

***Review of Ozone Performance in Previous WRAP  
Modeling and Relevance to Future Regional Ozone  
Planning***

Submitted to:

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July 25, 2008

## 1. Introduction

The Regional Haze Rule (EPA, 1999) mandates the development of State and Tribe Implementation Plans (SIPs and TIPs) to demonstrate progress toward attainment of visibility goals in National Parks and Wilderness Areas. The Western Regional Air Partnership (WRAP) has supported a variety of air quality studies to evaluate the sources of fine particulate matter (PM<sub>2.5</sub>) and gas phase NO<sub>2</sub> that contribute to poor visibility and regional haze. Some of these studies include air quality model simulations that represent the emissions, transport chemical transformations and fate of PM<sub>2.5</sub> and its precursors. Although ozone does not directly affect atmospheric visibility, ozone and related oxidant species do affect the conversion of several gas species including nitrogen oxides (NO<sub>x</sub>), sulfur oxides (SO<sub>x</sub>) and volatile organic compounds (VOC) to their oxidized forms, nitric acid (HNO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and oxygenated organic species, respectively. All of these species can either condense or interact with ambient ammonia (NH<sub>3</sub>) to form the secondary fine particulate species sulfates, nitrate and organic carbon, respectively. Thus, an air quality model must accurately simulate ambient ozone concentrations to represent correctly the formation of these secondary PM<sub>2.5</sub> species. Therefore, WRAP's previously completed air quality model simulations have also included model simulated ambient ozone concentrations.

There is increasing concern that regions in the rural western U.S. might not attain the National Ambient Air Quality Standards (NAAQS) for ambient ozone concentrations. This concern has increased with the recent reduction in the 8-hour average NAAQS from 0.08 parts per million (ppm) (compliance value of 85 parts per billion, ppb) to 0.075 ppm (75 ppb) (Federal Register, 2008). Given these concerns, the WRAP has decided to review the previously completed photochemical air quality model simulations to determine how they can be used to assist in future planning efforts for SIPs and TIPs for the 8-hour average ozone NAAQS. The previous WRAP visibility simulations were mostly performed using the USEPA's Community Multiscale Air Quality (CMAQ) (Byun and Ching, 1999) model coarse resolution 36-km grid, with limited model comparison studies also performed with a 12-km grid. Some model simulations were also completed using ENVIRON Corporation's Comprehensive Air Quality Model with extensions (CAMx) (ENVIRON, 2008). Those model simulations are described in section 2 of this paper. It is expected that state and tribal air pollution agencies will perform additional ozone modeling studies in the future, possibly with finer grid resolutions, to evaluate attainment strategies for the 8-hr ozone standard. The objective of this white paper is to:

1. Review previously completed WRAP regional scale modeling studies for ozone performance;
2. Assess whether the 2002 Base Case and 2018 WRAP model scenarios are adequate for use in specifying boundary conditions for future ozone modeling simulations; and
3. Recommend updates and boundary condition values to be used in future ozone modeling studies.

WRAP has completed visibility modeling studies using a trajectory model and two different grid models. The trajectory model simulations were performed using the CALPUFF modeling system (Scire et al., 2000) which uses observed ozone concentrations as input and does not simulate ambient ozone concentrations, so the CALPUFF simulations can not be used to further evaluate ambient ozone. However, the grid model simulations performed using CMAQ and CAMx do simulate full ozone photochemistry and predict ambient ozone concentrations, and it is those model results that will be reviewed here.

## 2. Description of WRAP 2002 Base Case Modeling

Photochemical grid models such as CMAQ and CAMx are deterministic models in which initial and boundary concentrations are specified, meteorology and emissions are provided as inputs and numerical methods are used to solve a system of coupled partial differential equations (PDE) to predict the species concentrations by computing the species rate of change at small, incremental time steps. The physical processes that effect species concentrations and that must be represented in the coupled PDEs and in the air quality model include the following: emissions, horizontal and vertical transport, horizontal and vertical dispersion, aqueous processes, convective cloud processes, chemical transformations, thermodynamic phase transformations and deposition. All of these processes are defined and numerically represented on a specific spatial domain with consistent spatial grid resolution and for a given time period. The domain definition and key input data used in the WRAP visibility modeling are described next.

### 2.1 WRAP Model Domains

WRAP used a coarse resolution 36-km modeling domain that includes the conterminous U.S. and large areas of Mexico and Canada. Model domains were defined for both the meteorology modeling (using MM5, described below) and for air quality modeling, with the air quality model domain nested in the MM5 domain. Figure 4-1 shows the MM5 horizontal domain as the outer most, blue grid. The CMAQ 36km domain is shown as the grey grid nested within the MM5 domain. Some model simulations were also performed using a fine resolution 12-km domain, shown in Figure 2-2, which includes only the western States. The 36-km coarse grid horizontal domain adopted the RPO unified grid map projection as shown in Table 2-1. The unified grid resulted from negotiations between the 5 RPOs and represents a compromise designed to provide acceptable map projection for all regions in the conterminous US. The selection of the MM5 domain is described in the VISTAS MM5 modeling protocol (Olerud, 2003).

Table 2-2 lists the number of rows and columns and the definition of the X and Y origin (i.e., the southwest corner) for the 36km and 12km grids for both MM5 and CMAQ. Note that the CMAQ grid is rotated 90 degrees relative to the MM5 grid, so rows and columns are reversed. In Table 4-2 “Dot” refers to the grid mesh defined at the vertices of the grid cells while “cross” refers to the grid mesh defined by the grid cell centers. Thus, the dimension of the dot mesh is equal to the cross mesh plus one. Finally, we note that the grid definition for the CMAQ Meteorology Chemistry Interface Processor (MCIP) and CMAQ Chemical Transport Model (CCTM) are identical.

