

# Eta-CMAQ air quality forecasts for O<sub>3</sub> and related species using three different photochemical mechanisms (CB4, CB05, SAPRC-99): comparisons with measurements during the 2004 ICARTT study

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**Abstract.** A critical module of air quality models is the photochemical mechanism. In this study, the impact of the three photochemical mechanisms (CB4, CB05, SAPRC-99) on the Eta-Community Multiscale Air Quality (CMAQ) model's forecast performance for O<sub>3</sub>, and its related precursors has been assessed over the eastern United States with observations obtained by aircraft (NOAA P-3 and NASA DC-8) flights, ship and two surface networks (AIRNow and AIRMAP) during the 2004 International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) study. The results show that overall none of the mechanisms performs systematically better than the others. On the other hand, at the AIRNow surface sites, CB05 has the best performance with the normalized mean bias (NMB) of 3.9%, followed by CB4 (NMB=−5.7%) and SAPRC-99 (NMB=10.6%) for observed O<sub>3</sub> ≥ 75 ppb, whereas CB4 has the best performance with the least overestimation for observed O<sub>3</sub> < 75 ppb. On the basis of comparisons with aircraft P-3 measurements, there were consistent overestimations of O<sub>3</sub>, NO<sub>z</sub>, PAN and NO<sub>y</sub> and consistent underestimations of CO, HNO<sub>3</sub>, NO<sub>2</sub>, NO, SO<sub>2</sub> and terpenes for all three mechanisms although the NMB values for each species and mechanisms were different. The results of aircraft DC-8 show that CB05 predicts the H<sub>2</sub>O<sub>2</sub> mixing ratios

most closely to the observations (NMB=10.8%), whereas CB4 and SAPRC-99 overestimated (NMB=74.7%) and underestimated (NMB=−25.5%) H<sub>2</sub>O<sub>2</sub> mixing ratios significantly, respectively. For different air mass flows over the Gulf of Maine on the basis of the ship data, the three mechanisms have relatively better performance for O<sub>3</sub>, isoprene and SO<sub>2</sub> for the clean marine or continental flows but relatively better performance for CO, NO<sub>2</sub> and NO for southwesterly/westerly offshore flows. The results of the O<sub>3</sub>-NO<sub>z</sub> slopes over the ocean indicate that SAPRC-99 has the highest upper limits of the ozone production efficiency ( $\epsilon_N$ ) (5.8), followed by CB05 (4.5) and CB4 (4.0) although they are much lower than that inferred from the observation (11.8), being consistent with the fact that on average, SAPRC-99 produces the highest O<sub>3</sub>, followed by CB05 and CB4, across all O<sub>3</sub> mixing ratio ranges

## 1 Introduction

One of the most important components of air quality models (AQMs) is the photochemical mechanism which describes how volatile organic compounds (VOCs) and oxides of nitrogen (NO<sub>x</sub>) interact to produce O<sub>3</sub> and other oxidants. Photochemical mechanisms were first used in AQMs more than 30 years ago (e.g., Reynolds et al., 1973). Highly detailed and explicit photochemical mechanisms such as the Master Chemical Mechanism (MCM) (Jenkin et al., 1997),



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which includes over 2400 chemical species and over 7100 chemical reactions for 120 of the most important emitted organic compounds, exist. The chemistry of atmospheric systems involves reactions whose characteristic time scales vary by orders of magnitude, resulting in a set of nonlinear stiff ordinary differential equations (ODEs), the numerical integration of which often comprises a large fraction of the overall chemical transport model computational time (Mathur et al., 1998; McRae et al., 1982). Thus, for practical reasons, the representation of photochemical mechanism in AQMs employs different methods including various types of parameterizations, approximations and condensations (Dodge, 2000). Uncertainties in the model's chemical mechanisms can range to 30% or more when new techniques are applied to re-measure reaction rate constants and yields (Russell and Dennis, 2000).

Three of the most commonly used chemical mechanisms in current AQMs for both regulatory and research applications include the Carbon Bond 4 (CB4) (Gery et al., 1989), SAPRC-99 (Carter, 2000) and CB05 (an update to CB4, Yarwood et al., 2005). All three mechanisms have been evaluated against measurements from a large number of chamber experiments and have been demonstrated to be reasonably successful in predicting ozone and related species from complex mixtures in "typical" urban atmospheres (Gery et al., 1989; Yarwood et al., 2005; Carter, 2000). The Carbon Bond (CB) mechanisms mostly use the lumped structure technique to condense the reactions of individual VOCs, whereas the SAPRC mechanism uses the lumped molecule technique to condense VOCs. In the lumped molecule technique, a generalized or surrogate species is used to represent similar organic compounds, whereas in the lumped structure technique, organic compounds are grouped according to bond type. Given the fact that different chemical schemes can have different formulations of the reaction mechanism, different rate constants and temperature and pressure dependencies for the reactions (Kuhn et al., 1998), it is not surprising that they sometimes yield different results. Several intercomparison studies of different chemical mechanisms have been performed with box and trajectory models, and 3-D AQMs over the last decade and the results have been summarized in detail by many investigators (Dunker et al., 1984; Stockwell, 1986; Jimenez et al., 2003; Gross and Stockwell, 2003; Kuhn et al., 1998; Luecken et al., 1999, 2008). For example, with box model calculation, Jimenez et al. (2003) compared seven different photochemical mechanisms (including LCC, CBM-IV, RADM2, EMEP, RACM, SAPRC-99 and CACM) and indicated that most chemical schemes yield similar O<sub>3</sub> mixing ratios. However, they also found significant discrepancies, mainly in predicted mixing ratios of HNO<sub>3</sub>, HO<sub>2</sub> and total PAN among the model simulations, even under extremely simple situations. With the simulations of 3-D AQMs, Faraji et al. (2008) compared CB4 and SAPRC-99 in southeast Texas and found that for most urban areas, the CB4 and SAPRC-99 mechanisms yield similar

results, but for 2000 summer in southeast Texas, the SAPRC-99 mechanism leads to O<sub>3</sub> mixing ratios that are 30–45 ppb higher than CB4. Faraji et al. (2008) attributed these discrepancies to differences in both reaction rate/stoichiometry parameters and condensation methods in the mechanisms. On the other hand, Luecken et al. (2008) recently examined the differences in predictions of O<sub>3</sub> and its O<sub>3</sub> precursors among CB4, CB05 and SAPRC-99 in a 3-D MM5-CMAQ model over the continental US. They show that the predicted O<sub>3</sub> mixing ratios are similar for most of the US, but statistically significant differences occur over many urban areas and the central US among the predictions by the three mechanisms, depending on location, the VOC/NO<sub>x</sub> ratio, and precursor concentrations. They also found that on average, SAPRC-99 predicts the highest O<sub>3</sub>, followed by CB05 and CB4.

In this study, we compare the CB4, CB05 and SAPRC-99 mechanisms by examining the impact of these different chemical mechanisms on the Eta-CMAQ air quality forecast model simulations for O<sub>3</sub> and its related precursors over the eastern US through comparisons with the intensive observational data obtained during the 2004 International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) study. The 2004 ICARTT experiment provided a comprehensive set of measurements of chemical constituents, both from surface and aircraft based platforms, which can be used to examine in detail the impact of chemical mechanisms from a multi-pollutant perspective, both in terms of their surface concentrations as well as vertical structure. This aspect constitutes the primary difference of this study from the previous comparative analyses of these mechanisms. The objective of this study is to assess the influence of the three photochemical mechanisms on the Eta-Community Multiscale Air Quality (CMAQ) model's ability to simulate O<sub>3</sub>, its related chemical species over the eastern United States with observations obtained by aircraft (NOAA P-3 and NASA DC-8) flights, ship and two surface networks (AIRNow and Atmospheric Investigation, Regional Modeling, Analysis, and Prediction (AIRMAP)) during the 2004 ICARTT study.

## 2 Description of the photochemical mechanisms, Eta-CMAQ model and observation database

### 2.1 Photochemical mechanisms

Detailed description of the CB4, CB05 and SAPRC-99 chemical mechanisms (species and reaction rates) and their evaluations against smog chamber experimental data can be found in Gery et al. (1989), Yarwood et al. (2005) and Carter (2000), respectively. Luecken et al. (2008) previously summarized the general characteristics of the three mechanisms used in this study; a brief summary relevant to this study is presented here. The version of CB4 in CMAQ (<http://www.cmaq-model.org>) has 46 species (30 organic species)

and 96 reactions (45 inorganic reactions). In contrast, CB05, an updated version of the CB4, includes 59 species and 156 reactions, with updated reaction rate constants, additional inorganic reactions and more organic species relative to CB4. Both CB4 and CB05 mostly use the lumped-structure technique to condense the organic chemistry. On the other hand, SAPRC-99 has 80 species and 214 reactions and uses a lumped molecule approach to condense the organic chemistry, i.e., surrogate species are used to represent similar organic compound. Tables 1 and 2 compare the reaction rates of inorganic and organic species at 298 K and 1 atmosphere, respectively, for the three mechanisms. Inorganic chemistry describes the chemistry of  $O_3$ , various  $NO_x$  species,  $H_2O_2$ , OH and  $HO_2$  radicals, CO,  $HNO_3$ ,  $HNO_2$ ,  $HNO_4$  and PNA. Organic chemistry includes the chemistry of formaldehyde, higher molecular weight aldehydes, alkanes, alkenes, aromatics, isoprene, terpene, ketone, and other organic compounds. As can be seen, there are many differences among CB4, CB05 and SAPRC-99 chemical mechanisms. SAPRC-99 includes more detailed organic chemistry than Carbon Bond mechanisms as SAPRC-99 was developed with the additional capability of representing reactions of a wide variety of individual VOCs (Carter, 1999). Updates to inorganic chemistry in CB05 compared to CB4 mechanism include (Yarwood et al., 2005): (1) updated rate constants based on recent (2003–2005) IUPAC and NASA evaluations, (2) an extended inorganic reaction set for urban to remote tropospheric conditions, (3)  $NO_x$  recycling reactions to represent the fate of  $NO_x$  over multiple days. Updates to organic chemistry in CB05 compared to CB4 mechanism include (Yarwood et al., 2005): (1) explicit organic chemistry for methane and ethane, (2) explicit methylperoxy radical, methyl hydroperoxide and formic acid, (3) lumped higher organic peroxides, organic acids and peracids, (4) internal olefin (R-HC=CH-R) species called IOLE, (5) higher aldehyde species ALDX, making ALD2 explicitly acetaldehyde, (6) higher peroxyacyl nitrate species from ALDX called PANX. As analyzed by Luecken et al. (2008), the reasons for CB05 to produce more  $O_3$  relative to CB4 include (1) the ALDX (aldehydes with more than two carbons) species in CB05 can produce about 50% more conversions of NO to  $NO_2$ , (2) the photolysis rate of ALDX in CB05 is higher compared to ALD2, leading to higher production of  $HO_x$ , (3) the additional acyl peroxy radicals (CXO3) in CB05 (e.g., CB05 uses two species (acetyl peroxy radical (C2O3) and other acyl peroxy radicals (CXO3) while CB4 only uses one species to represent all acyl peroxy radicals (C2O3)) can produce 50% more conversions of NO to  $NO_2$  than C2O3; this effect is apparent in the reactions of alkenes, including isoprene, with  $O_3$  and  $NO_3$ , (4) CB05 uses methyl peroxy radical (MEO2) to replace the alkyl peroxy radical operator (XO2) in some reactions to better represent reactions under low  $NO_x$  conditions, (5) CB05 adds a model species to represent internal alkenes, which are allowed to react with  $O_3$  and can change the temporal production of  $O_3$ , (6) CB05 allows

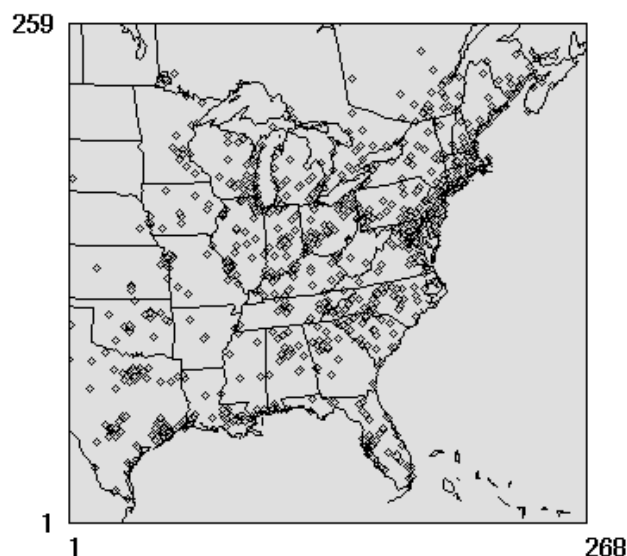


Fig. 1. The model domain and locations of AIRNow monitoring sites.

$HNO_3$  and organic nitrate to photolyze and produce  $HO_x$  and  $NO_2$ , providing additional organic radicals.

## 2.2 Eta-CMAQ forecast model

The developmental Eta-CMAQ air quality forecasting system for  $O_3$ , created by linking the Eta model (Rogers et al., 1996) and the CMAQ modeling system (Byun and Schere, 2006), was applied over a domain encompassing the eastern US (see Fig. 1) during summer 2004. The detailed description of model configurations can be found in Yu et al. (2007). The Eta model provided the meteorological fields for input to CMAQ. The model domain has a horizontal grid spacing of 12 km with twenty-two vertical layers between the surface and 100 mb. The boundary conditions for various species were based on a static vertical profile that was uniformly applied along all lateral boundaries. The species profiles are representative of continental “clean” conditions except  $O_3$  whose lateral boundary conditions are derived from the Global Forecast System (GFS) model. The primary Eta-CMAQ model forecast for next-day is based on the current day’s 12:00 UTC Eta simulation cycle. The area source emissions are based on the 2001 National Emission Inventory (NEI). The point source emissions are based on the 2001 NEI with  $SO_2$  and  $NO_x$  projected to 2004 on a regional basis using the Department of Energy’s 2004 Annual Energy Outlook issued in January of 2004. The mobile source emissions were generated by EPA’S MOBILE6 model using 1999 vehicle miles traveled (VMT) data and a fleet year of 2004. Daily temperatures from the Eta model were used to drive the inputs into the MOBILE6 model using a nonlinear least squares relationship described in Pouliot (2005). The

**Table 1.** Comparison of the reaction rates of inorganic species at 298 K and 1 atm ( $s^{-1}$  for first order reactions,  $cm^3 \text{ molecule}^{-1} s^{-1}$  for second-order,  $cm^6 \text{ molecule}^{-2} s^{-1}$  for third-order reactions) in CB4, CB05 and SAPRC-99. Details on reaction rates and species can be found in Gery et al. (1989), Yarwood et al. (2005) and Carter (2000) for CB4, CB05 and SAPRC-99, respectively.

