9/18/97 Carey Jang

ICF KAISER
Consulting Group
Systems Applications International, Inc.

MEMORANDUM

TO: OTAG Participants

FROM: Gary Z. Whitten, Hans P. Deuel, C. Shepherd Burton, Jay L. Haney, SAI

DATE: 28 June 1996

SUBJECT: Overview of the Implementation of an Updated Isoprene Chemistry Mechanism in CB4/UAM-V

Abstract

A condensed (one-product) isoprene chemistry mechanism, one of two recently developed by Carter (1996), has been substituted for the original isoprene reaction set included with CB4 (Gery et al., 1989). Carter (1996) noted that his new reaction sets and the original CB4 reaction set reproduce existing smog chamber data similarly; however, he found that the new chemistry produces considerably <u>less</u> incremental ozone from isoprene when isoprene is not the major VOC constituent. We find similar results in that readily available smog chamber data were equally well simulated by both the original CB4 chemistry and a version of CB4 that uses Carter's new condensed reactions for isoprene, but incremental reactivity estimates and the UAM-V yield <u>less</u> ozone from isoprene with the new reactions. Because the newly updated CB4 fits smog chamber data equally well <u>and</u> more correctly accounts for newly discovered secondary products, we conclude that the new chemistry should be used in the UAM-V.

Background

Ozone production in the troposphere is the result of a series of chemical transformations, in the presence of sunlight, of NO_x and VOCs, which are emitted into the atmosphere from both biogenic and anthropogenic sources. The complex physical and chemical processes leading to ozone production can be simulated using a photochemical air quality model. The quality of the estimates provided by photochemical air quality models, which have been applied to support planning efforts for ozone attainment, rely heavily on the quality of the inputs, particularly the emissions estimates. Recent advances in estimating biogenic emission factors have provided information for revising existing biogenic emission processors. For example, in 1995, the EPA updated the Biogenic Emission Inventory System (BEIS) and released the revised processor (BEIS2). The incorporation of more tree and crop species, the use of updated emission factors, and the revisions to the canopy model are expected to result in increased VOC emission estimates, especially for isoprene. These recent changes have focused concern on the accuracy of isoprene treatment in current photochemical grid models. Two aspects under review are the atmospheric chemistry of isoprene and the role of grid size resolution. This memorandum focuses on the chemistry. In this area, new analytical instruments have revealed the presence of important secondary photooxidation products not accounted for in the original Carbon Bond 4 (CB4) mechanism used in the Urban Airshed Model (UAM). A paper, soon to be published by Carter (1996), provides an updated and condensed set of reactions for isoprene photooxidation which account for these newly discovered secondary products. Although the original CB4 isoprene reactions were capable of adequately simulating smog chamber data, we have now learned that the updated chemistry simulates the same data for different reasons. These reasons lead to different impacts of isoprene in atmospheric settings where isoprene is not the sole organic ozone precursor (as is the case in the present smog chamber database used for testing isoprene reactions).

The CB4 mechanism is also contained in the variable-grid version of the UAM, known as the UAM-V. That modeling system is currently being applied to assess ozone production and transport in the eastern U.S. as part of the Ozone Transport and Assessment Group's (OTAG) regional modeling effort. The revised biogenic emissions estimates provided by the more technically advanced BEIS2 processor and the updated isoprene chemistry mechanism in the UAM-V are expected to provide more accurate representations of the role of biogenic emissions in ozone production in the OTAG study domain.

This memorandum summarizes the selection, implementation, and testing of a condensed version of Carter's isoprene mechanism into CB4. Data from 12 experiments from the University of North Carolina (UNC) outdoor chambers have been used to compare the performance of the original and the updated versions of CB4 isoprene chemistry. The results of these experiments are contained in Appendix A. Preliminary results of simulating the 1988 and 1993 OTAG episodes with the original and updated isoprene mechanisms in UAM-V are also provided.

Carter and Atkinson (1996) developed a detailed treatment of atmospheric isoprene chemistry that accounts for several reaction products recently revealed with new analytical instruments by Kwok et al. (1995) and Yu et al. (1995). Isoprene itself reacts very quickly during daylight, with a half-life from reaction with the hydroxyl radical (OH) as short as 20 minutes.[Smog chamber tests and computer simulations using isoprene as the sole VOC constituent show an accumulation of ozone throughout the day.] Similarly, computer simulations using a small incremental addition of isoprene to a urban-like mixture of VOC also show a day-long accumulation of incremental ozone due to the added isoprene. Hence, the reactivity from the products of the isoprene reactions appear to be important compared to the reactivity of isoprene itself. In the real atmosphere, and in regional models like the UAM-V, isoprene would rarely be the sole VOC present, but in smog chamber experiments used to test isoprene chemistry isoprene has been the only initial VOC present.

Urban mixtures of reacting VOCs can be sensitive to incremental additions of free radicals such as might occur from secondary products like formaldehyde[1]. These extra free radicals cause the VOCs in the urban mixture to react faster and generate more ozone. The conditions used by Carter to theoretically estimate Maximum Incremental Reactivity (MIR) have been shown by Jeffries and others to give the highest MIR estimates for those species that lead to the most extra free radicals. The new isoprene reactions developed by Carter (1996) and recently implemented in the UAM-V version of the CB4 show about a 38 percent lower MIR estimate compared to the original CB4 isoprene chemistry of Gery et al. (1989). Since both isoprene reaction sets seem to give virtually identical performance statistics (see Tables 1 and 2) in the smog chamber tests, it appears that free radical production is either much less from the secondary products in the new Carter isoprene reaction scheme, or these products themselves are capable of reacting faster with fewer radicals than the set of secondary products used in the original version of CB4.

The original CB4 isoprene reactions are a condensation of a detailed set of reactions developed by Killus and Whitten (1984). At that time only 2 of 12 possible reaction channels from the OH addition to isoprene were believed to be important. Carter and Atkinson's (1996) use of new instrumentation (Kwok et al., 1995; Yu et al., 1995) to monitor secondary products of isoprene decay revealed that 10 of the 12 possible reaction channels are actually important. Carter and Atkinson also noted that these newly discovered compounds apparently react faster than the two products previously believed sufficient to fully explain the behavior of secondary products of isoprene decay. Hence, we can now explain how it was possible to "fit" the pure isoprene smog chamber database with two alternative reaction sets, yet have one set give an MIR of 38 percent less. This explanation is that the secondary products in the new Carter reaction set produce less free radicals and react faster than the older CB4 reaction set; the combination of faster-reacting and fewer radicals gives the same smog chamber fit, but the MIR is affected only by the fewer radicals.

The Isoprene Reactions

Carter (1996) developed and tested two condensed versions of isoprene chemistry: the first version uses four new secondary products specific to isoprene and the second requires only one new special product. The original CB4 treatment of isoprene by Gery et al. (1989) was even more con-

---

[1] Terminal olefinic bonds generally react to give formaldehyde as a secondary product under smog-like conditions. Isoprene has two such bonds and formaldehyde has always been identified as a major secondary product from isoprene photooxidation. The photolysis of formaldehyde can yield two free radicals.

densed in that no new special products were used. To minimize the computer impact for OTAG, the single-product version of Carter's was chosen. Two other reasons to support this choice are shown by Carter: (1) it is very close in performance for reproducing smog chamber data to either the full detailed treatment or the four-product condensed version, and (2) the PAN production of the one-product version is somewhat higher than the other versions. For simulating ozone transport such as in OTAG, PAN and other PAN-like analogs are known to have an important role as species which carry nitrogen oxide, a key precuror to ozone formation. Hence, formation of PAN and its analogs should be simulated as accurately as possible. In the CB4 and the one-product condensed isoprene scheme, PAN is used as a surrogate for the sum of PAN itself and other PAN-like compounds. Therefore, we believe that any apparent errors in comparing the simulated PAN concentrations with observed concentrations of only PAN itself should be towards overprediction so as to account at least in some way for the other (often unmeasured) PAN analogs.

The condensed reactions for isoprene developed by Carter (1996) were designed to be used with the complete atmospheric mechanism known as the SAPRC-90 or SAPRC-93, developed at the Statewide Air Pollution Research Center (SAPRC) by Carter (1990 and 1995). In order to use the Carter isoprene reaction subset with the full CB4 mechanism, several product species used by Carter (1996), specific to the SAPRC mechanisms, required conversion to the closest possible equivalent counterpart species used in the full CB4 mechanism. Table 3 shows the SAPRC-93 species and their CB4 counterparts used. The single product isoprene reactions given by Carter (1996) and some of the products described by Carter for the SAPRC-90 and SAPRC-93 mechanisms (Carter, 1990 and 1995) were then converted using Table 3 to form the reactions shown in Tables 4 through 7. In these tables we have included for comparison the original CB4 isoprene reactions by Gery et al. (1989).

Smog Chamber Tests

Carter (1996) used the data from at least 28 experiments in five different smog chambers to test the new detailed and condensed versions of the isoprene chemistry. One of these five chambers, the University of North Carolina (UNC) chamber, was the same as used by Gery et al. (1989) to test the original CB4 reactions for isoprene with 12 experiments. Carter (1996) concluded that the CB4 mechanism "actually simulates isoprene environmental chamber data somewhat better than the other previously published mechanisms (though not as well as the new mechanisms)." In the time available for this project, we were able to use 12 experiments from the UNC chamber (7 from the original set used by Gery et al. in 1989 and 5 newly available experiments) to test both the original CB4 and the new version with Carter's new condensed reactions for isoprene. Appendix A shows the detailed results for all 12 experiments. Tables 1 and 2 provide a summary of the initial conditions and the performance statistics between the new and old versions of isoprene chemistry in the CB4 mechanism. Figures 1 through 3 show summary "scatter" plots of the performance for ozone, PAN, and formaldehyde, respectively.

At least for these 12 UNC experiments, we see no significant difference in performance for ozone and PAN between the original CB4 and the new version using our adaptation of Carter's one-product condensed scheme for isoprene. The figures presented by Carter (1996), showing some UNC experiments identical to the ones we use here, indicate that our simulations using the original CB4 do not quite match Carter's simulations. It is our understanding that differences in treatment of chamber characterization (mainly wall and background contamination effects) might explain the differences in these simulations. The chamber characterization treatment we used came directly from UNC without modification, but we understand that Carter uses his own special treatment of chamber effects developed at SAPRC.

There is a significant difference between the original CB4 and the new version regarding the production of formaldehyde. Carter and Atkinson (1996), after studying the performance of their detailed isoprene chemistry in several smog chambers, stated that they "consider the present data set inadequate to evaluate this aspect [formaldehyde performance] of the isoprene mechanism." They indicated that the formaldehyde data from the recent UNC chamber experiments may be the best in this regard. In Figure 3 we show that the original CB4 shows a significant overprediction of the most recent UNC data for formaldehyde, but the new version with the updated isoprene chemistry appears to simulate the newest formaldehyde data quite well.

Incremental Reactivity Tests

Carter (1996) concluded that "one cannot always use results of compound-NO_x simulations [i.e., smog chamber simulations] alone as a guide to how mechanisms may differ in their predictions of relative reactivity." He based his conclusion mainly on the fact that he found the original CB4 mechanism produced an incremental reactivity for isoprene that is nearly a factor of two greater (regardless of NO_x level) than his new isoprene chemistry with the SAPRC-90 mechanism. This is in contrast to the fact that the two mechanisms (1) produced quite similar performance in simulating isoprene smog chamber experiments, (2) give quite similar overall incremental reactivity results for urban mixtures, and (3) give similar MIR results (and other reactivity measures) for several other individual compounds. Our own tests indicate a reduction of over 35 percent in isoprene incremental reactivity using the updated CB4 (with the Carter isoprene reactions) compared to the original CB4 mechanism. Carter (1996) speculated that the Carbon Bond mechanism has a greater sensitivity to radical inputs in general than his SAPRC mechanisms, and this greater sensitivity may explain the higher incremental reactivity seen by the original CB4 for isoprene. We tend to disagree with this speculation in light of the significantly reduced incremental reactivity we now see when using the new Carter reaction set substituted for the isoprene reactions in the CB4 mechanism. Carter's speculation about the higher sensitivity of the Carbon Bond mechanism to radical inputs (than the SAPRC mechanism) can only partially explain why the incremental reactivity comparisons did show somewhat greater reductions in incremental reactivity for isoprene (38 to 46 percent over a range of NO_x conditions compared to our present

35 to 38 percent reductions over a similar range for the old to the new CB4); Carter was comparing the full SAPRC mechanism using the new condensed isoprene scheme to the original CB4 full mechanism using the old isoprene chemistry. However, we do not have the full set of conditions that Carter used to compute his various incremental reactivity factors. Nevertheless, it seems clear that two versions of isoprene chemistry (the original CB4 and the newly modified version reported here) can show quite significant differences in incremental reactivity yet show very similar performance in the existing smog chamber database.

We believe that the differences in incremental reactivity are explained by the differences in radical yield (the new scheme appears much lower). In incremental reactivity tests, radicals produced by an incremental addition to the total VOC mixture react, for the most part, not with the added increment of VOC, but with various other VOCs in the mixture instead. In the existing smog chamber database for isoprene testing, isoprene is always the sole VOC present. The new isoprene scheme has significantly higher hydroxyl radical reaction rate constants for the secondary products than the old CB4 scheme (see Tables 4 through 7). The isoprene reaction rate constants (especially for reaction with the hydroxyl radical) do not differ as much between the old and new versions, but isoprene is reacted away very quickly in these experiments, so the overall long-term chemistry seen depends strongly on the reactivity of the secondary products. The impact of the secondary products depends strongly on the product of the hydroxyl radical concentration times the hydroxyl radical rate constants. Hence, less hydroxyl radicals need to be present with the new scheme to produce the same smog chamber results, but as just noted the incremental reactivity results depend mainly on the hydroxyl radicals produced and not on the reactions of the secondary products.

Recommendations for Experiments to Test Isoprene Chemistry

If we have correctly explained why the smog chamber database cannot clearly show the importance of radical production from isoprene, then new experiments should be done with the sensitivity to show whether the new or old chemical scheme is correct. Experiments with only carbon monoxide (CO) and NO_x show that these act as chemical amplifiers to enhance the sensitivity to radical sources (Glasson and Dunker, 1989). CO reacts with hydroxyl radical to generate ozone in the presence of NO_x, but CO and NO_x (in clean and reasonably dry conditions) have no known sources of free radical production leading to hydroxyl radical. These experiments were designed (Killus and Whitten, 1981) to detect background radical sources in smog chambers. We believe that new experiments could be set up using a significant level of CO (e.g., 100 ppm) and a small amount of isoprene (e.g., a few ppb) so that the radicals contributed from the added isoprene (or its secondary products) are significantly greater than radicals produced from chamber background sources, and are sufficient to generate significant ozone when amplified by CO. The optimal set of conditions depends on the cleanliness of the smog chamber, and "blank" experiments without isoprene are needed to ensure the quality of the data. In such experiments the hydroxyl-CO reaction should be significantly more important than reactions with isoprene or any of its secondary products.

Preliminary UAM-V Simulation Results Using the Updated CB4 Isoprene Mechanism

After testing the updated CB4 isoprene mechanism with the PKSS smog chamber simulation software and assessing the resulting incremental reactivity, the CB4 isoprene mechanism was updated in the fast-solver version of UAM-V. A series of test simulations were conducted for a subset of the 1993 episode days for a subregional area centering on Atlanta, Georgia, referred to as the Atlanta test-bed simulation, and for a full SUPROXA-domain simulation of the 1988 and 1993 OTAG episodes.

Atlanta Test Bed Results

The original and updated versions of UAM-V were applied to simulate the first four episode days (20–23 July 1993) of the 1993 OTAG episode for the Atlanta test bed using the BaseA2 emissions inventory. This inventory, which includes biogenic emission estimates provided by BEIS2, represents an earlier version of the anthropogenic inventory that is slightly different than the one currently being used in the OTAG base case modeling. To examine the results of the updated isoprene chemistry, Figure 4 presents time series plots for 20–23 July 1993 for three sites (Columbus, GA - 132151003, Tilesboro, GA - 130150002, and Chattanooga, TN - 4760650028) for ozone, CO, formaldehyde, isoprene, NO_x, and PAN, comparing the results of the original and updated CB4 mechanisms. Ozone, CO, isoprene, and NO_x concentrations are slightly lower for all hours, while simulated formaldehyde and PAN concentrations are reduced nearly 50 percent with the updated CB4. Given the changes to the isoprene chemical mechanism and the resulting reduction in the incremental reactivity of isoprene, these results are expected and appear reasonable.