The CMAQ vertical structure is primarily defined by the vertical grid used in the MM5 modeling. The MM5 simulation used a terrain following coordinate system defined by pressure, using 34 layers that extend from the surface to the model top at 100 mb. Table 2-3 lists the layer definitions for both MM5 and for CMAQ. To reduce computational cost in the air quality modeling, a layer averaging scheme was adopted for CMAQ simulations. The effects of layer averaging were previously evaluated and found to have a

relatively minor effect on the model performance metrics when both the 34 layer and a 19 layer CMAQ models were compared to ambient monitoring data.

Table 2-1. Regional Planning Organization Unified grid definition.

PARAMETER	VALUE
Map projection	Lambert-conformal
alpha	33 degrees
beta	45 degrees
x center	97 degrees
y center	40 degrees

Table 2-2. Grid definitions for MM5 and CMAQ.

MODEL	COLUMNS DOT(CROSS) <sup>1</sup>	ROWS DOT(CROSS) <sup>1</sup>	SOUTH-WEST CORNER	
			XORIGIN	YORIGIN
MM5 36-km	129 (128)	165 (164)	-2,952,000	-2,304,000
CMAQ 36-km	149 (148)	113 (112)	-2,736,000	-2,088,000
MM5 12-km	220 (219)	199 (198)	xxxxx	xxxxx
CMAQ 12-km	208 (207)	187 (186)	-2,376,000	-936,000

<sup>1</sup>Dot nodes are defined at grid cell vertices and cross nodes are defined a grid cell centers

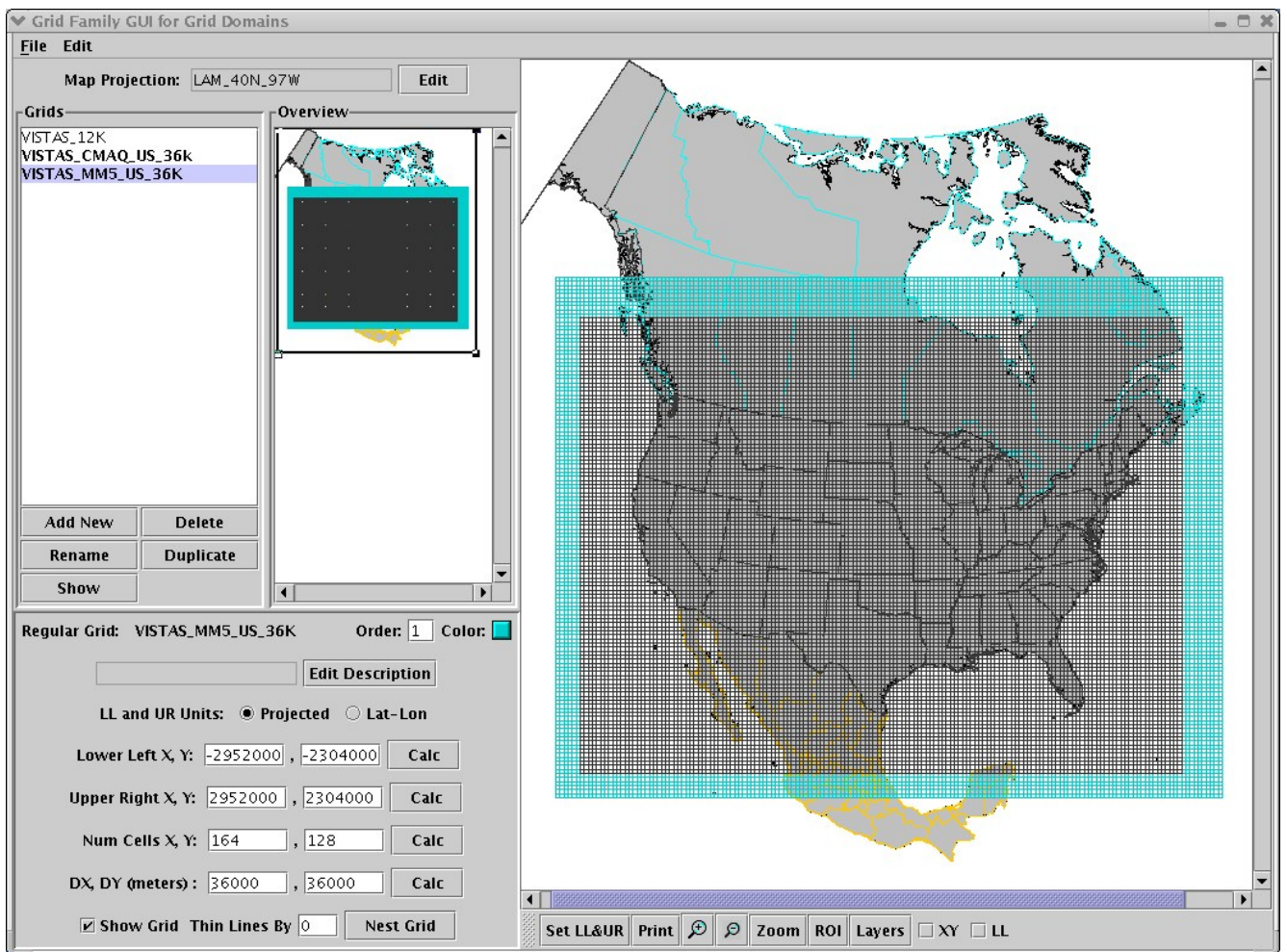
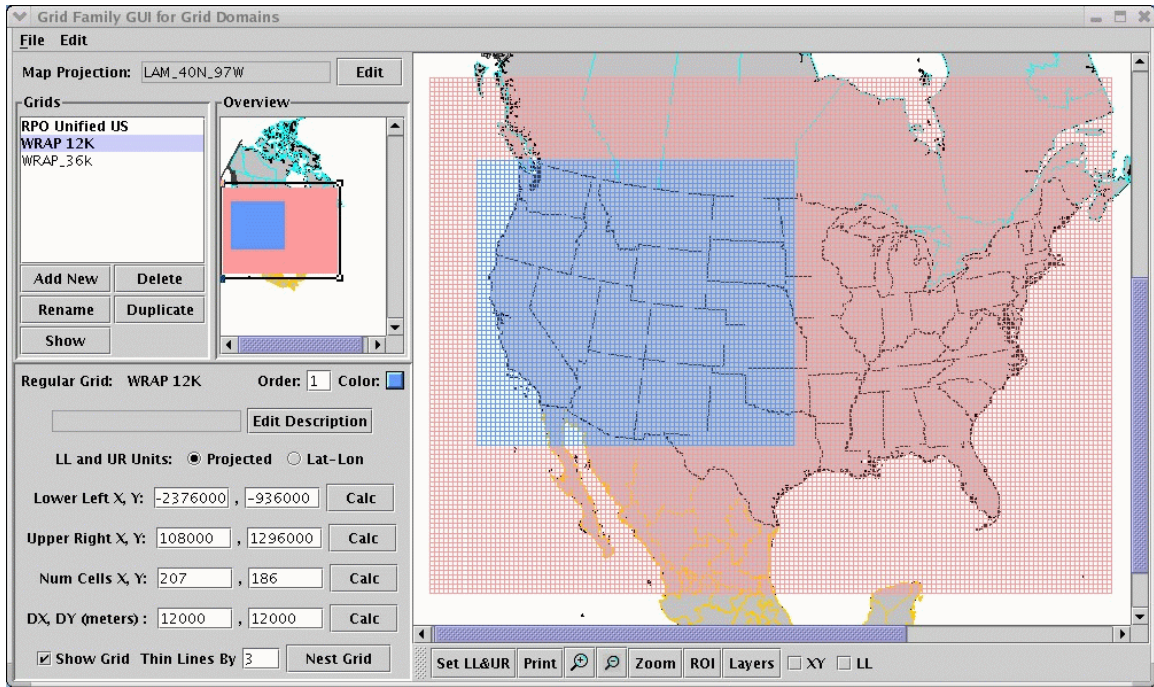


