Work Order No. 582-21-21802-020
Contract No. 582-19-90500
Tracking No. 2021-11
Task 6.2

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June 30, 2021

Develop CB7 Chemical Mechanism for CAMx Ozone Modeling

Final Report

PREPARED UNDER A CONTRACT FROM THE
TEXAS COMMISSION ON ENVIRONMENTAL QUALITY

The preparation of this document was financed through a contract from the State of Texas through the Texas Commission on Environmental Quality.
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LIST OF ACRONYMS AND ABBREVIATIONS

ANOx	Anthropogenic Nitrogen Oxides
AVOC	Anthropogenic Volatile Organic Compounds
BEIS	Biogenic Emission Inventory System
BELD	Biogenic Emissions Landcover Database
BNOx	Biogenic Nitrogen Oxides
BVOC	Biogenic Volatile Organic Compounds
CAMS	Continuous Ambient Monitoring Station
CAMx	Comprehensive Air Quality Model with Extensions
CB	Carbon Bond mechanism
CB4	Carbon Bond mechanism Version 4
CB05	Carbon Bond mechanism, 2005 version
CB6r2	Carbon Bond mechanism Version 6 Revision 2
CB6r5	Carbon Bond mechanism Version 6 Revision 5
CB7	Carbon Bond mechanism Version 7
CIM	Caltech Isoprene Mechanism
CONUS	Continental United States
GEOS-Chem	Goddard Earth Observing System Chemistry
HO_2	Hydroperoxy radical
IUPAC	International Union of Pure and Applied Chemistry
JPL	Jet Propulsion Laboratory
MCM	Master Chemical Mechanism
MDA8	Maximum Daily 8-hour Average
NASA	National Aeronautics and Space Administration
NO	Nitric oxide
NO_2	Nitrogen Dioxide
NOx	Nitrogen Oxides
O_3	Ozone
OH	Hydroxyl radical
PAN	Peroxyacetyl nitrate
RO2	Organic peroxy radical
SIP	State Implementation Plan
TCEQ	Texas Commission on Environmental Quality
VOC	Volatile Organic Compound
WRF	Weather Research and Forecasting

EXECUTIVE SUMMARY

The Texas Commission on Environmental Quality (TCEQ) uses the Comprehensive Air Quality Model with Extensions (CAMx) for state implementation plan (SIP) modeling. Chemical mechanisms need periodic review and update so that new scientific data and insights are incorporated as they become available. At the same time, continuity in chemical mechanism design and performance also has value in a policy context so that any consequences of mechanism changes for emission strategies are understood and can be attributed to justified updates.

We updated the Carbon Bond chemical mechanism that is used by the TCEQ from CB6r5 to CB7. Many parts of CB6r5 were recently reviewed and updated and for CB7 we prioritized updates to portions of the organic chemistry that are important and where newer information is available.

We tested CB7 in CAMx using an ozone (O_3) modeling database for June 2012 developed by the TCEQ. Changes in O_3 between CB7 and CB6r5 are relatively small and include areas of increase and decrease. Urban areas are not apparent in the O_3 differences over the Texas 4 km grid suggesting that O_3 differences are associated with mechanism updates for biogenic volatile organic compounds (VOC). O_3 decreases over land tend to be larger (1 - 2 ppb reduction) over forested areas of eastern Texas and the South-eastern US. Larger O_3 decreases (1.5 - 2.5 ppb reduction) occur over the Gulf of Mexico due to an iodine chemistry update, i.e., somewhat increased O_3 destruction by iodine, as well as reduced O_3 transport from land to over the Gulf. O_3 increases (up to 0.5 ppb) are confined to land areas of the Great Plains from West Texas to South Dakota as well as Eastern Mexico. These areas have terpene and sesquiterpene emissions from croplands and relatively low isoprene emission. We performed a statistical evaluation of CAMx model performance for maximum daily 8-hour average (MDA8) O_3 using TCEQ monitoring data and found that CB7 agrees slightly better with observation than CB6r5. We consider this improvement to be small and therefore conclude that CB7 and CB6r5 show equivalent performance for O_3 in Texas.

MDA8 O_3 concentrations on high O_3 days are somewhat less responsive to nitrogen oxide (NOx) emission reduction with CB7 than CB6r5. Therefore, CB7 could be expected to produce somewhat higher future O_3 design values for emission reduction scenarios that rely on reducing NOx emissions. CB7 and CB6r5 show similar responses of MDA8 O_3 to reducing anthropogenic VOC emissions with modest O_3 reductions in and downwind of major cities and minimal O_3 reductions elsewhere. Both CB6r5 and CB7 show that VOC reduction can help mitigate O_3 disbenefits associated with NOx emission reduction in some urban areas.

We recommend further evaluation of the CB7 terpene mechanism with consideration of the extent to which NOx is sequestered at night and then returned during the day where it can sustain O_3 production in NOx-limited environments.

INTRODUCTION

The Texas Commission on Environmental Quality (TCEQ) uses the Comprehensive Air Quality Model with Extensions (CAMx) for state implementation plan (SIP) modeling. The CAMx chemical mechanism is critical in determining how modeled ozone responds to emission changes. Chemical mechanisms need periodic review and update so that new scientific data and insights are incorporated as they become available. At the same time, continuity in chemical mechanism design and performance also has value in a policy context so that any consequences of mechanism changes for emission strategies are understood and can be attributed to justified updates. The TCEQ has used the Carbon Bond (CB) series of chemical mechanisms for ozone (O_3) modelling and SIP development. Here, we develop a major update to the CB mechanism and test the impact on O_3 response to emission changes in CAMx. The new mechanism is Carbon Bond version 7 (CB7).

The starting point for CB7 was CB6r5 which we developed in 2020 following a literature review focused on the chemistry of inorganic and simpler organic species (Yarwood and Beardsley, 2020). The CB6r5 update revised 47 reactions and added one reaction (Yarwood and Beardsley, 2020). For CB7, the following mechanism updates were prioritized and implemented:

- Isoprene chemistry is completely updated because it dominates the oxidizing potential of the atmosphere in many parts of Texas and elsewhere and new information has become available since the CB6r5 isoprene scheme was implemented nearly 10 years ago (in CB6 revision 2).
- Terpene chemistry is completely updated because the scheme in CB6r5 is essentially from CB05 (more than 15 years old) and more detailed reaction mechanisms of terpenes were recently published.
- The chemistry of alkanes larger than propane (represented by PAR) and associated ketones (KET) is updated because these compounds represent a large fraction of anthropogenic volatile organic compound (VOC) emissions and the current PAR chemistry is essentially from CB05.
- Rate constants for organic peroxy radical (collectively RO2) reactions are updated to reflect current information and improve mechanism efficiency.

Several other updates were made in developing CB7 and, in all, 74 reactions in CB7 are updated or new as compared to CB6r5, and 23 reactions in CB6r5 were eliminated from CB7. The isoprene update affects 20 reactions, the terpene update affects 19 reactions, the larger alkane (PAR) update affects 7 reactions and the RO2 update affects 16 reactions in CB7. The CB7 mechanism has 229 reactions among 92 species as compared to CB6r5 which has 234 reactions among 86 species.

CB7 DESIGN AND UPDATES

1.1 Data Sources for CB7

The types of chemical reaction data that are needed to develop gas-phase chemical mechanisms, such as CB7, include:

- Rate constants for thermal reactions, i.e., reactions that occur when atoms and/or molecules collide with each other in the atmosphere
- Absorption cross-sections and quantum yields for photolysis reactions, i.e., reactions that occur when molecules absorb sunlight and chemical bonds are broken
- Stoichiometric coefficients that define the amount (yield) of products that are formed for thermal and photolysis reactions

Two panels of atmospheric scientists review chemical reaction data that are needed for atmospheric modeling:

- The International Union of Pure and Applied Chemistry (IUPAC) Task Group on Atmospheric Chemical Kinetic Data Evaluation. New reviews are produced continuously and are disseminated via http://iupac.pole-ether.fr/?cmd=redirect&arubalp=12345#. The recommended citation for this data (Atkinson et al., 2004) does not reflect the current panel membership or the currency of the data (i.e., more recent than 2004).
- The National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory (JPL) Panel for Data Evaluation. New reviews are produced periodically (most recently in 2015) and disseminated via http://jpldataeval.jpl.nasa.gov. The current evaluation is number 19 in the series and the citation is Burkholder et al., 2019.

These panels serve the important functions of:

- Identifying new information as it is published in the scientific literature
- Comparing new information to existing information
- Critically evaluating the body of scientific knowledge for each chemical reaction
- Providing recommendations for many, but not all, chemical reactions.

The products of both panels are quality assured and ready for use in chemical mechanisms such as CB7. The panels are independent and their recommendations for a specific chemical reaction may differ, but not by an amount that is greater than the uncertainty for that reaction. CB mechanism versions since CB6 have generally relied more on recommendations from the IUPAC panel than the JPL panel, and this remains the case for CB7. However, we consulted recommendations from both panels and relied on the JPL panel when there were specific reasons to do so, e.g., no recommendation from the IUPAC panel for a reaction included in CB7.

Some of the CB7 updates made use of additional data sources as discussed below.

1.2 Order of Reactions in CB7

The CB7 reactions are ordered as follows:

1. Inorganic radical chemistry. The inorganic reactions have almost the same ordering as CB6, namely:
    a. NOx-O_3 photo-stationary state
    b. NO_3 production
    c. O_3 photolysis
    d. Hydrogen-oxygen species
    e. Nitrogen-oxygen species.
2. Reactions of small inorganic molecules, namely H_2, CO, SO_2, dimethyl sulfide (DMS)
3. Peroxyacetyl nitrate (PAN) and analogues (PANX, OPAN)
4. RO2 radicals that are produced throughout CB7 with associated organic peroxides and organic nitrates. RO2 radicals that are associated with a specific organic compound (e.g., ISO2 from isoprene) are grouped with that compound.
5. Oxygenated compounds (alcohols, aldehydes, ketones, acids) except that oxygenates associated with a specific organic compound (e.g., HPLD from isoprene) are grouped with that compound.
6. Anthropogenic VOCs
    a. Alkanes
    b. Alkenes
    c. Acetylene
    d. Aromatics.
7. Biogenic VOCs
    a. Isoprene
    b. Terpenes
    c. Sesquiterpenes.
8. Iodine scheme for O_3 depletion

1.3 Isoprene Mechanism Update

The Caltech Isoprene Mechanism (CIM; Wennberg et al., 2018) is one of several current isoprene mechanisms that aim to represent known isoprene chemistry in explicit detail. The explicit CIM has 810 reactions of 385 species (Bates and Jacob, 2019). Bates and Jacob derived a reduced CIM mechanism with 345 reactions of 108 species although this reduced mechanism remains larger than the entire CB7 mechanism.

We recently updated the CB6r2 isoprene scheme (which is unchanged in CB6r5) to emulate the CIM for simulating important species such as isoprene, OH, HO_2, NO_2, formaldehyde, isoprene epoxydiols (IEPOX) and isoprene-derived hydroperoxy aldehydes (HPALD). HPALD is an important precursor to OH that is formed under low NOx conditions and IEPOX is an important precursor to secondary organic aerosol. Using box model simulations for lower and higher NOx conditions, we updated the CB6 isoprene scheme to improve agreement with the CIM. Rate constant updates were based on rate constants in the CIM considering that CB6 lumped model species (ISPX, ISPD, HPLD, INTR) each correspond to several CIM species and so their rate constants were set to weighted averages of CIM rate constants. Similarly, the updated reaction products were initially set to weighted averages of CIM reaction products and then iteratively refined to improve agreement with the CIM for important species (isoprene, OH, HO_2, NO_2, formaldehyde, IEPOX and HPALD) in the box model simulations. Conducting box model simulations for higher and lower NOx conditions strongly differentiates between reaction pathways that are dominant under these different conditions and facilitated optimizing the compact isoprene mechanism.

This updated isoprene mechanism developed for CB6 (derived from the CIM) is included in CB7 as reactions 178 to 195. The CB7 implementation was made even smaller (reduced from 21 to 18 reactions) because we deleted two reactions of RO2 radicals with C2O3 (see the RO2 radical update, below) and deleted the reaction of ISPD with O_3 which is expected to be dominated by ISPD reactions with OH and NO_3.

1.4 Terpene Mechanism Update

The CB6 terpene mechanism was old having been developed for CB05 by adapting the SAPRC99 terpene mechanism. Schwantes et al. (2020) recently published detailed reaction mechanisms of four terpenes (α-pinene, β-pinene, limonene and myrcene) and one sesquiterpene (β-caryophyllene) and tested them in model simulations for the US finding reasonable model performance. We translated these mechanisms for CB7 (reactions 195 to 212) as follows:

- Include α-pinene explicitly (APIN) because it tends to dominate terpene emissions and combine β-pinene, limonene and myrcene to represent other terpenes (TERP).
- Include β-caryophyllene to represent sesquiterpenes (SQT).
- For reactions with OH, include the RO_2 radicals formed (APO2, TPO2 and SQO2) and their reactions with NO, HO_2 and RO_2 to account for important interactions between terpene and NOx emissions.
- For reactions with NO_3, omit the RO_2 radicals formed to manage mechanism size. We assume these RO_2 radicals always react with HO_2 because NO tends to be scarce when NO_3 is abundant.
- Directly include reaction products that are part of the CB7 mechanism (including OH, HO_2, CO, H_2O_2, MEO2, C2O3, formaldehyde, acetone).
- Add hydroxyacetone (HACT) so that it can be produced by the terpene mechanism and noting that only one reaction is required (CB7 reaction 123). In the future, the isoprene also could be updated to produce HACT.
- Represent the organic nitrate products using CB7 species NTR2 that represents larger multi-functional organic nitrates.
- Represent the larger oxygenated organic products using CB7 species ISPD for oxygenated products from isoprene. This assumption could be improved in the future because the terpene products have greater tendency to form organic nitrates (typically 30% organic nitrate yield in Schwantes et al., 2020) than does ISPD (zero organic nitrate yield).

The new terpene and sesquiterpene mechanisms are CB7 reactions 196 to 213. This scheme has advantages over CB6 but note that it required testing (performed in this project) by examining model performance in regions with higher terpene emission, e.g., East Texas.

1.5 Larger Alkanes (PAR) Mechanism Updates

Alkanes larger than propane are represented by model species PAR in CB6r5 using a highly compact scheme that originated with CB4 (Gery et al., 1989). This scheme is efficient and has desirable design attributes such explicitly representing that alkoxy radicals (ROR) can react with oxygen (tending to form ketones) or decompose via unimolecular reactions that have strong temperature dependence. Updates for CB05 (Yarwood et al, 2005) differentiated aldehyde products from PAR between acetaldehyde (ALD2) and larger aldehydes (ALDX). CB6 added a model species to represent ketones (KET) and explicitly represented acetone (ACET). CB6r3 added temperature and pressure dependence of organic nitrate yields from alkanes.

The objectives for the CB7 PAR update were to update the temperature dependencies of ROR reactions and to update the yields of aldehydes and ketones. We updated rate constants for ROR reactions as well OH reactions for PAR and KET using rate constants from MCM version 3.3.1 (Jenkin et al., 2015) together with the alkane composition profile assumed for PAR in CB4. The rate constants for reactions of ROR in CB7 (reactions 136 and 137) are fitted to the weighted average of corresponding reactions in MCM over the temperature range 260 K to 310 K as shown in Figure 1. The branching ratio shown in this figure is the fraction of ROR proceeding via each reaction pathway (i.e., reaction with O_2 or unimolecular decomposition) which is dependent on temperature. We updated the yields of aldehydes, ketones and other reaction products of PAR to be consistent with SAPRC07 (Carter, 2010). The SAPRC07 mechanism for regional modelling uses 3 model species to represent alkanes larger than propane (namely ALK3, ALK4 and ALK5), and we used the simple average of these species as the basis for the CB7 PAR update (reactions 133 to 137).

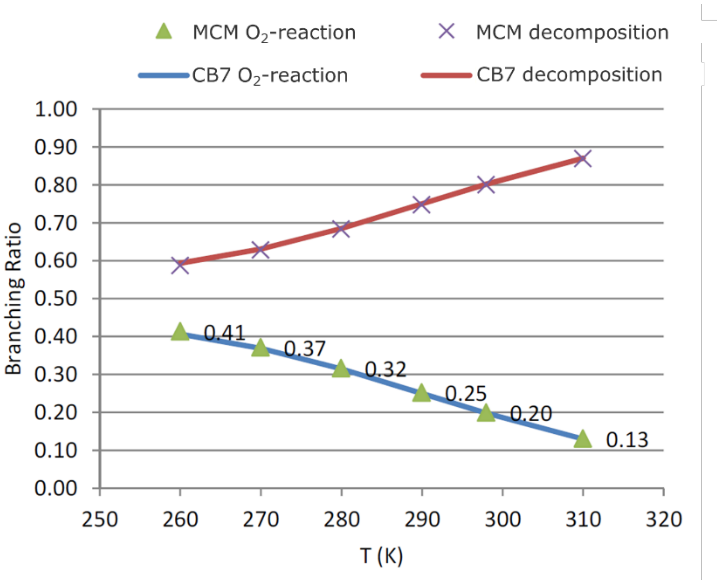

Figure 1. Branching ratios for alkoxy radical (ROR) reaction by unimolecular decomposition or O_2-reaction based on the Master Chemical Mechanism (MCM; symbols) and in CB7 (lines).

In CB6 KET is removed only by photolysis which tends to allow too much KET to accumulate from PAR degradation. In CB7 we added removal of KET by reaction with OH (reaction 122). Since ketone groups have no C-H bond they don’t react directly with OH but they do tend to enhance OH reaction with C-H bonds near the ketone group. The rate constant for OH reaction with KET in CB7 is an estimate of this enhancement determined from the difference in OH rate constants between matched alkane-ketone pairs in MCM version 3.3.1. The products of OH reaction with KET in CB7 are determined from the reactions of the ketone products formed from ALK3, ALK4 and ALK5 in SAPRC07. The products of KET photolysis in CB7 (reaction 121) were updated in the same way.

1.6 RO2 Radical Reaction Updates

We updated rate constants for reactions that remove organic peroxy (RO2) radicals to use newer rate values and be more consistent across RO2 species. We also eliminated all reactions of RO2 radicals with peroxyacetyl radical (C2O3).

All reactions of RO2 with NO (except methylperoxy radical, MEO2) use the same rate constant (see CB7 reaction 75) from the Master Chemical Mechanism (MCM) version 3.3.1 (Jenkin et al., 2015) except for the isoprene mechanism where Wennberg et al. (2018) had used a slightly different value that is retained in CB7.

Reactions of RO2 with HO_2 (except methylperoxy radical, MEO2) use the rate expression of Wennberg et al. (2018) which is consistent with MCM 3.3.1, namely

$$k_{(RO2+HO2)} = 2.82\text{E-}13 \times \exp(1300/T) \times [1 - \exp(-0.231 \times n)] \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

where n is the number of heavy atoms in the RO2 radical (usually C + O + N) and 2 is subtracted to remove the influence of the peroxy group (-OO). This formulation has the effect that larger (heavier) RO2 radicals react somewhat faster with HO_2 than smaller RO2 radicals.

Under most conditions the dominant fate of RO2 radicals is reaction either with NO or HO_2 except when both NO and HO_2 are scarce and RO2 radicals react with themselves (RO2 + RO2). CB7 includes several individual RO2 radicals (MEO2, XO2, ISO2, TPO2, etc.) that could react with each other but explicitly including all possible RO2-RO2 reactions (i.e., N! permutations among N model species) would be inefficient. Therefore, CB7 has a model species named RO2 that is designed to approximate the sum of individual RO2 radicals (RO2 ≈ MEO2 + XO2 + ISO2 + TPO2 …), as in CB6. This scheme greatly reduces the number of RO2 reactions that must be included (from N! to N+4). CB7 uses a somewhat faster RO2 + RO2 rate constant than CB6r5 (by about 40%) and adjusts the rate constants at which specific RO2 radicals react with the total RO2 species according to their size so that larger RO2 radicals react more slowly, which is similar to the MCM scheme.

CB6 included reactions of RO2 radicals with peroxyacetyl radical (C2O3) that only become important when RO2-RO2 self-reactions are important, i.e., when both NO and HO_2 are scarce. CB7 assumes that the included RO2-RO2 reactions (discussed above) can describe this situation and eliminates all C2O3 reactions with individual RO2 radicals which allowed 11 reactions from CB6r5 to be removed in CB7 and saved adding 4 new reactions with the terpene update.

We added a new model species to track aromatic hydroperoxides (ARPX) that are formed when aromatic RO2 radicals (i.e., BZO2, TO2 and XLO2) react with HO_2.

1.7 Ozone Destruction by Iodine

We made two changes to the iodine reaction mechanism to slightly simplify the scheme. Iodine is removed from the gas phase when larger iodine oxides are formed that condense to aerosol as represented by species IXOY in the CB6r5 scheme. CB6r5 parameterizes iodine aerosol formation as a reaction with O_3 (CB6r5 reaction 222: I2O2 + O3 = IXOY) following Kaltsoyannis and Plane (2008) although other models (e.g., GEOS-Chem) parameterize this process as iodine oxide condensation to existing aerosol. CB7 uses a unimolecular reaction (CB7 reaction 227: I2O2 = IXOY) which removes the uncertain dependency on O_3 concentration and is likely to enhance O_3 destruction by iodine emissions from the Gulf of Mexico and tend to improve model performance for O_3 along the Texas Gulf Coast. In the future, the rate constant for this reaction could be formulated in CAMx as an aerosol uptake process. We also replaced iodic acid (HIO3) by IXOY because both are assumed to form aerosol.

1.8 Corrections

The photolysis rate of glyoxal (GLY) was revised in CB6r5 using data evaluated by IUPAC (Atkinson et al., 2004) which increased GLY photolysis by an order of magnitude over CB6r4, which was surprising. We further reviewed the IUPAC data sheet and determined that by misunderstanding how the data are presented we had omitted a pressure dependence and overestimated the GLY photolysis rate. Correcting this error reduces GLY photolysis rate and the increase over CB6r4 is now approximately 45% which is much more reasonable than the previous order of magnitude increase.

Model species CXO3 represents larger acyl peroxy radicals and the most direct precursor of CXO3 is ALDX. ALDX represents larger aldehydes and formally contains 2 carbons because this provides flexibility in mapping organic compounds to CB model species. Accordingly, CXO3 formally contains 2 carbons. Several CXO3 reactions treated it as having 3 carbon atoms in CB6r5 and this is corrected in CB7.

THE CB7 MECHANISM

A complete listing of the updated CB7 mechanism is shown in Table 1 with changes from CB6r5 shown in red (additions) and strikeout (deletions). Some reactions in CB6r5 were deleted entirely from CB7 as shown in Table 2. A clean listing of CB7 (i.e., without changes marked) is in Table 3 with model species names defined in Table 4 and photolysis rates at several zenith angles presented in Table 5.

Table 1. The CB7 mechanism with changes from CB6r5 marked.

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
1	NO2 = NO + O	Photolysis	6.30E-3	
2	~~O +~~ O2 + O + M = O3 + M	k = 6.00E-34 (T/300)^-2.6	6.11E-34	1
3	NO + O3 ~~+ NO~~ = NO2	k = 2.07E-12 exp(-1400/T)	1.89E-14	1
4	~~O +~~ NO + O = NO2	Falloff: F=0.85; n=0.84 k(0) = 1.00E-31 (T/300)^-1.6 k(inf) = 5.00E-11 (T/300)^-0.3	2.26E-12	1
5	~~O +~~ NO2 + O = NO	k = 5.10E-12 exp(198/T)	9.91E-12	1
6	~~O +~~ NO2 + O = NO3	Falloff: F=0.6; n=1.03 k(0) = 1.30E-31 (T/300)^-1.5 k(inf) = 2.30E-11 (T/300)^0.24	2.09E-12	1
7	~~O +~~ O3 + O =	k = 8.00E-12 exp(-2060/T)	7.96E-15	1
8	O3 = O	Photolysis	3.33E-4	
9	O3 = O1D	Photolysis	8.78E-6	
10	O1D + M = O + M	k = 2.23E-11 exp(115/T)	3.28E-11	
11	O1D + H2O = 2 OH	k = 2.14E-10	2.14E-10	
12	O3 + OH = HO2	k = 1.70E-12 exp(-940/T)	7.25E-14	
13	O3 + HO2 = OH	k = 2.03E-16 (T/300)^4.57 exp(693/T)	2.01E-15	
14	OH + O = HO2	k = 2.40E-11 exp(110/T)	3.47E-11	
15	HO2 + O = OH	k = 3.00E-11 exp(200/T)	5.87E-11	

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
16	OH + OH = O	k = 6.20E-14 (T/298)^2.6 exp(945/T)	1.48E-12	
17	OH + OH = H2O2	Falloff: F=0.42; n=1.23 k(0) = 9.00E-31 (T/300)^-3.2 k(inf) = 3.90E-11 (T/300)^-0.47	6.21E-12	
18	OH + HO2 =	k = 4.80E-11 exp(250/T)	1.11E-10	
19	HO2 + HO2 = H2O2	k = k1 + k2 [M] k1 = 2.20E-13 exp(600/T) k2 = 1.90E-33 exp(980/T)	2.90E-12	
20	HO2 + HO2 + H2O = H2O2	k = k1 + k2 [M] k1 = 3.08E-34 exp(2800/T) k2 = 2.66E-54 exp(3180/T)	6.53E-30	
21	H2O2 = 2 OH	Photolysis	3.78E-6	
22	H2O2 + OH = HO2	k = 1.80E-12	1.80E-12	
23	H2O2 + O = OH + HO2	k = 1.40E-12 exp(-2000/T)	1.70E-15	
24	NO + NO + O2 = 2. NO2	k = 4.25E-39 exp(664/T)	3.95E-38	
25	NO + HO2 ~~+ NO~~ = OH + NO2	k = 3.45E-12 exp(270/T)	8.54E-12	1
26	NO2 + O3 = NO3	k = 1.40E-13 exp(-2470/T)	3.52E-17	
27	NO3 = NO2 + O	Photolysis	1.56E-1	
28	NO3 = NO	Photolysis	1.98E-2	
29	NO3 + NO = 2. NO2	k = 1.80E-11 exp(110/T)	2.60E-11	
30	NO3 + NO2 = NO + NO2	k = 4.50E-14 exp(-1260/T)	6.56E-16	
31	NO3 + OH = HO2 + NO2	k = 2.00E-11	2.00E-11	
32	NO3 + HO2 = OH + NO2	k = 4.00E-12	4.00E-12	
33	NO3 + NO3 = 2. NO2	k = 8.50E-13 exp(-2450/T)	2.28E-16	
34	NO3 + NO2 = N2O5	Falloff: F=0.35; n=1.33 k(0) = 3.60E-30 (T/300)^-4.1	1.24E-12	

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
		k(inf) = 1.90E-12 (T/300)^0.2		
35	N2O5 = NO3 + NO2	Falloff: F=0.35; n=1.33 k(0) = 1.30E-3 (T/300)^-3.5 exp(-11000/T) k(inf) = 9.70E+14 (T/300)^0.1 exp(-11080/T)	4.46E-2	
36	N2O5 = NO2 + NO3	Photolysis	2.52E-5	
37	N2O5 + H2O = 2. HNO3	k = 1.00E-22	1.00E-22	
38	NO + OH = HONO	Falloff: F=0.81; n=0.87 k(0) = 7.40E-31 (T/300)^-2.4 k(inf) = 3.30E-11 (T/300)^-0.3	9.77E-12	
39	HONO = NO + OH	Photolysis	1.04E-3	
40	HONO + OH = NO2	k = 2.50E-12 exp(260/T)	5.98E-12	
41	NO2 + OH = HNO3	Falloff: F=0.6; n=1 k(0) = 1.80E-30 (T/300)^-3 k(inf) = 2.80E-11	1.06E-11	
42	NO2 + OH + H2O = HNO3 + H2O	k = 1.10E-30	1.10E-30	
43	HNO3 + OH = NO3	k = k1 + k3 [M] / (1 + k3 [M] / k2) k1 = 2.40E-14 exp(460/T) k2 = 2.70E-17 exp(2199/T) k3 = 6.50E-34 exp(1335/T)	1.54E-13	
44	HNO3 = OH + NO2	Photolysis	2.54E-7	
45	NO2 + HO2 ~~+ NO2~~ = PNA	Falloff: F=0.4; n=1.26 k(0) = 1.40E-31 (T/300)^-3.1 k(inf) = 4.00E-12	7.50E-13	1
46	PNA = HO2 + NO2	Falloff: F=0.4; n=1.26 k(0) = 4.10E-5 exp(-10650/T) k(inf) = 6.00E+15 exp(-11170/T)	6.20E-2	
47	PNA = 0.59 HO2 + 0.59 NO2 + 0.41 OH + 0.41 NO3	Photolysis	2.36E-6	