Preliminary Results for the 1988 OTAG Episode

The original and updated versions of UAM-V were also applied to simulate the full July 1988 OTAG episode on the SUPROXA domain using the BASEB2 emissions inventory. This inventory also includes biogenic emission estimates provided by BEIS2. To illustrate the effects of the updated CB4 on ozone concentrations, Figures 5 and 6 present isopleth plots of UAM-V simulated maximum daily ozone concentrations for 8 July 1988 for the original and updated CB4 chemistry, respectively. The peak simulated concentration using the original CB4 is 227 ppb, located in Atlanta; this peak is reduced to 194 ppb using the updated CB4 chemistry. The peak observed ozone concentration on this day in Atlanta was 187 ppb. As indicated in the figures, maximum simulated ozone concentrations are generally lower in all parts of the domain with the use of the updated CB4 isoprene chemistry. Figure 7 illustrates the differences in maximum simulated ozone concentrations: the dotted lines indicate reductions in maximum simulated ozone concentrations with the use of the updated CB4 isoprene mechanism, with a miximum reduction of 44 ppb for this day. 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 episode appear reasonable.

Preliminary Results for the 1983 OTAG Episode

The original and updated versions of the UAM-V were also applied to simulate the full July 1993 OTAG episode on the SUPROXA domain using the BASEB2 emissions inventory. To illustrate the effects of the updated CB4 on ozone concentrations, Figures 8 and 9 present isopleth plots of UAM-V simulated maximum daily ozone concentrations for 23 July 1993 for the original and updated CB4 chemistry, respectively. The peak simulated concentration using the original CB4 is 302 ppb, located in Atlanta; this peak is reduced to 256 ppb using the updated CB4 chemistry. The peak observed ozone concentration on this day in Atlanta was 180 ppb. As indicated in the figures, and similar to the 1988 episode, maximum simulated ozone concentrations are generally lower in all parts of the domain with the use of the updated CB4 isoprene chemistry. Figure 10 illustrates the differences in maximum simulated ozone concentrations: the dotted lines indicate reductions in maximum simulated ozone concentrations with the use of the updated CB4 isoprene mechanism, with a maximum reduction of 45 ppb for this day. 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 1993 episode appear reasonable.

TABLE 1. Summary of UNC smog chamber experiments.

Date	NO_x (ppb)	VOC/NO_x (ppbC/ppb)	O_3Meas (ppb)	CB4 (ppb)	Carter (ppb)
JN1780B	96	13.5	406	380	351
JN1780R	189	2.6	354	494	424
JN2080R	478	1.0	88	167	63
JL1680B	186	10.6	837	616	605
JL1680R	180	22.4	652	335	371
JL1780B	460	5.6	1297	1043	1046
JL1780R	466	2.1	806	822	673
SE0981R	165	6.1	506	537	502
JN2592B	361	16.6	667	563	667
JN2592R	357	8.3	784	870	913
JN1793B	537	1.3	1042	1192	1194
JN1793R	528	8.9	993	956	1044

TABLE 2. Performance statistics of the CB4 and new Carter formulations.

Statistic	Ozone	PAN	Form
R^2 (to data)			
Old CB4	0.771	0.981	0.692
Carter	0.819	0.979	0.645
R^2 (to CB4)			
Carter	0.951		
Accuracy % (± Std Error)			
Old CB4	−7.5±5.6	+0.5±2.4	+19±11
Carter	−7.0±5.4	+17±4	−28±8

TABLE 3. Species used in condensed isoprene reaction scheme developed by Carter (1996) and their closest counterpart species used in the CB4 mechanism.

SAPRC Species	CB4 Species	Comments
RO2-N	XO2N	Converts NO to organic nitrate
R2O2	XO2	Converts NO to NO2
RO2-R	XO2 + HO2	
RO2	(not used)	Counter species only
HCOOH	NR	Treated as inert in CB4
HCOCO-O2	C2O3+CO-FORM-XO2	
CCO-O2	C2O3	Makes PAN
C2CO-O2	C2O3 + PAR	Makes PPN or higher Pan
RCO3	(not used)	Counter species only
RNO3	NTR + 1 or 2 PAR	Number of PAR from parent
RCHO	ALD2 + PAR	
GLY	FORM + CO	
MEK	4 PAR	

ISOP + HO → 0.088 XO2N + 0.912 (XO2 + HO2) + 0.629 HCHO + 0.912 ISPD
+ 0.079 XO2 + [illegible]

ISOP + OH → 0.088 XO2N + 0.912 HO2 + 0.991 XO2 + 0.629 HCHO + 0.912 ISPD $2.54E{-11}\, e^{-4}$

$$T(K) = -0.81 \frac{\text{Kcal/mol}}{R} \quad \text{K·mol/KCAL}$$

$$R = 1.98717\ \text{cal}/(\text{K·mol}) \times \frac{1\ \text{kcal}}{1000\ \text{cal}}$$

$$.001\ 1.98717 \times 10^{-3} \frac{\text{Kcal}}{\text{K·mol}} = 503.2282 \frac{\text{mol·K}}{\text{kcal}}$$

ISOP + O_3

TABLE 4. Products of OH + Isoprene reactions.

New adapted Carter

For isoprene (k = 147600 ppm^{-1}min^{-1}):

0.912 ISOPRD + 0.629 FORM + 0.991 XO2 + 0.912 HO2 + 0.088 XO2N

For "ISOPRD" (k = 49660):

1.565 PAR + 0.167 FORM + 0.713 XO2 + 0.503 HO2 + 0.334 CO + 0.168 MGLY + 0.273 ALD2 + 0.498 C2O3

Old CB4, for isoprene (k = 142000):

1.0 ETH + 1.0 FORM + 1.0 XO2 + 0.67 HO2 + 0.13 XO2N + 0.4 MGLY + 0.2 ALD2 + 0.2 C2O3

TABLE 5. Products of O3 + Isoprene reactions.

New adapted Carter

For isoprene (k = 0.019):

0.65 ISOPRD + 0.60 FORM + 0.20 XO2 + 0.066 HO2 + 0.266 OH + 0.2 C2O3 + 0.15 ALD2 + 0.35 PAR + 0.066 CO

For "ISOPRD" (k = 0.0105):

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

Old CB4, for isoprene (k = 0.018):

0.55 ETH + 1.0 FORM + 0.~~4~~ MGLY + 0.44 HO2 + 0.1 OH + 0.4 ALD2 + 0.1 PAR + 0.060 CO

0.2

TABLE 6. Products of NO3/NO2 + Isoprene reactions.

New adapted Carter

For isoprene + NO3 (*k* = 996):

0.2 ISOPRD + 0.8 NTR + 1.0 XO2 + 0.8 HO2 + 0.2 NO2 + 0.8 ALD2 + 2.4 PAR

For isoprene + NO2 (*k* = 0.00022):

0.2 ISOPRD + 0.8 NTR + 1.0 XO2 + 0.8 HO2 + 0.2 NO + 0.8 ALD2 + 2.4 PAR

For "ISOPRD" + NO3 (*k* = 1.478):

0.357 ALD2 + 0.282 FORM + 1.282 PAR + 0.925 HO2 + 0.643 CO + 0.85 NTR + 0.075 C2O3 + 0.075 XO2 + 0.075 HNO3

Old CB4, for isoprene + NO3 (*k* = 470):

1.0 XO2N

TABLE 7. Products of O + Isoprene reactions.

New adapted Carter (*k* = 53200):

0.75 ISOPRD + 0.50 FORM + 0.25 XO2 + 0.25 HO2 + 0.25 C2O3 + 0.25 PAR

Old CB4 (*k* = 27000):

0.55 OLE + 0.8 ALD2 + 0.5 XO2 + 0.6 HO2 + 0.5 CO + 0.9 PAR + 0.45 ETH

References

Carter, W.P.L. 1996. Condensed atmospheric photooxidation mechanisms for isoprene. *Atmos. Environ.* (in press).

Carter, W.P.L., and R. Atkinson. 1996. Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x. *Int. J. Chem. Kinetics* (in press).

Killus, J.P., and G.Z. Whitten. 1984. Isoprene: A photochemical kinetic mechanism. *Environ. Sci. Technol.*, 18:142-148.

Kwok, E.S.C., R. Atkinson, and J. Arey. 1995. Observations of hydroxycarbonyls from the OH radical-initiated reaction of isoprene. *Environ. Sci. Technol.*, 29:2467-2469.

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

Glasson, W.A., and A.M. Dunker. 1989. Investigation of background radical sources in a teflon-film irradiation chamber. *Environ. Sci. Technol.*, 23:970-978.

Killus, J.P., and G.Z. Whitten. 1981. Comments on "A smog chamber and modeling study of the gas phase NO_x–air photooxidation of toluene and the cresols." *Int. J. Chem. Kinet.*, 13:1101-1103.

Yu, J., H.E. Jeffries, and R. M. Le Lacheur. 1995. Identifying airborne carbonyl compounds in isoprene atmospheric photooxidation products by their PFBHA oximes using gas chromatography/ion trap mass spectrometry. *Environ. Sci. Technol.*, 29:1923-1932.

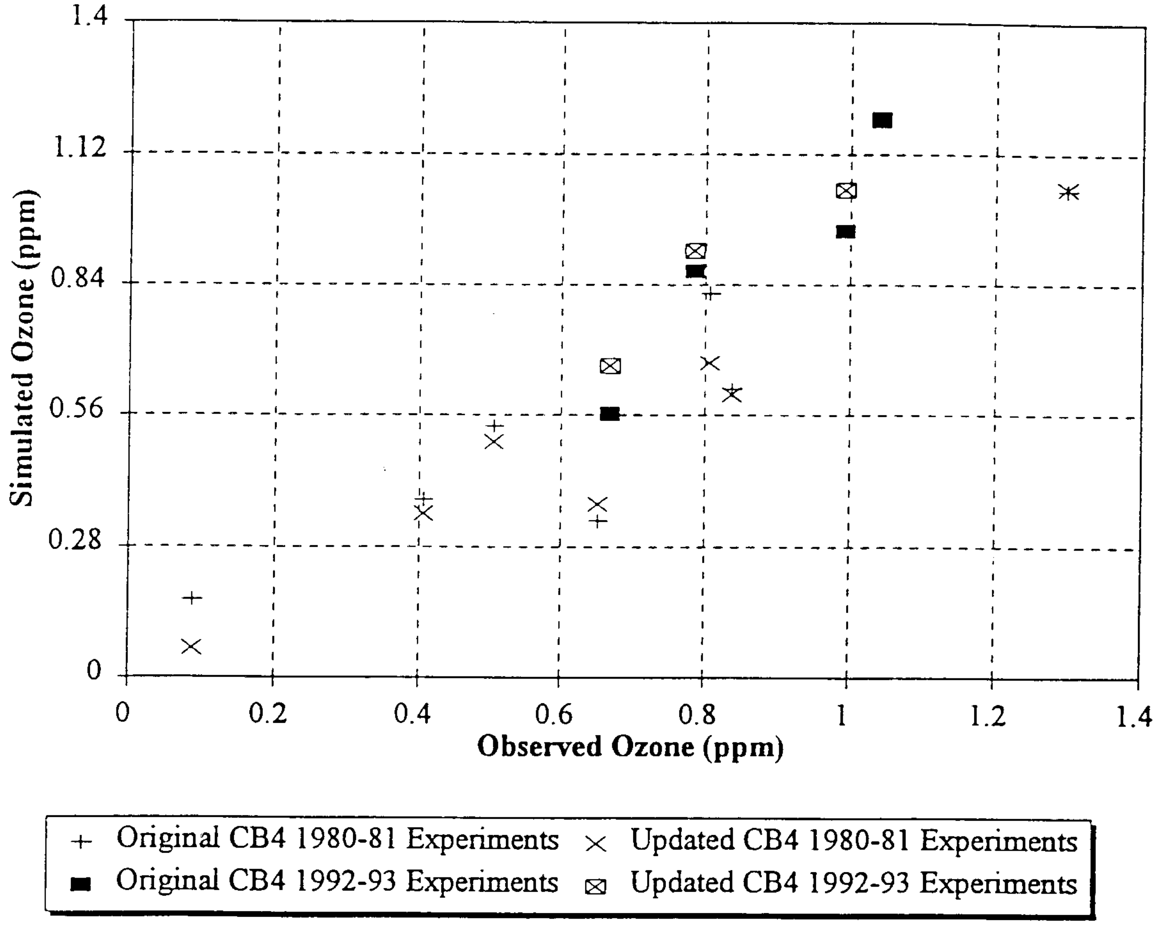


Figure 1. **Scatter plot of observed versus simulated peak ozone (ppm), comparing the original and updated CB4 isoprene mechanisms with smog chamber data.**

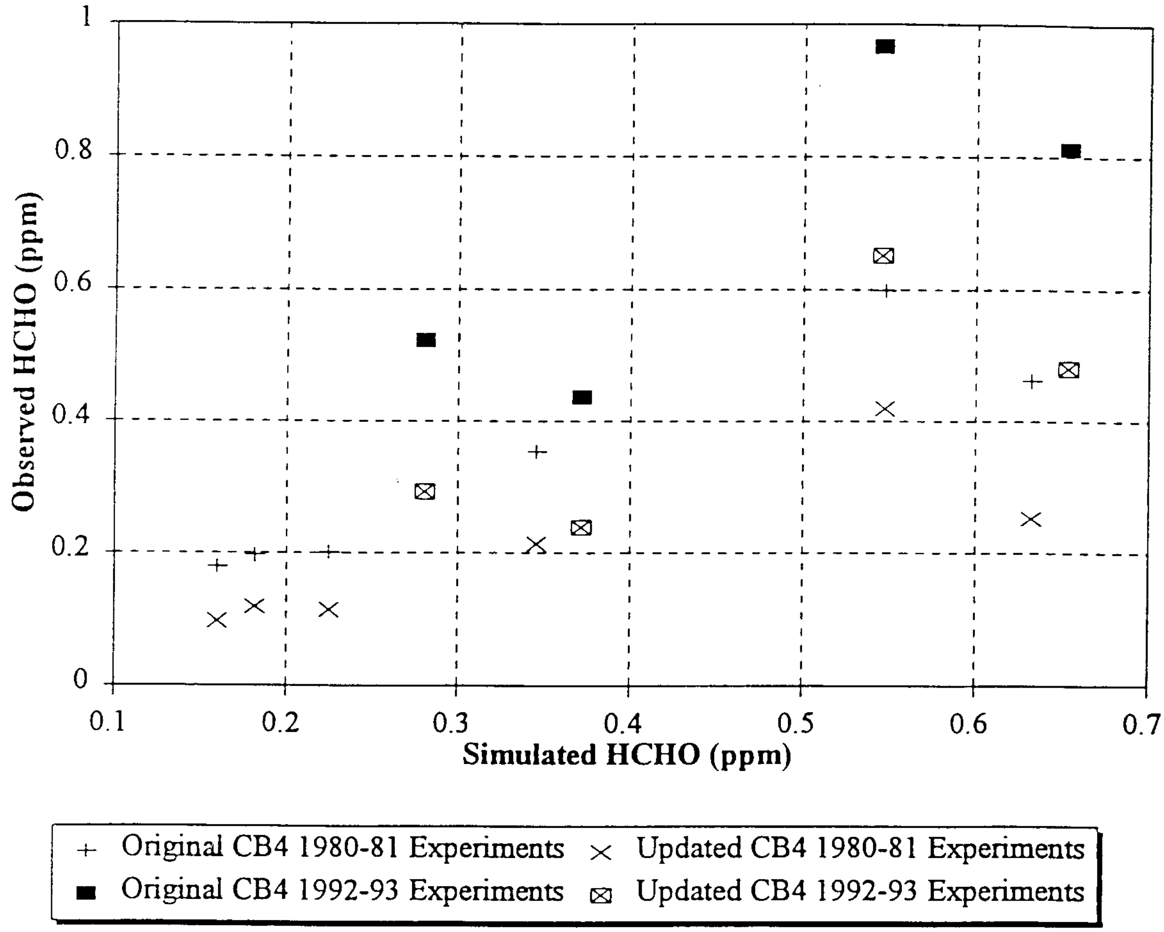


Figure 2. **Scatter plot of observed versus simulated peak formaldehyde (ppm), comparing the original and updated CB4 isoprene mechanisms with smog chamber data.**