Reaction	CB4	CB05	SAPRC-99	Comments
<b>NO<sub>x</sub> and O<sub>3</sub> chemistry</b>				
NO <sub>2</sub> +hν → NO+O	photolysis	photolysis	photolysis	
O <sub>3</sub> +hν → O+O <sub>2</sub>	photolysis	photolysis	photolysis	
O <sub>3</sub> +hν → OSD+O <sub>2</sub>	photolysis	photolysis	photolysis	
HONO+hν → NO+OH	photolysis	photolysis	photolysis	
HONO+hν → NO <sub>2</sub> +HO <sub>2</sub>			photolysis	Not in CB4, CB05
O+O <sub>2</sub> +M → O <sub>3</sub> +M	5.57E-34	6.11E-34	5.79E-34	
O+NO → NO <sub>2</sub>	1.66E-12	1.66E-12	2.48E-12	
O+NO <sub>2</sub> → NO+O <sub>2</sub>	9.30E-12	1.02E-11	9.72E-12	
O+O <sub>3</sub> → 2O <sub>2</sub>			7.96E-15	Not in CB4, CB05
O1D+H <sub>2</sub> O → 2OH	2.20E-10	2.20E-10	2.20E-10	
O1D+M → O+M	2.58E-11	2.96E-11	2.87E-11	
O <sub>3</sub> +OH → HO <sub>2</sub> +O <sub>2</sub>	6.83E-14	7.25E-14	6.63E-14	
O <sub>3</sub> +HO <sub>2</sub> → OH+2O <sub>2</sub>	2.00E-15	1.93E-15		Not in SAPRC-99
NO+NO+O <sub>2</sub> → 2NO <sub>2</sub>	1.95E-38	1.96E-38	1.95E-38	
NO+NO <sub>2</sub> +H <sub>2</sub> O → 2HONO	4.40E-40	5.00E-40		Not in SAPRC-99
NO+O <sub>3</sub> → NO <sub>2</sub> +O <sub>2</sub>	1.81E-14	1.95E-14	1.81E-14	
NO+OH+M → HONO+M	6.70E-12	7.41E-12	7.41E-12	
NO+HO <sub>2</sub> → NO <sub>2</sub> +OH	8.28E-12	8.10E-12	8.41E-12	
NO <sub>2</sub> +NO <sub>3</sub> → NO+NO <sub>2</sub> +O <sub>2</sub>	4.03E-16	6.56E-16	6.56E-16	
NO <sub>2</sub> +HO <sub>2</sub> +M → HNO <sub>4</sub> +M	1.48E-12	1.38E-12	1.38E-12	
HONO+OH → NO <sub>2</sub> +H <sub>2</sub> O	6.60E-12	4.86E-12	6.46E-12	
HONO+HONO → NO+NO <sub>2</sub>	1.00E-20	1.00E-20		Not in SAPRC-99
HNO <sub>4</sub> +M → NO <sub>2</sub> +HO <sub>2</sub> +M			7.55E-02	Not in CB4, CB05
HNO <sub>4</sub> +OH → NO <sub>2</sub> +O <sub>2</sub> +H <sub>2</sub> O			5.02E-12	Not in CB4, CB05
SO <sub>2</sub> +OH → H <sub>2</sub> SO <sub>4</sub> +HO <sub>2</sub>	8.89E-13	8.89E-13	9.77E-13	
CO+OH → HO <sub>2</sub> +CO <sub>2</sub>	2.40E-13	2.41E-13	2.09E-13	

biogenic emissions are calculated using Biogenic Emissions Inventory System (BEIS) version 3.12. The CB4, CB05 and SAPRC-99 chemical mechanisms as described in Sect. 2.2 have been used to represent photochemical reaction pathways in the three cases.

### 2.3 Observation database

The hourly, near real-time observed O<sub>3</sub> data at 614 sites in the eastern US are available from the US EPA's AIRNow (Fig. 1) for the study period. Note that AIRNow data have only gone through some preliminary data quality assessments. From 1 July to 15 August, 2004, measurements of vertical profiles of O<sub>3</sub> and its related chemical

Table 1. Continued.

Reaction	CB4	CB05	SAPRC-99	Comments
<b>NO<sub>3</sub> and HNO<sub>3</sub> chemistry</b>				
NO <sub>3</sub> +hν → NO+O <sub>2</sub>		photolysis	photolysis	Not in CB4
NO <sub>3</sub> +hν → NO <sub>2</sub> +O	photolysis	photolysis	photolysis	
HNO <sub>3</sub> +hν → NO <sub>2</sub> +OH		photolysis	photolysis	Not in CB4
HNO <sub>4</sub> +hν → 0.61HO <sub>2</sub> +0.61NO <sub>2</sub> +0.39OH+0.39NO <sub>3</sub>			photolysis	Not in CB4, CB05
O+NO <sub>2</sub> +M → NO <sub>3</sub> +M	1.58E-12	3.28E-12	1.82E-12	
NO <sub>2</sub> +O <sub>3</sub> → NO <sub>3</sub> +O <sub>2</sub>	3.23E-17	3.23E-17	3.52E-17	
NO <sub>2</sub> +OH → HNO <sub>3</sub>	1.15E-11	1.05E-11	8.98E-12	
HNO <sub>3</sub> +OH → NO <sub>3</sub> +H <sub>2</sub> O	1.47E-13	1.54E-13	1.47E-13	
NO <sub>3</sub> +OH → NO <sub>2</sub> +HO <sub>2</sub>		2.20E-11	2.00E-11	Not in CB4
NO <sub>3</sub> +HO <sub>2</sub> → HNO <sub>3</sub> +O <sub>2</sub>		3.50E-12		Not in CB4, SAPRC-99
NO <sub>3</sub> +HO <sub>2</sub> → 0.8NO <sub>2</sub> +0.2HNO <sub>3</sub> +0.8OH+O <sub>2</sub>			4.00E-12	Not in CB4, CB05
NO <sub>3</sub> +NO <sub>3</sub> → 2NO <sub>2</sub> +O <sub>2</sub>		2.28E-16	2.28E-16	Not in CB4
NO <sub>3</sub> +NO → 2NO <sub>2</sub>	3.01E-11	2.65E-11	2.60E-11	
NO <sub>3</sub> +NO <sub>2</sub> +M → N <sub>2</sub> O <sub>5</sub> +M	1.26E-12	1.18E-12	1.54E-12	
N <sub>2</sub> O <sub>5</sub> → NO <sub>2</sub> +NO <sub>3</sub>	4.36E-02	5.28E-02	5.28E-02	
N <sub>2</sub> O <sub>5</sub> +H <sub>2</sub> O → 2HNO <sub>3</sub>	0.00E+00	0.00E+00	0.00E+00	
<b>HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> chemistry</b>				
H <sub>2</sub> O <sub>2</sub> +hν → 2OH	photolysis	photolysis	photolysis	
HO <sub>2</sub> +OH → H <sub>2</sub> O+O <sub>2</sub>		1.11E-10	1.11E-10	Not in CB4
HO <sub>2</sub> +HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub>	2.80E-12	1.72E-12	1.64E-12	
HO <sub>2</sub> +HO <sub>2</sub> +H <sub>2</sub> O → H <sub>2</sub> O <sub>2</sub> +O <sub>2</sub> +H <sub>2</sub> O	6.24E-30	3.87E-30	3.78E-30	
H <sub>2</sub> O <sub>2</sub> +OH → HO <sub>2</sub> +H <sub>2</sub> O	1.66E-12	1.70E-12	1.70E-12	
OH+H <sub>2</sub> → HO <sub>2</sub>		6.69E-15	6.70E-15	Not in CB4

species (CO, NO, NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>O, HNO<sub>3</sub>, SO<sub>2</sub>, PAN, isoprene, terpenes) were carried out by instrumented aircraft (NOAA P-3 and NASA DC-8) deployed as part of the 2004 ICARTT field experiment. The observations of O<sub>3</sub> and its related chemical species along the coast of New Hampshire, Massachusetts and Maine were obtained by the NOAA ship Ronald H. Brown during the 2004 ICARTT field experiment. The detailed instrumentation and protocols for measurements are described in <http://www.al.noaa.gov/ICARTT/FieldOperations/>. The flight tracks of P-3, DC-8, and ship are presented in Fig. 2. Four sites of the AIRMAP (DeBell et al., 2004; Mao and Talbot, 2004) provided continuous measurements of O<sub>3</sub> and related photochemical species as well as meteorological parameters

during the study; the sites include Castle Springs (CS) (43.73° N, 71.33° W), New Hampshire (NH), Isle of Schoals (IS) (42.99° N, 69.33° W), Maine, Mount Washington Observatory (MWO) (44.27° N, 71.30° W), NH, and Thompson Farm (TF) (43.11° N, 70.95° W), NH. The comparison of the model results for the three mechanisms during the period of 15 July–18 August, 2004 is examined in this study.

### 3 Results and discussion

#### 3.1 O<sub>3</sub> comparison at the AQS sites

To gain insights into the model performance, the normalized mean bias (NMB) values (Yu et al., 2006) for maximum 8-h

**Table 2.** The same as Table 1 but for organic species.

Reactions	CB4	CB05	SAPRC-99	Comments
<b>Formaldehyde</b>				
$\text{HCHO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}$	1.00E-11	9.00E-12	9.20E-12	Formaldehyde
$\text{HCHO} \rightarrow 2\text{HO}_2 + \text{CO}$	photolysis	photolysis	photolysis	
$\text{HCHO} \rightarrow \text{CO}$	photolysis	photolysis	photolysis	
$\text{HCHO} + \text{O} \rightarrow \text{OH} + \text{HO}_2 + \text{CO}$	1.65E-13	1.58E-13		
$\text{HCHO} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{HO}_2 + \text{CO}$	6.30E-16	5.80E-16	5.73E-16	
$\text{HCHO} + \text{HO}_2 \rightarrow \text{HCO}_3$		7.90E-14	7.90E-14	
$\text{HCO}_3 \rightarrow \text{HCHO} + \text{HO}_2$		1.51E+02	1.51E+02	
$\text{HCO}_3 + \text{NO} \rightarrow \text{HCOOH} + \text{NO}_2 + \text{HO}_2$		5.60E-12	7.29E-12	
$\text{HCO}_3 + \text{HO}_2 \rightarrow \text{MEPX}$		1.26E-11		
$\text{HCOOH} + \text{OH} \rightarrow \text{HO}_2$		4.00E-13	4.50E-13	Formic acid
$\text{MEO}_2 + \text{NO} \rightarrow \text{HCHO} + \text{HO}_2 + \text{NO}_2$		7.66E-12	7.29E-12	Methylperoxy radical
$\text{MEO}_2 + \text{HO}_2 \rightarrow \text{MEPX}$		5.08E-12	5.21E-12	
$\text{MEO}_2 + \text{MEO}_2 \rightarrow 1.37\text{HCHO} + 0.74\text{HO}_2 + 0.63\text{MEOH}$		3.52E-13		
$\text{MEOH} + \text{OH} \rightarrow \text{HCHO} + \text{HO}_2$		9.12E-13	9.14E-13	Methanol
$\text{MEPX} \rightarrow \text{HCHO} + \text{HO}_2 + \text{OH}$		photolysis	photolysis	Methylhydroperoxide
$\text{MEPX} + \text{OH} \rightarrow 0.7\text{MEO}_2 + 0.3\text{XO}_2 + 0.3\text{HO}_2$		7.43E-12		
$\text{MEO}_2 + \text{MEO}_2 \rightarrow \text{MEOH} + \text{HCHO}$			2.65E-13	Methylperoxy radical
$\text{MEO}_2 + \text{MEO}_2 \rightarrow 2\text{HCHO} + 2\text{HO}_2$			1.07E-13	
$\text{MEO}_2 + \text{NO}_3 \rightarrow \text{HCHO} + \text{HO}_2 + \text{NO}_2$			1.30E-12	
$\text{MEPX} + \text{HO} \rightarrow 0.35\text{HCHO} + 0.35\text{HO} + 0.65\text{MEO}_2$			5.49E-12	Methylhydroperoxide
<b>Alkene reactions</b>				
$\text{OLE} + \text{O} \rightarrow 0.63\text{ALD}_2 + 0.38\text{HO}_2 + 0.28\text{XO}_2 + 0.3\text{CO} + 0.2\text{HCHO} + 0.02\text{XO}_2\text{N} + 0.22\text{PAR} + 0.2\text{OH}$	4.05E-12			Terminal Olefin
$\text{OLE} + \text{O} \rightarrow 0.2\text{ALD}_2 + 0.3\text{ALDX} + 0.3\text{HO}_2 + 0.2\text{XO}_2 + 0.2\text{CO} + 0.2\text{HCHO} + 0.01\text{XO}_2\text{N} + 0.2\text{PAR} + 0.1\text{OH}$		3.91E-12		
$\text{OLE} + \text{OH} \rightarrow \text{HCHO} + \text{ALD}_2 + \text{XO}_2 + \text{HO}_2 - \text{PAR}$	2.82E-11			
$\text{OLE} + \text{OH} \rightarrow 0.8\text{HCHO} + 0.33\text{ALD}_2 + 0.62\text{ALDX} + 0.8\text{XO}_2 + 0.95\text{HO}_2 - 0.7\text{PAR}$		3.20E-11		
$\text{OLE} + \text{O}_3 \rightarrow 0.5\text{ALD}_2 + 0.74\text{HCHO} + 0.33\text{CO} + 0.44\text{HO}_2 + 0.22\text{XO}_2 + 0.1\text{OH} + 0.2\text{HCOOH} + 0.2\text{AACD} - \text{PAR}$	1.20E-17			
$\text{OLE} + \text{O}_3 \rightarrow 0.18\text{ALD}_2 + 0.74\text{HCHO} + 0.32\text{ALDX} + 0.22\text{XO}_2 + 0.1\text{OH} + 0.33\text{CO} + 0.44\text{HO}_2 - 1.0\text{PAR}$		1.11E-17		
$\text{OLE} + \text{NO}_3 \rightarrow 0.91\text{XO}_2 + 0.09\text{XO}_2\text{N} + \text{HCHO} + \text{ALD}_2 - \text{PAR} + \text{NO}_2$	7.70E-15			
$\text{NO}_3 + \text{OLE} \rightarrow \text{NO}_2 + \text{HCHO} + 0.91\text{XO}_2 + 0.09\text{XO}_2\text{N} + 0.56\text{ALDX} + 0.35\text{ALD}_2 - 1\text{PAR}$		4.98E-16		

Table 2. Continued.