Figure 2-1. Nesting of 36-km CMAQ grid in the MM5 36-km grid.



**Figure 2-2. High resolution 12 km nested grid for the WRAP region, shown in blue.**

**Table 2-3. Vertical layer definition for MM5 simulations (left most columns), and approach for reducing CMAQ layers by collapsing multiple MM5 layers (right columns).**

<b>MM5</b>					<b>CMAQ 19L</b>				
Layer	Sigma	Pres(mb)	Height(m)	Depth(m)	Layer	Sigma	Pres(mb)	Height(m)	Depth(m)
<b>34</b>	<b>0.000</b>	<b>100</b>	<b>14662</b>	<b>1841</b>	<b>19</b>	<b>0.000</b>	<b>100</b>	<b>14662</b>	<b>6536</b>
33	0.050	145	12822	1466		0.050	145		
32	0.100	190	11356	1228		0.100	190		
31	0.150	235	10127	1062		0.150	235		
30	0.200	280	9066	939		0.200	280		
<b>29</b>	<b>0.250</b>	<b>325</b>	<b>8127</b>	<b>843</b>	<b>18</b>	<b>0.250</b>	<b>325</b>	<b>8127</b>	<b>2966</b>
28	0.300	370	7284	767		0.300	370		
27	0.350	415	6517	704		0.350	415		
26	0.400	460	5812	652		0.400	460		
<b>25</b>	<b>0.450</b>	<b>505</b>	<b>5160</b>	<b>607</b>	<b>17</b>	<b>0.450</b>	<b>505</b>	<b>5160</b>	<b>1712</b>
24	0.500	550	4553	569		0.500	550		
23	0.550	595	3984	536		0.550	595		
<b>22</b>	<b>0.600</b>	<b>640</b>	<b>3448</b>	<b>506</b>	<b>16</b>	<b>0.600</b>	<b>640</b>	<b>3448</b>	<b>986</b>
21	0.650	685	2942	480		0.650	685		
<b>20</b>	<b>0.700</b>	<b>730</b>	<b>2462</b>	<b>367</b>	<b>15</b>	<b>0.700</b>	<b>730</b>	<b>2462</b>	<b>633</b>
19	0.740	766	2095	266		0.740	766		
<b>18</b>	<b>0.770</b>	<b>793</b>	<b>1828</b>	<b>259</b>	<b>14</b>	<b>0.770</b>	<b>793</b>	<b>1828</b>	<b>428</b>
17	0.800	820	1569	169		0.800	820		
<b>16</b>	<b>0.820</b>	<b>838</b>	<b>1400</b>	<b>166</b>	<b>13</b>	<b>0.820</b>	<b>838</b>	<b>1400</b>	<b>329</b>
15	0.840	856	1235	163		0.840	856		
<b>14</b>	<b>0.860</b>	<b>874</b>	<b>1071</b>	<b>160</b>	<b>12</b>	<b>0.860</b>	<b>874</b>	<b>1071</b>	<b>160</b>
13	0.880	892	911	158		0.880	892		158
<b>12</b>	<b>0.900</b>	<b>910</b>	<b>753</b>	<b>78</b>	<b>10</b>	<b>0.900</b>	<b>910</b>	<b>753</b>	<b>155</b>
11	0.910	919	675	77		0.910	919		
<b>10</b>	<b>0.920</b>	<b>928</b>	<b>598</b>	<b>77</b>	<b>9</b>	<b>0.920</b>	<b>928</b>	<b>598</b>	<b>153</b>
9	0.930	937	521	76		0.930	937		
<b>8</b>	<b>0.940</b>	<b>946</b>	<b>445</b>	<b>76</b>	<b>8</b>	<b>0.940</b>	<b>946</b>	<b>445</b>	<b>76</b>
<b>7</b>	<b>0.950</b>	<b>955</b>	<b>369</b>	<b>75</b>	<b>7</b>	<b>0.950</b>	<b>955</b>	<b>369</b>	<b>75</b>
<b>6</b>	<b>0.960</b>	<b>964</b>	<b>294</b>	<b>74</b>	<b>6</b>	<b>0.960</b>	<b>964</b>	<b>294</b>	<b>74</b>
<b>5</b>	<b>0.970</b>	<b>973</b>	<b>220</b>	<b>74</b>	<b>5</b>	<b>0.970</b>	<b>973</b>	<b>220</b>	<b>74</b>
<b>4</b>	<b>0.980</b>	<b>982</b>	<b>146</b>	<b>37</b>	<b>4</b>	<b>0.980</b>	<b>982</b>	<b>146</b>	<b>37</b>
<b>3</b>	<b>0.985</b>	<b>986.5</b>	<b>109</b>	<b>37</b>	<b>3</b>	<b>0.985</b>	<b>986.5</b>	<b>109</b>	<b>37</b>
<b>2</b>	<b>0.990</b>	<b>991</b>	<b>73</b>	<b>36</b>	<b>2</b>	<b>0.990</b>	<b>991</b>	<b>73</b>	<b>36</b>
<b>1</b>	<b>0.995</b>	<b>995.5</b>	<b>36</b>	<b>36</b>	<b>1</b>	<b>0.995</b>	<b>995.5</b>	<b>36</b>	<b>36</b>
<b>0</b>	<b>1.000</b>	<b>1000</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>1.000</b>	<b>1000</b>	<b>0</b>	<b>0</b>