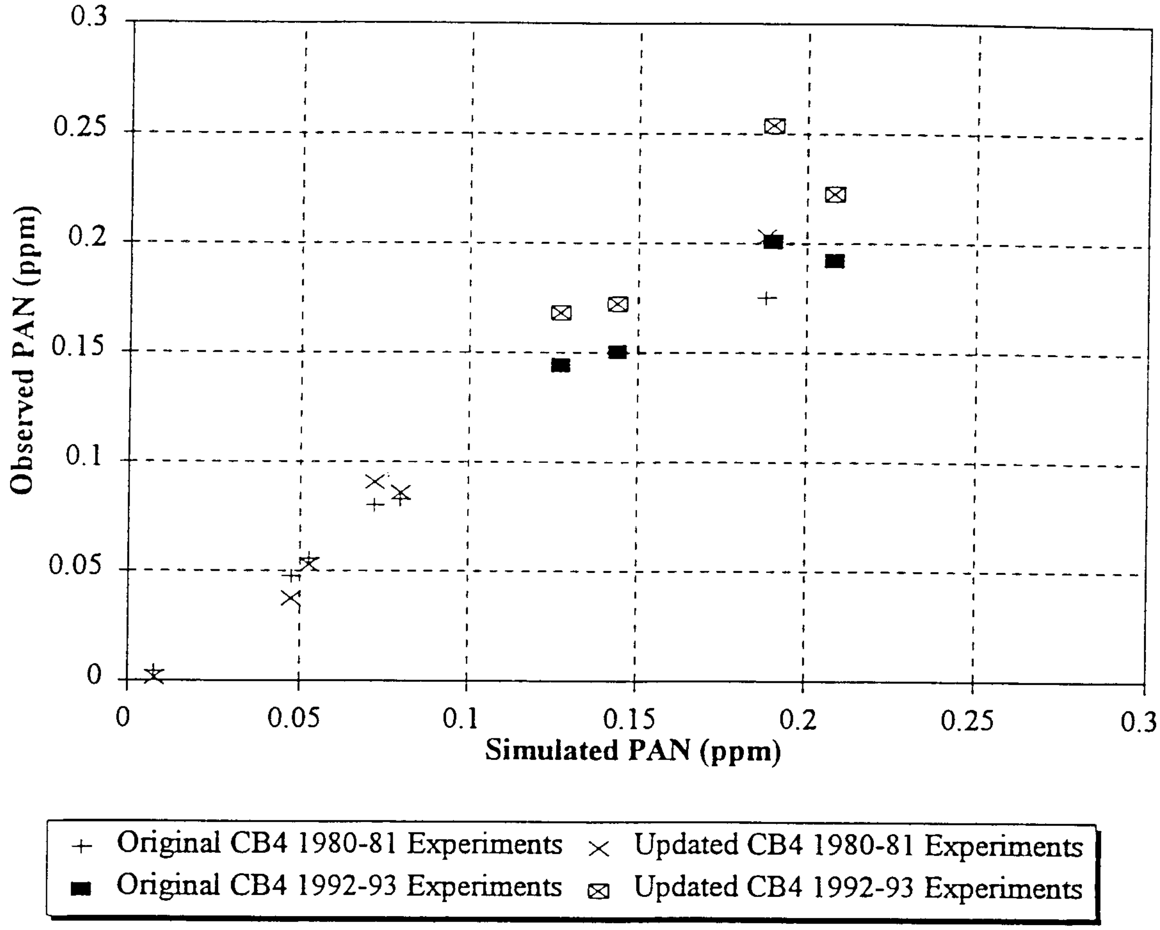


Figure 3. **Scatter plot of observed versus simulated peak PAN (ppm), comparing the original and updated CB4 isoprene mechanisms with smog chamber data.**

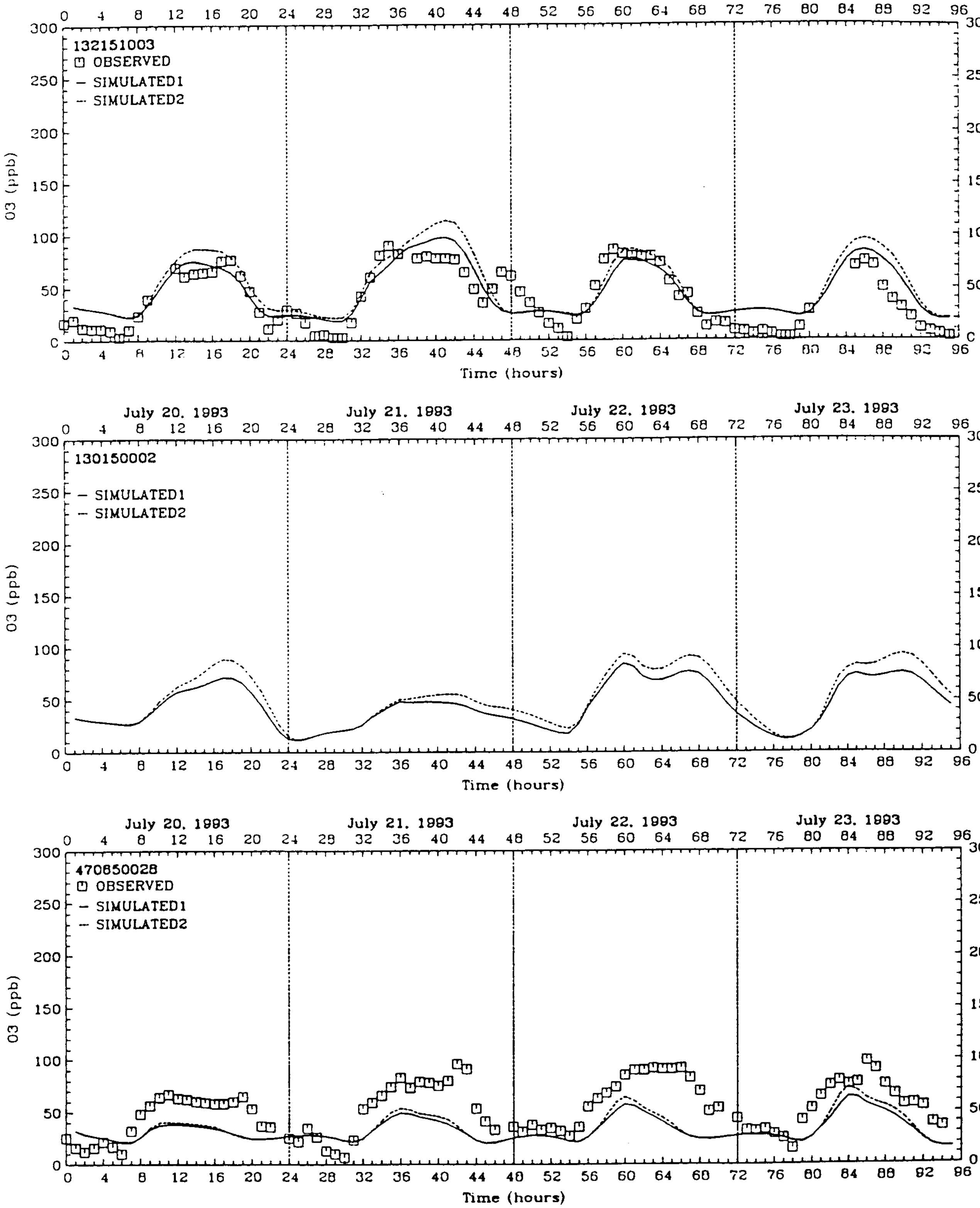


FIGURE 4a. UAM-V simulated and observed ozone concentrations (ppb) for three sites (Columbus, GA - 132151003, Tilesboro, GA - 130150002, and Chattanooga, TN - 4760650028) in the Atlanta test bed comparing the results of the original (Simulated2) and the updated (Simulated1) CB4 isoprene mechanisms.

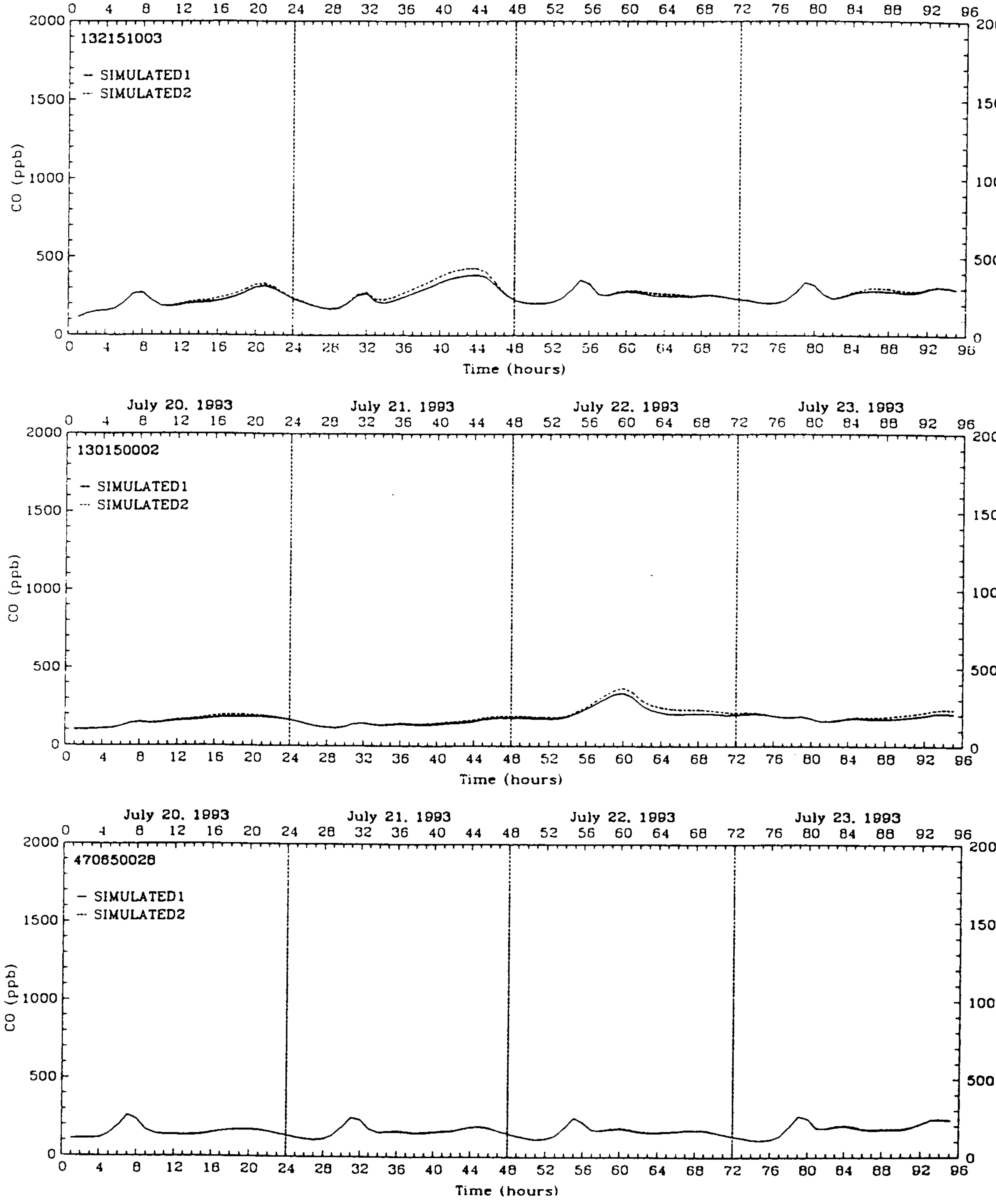


FIGURE 4b. UAM-V simulated and observed CO concentrations (ppb) for three sites (Columbus, GA - 132151003, Tilesboro, GA - 130150002, and Chattanooga, TN - 4760650028) in the Atlanta test bed comparing the results of the original (Simulated2) and the updated (Simulated1) CB4 isoprene mechanisms.

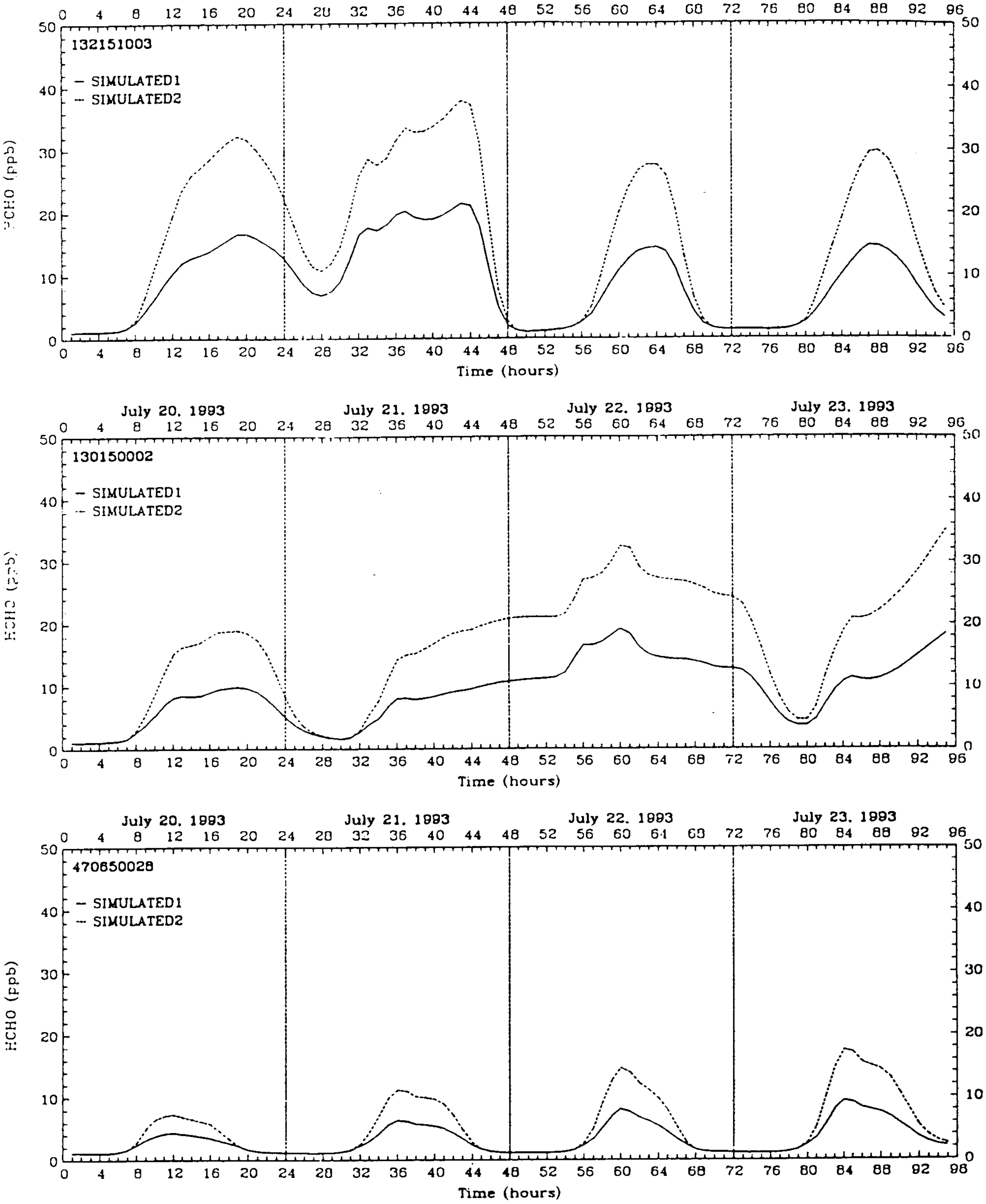


FIGURE 4c. UAM-V simulated and observed formaldehyde concentrations (ppb) for three sites (Columbu GA - 132151003, Tilesboro, GA - 130150002, and Chattanooga, TN - 4760650028) in the Atlanta test bed comparing the results of the original (Simulated2) and the updated (Simulated1) CB4 isoprene mechanisms.