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
48	PNA + OH = NO2	k = 3.20E-13 exp(690/T)	3.24E-12	
49	H2 + OH = HO2	k = 7.70E-12 exp(-2100/T)	6.70E-15	
50	CO + OH = HO2	k = k1 + k2 [M] k1 = 1.44E-13 k2 = 3.43E-33	2.28E-13	
51	SO2 + OH = SULF + HO2	Falloff: F=0.53; n=1.1 k(0) = 2.80E-31 (T/300)^-2.6 k(inf) = 2.00E-12	9.35E-13	
52	SO2 = SULF	k = 0.00E+0	0.00E+0	
53	DMS + OH = SO2 + FORM + MEO2	k = 1.12E-11 exp(-250/T)	4.84E-12	
54	DMS + OH + O2 = SULF + MEO2	k = 1.28E-37 exp(4480/T)	4.33E-31	
55	DMS + NO3 = SO2 + FORM + MEO2 + HNO3	k = 1.90E-13 exp(520/T)	1.09E-12	
56	C2O3 + NO = NO2 + MEO2 + RO2	k = 7.50E-12 exp(290/T)	1.98E-11	
57	C2O3 + NO2 = PAN	Falloff: F=0.3; n=1.41 k(0) = 3.61E-28 (T/300)^-6.87 k(inf) = 1.24E-11 (T/300)^-1.105	9.86E-12	
58	PAN = NO2 + C2O3	Falloff: F=0.3; n=1.41 k(0) = 1.10E-5 exp(-10100/T) k(inf) = 1.90E+17 exp(-14100/T)	4.31E-4	
59	PAN = 0.6 NO2 + 0.6 C2O3 + 0.4 NO3 + 0.4 MEO2 + 0.4 RO2	Photolysis	3.47E-7	
60	C2O3 + HO2 = 0.37 PACD + 0.13 AACD + 0.13 O3 + 0.5 OH + 0.5 MEO2 + 0.5 RO2	k = 3.14E-12 exp(580/T)	2.20E-11	
61	C2O3 + RO2 = 0.3 AACD + 0.7 MEO2 + 1.7 RO2	k = 4.40E-13 exp(1070/T)	1.60E-11	2
62	C2O3 + C2O3 = 2. MEO2 + 2. RO2	k = 2.90E-12 exp(500/T)	1.55E-11	
63	CXO3 + NO = NO2 + 0.5 ALD2 + XO2H + RO2	k = 6.70E-12 exp(340/T)	2.10E-11	3
64	CXO3 + NO2 = PANX	k = k(ref)/K k(ref) = k(~~54~~57) K = 1.19E+0	8.28E-12	12

No.	Reactants and Products [a, b]	Rate Constant Expression	k298 [c, d]	Comment
65	PANX = NO2 + CXO3	k = k(ref)/K k(ref) = k(~~55~~58) K = 1.19E+0	3.62E-4	12
66	PANX + OH = 0.5 ALD2 + NO2	k = 3.00E-12	3.00E-12	3
67	CXO3 + HO2 = 0.~~37~~19 PACD + 0.~~13~~06 AACD + 0.~~13~~25 ALD2 + 0.06 O3 + 0.~~5~~25 OH + 0.~~5 MEO2 + 0.5 RO2~~25 HO2	k = k(ref)/K k(ref) = k(~~57~~60) K = 1.00E+0	2.20E-11	3
68	CXO3 + RO2 = ~~MEO2~~0.35 ALD2 + 0.15 AACD + 0.35 HO2 + RO2	k = k(ref)/K k(ref) = k(~~58~~61) K = 1.00E+0	1.60E-11	2,3
69	OPO3 + NO = NO2 + 0.5 GLY + 0.5 CO + 0.8 HO2 + 0.2 CXO3	k = k(ref)/K k(ref) = k(~~61~~63) K = 1.00E+0	2.10E-11	12
70	OPO3 + NO2 = OPAN	k = k(ref)/K k(ref) = k(~~62~~64) K = 1.00E+0	8.28E-12	12
71	OPAN = OPO3 + NO2	k = k(ref)/K k(ref) = k(~~63~~65) K = 1.00E+0	3.62E-4	12
72	OPAN + OH = 0.5 NO2 + 0.5 NTR2 + 0.5 GLY + CO~~ + 0.5 NTR2~~	k = 3.60E-11	3.60E-11	4
73	OPO3 + HO2 = 0.37 PACD + 0.13 AACD + 0.13 O3 + 0.5 OH + 0.5 MEO2 + 0.5 RO2	k = k(ref)/K k(ref) = k(~~57~~60) K = 1.00E+0	2.20E-11	12
74	OPO3 + RO2 = 0.~~8 XO2H + 0.8~~7 ALDX + 0.3 AACD + 0.7 XO2H + 1.~~8~~7 RO2 ~~+ 0.2 AACD~~	k = k(ref)/K k(ref) = k(~~58~~61) K = 1.00E+0	1.60E-11	4
75	RO2 + NO = NO	k = 2.~~40E~~70E-12 exp(360/T)	~~8.03E~~9.04E-12	5
76	RO2 + HO2 = HO2	k = ~~4.80E~~2.12E-13 exp(~~800~~1300/T)	~~7.03E-12~~1.66E-11	5
77	RO2 + RO2 =	k = ~~6.50E-14~~1.55E-13 exp(~~500~~350/T)	~~3.48E~~5.00E-13	5
78	MEO2 + NO = FORM + HO2 + NO2	k = 2.30E-12 exp(360/T)	7.70E-12	
79	MEO2 + HO2 = 0.9 MEPX + 0.1 FORM	k = 3.80E-13 exp(780/T)	5.21E-12	
80	MEO2 + C2O3 = FORM + 0.9 HO2 + 0.9 MEO2 + 0.1 AACD + 0.9 RO2	k = 2.00E-12 exp(500/T)	1.07E-11	
81	MEO2 + RO2 = 0.685 FORM + 0.315 MEOH + 0.37 HO2 + RO2	k = k(ref)/K k(ref) = k(~~70~~77) K = 1.00E+0	~~3.48E~~5.00E-13	5
82	MEPX + OH = 0.6 MEO2 + 0.6 RO2 + 0.4 FORM + 0.4 OH	k = 5.30E-12 exp(190/T)	1.00E-11	

No.	**Reactants and Products** [a, b]	**Rate Constant Expression**	**k_{298}** [c, d]	**Comment**
83	MEPX = MEO2 + RO2 + OH	Photolysis	2.68E-6	
84	XO2H + NO = NO2 + HO2	~~k = 2.70E-12 exp(360/T)~~k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12	12
85	XO2H + HO2 = ROOH	k = ~~6.80E~~2.12E-13 exp(~~800~~1300/T)	~~9.96E-12~~1.67E-11	5
86	XO2H + RO2 = 0.6 HO2 + RO2	k = k(ref)/K k(ref) = k(~~70~~77) K = ~~1~~2.00E+0	~~3.48E~~2.50E-13	5
87	XO2 + NO = NO2	k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12	
88	XO2 + HO2 = ROOH	k = k(ref)/K k(ref) = k(~~76~~85) K = 1.00E+0	~~9.96E-12~~1.67E-11	5
89	XO2 + RO2 = RO2	k = k(ref)/K k(ref) = k(~~70~~77) K = ~~1~~2.00E+0	~~3.48E~~2.50E-13	5
90	XO2N + NO = 0.5 NTR1 + 0.5 NTR2	k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12	
91	XO2N + HO2 = ROOH	k = k(ref)/K k(ref) = k(~~76~~85) K = 1.00E+0	~~9.96E-12~~1.67E-11	5
92	XO2N + RO2 = RO2	k = k(ref)/K k(ref) = k(~~70~~77) K = ~~1~~2.00E+0	~~3.48E~~2.50E-13	5
93	ROOH + OH = 0.~~54~~56 XO2H + 0.~~06~~04 XO2N + 0.6 RO2 + 0.4 OH	k = 5.30E-12 exp(190/T)	1.00E-11	2
94	ROOH = HO2 + OH	Photolysis	2.68E-6	
95	NTR1 + OH = ~~NTR2~~NO2	k = 2.00E-12	2.00E-12	2,8
96	NTR1 = NO2	Photolysis	1.06E-6	
97	NTR2 = HNO3	k = 2.30E-5	2.30E-5	
98	MEOH + OH = FORM + HO2	k = 2.85E-12 exp(-345/T)	8.95E-13	
99	ETOH + OH = 0.95 ALD2 + 0.9 HO2 + 0.1 XO2H + 0.1 RO2 + 0.078 FORM + 0.011 GLYD	k = 3.00E-12 exp(20/T)	3.21E-12	
100	FORM + OH = HO2 + CO	k = 5.40E-12 exp(135/T)	8.49E-12	
101	FORM = 2. HO2 + CO	Photolysis	1.69E-5	
102	FORM = CO + H2	Photolysis	2.69E-5	
103	FORM + NO3 = HNO3 + HO2 + CO	k = 5.50E-16	5.50E-16	

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
104	ALD2 + OH = C2O3	k = 4.70E-12 exp(345/T)	1.50E-11	
105	ALD2 + NO3 = C2O3 + HNO3	k = 1.40E-12 exp(-1860/T)	2.73E-15	
106	ALD2 = MEO2 + RO2 + CO + HO2	Photolysis	1.96E-6	
107	ALDX + OH = CXO3	k = 4.90E-12 exp(405/T)	1.91E-11	
108	ALDX + NO3 = CXO3 + HNO3	k = 6.30E-15	6.30E-15	
109	ALDX = 0.5 ALD2 + XO2H + RO2 + CO + HO2	Photolysis	2.62E-5	3
110	GLYD + OH = 0.2 GLY + 0.2 HO2 + 0.8 C2O3	k = 8.00E-12	8.00E-12	
111	GLYD = 0.74 FORM + 0.89 CO + 1.4 HO2 + 0.15 MEOH + 0.19 OH + 0.11 GLY + 0.11 XO2H + 0.11 RO2	Photolysis	2.76E-6	
112	GLYD + NO3 = HNO3 + C2O3	k = k(ref)/K k(ref) = k(105) K = 1.00E+0	2.73E-15	
113	GLY + OH = 1.8 CO + 0.2 XO2 + 0.2 RO2 + HO2	k = 3.10E-12 exp(340/T)	9.70E-12	
114	GLY = 2. HO2 + 2. CO	Photolysis	7.95E-5~~.01E-4~~	6
115	GLY + NO3 = HNO3 + 1.5 CO + 0.5 XO2 + 0.5 RO2 + HO2	k = 4.00E-16	4.00E-16	
116	MGLY = C2O3 + HO2 + CO	Photolysis	1.46E-4	
117	MGLY + NO3 = HNO3 + C2O3 + XO2 + RO2	k = 5.00E-16	5.00E-16	
118	MGLY + OH = C2O3 + CO	k = 1.90E-12 exp(575/T)	1.31E-11	
119	ACET = 0.38 CO + 1.38 MEO2 + 1.38 RO2 + 0.62 C2O3	Photolysis	2.08E-7	
120	ACET + OH = FORM + C2O3 + XO2 + RO2	k = 1.41E-12 exp(-620.6/T)	1.76E-13	
121	KET = 0.~~5~~15 FORM + 0.58 ALD2 + 0.~~5~~34 ALDX + 0.96 HO2 + 0.7 C2O3 + 0.~~5 XO2H + 0.5~~3 CXO3 + ~~0.5 MEO2 +~~1.3 XO2 + 0.03 XO2N + 1.33 RO2 - ~~2.5~~3. PAR	Photolysis	2.27E-7	7
122	KET + OH = 0.06 KET + 0.15 FORM + 0.29 ALD2 + 0.46 ALDX + 0.61 HO2 + 0.27 C2O3 + 0.06 CXO3 + 0.72 XO2 + 0.04 XO2N + 0.76 RO2 - 1.38 PAR	k = 1.00E-12	1.00E-12	7

No.	Reactants and Products [a, b]	Rate Constant Expression	k298 [c, d]	Comment
123	HACT + OH = MGLY + HO2	k = 2.00E-12 exp(320/T)	5.85E-12	8,2
124	FACD + OH = HO2	k = 4.50E-13	4.50E-13	
125	AACD + OH = MEO2 + RO2	k = 4.00E-14 exp(850/T)	6.93E-13	
126	PACD + OH = C2O3	k = 5.30E-12 exp(190/T)	1.00E-11	
127	CH4 + OH = MEO2 + RO2	k = 1.85E-12 exp(-1690/T)	6.37E-15	
128	ECH4 + OH = MEO2 + RO2	k = 1.85E-12 exp(-1690/T)	6.37E-15	
129	ETHA + OH = 0.991 ALD2 + 0.991 XO2H + 0.009 XO2N + RO2	k = 6.90E-12 exp(-1000/T)	2.41E-13	
130	PRPA + OH = XPRP	k = 7.60E-12 exp(-585/T)	1.07E-12	
131	XPRP = XO2N + RO2	Falloff: F=0.41; n=1 k(0) = 2.37E-21 k(inf) = 4.30E-1 (T/298)^-8	3.09E-2	
132	XPRP = 0.732 ACET + 0.268 ALDX + 0.268 PAR + XO2H + RO2	k = 1.00E+0	1.00E+0	
133	PAR + OH = XPAR	k = ~~8.10E~~3.09E-13 (T/300)^2 exp(300/T)	8.~~10E~~34E-13	7
134	XPAR = XO2N + RO2 - 3. PAR	Falloff: F=0.41; n=1 k(0) = 4.81E-20 k(inf) = 4.30E-1 (T/298)^-8	1.49E-1	7
135	XPAR = 0.~~126~~87 ROR + 0.13 ALDX + 0.~~874 ROR + 0.126~~13 XO2H + 0.~~874 XO2 +~~13 RO2 - 0.~~126~~13 PAR	k = 1.00E+0	1.00E+0	7
136	ROR = 0.~~2 KET + 0.42~~32 ACET + 0.~~74~~3 KET + 0.04 FORM + 0.46 ALD2 + 0.~~37~~1 ALDX + 0.~~04 XO2N~~62 HO2 + 0.~~94~~11 MEO2 + 1.75 XO2 + 0.25 XO2H + 0.~~98~~02 XO2N + 2.13 RO2 ~~+ 0.02 ROR – 2.7~~ - 1.63 PAR	k = ~~5.70E~~k1 + k2 [M] k1 = 2.40E+12 exp(-~~5780~~5000/T) k2 = 5.00E-15 exp(-250/T)	~~2.15E+4~~1.77E+5	7
137	ROR + O2 = 0.15 ACET + 0.85 KET + HO2 - 0.3 PAR	k = ~~1.50E~~2.00E-14 exp(-~~200~~250/T)	~~7.67E~~8.64E-15	7
138	ETHY + OH = 0.7 GLY + 0.7 OH + 0.3 FACD + 0.3 CO + 0.3 HO2	Falloff: F=0.37; n=1.3 k(0) = 5.00E-30 (T/300)^-1.5 k(inf) = 1.00E-12	7.52E-13	

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
139	ETH + OH = XO2H + RO2 + 1.56 FORM + 0.22 GLYD	Falloff: F=0.48; n=1.15 k(0) = 8.60E-29 (T/300)^-3.1 k(inf) = 9.00E-12 (T/300)^-0.85	7.84E-12	
140	ETH + O3 = FORM + 0.35 CO + 0.27 HO2 + 0.17 OH + 0.42 FACD	k = 6.82E-15 exp(-2500/T)	1.55E-18	
141	ETH + NO3 = 0.5 NO2 + 0.5 NTR1 + 0.5 XO2H + 0.5 XO2 + RO2 + 1.125 FORM	k = 3.30E-12 exp(-2880/T)	2.10E-16	
142	OLE + OH = 0.781 FORM + 0.488 ALD2 + 0.488 ALDX + 0.976 XO2H + 0.195 XO2 + 0.024 XO2N + 1.195 RO2 - 0.73 PAR	Falloff: F=0.5; n=1.13 k(0) = 8.00E-27 (T/300)^-3.5 k(inf) = 3.00E-11 (T/300)^-1	2.86E-11	
143	OLE + O3 = 0.295 ALD2 + 0.555 FORM + 0.27 ALDX + 0.15 XO2H + 0.15 RO2 + 0.334 OH + 0.08 HO2 + 0.378 CO + 0.075 GLY + 0.075 MGLY + 0.09 FACD + 0.13 AACD + 0.04 H2O2 - 0.79 PAR	k = 5.50E-15 exp(-1880/T)	1.00E-17	
144	OLE + NO3 = 0.5 NO2 + 0.5 NTR1 + 0.48 XO2 + 0.48 XO2H + 0.04 XO2N + RO2 + 0.5 FORM + 0.25 ALD2 + 0.375 ALDX - PAR	k = 4.60E-13 exp(-1155/T)	9.54E-15	
145	IOLE + OH = 1.3 ALD2 + 0.7 ALDX + XO2H + RO2	k = 1.05E-11 exp(519/T)	5.99E-11	
146	IOLE + O3 = 0.732 ALD2 + 0.442 ALDX + 0.128 FORM + 0.245 CO + 0.5 OH + 0.3 XO2H + 0.3 RO2 + 0.24 GLY + 0.06 MGLY + 0.29 PAR + 0.08 AACD + 0.08 H2O2	k = 4.70E-15 exp(-1013/T)	1.57E-16	
147	IOLE + NO3 = 0.5 NO2 + 0.5 NTR1 + 0.48 XO2 + 0.48 XO2H + 0.04 XO2N + RO2 + 0.5 ALD2 + 0.625 ALDX + PAR	k = 3.70E-13	3.70E-13	
148	BENZ + OH = 0.53 CRES + 0.352 BZO2 + 0.352 RO2 + 0.118 OPEN + 0.118 OH + 0.53 HO2	k = 2.30E-12 exp(-190/T)	1.22E-12	
149	BZO2 + NO = 0.918 NO2 + 0.082 NTR2 + 0.918 GLY + 0.918 OPEN + 0.918 HO2	~~k = 2.70E-12 exp(360/T)~~k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12	12
150	BZO2 + HO2 = ARPX	k = ~~1.90E~~2.24E-13 exp(1300/T)	1.~~49E~~76E-11	5,9

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
151	BZO2 + RO2 = GLY + OPEN + HO2 + RO2	k = k(ref)/K k(ref) = k(~~70~~77) K = ~~1~~2.00E+0	~~3.48E~~2.50E-13	5
152	TOL + OH = 0.18 CRES + 0.65 TO2 + 0.72 RO2 + 0.1 OPEN + 0.1 OH + 0.07 XO2H + 0.18 HO2	k = 1.80E-12 exp(340/T)	5.63E-12	
153	TO2 + NO = 0.86 NO2 + 0.14 NTR2 + 0.417 GLY + 0.443 MGLY + 0.66 OPEN + 0.2 XOPN + 0.86 HO2	~~k = 2.70E-12 exp(360/T)~~k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12	12
154	TO2 + HO2 = ARPX	k = ~~1.90E~~2.39E-13 exp(1300/T)	1.~~49E~~87E-11	5,9
155	TO2 + RO2 = 0.48 GLY + 0.52 MGLY + 0.77 OPEN + 0.23 XOPN + HO2 + RO2	k = k(ref)/K k(ref) = k(~~70~~77) K = ~~1~~2.00E+0	~~3.48E~~2.50E-13	5
156	XYL + OH = 0.155 CRES + 0.544 XLO2 + 0.602 RO2 + 0.244 XOPN + 0.244 OH + 0.058 XO2H + 0.155 HO2	k = 1.85E-11	1.85E-11	
157	XLO2 + NO = 0.86 NO2 + 0.14 NTR2 + 0.221 GLY + 0.675 MGLY + 0.3 OPEN + 0.56 XOPN + 0.86 HO2	~~k = 2.70E-12 exp(360/T)~~k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12	12
158	XLO2 + HO2 = ARPX	k = ~~1.90E~~2.50E-13 exp(1300/T)	1.~~49E~~96E-11	5,9
159	XLO2 + RO2 = 0.26 GLY + 0.77 MGLY + 0.35 OPEN + 0.65 XOPN + HO2 + RO2	k = k(ref)/K k(ref) = k(~~70~~77) K = ~~1~~2.00E+0	~~3.48E~~2.50E-13	5
160	OPEN = OPO3 + HO2 + CO	Photolysis	5.04E-4	
161	OPEN + OH = 0.6 OPO3 + 0.4 XO2H + 0.4 RO2 + 0.4 GLY	k = 4.40E-11	4.40E-11	
162	OPEN + O3 = 1.4 GLY + 0.24 MGLY + 0.5 OH + 0.12 C2O3 + 0.08 FORM + 0.02 ALD2 + 1.98 CO + 0.56 HO2	k = 5.40E-17 exp(-500/T)	1.01E-17	
163	OPEN + NO3 = OPO3 + HNO3	k = 3.80E-12	3.80E-12	
164	XOPN = 0.4 GLY + XO2H + 0.7 HO2 + 0.7 CO + 0.3 C2O3	Photolysis	5.04E-4	
165	XOPN + OH = MGLY + 0.4 GLY + 2. XO2H + 2. RO2	k = 9.00E-11	9.00E-11	
166	XOPN + O3 = 1.2 MGLY + 0.5 OH + 0.6 C2O3 + 0.1 ALD2 + 0.5 CO + 0.3 XO2H + 0.3 RO2	k = 1.08E-16 exp(-500/T)	2.02E-17	

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
167	XOPN + NO3 = 0.5 NO2 + 0.5 NTR2 + 0.45 XO2H + 0.45 XO2 + 0.1 XO2N + RO2 + 0.25 OPEN + 0.25 MGLY	k = 3.00E-12	3.00E-12	
168	CRES + OH = 0.025 GLY + 0.025 OPEN + HO2 + 0.2 CRO + 0.732 CAT1 + 0.02 XO2N + 0.02 RO2	k = 1.70E-12 exp(950/T)	4.12E-11	
169	CRES + NO3 = 0.3 CRO + HNO3 + 0.48 XO2 + 0.12 XO2H + 0.24 GLY + 0.24 MGLY + 0.48 OPO3 + 0.1 XO2N + 0.7 RO2	k = 1.40E-11	1.40E-11	
170	CRO + NO2 = CRON	k = 2.10E-12	2.10E-12	
171	CRO + HO2 = CRES	k = 5.50E-12	5.50E-12	
172	CRON + OH = NTR2 + 0.5 CRO	k = 1.53E-12	1.53E-12	
173	CRON + NO3 = NTR2 + 0.5 CRO + HNO3	k = 3.80E-12	3.80E-12	
174	CRON = HONO + HO2 + FORM + OPEN	Photolysis	9.45E-5	
175	CAT1 + OH = 0.14 FORM + 0.2 HO2 + 0.5 CRO	k = 5.00E-11	5.00E-11	
176	CAT1 + NO3 = CRO + HNO3	k = 1.70E-10	1.70E-10	
177	ARPX + OH = 0.5 OH + 0.2 BZO2 + 0.15 TO2 + 0.15 XLO2 + 0.5 RO2	k = 8.00E-11	8.00E-11	9
178	ISOP + OH = ISO2 + RO2	k = 2.70E-11 exp(390/T)	9.99E-11	4
179	ISO2 + NO = 0.9 NO2 + 0.1 INTR + 0.9 ~~NO2 + 0.673~~ FORM + 0.9 ISPD + 0.~~818~~9 HO2~~ + 0.082 XO2H + 0.082 RO2~~	~~k = 2.39E-12 exp(365/T)~~k = k(ref)/K k(ref) = k(75) K = 1.00E+0	~~8.13E~~9.04E-12	4
180	ISO2 + HO2 = 0.~~88~~94 ISPX + 0.~~12 OH + 0.12 HO2 + 0.12~~06 FORM + 0.~~12~~06 ISPD + 0.06 OH + 0.06 HO2	k = ~~7.43E~~2.12E-13 exp(~~700~~1300/T)	~~7.78E-12~~1.66E-11	4
181	ISO2 + RO2 = ~~0.598 FORM + 1~~ ISPD + ~~0.728 HO2 + 0.072 XO2H + 1.072~~ RO2	k = k(ref)/K k(ref) = k(~~70~~77) K = ~~1~~2.00E+0	~~3.48E~~2.50E-13	4
182	ISO2 = ~~HO2 +~~0.4 HPLD + 0.1 ISPD + 0.1 GLY + 0.1 GLYD + CO + 1.7 OH + 0.35 HO2	k = 3.30E+9 exp(-8300/T)	2.64E-3	4
183	ISOP + O3 = 0.~~6~~8 FORM + 0.~~65~~5 ISPD + 0.~~15 ALDX~~58 FACD + 0.~~2 CXO3~~5 CO + 0.~~35 PAR + 0.266~~28 OH + 0.~~2 XO2 + 0.2 RO2 + 0.066~~5 HO2 + 0.~~066 CO~~4 MEO2 + 0.4 RO2	k = 1.03E-14 exp(-1995/T)	1.27E-17	4

No.	**Reactants and Products** $^{a, b}$	**Rate Constant Expression**	**k**$_{298}$ $^{c, d}$	**Comment**
184	ISOP + NO3 = 0.~~35~~25 NO2 + 0.~~65~~75 NTR2 + 0.~~64 XO2H + 0.33 XO2 + 0.03 XO2N + RO2 + 0.35~~25 FORM + 0.~~35~~25 ISPD + 0.25 OH + 0.25 XO2 + 0.25 RO2	k = ~~3.03E~~2.95E-12 exp(-~~448~~450/T)	6.~~74E~~52E-13	4
185	ISPD + OH = 0.~~022 XO2N + 0.521 XO2 + 0.115~~4 MGLY + 0.~~115 MEO2 + 0.269~~2 GLYD + 0.~~269 C2O3 + 0.457 OPO3 + 0.117 PAR + 0.137 ACET + 0.137~~1 FORM + CO + 0.~~137~~1 OH + 0.1 HO2 + 0.~~658 RO2~~1 OPO3 + 0.4 C2O3	k = ~~5.58E~~7.00E-12 exp(~~511~~430/T)	~~3.10E~~2.96E-11	4
186	ISPD + NO3 = 0.~~717~~9 NTR2 + 0.1 HNO3 + 0.~~142 NTR2 + 0.142 NO2~~1 CO + 0.~~142 XO2 + 0.142 XO2H + 0.113 GLYD + 0.113 MGLY + 0.717 PAR + 0.717 CXO3 + 0.284 RO2~~1 C2O3	k = ~~4.10E-12~~3.94E-14 exp~~(-1860~~(475/T)	~~7.98E-15~~1.94E-13	4
187	ISPD = 0.~~76 HO2~~8 ISPD + 0.~~34 XO2H~~15 MGLY + 0.~~16 XO2~~1 GLYD + 0.~~34 MEO2 + 0.208 C2O3 + 0.26~~1 FORM + 0.~~24 OLE + 0.24 PAR + 0.17 ACET + 0.128 GLYD + 0.84 RO2~~2 OH	Photolysis	1.60E-5	4
188	ISPX + OH = 0.~~904~~6 EPOX + 0.~~933~~2 MGLY + 0.2 FORM + 0.2 ROOH + OH + 0.~~067 ISO2 + 0.067 RO2 + 0.029 IOLE + 0.029 ALDX~~5 HO2	k = 2.~~23E~~80E-11 exp(~~372~~370/T)	~~7.77E~~9.69E-11	4
189	HPLD = 0.6 HPLD + 0.3 ISPD + 1.65 OH + ~~ISPD~~0.2 HO2 + 0.8 CO	Photolysis	~~4.41E-4~~#N/A	4
190	HPLD + ~~NO3 = HNO3 +~~OH = ISPD + 0.2 HCHO + 0.5 CO + 1.1 OH	k = ~~6.00E-12~~1.17E-11 exp~~(-1860~~(450/T)	~~1.17E-14~~5.30E-11	4
191	EPOX + OH = 0.2 ISPD + 0.2 HO2 + 0.8 EPX2 + 0.8 RO2	k = 5.~~78E~~43E-11 exp(-~~400~~450/T)	1.~~51E~~20E-11	4
192	EPX2 + NO = 0.~~275~~98 NO2 + 0.02 NTR2 + 0.7 MGLY + 0.7 GLYD + 0.~~275~~2 GLY + 0.~~275 MGLY~~2 CO + 0.~~125~~2 ISPD + 0.7 OH + ~~0.825~~ HO2~~ + 0.375 FORM + NO2 + 0.251 CO + 2.175 PAR~~	~~k = 2.39E-12 exp(365/T)~~k = k(ref)/K k(ref) = k(75) K = 1.00E+0	~~8.13E~~9.04E-12	4
193	EPX2 + HO2 = 0.~~275 GLYD~~3 ISPD + 0.~~275~~3 MGLY + 0.1 GLY + 0.~~275 MGLY~~2 GLYD + 1.~~125 OH + 0.825 HO2 + 0.375~~5 FORM + ROOH +	k = ~~7.43E~~2.38E-13 exp(~~700~~1300/T)	~~7.78E-12~~1.87E-11	4