## 2.2 WRAP Model Scenarios

WRAP has completed emissions and air quality modeling for several different emissions scenarios, with the particular configuration of each scenario being determined by

planning needs for the regional haze SIPs and TIPS. Model scenarios include the following:

**2002 Base Case Version B:** this scenario was developed for use in the model performance evaluation, to determine whether the gridded air quality models performed was sufficiently well to justify continuing to use the model for planning purposes. The emissions configuration included actual point source, area sources, mobile sources from MOBILE6 with California mobile sources from EMFAC, biogenic emissions from the BEIS3 model, ammonia emissions and wind blown dust emissions were from models developed with WRAP funding, and actual wildfire, prescribed fires, and agricultural burning emissions for 2002 were used in this scenario. The model was extensively evaluated by comparing simulated concentrations of PM<sub>2.5</sub> to ambient monitoring data for all available monitoring networks, and WRAP concluded that the model did perform sufficiently well to continue using either the CMAQ or the CAMx models for planning purposes. The input data and model performance evaluation for this case are described in detail in Tonnesen et. al (2006).

**2002 Planning Case version B:** For regional haze planning purposes, the base case model emissions scenario was designed to represent the five-year baseline period of 2001-2004. Therefore, instead of using actual fire emissions for 2002, WRAP developed a new fire emissions inventory that was designed to represent typical fire conditions for the 2001-2004 period. Because this model scenario was not intended to represent actual 2002 visibility (and because the model performance evaluation had already been completed) this and subsequent model scenarios should not be compared to ambient monitoring data for 2002. However, the 2002 Planning Case version D was used as the basis for comparison to all future projected visibility scenarios. This model scenario is described in Tonnesen et. al. (2007).

**2018 Base Case Version B:** This model scenario was designed to evaluate regional haze air quality for future year 2018 conditions with currently projected 2018 emissions that include planned or “on the books” emissions control strategies.

**2018 Preliminary Reasonable Progress Case version B:** This scenario was designed to evaluate regional haze air quality for future year 2018 conditions with all known and expected controls as of March 2007. The emissions will be updated to develop a Final Reasonable Progress Case later in 2008.

### **2.3 Boundary and Initial Concentrations**

Global transport of gas and particulate species into the WRAP modeling domain are represented by specifying the species concentrations at the boundaries of the domain. The WRAP RMC adapted data from GEOS-CHEM, a coarse resolution global scale atmospheric chemistry and transport model (Jacob et al., , 2005). Annual GEOS-CHEM simulations were completed for calendar year 2002 by Jacobs et. al (2005) with funding from the Regional Planning Organizations (RPOs). The RMC used procedures developed

by Byun (2004) to extract GEOS-CHEM species concentrations and to convert them to the model grid definition and consistent chemical species used in the WRAP CMAQ modeling. Another widely used global scale atmospheric chemistry and transport model is the Model for Ozone And Related chemical Tracers (MOZART) which is described at <http://gctm.acd.ucar.edu/mozart/index.shtml>.

The WRAP visibility modeling was performed for calendar year 2002. Initial concentrations for model simulations were prepared using a set of default species concentrations based on typical ambient concentrations. The effects of the choice of initial concentrations decay rapidly and have no significant effect on model predictions for gas species after the first few days of the model simulation.

## **2.4 Emissions Inventory Data**

The starting point for the 2002 WRAP emissions inventory was the 2002 National Emissions Inventory (NEI) data with significant updates and new data developed by WRAP. Mobile source emissions inventories were developed using the EMFAC model for California and the MOBILE6 model for estimating on-road mobile emissions fluxes from county-level vehicle activity data (U.S. EPA, 2003). The Biogenic Emissions Inventory System version 3 (BEIS3.12) was used to model the biogenic VOC emissions inventory (described at <http://www.epa.gov/asmdnerl/biogen.html>). The WRAP funded the development of new emissions models for ammonia (Mansell, 2005) and for windblown dust (Mansell et al., 2005). Emissions inventory data were obtained for commercial shipping (reference) and off-shore point and area source (Wilson et al., 2004). Emissions data were also included for Canada and Mexico mobile sources, point sources and fires, although complete data was not available for Mexico. The Sparse Matrix Operator Kernel Emissions (SMOKE) version 2.1 processing system (CEP, 2004) was used to process all of the raw emissions inventory data. Emissions processing included gridding, speciation, temporalization and merging all of the raw input data into binary files for input to the air quality modeling system. The emissions modeling and quality assurance (QA) review was based on the WRAP RMC emissions QA protocol (Adelman, 2004). The development of the emission inventory data are described in detail in Tonnesen et al. (2006).