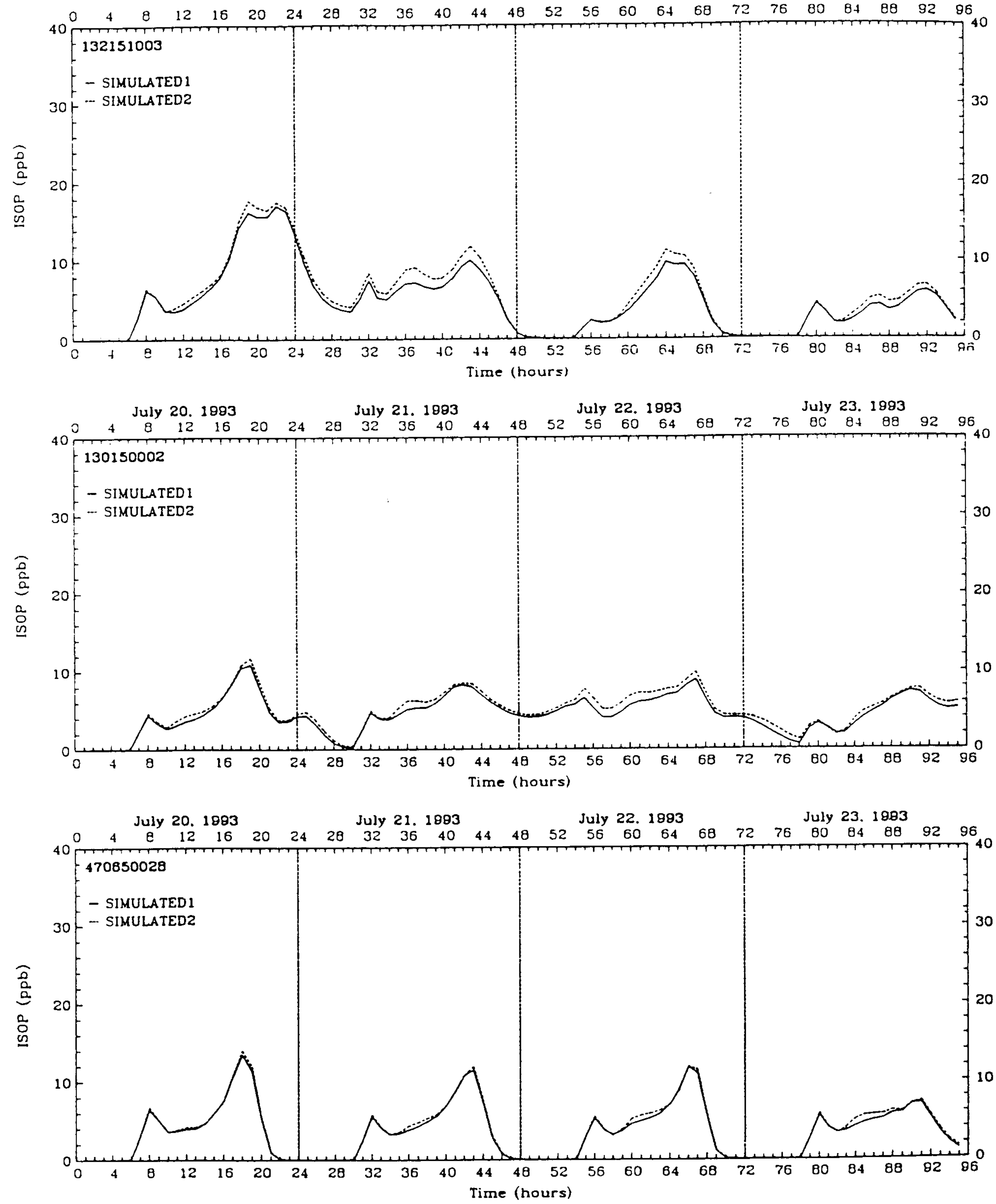


FIGURE 4d. UAM-V simulated and observed isoprene concentrations (ppb) for three sites (Columbus, GA - 132151003, Tilesboro, GA - 130150002, and Chattanooga, TN - 4760650028) in the Atlanta test bed comparing the results of the original (Simulated2) and the updated (Simulated1) CB4 isoprene mechanisms.

PLT. Mon Jun 10 11:44:43 1996

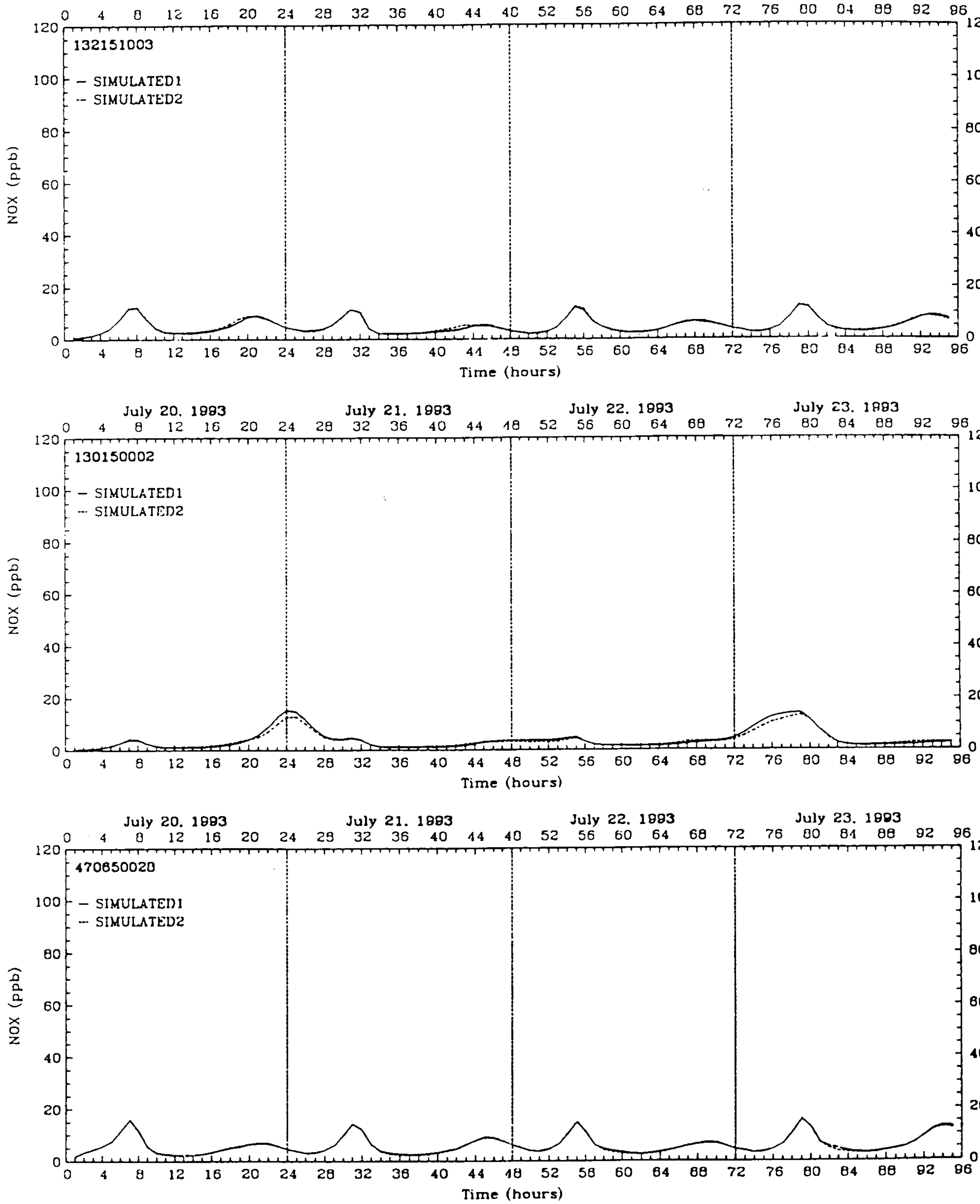


FIGURE 4e. UAM-V simulated and observed NOx concentrations (ppb) for three sites (Columbus, GA - 132151003, Tilesboro, GA - 130150002, and Chattanooga, TN - 4760650028) in the Atlanta test bed comparing the results of the original (Simulated2) and the updated (Simulated1) CB4 isoprene mechanisms.

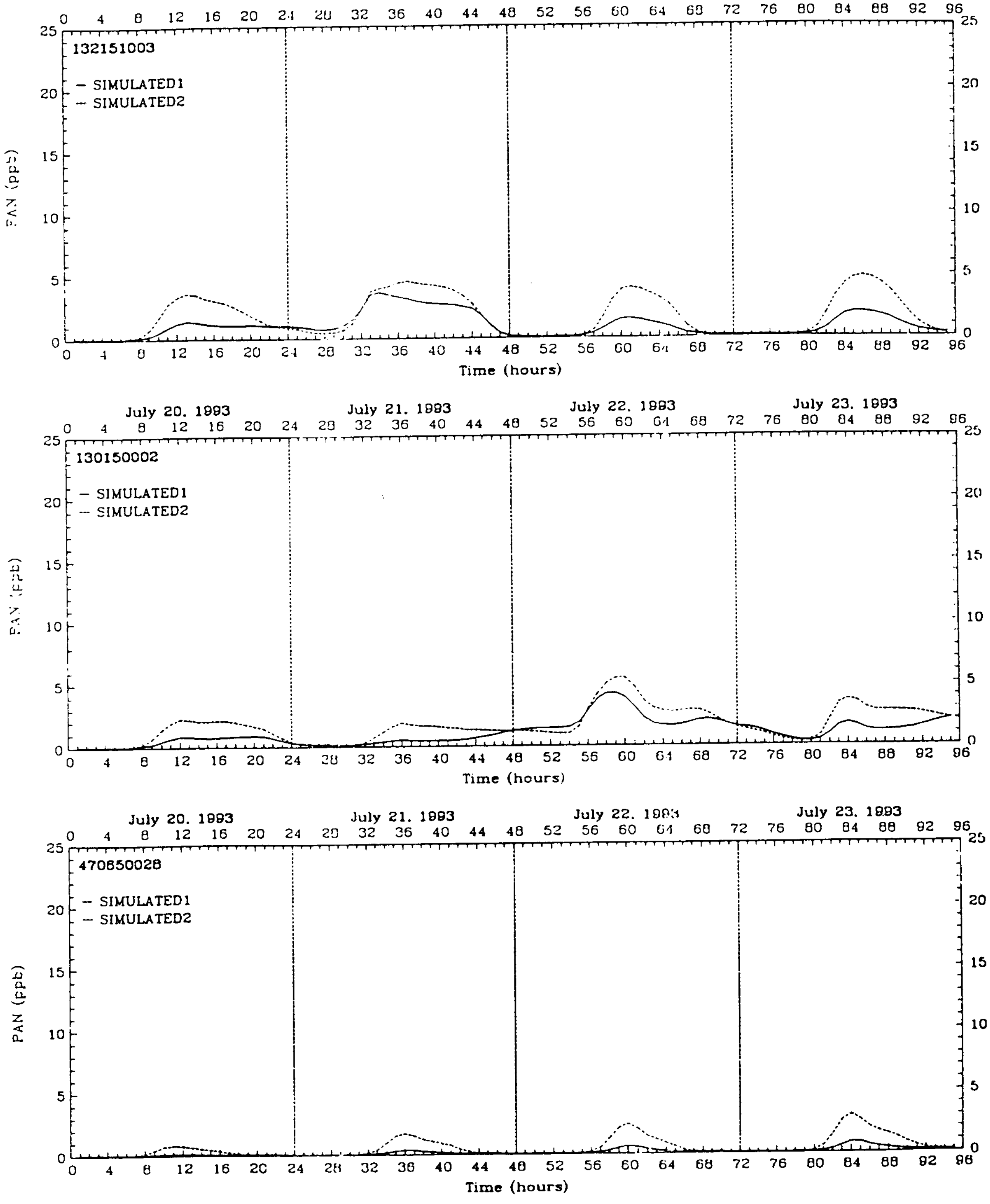


FIGURE 4f. UAM-V simulated and observed PAN concentrations (ppb) for three sites (Columbus, GA - 132151003, Tilesboro, GA - 130150002, and Chattanooga, TN - 4760650028) in the Atlanta test bed comparing the results of the original (Simulated2) and the updated (Simulated1) CB4 isoprene mechanisms.

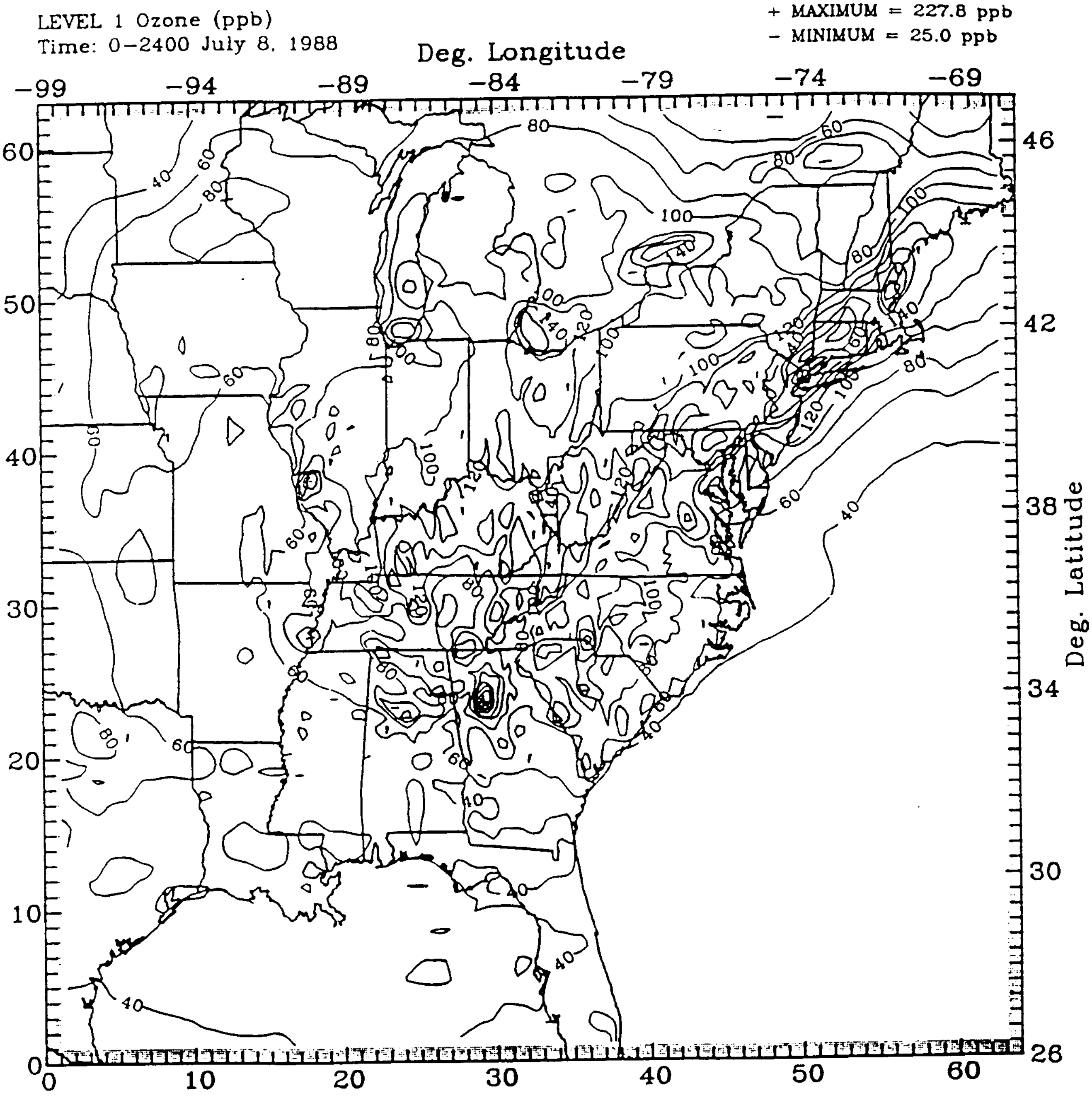


FIGURE 5. UAM-V simulated maximum daily ozone concentrations (ppb) for 8 July 1988 using the BaseB2 emissions and the original CB4 isoprene chemistry.