Reactions	CB4	CB05	SAPRC-99	Comments
OLE1 + HO → 0.91RO2_R + 0.09RO2_N + 0.205R2O2 + 0.732HCHO + 0.294ALD2 + 0.497RCHO + 0.005ACET + 0.119PROD2			3.23E-11	Alkene 1
OLE1 + O3 → 0.155HO + 0.056HO2 + 0.022RO2_R + 0.001RO2_N + 0.076MEO2 + 0.345CO + 0.5HCHO + 0.154ALD2 + 0.363RCHO + 0.001ACET + 0.215PROD2 + 0.185HCOOH + 0.05CCO.OH + 0.119RCO.OH			1.07E-17	
OLE1 + NO3 → 0.824RO2_R + 0.176RO2_N + 0.488R2O2 + 0.009ALD2 + 0.037RCHO + 0.024ACET + 0.511NTR			1.26E-14	
OLE1 + O → 0.45RCHO + 0.437MEK + 0.113PROD2			4.88E-12	
OLE2 + HO → 0.918RO2_R + 0.082RO2_N + 0.001R2O2 + 0.244HCHO + 0.732ALD2 + 0.511RCHO + 0.127ACET + 0.072MEK + 0.061BALD + 0.025METHACRO + 0.025ISOPROD + OLE2AER			6.31E-11	Alkene 2
OLE2 + O3 → 0.378HO + 0.003HO2 + 0.033RO2_R + 0.002RO2_N + 0.137R2O2 + 0.197MEO2 + 0.137C2O3 + 0.006RCO.O2 + 0.265CO + 0.269HCHO + 0.456ALD2 + 0.305RCHO + 0.045ACET + 0.026MEK + 0.006PROD2 + 0.042BALD + 0.026METHACRO + 0.073HCOOH + 0.129CCO.OH + 0.303RCO.OH + OLE2AER			1.07E-16	
OLE2 + NO3 → 0.391NO2 + 0.442RO2_R + 0.136RO2_N + 0.711R2O2 + 0.03MEO2 + 0.079HCHO + 0.507ALD2 + 0.151RCHO + 0.102ACET + 0.001MEK + 0.015BALD + 0.048MVK + 0.321NTR + OLE2AER			7.26E-13	
OLE2 + O → 0.013HO2 + 0.012RO2_R + 0.001RO2_N + 0.012CO + 0.069RCHO + 0.659MEK + 0.259PROD2 + 0.012METHACRO			2.09E-11	
ETH + O → HCHO + 0.7XO2 + CO + 1.7HO2 + 0.3OH	7.01E-13	7.29E-13		Ethene
ETH + O → 0.5HO2 + 0.2RO2_R + 0.3MEO2 + 0.491CO + 0.191HCHO + 0.25ALD2 + 0.009GLY			7.29E-13	
ETH + OH → XO2 + 1.56HCHO + HO2 + 0.22ALD2	7.94E-12	8.15E-12		
ETH + OH → RO2_R + 1.61HCHO + 0.195ALD2			8.52E-12	
ETH + O3 → HCHO + 0.42CO + 0.12HO2 + 0.4HCOOH	1.89E-18			
ETH + O3 → HCHO + 0.63CO + 0.13HO2 + 0.13OH + 0.37HCOOH		1.76E-18		
ETH + O3 → 0.12HO + 0.12HO2 + 0.5CO + HCHO + 0.37HCOOH			1.59E-18	
ETH + NO3 → NO2 + XO2 + 2HCHO		2.10E-16		
ETH + NO3 → RO2_R + RCHO			2.05E-16	
IOLE + O → 1.24ALD2 + 0.66ALDX + 0.1HO2 + 0.1XO2 + 0.1CO + 0.1PAR		2.30E-11		Internal olefin
IOLE + OH → 1.300ALD2 + 0.700ALDX + HO2 + XO2		6.33E-11		
IOLE + O3 → 0.65ALD2 + 0.35ALDX + 0.25HCHO + 0.25CO + 0.5O + 0.5OH + 0.5HO2			2.09E-16	
IOLE + NO3 → 1.180ALD2 + 0.640ALDX + HO2 + NO2		3.88E-13		
METHACRO + HO → 0.5RO2_R + 0.416CO + 0.084HCHO + 0.416MEK + 0.084MGLY + 0.5MA_RCO3			3.36E-11	Methacrolein

Table 2. Continued.

Reactions	CB4	CB05	SAPRC-99	Comments
METHACRO + O <sub>3</sub> → 0.008HO <sub>2</sub> + 0.1RO <sub>2</sub> _R + 0.208HO + 0.1RCO_O2 + 0.45CO + 0.2HCHO + 0.9MGLY + 0.333HCOOH			1.13E-18	
METHACRO + NO <sub>3</sub> → 0.5HNO <sub>3</sub> + 0.5RO <sub>2</sub> _R + 0.5CO + 0.5MA_RCO3			4.58E-15	
METHACRO + O <sub>3</sub> P → RCHO			6.34E-12	
METHACRO → 0.34HO <sub>2</sub> + 0.33RO <sub>2</sub> _R + 0.33HO + 0.67C <sub>2</sub> O <sub>3</sub> + 0.67CO + 0.67HCHO + 0.33MA_RCO3			photolysis	
MA_RCO3 + NO <sub>2</sub> → MA_PAN			1.21E-11	Peroxyacyl radicals from methacrolein
MA_RCO3 + NO → NO <sub>2</sub> + HCHO + C <sub>2</sub> O <sub>3</sub>			2.80E-11	
MA_RCO3 + HO <sub>2</sub> → 0.75RCO_OOH + 0.25RCO_OH + 0.25O <sub>3</sub>			1.41E-11	
MA_RCO3 + NO <sub>3</sub> → NO <sub>2</sub> + HCHO + C <sub>2</sub> O <sub>3</sub>			4.00E-12	
MA_RCO3 + MEO <sub>2</sub> → RCO_OH + HCHO			9.64E-12	
MA_RCO3 + RO <sub>2</sub> _R → RCO_OH			7.50E-12	
MA_RCO3 + R <sub>2</sub> O <sub>2</sub> → MA_RCO3			7.50E-12	
MA_RCO3 + RO <sub>2</sub> _N → 2RCO_OH			7.50E-12	
MA_RCO3 + C <sub>2</sub> O <sub>3</sub> → MEO <sub>2</sub> + HCHO + C <sub>2</sub> O <sub>3</sub>			1.55E-11	
MA_RCO3 + RCO_O2 → HCHO + C <sub>2</sub> O <sub>3</sub> + ALD <sub>2</sub> + RO <sub>2</sub> _R			1.55E-11	
MA_RCO3 + BZCO_O2 → HCHO + C <sub>2</sub> O <sub>3</sub> + BZ_O + R <sub>2</sub> O <sub>2</sub>			1.55E-11	
MA_RCO3 + MA_RCO3 → 2HCHO + 2C <sub>2</sub> O <sub>3</sub>			1.55E-11	
<b>Isoprene reactions</b>				
ISOP + O → 0.75ISPD + 0.50HCHO + 0.25XO <sub>2</sub> + 0.25HO <sub>2</sub> + 0.25C <sub>2</sub> O <sub>3</sub> + 0.25PAR	3.60E-11	3.60E-11		Isoprene
ISOP + O → 0.01RO <sub>2</sub> _N + 0.24R <sub>2</sub> O <sub>2</sub> + 0.25MEO <sub>2</sub> + 0.24MA_RCO3 + 0.24HCHO + 0.75PROD <sub>2</sub>			3.60E-11	
ISOP + OH → 0.912ISPD + 0.629HCHO + 0.991XO <sub>2</sub> + 0.912HO <sub>2</sub> + 0.088XO <sub>2</sub> N	9.97E-11	9.97E-11		
ISOP + HO → 0.907RO <sub>2</sub> _R + 0.093RO <sub>2</sub> _N + 0.079R <sub>2</sub> O <sub>2</sub> + 0.624HCHO + 0.23METHACRO + 0.32MVK + 0.357ISOPROD			9.83E-11	
ISOP + O <sub>3</sub> → 0.65ISPD + 0.60HCHO + 0.20XO <sub>2</sub> + 0.066HO <sub>2</sub> + 0.266OH + 0.20C <sub>2</sub> O <sub>3</sub> + 0.15ALD <sub>2</sub> + 0.35PAR + 0.066CO	1.29E-17	1.29E-17		
ISOP + O <sub>3</sub> → 0.266HO + 0.066RO <sub>2</sub> _R + 0.008RO <sub>2</sub> _N + 0.126R <sub>2</sub> O <sub>2</sub> + 0.192MA_RCO3 + 0.275CO + 0.592HCHO + 0.1PROD <sub>2</sub> + 0.39METHACRO + 0.16MVK + 0.204HCOOH + 0.15RCO_OH			1.29E-17	
ISOP + NO <sub>3</sub> → 0.2ISPD + 0.8NTR + 1XO <sub>2</sub> + 0.8HO <sub>2</sub> + 0.2NO <sub>2</sub> + 0.8ALD <sub>2</sub> + 2.4PAR	6.74E-13	6.74E-13	6.74E-13	
ISOP + NO <sub>2</sub> → 0.2ISPD + 0.8NTR + 1XO <sub>2</sub> + 0.8HO <sub>2</sub> + 0.2NO + 0.8ALD <sub>2</sub> + 2.4PAR	1.49E-19	1.50E-19		



Table 2. Continued.

Reactions	CB4	CB05	SAPRC-99	Comments
ISPD + OH → 1.565PAR + 0.167HCHO + 0.713XO2 + 0.503HO <sub>2</sub> + 0.334CO + 0.168MGLY + 0.273ALD2 + 0.498C2O3	3.36E-11			Isoprene product
ISPD + OH → 1.565PAR + 0.167HCHO + 0.713XO2 + 0.503HO <sub>2</sub> + 0.334CO + 0.168MGLY + 0.252ALD2 + 0.21C2O3 + 0.25CXO3 + 0.12ALDX		3.36E-11		
ISPD + OH → 0.67RO2_R + 0.041RO2_N + 0.289MA_RCO3 + 0.336CO + 0.055HCHO + 0.129ALD2 + 0.013RCHO + 0.15MEK + 0.332PROD2 + 0.15GLY + 0.174MGLY			6.19E-11	
ISPD + O3 → 0.114C2O3 + 0.15HCHO + 0.85MGLY + 0.154HO <sub>2</sub> + 0.268OH + 0.064XO2 + 0.02ALD2 + 0.36PAR + 0.225CO	7.11E-18	7.10E-18		
ISPD + O3 → 0.4HO <sub>2</sub> + 0.048RO2_R + 0.048RCO_O2 + 0.285HO + 0.498CO + 0.125HCHO + 0.047ALD2 + 0.21MEK + 0.023GLY + 0.742MGLY + 0.1HCOOH + 0.372RCO_OH			4.18E-18	
ISPD + NO <sub>3</sub> → 0.357ALD2 + 0.282HCHO + 1.282PAR + 0.925HO <sub>2</sub> + 0.643CO + 0.850NTR + 0.075C2O3 + 0.075XO2 + 0.075HNO <sub>3</sub>	1.00E-15			
ISPD + NO <sub>3</sub> → 0.357ALDX + 0.282HCHO + 1.282PAR + 0.925HO <sub>2</sub> + 0.643CO + 0.85NTR + 0.075CXO3 + 0.075XO2 + 0.15HNO <sub>3</sub>		1.00E-15		
ISPD + NO <sub>3</sub> → 0.799RO2_R + 0.051RO2_N + 0.15MA_RCO3 + 0.572CO + 0.15HNO <sub>3</sub> + 0.227HCHO + 0.218RCHO + 0.008MGLY + 0.572NTR			1.00E-13	
ISPD → 0.333CO + 0.067ALD2 + 0.900HCHO + 0.832PAR + 1.033HO <sub>2</sub> + 0.700XO2 + 0.967C2O3	photolysis	photolysis		
ISPD → 1.233HO <sub>2</sub> + 0.467C2O3 + 0.3RCO_O2 + 1.233CO + 0.3HCHO + 0.467ALD2 + 0.233MEK			photolysis	
<b>Terpene reactions</b>				
TERP + O → 0.150ALDX + 5.12PAR + TERPAER		3.60E-11		Terpenes
TRP1 + O → 0.147RCHO + 0.853PROD2 + TRP1AER			3.27E-11	Terpenes
TERP + OH → TERPAER + OH	8.26E-11			
TERP + OH → 0.750HO <sub>2</sub> + 1.250XO2 + 0.250XO2N + 0.280HCHO + 1.66 PAR + 0.470ALDX + TERPAER		6.77E-11	8.26E-11	
TERP + NO <sub>3</sub> → TERPAER + NO <sub>3</sub>	6.58E-12			
TERP + NO <sub>3</sub> → 0.47NO <sub>2</sub> + 0.28HO <sub>2</sub> + 1.03XO2 + 0.25XO2N + 0.47ALDX + 0.53NTR + TERPAER		6.66E-12		
TRP1 + NO <sub>3</sub> → 0.474NO <sub>2</sub> + 0.276RO2_R + 0.25RO2_N + 0.75R2O2 + 0.474RCHO + 0.276NTR + TRP1AER			6.58E-12	
TERP + O3 → TERPAER + O3	6.87E-17			
TERP + O3 → 0.57OH + 0.07HO <sub>2</sub> + 0.76XO2 + 0.18XO2N + 0.24HCHO + 0.001CO + 7PAR + 0.21ALDX + 0.39CXO3 + TERPAER		7.63E-17		
TRP1 + O3 → 0.567HO + 0.033HO <sub>2</sub> + 0.031RO2_R + 0.18RO2_N + 0.729R2O2 + 0.123C2O3 + 0.201RCO_O2 + 0.157CO + 0.235HCHO + 0.205RCHO + 0.13ACET + 0.276PROD2 + 0.001GLY + 0.031BACL + 0.103HCOOH + 0.189RCO_OH + TRP1AER			6.87E-17	

Table 2. Continued.