No.	Reactants and Products $^{a, b}$	Rate Constant Expression	k_{298} $^{c, d}$	Comment
	0.~~074 FACD + 0.251~~2 CO + ~~2.175 PAR~~1.7 OH + HO2			
194	EPX2 + RO2 = 0.~~275 GLYD + 0.275 GLY + 0.275~~6 MGLY + 0.~~125 OH~~5 GLY + 0.~~825 HO2 + 0.375~~5 FORM + 0.~~251~~3 GLYD + 0.1 ISPD + 0.2 CO + ~~2.175 PAR~~0.85 OH + HO2 + RO2	k = k(ref)/K k(ref) = k(~~70~~77) K = ~~1~~2.00E+0	~~3.48E~~2.50E-13	4
195	INTR + OH = 0.~~63 XO2 + 0.37 XO2H + RO2 + 0.444~~5 NO2 + 0.~~185 NO3~~4 NTR2 + 0.~~104~~1 INTR + 0.~~592 FORM + 0.331 GLYD + 0.185 FACD + 2.7 PAR + 0.098 OLE + 0.078 ALDX + 0.266 NTR2~~4 ISPD + 0.1 EPOX	k = ~~3.10E~~1.34E-11 exp(410/T)	~~3.10E~~5.30E-11	4
196	APIN + OH = APO2	k = 1.00E-11 exp(300/T)	2.74E-11	8
197	APO2 + NO = 0.77 NO2 + 0.23 NTR2 + 0.21 FORM + 0.09 ACET + 0.62 ISPD + 0.77 HO2 + 0.11 ROOH + 0.19 XO2N + 0.19 RO2	k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12	8
198	APO2 + HO2 = 0.08 FORM + 0.06 ACET + 0.35 ISPD + 0.48 HO2 + 0.35 OH + 0.65 ROOH	k = 2.60E-13 exp(1300/T)	2.04E-11	8
199	APO2 + RO2 = 0.06 ACET + 0.87 ISPD + 0.5 HO2 + 0.13 ROOH + RO2	k = k(ref)/K k(ref) = k(77) K = 2.00E+0	2.50E-13	8
200	APIN + O3 = 0.27 FORM + 0.22 ISPD + 0.22 H2O2 + 0.17 CO + 0.77 OH + 0.17 HO2 + 0.33 XO2 + 0.07 XO2N + 0.27 OPO3 + 0.4 RO2	k = 8.22E-16 exp(-640/T)	9.60E-17	8
201	APIN + NO3 = 0.7 NO2 + 0.3 NTR2 + 0.7 ISPD + 0.7 OH + 0.7 HO2	k = 1.20E-12 exp(490/T)	6.21E-12	8
202	~~TERP + OH = 0.75 XO2H + 0.5 XO2 + 0.25 XO2N + 1.5 RO2 + 0.28 FORM + 1.66 PAR + 0.47 ALDX~~TERP + OH = TPO2	k = ~~1.50E~~4.07E-11 exp(~~449~~350/T)	~~6.77E-11~~1.32E-10	8
203	TPO2 + NO = 0.75 NO2 + 0.26 NTR2 + 0.43 FORM + 0.12 ACET + 0.63 ISPD + 0.75 HO2 + 0.19 XO2N + 0.19 RO2	k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12	8

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
204	TPO2 + HO2 = 0.04 FORM + 0.01 ACET + 0.07 ISPD + 0.07 HO2 + 0.07 OH + 0.94 ROOH	k = 2.60E-13 exp(1300/T)	2.04E-11	8
205	TPO2 + RO2 = 0.27 FORM + 0.04 ACET + ISPD + 0.5 HO2 + RO2	k = k(ref)/K k(ref) = k(77) K = 2.00E+0	2.50E-13	8
206	TERP + O3 = 0.~~57~~59 FORM + 0.06 ACET + 0.05 HACT + 0.25 ISPD + 0.24 H2O2 + 0.47 OH + 0.~~07 XO2H~~16 HO2 + 0.~~69~~04 FACD + 0.06 XO2 + 0.~~18~~07 XO2N + ~~0.94~~ 0.25 C2O3 + 0.4 OPO3 + 0.13 RO2 ~~+ 0.24 FORM + 0.001 CO + 7 PAR + 0.21 ALDX + 0.39 CXO3~~	k = ~~1.20E~~4.46E-15 exp(-~~821~~960/T)	~~7.63E-17~~1.78E-16	8
207	TERP + NO3 = 0.~~47~~3 NO2 + 0.~~28 XO2H~~7 NTR2 + 0.~~75 XO2~~12 ACET + 0.~~25 XO2N + 1.28 RO2~~3 ISPD + 0.~~47 ALDX~~48 OH + 0.~~53 NTR2~~3 HO2	k = ~~3.70E~~7.00E-12 ~~exp(175/T)~~	~~6.66E~~7.00E-12	8
208	SQT + OH = SQO2	k = 2.00E-10	2.00E-10	8
209	SQO2 + NO = 0.6 NO2 + 0.4 NTR2 + 0.6 ISPD + 0.6 HO2 + 0.18 XO2N + 0.18 RO2	k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12	8
210	SQO2 + HO2 = 0.1 ISPD + 0.1 HO2 + 0.1 OH + 0.9 ROOH	k = 2.60E-13 exp(1300/T)	2.04E-11	8
211	SQO2 + RO2 = ISPD + 0.5 HO2 + RO2	k = k(ref)/K k(ref) = k(77) K = 2.00E+0	2.50E-13	8
212	SQT + O3 = 0.08 FORM + 0.87 ISPD + 0.17 H2O2 + 0.08 OH + 0.08 HO2 + 0.26 XO2N + 0.26 RO2	k = 1.20E-14	1.20E-14	8
213	SQT + NO3 = 0.24 NO2 + 0.76 NTR2 + 0.24 ISPD + 0.47 OH	k = 1.90E-11	1.90E-11	8
214	I2 = 2. I	Photolysis	1.44E-1	
215	HOI = I + OH	Photolysis	6.36E-2	
216	I + O3 = IO	k = 2.10E-11 exp(-830/T)	1.30E-12	
217	IO = I + O	Photolysis	1.18E-1	
218	IO + IO = 0.4 I + 0.4 OIO + 0.6 I2O2	k = 5.40E-11 exp(180/T)	9.88E-11	
219	IO + HO2 = HOI	k = 1.40E-11 exp(540/T)	8.57E-11	

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]	Comment
220	IO + NO = I + NO2	k = 7.15E-12 exp(300/T)	1.96E-11	
221	IO + NO2 = INO3	Falloff: F=0.4; n=1.26 k(0) = 7.70E-31 (T/300)^-5 k(inf) = 1.60E-11	3.54E-12	
222	OIO = I	Photolysis	1.41E-1	
223	OIO + OH = ~~HIO3~~0.5 IXOY	Falloff: F=0.3; n=1.41 k(0) = 1.50E-27 (T/300)^-3.93 k(inf) = 5.50E-10 exp(46/T)	3.96E-10	10
224	OIO + IO = IXOY	k = 1.00E-10	1.00E-10	
225	OIO + NO = IO + NO2	k = 1.10E-12 exp(542/T)	6.78E-12	
226	I2O2 = I + OIO	k = 1.00E+1	1.00E+1	
227	I2O2 ~~+ O3~~ = IXOY	k = ~~1~~3.00E-~~12~~1	~~1~~3.00E-~~12~~1	11
228	INO3 = I + NO3	Photolysis	1.25E-2	
229	INO3 + H2O = HOI + HNO3	k = 2.50E-22	2.50E-22	

Footnotes:
(a) Products O2, CO2 and H2O are not listed
(b) Pressure-dependent reactions with a rate constant described by a falloff expression don't have M as a reactant because the rate constant expression contains M
(c) k_{298} is the rate constant at 298 K and 1 atmosphere using units in molecules/cm^3 and 1/s
(d) For photolysis reactions k_{298} shows the photolysis rate at a solar zenith angle of 60° and height of 600 m MSL/AGL.

Key to Table 1 comments on mechanism updates from CB6r5 to CB7:

1. Reordered the reactants so that stable species are first, except that M is last, e.g., O2 + O + M rather than O + O2 + M
2. Updated products according to MCM v3.3.1
3. For reactions of CXO3, reduced the product yields to 50% when 1 of the 2 carbons in CXO3 is converted to CO2
4. Isoprene (ISOP) update, including update to OPAN (other PAN compounds)
5. RO2 reaction rate update
6. Correct error in GLY photolysis rate made in CB6r5
7. Alkane (PAR) and ketone (KET) update
8. Terpene update (APIN, TERP and SQT) includes adding hydroxyacetone (HACT)
9. Added aromatic hydroperoxides (ARPX)
10. Replaced HIO3 by IXOY and reduce yield to 50% because IXOY contains 2 I-atoms
11. Reformulated I2O2 conversion to aerosol (IXOY) as a unimolecular reaction while keeping the conversion rate comparable to the CB6 formulation
12. No change to the rate constant but the rate constant expression was revised, e.g., to account for new reaction ordering.

Table 2. Reactions in CB6r5 that aren’t in CB7.

Reactants and Products	**k_{298}**	**Comment**
C2O3 + CXO3 = MEO2 + ALD2 + XO2H + 2 RO2	1.55E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
CXO3 + CXO3 = 2 MEO2 + 2 RO2	1.55E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
XO2H + C2O3 = 0.8 HO2 + 0.8 MEO2 + 0.2 AACD + 0.8 RO2	1.6E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
XO2 + C2O3 = 0.8 MEO2 + 0.2 AACD + 0.8 RO2	1.6E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
XO2N + C2O3 = 0.8 HO2 + 0.8 MEO2 + 0.2 AACD + 0.8 RO2	1.6E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
ISO2 + C2O3 = 0.598 FORM + ISPD + 0.728 HO2 + 0.072 XO2H + 0.8 MEO2 + 0.2 AACD + 0.872 RO2	1.6E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
EPX2 + C2O3 = 0.22 GLYD + 0.22 GLY + 0.22 MGLY + 0.1 OH + 0.66 HO2 + 0.3 FORM + 0.2 CO + 1.74 PAR + 0.8 MEO2 + 0.2 AACD + 0.8 RO2	1.6E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
BZO2 + C2O3 = GLY + OPEN + HO2 + MEO2 + RO2	1.6E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
TO2 + C2O3 = 0.48 GLY + 0.52 MGLY + 0.77 OPEN + 0.23 XOPN + HO2 + MEO2 + RO2	1.6E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
XLO2 + C2O3 = 0.26 GLY + 0.77 MGLY + 0.35 OPEN + 0.65 XOPN + HO2 + MEO2 + RO2	1.6E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
OPO3 + C2O3 = MEO2 + XO2 + ALDX + 2 RO2	1.55E-11	Implicitly represented in CB7 by reactions of each reactant with RO2
FORM + HO2 = HCO3	7.9E-14	Not competitive with other reactions of FORM
HCO3 = FORM + HO2	1.51E2	Not needed when FORM + HO2 is deleted
HCO3 + NO = FACD + NO2 + HO2	5.6E-12	Not needed when FORM + HO2 is deleted
HCO3 + HO2 = 0.5 MEPX + 0.5 FACD + 0.2 OH + 0.2 HO2	1.26E-11	Not needed when FORM + HO2 is deleted
NO3 + O = NO2	1.7E-11	Not competitive with other reactions of NO3
NO3 + O3 = NO2	1.0E-17	Not competitive with other reactions of NO3
PANX = 0.6 NO2 + 0.6 CXO3 + 0.4 NO3 + 0.4 ALD2 + 0.4 XO2H + 0.4 RO2	3.47E-07	PANX photolysis not competitive with OH + PANX
NO + NO2 + H2O = 2 HONO	5.0E-40	Heterogeneous HONO formation should be represented explicitly rather than implicitly using this reaction
HONO + HONO = NO + NO2	1.0E-20	Only useful for modeling chamber experiments
ROR + NO2 = NTR1	3.29E-11	Not competitive with other reactions of ROR
ISPD + O3 = 0.04 ALD2 + 0.231 FORM + 0.531 MGLY + 0.17 GLY + 0.17 ACET + 0.543 CO + 0.461 OH + 0.15 FACD + 0.398 HO2 + 0.143 C2O3	1.02E-17	Not competitive with OH + ISPD

Reactants and Products	**k_{298}**	**Comment**
INTR = HNO3	1.4E-4	INTR heterogeneous reaction not competitive with OH + INTR

Table 3. The CB7 mechanism.

No.	**Reactants and Products** [a, b]	**Rate Constant Expression**	**k_{298}** [c, d]
1	NO2 = NO + O	Photolysis	6.30E-3
2	O2 + O + M = O3 + M	k = 6.00E-34 (T/300)^-2.6	6.11E-34
3	NO + O3 = NO2	k = 2.07E-12 exp(-1400/T)	1.89E-14
4	NO + O = NO2	Falloff: F=0.85; n=0.84 k(0) = 1.00E-31 (T/300)^-1.6 k(inf) = 5.00E-11 (T/300)^-0.3	2.26E-12
5	NO2 + O = NO	k = 5.10E-12 exp(198/T)	9.91E-12
6	NO2 + O = NO3	Falloff: F=0.6; n=1.03 k(0) = 1.30E-31 (T/300)^-1.5 k(inf) = 2.30E-11 (T/300)^0.24	2.09E-12
7	O3 + O =	k = 8.00E-12 exp(-2060/T)	7.96E-15
8	O3 = O	Photolysis	3.33E-4
9	O3 = O1D	Photolysis	8.78E-6
10	O1D + M = O + M	k = 2.23E-11 exp(115/T)	3.28E-11
11	O1D + H2O = 2 OH	k = 2.14E-10	2.14E-10
12	O3 + OH = HO2	k = 1.70E-12 exp(-940/T)	7.25E-14
13	O3 + HO2 = OH	k = 2.03E-16 (T/300)^4.57 exp(693/T)	2.01E-15
14	OH + O = HO2	k = 2.40E-11 exp(110/T)	3.47E-11
15	HO2 + O = OH	k = 3.00E-11 exp(200/T)	5.87E-11
16	OH + OH = O	k = 6.20E-14 (T/298)^2.6 exp(945/T)	1.48E-12
17	OH + OH = H2O2	Falloff: F=0.42; n=1.23 k(0) = 9.00E-31 (T/300)^-3.2 k(inf) = 3.90E-11 (T/300)^-0.47	6.21E-12
18	OH + HO2 =	k = 4.80E-11 exp(250/T)	1.11E-10
19	HO2 + HO2 = H2O2	k = k1 + k2 [M] k1 = 2.20E-13 exp(600/T) k2 = 1.90E-33 exp(980/T)	2.90E-12
20	HO2 + HO2 + H2O = H2O2	k = k1 + k2 [M] k1 = 3.08E-34 exp(2800/T) k2 = 2.66E-54 exp(3180/T)	6.53E-30
21	H2O2 = 2 OH	Photolysis	3.78E-6
22	H2O2 + OH = HO2	k = 1.80E-12	1.80E-12
23	H2O2 + O = OH + HO2	k = 1.40E-12 exp(-2000/T)	1.70E-15
24	NO + NO + O2 = 2 NO2	k = 4.25E-39 exp(664/T)	3.95E-38
25	NO + HO2 = OH + NO2	k = 3.45E-12 exp(270/T)	8.54E-12
26	NO2 + O3 = NO3	k = 1.40E-13 exp(-2470/T)	3.52E-17
27	NO3 = NO2 + O	Photolysis	1.56E-1

No.	**Reactants and Products** [a, b]	**Rate Constant Expression**	**k_{298}** [c, d]
28	NO3 = NO	Photolysis	1.98E-2
29	NO3 + NO = 2 NO2	k = 1.80E-11 exp(110/T)	2.60E-11
30	NO3 + NO2 = NO + NO2	k = 4.50E-14 exp(-1260/T)	6.56E-16
31	NO3 + OH = HO2 + NO2	k = 2.00E-11	2.00E-11
32	NO3 + HO2 = OH + NO2	k = 4.00E-12	4.00E-12
33	NO3 + NO3 = 2 NO2	k = 8.50E-13 exp(-2450/T)	2.28E-16
34	NO3 + NO2 = N2O5	Falloff: F=0.35; n=1.33 k(0) = 3.60E-30 (T/300)^-4.1 k(inf) = 1.90E-12 (T/300)^0.2	1.24E-12
35	N2O5 = NO3 + NO2	Falloff: F=0.35; n=1.33 k(0) = 1.30E-3 (T/300)^-3.5 exp(-11000/T) k(inf) = 9.70E+14 (T/300)^0.1 exp(-11080/T)	4.46E-2
36	N2O5 = NO2 + NO3	Photolysis	2.52E-5
37	N2O5 + H2O = 2 HNO3	k = 1.00E-22	1.00E-22
38	NO + OH = HONO	Falloff: F=0.81; n=0.87 k(0) = 7.40E-31 (T/300)^-2.4 k(inf) = 3.30E-11 (T/300)^-0.3	9.77E-12
39	HONO = NO + OH	Photolysis	1.04E-3
40	HONO + OH = NO2	k = 2.50E-12 exp(260/T)	5.98E-12
41	NO2 + OH = HNO3	Falloff: F=0.6; n=1 k(0) = 1.80E-30 (T/300)^-3 k(inf) = 2.80E-11	1.06E-11
42	NO2 + OH + H2O = HNO3 + H2O	k = 1.10E-30	1.10E-30
43	HNO3 + OH = NO3	k = k1 + k3 [M] / (1 + k3 [M] / k2) k1 = 2.40E-14 exp(460/T) k2 = 2.70E-17 exp(2199/T) k3 = 6.50E-34 exp(1335/T)	1.54E-13
44	HNO3 = OH + NO2	Photolysis	2.54E-7
45	NO2 + HO2 = PNA	Falloff: F=0.4; n=1.26 k(0) = 1.40E-31 (T/300)^-3.1 k(inf) = 4.00E-12	7.50E-13
46	PNA = HO2 + NO2	Falloff: F=0.4; n=1.26 k(0) = 4.10E-5 exp(-10650/T) k(inf) = 6.00E+15 exp(-11170/T)	6.20E-2
47	PNA = 0.59 HO2 + 0.59 NO2 + 0.41 OH + 0.41 NO3	Photolysis	2.36E-6
48	PNA + OH = NO2	k = 3.20E-13 exp(690/T)	3.24E-12
49	H2 + OH = HO2	k = 7.70E-12 exp(-2100/T)	6.70E-15
50	CO + OH = HO2	k = k1 + k2 [M] k1 = 1.44E-13 k2 = 3.43E-33	2.28E-13
51	SO2 + OH = SULF + HO2	Falloff: F=0.53; n=1.1 k(0) = 2.80E-31 (T/300)^-2.6 k(inf) = 2.00E-12	9.35E-13
52	SO2 = SULF	k = 0.00E+0	0.00E+0

No.	**Reactants and Products** [a, b]	**Rate Constant Expression**	**k_{298}** [c, d]
53	DMS + OH = SO2 + FORM + MEO2	k = 1.12E-11 exp(-250/T)	4.84E-12
54	DMS + OH + O2 = SULF + MEO2	k = 1.28E-37 exp(4480/T)	4.33E-31
55	DMS + NO3 = SO2 + FORM + MEO2 + HNO3	k = 1.90E-13 exp(520/T)	1.09E-12
56	C2O3 + NO = NO2 + MEO2 + RO2	k = 7.50E-12 exp(290/T)	1.98E-11
57	C2O3 + NO2 = PAN	Falloff: F=0.3; n=1.41 k(0) = 3.61E-28 (T/300)^-6.87 k(inf) = 1.24E-11 (T/300)^-1.105	9.86E-12
58	PAN = NO2 + C2O3	Falloff: F=0.3; n=1.41 k(0) = 1.10E-5 exp(-10100/T) k(inf) = 1.90E+17 exp(-14100/T)	4.31E-4
59	PAN = 0.6 NO2 + 0.6 C2O3 + 0.4 NO3 + 0.4 MEO2 + 0.4 RO2	Photolysis	3.47E-7
60	C2O3 + HO2 = 0.37 PACD + 0.13 AACD + 0.13 O3 + 0.5 OH + 0.5 MEO2 + 0.5 RO2	k = 3.14E-12 exp(580/T)	2.20E-11
61	C2O3 + RO2 = 0.3 AACD + 0.7 MEO2 + 1.7 RO2	k = 4.40E-13 exp(1070/T)	1.60E-11
62	C2O3 + C2O3 = 2 MEO2 + 2 RO2	k = 2.90E-12 exp(500/T)	1.55E-11
63	CXO3 + NO = NO2 + 0.5 ALD2 + XO2H + RO2	k = 6.70E-12 exp(340/T)	2.10E-11
64	CXO3 + NO2 = PANX	k = k(ref) K k(ref) = k(57) K = 1.19E+0	8.28E-12
65	PANX = NO2 + CXO3	k = k(ref) K k(ref) = k(58) K = 1.19E+0	3.62E-4
66	PANX + OH = 0.5 ALD2 + NO2	k = 3.00E-12	3.00E-12
67	CXO3 + HO2 = 0.19 PACD + 0.06 AACD + 0.25 ALD2 + 0.06 O3 + 0.25 OH + 0.25 HO2	k = k(ref) K k(ref) = k(60) K = 1.00E+0	2.20E-11
68	CXO3 + RO2 = 0.35 ALD2 + 0.15 AACD + 0.35 HO2 + RO2	k = k(ref) K k(ref) = k(61) K = 1.00E+0	1.60E-11
69	OPO3 + NO = NO2 + 0.5 GLY + 0.5 CO + 0.8 HO2 + 0.2 CXO3	k = k(ref) K k(ref) = k(63) K = 1.00E+0	2.10E-11
70	OPO3 + NO2 = OPAN	k = k(ref) K k(ref) = k(64) K = 1.00E+0	8.28E-12
71	OPAN = OPO3 + NO2	k = k(ref) K k(ref) = k(65) K = 1.00E+0	3.62E-4
72	OPAN + OH = 0.5 NO2 + 0.5 NTR2 + 0.5 GLY + CO	k = 3.60E-11	3.60E-11
73	OPO3 + HO2 = 0.37 PACD + 0.13 AACD + 0.13 O3 + 0.5 OH + 0.5 MEO2 + 0.5 RO2	k = k(ref) K k(ref) = k(60) K = 1.00E+0	2.20E-11

No.	**Reactants and Products** [a, b]	**Rate Constant Expression**	**k_{298}** [c, d]
74	OPO3 + RO2 = 0.7 ALDX + 0.3 AACD + 0.7 XO2H + 1.7 RO2	k = k(ref) K k(ref) = k(61) K = 1.00E+0	1.60E-11
75	RO2 + NO = NO	k = 2.70E-12 exp(360/T)	9.04E-12
76	RO2 + HO2 = HO2	k = 2.12E-13 exp(1300/T)	1.66E-11
77	RO2 + RO2 =	k = 1.55E-13 exp(350/T)	5.00E-13
78	MEO2 + NO = FORM + HO2 + NO2	k = 2.30E-12 exp(360/T)	7.70E-12
79	MEO2 + HO2 = 0.9 MEPX + 0.1 FORM	k = 3.80E-13 exp(780/T)	5.21E-12
80	MEO2 + C2O3 = FORM + 0.9 HO2 + 0.9 MEO2 + 0.1 AACD + 0.9 RO2	k = 2.00E-12 exp(500/T)	1.07E-11
81	MEO2 + RO2 = 0.685 FORM + 0.315 MEOH + 0.37 HO2 + RO2	k = k(ref) K k(ref) = k(77) K = 1.00E+0	5.00E-13
82	MEPX + OH = 0.6 MEO2 + 0.6 RO2 + 0.4 FORM + 0.4 OH	k = 5.30E-12 exp(190/T)	1.00E-11
83	MEPX = MEO2 + RO2 + OH	Photolysis	2.68E-6
84	XO2H + NO = NO2 + HO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
85	XO2H + HO2 = ROOH	k = 2.12E-13 exp(1300/T)	1.67E-11
86	XO2H + RO2 = 0.6 HO2 + RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
87	XO2 + NO = NO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
88	XO2 + HO2 = ROOH	k = k(ref) K k(ref) = k(85) K = 1.00E+0	1.67E-11
89	XO2 + RO2 = RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
90	XO2N + NO = 0.5 NTR1 + 0.5 NTR2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
91	XO2N + HO2 = ROOH	k = k(ref) K k(ref) = k(85) K = 1.00E+0	1.67E-11
92	XO2N + RO2 = RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
93	ROOH + OH = 0.56 XO2H + 0.04 XO2N + 0.6 RO2 + 0.4 OH	k = 5.30E-12 exp(190/T)	1.00E-11
94	ROOH = HO2 + OH	Photolysis	2.68E-6
95	NTR1 + OH = NO2	k = 2.00E-12	2.00E-12
96	NTR1 = NO2	Photolysis	1.06E-6
97	NTR2 = HNO3	k = 2.30E-5	2.30E-5