T: Thu Jun 27 16:10:32 1996

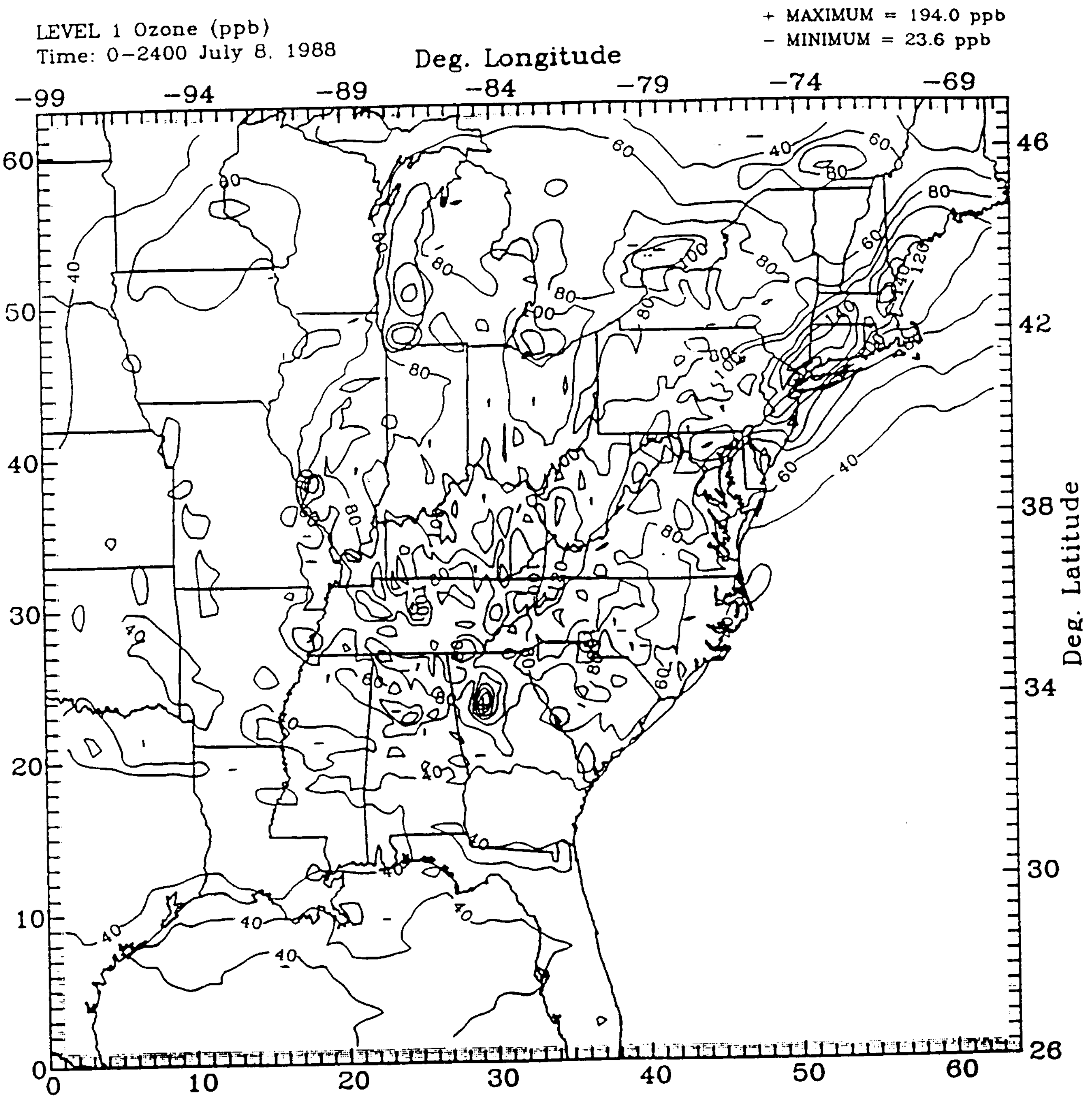


FIGURE 6. UAM-V simulated maximum daily ozone concentrations (ppb) for 8 July 1988 using the BaseB2 emissions and the updated CB4 isoprene chemistry.

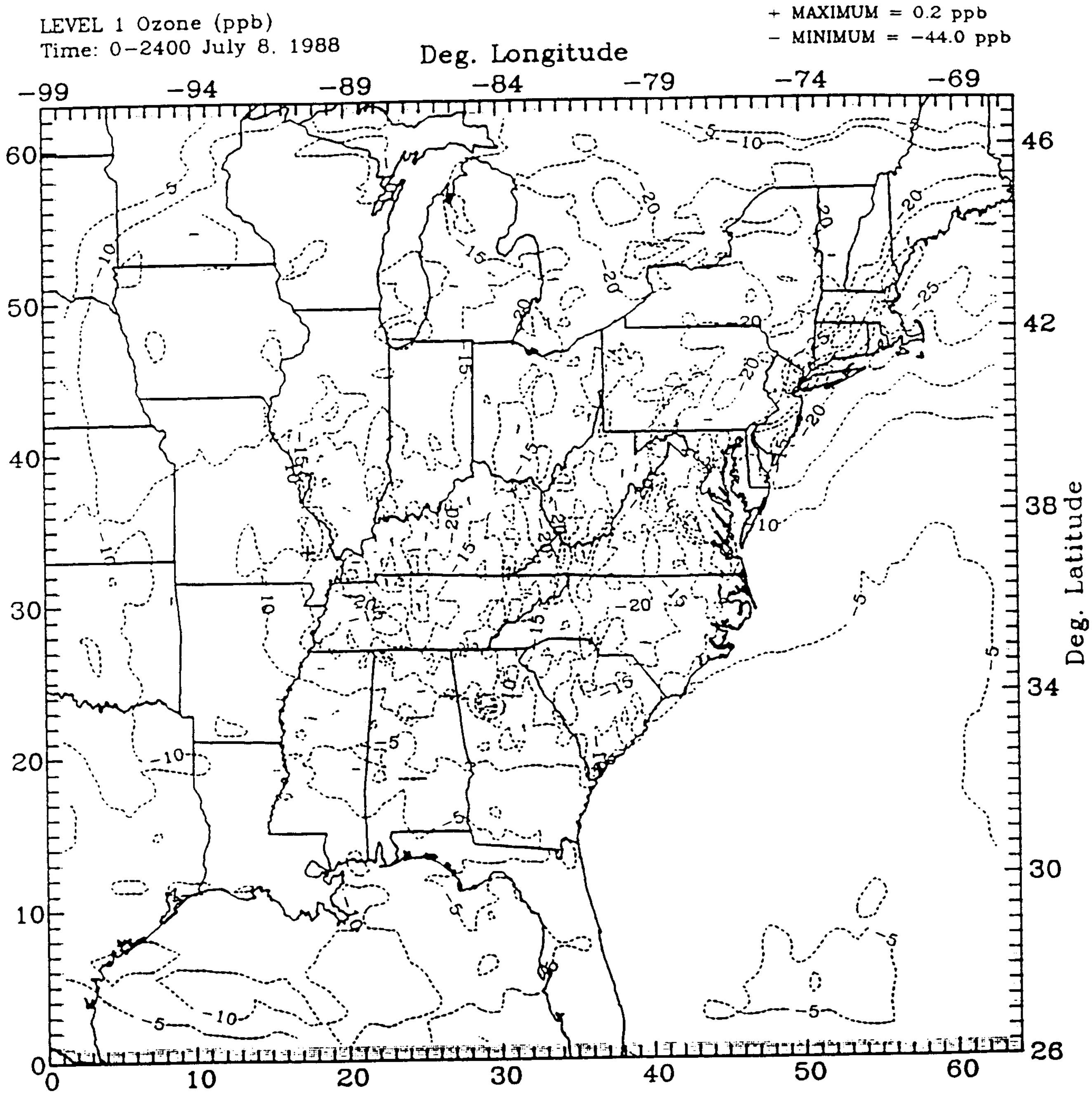
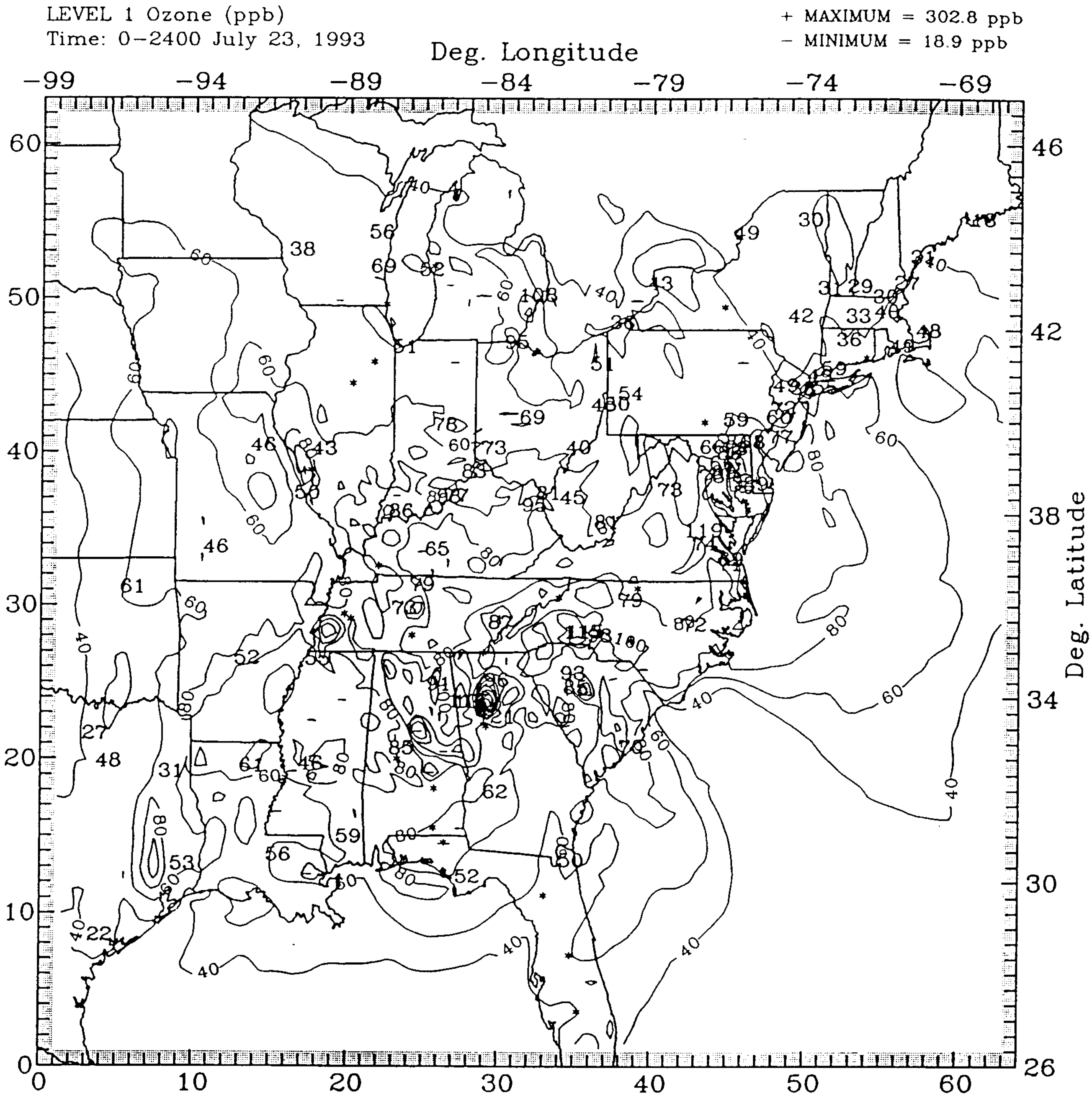


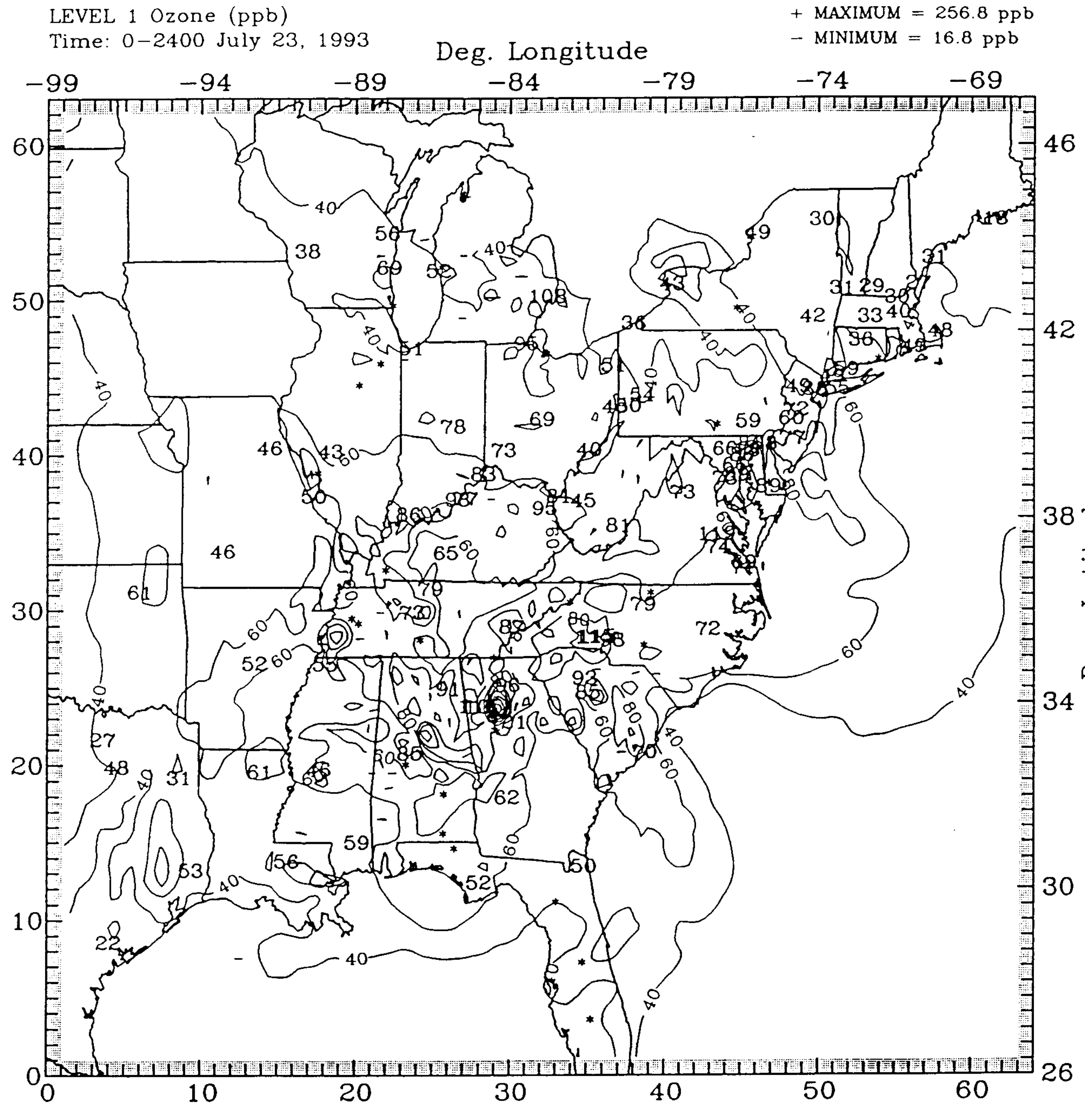
FIGURE 7. Differences in the maximum simulated ozone concentrations (ppb) for 8 July 1988: (Updated CB4 minus Original CB4)