Reactions	CB4	CB05	SAPRC-99	Comments
<b>Higher molecular weight Aldehyde</b>				
ALD2 + O → C2O3 + OH	4.39E-13	4.49E-13		Acetaldehyde
ALD2 + OH → C2O3	1.62E-11	1.39E-11	1.58E-11	
ALD2 + NO <sub>3</sub> → C2O3 + HNO <sub>3</sub>	2.50E-15	2.38E-15	2.73E-15	
ALD2 → MEO2 + CO + HO <sub>2</sub>		photolysis	photolysis	
ALD2 → XO <sub>2</sub> + 2HO <sub>2</sub> + CO + HCHO	photolysis			
C2O3 + NO → NO <sub>2</sub> + XO <sub>2</sub> + HCHO + HO <sub>2</sub>	1.91E-11	2.00E-11	2.13E-11	Acetylperoxy radical
C2O3 + NO <sub>2</sub> → PAN	9.41E-12	1.05E-11	1.05E-11	
C2O3 + C2O3 → 2XO <sub>2</sub> + 2HCHO + 2HO <sub>2</sub>	2.50E-12		1.55E-11	
C2O3 + C2O3 → 2MEO2		1.55E-11		
C2O3 + HO <sub>2</sub> → 0.79HCHO + 0.79XO <sub>2</sub> + 0.79HO <sub>2</sub> + 0.79OH + 0.21PACD	6.50E-12			
C2O3 + HO <sub>2</sub> → 0.8PACD + 0.2AACD + 0.2O <sub>3</sub>		1.41E-11		
C2O3 + MEO2 → 0.9MEO2 + 0.9HO <sub>2</sub> + HCHO + 0.1AACD		1.07E-11		
C2O3 + XO <sub>2</sub> → 0.9MEO2 + 0.1AACD		1.60E-11		
C2O3 + MEO2 → CCO.OH + HCHO			9.64E-12	
C2O3 + HO <sub>2</sub> → 0.75CCO.OOH + 0.25CCO.OH + 0.25O <sub>3</sub>			1.41E-11	
C2O3 + NO <sub>3</sub> → MEO2 + NO <sub>2</sub>			4.00E-12	
C2O3 + RO <sub>2</sub> .R → CCO.OH			7.50E-12	
C2O3 + R <sub>2</sub> O <sub>2</sub> → C2O3			7.50E-12	
C2O3 + RO <sub>2</sub> .N → CCO.OH + PROD2			7.50E-12	
PAN → C2O3 + NO <sub>2</sub>	4.23E-04	3.31E-04	5.21E-04	Peroxy acyl nitrate
PAN → C2O3 + NO <sub>2</sub>		photolysis		
PAN2 → RCO.O <sub>2</sub> + NO <sub>2</sub>			4.43E-04	PPN and other higher alky PAN analogues
MA.PAN → MA.RCO <sub>3</sub> + NO <sub>2</sub>			3.55E-04	
PACD + OH → C2O3		7.83E-13		Peroxy carboxylic acid
PACD → MEO2 + OH		photolysis		
AACD + OH → MEO2		7.83E-13		Carboxylic acid
ALDX + O → CXO <sub>3</sub> + OH		7.02E-13		Propionaldehyde and higher aldehydes
ALDX + OH → CXO <sub>3</sub>		1.99E-11		
ALDX + NO <sub>3</sub> → CXO <sub>3</sub> + HNO <sub>3</sub>		6.50E-15		
ALDX → MEO2 + CO + HO <sub>2</sub>		photolysis		

Table 2. Continued.

Reactions	CB4	CB05	SAPRC-99	Comments
$CXO_3 + NO \rightarrow ALD_2 + NO_2 + HO_2 + XO_2$		2.10E-11		C3 and higher acylperoxy radical
$CXO_3 + NO_2 \rightarrow PANX$		1.05E-11		
$CXO_3 + HO_2 \rightarrow 0.8PACD + 0.2AACD + 0.2O_3$		1.41E-11		
$CXO_3 + MEO_2 \rightarrow 0.9ALD_2 + 0.9XO_2 + HO_2 + 0.1AACD + 0.1HCHO$		1.07E-11		
$CXO_3 + XO_2 \rightarrow 0.9ALD_2 + 0.1AACD$		1.60E-11		
$CXO_3 + CXO_3 \rightarrow 2ALD_2 + 2XO_2 + 2HO_2$		1.55E-11		
$CXO_3 + C_2O_3 \rightarrow MEO_2 + XO_2 + HO_2 + ALD_2$		1.55E-11		
$PANX \rightarrow CXO_3 + NO_2$		3.31E-04		C3 and higher peroxyacyl nitrates
$PANX \rightarrow CXO_3 + NO_2$		photolysis		
$PANX + OH \rightarrow ALD_2 + NO_2$		3.00E-13		
$NTR + OH \rightarrow HNO_3 + HO_2 + 0.33HCHO + 0.33ALD_2 + 0.33ALDX - 0.66PAR$		1.76E-13		Organic nitrate (RNO <sub>3</sub> )
$NTR \rightarrow NO_2 + HO_2 + 0.33HCHO + 0.33ALD_2 + 0.33ALDX - 0.66PAR$		photolysis		
$NTR + HO \rightarrow 0.338NO_2 + 0.113HO_2 + 0.376RO_2\_R + 0.173RO_2\_N + 0.596R_2O_2 + 0.01HCHO + 0.439ALD_2 + 0.213RCHO + 0.006ACET + 0.177MEK + 0.048PROD_2 + 0.31NTR$			7.80E-12	
$NTR \rightarrow NO_2 + 0.341HO_2 + 0.564RO_2\_R + 0.095RO_2\_N + 0.152R_2O_2 + 0.134HCHO + 0.431ALD_2 + 0.147RCHO + 0.02ACET + 0.243MEK + 0.435PROD_2$			photolysis	
$ROOH + OH \rightarrow XO_2 + 0.5ALD_2 + 0.5ALDX$		5.69E-12		Higher organic peroxide
$ROOH + HO \rightarrow RCHO + 0.34RO_2\_R + 0.66HO$			1.10E-11	
$ROOH \rightarrow OH + HO_2 + 0.5ALD_2 + 0.5ALDX$		photolysis		
$ETOH + OH \rightarrow HO_2 + 0.9ALD_2 + 0.05ALDX + 0.1HCHO + 0.1XO_2$		3.19E-12		Ethanol
$ROOH \rightarrow RCHO + HO_2 + HO$			photolysis	Lumped C3+ aldehydes
$RCHO + HO \rightarrow 0.034RO_2\_R + 0.001RO_2\_N + 0.965RCO\_O_2 + 0.034CO + 0.034ALD_2$			2.00E-11	
$RCHO + NO_3 \rightarrow HNO_3 + RCO\_O_2$			3.67E-15	
$RCHO \rightarrow ALD_2 + RO_2\_R + CO + HO_2$			photolysis	
$CCO\_OH + HO \rightarrow 0.13RO_2\_R + 0.87MEO_2 + 0.13MGly$			8.00E-13	Peroxy acetic acid
$RCO\_OH + HO \rightarrow RO_2\_R + 0.605ALD_2 + 0.21RCHO + 0.185BACL$			1.16E-12	Higher organic acids

Table 2. Continued.

Reactions	CB4	CB05	SAPRC-99	Comments
<b>Alkane reactions</b>				
CH <sub>4</sub> + OH → XO <sub>2</sub> + HCHO + HO <sub>2</sub>	7.73E-15			Methane
CH <sub>4</sub> + OH → MEO <sub>2</sub>		6.34E-15	6.37E-15	
ETHA + OH → 0.991ALD <sub>2</sub> + 0.991XO <sub>2</sub> + 0.009XO <sub>2</sub> N + HO <sub>2</sub>		2.40E-13		Ethane
PAR + OH → 0.87XO <sub>2</sub> + 0.13XO <sub>2</sub> N + 0.11HO <sub>2</sub> + 0.11ALD <sub>2</sub> + 0.76ROR - 0.11PAR	8.10E-13			Paraffin carbon bond
PAR + OH → 0.87XO <sub>2</sub> + 0.13XO <sub>2</sub> N + 0.11HO <sub>2</sub> + 0.06ALD <sub>2</sub> - 0.11PAR + 0.76ROR + 0.05ALDX		8.10E-13		
ROR → 1.1ALD <sub>2</sub> + 0.96XO <sub>2</sub> + 0.94HO <sub>2</sub> - 2.10PAR + 0.04XO <sub>2</sub> N + 0.02ROR	2.19E+03			Secondary alkoxy radical
ROR → 0.96XO <sub>2</sub> + 0.6ALD <sub>2</sub> + 0.94HO <sub>2</sub> - 2.1PAR + 0.04XO <sub>2</sub> N + 0.02ROR + 0.5ALDX		2.19E+03		
ROR → HO <sub>2</sub>	1.60E+03	1.60E+03		
ROR + NO <sub>2</sub> → NTR	1.50E-11	1.50E-11		
ALK1 + HO → RO <sub>2</sub> _R + ALD <sub>2</sub>			2.54E-13	Alkane 1
ALK2 + HO → 0.246HO + 0.121HO <sub>2</sub> + 0.612RO <sub>2</sub> _R + 0.021RO <sub>2</sub> _N + 0.16CO + 0.039HCHO + 0.155RCHO + 0.417ACET + 0.248GLY + 0.121HCOOH			1.04E-12	Alkane 2
ALK3 + HO → 0.695RO <sub>2</sub> _R + 0.07RO <sub>2</sub> _N + 0.559R <sub>2</sub> O <sub>2</sub> + 0.236TBU_O + 0.026HCHO + 0.445ALD <sub>2</sub> + 0.122RCHO + 0.024ACET + 0.332MEK			2.38E-12	Alkane 3
ALK4 + HO → 0.835RO <sub>2</sub> _R + 0.143RO <sub>2</sub> _N + 0.936R <sub>2</sub> O <sub>2</sub> + 0.011MEO <sub>2</sub> + 0.011C <sub>2</sub> O <sub>3</sub> + 0.002CO + 0.024HCHO + 0.455ALD <sub>2</sub> + 0.244RCHO + 0.452ACET + 0.11MEK + 0.125PROD <sub>2</sub>			4.38E-12	Alkane 4
ALK5 + HO → 0.653RO <sub>2</sub> _R + 0.347RO <sub>2</sub> _N + 0.948R <sub>2</sub> O <sub>2</sub> + 0.026HCHO + 0.099ALD <sub>2</sub> + 0.204RCHO + 0.072ACET + 0.089MEK + 0.417PROD <sub>2</sub> + ALK5AER			9.32E-12	Alkane 5
<b>Aromatic reactions</b>				
TOL + OH → 0.08XO <sub>2</sub> + 0.36CRES + 0.44HO <sub>2</sub> + 0.56TO <sub>2</sub> + TO-LAER	6.19E-12	5.92E-12		Toluene
ARO1 + OH → 0.224HO <sub>2</sub> + 0.765RO <sub>2</sub> _R + 0.011RO <sub>2</sub> _N + 0.055PROD <sub>2</sub> + 0.118GLY + 0.119MGLY + 0.017PHEN + 0.207CRES + 0.059BALD + 0.491DCB1 + 0.108DCB2 + 0.051DCB3 + ARO1AER			5.96E-12	Aromatic 1
TO <sub>2</sub> + NO → 0.9NO <sub>2</sub> + 0.9HO <sub>2</sub> + 0.9OPEN + 0.1NTR	8.10E-12	8.10E-12		Toluene-hydroxyl radical adduct
TO <sub>2</sub> → CRES + HO <sub>2</sub>	4.20E+00	4.20E+00		
ARO2 + HO → 0.187HO <sub>2</sub> + 0.804RO <sub>2</sub> _R + 0.009RO <sub>2</sub> _N + 0.097GLY + 0.287MGLY + 0.087BACL + 0.187CRES + 0.05BALD + 0.561DCB1 + 0.099DCB2 + 0.093DCB3 + ARO2AER			2.64E-11	Aromatic 2
CRES + OH → 0.4CRO + 0.6XO <sub>2</sub> + 0.6HO <sub>2</sub> + 0.3OPEN + CSLAER	4.10E-11	4.10E-11		Cresols
CRES + OH → 0.24BZ_O + 0.76RO <sub>2</sub> _R + 0.23MGLY + CRESAER			4.20E-11	

Table 2. Continued.