Subsequent to the initial visibility simulations, WRAP has spent considerable time and resources on additional inventory development efforts, specifically to characterize a number of natural and anthropogenic emission sources including wild and prescribed fires, oil and gas development and off-shore marine vessels.

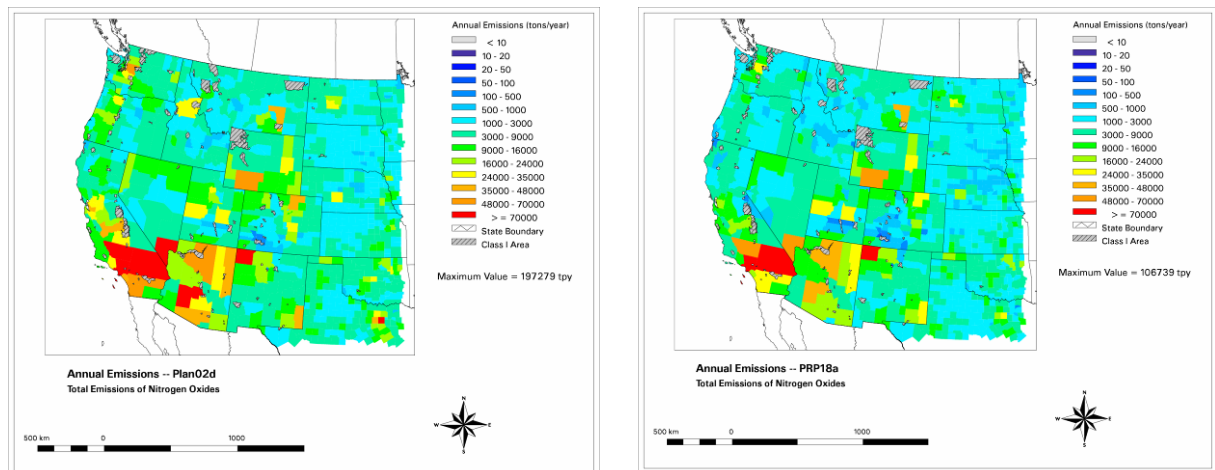
The most recent versions of the 2002 and 2018 WRAP emission inventories for regional modeling include:

- Plan 2002d – The 2002 Planning (Plan02d) emission inventory represents a typical 2002 annual inventory of emissions from all source sectors derived from a number of sources, including state/county emission inventory submittals, permits, MOBILE6 modeling, or other modeled estimates based on activity levels. The

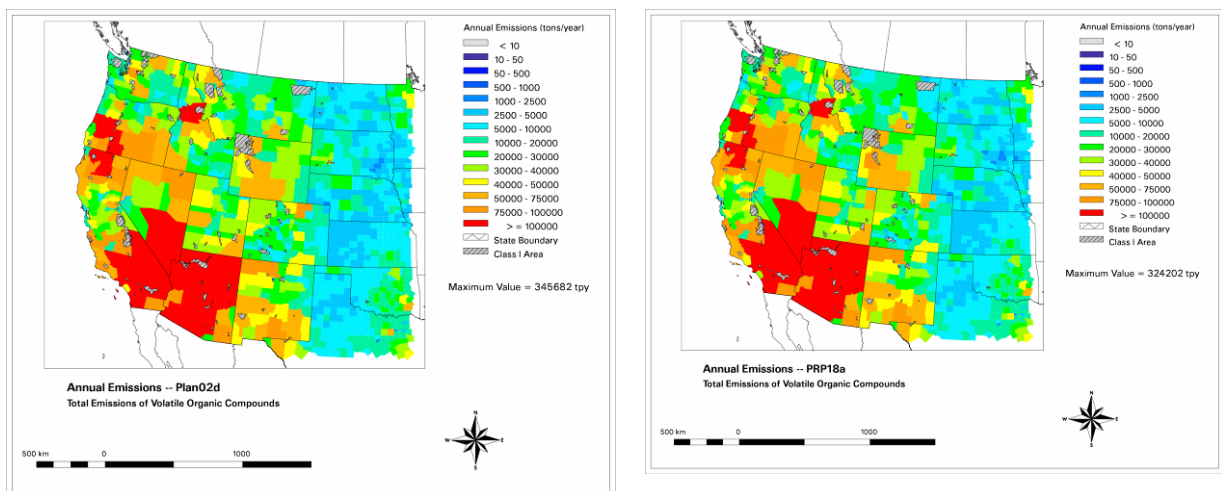
planning inventories are used to provide representative baseline visibility conditions for comparisons and assessments of progress towards achieving natural visibility conditions in the future years.

- PRP 2018a – The Preliminary Reasonable Progress emission inventory for 2018 (PRP18a), which incorporates growth and existing and/or planned emission controls and all projected BART emission reductions across the WRAP region.

The 2002 and 2018 WRAP emission inventories for NOx and VOC are displayed in Figures 2-3 and 2-4, respectively. Presented are annual, county-level emission estimates for all emission source sectors, including biogenic emissions, in units of tons per year. Although emissions of NOx and VOC are projected to decrease from 2002 to 2018, significant sources of these ozone precursors are still present and distributed across the Western States in calendar 2018, illustrating the regional nature of the air quality problem.