LT: Tue Jun 18 13:52:29 1996



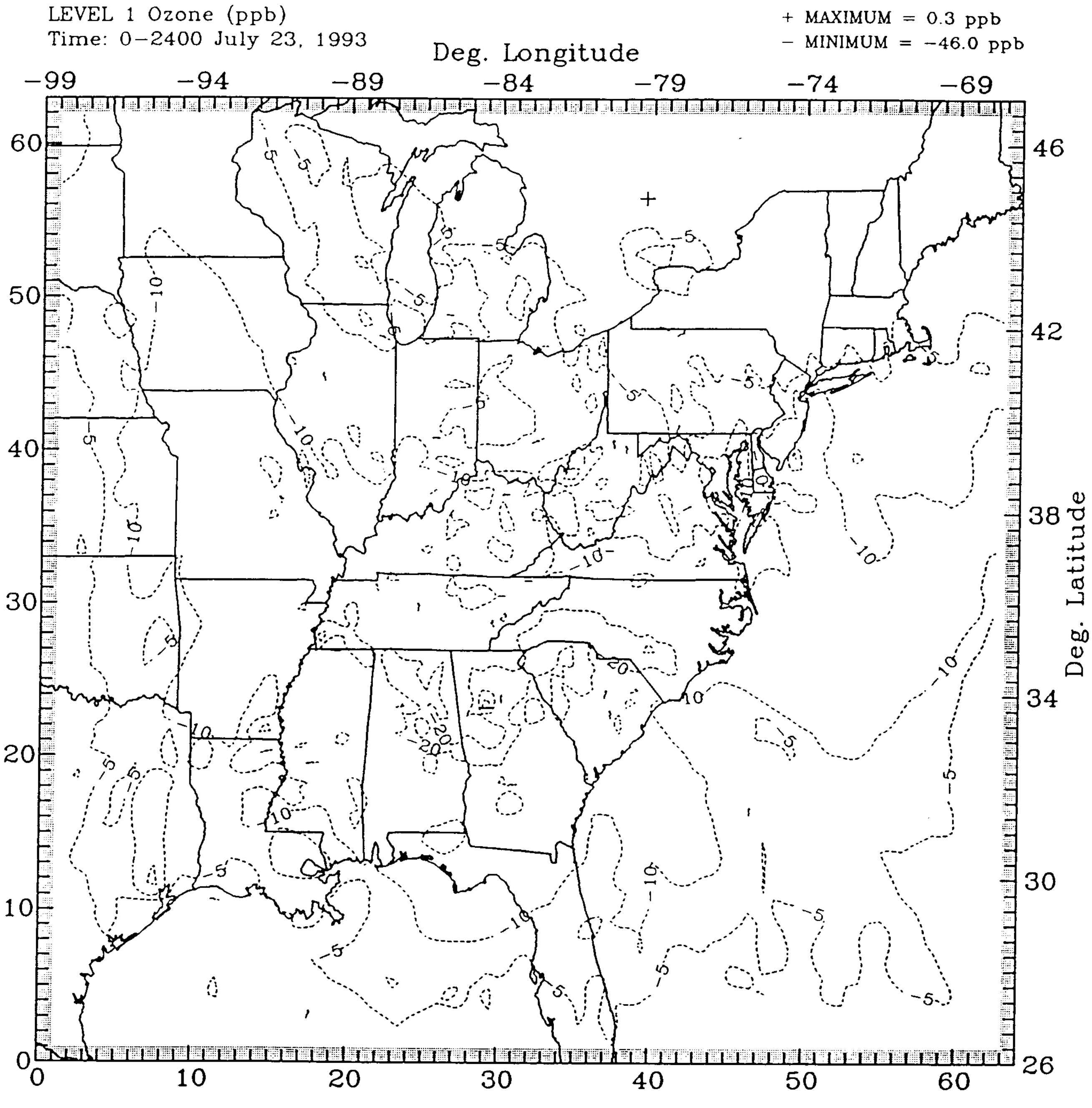
OTAG UAM-V Model Predictions of Maximum Daily Ozone:
-- 23jul93 -- 93-Base_Case --
1993_Base_OLD_Chemistry____SAIMM
(23jul93-93.tv.93basC2)

FIGURE 8 UAM V



OTAG UAM-V Model Predictions of Maximum Daily Ozone:
-- 23jul93 -- 93-Base_Case --
1993_Base_Updated_Chemistry____SAIMM
(23jul93-93.tv.93basC2uc)

FIGURE 9. UAM-V simulated maximum daily ozone concentrations (ppb) for 23 July 1993 using the BaseB2 emissions and the updated CB4 isoprene



UAM-V Difference Plot of Maximum Ozone
93basC2uc minus 93basC2
(93basC2uc−93basC2)

FIGURE 10. Differences in the maximum simulated ozone concentrations (ppb) for 23 July 1993: (Updated CB4 minus original CB4).

APPENDIX A

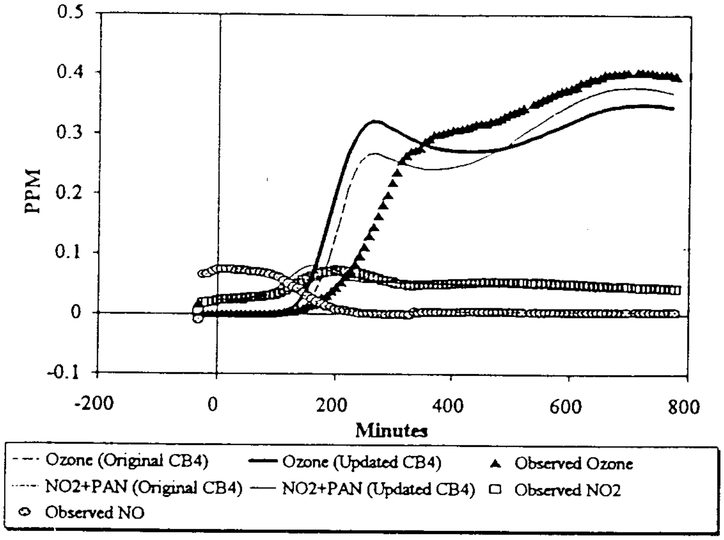
Results of Simulations of an Updated Isoprene Chemical Mechanism in CB4 Using Smog Chamber Data

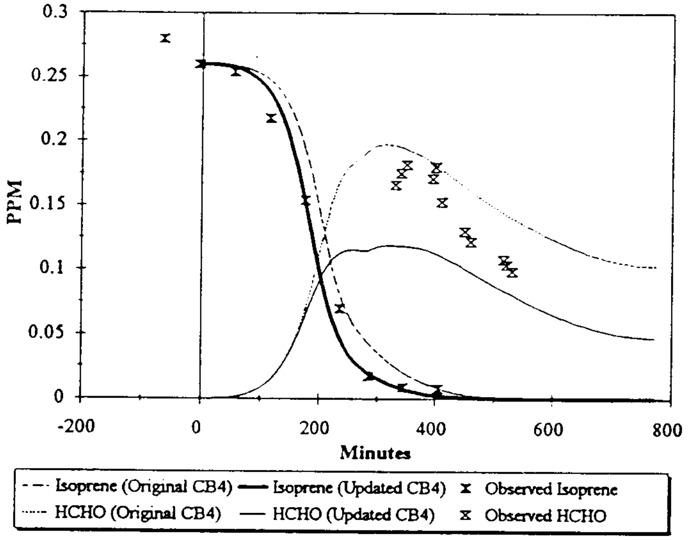
SUMMARY OF UNC SMOG CHAMBER EXPERIMENTS

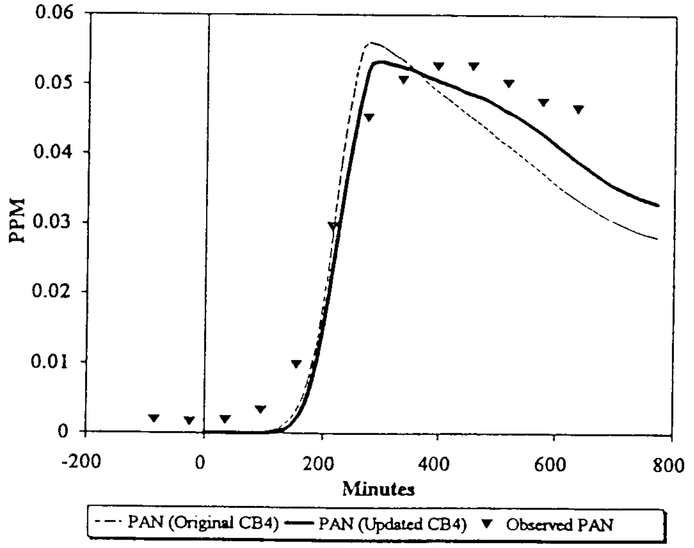
Experiment	Description
JN1780B	June 17, 1980, Blue chamber
JN1780R	June 17, 1980, Red chamber
JN2080R	June 20, 1980, Red chamber
JL1680B	July 16, 1980, Blue chamber
JL1680R	July 16, 1980, Red chamber
JL1780B	July 17, 1980, Blue chamber
JL1780R	July 17, 1980, Red chamber
SE0981R	September 9, 1981, Red chamber
JN2592B	June 25, 1992, Blue chamber
JN2592R	June 25, 1992, Red chamber
JN1793B	June 17, 1993, Blue chamber
JN1793R	June 17, 1993, Red chamber