No.	**Reactants and Products** [a, b]	**Rate Constant Expression**	**k_{298}** [c, d]
98	MEOH + OH = FORM + HO2	k = 2.85E-12 exp(-345/T)	8.95E-13
99	ETOH + OH = 0.95 ALD2 + 0.9 HO2 + 0.1 XO2H + 0.1 RO2 + 0.078 FORM + 0.011 GLYD	k = 3.00E-12 exp(20/T)	3.21E-12
100	FORM + OH = HO2 + CO	k = 5.40E-12 exp(135/T)	8.49E-12
101	FORM = 2 HO2 + CO	Photolysis	1.69E-5
102	FORM = CO + H2	Photolysis	2.69E-5
103	FORM + NO3 = HNO3 + HO2 + CO	k = 5.50E-16	5.50E-16
104	ALD2 + OH = C2O3	k = 4.70E-12 exp(345/T)	1.50E-11
105	ALD2 + NO3 = C2O3 + HNO3	k = 1.40E-12 exp(-1860/T)	2.73E-15
106	ALD2 = MEO2 + RO2 + CO + HO2	Photolysis	1.96E-6
107	ALDX + OH = CXO3	k = 4.90E-12 exp(405/T)	1.91E-11
108	ALDX + NO3 = CXO3 + HNO3	k = 6.30E-15	6.30E-15
109	ALDX = ALD2 + XO2H + RO2 + CO + HO2	Photolysis	2.62E-5
110	GLYD + OH = 0.2 GLY + 0.2 HO2 + 0.8 C2O3	k = 8.00E-12	8.00E-12
111	GLYD = 0.74 FORM + 0.89 CO + 1.4 HO2 + 0.15 MEOH + 0.19 OH + 0.11 GLY + 0.11 XO2H + 0.11 RO2	Photolysis	2.76E-6
112	GLYD + NO3 = HNO3 + C2O3	k = k(ref) K k(ref) = k(105) K = 1.00E+0	2.73E-15
113	GLY + OH = 1.8 CO + 0.2 XO2 + 0.2 RO2 + HO2	k = 3.10E-12 exp(340/T)	9.70E-12
114	GLY = 2 HO2 + 2 CO	Photolysis	7.95E-5
115	GLY + NO3 = HNO3 + 1.5 CO + 0.5 XO2 + 0.5 RO2 + HO2	k = 4.00E-16	4.00E-16
116	MGLY = C2O3 + HO2 + CO	Photolysis	1.46E-4
117	MGLY + NO3 = HNO3 + C2O3 + XO2 + RO2	k = 5.00E-16	5.00E-16
118	MGLY + OH = C2O3 + CO	k = 1.90E-12 exp(575/T)	1.31E-11
119	ACET = 0.38 CO + 1.38 MEO2 + 1.38 RO2 + 0.62 C2O3	Photolysis	2.08E-7
120	ACET + OH = FORM + C2O3 + XO2 + RO2	k = 1.41E-12 exp(-620.6/T)	1.76E-13
121	KET = 0.15 FORM + 0.58 ALD2 + 0.34 ALDX + 0.96 HO2 + 0.7 C2O3 + 0.3 CXO3 + 1.3 XO2 + 0.03 XO2N + 1.33 RO2 - 3. PAR	Photolysis	2.27E-7
122	KET + OH = 0.06 KET + 0.15 FORM + 0.29 ALD2 + 0.46 ALDX + 0.61 HO2 + 0.27 C2O3 + 0.06 CXO3 + 0.72 XO2 + 0.04 XO2N + 0.76 RO2 - 1.38 PAR	k = 1.00E-12	1.00E-12
123	HACT + OH = MGLY + HO2	k = 2.00E-12 exp(320/T)	5.85E-12
124	FACD + OH = HO2	k = 4.50E-13	4.50E-13
125	AACD + OH = MEO2 + RO2	k = 4.00E-14 exp(850/T)	6.93E-13

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]
126	PACD + OH = C2O3	k = 5.30E-12 exp(190/T)	1.00E-11
127	CH4 + OH = MEO2 + RO2	k = 1.85E-12 exp(-1690/T)	6.37E-15
128	ECH4 + OH = MEO2 + RO2	k = 1.85E-12 exp(-1690/T)	6.37E-15
129	ETHA + OH = 0.991 ALD2 + 0.991 XO2H + 0.009 XO2N + RO2	k = 6.90E-12 exp(-1000/T)	2.41E-13
130	PRPA + OH = XPRP	k = 7.60E-12 exp(-585/T)	1.07E-12
131	XPRP = XO2N + RO2	Falloff: F=0.41; n=1 k(0) = 2.37E-21 k(inf) = 4.30E-1 (T/298)^-8	3.09E-2
132	XPRP = 0.732 ACET + 0.268 ALDX + 0.268 PAR + XO2H + RO2	k = 1.00E+0	1.00E+0
133	PAR + OH = XPAR	k = 3.09E-13 (T/300)^2 exp(300/T)	8.34E-13
134	XPAR = XO2N + RO2 - 3. PAR	Falloff: F=0.41; n=1 k(0) = 4.81E-20 k(inf) = 4.30E-1 (T/298)^-8	1.49E-1
135	XPAR = 0.87 ROR + 0.13 ALDX + 0.13 XO2H + 0.13 RO2 - 0.13 PAR	k = 1.00E+0	1.00E+0
136	ROR = 0.32 ACET + 0.3 KET + 0.04 FORM + 0.46 ALD2 + 0.1 ALDX + 0.62 HO2 + 0.11 MEO2 + 1.75 XO2 + 0.25 XO2H + 0.02 XO2N + 2.13 RO2 - 1.63 PAR	k = k1 + k2 [M] k1 = 2.40E+12 exp(-5000/T) k2 = 5.00E-15 exp(-250/T)	1.77E+5
137	ROR + O2 = 0.15 ACET + 0.85 KET + HO2 - 0.3 PAR	k = 2.00E-14 exp(-250/T)	8.64E-15
138	ETHY + OH = 0.7 GLY + 0.7 OH + 0.3 FACD + 0.3 CO + 0.3 HO2	Falloff: F=0.37; n=1.3 k(0) = 5.00E-30 (T/300)^-1.5 k(inf) = 1.00E-12	7.52E-13
139	ETH + OH = XO2H + RO2 + 1.56 FORM + 0.22 GLYD	Falloff: F=0.48; n=1.15 k(0) = 8.60E-29 (T/300)^-3.1 k(inf) = 9.00E-12 (T/300)^-0.85	7.84E-12
140	ETH + O3 = FORM + 0.35 CO + 0.27 HO2 + 0.17 OH + 0.42 FACD	k = 6.82E-15 exp(-2500/T)	1.55E-18
141	ETH + NO3 = 0.5 NO2 + 0.5 NTR1 + 0.5 XO2H + 0.5 XO2 + RO2 + 1.125 FORM	k = 3.30E-12 exp(-2880/T)	2.10E-16
142	OLE + OH = 0.781 FORM + 0.488 ALD2 + 0.488 ALDX + 0.976 XO2H + 0.195 XO2 + 0.024 XO2N + 1.195 RO2 - 0.73 PAR	Falloff: F=0.5; n=1.13 k(0) = 8.00E-27 (T/300)^-3.5 k(inf) = 3.00E-11 (T/300)^-1	2.86E-11
143	OLE + O3 = 0.295 ALD2 + 0.555 FORM + 0.27 ALDX + 0.15 XO2H + 0.15 RO2 + 0.334 OH + 0.08 HO2 + 0.378 CO + 0.075 GLY + 0.075 MGLY + 0.09 FACD + 0.13 AACD + 0.04 H2O2 - 0.79 PAR	k = 5.50E-15 exp(-1880/T)	1.00E-17
144	OLE + NO3 = 0.5 NO2 + 0.5 NTR1 + 0.48 XO2 + 0.48 XO2H + 0.04 XO2N + RO2 + 0.5 FORM + 0.25 ALD2 + 0.375 ALDX - 1 PAR	k = 4.60E-13 exp(-1155/T)	9.54E-15
145	IOLE + OH = 1.3 ALD2 + 0.7 ALDX + XO2H + RO2	k = 1.05E-11 exp(519/T)	5.99E-11

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]
146	IOLE + O3 = 0.732 ALD2 + 0.442 ALDX + 0.128 FORM + 0.245 CO + 0.5 OH + 0.3 XO2H + 0.3 RO2 + 0.24 GLY + 0.06 MGLY + 0.29 PAR + 0.08 AACD + 0.08 H2O2	k = 4.70E-15 exp(-1013/T)	1.57E-16
147	IOLE + NO3 = 0.5 NO2 + 0.5 NTR1 + 0.48 XO2 + 0.48 XO2H + 0.04 XO2N + RO2 + 0.5 ALD2 + 0.625 ALDX + PAR	k = 3.70E-13	3.70E-13
148	BENZ + OH = 0.53 CRES + 0.352 BZO2 + 0.352 RO2 + 0.118 OPEN + 0.118 OH + 0.53 HO2	k = 2.30E-12 exp(-190/T)	1.22E-12
149	BZO2 + NO = 0.918 NO2 + 0.082 NTR2 + 0.918 GLY + 0.918 OPEN + 0.918 HO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
150	BZO2 + HO2 = ARPX	k = 2.24E-13 exp(1300/T)	1.76E-11
151	BZO2 + RO2 = GLY + OPEN + HO2 + RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
152	TOL + OH = 0.18 CRES + 0.65 TO2 + 0.72 RO2 + 0.1 OPEN + 0.1 OH + 0.07 XO2H + 0.18 HO2	k = 1.80E-12 exp(340/T)	5.63E-12
153	TO2 + NO = 0.86 NO2 + 0.14 NTR2 + 0.417 GLY + 0.443 MGLY + 0.66 OPEN + 0.2 XOPN + 0.86 HO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
154	TO2 + HO2 = ARPX	k = 2.39E-13 exp(1300/T)	1.87E-11
155	TO2 + RO2 = 0.48 GLY + 0.52 MGLY + 0.77 OPEN + 0.23 XOPN + HO2 + RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
156	XYL + OH = 0.155 CRES + 0.544 XLO2 + 0.602 RO2 + 0.244 XOPN + 0.244 OH + 0.058 XO2H + 0.155 HO2	k = 1.85E-11	1.85E-11
157	XLO2 + NO = 0.86 NO2 + 0.14 NTR2 + 0.221 GLY + 0.675 MGLY + 0.3 OPEN + 0.56 XOPN + 0.86 HO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
158	XLO2 + HO2 = ARPX	k = 2.50E-13 exp(1300/T)	1.96E-11
159	XLO2 + RO2 = 0.26 GLY + 0.77 MGLY + 0.35 OPEN + 0.65 XOPN + HO2 + RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
160	OPEN = OPO3 + HO2 + CO	Photolysis	5.04E-4
161	OPEN + OH = 0.6 OPO3 + 0.4 XO2H + 0.4 RO2 + 0.4 GLY	k = 4.40E-11	4.40E-11
162	OPEN + O3 = 1.4 GLY + 0.24 MGLY + 0.5 OH + 0.12 C2O3 + 0.08 FORM + 0.02 ALD2 + 1.98 CO + 0.56 HO2	k = 5.40E-17 exp(-500/T)	1.01E-17
163	OPEN + NO3 = OPO3 + HNO3	k = 3.80E-12	3.80E-12
164	XOPN = 0.4 GLY + XO2H + 0.7 HO2 + 0.7 CO + 0.3 C2O3	Photolysis	5.04E-4
165	XOPN + OH = MGLY + 0.4 GLY + 2 XO2H + 2 RO2	k = 9.00E-11	9.00E-11

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]
166	XOPN + O3 = 1.2 MGLY + 0.5 OH + 0.6 C2O3 + 0.1 ALD2 + 0.5 CO + 0.3 XO2H + 0.3 RO2	k = 1.08E-16 exp(-500/T)	2.02E-17
167	XOPN + NO3 = 0.5 NO2 + 0.5 NTR2 + 0.45 XO2H + 0.45 XO2 + 0.1 XO2N + RO2 + 0.25 OPEN + 0.25 MGLY	k = 3.00E-12	3.00E-12
168	CRES + OH = 0.025 GLY + 0.025 OPEN + HO2 + 0.2 CRO + 0.732 CAT1 + 0.02 XO2N + 0.02 RO2	k = 1.70E-12 exp(950/T)	4.12E-11
169	CRES + NO3 = 0.3 CRO + HNO3 + 0.48 XO2 + 0.12 XO2H + 0.24 GLY + 0.24 MGLY + 0.48 OPO3 + 0.1 XO2N + 0.7 RO2	k = 1.40E-11	1.40E-11
170	CRO + NO2 = CRON	k = 2.10E-12	2.10E-12
171	CRO + HO2 = CRES	k = 5.50E-12	5.50E-12
172	CRON + OH = NTR2 + 0.5 CRO	k = 1.53E-12	1.53E-12
173	CRON + NO3 = NTR2 + 0.5 CRO + HNO3	k = 3.80E-12	3.80E-12
174	CRON = HONO + HO2 + FORM + OPEN	Photolysis	9.45E-5
175	CAT1 + OH = 0.14 FORM + 0.2 HO2 + 0.5 CRO	k = 5.00E-11	5.00E-11
176	CAT1 + NO3 = CRO + HNO3	k = 1.70E-10	1.70E-10
177	ARPX + OH = 0.5 OH + 0.2 BZO2 + 0.15 TO2 + 0.15 XLO2 + 0.5 RO2	k = 8.00E-11	8.00E-11
178	ISOP + OH = ISO2 + RO2	k = 2.70E-11 exp(390/T)	9.99E-11
179	ISO2 + NO = 0.9 NO2 + 0.1 INTR + 0.9 FORM + 0.9 ISPD + 0.9 HO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
180	ISO2 + HO2 = 0.94 ISPX + 0.06 FORM + 0.06 ISPD + 0.06 OH + 0.06 HO2	k = 2.12E-13 exp(1300/T)	1.66E-11
181	ISO2 + RO2 = ISPD + RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
182	ISO2 = 0.4 HPLD + 0.1 ISPD + 0.1 GLY + 0.1 GLYD + CO + 1.7 OH + 0.35 HO2	k = 3.30E+9 exp(-8300/T)	2.64E-3
183	ISOP + O3 = 0.8 FORM + 0.5 ISPD + 0.58 FACD + 0.5 CO + 0.28 OH + 0.5 HO2 + 0.4 MEO2 + 0.4 RO2	k = 1.03E-14 exp(-1995/T)	1.27E-17
184	ISOP + NO3 = 0.25 NO2 + 0.75 NTR2 + 0.25 FORM + 0.25 ISPD + 0.25 OH + 0.25 XO2 + 0.25 RO2	k = 2.95E-12 exp(-450/T)	6.52E-13
185	ISPD + OH = 0.4 MGLY + 0.2 GLYD + 0.1 FORM + CO + 0.1 OH + 0.1 HO2 + 0.1 OPO3 + 0.4 C2O3	k = 7.00E-12 exp(430/T)	2.96E-11
186	ISPD + NO3 = 0.9 NTR2 + 0.1 HNO3 + 0.1 CO + 0.1 C2O3	k = 3.94E-14 exp(475/T)	1.94E-13
187	ISPD = 0.8 ISPD + 0.15 MGLY + 0.1 GLYD + 0.1 FORM + 0.2 OH	Photolysis	1.60E-5

No.	**Reactants and Products** [a, b]	**Rate Constant Expression**	**k_{298}** [c, d]
188	ISPX + OH = 0.6 EPOX + 0.2 MGLY + 0.2 FORM + 0.2 ROOH + OH + 0.5 HO2	k = 2.80E-11 exp(370/T)	9.69E-11
189	HPLD = 0.6 HPLD + 0.3 ISPD + 1.65 OH + 0.2 HO2 + 0.8 CO	Photolysis	4.41E-4
190	HPLD + OH = ISPD + 0.2 HCHO + 0.5 CO + 1.1 OH	k = 1.17E-11 exp(450/T)	5.30E-11
191	EPOX + OH = 0.2 ISPD + 0.2 HO2 + 0.8 EPX2 + 0.8 RO2	k = 5.43E-11 exp(-450/T)	1.20E-11
192	EPX2 + NO = 0.98 NO2 + 0.02 NTR2 + 0.7 MGLY + 0.7 GLYD + 0.2 GLY + 0.2 CO + 0.2 ISPD + 0.7 OH + HO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
193	EPX2 + HO2 = 0.3 ISPD + 0.3 MGLY + 0.1 GLY + 0.2 GLYD + 1.5 FORM + ROOH + 0.2 CO + 1.7 OH + HO2	k = 2.38E-13 exp(1300/T)	1.87E-11
194	EPX2 + RO2 = 0.6 MGLY + 0.5 GLY + 0.5 FORM + 0.3 GLYD + 0.1 ISPD + 0.2 CO + 0.85 OH + HO2 + RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
195	INTR + OH = 0.5 NO2 + 0.4 NTR2 + 0.1 INTR + 0.4 ISPD + 0.1 EPOX	k = 1.34E-11 exp(410/T)	5.30E-11
196	APIN + OH = APO2	k = 1.00E-11 exp(300/T)	2.74E-11
197	APO2 + NO = 0.77 NO2 + 0.23 NTR2 + 0.21 FORM + 0.09 ACET + 0.62 ISPD + 0.77 HO2 + 0.11 ROOH + 0.19 XO2N + 0.19 RO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
198	APO2 + HO2 = 0.08 FORM + 0.06 ACET + 0.35 ISPD + 0.48 HO2 + 0.35 OH + 0.65 ROOH	k = 2.60E-13 exp(1300/T)	2.04E-11
199	APO2 + RO2 = 0.06 ACET + 0.87 ISPD + 0.5 HO2 + 0.13 ROOH + RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
200	APIN + O3 = 0.27 FORM + 0.22 ISPD + 0.22 H2O2 + 0.17 CO + 0.77 OH + 0.17 HO2 + 0.33 XO2 + 0.07 XO2N + 0.27 OPO3 + 0.4 RO2	k = 8.22E-16 exp(-640/T)	9.60E-17
201	APIN + NO3 = 0.7 NO2 + 0.3 NTR2 + 0.7 ISPD + 0.7 OH + 0.7 HO2	k = 1.20E-12 exp(490/T)	6.21E-12
202	TERP + OH = TPO2	k = 4.07E-11 exp(350/T)	1.32E-10
203	TPO2 + NO = 0.75 NO2 + 0.26 NTR2 + 0.43 FORM + 0.12 ACET + 0.63 ISPD + 0.75 HO2 + 0.19 XO2N + 0.19 RO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
204	TPO2 + HO2 = 0.04 FORM + 0.01 ACET + 0.07 ISPD + 0.07 HO2 + 0.07 OH + 0.94 ROOH	k = 2.60E-13 exp(1300/T)	2.04E-11
205	TPO2 + RO2 = 0.27 FORM + 0.04 ACET + ISPD + 0.5 HO2 + RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
206	TERP + O3 = 0.59 FORM + 0.06 ACET + 0.05 HACT + 0.25 ISPD + 0.24 H2O2 + 0.47 OH + 0.16 HO2 + 0.04 FACD +	k = 4.46E-15 exp(-960/T)	1.78E-16

No.	Reactants and Products [a, b]	Rate Constant Expression	k_{298} [c, d]
	0.06 XO2 + 0.07 XO2N + 0.25 C2O3 + 0.4 OPO3 + 0.13 RO2		
207	TERP + NO3 = 0.3 NO2 + 0.7 NTR2 + 0.12 ACET + 0.3 ISPD + 0.48 OH + 0.3 HO2	k = 7.00E-12	7.00E-12
208	SQT + OH = SQO2	k = 2.00E-10	2.00E-10
209	SQO2 + NO = 0.6 NO2 + 0.4 NTR2 + 0.6 ISPD + 0.6 HO2 + 0.18 XO2N + 0.18 RO2	k = k(ref) K k(ref) = k(75) K = 1.00E+0	9.04E-12
210	SQO2 + HO2 = 0.1 ISPD + 0.1 HO2 + 0.1 OH + 0.9 ROOH	k = 2.60E-13 exp(1300/T)	2.04E-11
211	SQO2 + RO2 = ISPD + 0.5 HO2 + RO2	k = k(ref) K k(ref) = k(77) K = 2.00E+0	2.50E-13
212	SQT + O3 = 0.08 FORM + 0.87 ISPD + 0.17 H2O2 + 0.08 OH + 0.08 HO2 + 0.26 XO2N + 0.26 RO2	k = 1.20E-14	1.20E-14
213	SQT + NO3 = 0.24 NO2 + 0.76 NTR2 + 0.24 ISPD + 0.47 OH	k = 1.90E-11	1.90E-11
214	I2 = 2 I	Photolysis	1.44E-1
215	HOI = I + OH	Photolysis	6.36E-2
216	I + O3 = IO	k = 2.10E-11 exp(-830/T)	1.30E-12
217	IO = I + O	Photolysis	1.18E-1
218	IO + IO = 0.4 I + 0.4 OIO + 0.6 I2O2	k = 5.40E-11 exp(180/T)	9.88E-11
219	IO + HO2 = HOI	k = 1.40E-11 exp(540/T)	8.57E-11
220	IO + NO = I + NO2	k = 7.15E-12 exp(300/T)	1.96E-11
221	IO + NO2 = INO3	Falloff: F=0.4; n=1.26 k(0) = 7.70E-31 (T/300)^-5 k(inf) = 1.60E-11	3.54E-12
222	OIO = I	Photolysis	1.41E-1
223	OIO + OH = 0.5 IXOY	Falloff: F=0.3; n=1.41 k(0) = 1.50E-27 (T/300)^-3.93 k(inf) = 5.50E-10 exp(46/T)	3.96E-10
224	OIO + IO = IXOY	k = 1.00E-10	1.00E-10
225	OIO + NO = IO + NO2	k = 1.10E-12 exp(542/T)	6.78E-12
226	I2O2 = I + OIO	k = 1.00E+1	1.00E+1
227	I2O2 = IXOY	k = 3.00E-1	3.00E-1
228	INO3 = I + NO3	Photolysis	1.25E-2
229	INO3 + H2O = HOI + HNO3	k = 2.50E-22	2.50E-22

Notes:
(a) Products O2, CO2 and H2O are not listed
(b) Pressure-dependent reactions with a rate constant described by a falloff expression don't have M as a reactant because the rate constant expression contains M
(c) k_{298} is the rate constant at 298 K and 1 atmosphere using units in molecules/cm^3 and 1/s
(d) For photolysis reactions k_{298} shows the photolysis rate at a solar zenith angle of 60° and height of 600 m MSL/AGL.

Table 4. CB7 model species names and molecular weights.

Name	Description	C	H	O	N	S	I	M Wt
APO2	Peroxy radical from OH addition to α-pinene	10	17	3				185.2
BZO2	Peroxy radical from OH addition to benzene	6	7	5				159.1
C2O3	Acetylperoxy radical	2	3	3				75.0
CRO	Alkoxy radical from cresol	7	7	1				107.1
CXO3	C3 and higher acylperoxy radicals	3	5	3				89.0
EPX2	Peroxy radical from EPOX reaction with OH	5	9	5				149.1
HO2	Hydroperoxy radical		1	2				33.0
ISO2	Peroxy radical from OH addition to isoprene	5	9	3				117.1
MEO2	Methylperoxy radical	1	3	2				47.0
NO3	Nitrate radical			3	1			62.0
O	Oxygen atom in the $O^3(P)$ electronic state			1				16.0
O1D	Oxygen atom in the $O^1(D)$ electronic state			1				16.0
OH	Hydroxyl radical		1	1				17.0
OPO3	Peroxyacyl radical from OPEN	4	3	4				115.0
RO2	Operator to approximate total peroxy radical concentration	4	7	2				87.1
ROR	Secondary alkoxy radical	4	7	1				71.1
TPO2	Peroxy radical from OH addition to TERP	10	17	3				185.2
TO2	Peroxy radical from OH addition to TOL	7	9	5				173.1
SQO2	Peroxy radical from OH addition to SQT	15	25	3				253.3
XLO2	Peroxy radical from OH addition to XYL	8	11	5				187.1
XO2	NO to NO2 conversion from alkylperoxy (RO2) radical	4	7	2				87.1
XO2H	NO to NO2 conversion (XO2) accompanied by HO2 production	4	7	2				87.1
XO2N	NO to organic nitrate conversion from RO2 radical	4	7	2				87.1
AACD	Acetic acid	2	4	2				60.0
ACET	Acetone	3	6	1				58.1
ALD2	Acetaldehyde	2	4	1				44.0
ALDX	Propionaldehyde and higher aldehydes	3	6	1				58.1
APIN	α-Pinene	10	16					136.2
BENZ	Benzene	6	6					78.1
CAT1	Methyl-catechols	7	8	2				124.1
CO	Carbon monoxide	1		1				28.0
CH4	Methane	1	4					16.0
CRES	Cresols	7	8	1				108.1
CRON	Nitro-cresols	7	7	3	1			153.1

Name	**Description**	**C**	**H**	**O**	**N**	**S**	**I**	**M Wt**
EPOX	Epoxide formed from ISPX reaction with OH	5	10	3				118.1
ETH	Ethene	2	4					28.0
ETHA	Ethane	2	6					30.1
ETHY	Ethyne	2	2					26.0
ETOH	Ethanol	2	6	1				46.1
FACD	Formic acid	1	2	2				46.0
FORM	Formaldehyde	1	2	1				30.0
GLY	Glyoxal	2	2	2				58.0
GLYD	Glycolaldehyde	2	4	2				60.0
H2O2	Hydrogen peroxide		2	2				34.0
HACT	Hydroxyacetone	3	6	2				74.1
HNO3	Nitric acid		1	3	1			63.0
HONO	Nitrous acid		1	2	1			47.0
HPLD	hydroperoxyaldehyde	5	8	3				116.1
INTR	Organic nitrates from ISO2 reaction with NO	5	9	4	1			147.1
IOLE	Internal olefin carbon bond (R-C=C-R)	4	8					56.1
ISOP	Isoprene	5	8					68.1
ISPD	Isoprene product (lumped methacrolein, methyl vinyl ketone, etc.)	4	6	1				70.1
ISPX	Hydroperoxides from ISO2 reaction with HO2	5	10	3				118.1
KET	Ketone carbon bond (C=O)	4	8	1				72.1
MEOH	Methanol	1	4	1				32.0
MEPX	Methylhydroperoxide	1	4	2				48.0
MGLY	Methylglyoxal	3	4	2				72.0
N2O5	Dinitrogen pentoxide			5	2			108.0
NO	Nitric oxide			1	1			30.0
NO2	Nitrogen dioxide			2	1			46.0
O3	Ozone			3				48.0
OLE	Terminal olefin carbon bond (R-C=C)	3	6					42.1
OPAN	Peroxyacyl nitrate (PAN compound) from OPO3	4	3	6	1			161.0
OPEN	Aromatic ring opening product (unsaturated dicarbonyl)	4	4	2				84.0
PACD	Peroxyacetic and higher peroxycarboxylic acids	2	4	3				76.0
PAN	Peroxyacetyl Nitrate	2	3	5	1			121.0
PANX	C3 and higher peroxyacyl nitrate	3	5	5	1			135.0
PAR	Paraffin carbon bond (C-C)	5	12					72.1
PNA	Peroxynitric acid		1	4	1			79.0
PRPA	Propane	3	8					44.1

Name	Description	C	H	O	N	S	I	M Wt
ROOH	Higher organic peroxide	4	10	2				90.1
SO2	Sulfur dioxide			2		1		64.0
SULF	Sulfuric acid (gaseous)		2	4		1		98.0
SQT	Sesquiterpenes	15	24					204.3
TERP	Monoterpenes	10	16					136.2
TOL	Toluene and other monoalkyl aromatics	7	8					92.1
XOPN	Aromatic ring opening product (unsaturated dicarbonyl)	5	6	2				98.1
XYL	Xylene and other polyalkyl aromatics	8	10					106.2
ARPX	Aromatic peroxide from BZO2, TO2 and XLO2	6	8	6				176.1
NTR1	Simple organic nitrates	4	9	3	1			119.1
NTR2	Multi-functional organic nitrates	4	9	4	1			135.1
ECH4	Emitted methane (to enable tracking seperate from CH4)	1	4					16.0
XPRP	Operator for organic nitrates from PRPA	3	7	2				75.1
XPAR	Operator for organic nitrates from PAR	5	11	2				103.1
I2	Molecular iodine						2	253.8
I	Iodine atom						1	126.9
IO	Iodine monoxide			1			1	142.9
OIO	Iodine dioxide			2			1	158.9
I2O2	Diiodine dioxide			2			2	285.8
IXOY	Condensable iodine oxides			3			2	301.8
HOI	Hypoiodous acid		1	1			1	143.9
INO3	Iodine nitrate			3	1		1	188.9
DMS	Dimethyl sulfide	2	6			1		62.1

Table 5. Zenith angle dependence of photolysis rates (s^{-1}) for CB7 reactions.