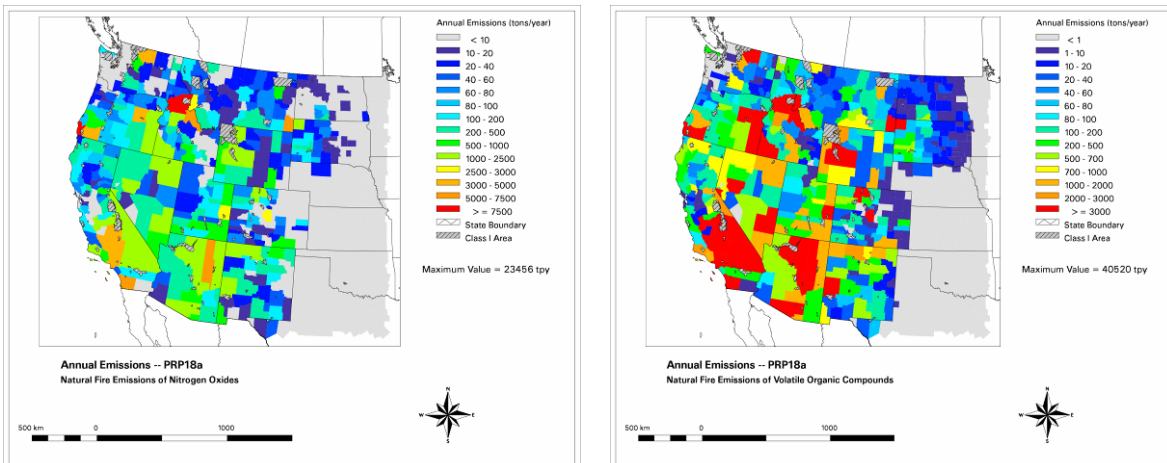


**Figure 2-3.** WRAP annual county-level NOx emissions. Plan02d (left); PRP18a (right)

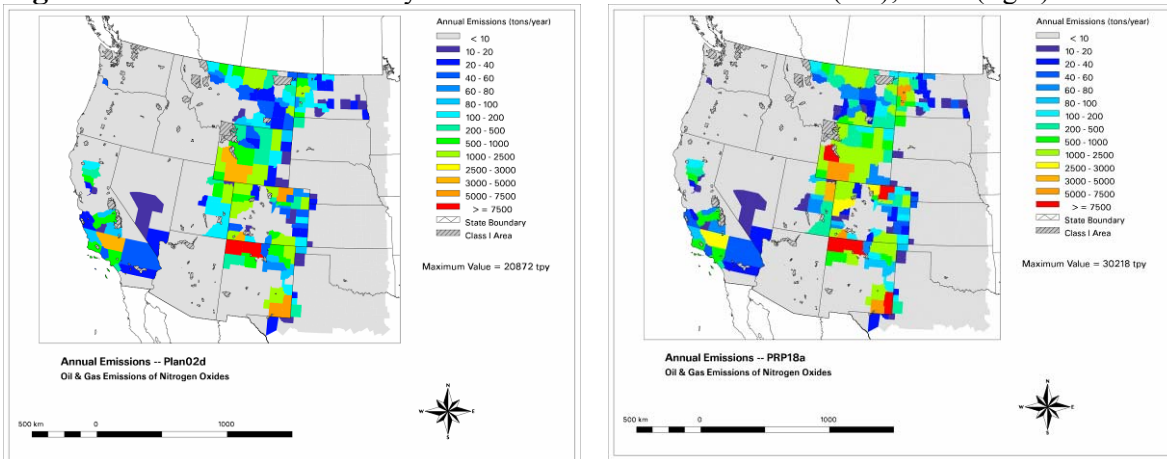


**Figure 2-4.** WRAP annual county-level VOC emissions. Plan02d (left); PRP18a (right)

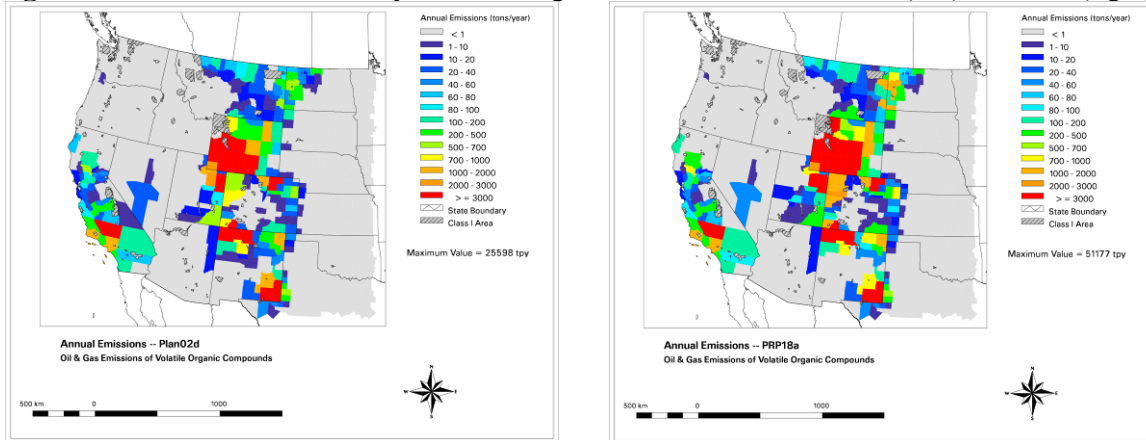
Both the 2002 and 2018 inventories incorporate emission estimates from previously uncharacterized sources including natural fires, offshore marine shipping in the Eastern Pacific, and oil and gas development and production. Note that both the offshore shipping and natural fire emission inventories were held constant from 2002 to 2018 for regional air quality modeling purposes. Figure 2-5 presents the estimated annual, county-level NOx and VOC emissions from natural fire sources. By definition, natural fires (e.g., wild fires caused by lightning strikes) are clearly unpredictable, unlike other fire sources (e.g., agricultural burning, prescribed fires, etc.) and uncontrollable with respect to air quality planning. Annual NOx and VOC emission estimates from oil and gas development in the WRAP region are displayed in Figures 2-6 and 2-7, respectively. Emissions from this source sector are seen to be increasing from 2002 to 2018, particularly in the Inter-Mountain and Southwestern States, and are predicted to increase over time. These emission sources have not been characterized, or quantified, in previous inventories to the degree to which they currently have been by the WRAP and, as noted above, were not considered in EPA’s modeling efforts associated with assessments of the revised ozone standard. As these sources are generally far removed from urban centers, and due to their wide-spread geographic distribution, they are likely to become a key component in regional control strategies for ozone air quality.