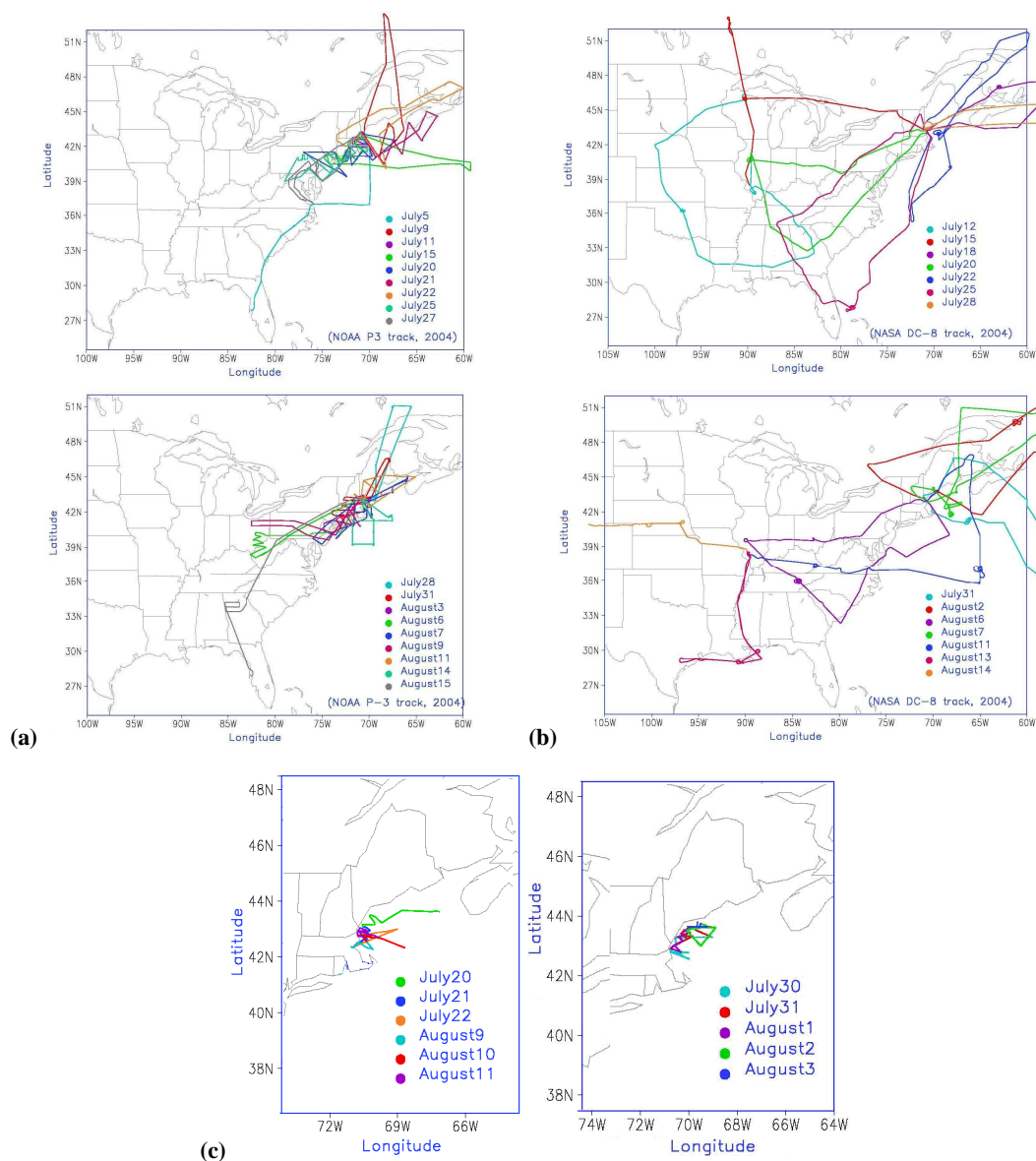
Reactions	CB4	CB05	SAPRC-99	Comments
$\text{CRES} + \text{NO}_3 \rightarrow \text{CRO} + \text{HNO}_3 + \text{CSLAER}$	2.20E-11	2.20E-11		
$\text{CRES} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{BZ}_2\text{O} + \text{CRESAER}$			1.37E-11	
$\text{CRO} + \text{NO}_2 \rightarrow \text{NTR}$	1.40E-11	1.40E-11		
$\text{CRO} + \text{HO}_2 \rightarrow \text{CRES}$		5.50E-12		Methylphenoxy radical
$\text{XYL} + \text{OH} \rightarrow 0.7\text{HO}_2 + 0.5\text{XO}_2 + 0.2\text{CRES} + 0.8\text{MGLY} + 1.1\text{PAR} + 0.3\text{TO}_2 + \text{XYLAER}$	2.51E-11	2.51E-11		Xylene
$\text{OPEN} + \text{OH} \rightarrow \text{XO}_2 + 2\text{CO} + 2\text{HO}_2 + \text{C}_2\text{O}_3 + \text{HCHO}$	3.00E-11	3.00E-11		Aromatic ring opening product
$\text{OPEN} \rightarrow \text{C}_2\text{O}_3 + \text{HO}_2 + \text{CO}$	photolysis	photolysis		
$\text{OPEN} + \text{O}_3 \rightarrow 0.03\text{ALD}_2 + 0.62\text{C}_2\text{O}_3 + 0.7\text{HCHO} + 0.03\text{XO}_2 + 0.69\text{CO} + 0.08\text{OH} + 0.76\text{HO}_2 + 0.2\text{MGLY}$	1.01E-17	1.01E-17		
$\text{MGLY} + \text{OH} \rightarrow \text{XO}_2 + \text{C}_2\text{O}_3$	1.70E-11	1.80E-11		Methylglyoxal
$\text{MGLY} + \text{HO} \rightarrow \text{CO} + \text{C}_2\text{O}_3$			1.50E-11	
$\text{MGLY} \rightarrow \text{C}_2\text{O}_3 + \text{HO}_2 + \text{CO}$	photolysis	photolysis	photolysis	
$\text{MGLY} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{CO} + \text{C}_2\text{O}_3$			2.42E-15	Glyoxal
$\text{GLY} \rightarrow 2\text{CO} + 2\text{HO}_2$			photolysis	
$\text{GLY} \rightarrow \text{HCHO} + \text{CO}$			photolysis	
$\text{GLY} + \text{HO} \rightarrow 0.63\text{HO}_2 + 1.26\text{CO} + 0.37\text{RCO}_2\text{O}_2$			1.10E-11	
$\text{GLY} + \text{NO}_3 \rightarrow \text{HNO}_3 + 0.63\text{HO}_2 + 1.26\text{CO} + 0.37\text{RCO}_2\text{O}_2$			9.65E-16	
$\text{DCB1} + \text{HO} \rightarrow \text{RCHO} + \text{RO}_2\text{R} + \text{CO}$			5.00E-11	Reactive aromatic fragmentation product 1
$\text{DCB1} + \text{O}_3 \rightarrow 1.5\text{HO}_2 + 0.5\text{HO} + 1.5\text{CO} + \text{GLY}$			2.00E-18	
$\text{DCB2} + \text{HO} \rightarrow \text{R}_2\text{O}_2 + \text{RCHO} + \text{C}_2\text{O}_3$			5.00E-11	Reactive aromatic fragmentation product 2
$\text{DCB2} \rightarrow \text{RO}_2\text{R} + 0.5\text{C}_2\text{O}_3 + 0.5\text{HO}_2 + \text{CO} + \text{R}_2\text{O}_2 + 0.5\text{GLY} + 0.5\text{MGLY}$			photolysis	
$\text{DCB3} + \text{HO} \rightarrow \text{R}_2\text{O}_2 + \text{RCHO} + \text{C}_2\text{O}_3$			5.00E-11	Reactive aromatic fragmentation product 3
$\text{DCB3} \rightarrow \text{RO}_2\text{R} + 0.5\text{C}_2\text{O}_3 + 0.5\text{HO}_2 + \text{CO} + \text{R}_2\text{O}_2 + 0.5\text{GLY} + 0.5\text{MGLY}$			photolysis	
$\text{PHEN} + \text{HO} \rightarrow 0.24\text{BZ}_2\text{O} + 0.76\text{RO}_2\text{R} + 0.23\text{GLY}$			2.63E-11	Phenol
$\text{PHEN} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{BZ}_2\text{O}$			3.78E-12	

Table 2. Continued.

Reactions	CB4	CB05	SAPRC-99	Comments
<b>Ketone</b>				
ACET + HO → HCHO + C2O3 + R2O2			1.92E-13	Acetone
ACET → C2O3 + MEO2			photolysis	
MEK + HO → 0.37RO2_R + 0.042RO2_N + 0.616R2O2 + 0.492C2O3 + 0.096RCO_O2 + 0.115HCHO + 0.482ALD2 + 0.37RCHO			1.18E-12	Ketones
MEK → C2O3 + ALD2 + RO2_R			photolysis	
MVK + HO → 0.3RO2_R + 0.025RO2_N + 0.675R2O2 + 0.675C2O3 + 0.3HCHO + 0.675RCHO + 0.3MGLY			1.89E-11	Methyl vinyl ketones
MVK + O3 → 0.064HO2 + 0.05RO2_R + 0.164HO + 0.05RCO_O2 + 0.475CO + 0.1HCHO + 0.95MGLY + 0.351HCOOH			4.58E-18	
MVK + O3P → 0.45RCHO + 0.55MEK			4.32E-12	
MVK → 0.3MEO2 + 0.7CO + 0.7PROD2 + 0.3MA_RCO3			photolysis	
PROD2 + HO → 0.379HO2 + 0.473RO2_R + 0.07RO2_N + 0.029C2O3 + 0.049RCO_O2 + 0.213HCHO + 0.084ALD2 + 0.558RCHO + 0.115MEK + 0.329PROD2			1.50E-11	
PROD2 → 0.96RO2_R + 0.04RO2_N + 0.515R2O2 + 0.667C2O3 + 0.333RCO_O2 + 0.506HCHO + 0.246ALD2 + 0.71RCHO			photolysis	
<b>other</b>				
RO2_R + NO → NO2 + HO2			9.04E-12	Peroxy radical operator
RO2_R + HO2 → ROOH			1.49E-11	
RO2_R + NO3 → NO2 + HO2			2.30E-12	
RO2_R + MEO2 → HO2 + 0.75HCHO + 0.25MEOH			2.00E-13	
RO2_R + RO2_R → HO2			3.50E-14	
R2O2 + NO → NO2			9.04E-12	Peroxy radical operator
R2O2 + HO2 → HO2			1.49E-11	
R2O2 + NO3 → NO2			2.30E-12	
R2O2 + MEO2 → MEO2			2.00E-13	
R2O2 + RO2_R → RO2_R			3.50E-14	
R2O2 + R2O2 →			3.50E-14	
RO2_N + NO → NTR			9.04E-12	Peroxy radical operator
RO2_N + HO2 → ROOH			1.49E-11	
RO2_N + MEO2 → HO2 + 0.25MEOH + 0.5MEK + 0.5PROD2 + 0.75HCHO			2.30E-12	
RO2_N + NO3 → NO2 + HO2 + MEK			2.00E-13	
RO2_N + RO2_R → HO2 + 0.5MEK + 0.5PROD2			3.50E-14	
RO2_N + R2O2 → RO2_N			3.50E-14	
RO2_N + RO2_N → MEK + HO2 + PROD2			3.50E-14	

Table 2. Continued.

Reactions	CB4	CB05	SAPRC-99	Comments
$\text{RCO.O2} + \text{NO}_2 \rightarrow \text{PAN2}$			1.21E-11	Peroxy propionyl radicals
$\text{RCO.O2} + \text{NO} \rightarrow \text{NO}_2 + \text{ALD2} + \text{RO2.R}$			2.80E-11	
$\text{RCO.O2} + \text{HO}_2 \rightarrow 0.75\text{RCO.OOH} + 0.25\text{RCO.OH} + 0.25\text{O3}$			1.41E-11	
$\text{RCO.O2} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{ALD2} + \text{RO2.R}$			4.00E-12	
$\text{RCO.O2} + \text{MEO2} \rightarrow \text{RCO.OH} + \text{HCHO}$			9.64E-12	
$\text{RCO.O2} + \text{RO2.R} \rightarrow \text{RCO.OH}$			7.50E-12	
$\text{RCO.O2} + \text{R2O2} \rightarrow \text{RCO.O2}$			7.50E-12	
$\text{RCO.O2} + \text{RO2.N} \rightarrow \text{RCO.OH} + \text{PROD2}$			7.50E-12	
$\text{RCO.O2} + \text{C2O3} \rightarrow \text{MEO2} + \text{ALD2} + \text{RO2.R}$			1.55E-11	
$\text{RCO.O2} + \text{RCO.O2} \rightarrow 2\text{ALD2} + 2\text{RO2.R}$			1.55E-11	
$\text{BZCO.O2} + \text{NO}_2 \rightarrow \text{PBZN}$			1.37E-11	Peroxy radicals from aromatic aldehyde
$\text{PBZN} \rightarrow \text{BZCO.O2} + \text{NO}_2$			3.12E-04	
$\text{BZCO.O2} + \text{NO} \rightarrow \text{NO}_2 + \text{BZ.O} + \text{R2O2}$			2.80E-11	
$\text{BZCO.O2} + \text{HO}_2 \rightarrow 0.75\text{RCO.OOH} + 0.25\text{RCO.OH} + 0.25\text{O3}$			1.41E-11	
$\text{BZCO.O2} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{BZ.O} + \text{R2O2}$			4.00E-12	
$\text{BZCO.O2} + \text{MEO2} \rightarrow \text{RCO.OH} + \text{HCHO}$			9.64E-12	
$\text{BZCO.O2} + \text{RO2.R} \rightarrow \text{RCO.OH}$			7.50E-12	
$\text{BZCO.O2} + \text{R2O2} \rightarrow \text{BZCO.O2}$			7.50E-12	
$\text{BZCO.O2} + \text{RO2.N} \rightarrow \text{RCO.OH} + \text{PROD2}$			7.50E-12	
$\text{BZCO.O2} + \text{C2O3} \rightarrow \text{MEO2} + \text{BZ.O} + \text{R2O2}$			1.55E-11	
$\text{BZCO.O2} + \text{RCO.O2} \rightarrow \text{ALD2} + \text{RO2.R} + \text{BZ.O} + \text{R2O2}$			1.55E-11	
$\text{BZCO.O2} + \text{BZCO.O2} \rightarrow 2\text{BZ.O} + 2\text{R2O2}$			1.55E-11	
$\text{TBU.O} + \text{NO}_2 \rightarrow \text{NTR}$			2.40E-11	t-Butoxy radicals
$\text{TBU.O} \rightarrow \text{ACET} + \text{MEO2}$			9.88E+02	
$\text{BZ.O} + \text{NO}_2 \rightarrow \text{NPHE}$			3.80E-11	Phenoxy radicals
$\text{BZ.O} + \text{HO}_2 \rightarrow \text{PHEN}$			1.49E-11	
$\text{BZ.O} \rightarrow \text{PHEN}$			1.00E-03	
$\text{BZNO}_2\text{-O} + \text{NO}_2 \rightarrow$			3.80E-11	Nitro-substituted phenoxy radicals
$\text{BZNO}_2\text{-O} + \text{HO}_2 \rightarrow \text{NPHE}$			1.49E-11	
$\text{BZNO}_2\text{-O} \rightarrow \text{NPHE}$			1.00E-03	
$\text{NPHE} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{BZNO}_2\text{-O}$			3.78E-12	Nitrophenols
$\text{BACL} \rightarrow 2\text{C2O3}$			photolysis	Biacetyl
$\text{BALD} + \text{HO} \rightarrow \text{BZCO.O2}$			1.29E-11	Benzaldehyde
$\text{BALD} \rightarrow$			photolysis	
$\text{BALD} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{BZCO.O2}$			2.62E-15	

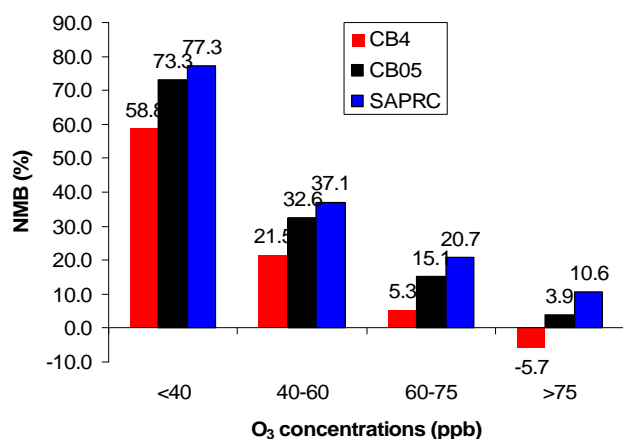


**Fig. 2.** Tracks of (a) P-3, (b) DC-8 and (c) ship tracks during the 2004 ICARTT period.

$O_3$  as a function of the different observed  $O_3$  mixing ratio ranges are calculated for the three mechanisms and are displayed in Fig. 3. As can be seen, for  $O_3$  mixing ratios greater than 75 ppb, CB05 exhibits the best performance with the NMB of 3.9%, followed by CB4 (NMB=-5.7%) and SAPRC-99 (NMB=10.6%). In contrast, for  $O_3$  mixing ratios less than 75 ppb, CB4 exhibited the least overestimation amongst the three mechanisms; CB05 and SAPRC-99 produce more  $O_3$  than CB4 for all  $O_3$  mixing ratio ranges (see Fig. 3). As analyzed by Yu et al. (2007), one of the reasons for the overestimation of observations in the low  $O_3$  mixing ratio ranges could be indicative of titration by NO in urban plumes that the model does not resolve because majority of the AIRNow sites are located in urban or suburban areas.

Another one is because of the significant overestimation in areas of cloud cover mainly caused by the unrealistic vertical transport of excessive amounts of high  $O_3$  concentrations near the tropopause to the ground associated with downward entrainment in CMAQ's convective cloud scheme (Yu et al., 2007). The spatial distributions of NMB values indicate that large overestimation of the observed daily max 8-h  $O_3$  mixing ratios was in the northeast for all three mechanisms where very low  $O_3$  mixing ratios were observed for all three mechanisms (not shown). Spatially, SAPRC-99 is more similar to CB05 with the exception that SAPRC-99 has slightly more overpredictions.