No.	Zenith Angle 0 Degrees	Zenith Angle 20 Degrees	Zenith Angle 40 Degrees	Zenith Angle 60 Degrees	Zenith Angle 78 Degrees	Zenith Angle 86 Degrees
1	1.01E-02	9.77E-03	8.75E-03	6.30E-03	2.09E-03	5.12E-04
8	4.26E-04	4.19E-04	3.94E-04	3.33E-04	1.79E-04	4.27E-05
9	4.55E-05	3.99E-05	2.54E-05	8.78E-06	9.20E-07	1.52E-07
21	8.79E-06	8.26E-06	6.64E-06	3.78E-06	8.81E-07	2.03E-07
27	1.88E-01	1.86E-01	1.79E-01	1.56E-01	8.22E-02	1.79E-02
28	2.32E-02	2.31E-02	2.23E-02	1.98E-02	1.12E-02	2.63E-03
36	5.54E-05	5.23E-05	4.26E-05	2.52E-05	6.30E-06	1.48E-06
39	1.74E-03	1.68E-03	1.49E-03	1.04E-03	3.29E-04	8.35E-05

No.	Zenith Angle 0 Degrees	Zenith Angle 20 Degrees	Zenith Angle 40 Degrees	Zenith Angle 60 Degrees	Zenith Angle 78 Degrees	Zenith Angle 86 Degrees
44	8.47E-07	7.70E-07	5.57E-07	2.54E-07	4.20E-08	7.98E-09
47	7.02E-06	6.46E-06	4.84E-06	2.36E-06	4.16E-07	7.73E-08
59	9.53E-07	8.81E-07	6.72E-07	3.47E-07	7.05E-08	1.52E-08
83	6.02E-06	5.68E-06	4.61E-06	2.68E-06	6.52E-07	1.53E-07
94	3.29E-06	3.01E-06	2.22E-06	1.06E-06	1.85E-07	3.60E-08
96	4.16E-05	3.90E-05	3.10E-05	1.69E-05	3.55E-06	7.35E-07
101	5.43E-05	5.18E-05	4.35E-05	2.69E-05	7.06E-06	1.73E-06
102	7.29E-06	6.59E-06	4.65E-06	1.96E-06	2.54E-07	3.93E-08
106	6.88E-05	6.41E-05	4.99E-05	2.62E-05	5.17E-06	1.04E-06
109	9.03E-06	8.24E-06	6.01E-06	2.76E-06	4.40E-07	7.94E-08
111	1.35E-04	1.30E-04	1.14E-04	7.95E-05	2.57E-05	6.08E-06
114	2.36E-04	2.29E-04	2.04E-04	1.46E-04	4.92E-05	1.16E-05
116	1.16E-06	1.02E-06	6.50E-07	2.27E-07	2.34E-08	3.59E-09
119	1.02E-06	9.02E-07	5.83E-07	2.08E-07	2.25E-08	3.51E-09
121	2.96E-05	2.84E-05	2.45E-05	1.60E-05	4.60E-06	1.16E-06
160	6.02E-06	5.68E-06	4.61E-06	2.68E-06	6.52E-07	1.53E-07
164	7.04E-04	6.84E-04	6.12E-04	4.41E-04	1.46E-04	3.58E-05
174	1.51E-04	1.47E-04	1.31E-04	9.45E-05	3.13E-05	7.68E-06
187	8.04E-04	7.82E-04	7.00E-04	5.04E-04	1.67E-04	4.09E-05
189	8.04E-04	7.82E-04	7.00E-04	5.04E-04	1.67E-04	4.09E-05
214	1.73E-01	1.72E-01	1.65E-01	1.44E-01	7.58E-02	1.65E-02
215	1.02E-01	9.87E-02	8.84E-02	6.36E-02	2.11E-02	5.17E-03
217	1.88E-01	1.83E-01	1.64E-01	1.18E-01	3.91E-02	9.57E-03
222	1.71E-01	1.69E-01	1.62E-01	1.41E-01	7.46E-02	1.63E-02
228	2.51E-02	2.40E-02	2.01E-02	1.25E-02	3.27E-03	8.00E-04

Notes:
(a) Photolysis rates at an altitude of 600 m MSL/AGL with surface albedo of 0.04 and stratospheric O_3 column of 300 Dobson Units.

MODEL SETUP AND EMISSION SENSITIVITY TESTS

1.9 CAMx Setup

We used CAMx version 7.1 to simulate O_3 formation in Texas during June 2012, a period of elevated O_3 throughout much of Texas. The CAMx model options are summarized in Table 6. Two weeks at the end of May were used as the spin-up days for the simulation (i.e., starting May 16th). Input data were developed by the TCEQ for the State Implementation Plan (SIP) to attain the 8-h O_3 standard in Houston-Galveston-Brazoria (TCEQ, 2016; TCEQ, 2019). The modeling domain has a 36-km grid covering the continental U.S. (CONUS) and parts of Canada and Mexico, a 12-km grid covering Texas and parts of adjacent states, and a large 4-km grid covering eastern Texas and part of Louisiana (Figure 2). The Weather Research and Forecasting (WRF) model version 3.7.1 (Skamarock et al., 2008) was used to develop the meteorological inputs for CAMx. Nopmongcol et al. (2016) prepared initial concentrations and boundary conditions for the 36-km grid using the Goddard Earth Observing System Chemistry (GEOS-Chem) global model v10-01 with updated iodine reactions.

Table 6. CAMx model options

Science Options	**CAMx Base Case setup**
Version	Version 7.1
Time Zone	Central Standard Time
Vertical Grid Mesh	29 Layers with 34 m deep surface layer and 15 layers in the lowest 1.6 km (TCEQ's CAMx 2012 vertical layer structure)
Horizontal Grids	Two-way grid nesting with spacings of 36 km, 12 km, and 4 km
Meteorology	TCEQ's 2012 WRF meteorology
Chemistry Mechanism	CB7 or CB6r5 gas-phase mechanism
Chemistry Solver	Euler Backward Iterative (EBI)
Photolysis Rates	TUV version 4.8 with TOMS stratospheric O_3 column adjustment and in-line adjustment for clouds
Advection Scheme	Piecewise Parabolic Method (PPM)
Planetary Boundary Layer (PBL) mixing	K-theory with CMAQ Kv and KV100 patch to enhance vertical mixing over urban areas within the lowest 100 m
In-line Ix Emissions On	Inorganic iodine (Ix) emissions computed from saltwater masks
Parallelization	MPI (8 threads) and OMP (3 threads)

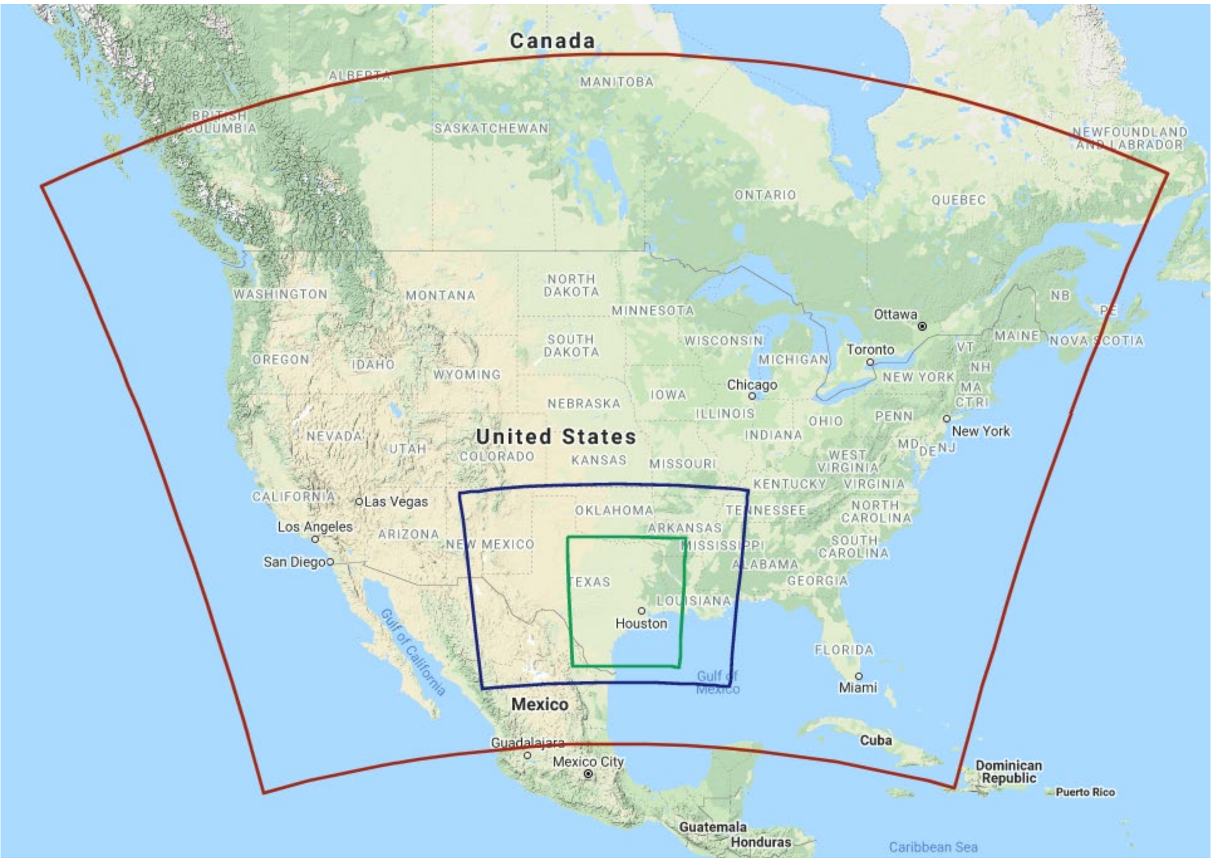

Figure 2. Extents of the CAMx 36 km (red), 12 km (blue), and 4 km (green) modeling domains (Figure from the TCEQ).

1.10 Emission Sensitivity Tests

Ramboll and the TCEQ conducted 6 CAMx model simulations for both CB6r5 and CB7 for a total of 12 simulations, namely the base case, 3 anthropogenic emission scenarios, and 2 biogenic emission scenarios for each mechanism. Ramboll performed both base case simulations, all anthropogenic emission scenarios, and one (of two) biogenic emission scenarios for both CB7 and CB6r5. The TCEQ conducted the remaining biogenic emissions scenario simulation for both mechanisms.

To ensure consistency between the results generated by different computing systems, Ramboll and the TCEQ performed a CAMx test run using the same model inputs. The tests gave comparable results so that simulations performed by the TCEQ can be compared to simulations performed by Ramboll with confidence.

The base case emission inventories were prepared for use with CB6r5 and consequently lacked explicit speciation of α-pinene (APIN) that can be used by CB7. For simulations with CB7, we equally split the CB6r5 terpene (TERP) emissions into APIN and TERP to differentiate α-pinene while preserving the total mass of terpene emissions. Simulations with CB7 used SQT emissions but simulations with CB6r5 did not (CB6r5 has no SQT model species) but this difference is considered minor because the mass of sesquiterpene emissions is a small fraction of terpene emissions and the chemical reactions of terpenes and sesquiterpenes are generally similar.

1.10.1 Anthropogenic Sensitivity Tests

We performed sensitivity simulations with emissions of anthropogenic NOx (NO, NO_2 and HONO) and anthropogenic VOC (any VOC except isoprene, terpenes or sesquiterpenes) reduced as follows:

- 25% reduction in anthropogenic NOx
- 25% reduction in anthropogenic VOC
- 25% reduction in anthropogenic NOx and VOC

Emissions of CO, SO_2 and biogenic VOC and NOx were unchanged from the base case in these sensitivity simulations. Maps of ground-level VOC and NOx emissions (anthropogenic plus biogenic) for the 36 km grid are shown in Figure 3 together with maps showing the effects of 25% reductions in anthropogenic VOC and NOx emissions. Maps of ground-level VOC and NOx anthropogenic emissions for the 4 km grid are shown in Figure 4 together with maps showing the effects of 25% reductions in anthropogenic VOC and NOx emissions.

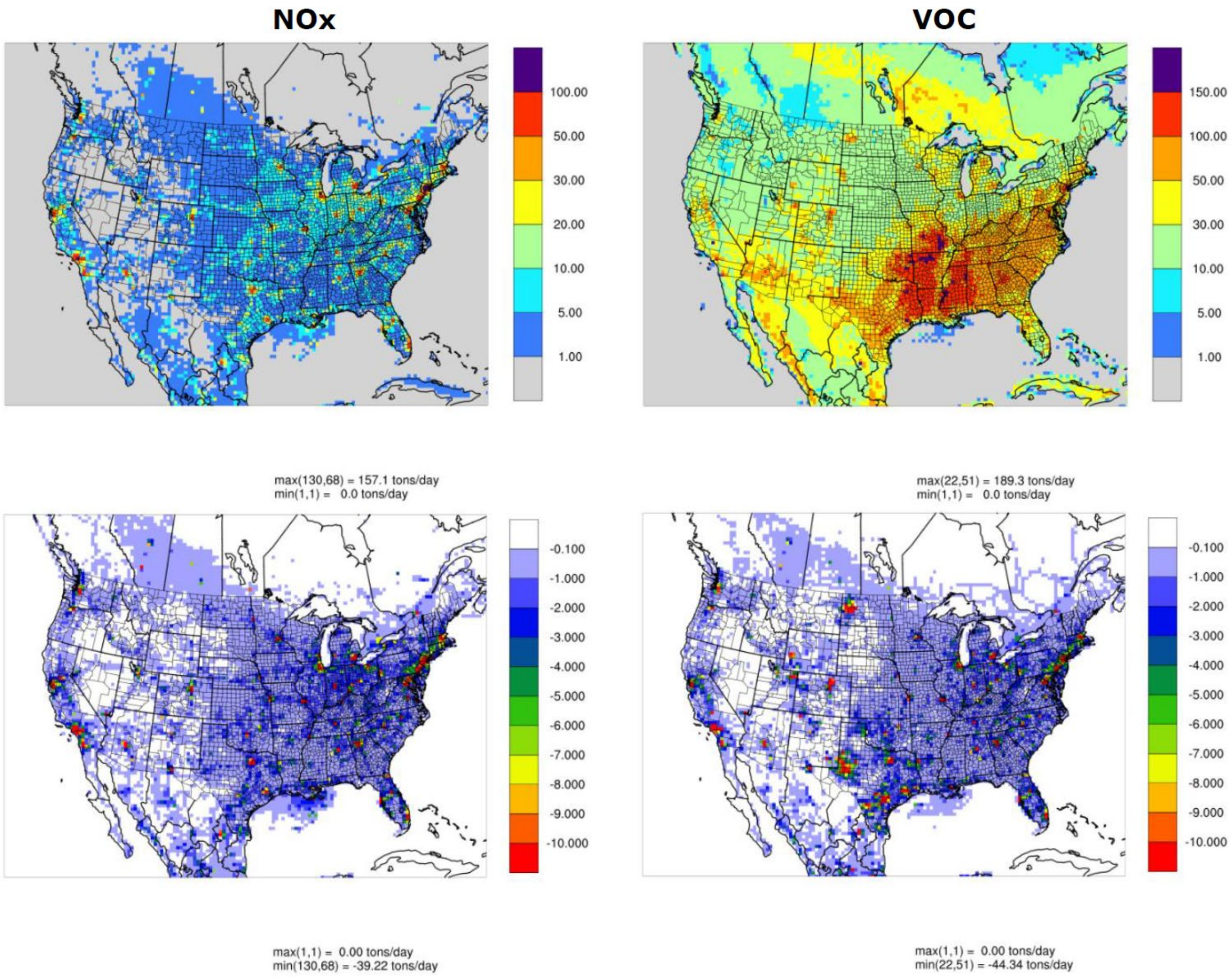

Figure 3. Maps of ground-level emissions (ton/day) for the CONUS 36 km grid cells on the Top10 days showing NOx (left) and VOC (right) for the base case anthropogenic plus biogenic (top) and the change due to 25% reduction in anthropogenic (bottom).

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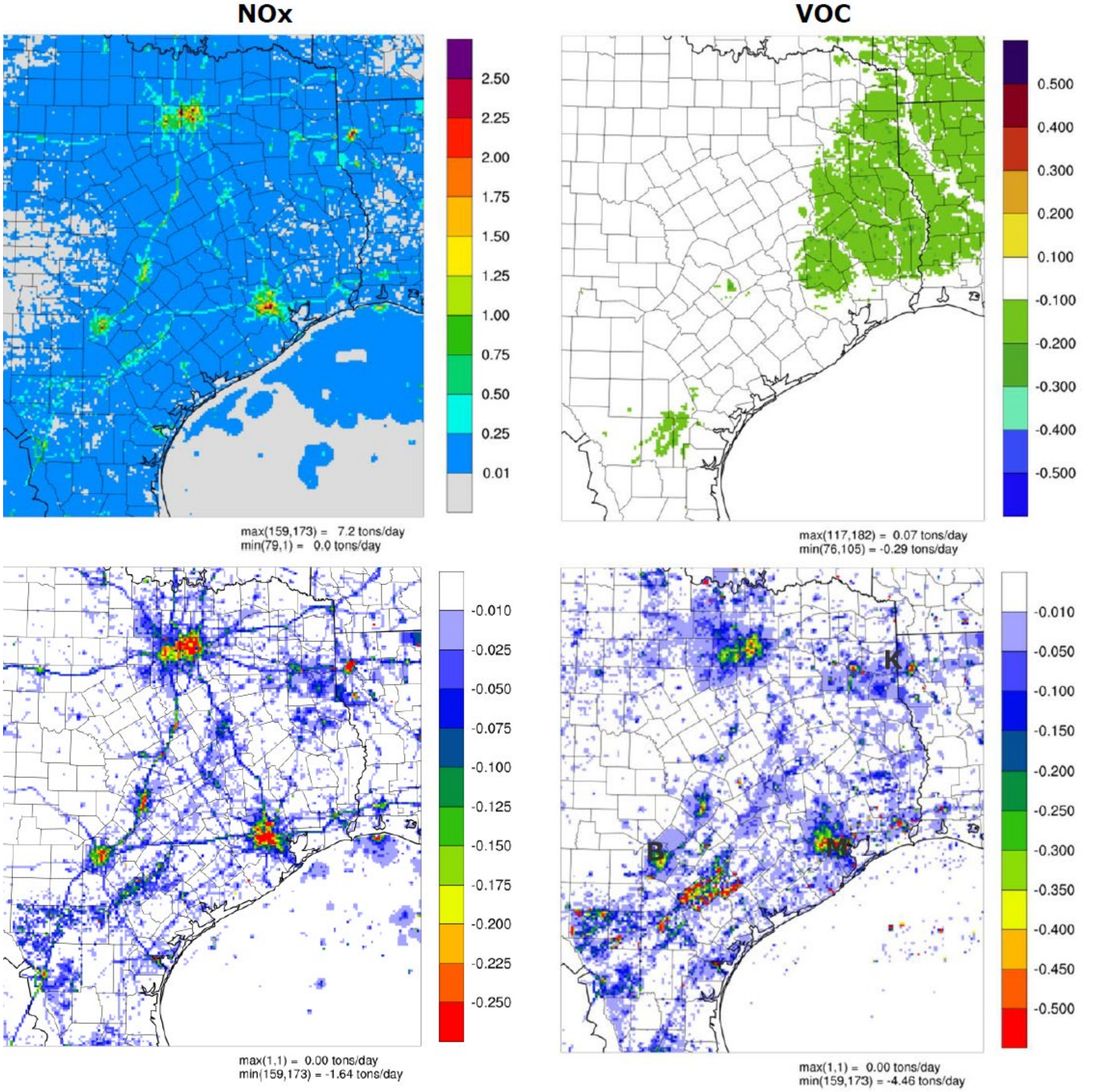


Figure 4. Maps of anthropogenic ground-level emissions (ton/day) for the Texas 4 km grid cells on the Top10 days showing NOx (left) and VOC (right) for the base case (top) and the change due to 25% reduction (bottom). The locations of Karnack, Camp Bullis and UH Moody Tower are marked by the letters K, B and M on the bottom-right map.

1.10.2Biogenic Sensitivity Tests

The biogenic sensitivity simulations changed the biogenic VOC or NOx emissions. The base case biogenic emissions were prepared by TCEQ using Biogenic Emission Inventory System (BEIS) version 3.61 with Biogenic Emissions Landcover Database version 4 (hereafter BEIS/BELD4). Recently, EPA released an update to BEIS version 3.70 along with updated biomass and emissions factors and Biogenic Emissions Landcover Database version 5 (hereafter BEIS/BELD5) that changes both VOC and NOx emission rates. To clearly differentiate between the effects of updating biogenic VOC and NOx emissions we performed two biogenic sensitivity tests:

- Update biogenic VOC to BELD5 while keeping biogenic NOx emissions unchanged from BELD4
- Update biogenic NOx to BELD5 while keeping biogenic VOC emissions unchanged from BELD4

Emissions of CO, SO_2 and anthropogenic VOC and NOx were unchanged from the base case in these sensitivity simulations. Emissions from BEIS/BELD5 were available only for the 4 km grid, and therefore, CAMx results for the biogenic sensitivity tests are only analyzed for the 4 km grid.

Maps of biogenic isoprene and terpene emissions for the 4 km grid are shown in Figure 5, with the base case emissions shown at the top and differences (BEIS/BELD5 – base case) shown at the bottom. In general, biogenic VOC emissions are dominated by trees because they have large biomass, terpene emissions are more strongly associated with coniferous than deciduous trees, whereas isoprene emissions are more associated with deciduous than coniferous trees. The region of higher terpene emission in the base case is the mixed conifer/hardwood forest of East Texas known as the "Piney Woods" and the BEIS/BELD5 update lowers terpene emissions in this region. Areas with higher isoprene emissions are widespread in the 4 km grid and are particularly associated with oak trees including the Texas "Hill Country" (north and west of Austin and San Antonio) and the western margin of the Piney Woods. The BEIS/BELD5 update tends to lower isoprene emissions in areas where the base case has higher isoprene emissions. The BEIS/BELD5 update also tends to increase isoprene emission in the urban areas of Houston and Dallas/Fort-Worth. The BEIS/BELD5 update tends to decrease isoprene emissions in the Piney Woods of East Texas and extending into Louisiana and Arkansas.

Maps of biogenic NOx emissions for the 4 km grid are shown in Figure 6, with the base case emissions shown on the left and the differences (BEIS/BELD5 – base case) shown on the right. The BEIS/BELD5 update increased biogenic NOx emissions across most of the 4 km domain with larger increases in wooded areas of East Texas, the Hill Country of the Edwards Plateau, and near the Gulf Coast. These areas had relatively low biogenic NOx emissions in the base case. The urban areas of Dallas-Fort Worth (DFW) and Houston had relatively low biogenic NOx emissions in the base case and saw increases with the BEIS/BELD5 update.

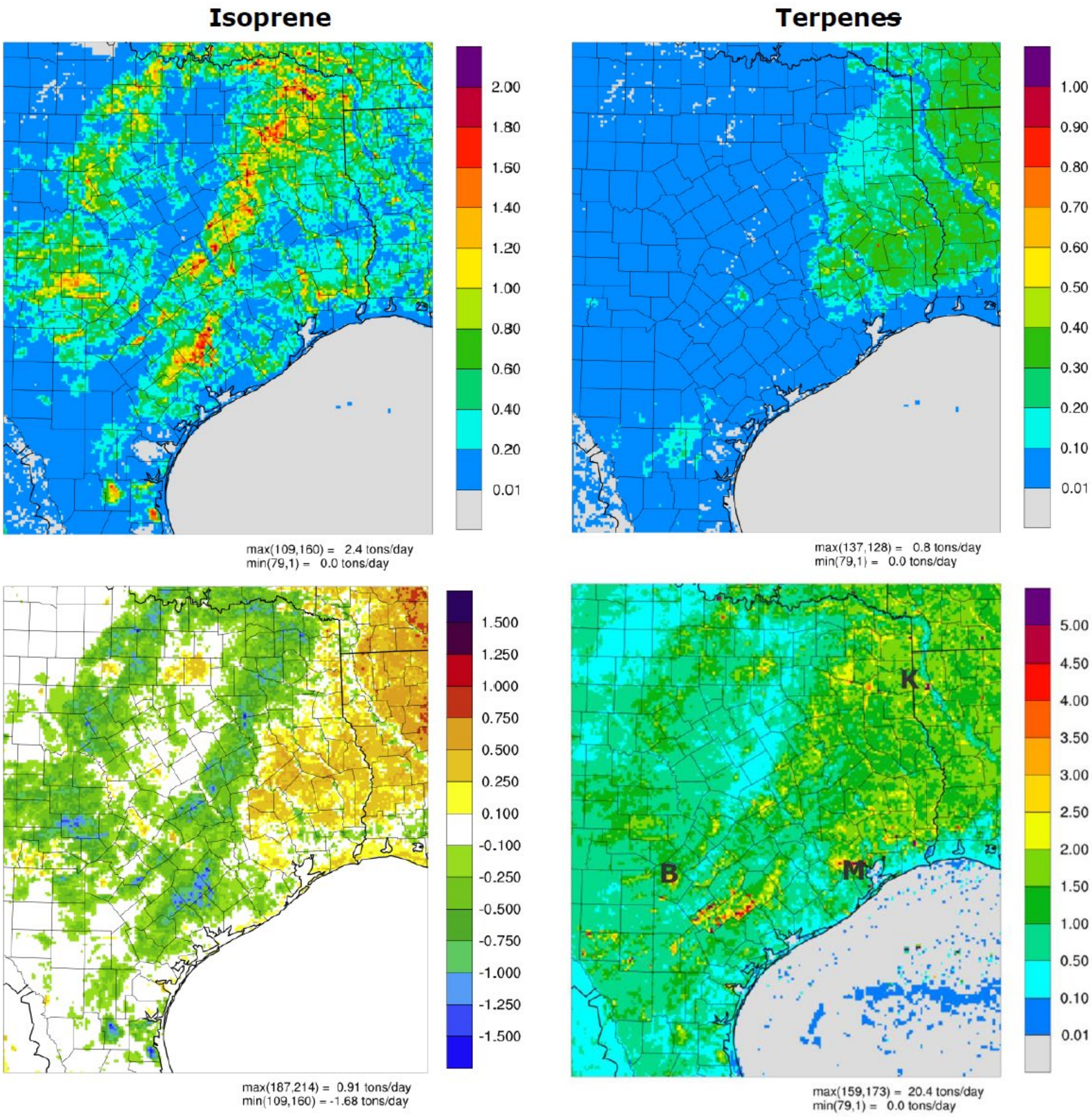


Figure 5. Maps of biogenic emissions (ton/day) for the Texas 4 km grid cells on the Top10 days showing isoprene (left) and terpenes (right) for the base case (top) and the change due to the BEIS/BELD5 sensitivity case (bottom). The locations of Karnack, Camp Bullis and UH Moody Tower are marked by the letters K, B and M on the bottom-right map.

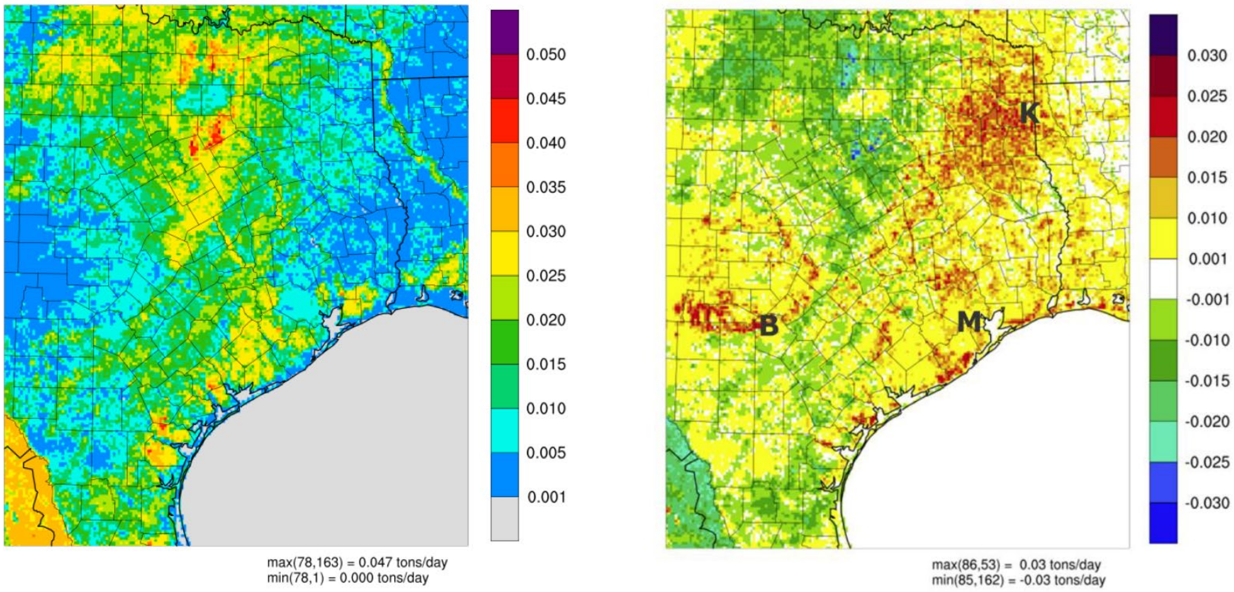


Figure 6. Maps of biogenic NOx emissions (ton/day) for the Texas 4 km grid cells on the Top10 days for the base case (left) and the change due to the BEIS/BELD5 sensitivity case (right). The locations of Karnack, Camp Bullis and UH Moody Tower are marked by the letters K, B and M on the right map.