UNC ISOPRENE - NOx EXPERIMENT

17 June 1980 - Blue Chamber

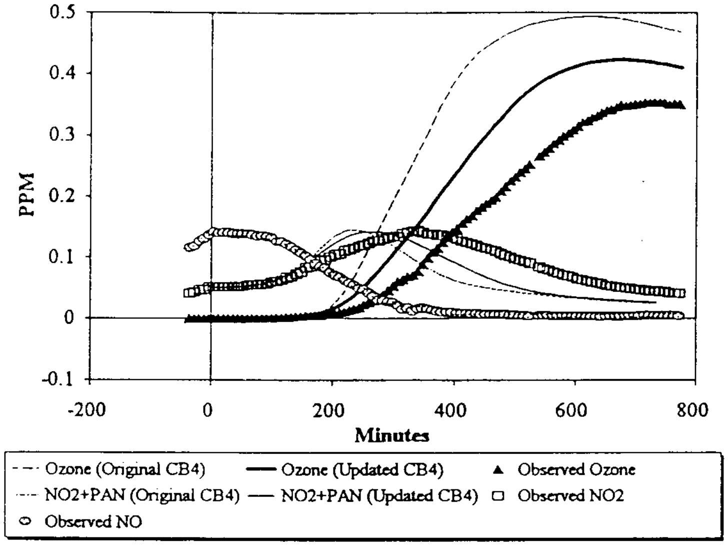


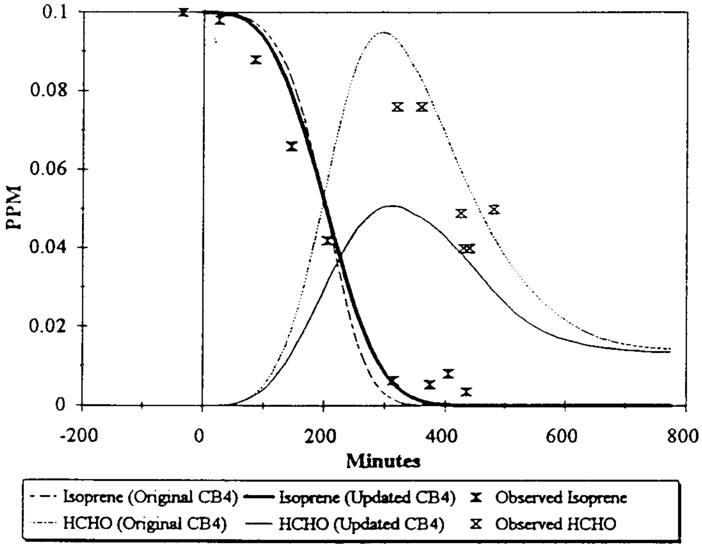


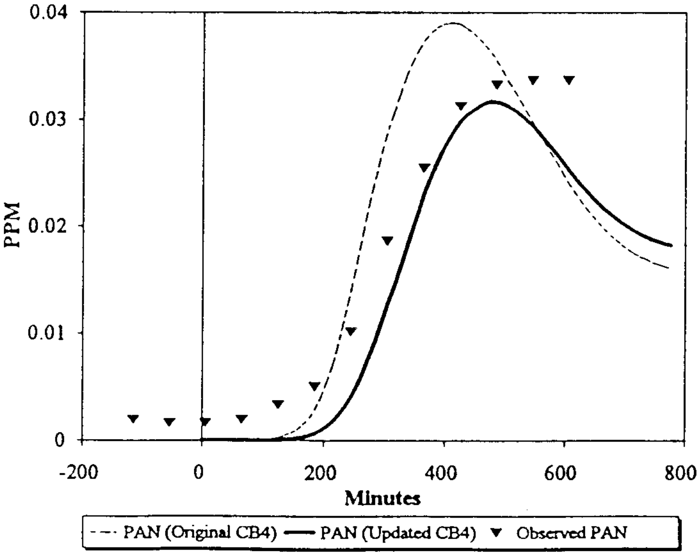


UNC ISOPRENE - NOx EXPERIMENT

17 June 1980 - Red Chamber

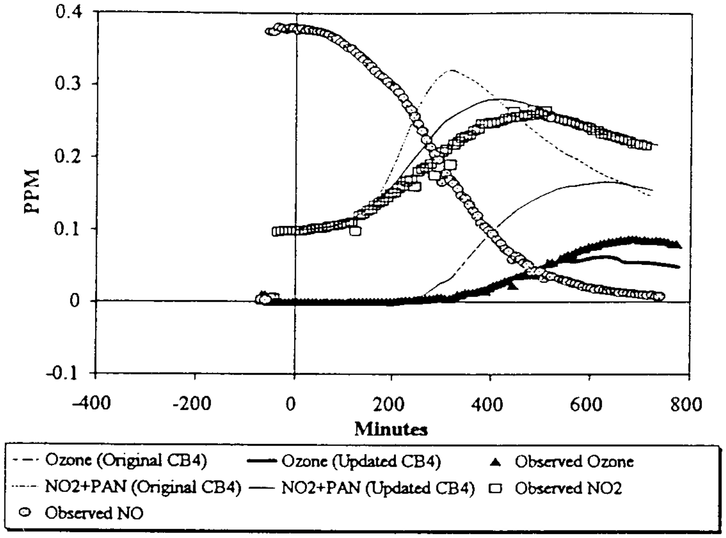


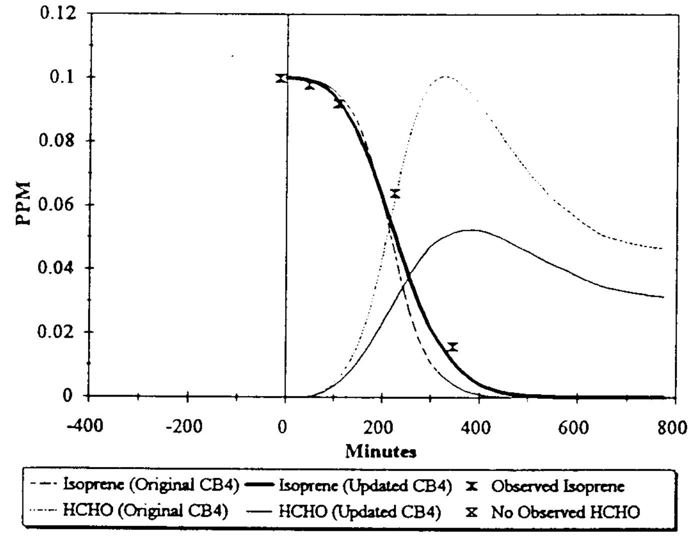


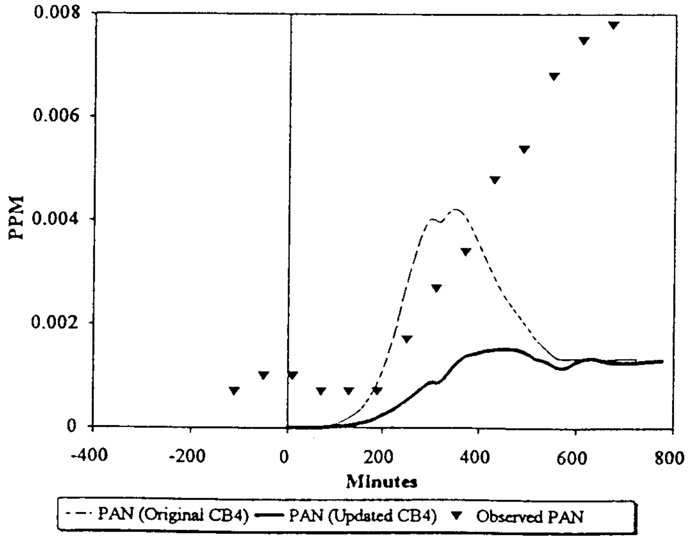


UNC ISOPRENE - NOx EXPERIMENT

20 June 1980 - Red Chamber

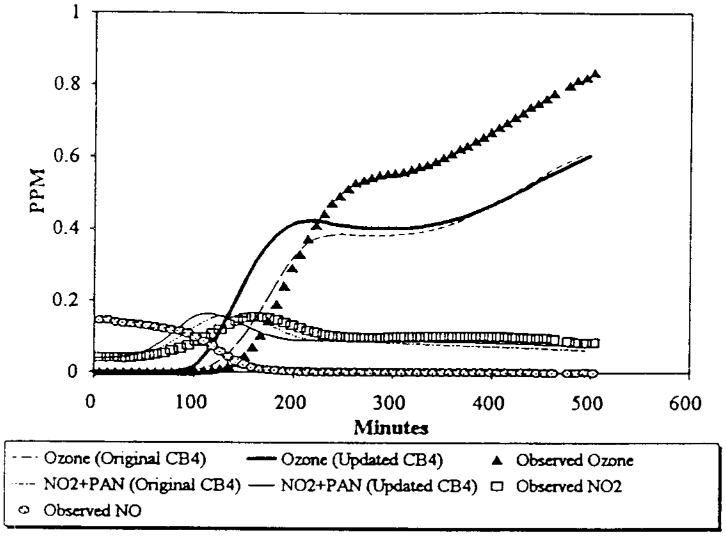


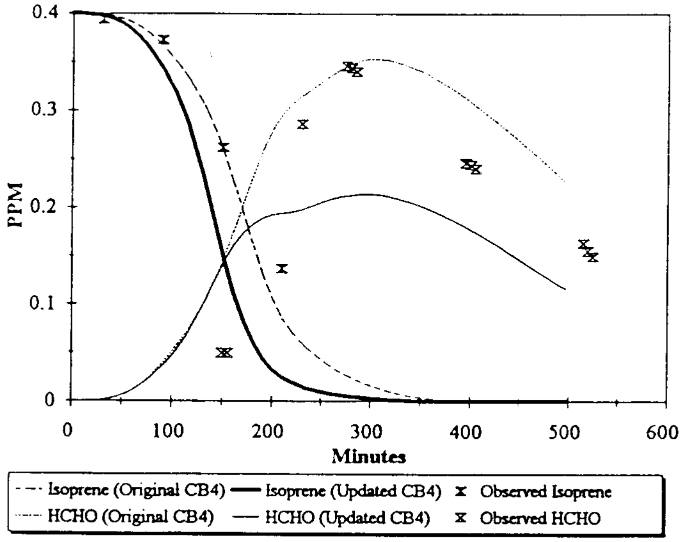


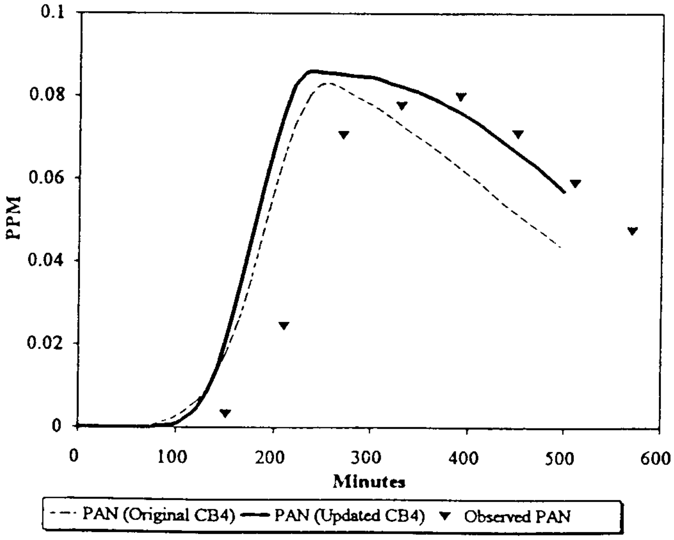


UNC ISOPRENE - NOx EXPERIMENT

16 July 1980 - Blue Chamber

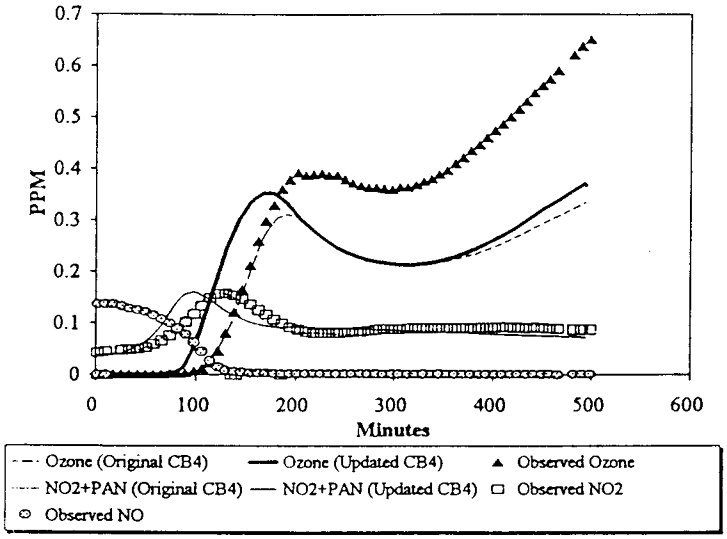


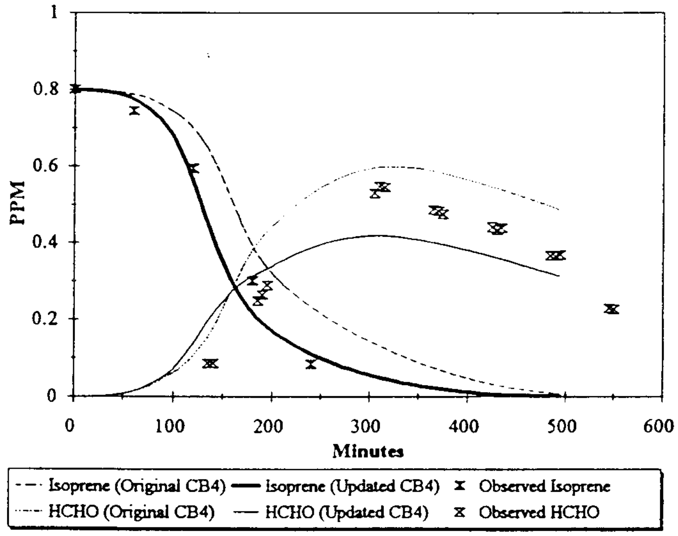


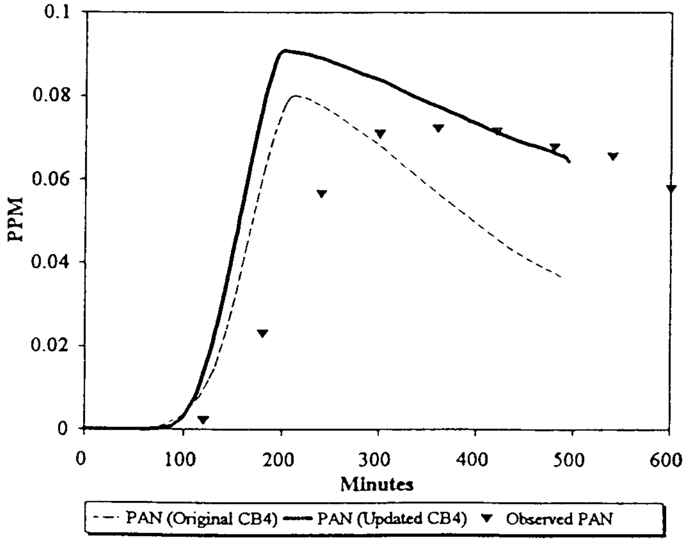


UNC ISOPRENE - NOx EXPERIMENT

16 July 1980 - Red Chamber

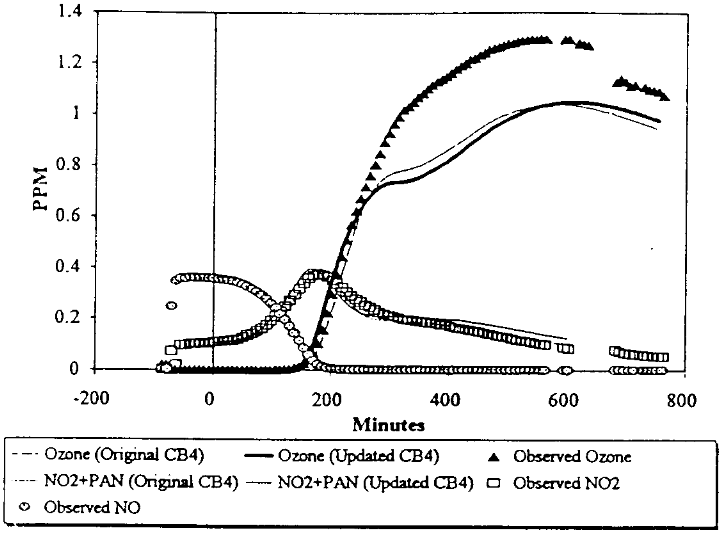


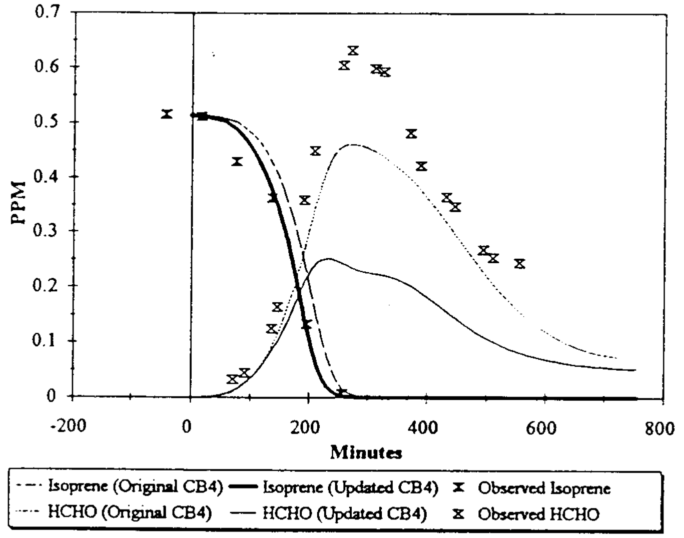


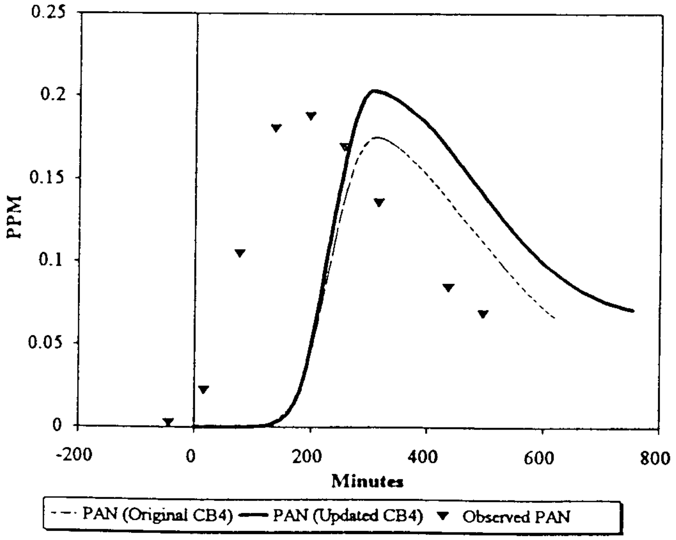


UNC ISOPRENE - NOx EXPERIMENT

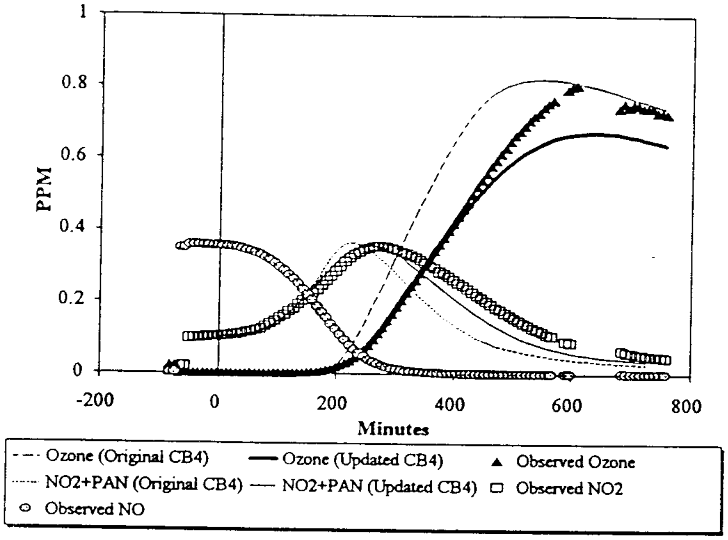