**Fig. 3.** Comparison of the modeled (CB4, CB05 and SAPRC-99) and observed maximum 8-h O<sub>3</sub> concentrations at the AIRNow monitoring sites: the NMB values of each model as a function of the observed maximum 8-h O<sub>3</sub> concentration ranges during the period of 15 July and 18 August, 2004.

### 3.2 Vertical profile comparisons for different species

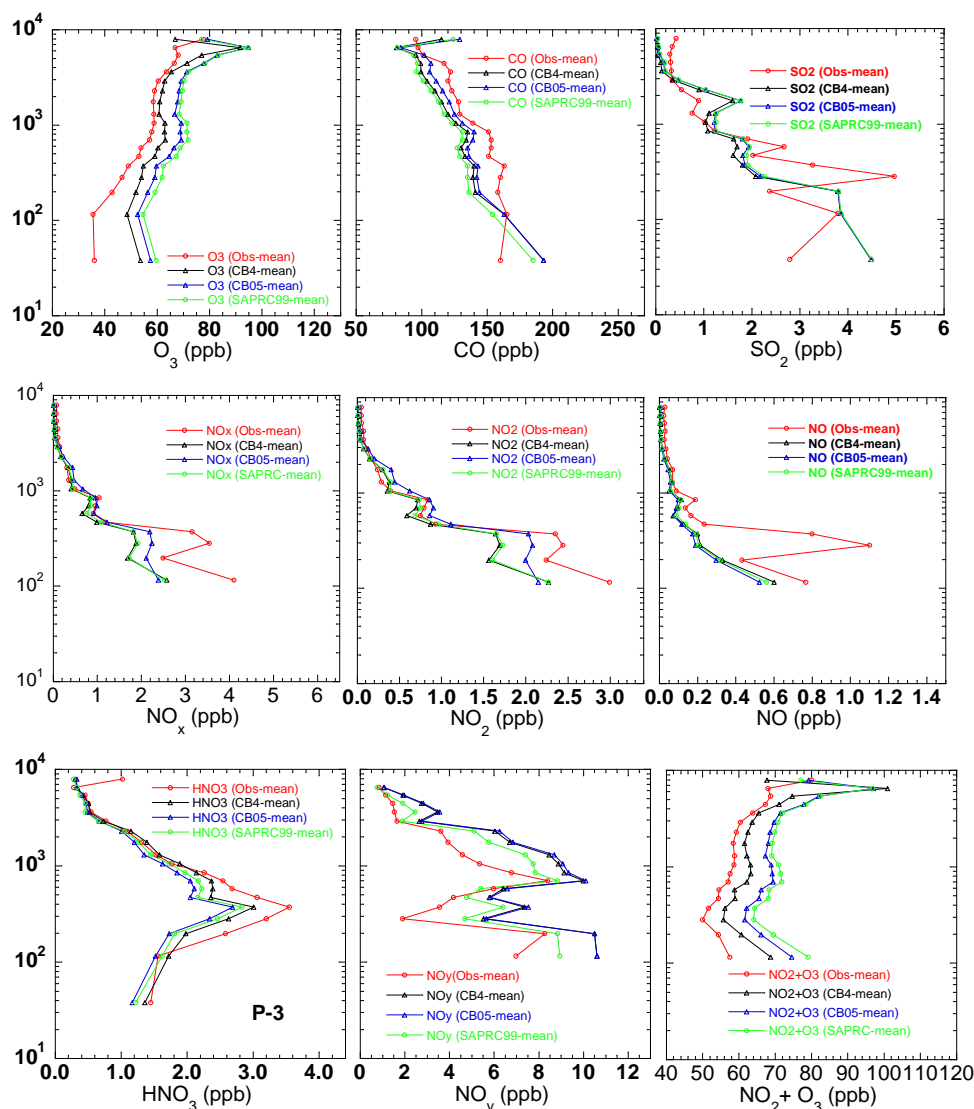
To compare the modeled and observed vertical profiles, the observed and modeled data were grouped according to the model layer for each day and each flight: that is, both observations and predictions were averaged along the aircraft transect according to layer height, representing the average conditions encountered over the study area. The aircraft flight tracks in Fig. 2 show that observations onboard the P-3 cover a regional area over the northeast around NY and Boston, whereas the DC-8 aircraft covers a broader regional area over the eastern US. Figures 4–6 present observed and modeled (CB4, CB05, SAPRC-99) vertical profiles for O<sub>3</sub>, CO, SO<sub>2</sub>, NO<sub>x</sub>, NO, NO<sub>2</sub>, HNO<sub>3</sub>, NO<sub>y</sub>, NO<sub>2</sub>+O<sub>3</sub>, HCHO, terpenes, isoprene, PAN, and H<sub>2</sub>O<sub>2</sub> on the daily basis during the 2004 ICARTT period. Table 3 summarizes the results of comparison for all observation and model data during the 2004 ICARTT period.

As shown in Figs. 4 and 6, and Table 3, all three mechanisms tend to consistently overestimate O<sub>3</sub> from low altitude to high altitude with the highest for SAPRC-99, followed by CB05 and CB4, similar to trends noted relative to AIRNow measurement at the surface, although they reproduce the vertical variation patterns of O<sub>3</sub> well. All three mechanisms tend to overestimate more in the upper layers at altitude >6 km on the basis of DC-8 observations (see Fig. 6) due to effects of the lateral boundary conditions derived from the Global Forecast System (GFS) model and coarse vertical model resolution in the free troposphere (Yu et al., 2007). Figures 4–6 and Table 3 also indicate that there are many noticeable consistencies and discrepancies for different species among the three chemical mechanisms. Noticeable among these are consistent overestimations of O<sub>3</sub>, NO<sub>z</sub>, PAN, NO<sub>y</sub>,

and O<sub>3</sub>+NO<sub>2</sub> and consistent underestimations of CO, HNO<sub>3</sub>, NO<sub>2</sub>, NO, SO<sub>2</sub>, and terpenes relative to the P3 observations. There were consistent overestimations of O<sub>3</sub>, HNO<sub>3</sub>, and HCHO and consistent underestimations of CO, NO<sub>2</sub>, SO<sub>2</sub>, and NO relative to DC-8 observations for all three mechanisms although the NMB values for each species and mechanism are somewhat different as listed in Table 3. One reason for the consistent underestimations of CO relative to both P3 and DC8 observations for the three model configurations can be the inadequate representation of the transport of pollution associated with biomass burning from outside the domain, especially from large Alaska forest fires during this period (Yu et al., 2007; Mathur, 2008).

In terms of the NMB values for each species relative to P3 observations in Table 3, CB4 has relatively better performance for O<sub>3</sub> and HNO<sub>3</sub>, whereas CB05 has the relatively better performance for CO, NO<sub>2</sub>, and NO<sub>x</sub>, and SAPRC-99 has the relatively better performance for SO<sub>2</sub>. The speciation of NO<sub>y</sub> in the different mechanisms is different, i.e., CB4: NO<sub>y</sub> = NO + NO<sub>2</sub> + NO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> + HONO + HNO<sub>3</sub> + PAN + PNA + NTR, CB05: NO<sub>y</sub> = NO + NO<sub>2</sub> + NO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> + HONO + HNO<sub>3</sub> + PAN + PNA + NTR + PANX, and SAPRC-99: NO<sub>y</sub> = NO + NO<sub>2</sub> + NO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> + HONO + HNO<sub>3</sub> + HNO<sub>4</sub> + PAN + PAN2 + PBZN + MA\_PAN + BZNO<sub>2</sub>-O + NPHE. Despite the fact that CB4 apportions PAN (peroxyacetyl nitrate) and homologs (peroxypropionyl nitrate and larger compounds) differently from the CB05 and SAPRC-99 (Luecken et al., 2008), both CB4 and CB05 overestimated observed PAN from low to high altitudes (see Figure 5) by about a factor of 2 while SAPRC-99 results are more close to the observations (see Table 3). Henderson et al. (2009) suggested several reasons for model over-prediction of PAN; possible reasons include the uncertainty in the reaction rate of per-acetic acid with hydroxyl radicals, over-estimation of acetone photolysis, the omission of PAN photolysis, and omission of hydroxyl reaction with PAN. There are consistent underestimations of NO<sub>x</sub> relative to both P3 and DC-8 observations (see Table 3 and Figs. 4 and 6) for all three mechanisms, being in agreement with Singh et al. (2007). This is likely due to the fact that the aircraft and lightning NO emissions are not included in the current model emission inventory. Ridley et al. (2005) suggested that cloud-to-cloud discharges may be a far greater source of NO<sub>x</sub> than what has traditionally been believed. The three mechanisms slightly underestimated HNO<sub>3</sub> relative to P3 observations while they slightly overestimated HNO<sub>3</sub> relative to DC-8 observation as shown in Table 3. One of the reasons for this different performance is because of different areas measured by P3 and DC-8 as shown in Fig. 2.

On the basis of DC-8 observations, CB05 performs relatively better for H<sub>2</sub>O<sub>2</sub> and CO than CB4 and SAPRC-99. H<sub>2</sub>O<sub>2</sub> and hydroperoxide radical (HO<sub>2</sub>) are photochemical products and are affected by the levels of chemical components such as NO<sub>x</sub>, CO, methane and non-methane hydrocarbons (Lee et al., 2000). Kuhn et al. (1998) pointed out

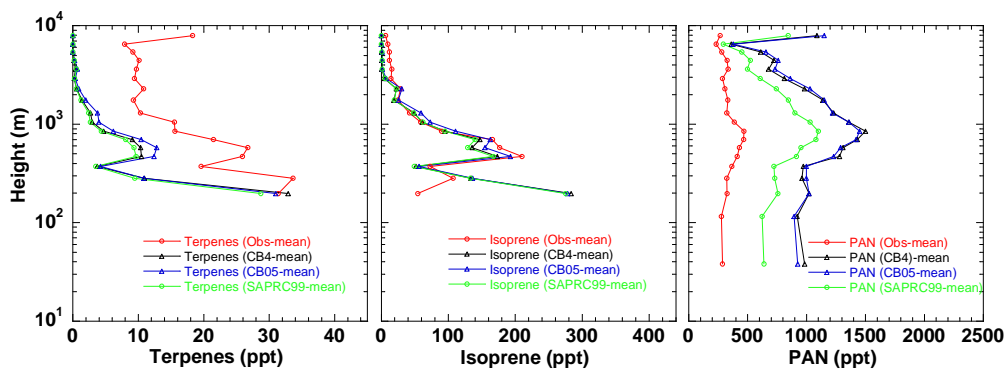


**Fig. 4.** Comparison of means of vertical  $\text{O}_3$ , CO,  $\text{NO}_x$ , NO,  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{NO}_y$  and  $\text{NO}_2+\text{O}_3$  for the P-3 observations and model predictions during 2004 ICARTT period.

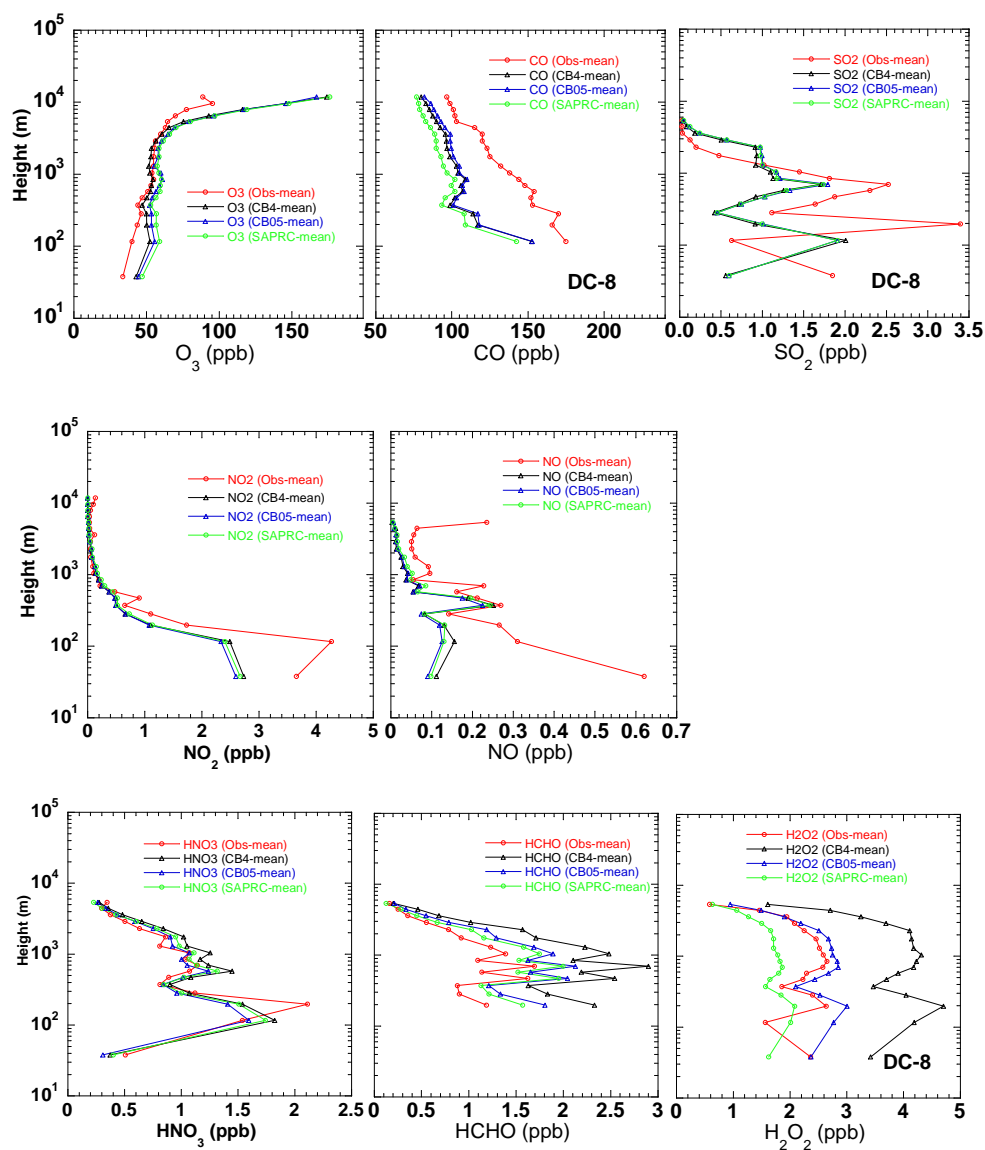
that  $\text{H}_2\text{O}_2$  and organic peroxides chemistry is a weak point in most mechanisms due to the fact that there are many complex reactions and possibly important unknowns like the incorrect use of the  $\text{HO}_2+\text{HO}_2$  rate constant and different treatment of the peroxy radical interactions. Among the three mechanisms, the  $\text{H}_2\text{O}_2$  mixing ratios from CB05 are the closest to the observations with a NMB value of 10.8%, whereas CB4 significantly overestimated the  $\text{H}_2\text{O}_2$  mixing ratios from low to high altitudes (see Fig. 6) with the NMB value of 74.7% (see Table 3) due to the fact that the  $\text{H}_2\text{O}_2$  formation rate in CB4 is 62% higher than CB05 or SAPRC-99 (Luecken et al., 2008). On the other hand, SAPRC-99 underestimated  $\text{H}_2\text{O}_2$  mixing ratios with a NMB value of  $-25.5\%$ . Compared to SAPRC-99, CB05 can produce more new  $\text{HO}_2$ , enhancing formation of  $\text{H}_2\text{O}_2$  as pointed out by Luecken et al. (2008).