MECHANISM TESTING

1.11 Base Case Ozone and Model Performance for Ozone

We compared the monthly averages of the maximum daily 8-hour average (MDA8) O_3 in June for base case simulations with CB7 and CB6r5 over the Texas 4 km grid (Figure 7) and the CONUS 36 km grid (Figure 8). June average MDA8 O_3 is very similar with CB7 and CB6r5 and differences are seen from the difference plots. The O_3 changes are relatively small and include areas of increase and decrease. Over the Texas 4 km grid, O_3 concentration differences (CB7 – CB6r5) range from +0.4 ppb to -2.3 ppb (+1.0% to -4.2%). A similar range of differences is seen over the 36 km grid (+0.5 ppb to -2.6 ppb; +0.9% to -5.9%). Urban areas are not apparent in the O_3 differences over the Texas 4 km grid suggesting that differences are associated with updates to reactions of biogenic VOC, namely isoprene, terpenes and sesquiterpenes. O_3 decreases over land tend to be larger (1 - 2 ppb reduction) over forested areas of eastern Texas and the Southeast where forests include conifers that tend to emit terpenes and sesquiterpenes and isoprene emissions also are strong. Larger O_3 decreases (1.5 - 2.5 ppb reduction) occur over the Gulf of Mexico near the coastline that are caused by the iodine chemistry update, i.e., somewhat increased O_3 destruction by iodine, as well as reduced O_3 transport from land to over the Gulf. Similar over-water O_3 decreases occur near the mid-Atlantic and Northeast States. O_3 increases (up to 0.5 ppb) are confined to land areas of the plains from West Texas to South Dakota as well as Eastern Mexico. These areas have terpene and sesquiterpene emissions from croplands and relatively low isoprene emission. We conclude that O_3 differences are mainly associated with the CB7 updates to reactions of biogenic VOCs with small O_3 reductions predominating except in areas dominated by croplands and prairies that show small O_3 increases.

We also compared the monthly maximum MDA8 O_3 for base case simulations with CB7 and CB6r5 over the Texas 4 km grid (Figure 9) and the CONUS 36 km grid (Figure 10). Changes in maximum MDA8 O_3 show more variation and fine structure than changes in monthly average MDA8 O_3 but, overall, both metrics show similar regional patterns of O_3 increase and decrease. CB7 tends to decrease O_3 peaks over water, for example offshore from Galveston where a peak of 124.8 ppb with CB6r5 is reduced to 114.4 ppb with CB7 (Figure 9).

We performed a statistical evaluation of model performance (MPE) using O_3 data from TCEQ Continuous Air Monitoring Stations (CAMS) as reported in Table 6. The statistical metrics indicate that CB7 agrees slightly better with observation than CB6r5. However, these differences are too small to be considered meaningful and, therefore, we conclude that CB7 and CB6r5 have equivalent performance.

Table 6. CAMx performance statistics for maximum daily 8-hour average (MDA8) O_3 at Continuous Ambient Monitoring Stations (CAMS) in the 4-km grid for June 2012.

Statistical Metric	**CB7**	**CB6r5**
Number of Observations	3012	3012
Average Concentration - Observations (ppb)	46.1	46.1
Average Concentration - Model (ppb)	51.5	51.8
r^2	0.828	0.828
Mean Bias (ppb)	5.34	5.68
Mean Error (ppb)	7.76	7.98
Normalized Mean Bias (%)	11.6	12.3
Normalized Mean Error (%)	16.8	17.3
Mean Fractional Bias (%)	14.9	15.6
Mean Fractional Error (%)	18.7	19.2

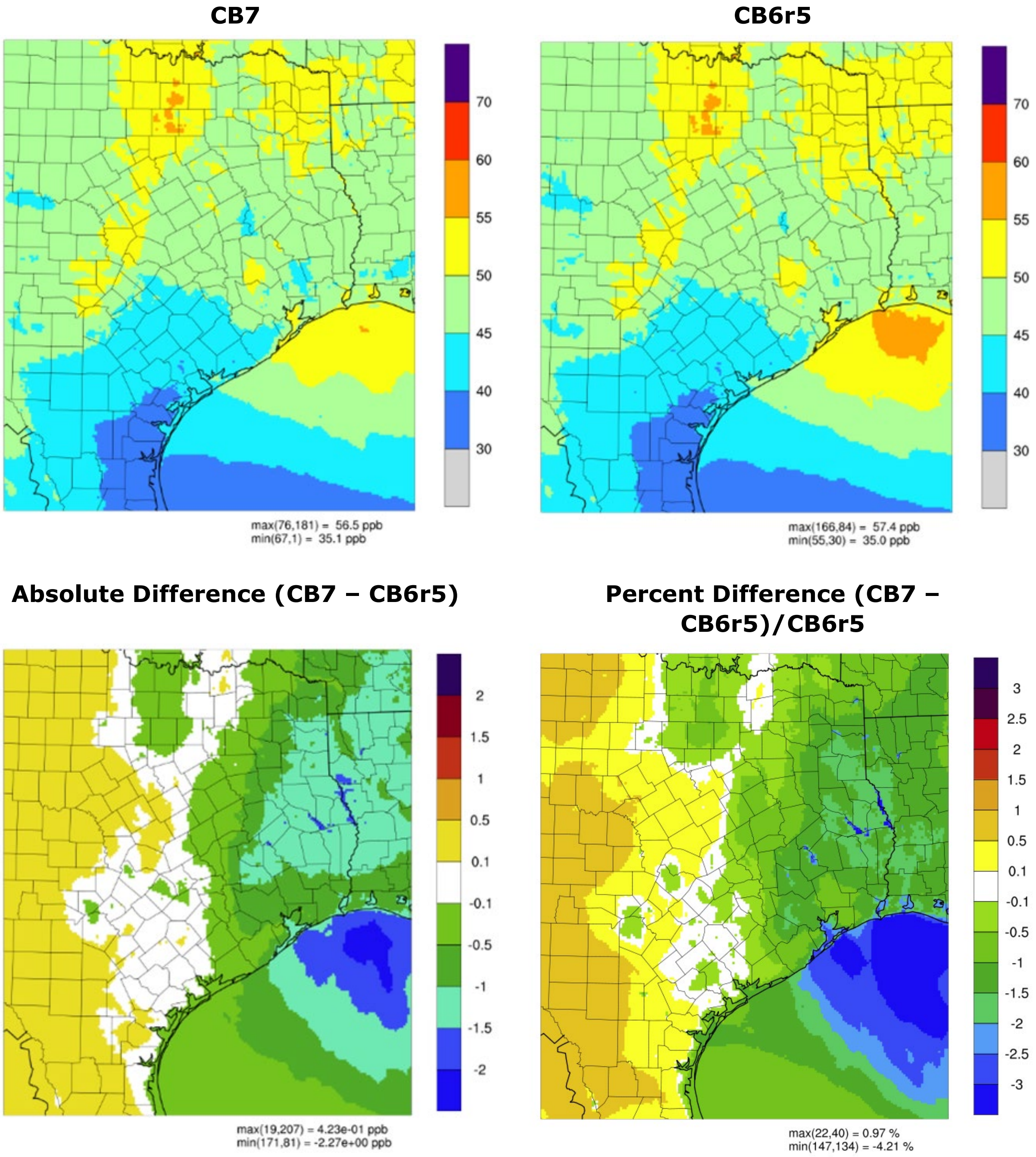
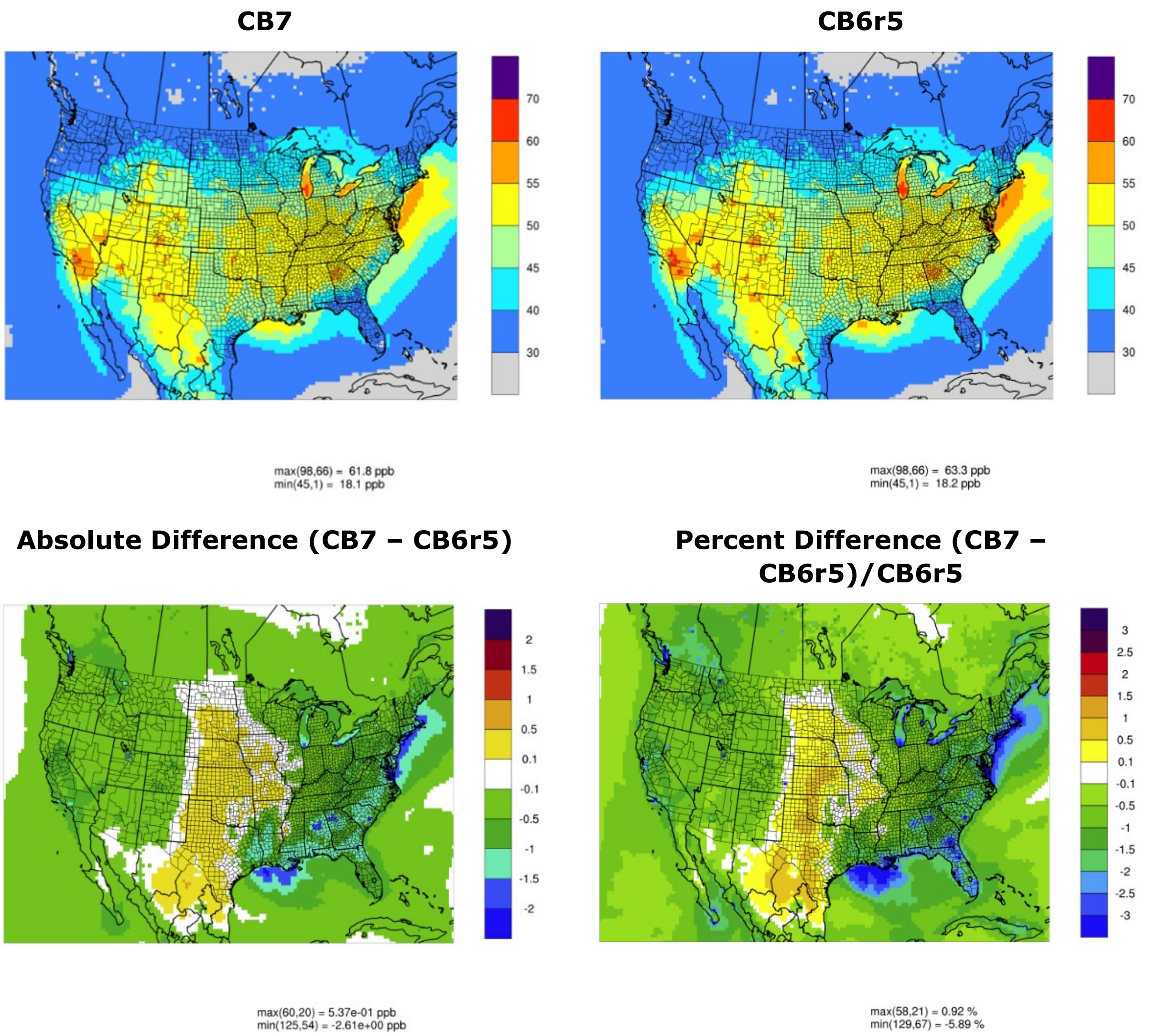


Figure 7. June 2012 base case average maximum daily 8-hour average (MDA8) O_3 (ppb) over 4 km grid with CB7 (top left) and CB6r5 (top right), and the absolute (bottom left) and percent difference (bottom right) between CB7 and CB6r5.



CB7

CB6r5

max(98,66) = 61.8 ppb
min(45,1) = 18.1 ppb

max(98,66) = 63.3 ppb
min(45,1) = 18.2 ppb

Absolute Difference (CB7 – CB6r5)

Percent Difference (CB7 – CB6r5)/CB6r5

max(60,20) = 5.37e-01 ppb
min(125,54) = -2.61e+00 ppb

max(58,21) = 0.92 %
min(129,67) = -5.89 %

Figure 8. June 2012 base case average maximum daily 8-hour average (MDA8) O_3 (ppb) over the 36 km grid with CB7 (top left) and CB6r5 (top right), and the absolute (bottom left) and percent difference (bottom right) between CB7 and CB6r5.

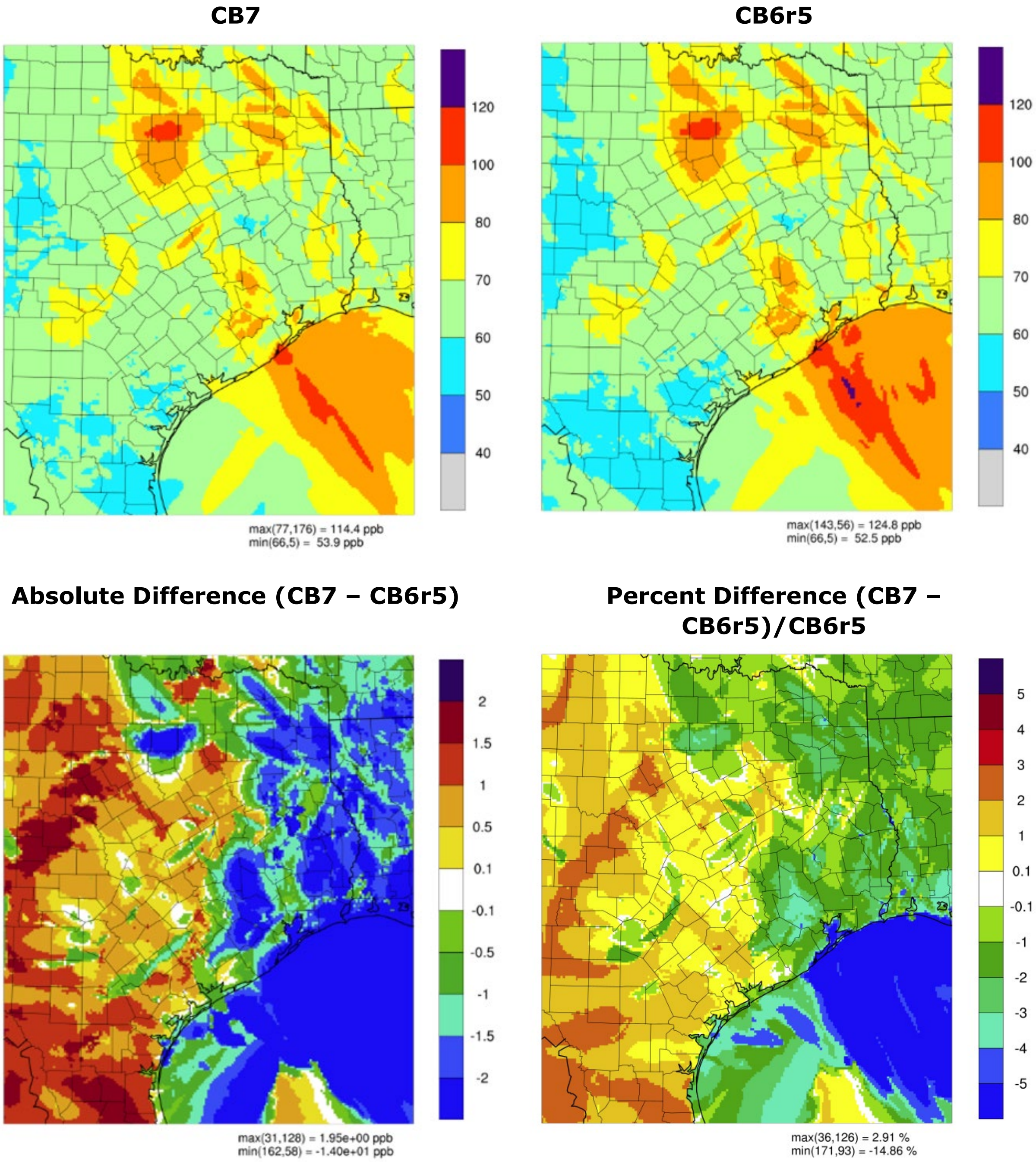
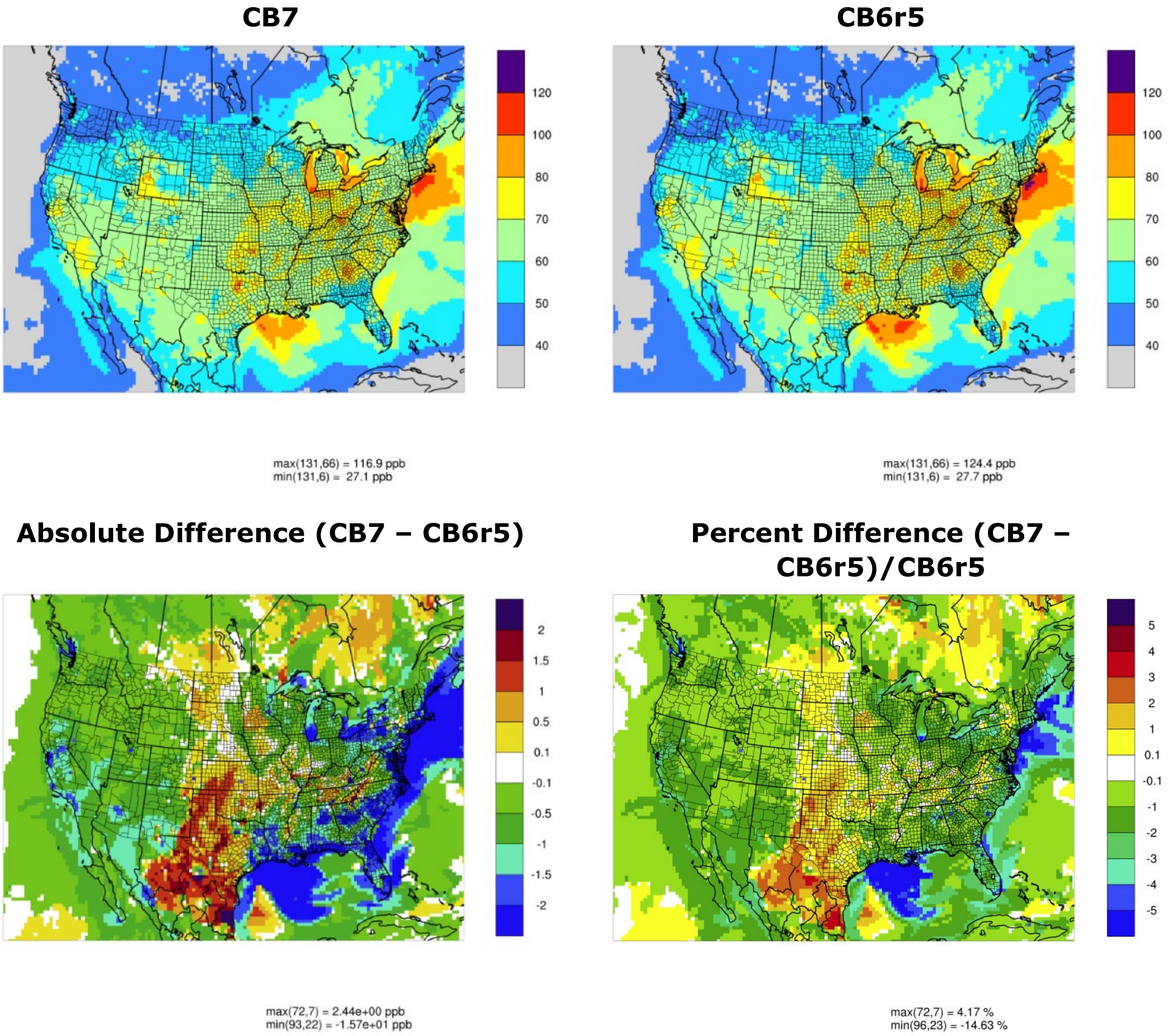


Figure 9. June 2012 base case highest maximum daily 8-hour average (MDA8) O_3 (ppb) over the 4 km grid with CB7 (top left) and CB6r5 (top right), and the absolute (bottom left) and percent difference (bottom right) between CB7 and CB6r5.


CB7

CB6r5

Absolute Difference (CB7 – CB6r5)

Percent Difference (CB7 – CB6r5)/CB6r5

Figure 10. June 2012 base case highest maximum daily 8-hour average (MDA8) O_3 (ppb) over the 36 km grid with CB7 (top left) and CB6r5 (top right), and the absolute (bottom left) and percent difference (bottom right) between CB7 and CB6r5

1.12 Multi-Species Comparison at Monitor Locations in Texas

We compared average diurnal profiles of several species with CB7 and CB6r5 at three locations with a TCEQ CAMS that have different emission characteristics:

- Karnack (CAMS 0085) is a rural location in Northeast Texas (32.6690 North, -94.1675 West) influenced by biogenic VOC emissions from surrounding forest and anthropogenic emissions from nearby roads, oil and gas wells, and other sources.
- UH Moody Tower (CAMS 0695) is an urban location on the campus of the University of Houston (29.7176 North, -95.3414 West) influenced by anthropogenic emissions from Houston’s urban and industrial activities.

- Camp Bullis (CAMS 0058) is a suburban/rural location (29.6321 North, -98.5649 West) frequently downwind of the San Antonio urban core on higher O_3days but with relatively low emissions nearby.

The locations of these sites are marked in Figures 4, 5 and 6, for reference.

To focus on O_3conducive conditions, we averaged concentrations at each site over 10 days with higher O_3across East Texas (the "Top 10" days), namely June 7-9 and June 22-28. The resulting average diurnal profiles for several species are shown below in Figure 11 to Figure 16.

The average diurnal profiles for O_3 at all three sites show similar day-time maximums and night-time minimums except for Karnack at night where CB7 depletes O_3 more rapidly than CB6r5 due to updated terpene chemistry in CB7. The CB7 terpene updates are more influential at Karnack than the other sites because the total terpene concentration (i.e., APIN + TERP for CB7 vs. TERP for CB6r5) is an order of magnitude larger at Karnack than the other locations (Figure 11 to Figure 16). Representative half-lives for CB6 and CB7 terpenes with respect to reaction with oxidants are compared for CB6 and CB7 in Table 7 for evening hours at Karnack, showing that O_3 dominates terpene destruction under these conditions and that terpenes have shorter half-life in CB7 than CB6. It is important to include terpene reactions with OH and NO_3 (as well as O_3) in CB7 because terpene reactions with OH are important during daytime due to higher OH concentrations and terpene reactions with NO_3 are the dominant night-time removal pathway at the urban Moody Tower and suburban Camp Bullis locations.

Table 7. Rate constants (cm^3 $molec^{-1}$ s^{-1}) at 298 K for terpene reactions in CB6 and CB7 along with atmospheric half-lives for evening hours at Karnack, Camp Bullis and UH Moody Tower on the "Top 10" days in June 2012.

Oxidant	Mixing Ratio	CB6r5 TERP	CB7 TERP	CB7 APIN
Rate Constant				
OH		6.8E-11	1.3E-10	2.7E-11
O_3		7.6E-17	1.8E-16	9.6E-17
NO_3		6.7E-12	7.0E-12	6.2E-12
Half-life (h) at Karnack				
OH	0.02 ppt	5.8	3.0	14.5
O_3	40 ppb	2.6	1.1	2.0
NO_3	0.1 ppt	11.7	11.2	12.6
Half-life (h) at Camp Bullis				
OH	0.02 ppt	5.8	3.0	14.5
O_3	30 ppb	3.4	1.4	2.7
NO_3	5 ppt	0.2	0.2	0.3
Half-life (h) at Moody Tower				
OH	0.02 ppt	5.8	3.0	14.5
O_3	40 ppb	4.1	1.7	3.3
NO_3	2 ppt	0.6	0.6	0.6

Note: Half-lives are for oxidant concentrations that represent evening hours on the "Top 10" days in June 2012.

The multi-species comparisons shown in Figure 11 and Figure 12 for Karnack are representative of the forested rural areas of Eastern Texas (the "Piney Woods") and the South-eastern US where combinations of pine and hardwood tree species emit both terpenes and isoprene. The daytime O_3 maximums with CB7 and CB6r5 are very similar although the diurnal profile of O_3 reveals that slightly greater daytime O_3 production is being offset by greater nighttime O_3 destruction, as discussed above. The daytime NO_2 concentration at Karnack of less than 1 ppb leads to a photochemical environment where O_3 production is NOx-limited. Close comparison of the daytime NO_2 and NO at Karnack shows slightly higher NOx with CB7 than CB6r5 which can explain greater daytime O_3 production with CB7. Slightly higher daytime NOx with CB7 at Karnack probably is attributable to the terpene chemistry update and its influence on peroxyacyl nitrates (PANs). The total PAN concentration at Karnack during the night is substantially higher with CB7 than CB6r5 (nearly double) and PANs tend to sequester NO_2 at night and return NO_2 during the day when warmer temperatures decompose PANs. Much of increase in total PANs at night with CB7 results from model species OPAN (representing other PAN compounds) produced via O_3 plus terpene reactions that are faster in CB7, as discussed above.

OH concentrations are higher with CB7 than CB6r5 at Karnack during the day and at night. Higher OH at night is partly attributable to more active terpene oxidation by O_3 in CB7 because OH is a product of O_3 reactions with terpenes. During the day, higher OH with CB7 results from the isoprene chemistry update which produces more secondary OH under low NOx conditions than the CB6r5 isoprene mechanism. Higher OH leads to more nitric acid (HNO_3), produced when OH reacts with NO_2, and less isoprene. The daytime isoprene reduction with CB7 is smaller (in relative terms) than the daytime OH increase suggesting that the CB7 isoprene chemistry update will not substantially change model performance for isoprene.

The CB7 terpene chemistry update changes O_3 in several ways: More O_3 destruction at night; slightly more NOx during the day; slightly more O_3 production during the day. At Karnack, these changes have nearly cancelling effects on daily maximum O_3 but the balance between these competing effects is likely to change with the composition of biogenic VOC emissions which can explain the regional patterns of MDA8 O_3 changes between CB7 and CB6r5 (Figure 7 and Figure 8).

Species concentration differences are less pronounced at the urban Moody Tower location (Figure 13 and Figure 14) and suburban Camp Bullis location (Figure 15 and Figure 16) than at Karnack consistent with lower terpene emissions and concentrations at the urban/suburban locations. This suggests that CB7 updates for anthropogenic VOC, mainly alkanes (PAR) and associated ketones (KET) have only minor impacts and is consistent with urban areas not standing out in the spatial maps of MDA8 O_3 changes between CB7 and CB6r5 (Figure 7 and Figure 8).

Formaldehyde (FORM) is an important toxic air pollutant and secondary production (i.e., from VOC degradation) is an important source of FORM in addition to primary emission. FORM concentrations are slightly higher with CB7 than CB6r5 at all three locations (Figure 11 to Figure 16) but these differences are minor, e.g., uncertainty in VOC emission rates is likely to be more influential.

Hydroperoxy radical (HO_2) is tightly connected with OH and O_3, and HO_2 is a precursor to peroxides which are an important oxidant, e.g., converting sulfur dioxide (SO_2) to sulfate aerosol. CB7 tends to lower HO_2 during the day and increase HO_2 during the night compared to CB6r5. HO_2 increases at night can be partly attributed to more active terpene reactions with O_3 in CB7. HO_2 decreases during the day can be partly attributed to slightly higher NO with CB7 shifting the HO_2/OH ratio (these two species interconvert rapidly) in favor of less HO_2 and more OH. Changes in total peroxides (i.e., 2 x H_2O_2 plus the sum of organic peroxides) tend to follow the changes in HO_2.

RO2 concentrations tend to be lower with CB7 than CB6r5 in accordance with updates to the rate constants of RO2 reactions in CB7. For the most part, RO_2 radicals react either with NO (producing NO_2) or HO_2 (often forming organic peroxides). When both NO and HO_2 are scarce, usually at night, RO_2 radicals tend to react with themselves (called self-reaction) and changing the RO_2 concentration may not alter how RO_2 radicals react (i.e., mainly by self-reaction). This can explain why relatively large changes in RO2 concentration at night with CB7 are not associated with corresponding changes in NO_2 or total peroxides.