**Figure 2-5.** WRAP annual county-level natural fire emissions. NOx (left); VOC (right)



**Figure 2-6.** WRAP annual county-level oil & gas NOx emissions. Plan02d (left); PRP18a (right)



**Figure 2-7.** WRAP annual county-level oil & gas VOC emissions. Plan02d (left); PRP18a (right)

## 2.5 MM5 simulations and MM5 performance evaluation.

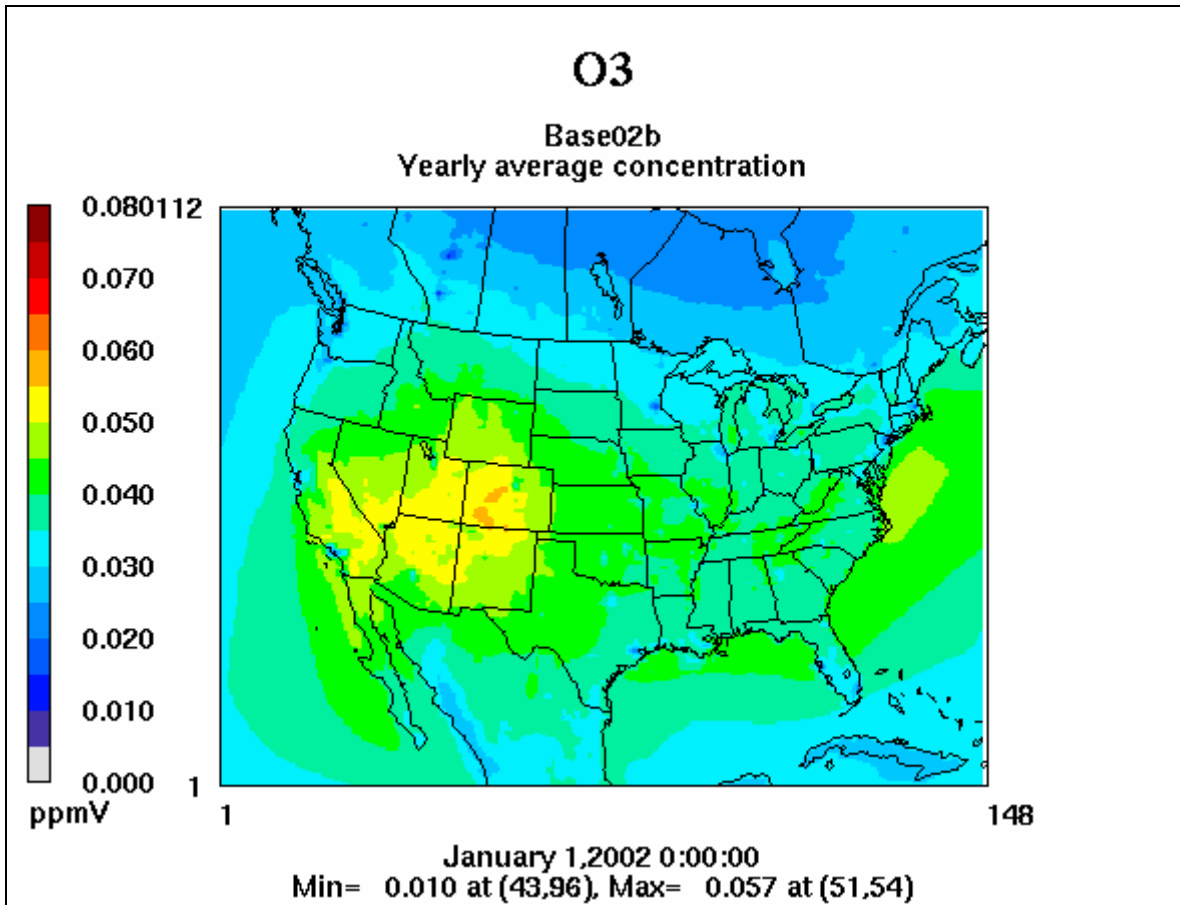
Along with emissions inventories, meteorology data is the input data that has the greatest effect on model uncertainty. Meteorology data includes wind speed and direction, vertical mixing and boundary layer height, temperature, humidity, cloud cover and precipitation. MM5 simulations were used to provide all of these input data. WRAP funded an MM5 sensitivity study to optimize the MM5 performance for the western US on both the 36 km and 12 km grid (Kemball-Cook et al., 2005). That study concluded that the final 36 km and 12 km WRAP MM5 runs exhibited reasonably good performance and is certainly within the bounds of other meteorological databases used for prior air quality modeling efforts. It was therefore reasonable to proceed with their use as inputs for visibility modeling. However, all of the MM5 variables do have error and bias that limit the accuracy of the air quality modeling for both PM<sub>2.5</sub> and ozone. While it is not easy to quantify the effect of those errors, we can conclude that error and bias in wind direction and vertical mixing will introduce significant errors in the air quality model performance for ozone

### **3. WRAP 2002 Base Case Ozone MPE**

Although some limited model performance evaluation was completed as part of the WRAP visibility modeling study, the primary emphasis of that work was on the speciated PM<sub>2.5</sub> performance evaluation. Although error or bias in simulated ozone concentration does affect the rate of oxidation of SO<sub>2</sub>, NO<sub>2</sub> and VOC, the error and uncertainties that this introduces to simulated concentrations of PM<sub>2.5</sub> species is probably smaller than uncertainties resulting from errors in emissions and meteorology. Moreover, most of the ambient ozone monitoring data is located in or near urban areas for which the coarse resolution 36 km model is not expected to perform well. Therefore, only limited efforts were made to evaluate the ozone performance for the regional scale modeling. Future model evaluation efforts can be performed by identifying only those monitoring sites located in rural and remote areas. Alternatively, higher resolution modeling can be performed to more accurately represent strong concentration gradients of ozone and its precursors in urban influenced areas.

