAM-V 1.24

PAVE by MCNC

Impact of New ISOP Chem ONLY

O3 Maxdif- Isoprene changes w/Rx14 and 81 correction
NC DAQ (rad-or1481-Jul22.1993.18.grey.gif)

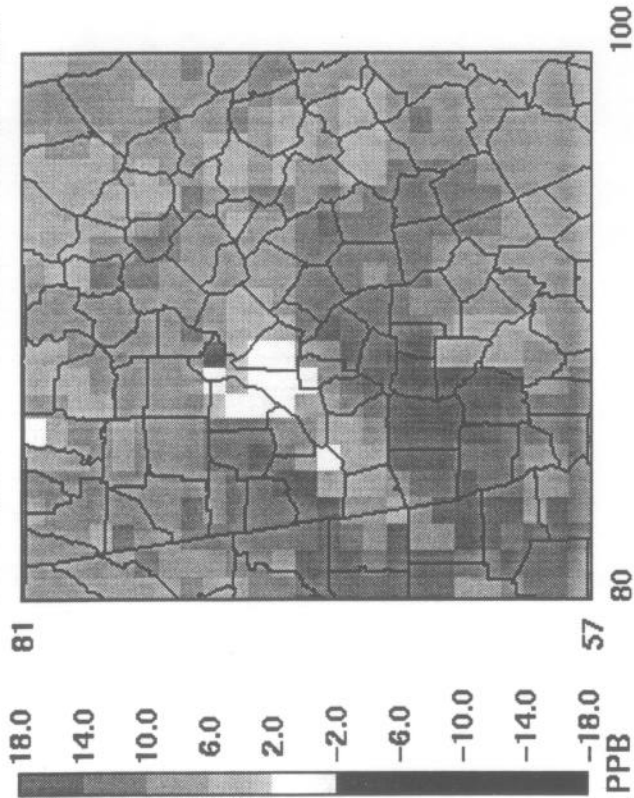


July 22, 1993 0:00:00
Min=-29.3 at (55,82), Max=18.9 at (82,59)

PAVE by MCNC

Impact of New ISOP Chem ONLY

O3 Maxdif- Isoprene changes w/Rx14 and 81 correction
NC DAQ (rad-or1481-Jul22.1993.18.grey.gif)



July 22, 1993 0:00:00
Min=-1.1 at (88,70), Max=18.9 at (82,59)

Figure 7. Maximum ozone difference on July 22nd due to the isoprene chemistry update with correct rate constants for reactions 14 and 81. (The light gray areas in the South are ozone increases).

Figure 8. Same as figure 7 except a zoom of the Atlanta area

PAVE by MCNC

Isoprene Max 1993 OTAG Base Case

ISOP Max July 22, 1993 only
NC DAQ (finl.Jul22.1993.18.isop.grey.gif)

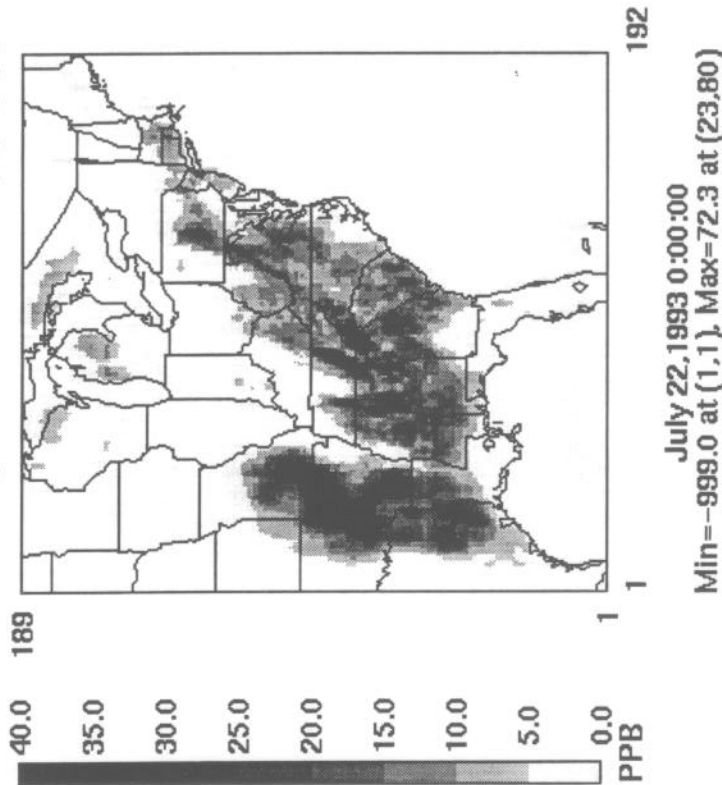


Figure 9. Maximum isoprene concentration (in ppbV) on July 22nd in the OTAG 1993 base case.

O3b - O3a

(O3a : Original CB4, O3b : Updated CB4)

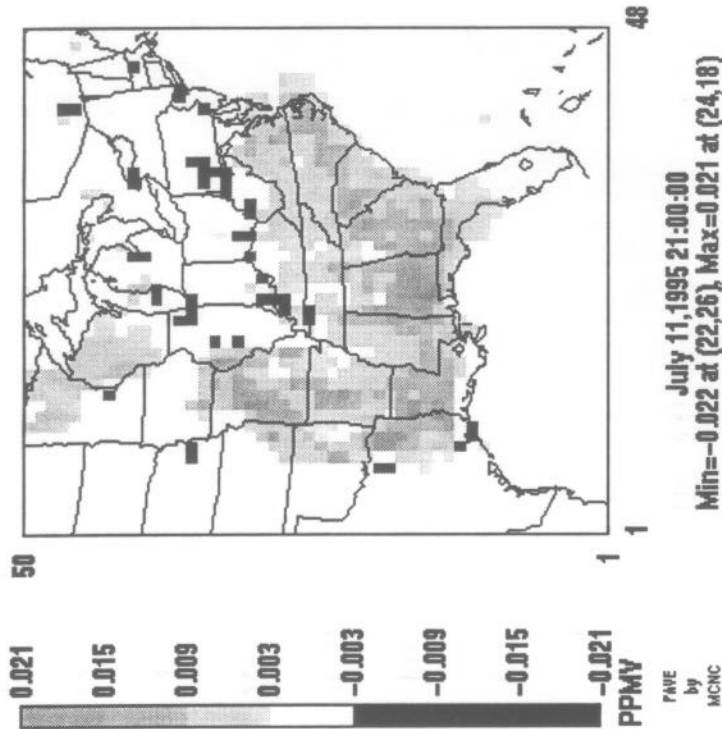


Figure 10. Ozone difference due to the isoprene chemistry update using the MAQSIP model on July 11, 1995 at 4:00 PM (2100 GMT). The horizontal resolution is 54 km (Jang, 1997)