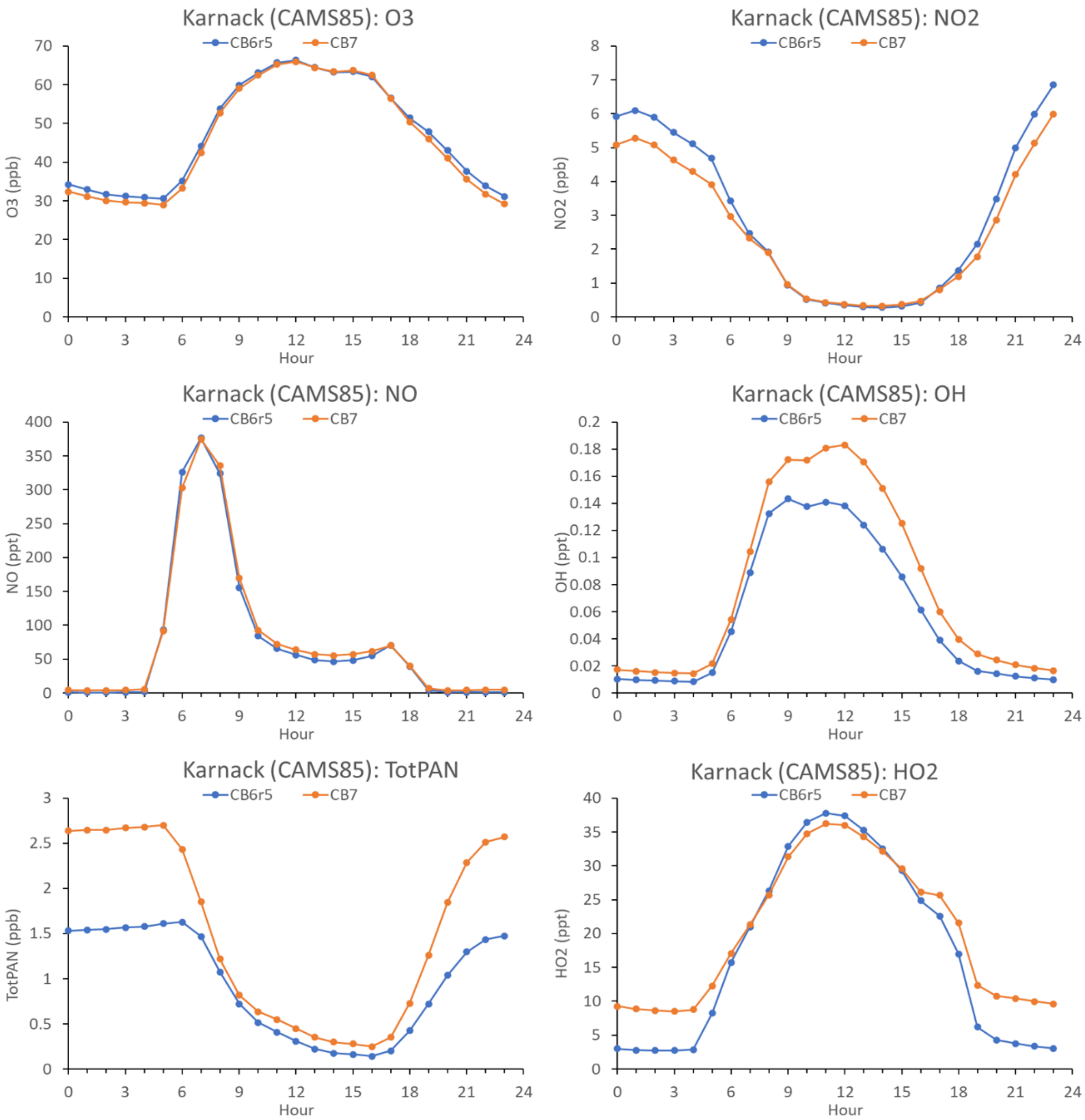


Figure 11. Diurnal profiles at Karnack, Northeast Texas (CAMS 0085) for the "Top10" O_3 days in June 2012 with both CB7 and CB6r5: O_3, NO_2, NO, OH radical, total PAN and HO_2 radical.

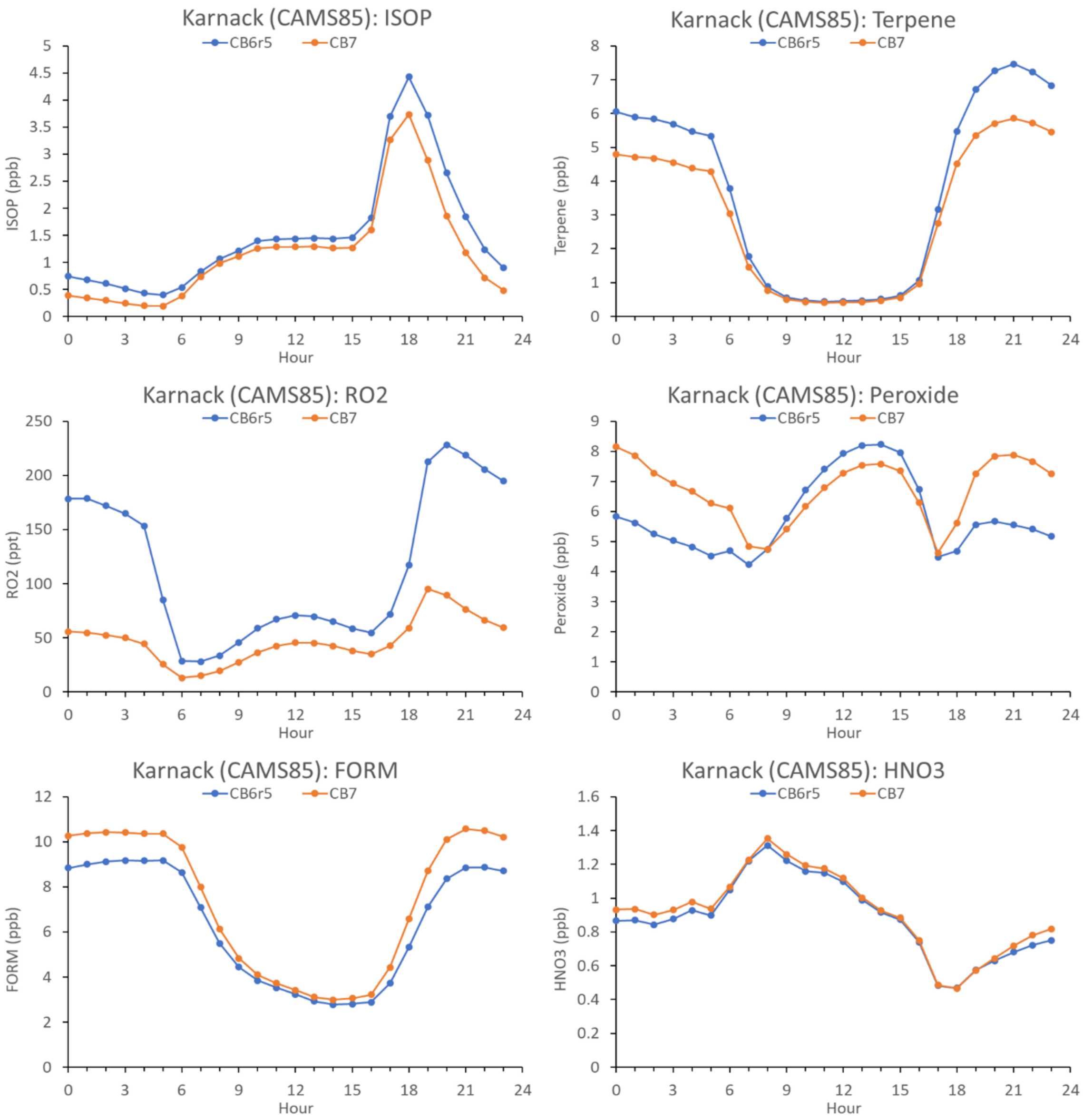


Figure 12. Diurnal profiles at Karnack, Northeast Texas (CAMS 0085) for the "Top10" O_3 days in June 2012 with both CB7 and CB6r5: isoprene, terpenes, total RO2 radicals, total peroxide, formaldehyde and nitric acid.

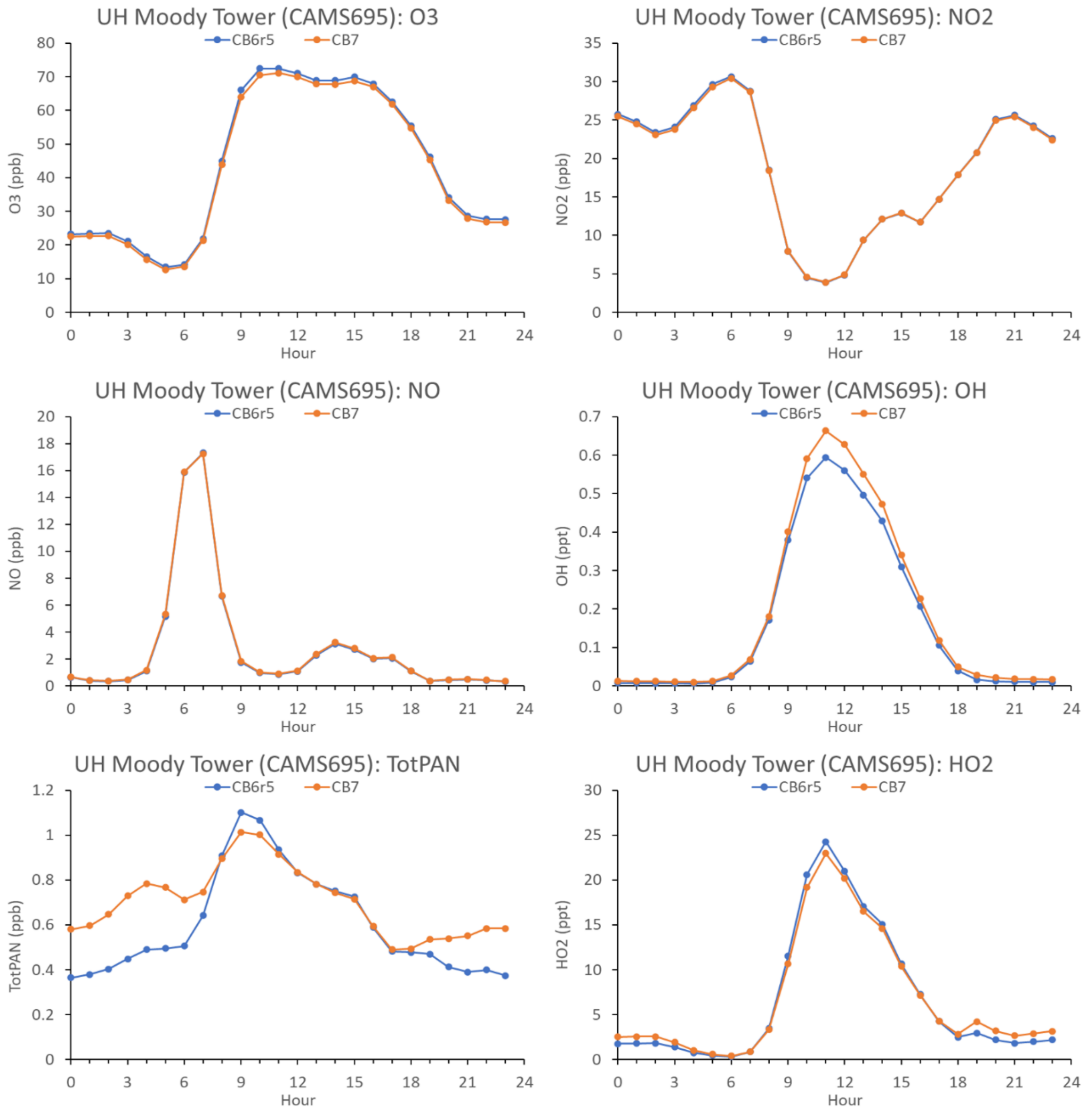


Figure 13. **Diurnal profiles at Moody Tower, Houston (CAMS 0695) for the "Top10" O_3 days in June 2012 with both CB7 and CB6r5: O_3, NO_2, NO, OH radical, total PAN and HO_2 radical.**

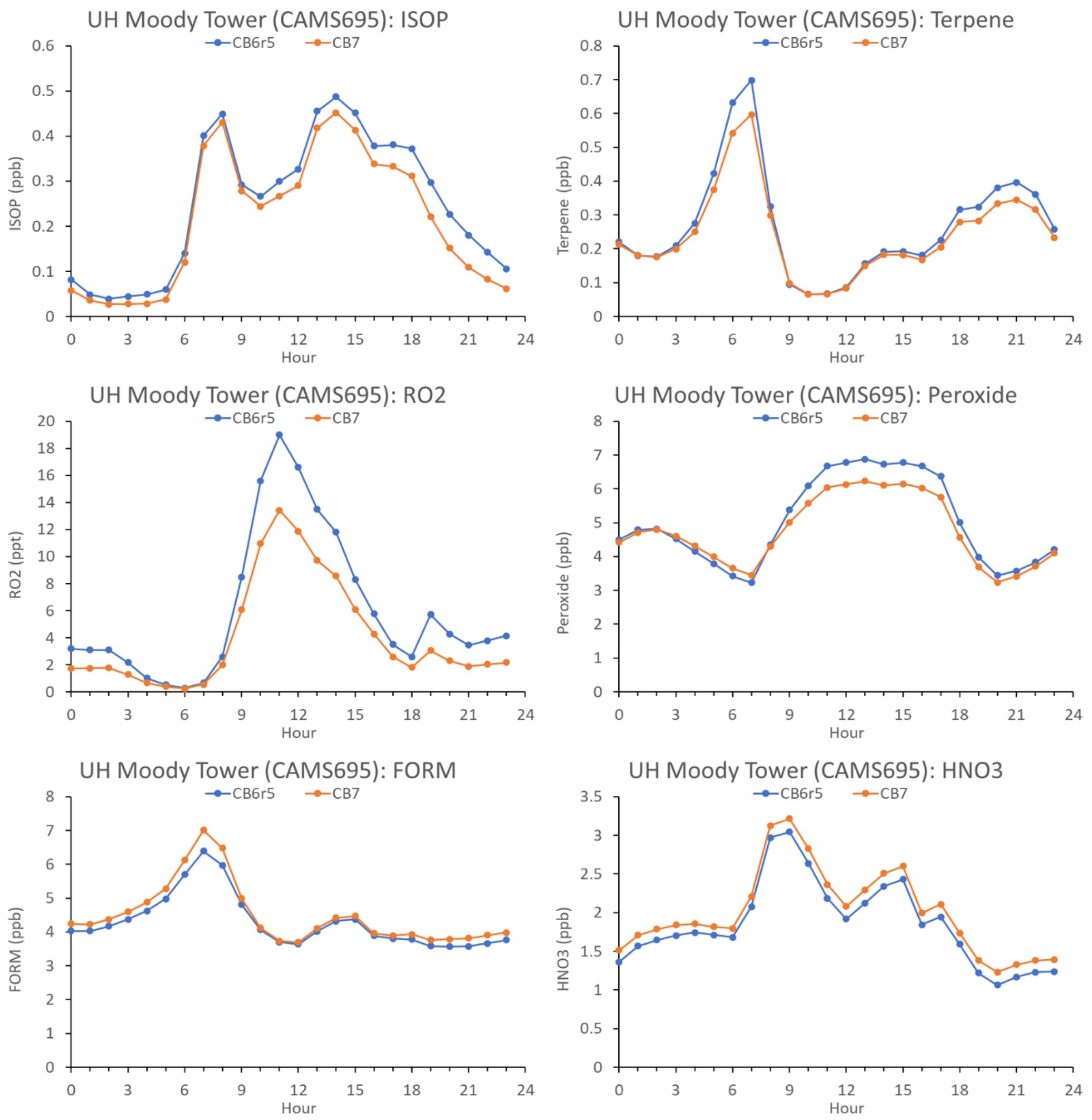


Figure 14. Diurnal profiles at Moody Tower, Houston (CAMS 0695) for the "Top10" O_3 days in June 2012 with both CB7 and CB6r5: isoprene, terpenes, total RO2 radicals, total peroxide, formaldehyde, and nitric acid.

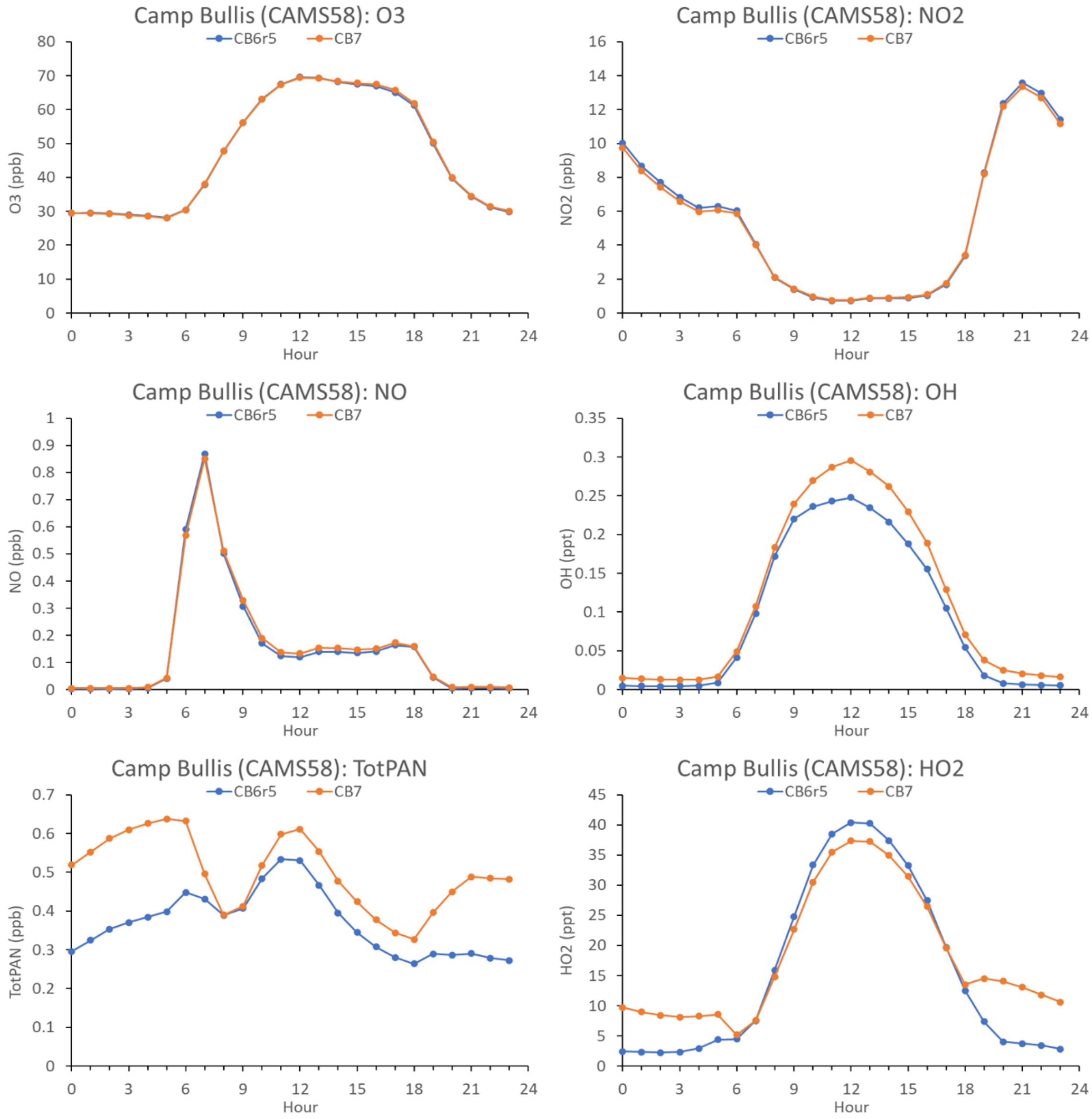


Figure 15. Diurnal profiles at Camp Bullis, San Antonio (CAMS 0058) for the “Top10” O_3 days in June 2012 with both CB7 and CB6r5: O_3, NO_2, NO, OH radical, total PAN and HO_2 radical.

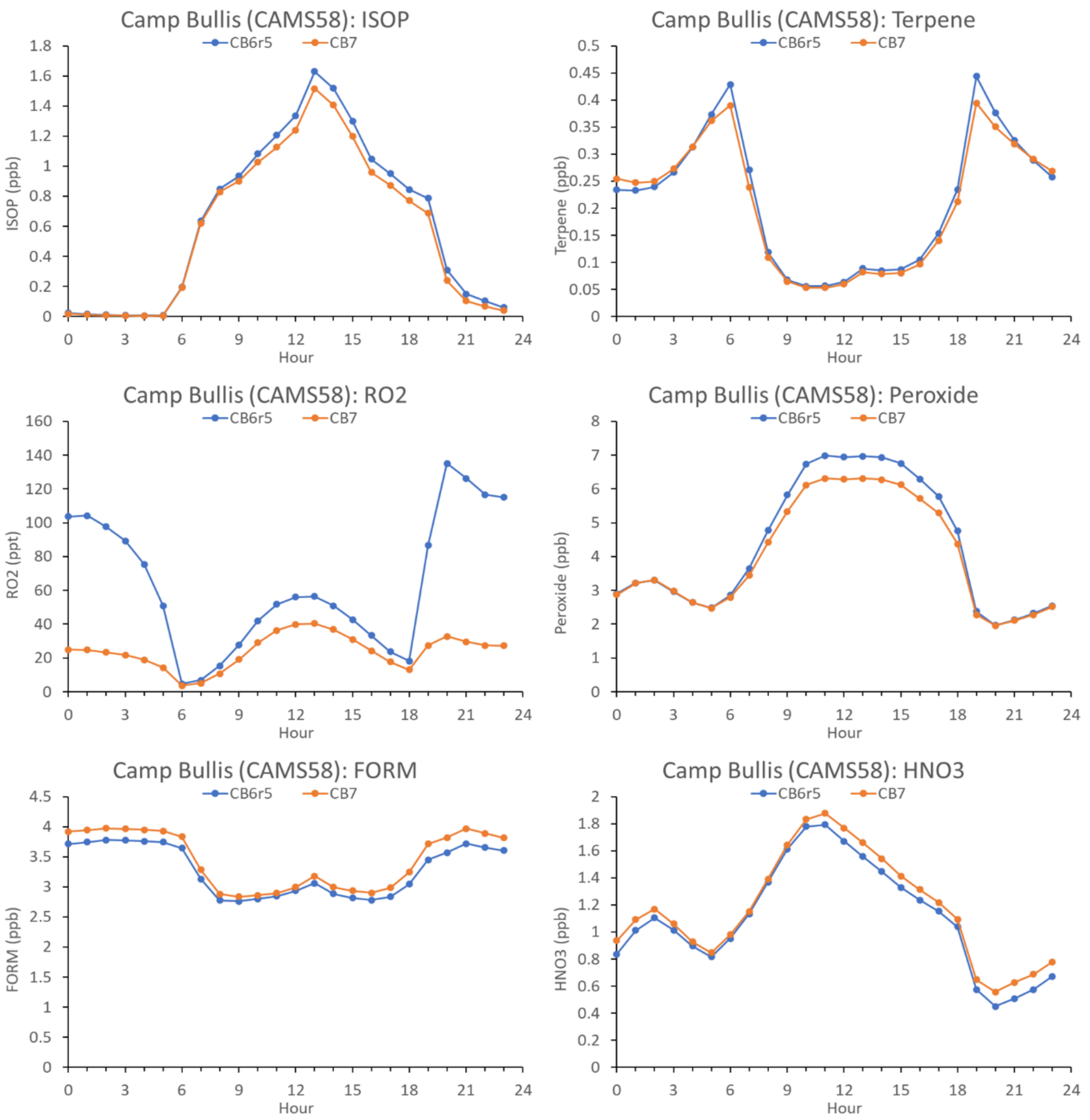


Figure 16. Diurnal profiles at Camp Bullis, San Antonio (CAMS 0058) for the "Top10" O_3 days in June 2012 with both CB7 and CB6r5: isoprene, terpenes, total RO2 radicals, total peroxide, formaldehyde, and nitric acid.

1.13 Examination of the CB7 Terpene Update

Consequences of the terpene chemistry update for CB7 are investigated in more detail through Figure 17 (which complements Figures 11 and Figure 12) for Karnack in a location where terpene emissions are important (see Figure 5; the location of Karnack is marked in this figure). The total mass of terpene emissions is the same for CB7 and CB6r5 but the total terpene concentration (i.e., APIN plus TERP for CB7 and TERP for CB6r5) is lower with CB7 (Figure 17) because terpenes are removed more rapidly by chemical reactions in the updated mechanism. Terpene concentrations are higher at night because they are emitted throughout the day and the boundary layer is shallow at night. In contrast, isoprene concentrations are higher during the day because isoprene emissions increase strongly with sunlight and photosynthesis.

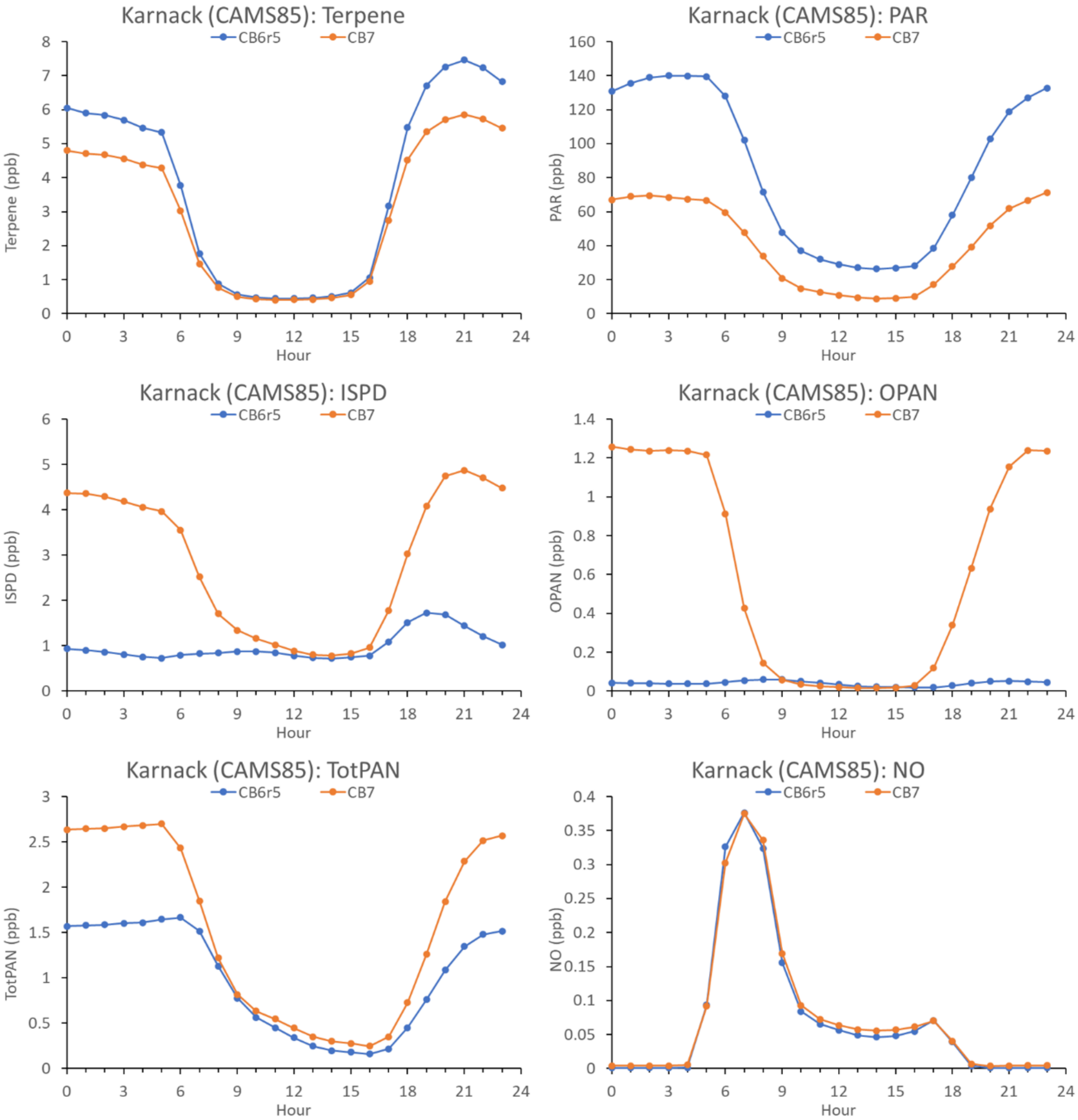


Figure 17. Diurnal profiles at Karnack, Northeast Texas (CAMS 0085) for the "Top10" O_3 days in June 2012 with both CB7 and CB6r5: terpenes, PAR, ISPD, OPAN, total PAN compounds and PAN.