In addition, Table 3 shows that on the basis of DC-8 observations, CB4 has relatively better performance for  $\text{O}_3$ , whereas CB05 has the relatively better performance for  $\text{HNO}_3$  and  $\text{SO}_2$ , and SAPRC-99 has the relatively better performance for HCHO and NO. The different model performance for the same species relative to P3 and DC-8 observations can be attributed to the difference in the studying areas of P3 and DC-8 as indicated in Fig. 2.

Biogenic monoterpene and isoprene emission rates are high over the coniferous forests of northeastern North America, especially in the summer months (Guenther et al., 2000). Isoprene is the most significant biogenic compound regarding photochemistry and terpene is a significant gas precursor for the formation of biogenic secondary organic aerosols (SOA). Isoprene is highly reactive in the atmosphere with a



**Fig. 5.** Comparison of means of vertical terpenes, isoprene and PAN for the P-3 observations and model predictions during 2004 ICARTT period.



**Fig. 6.** The same as Fig. 3 but for vertical  $\text{O}_3$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{SO}_2$  and  $\text{HCHO}$  profiles based on DC-8.

**Table 3.** Comparison of observations and models (CB4, CB05 and SAPRC-99) for different gaseous species ( $O_3$ , CO, PAN,  $NO_x$ , NO,  $NO_2$ ,  $HNO_3$ ,  $NO_y$ , ethylene,  $NO_z$ , and  $NO_2+O_3$ ) on the basis of all P-3 and DC-8 aircraft measurements during the 2004 ICARTT (mean  $\pm$  standard deviation, all units are ppbv except that PAN, isoprene, and terpenes units are pptv).

	Obs	Mean $\pm$ standard deviation			NMB (%)		
		CB4	CB05	SAPRC-99	CB4	CB05	SAPRC-99
<b>P3</b>							
$O_3$	55.4 $\pm$ 16.2	61.3 $\pm$ 16.1	67.1 $\pm$ 17.4	68.9 $\pm$ 18.0	10.8	21.1	24.3
$O_3+NO_2$	58.5 $\pm$ 14.9	63.4 $\pm$ 16.5	69.6 $\pm$ 17.4	71.3 $\pm$ 17.8	8.3	19.0	22.0
$NO_z$	2.7 $\pm$ 1.4	5.4 $\pm$ 2.4	5.5 $\pm$ 2.5	4.3 $\pm$ 2.1	101.2	108.0	63.1
PAN	348.1 $\pm$ 176.7	1047.8 $\pm$ 525.0	1054.0 $\pm$ 544.1	768.9 $\pm$ 445.0	201.0	202.8	120.9
$NO_y$	4.1 $\pm$ 2.5	6.3 $\pm$ 3.1	6.4 $\pm$ 3.1	5.3 $\pm$ 2.8	53.0	55.8	28.3
CO	139.3 $\pm$ 36.0	124.8 $\pm$ 33.2	129.6 $\pm$ 33.2	121.2 $\pm$ 35.5	-10.4	-6.9	-13.0
$HNO_3$	1.8 $\pm$ 1.8	1.6 $\pm$ 1.6	1.4 $\pm$ 1.4	1.5 $\pm$ 1.5	-8.9	-19.9	-16.1
$NO_2$	0.8 $\pm$ 1.4	0.6 $\pm$ 0.9	0.8 $\pm$ 1.2	0.7 $\pm$ 0.9	-22.5	-2.4	-19.3
NO	0.2 $\pm$ 0.8	0.1 $\pm$ 0.2	0.1 $\pm$ 0.2	0.1 $\pm$ 0.2	-56.2	-61.0	-56.8
$NO_x$	1.0 $\pm$ 2.1	0.7 $\pm$ 1.0	0.8 $\pm$ 1.2	0.7 $\pm$ 1.0	-32.8	-17.9	-30.4
$SO_2$	1.7 $\pm$ 2.7	1.5 $\pm$ 2.0	1.6 $\pm$ 2.0	1.7 $\pm$ 2.0	-9.7	-2.9	-1.4
isoprene	69.7 $\pm$ 100.4	65.5 $\pm$ 140.9	73.5 $\pm$ 145.7	63.8 $\pm$ 138.5	-6.0	5.5	-8.4
terpenes	15.6 $\pm$ 12.4	4.3 $\pm$ 11.1	5.1 $\pm$ 11.5	3.9 $\pm$ 9.9	-72.2	-67.3	-74.9
<b>DC-8</b>							
$O_3$	57.5 $\pm$ 19.9	68.6 $\pm$ 37.5	72.0 $\pm$ 36.3	73.8 $\pm$ 37.1	19.2	25.2	28.4
$HNO_3$	0.8 $\pm$ 0.8	0.9 $\pm$ 0.9	0.8 $\pm$ 0.8	0.9 $\pm$ 0.9	13.5	0.7	4.7
HCHO	0.9 $\pm$ 0.6	1.6 $\pm$ 1.1	1.2 $\pm$ 0.8	1.1 $\pm$ 0.8	82.1	39.0	26.2
$H_2O_2$	2.1 $\pm$ 1.0	3.7 $\pm$ 1.6	2.4 $\pm$ 1.0	1.6 $\pm$ 0.8	74.7	10.8	-25.5
CO	130.2 $\pm$ 35.4	99.6 $\pm$ 22.3	101.8 $\pm$ 23.4	93.2 $\pm$ 24.4	-23.5	-21.8	-28.4
$NO_2$	0.5 $\pm$ 1.3	0.3 $\pm$ 0.8	0.3 $\pm$ 0.7	0.4 $\pm$ 0.7	-33.9	-35.0	-30.5
$SO_2$	1.1 $\pm$ 1.5	0.8 $\pm$ 1.1	0.8 $\pm$ 1.1	0.8 $\pm$ 1.1	-26.1	-20.4	-21.5
NO	0.2 $\pm$ 0.3	0.1 $\pm$ 0.2	0.1 $\pm$ 0.2	0.1 $\pm$ 0.2	-58.6	-60.7	-55.3

relatively short lifetime compared to other reactive VOCs. Table 2 shows that all three mechanisms consider the reactions of isoprene with atomic oxygen, OH radicals,  $NO_3$  radicals, and  $O_3$  although the reaction products and propagation reactions are different amongst the mechanisms. The results in Fig. 5 show that the three mechanisms have similar performance for isoprene with significant overestimation at altitudes between  $\sim$ 200 and 300 m but slight underestimation above it. On average for all data as summarized in Table 3, CB05 has slightly better results for isoprene with the NMB value of 5.5%, whereas CB4 and SAPRC-99 have the negative NMB values of -6.0% and -8.4%, respectively. A close inspection of Fig. 5 shows that CB05 has slightly higher isoprene mixing ratios at the high altitudes (>layer 5) than CB4 and SAPRC-99. On the other hand, the three mechanisms systematically underestimated the observed terpenes by more than a factor of 2 from low to high altitudes except at the layer 3 ( $\sim$ 200 m) where the mean results of the three mechanisms are close to the observations due to high model terpenes mixing ratios at layer 3 on 7/22 when the P3 observations took place over the northeastern part as indicated in Fig. 2. Improvement of the VOC emission inventory is recommended in order to provide better model results for these species. For

instance, MEGAN (Guenther et al., 2006) provides different estimates for isoprene and other biogenic VOCs. Since MEGAN has higher isoprene estimates than BEIS and if the ozone production was VOC-limited, MEGAN would increase ozone. If ozone production is  $NO_x$ -limited, however, the differences in MEGAN and BEIS would have little impact on ozone.

### 3.3 Time series comparison over the ocean with the Ronald H. Brown ship observations

The cruise tracks of the NOAA ship Ronald H. Brown of Fig. 2 shows that most of ship's cruising time was spent sampling along the coast of New Hampshire, Massachusetts and Maine. The time-series of observations and model predictions (CB4, CB05 and SAPRC-99) for different species ( $O_3$ ,  $O_3+NO_2$ , CO,  $NO_y$ ,  $NO_2$ , NO, PAN,  $SO_2$ , and isoprene) along the ship tracks during the ICARTT period are shown in Fig. 7. As analyzed by Yu et al. (2007), the air mass flow patterns sampled in the Gulf of Maine can be divided into two groups for our study period: (1) offshore flows from the west and southwest that are significantly affected by anthropogenic sources from the Washington, DC/New York City/Boston urban corridor and biogenic

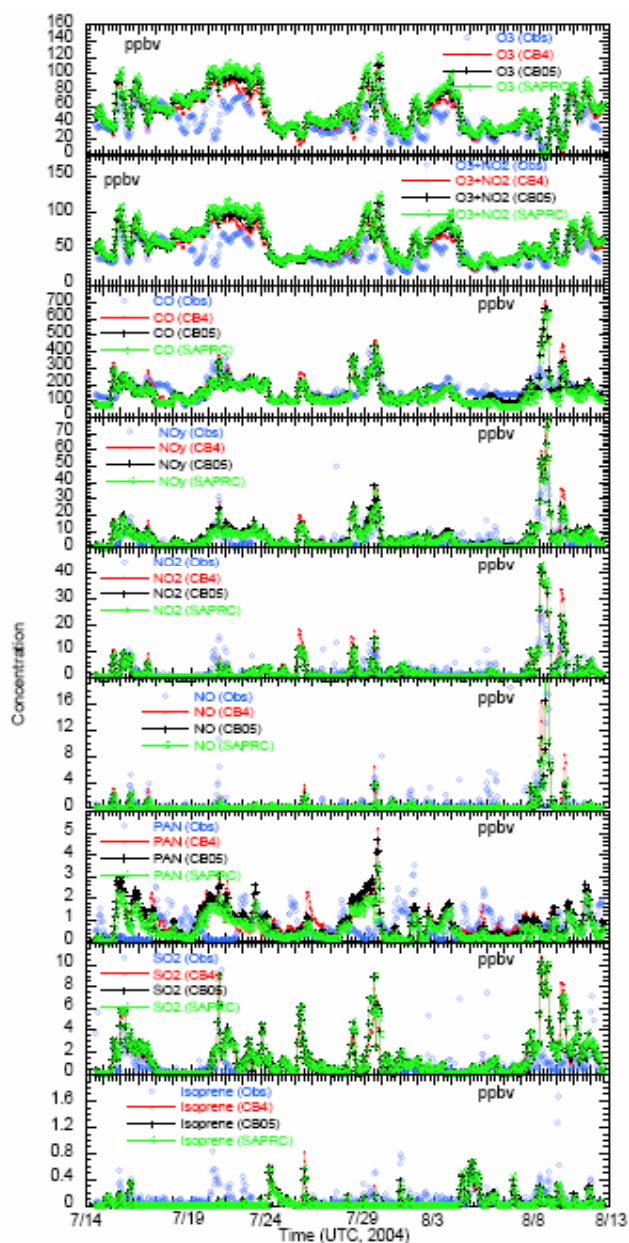
**Table 4.** Comparison of observations and model predictions (CB4, CB05 and SAPRC-99) for different gaseous species ( $O_3$ , CO, PAN, NO,  $NO_2$ ,  $NO_y$ ,  $SO_2$  and  $NO_2+O_3$  along the ship tracks for different offshore flows during the 2004 ICARTT (mean  $\pm$  standard deviation, all units are ppbv except that isoprene unit is pptv). Correlations between  $O_3$  and  $NO_z$  for the  $NO_x$  limited conditions indicated by the observational data with  $[O_3]/[NO_x]>46$  (aged air masses) (see text for explanation).

	Obs	Mean $\pm$ standard deviation			NMB (%)		
		CB4	CB05	SAPRC-99	CB4	CB05	SAPRC-99
<b>Southwesterly/westerly offshore flows</b>							
$O_3$	44.6 $\pm$ 18.9	56.9 $\pm$ 23.0	62.7 $\pm$ 25.2	65.6 $\pm$ 27.6	27.6	40.6	47.1
$O_3+NO_2$	48.1 $\pm$ 17.6	60.5 $\pm$ 19.5	66.0 $\pm$ 22.1	69.0 $\pm$ 24.7	25.6	37.1	43.4
isoprene	135.8 $\pm$ 164.3	41.4 $\pm$ 82.2	42.1 $\pm$ 84.4	39.8 $\pm$ 82.8	-69.5	-69.0	-70.7
CO	190.4 $\pm$ 63.3	197.1 $\pm$ 100.9	190.2 $\pm$ 90.8	179.9 $\pm$ 89.1	3.5	-0.1	-5.5
$NO_y$	6.7 $\pm$ 7.4	10.6 $\pm$ 10.8	10.2 $\pm$ 10.0	8.8 $\pm$ 9.8	58.1	52.6	31.8
$NO_2$	3.5 $\pm$ 4.5	3.6 $\pm$ 7.4	3.4 $\pm$ 6.9	3.5 $\pm$ 7.0	5.3	-2.6	1.4
NO	1.0 $\pm$ 2.5	1.1 $\pm$ 4.5	0.8 $\pm$ 3.9	0.8 $\pm$ 3.9	9.7	-16.0	-15.4
PAN	0.7 $\pm$ 0.6	1.1 $\pm$ 0.7	1.2 $\pm$ 0.8	0.8 $\pm$ 0.6	60.4	72.4	24.3
$SO_2$	1.1 $\pm$ 1.2	2.1 $\pm$ 2.2	2.3 $\pm$ 2.1	2.3 $\pm$ 2.1	97.5	113.3	117.1
<b>Easterly/northerly/northwesterly/southerly clean marine or continental flows</b>							
$O_3$	35.0 $\pm$ 12.5	37.2 $\pm$ 10.2	39.7 $\pm$ 10.0	41.2 $\pm$ 9.9	6.2	13.6	17.7
$O_3+NO_2$	36.8 $\pm$ 12.2	37.8 $\pm$ 10.3	40.4 $\pm$ 10.2	41.8 $\pm$ 10.1	3.0	9.9	14.0
isoprene	81.3 $\pm$ 95.8	71.4 $\pm$ 141.1	81.7 $\pm$ 148.6	78.8 $\pm$ 151.9	-12.2	0.5	-3.0
CO	146.5 $\pm$ 21.1	104.5 $\pm$ 15.4	101.0 $\pm$ 14.1	87.5 $\pm$ 18.6	-28.6	-31.1	-40.3
$NO_y$	3.3 $\pm$ 4.6	2.3 $\pm$ 1.1	2.0 $\pm$ 0.9	1.3 $\pm$ 0.8	-31.3	-41.8	-62.6
$NO_2$	1.6 $\pm$ 2.0	0.6 $\pm$ 0.8	0.4 $\pm$ 0.6	0.5 $\pm$ 0.6	-63.6	-72.5	-70.8
NO	1.5 $\pm$ 10.8	0.03 $\pm$ 0.07	0.02 $\pm$ 0.05	0.02 $\pm$ 0.05	-97.8	-98.5	-98.3
PAN	0.8 $\pm$ 0.5	0.7 $\pm$ 0.4	0.4 $\pm$ 0.2	0.3 $\pm$ 0.2	-11.7	-48.9	-65.6
$SO_2$	0.6 $\pm$ 0.9	0.39 $\pm$ 0.39	0.37 $\pm$ 0.36	0.38 $\pm$ 0.37	-36.0	-38.8	-36.7
<b>All data</b>							
Obs ( $n = 138$ ):	$[O_3]=11.8[NO_z]+36.8, r = 0.591$						
CB4 ( $n = 138$ ):	$[O_3]=4.0[NO_z]+38.3, r = 0.805$						
CB05 ( $n = 138$ ):	$[O_3]=4.5[NO_z]+42.1, r = 0.798$						
SAPRC-99 ( $n = 138$ ):	$[O_3]=5.8[NO_z]+45.8, r = 0.786$						