17 July 1980 - Blue Chamber

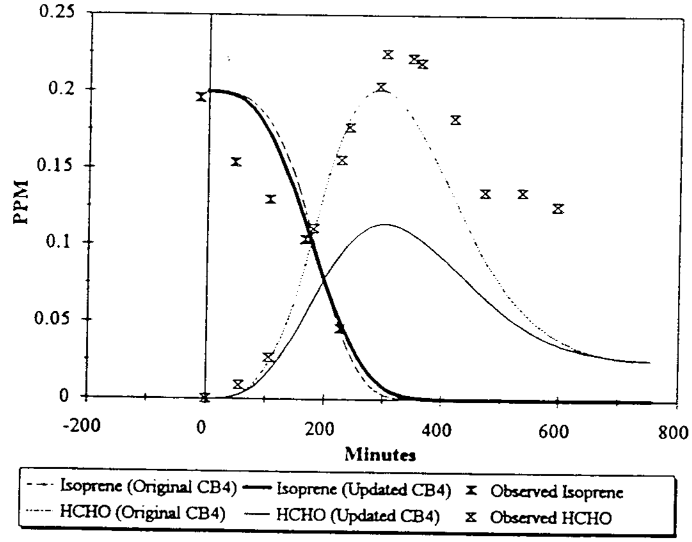


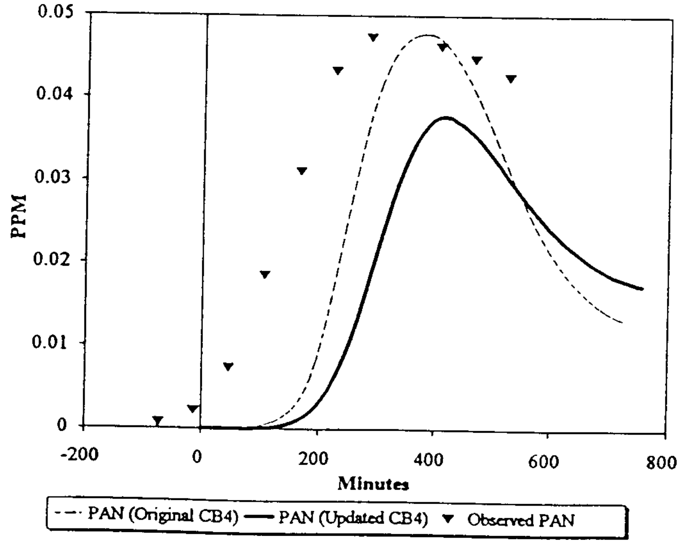




UNC ISOPRENE - NOx EXPERIMENT
17 July 1980 - Red Chamber

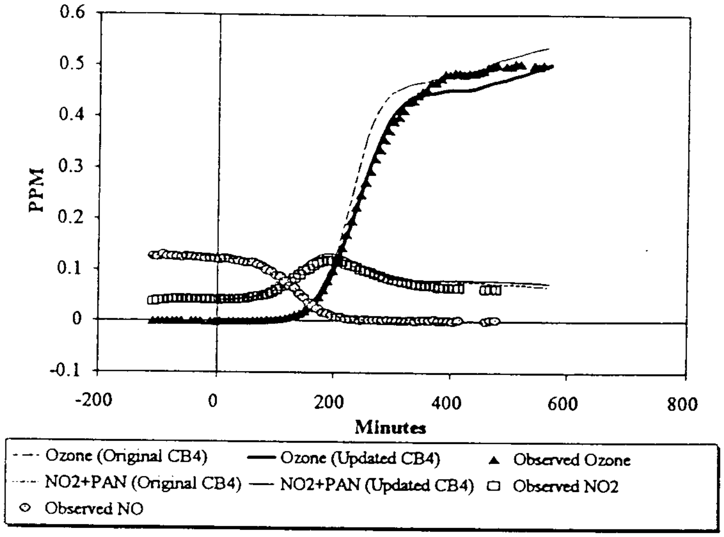


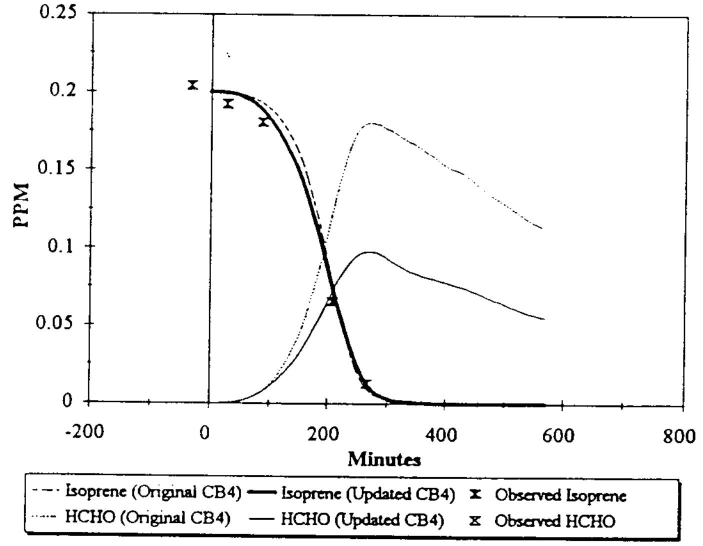


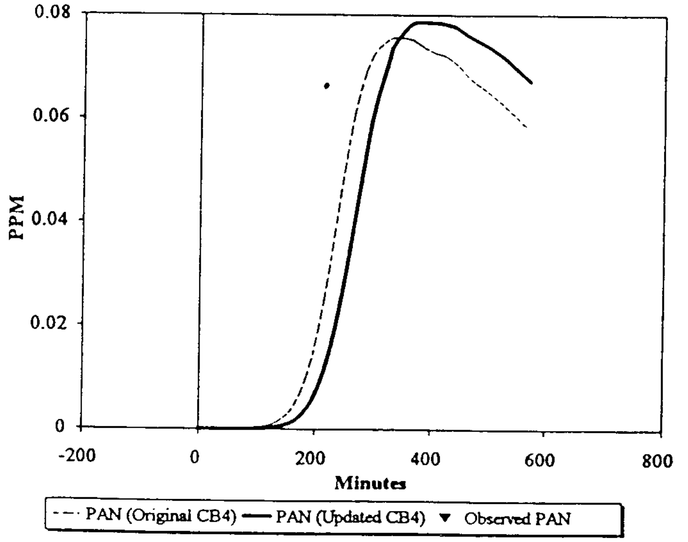


UNC ISOPRENE - NOx EXPERIMENT

9 September 1981 - Red Chamber

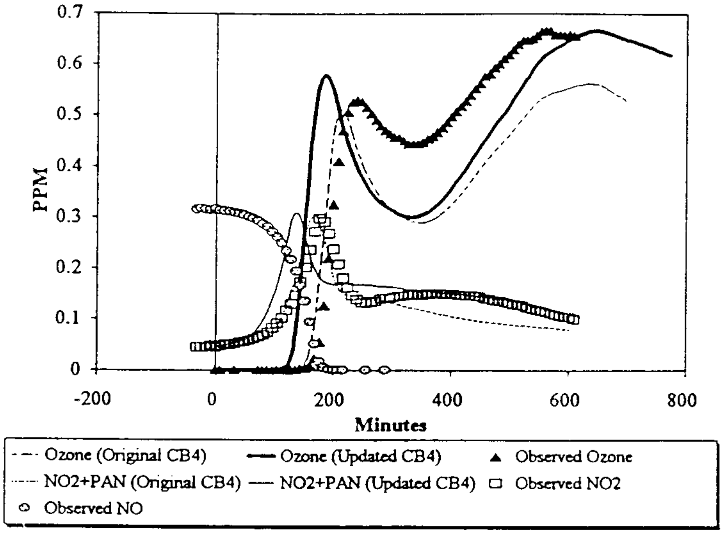


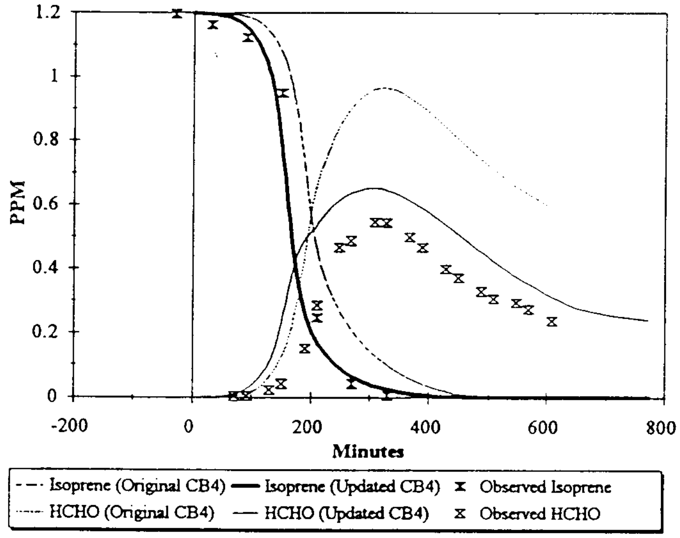


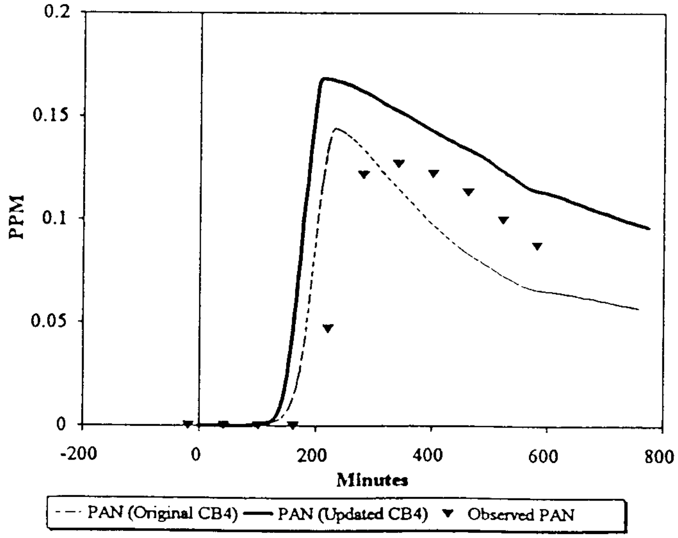


UNC ISOPRENE - NOx EXPERIMENT

25 June 1992 - Blue Chamber

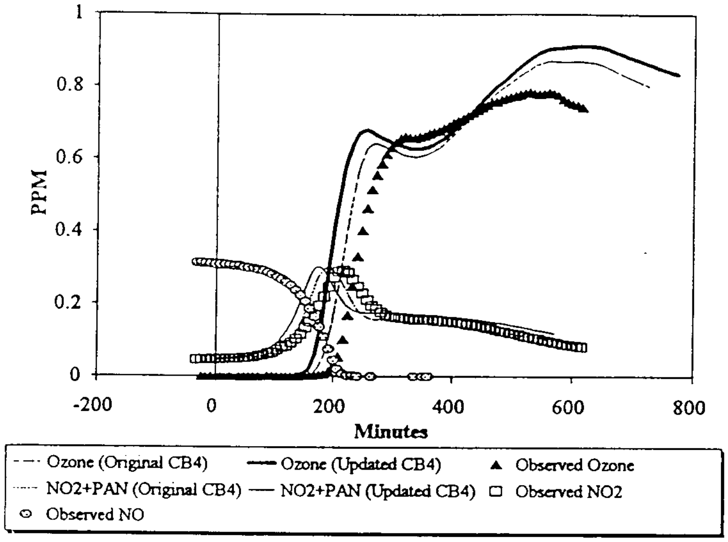


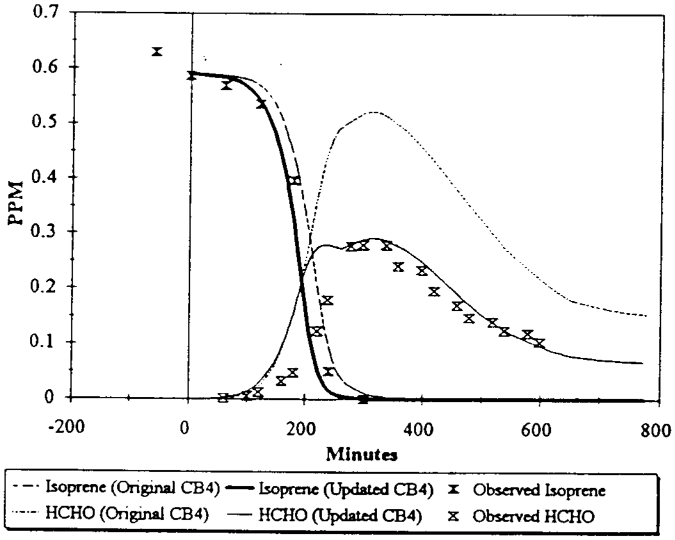


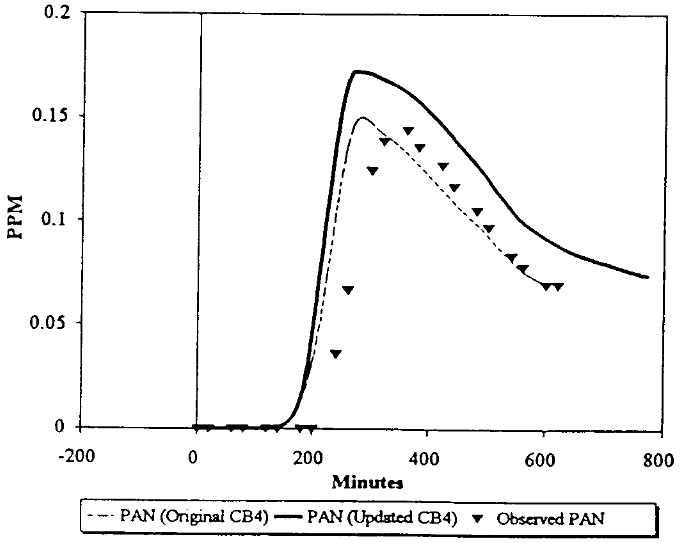


UNC ISOPRENE - NOx EXPERIMENT

25 June 1992 - Red Chamber

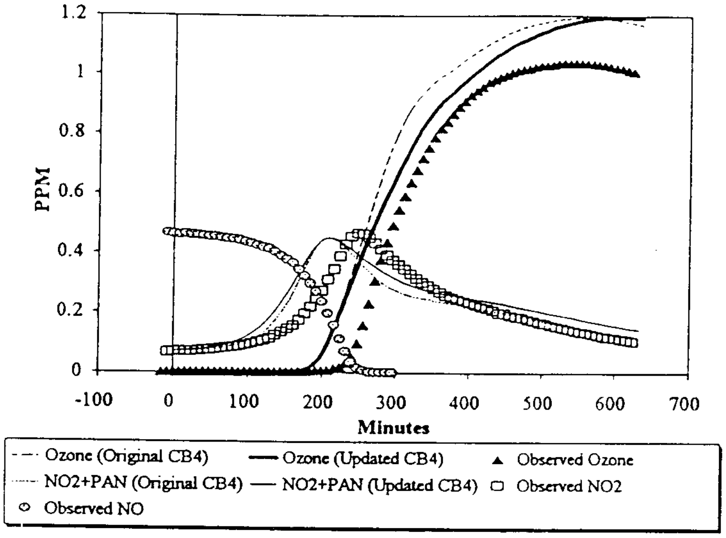


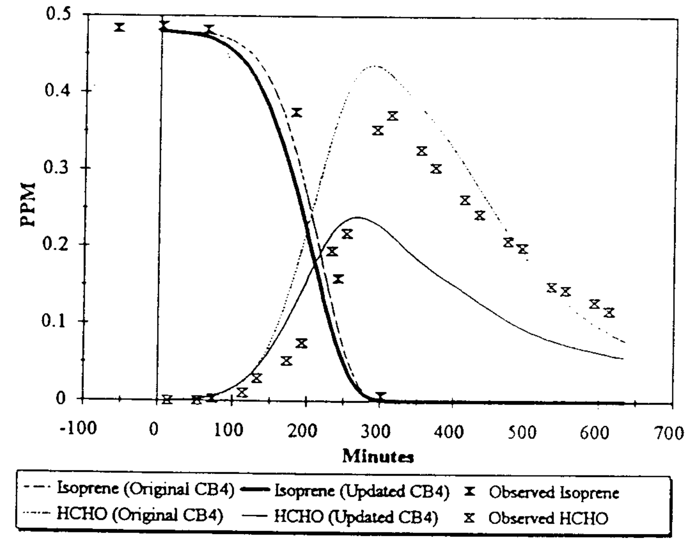


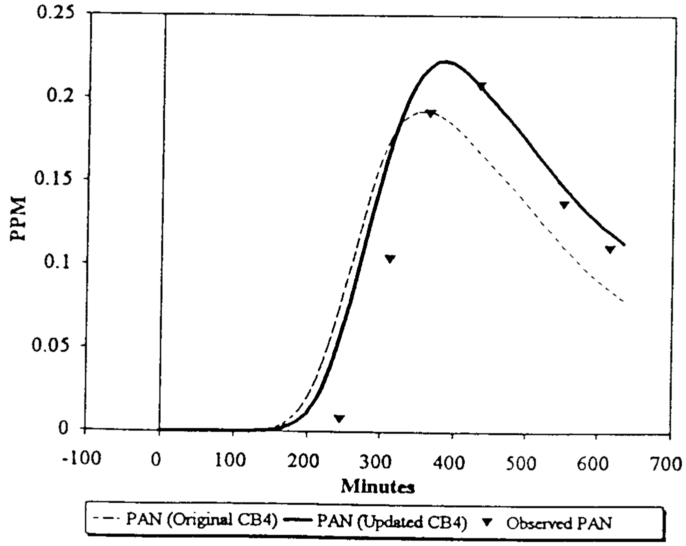


UNC ISOPRENE - NOx EXPERIMENT

17 June 1993 - Blue Chamber







UNC ISOPRENE - NOx EXPERIMENT

17 June 1993 - Red Chamber