Neither CB7 nor CB6r5 includes a model species specifically designed to represent organic products from terpene oxidation, e.g., pinonaldehyde, limonaldehyde and nopinone. CB6r5 represents these products using PAR as a surrogate (dating from CB05) whereas CB7 represents them using ISPD (designed to represent methacrolein, methylvinyl ketone and other isoprene oxidation products). Consequently, CB7 produces lower PAR concentrations than CB6r5 (Figure 17) but higher ISPD concentrations, especially at night. Eliminating secondary formation of PAR from terpene oxidation in CB7 improves mechanism clarity because PAR is associated with anthropogenic rather than biogenic VOC. However, the magnitude of ISPD increase at night with CB7 creates a potential for unintended consequences because ISPD was not specifically designed to represent products of terpene oxidation. In particular, the CB7 terpene mechanism forms OPAN (representing other peroxyacyl nitrates) at night which is destroyed by chemical reactions during the day which releases NOx and helps sustain O_3 production under NOx-limited conditions. We recommend further evaluation of this aspect of the CB7 terpene mechanism with consideration of whether the large contribution of OPAN to total PANs at night (about half at Karnack, Figure 17) is consistent with ambient measurements of PAN compounds made in pine forest environments.

1.14 Ozone Response to Anthropogenic Emission Reduction

The response of June average MDA8 O_3 to anthropogenic emission sensitivity tests with CB7 and CB6r5 is compared in Figure 18. Reducing anthropogenic NOx (ANOx) by 25% causes substantially larger O_3 changes than reducing anthropogenic VOC (AVOC) by 25% and consequently a different color scale is used to show the AVOC sensitivity test result.

CB7 and CB6r5 show similar responses of MDA8 O_3 to reducing AVOC emission by 25%, with modest O_3 reduction in and downwind of major cities and minimal O_3 reduction elsewhere. CB7 produces slightly greater O_3 reductions that extend further downwind of major cities. This difference is likely to be a consequence of the CB7 updates to the chemistry of alkanes (PAR) and associated ketones (KET). The 25% AVOC reduction mitigates localized O_3 increases associated with 25% ANOx reduction in some urban areas with both CB7 and CB6r5.

CB7 and CB6r5 show similar responses of MDA8 O_3 to reducing ANOx emission by 25%, with localized O_3 increases (sometimes called O_3 disbenefits) in some major cities and larger O_3 reductions elsewhere. The largest O_3 reductions occur in Northeast Texas where ANOx emissions interact with abundant BVOC emissions to form O_3 when atmospheric conditions are conducive. The O_3 reductions in Northeast Texas are somewhat smaller with CB7 than CB6r5 which is most likely a consequence of the updated terpene chemistry in CB7 altering how NOx is sequestered at night by OPAN and returned during the day (discussed above). However, difference plots for NO_2 (shown in Figure 19, with averaging times matched to Figure 18) show that CB7 and CB6r5 produce nearly identical NO_2 response to the 25% ANOx emission reduction and therefore differences in NO_2 between CB6r5 and CB7 are subtle.

Reducing ANOx and AVOC together has nearly the same effect on MDA8 O_3 as reducing ANOx on its own with both CB7 and CB6r5.

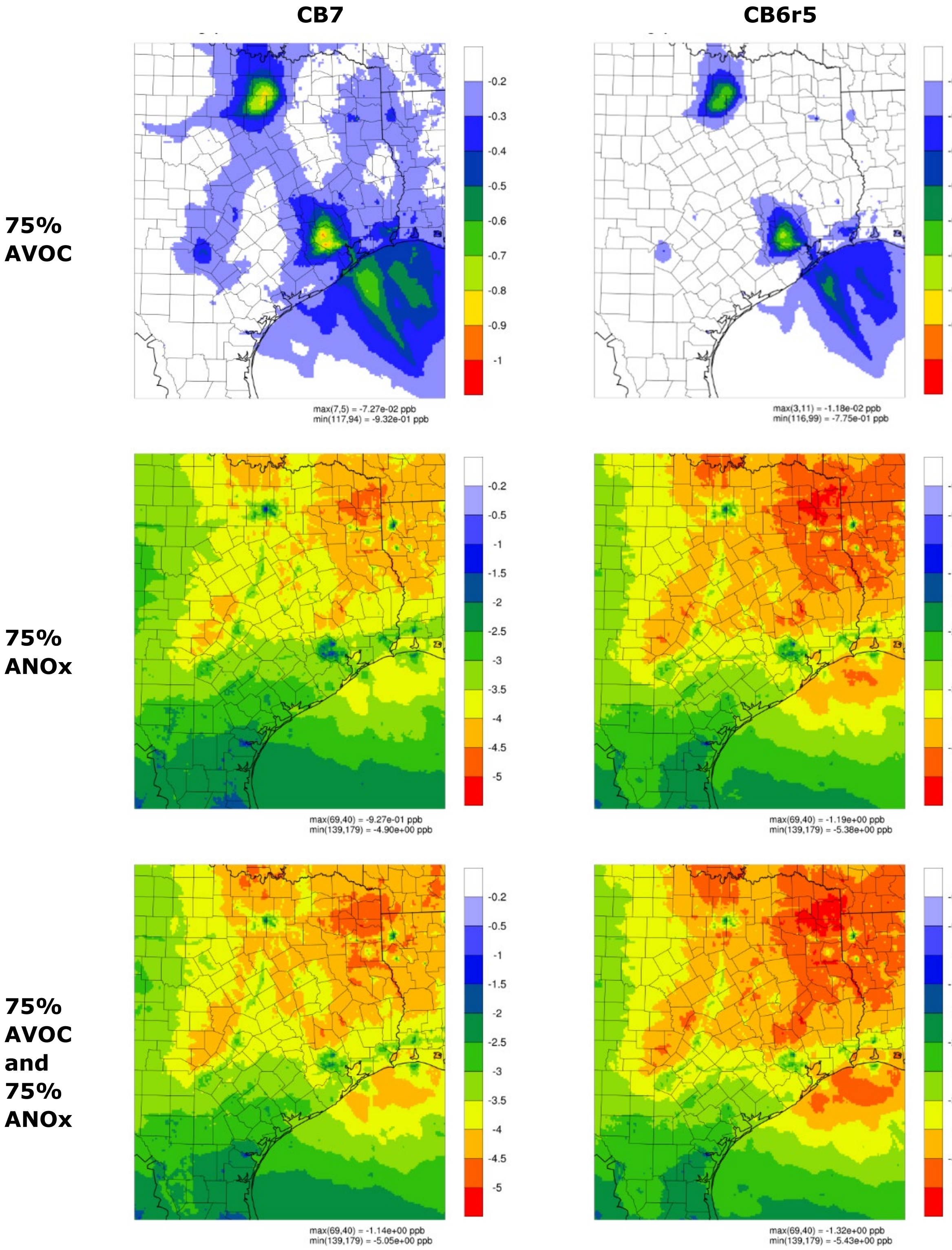


Figure 18. Differences in June average MDA8 O_3 (ppb) for anthropogenic emission scenarios – base case (rows) with CB7 and CB6r5 (columns). The top row has a different color scale.

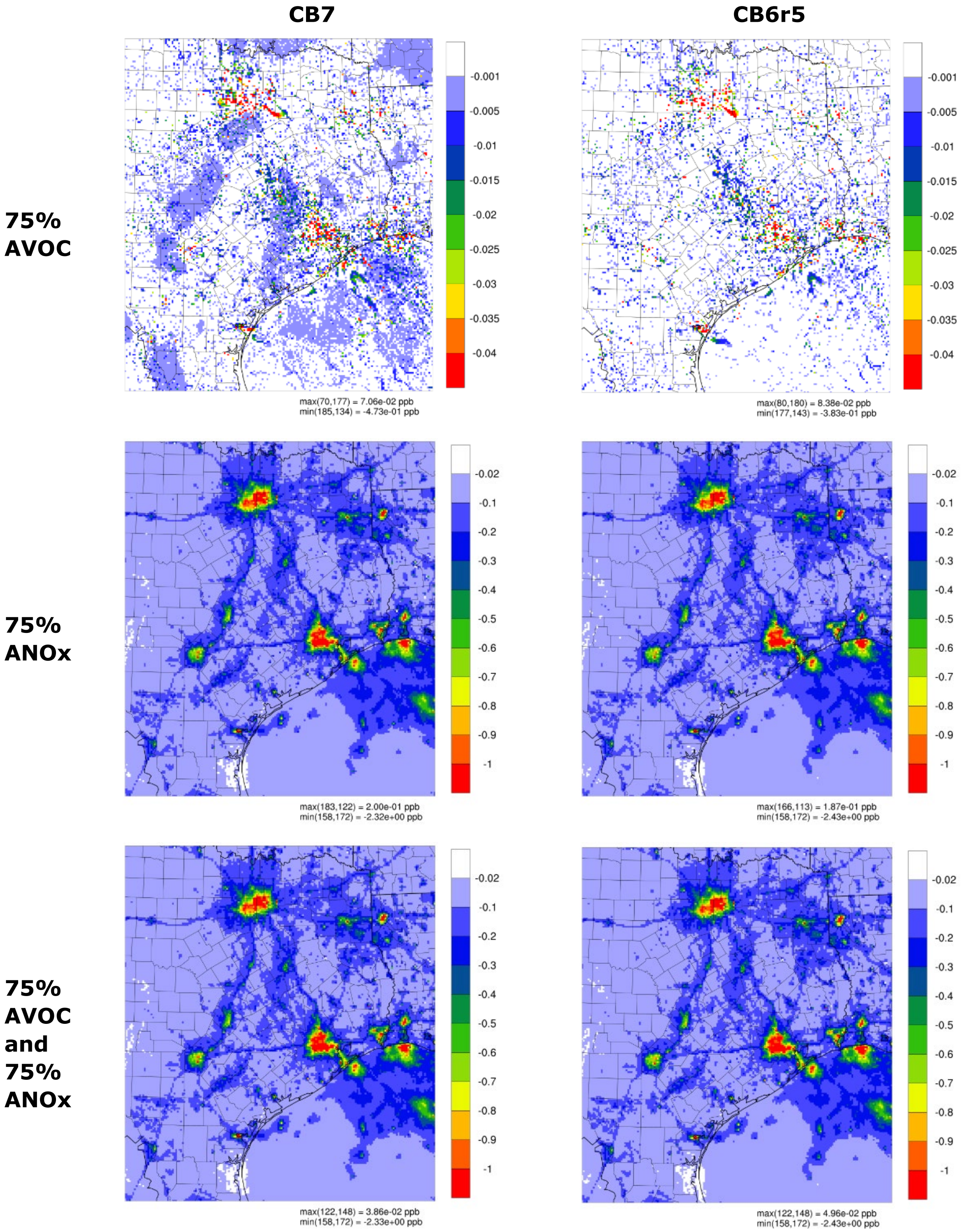


Figure 19. Differences in June average NO_2 (ppb), for hours matching MDA8 O_3, for anthropogenic emission scenarios – base case (rows) with CB7 and CB6r5 (columns). The top row has a different color scale.

To quantitatively evaluate the O_3 response to reducing anthropogenic emissions we computed emission response factors by taking the ratio of MDA8 O_3 in the sensitivity case to MDA8 O_3 in the base case. We computed representative emission response factors for Texas regions (Table 8) by averaging them over all CAMS within each region on the Top 10 days (June 7-9 and June 22-28). Data from Table 8 are plotted in Figure 20. This analysis has similarities with, but also important differences from, the relative response factor (RRF) methodology used to compute future O_3 design values based on model results. Figure 20 and Figure 18 are consistent in showing that CB7 is somewhat less responsive than CB6r5 to reducing anthropogenic NOx emissions and therefore could be expected to produce somewhat higher future O_3 design values for emission reduction scenarios that rely on reducing NOx emissions.

Table 8. Average maximum daily 8-hour average (MDA8) O_3 emission response factors on the Top 10 days by region.

Region	**75% ANOx CB7**	**75% ANOx CB6r5**	**75% AVOC CB7**	**75% AVOC CB6r5**	**75% ANOx and 75% AVOC CB7**	**75% ANOx and 75% AVOC CB6r5**
Austin	0.907	0.897	0.995	0.997	0.904	0.896
Dallas (DFW)	0.916	0.907	0.992	0.994	0.910	0.903
Beaumont (BPA)	0.915	0.904	0.992	0.995	0.909	0.900
Houston (HGB)	0.914	0.903	0.990	0.993	0.907	0.898
San Antonio	0.910	0.900	0.993	0.996	0.905	0.898
Corpus Christi	0.917	0.907	0.994	0.997	0.913	0.905
Northeast Texas	0.907	0.896	0.996	0.998	0.904	0.895

Note: Emission response factor is sensitivity case MDA8 O_3 / base case MDA8 O_3. The Top 10 days are June 7-9 and June 22-28.

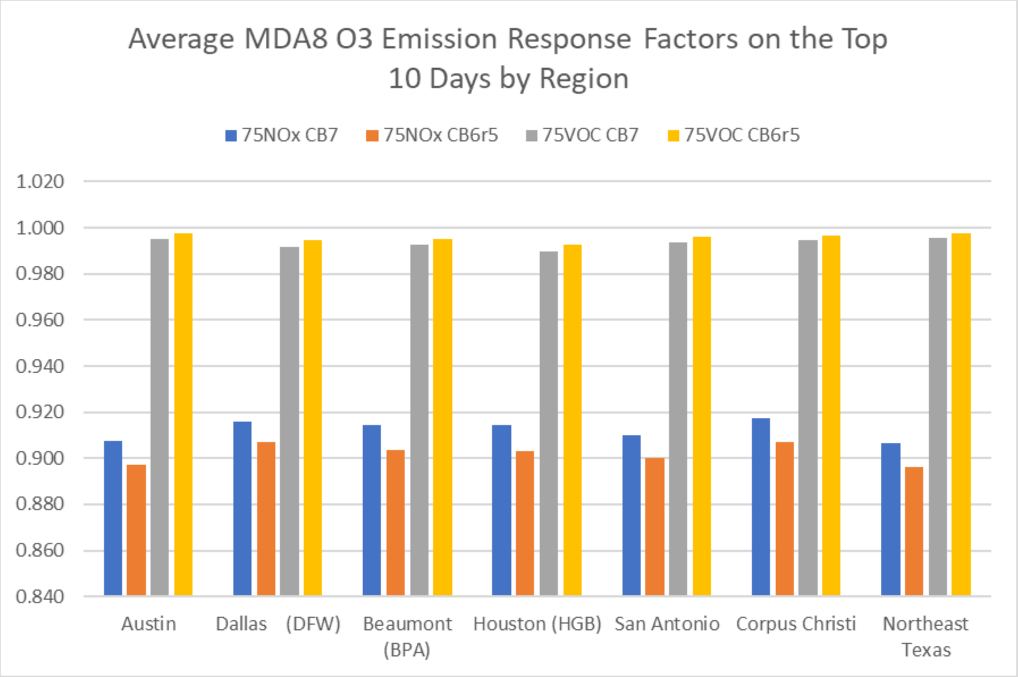


Figure 20. Average maximum daily 8-hour average (MDA8) O_3 emission response factors on the Top 10 days by region.

1.15 Ozone Response to Changing Biogenic Emissions

The response of June average MDA8 O_3 to biogenic emission sensitivity tests with CB7 and CB6r5 is compared in Figure 21. As discussed above, the biogenic emission sensitivity tests investigate the effects of recent updates to the BEIS biogenic emission model and its associated BELD vegetation cover database. Changes in biogenic VOC (BVOC) and NOx (BNOx) were evaluated separately and emission changes were applied only within the 4 km grid. The change in BVOC causes substantially greater O_3 response than the change in BNOx with both CB7 and CB6r5 (Figure 21). June average MDA8 O_3 is reduced over central Texas where isoprene emissions were reduced (Figure 5) and these O_3 reductions are slightly stronger with CB7 than CB6r5. We also looked into changes in Total PAN at the hours matching MDA8 O_3 (Figure 22), finding stronger reductions with CB7 than CB6r5, but this analysis did not provide additional insight (beyond the discussion above) as to the influence of the CB7 terpene mechanism update on O_3.

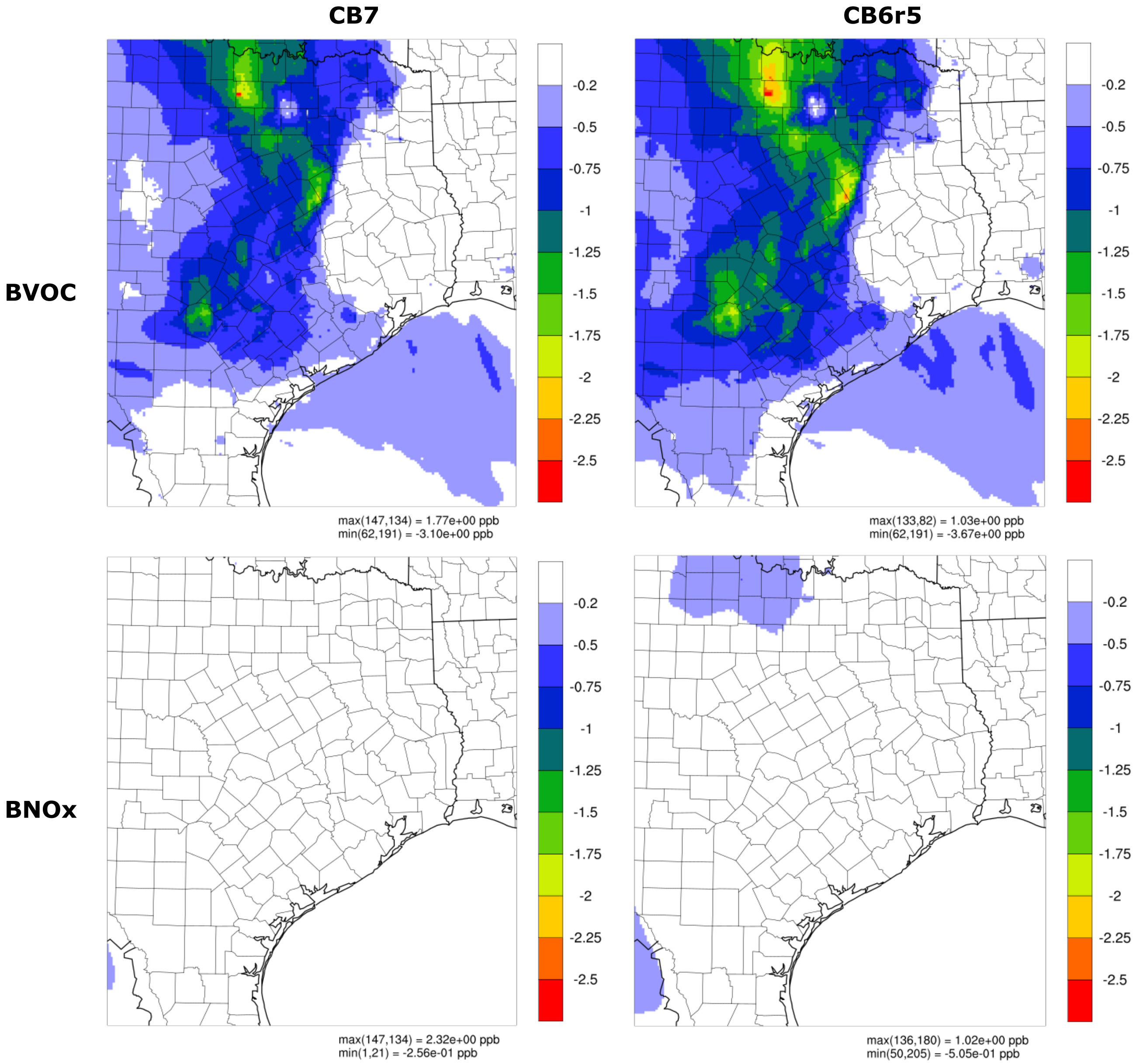


Figure 21. Differences in June average maximum daily 8-hour average (MDA8) O_3 (ppb) from the base case for the biogenic VOC and NOx emission sensitivity tests (rows) with CB7 and CB6r5 (columns).

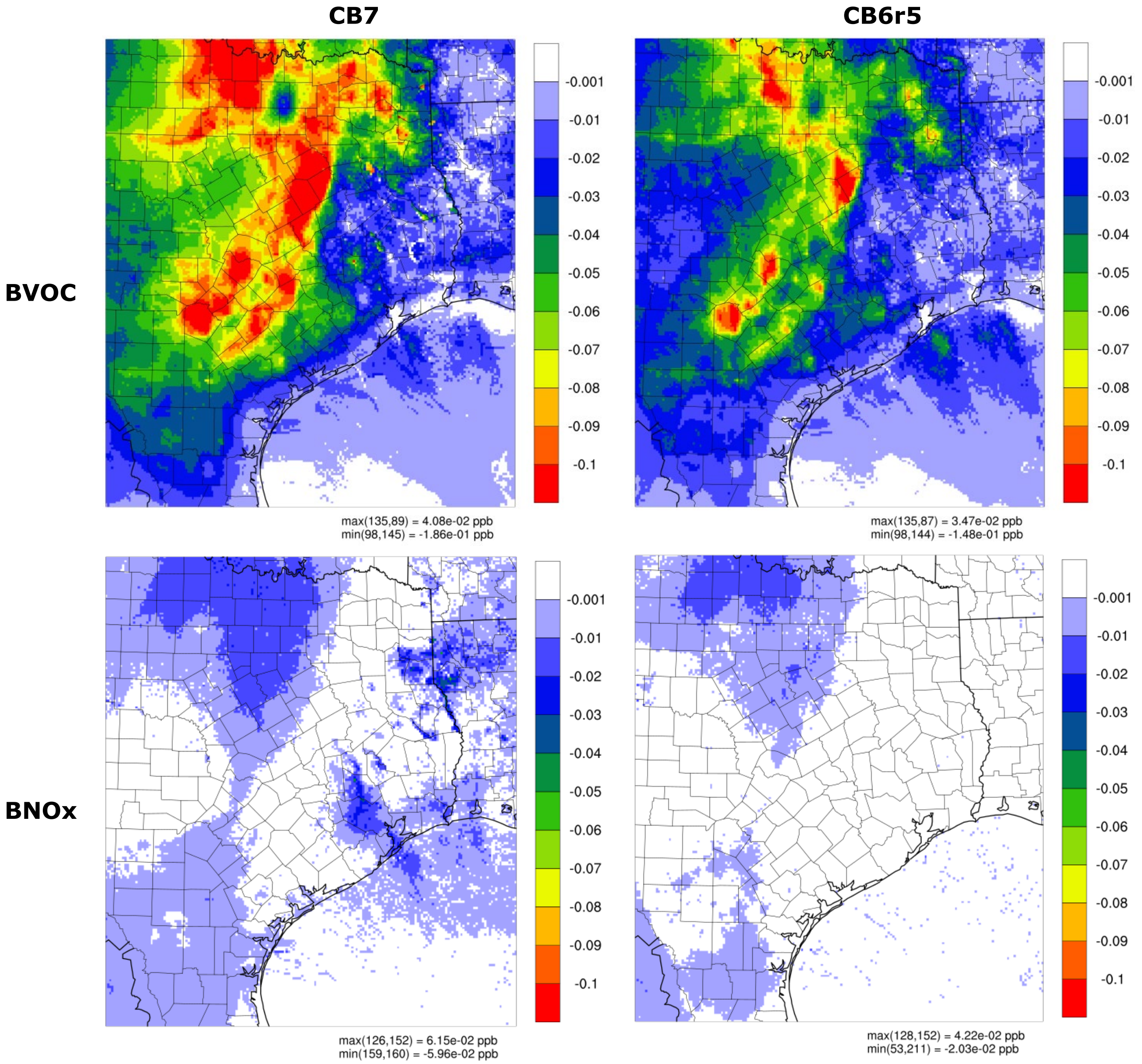


Figure 22. Differences in June average total PANs (ppb), for hours matching MDA8 O_3, for the biogenic VOC and NOx emission sensitivity tests (rows) with CB7 and CB6r5 (columns).

CONCLUSIONS

We updated the Carbon Bond chemical mechanism from CB6r5 to CB7. Many parts of CB6r5 were recently reviewed and updated (Yarwood and Beardsley, 2020) and for CB7 we prioritized updates to portions of the organic chemistry that are important and where newer information is available. We updated reactions for isoprene and terpenes, which are mainly biogenic, as well as for larger alkanes, which are mainly anthropogenic. We made other updates to improve efficiency and consistency. In all, 74 reactions in CB7 are updated or new as compared to CB6r5, and 23 reactions in CB6r5 were eliminated from CB7. The CB7 mechanism has 229 reactions among 92 species as compared to CB6r5 which has 234 reactions among 86 species.

We tested CB7 in CAMx using a modeling database for June 2012 developed by the TCEQ. Changes in MDA8 O_3 between CB7 and CB6r5 are relatively small and include areas of increase and decrease. Urban areas are not apparent in the O_3 differences over the Texas 4 km grid suggesting that differences are associated with updates to reactions of biogenic VOC, namely isoprene, terpenes and sesquiterpenes. MDA8 O_3 decreases over land tend to be larger (1 - 2 ppb reduction) over forested areas of eastern Texas and the Southeast where forests include conifers that tend to emit terpenes and sesquiterpenes, and isoprene emissions also are strong. Larger MDA8 O_3 decreases (1.5 - 2.5 ppb reduction) occur over the Gulf of Mexico near the coastline that are caused by the iodine chemistry update, i.e., somewhat increased O_3 destruction by iodine, as well as reduced O_3 transport from land to over the Gulf. Similar over-water O_3 decreases occur near the mid-Atlantic and Northeast States. MDA8 O_3 increases (up to 0.5 ppb) are confined to land areas of the plains from West Texas to South Dakota as well as Eastern Mexico. These areas have terpene and sesquiterpene emissions from croplands and relatively low isoprene emission. We conclude that O_3 differences are mainly associated with the CB7 updates to reactions of biogenic VOCs with small O_3 reductions predominating except in areas dominated by croplands and prairies that show small O_3 increases.

We performed a statistical evaluation of model performance for MDA8 O_3 using data from TCEQ CAMS and found that CB7 agrees slightly better with observation than CB6r5. We consider this improvement to be small and therefore conclude that CB7 and CB6r5 show equivalent performance for O_3 in Texas.

MDA8 O_3 concentrations on high O_3 days are somewhat less responsive to NOx emission reduction with CB7 than CB6r5. Therefore, CB7 could be expected to produce somewhat higher future O_3 design values for emission reduction scenarios that rely on reducing NOx emissions. CB7 and CB6r5 show similar responses of MDA8 O_3 to reducing anthropogenic VOC emissions with modest O_3 reductions in and downwind of major cities and minimal O_3 reductions elsewhere. Both CB6r5 and CB7 show that VOC reduction can help mitigate O_3 disbenefits associated with NOx emission reduction in some urban areas.

We recommend further evaluation of the CB7 terpene mechanism with consideration of the extent to which NOx is sequestered at night (particularly in PAN compounds) and returned during the day where it can sustain O_3 production in NOx-limited environments. Adding one or more model species that are specifically designed to represent terpene oxidation products would improve the CB7 terpene mechanism and could influence how the mechanism responds to anthropogenic emission changes.

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