emissions in New Hampshire and Maine, and (2) relatively clean marine and continental flows from the east, south, north and northwest. On days with the southwesterly/westerly offshore flows such as 10 July, 15–17 July, and 20–23 July, 29 July to 1 August, 3–4 August, 8–12 August, and 16–17 August, measured concentrations for each species were clearly seen above the background values. The easterly/northerly/northwesterly/southerly clean marine or continental flows impacted the ship observations on days 11–13 July, 18 July, and 25–28 July and 5–7 August which were characterized by low mixing ratios of  $O_3$ , CO,  $NO_y$ ,  $SO_2$ , and  $NO_x$ . Table 4 summarizes the mean results for these two different flows on the basis of wind fields observed by High-Resolution Doppler Lidar (HRDL) (Yu et al., 2007). As can be seen, all three mechanism model configurations exhibit relatively better model performance for the clean marine or continental flows for  $O_3$ ,  $O_3+NO_2$ , isoprene, and  $SO_2$  compared to southwesterly/westerly offshore flows. On the other hand, the three mechanisms exhibit relatively better model performance for CO,  $NO_2$ , and NO for southwest-

erly/westerly offshore flows. The clean marine or continental flows have significantly lower mixing ratios than the southwesterly/westerly polluted flows for all species except NO and PAN on the basis of observations. The three mechanisms have very similar performance for the clean marine or continental flows with general underestimations for all species except  $O_3$  as shown in Table 4 due to the fact that the mixing ratios of all those species are close to the background in these clean flows. This similarity is also consistent with the use of the same boundary conditions for all simulations. In contrast, all three mechanisms exhibit consistent overestimations of  $SO_2$ , PAN,  $NO_y$ , and  $O_3$  for the southwesterly/westerly polluted flows.

In terms of the NMB values for each species in Table 4, all three mechanisms reproduced the observations of CO,  $NO_2$ , and NO in the southwesterly/westerly polluted flows well with the NMB value  $< \pm 20\%$ . Comparing the results of Tables 3 and 4 for each species, the model performance statistics for the southwesterly/westerly polluted flow conditions are similar to those for the aircraft measurement



**Fig. 7.** Time series comparisons of model predictions and observations for different species on the basis of ship measurements.

comparisons. For example, in the southwesterly/westerly polluted flows, all three mechanisms tend to consistently overestimate  $O_3$  with the highest for SAPRC-99, followed by CB05 and CB4, and the three mechanisms tend to consistently overestimate  $NO_y$  and PAN with slightly better performance for SAPRC-99. Also noticeable in these comparisons is significant overestimation of  $SO_2$  but underestimation of isoprene during the southwesterly/westerly polluted flows. This suggests that the CMAQ modeling system may have overestimated some of emission sources of  $SO_2$  from urban plumes over Washington, DC/New York City/Boston

areas and underestimated biogenic emissions of isoprene on the basis of ship observations.

The upper limits of the ozone production efficiency ( $\epsilon_N$ ) values can be estimated by the  $O_3$ - $NO_z$  ( $NO_z=NO_y+NO_x$ ) slope because  $NO_z$  species (primarily  $HNO_3$ ) are removed from the atmosphere more rapidly than  $O_3$  (Yu et al., 2007). Following Arnold et al. (2003), both modeled and observed  $O_3$ - $NO_z$  slopes are obtained for only observational data with  $[O_3]/[NO_x]>46$ . The results of Table 4 reveal that the  $\epsilon_N$  values of the three mechanisms are much lower than the corresponding observation (11.8) with the highest for SAPRC-99 (5.8), followed by CB05 (4.5) and CB4 (4.0), whereas the intercepts of  $O_3$ - $NO_z$  relationships for the three mechanisms are higher than the observations, indicating that background  $O_3$  mixing ratios in the model are too high. The  $\epsilon_N$  values of SAPRC-99, CB05 and CB4 are consistent with the fact that SAPRC-99 produces the highest  $O_3$ , followed by CB05 and CB4 as previously discussed. The overpredictions of  $NO_z$  mixing ratios indicate that all three chemical mechanisms still produce more terminal oxidized nitrogen products than inferred from observations, thereby contributing in part to the noted underestimation of  $\epsilon_N$ .

### 3.4 Comparisons at the AIRMAP sites

Table 5 lists the comparison of observations and three mechanisms (CB4, CB05 and SAPRC-99) for different species ( $O_3$ , CO, NO,  $NO_y$ , and  $SO_2$ ) at the four AIRMAP (CS, IS, MWO and TF) sites on the basis of hourly time-series data during the 2004 ICARTT period. As can be seen, there are several consistent features in the model performance with of the three different mechanisms at each site. All three mechanisms underestimate NO, and CO but overestimate  $O_3$  at all four sites. The three mechanisms consistently overestimated  $NO_y$  at the CS and TF sites but underestimated  $NO_y$  at the MWO site. Compared to the other sites, relatively poor model performance for several species is noted at the MWO site (the highest mountain (1916 m) in the northeastern US). This, in part, arises from the inability of the model to capture the inherent sub-grid variability at this location. The models usually misrepresent mountain sites because they essentially sample free tropospheric air while the models can't resolve the terrain. Overall, CB4 has the smallest NMB values for  $O_3$  based on the entire hourly data, whereas SAPRC-99 has the better results for  $NO_y$  at the CS and TF sites. This also is in agreement with the previous results of P-3.

## 4 Summary and conclusions

A rigorous comparison of the three photochemical mechanisms (CB4, CB05 and SAPRC-99) for the Eta-CMAQ air quality forecast model for  $O_3$  and its related precursors has been carried out by comparing the model results with intensive observations over the eastern United States obtained

**Table 5.** Comparison of observations and model predictions (CB4, CB05 and SAPRC-99) for different gaseous species (O<sub>3</sub>, CO, NO, NO<sub>y</sub>, SO<sub>2</sub>) at four AIRMAP sites during the 2004 ICARTT (mean ± standard deviation, all units are ppbv).

	Mean ± standard deviation				NMB (%)		
	Obs	CB4	CB05	SAPRC-99	CB4	CB05	SAPRC-99
<b>Castle Springs (N = 842)</b>							
NO	0.14±0.2	0.05±0.07	0.04±0.05	0.04±0.05	-66.9	-73.7	-69.2
NO <sub>y</sub>	2.2±1.5	3.4±2.5	3.1±2.4	2.4±2.0	55.9	41.9	9.8
O <sub>3</sub>	35.2±13.0	46.8±15.0	51.9±16.1	52.7±16.8	33.2	47.5	50.0
CO	189.8±45.5	112.1±31.2	113.1±31.5	105.0±32.7	-40.9	-40.4	-44.7
SO <sub>2</sub>	1.3±2.3	1.0±1.4	1.2±1.7	1.1±1.7	-21.2	-7.3	-13.2
<b>Isle of Schoals (N = 864)</b>							
O <sub>3</sub>	36.8±17.1	52.4±16.9	57.7±19.8	58.9±21.9	42.2	56.6	59.9
CO	175.2±52.9	124.1±44.0	124.2±42.2	112.6±44.4	-29.1	-29.1	-35.7
NO	0.8±1.4	0.2±1.1	0.07±0.33	0.09±0.40	-74.5	-90.8	-88.1
<b>Mount Washington (N = 864)</b>							
O <sub>3</sub>	46.6±12.7	49.3±14.3	53.3±15.5	54.7±16.8	5.7	14.3	17.4
NO	4.3±15.5	0.01±0.01	0.01±0.01	0.01±0.03	-99.7	-99.7	-99.6
CO	157.5±45.8	96.2±19.8	98.5±20.9	91.1±23.8	-38.9	-37.4	-42.2
NO <sub>y</sub>	4.4±13.5	2.4±1.7	2.2±1.6	1.7±1.3	-44.4	-50.0	-61.0
SO <sub>2</sub>	0.9±1.6	0.4±0.5	0.5±0.7	0.5±0.7	-55.2	-44.8	-39.2
<b>Thompson Farm (N = 864)</b>							
O <sub>3</sub>	28.2±18.7	43.9±17.7	49.7±18.2	51.4±19.5	55.3	76.1	82.0
NO	0.3±0.7	0.2±0.4	0.2±0.2	0.2±0.3	-28.6	-48.2	-47.5
CO	173.4±48.6	160.8±57.9	154.1±50.5	150.0±57.1	-7.3	-11.1	-13.6
NO <sub>y</sub>	3.9±2.6	7.4±4.8	6.5±4.2	6.1±4.1	89.2	65.3	55.2
SO <sub>2</sub>	1.1±2.4	1.5±1.2	1.7±1.3	1.7±1.3	32.0	49.1	54.1

during the 2004 ICARTT study. All the three photochemical mechanisms are used as part of the chemical transport model in the Eta-CMAQ air quality forecast model. The main conclusions of the comparison results are summarized below. The comparisons with measurements at the AIRNow surface sites show that SAPRC-99 predicts the highest O<sub>3</sub> mixing ratios, followed by CB05 and CB4 for all O<sub>3</sub> mixing ratio ranges and that relative to observations for the O<sub>3</sub> mixing ratios ≥ 75 ppb, CB05 has the best performance with NMB=3.9%, followed by CB4 (NMB=-5.7%) and SAPRC-99 (NMB=10.6%), whereas CB4 has the best performance for observed O<sub>3</sub> mixing ratios < 75 ppb. On the basis of vertical results from P-3 and DC-8 aircraft, all three mechanisms tend to consistently overestimate O<sub>3</sub> from low altitude to high altitude with the highest for SAPRC-99, followed by CB05 and CB4. On the basis of P-3 observations, there were consistent overestimations of O<sub>3</sub>, NO<sub>z</sub>, PAN, and NO<sub>y</sub>, and consistent underestimations of CO, HNO<sub>3</sub>, NO<sub>2</sub>, NO, SO<sub>2</sub> and terpenes for the three mechanisms although the NMB values for each species and mechanism are somewhat different. On the basis of DC-8 observations, CB05 has relatively better performance for H<sub>2</sub>O<sub>2</sub> and CO than CB4 and SAPRC-99. Among the three mechanisms, CB05 predictions of H<sub>2</sub>O<sub>2</sub> are the closest to the observa-

tions with NMB=10.8%, whereas CB4 significantly overestimates H<sub>2</sub>O<sub>2</sub> with NMB=74.7% and SAPRC-99 significantly underestimates H<sub>2</sub>O<sub>2</sub> with NMB=-25.5%. This is due to the fact that the H<sub>2</sub>O<sub>2</sub> formation rate in CB4 is 62% higher than CB05, and relative to SAPRC-99, CB05 can produce more new HO<sub>2</sub>, enhancing formation of H<sub>2</sub>O<sub>2</sub>. On the basis of DC-8 observations, CB4 has relatively better performance for O<sub>3</sub>, whereas CB05 has the relatively better performance for HNO<sub>3</sub> and SO<sub>2</sub>, and SAPRC-99 has the relatively better performance for HCHO and NO. The three mechanisms overestimated isoprene below 300 m but slightly underestimated isoprene above 300 m. The three mechanisms systematically underestimated the observed terpenes by more than a factor of 2 most of time.

The capability of the three mechanisms to reproduce the observed pollutant concentrations over the ocean areas (Gulf of Maine) was found to be dependent on the offshore flow types. The three mechanisms exhibit relatively better performance for O<sub>3</sub>, isoprene and SO<sub>2</sub> for the clean marine or continental flows but relatively better performance for CO, NO<sub>2</sub> and NO for southwesterly/westerly offshore flows. Model performance during southwesterly/westerly polluted flow conditions was similar to that noted for aircraft measurements except isoprene. According to the ship data, the

upper limits of the ozone production efficiency ( $\epsilon_N$ ) values estimated on the basis of the  $O_3$ - $NO_z$  slope are 5.8, 4.5, and 4.0 for SAPRC-99, CB05 and CB4, respectively, much lower than the observation (11.8). This is also consistent with the fact that SAPRC-99 produces the highest  $O_3$ , followed by CB05 and CB4. The overpredictions of  $NO_z$  mixing ratios in the model also contribute in part to the noted underestimation of  $\epsilon_N$ .

In light of the uncertainties in the photochemical mechanisms, prognostic model forecasts of meteorological fields and emissions, the overall performance of the model system can be considered to be reasonable with NMB less than 30% in general. On the other hand, given the fact that the three mechanisms use different methods to condense the organic chemistry and have different number of species, leading to difficulty for defining completely equivalent emissions as well as complicating comparisons of chemistry in the three mechanisms, it is not obviously possible to prove which one is “correct” for  $O_3$  and its related precursor predictions. On the basis of this work, overall none of the mechanisms performs systematically better than the others. However, it is important and necessary that the older chemical mechanisms be revised periodically to be consistent with current scientific knowledge. The CB05 mechanism has more detailed treatment of both inorganic and organic reactions and more number of species according to the state-of-the-science than CB4.

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