We present examples below of the ozone MPE that was completed for the WRAP 2002 modeling. Model simulations and performance evaluations were performed with several different versions of the WRAP emissions data. The ozone MPE was originally completed for preliminary data sets and the Base 2002 version A emissions data. Because subsequent emissions updates were expected to have limited effect on the model simulated ozone concentration, only limited ozone MPE was performed on the 2002 Base version B case. In this section we summarize the ozone MPE for the WRAP CMAQ simulations primarily for the 36 km and 12 km simulations for the 2002 Base Case version A. Some results for Base 2002 B are also presented, when available. Figure 3-1 shows the annual average CMAQ model simulated ozone concentration for the 2002 Base Case version B using the 36 km grid. The elevated ozone level in the West, and in Rocky Mountain region in particular, is probably a result of elevated ozone production associated with the summer time NO<sub>x</sub> emissions from forest fires in the west and reduced chemical loss of ozone in the west from lower ambient concentrations of biogenic VOC. The urban areas show depressed ozone levels throughout the domain because of titration of ozone by urban NO emissions.

Typical ozone model evaluation analyses have relied primarily on compilations of model statistical metrics including bias and error, calculated in a variety of ways. Some of these results are presented in Section 3.1. It is also useful to evaluate ozone performance using both time-series plots and spatial plots of model and data comparisons, and examples of these plots are shown in Section 3.3.



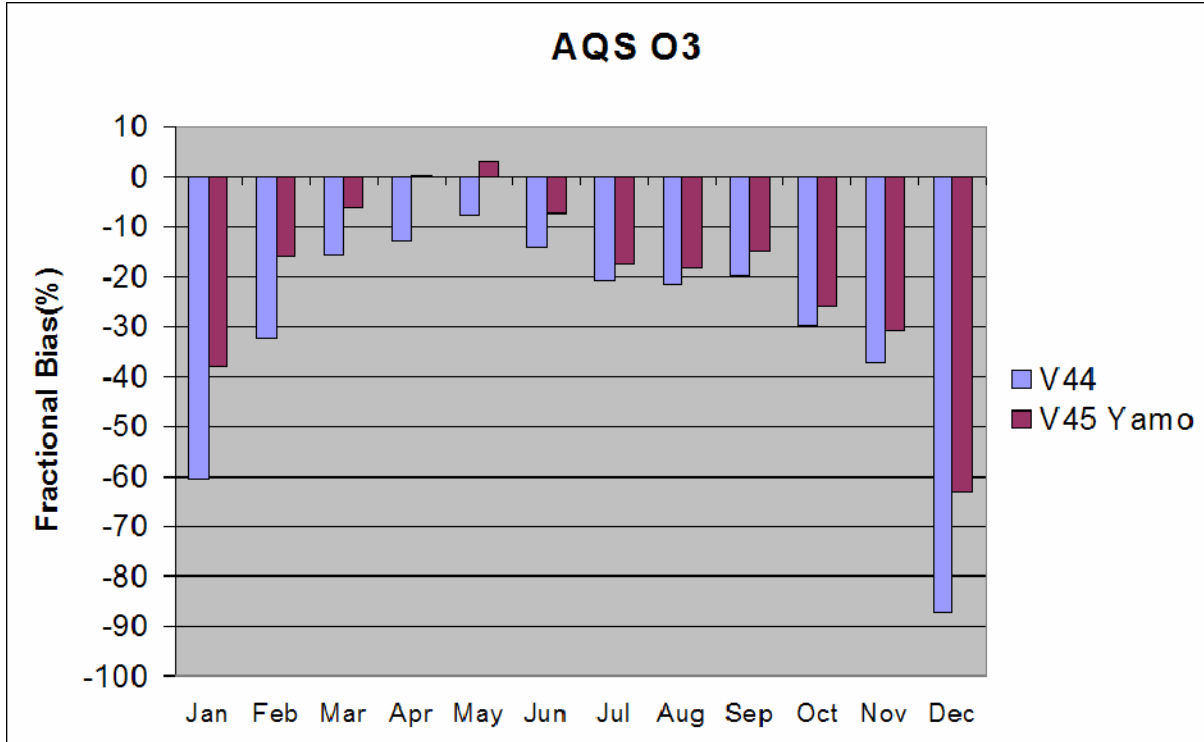
**Figure 3-1. Annual average CMAQ simulated ozone concentration for 2002 Base B.**

### 3.1 Ozone Statistical Performance Metrics

For ozone modeling, EPA has established performance goals for one-hour average ozone normalized mean bias and gross error of  $\leq \pm 15\%$  and  $\leq 35\%$ , respectively (U.S. EPA, 1991). Most previous regulatory applications of ozone modeling have been for the 120 ppb one-hour average ozone NAAQS. Because the focus was on high ozone concentrations for those applications, a filter was typically applied to exclude all data for which the monitored ozone concentration was less than 60 ppb, and statistical metric were calculated using only those ambient data greater than 60 ppb. For the new eight-hour ozone standard we are concerned with the model performance at lower concentrations. Therefore, we present here statistical performance metrics here for both approaches, i.e., using all ambient ozone data, and using only those data greater than 60 ppb. The EPA 1991 1-hr ozone performance goals are for Mean Normalized Bias and Gross Error (MNB and MNGE). The MFB and MNGE normalize the difference between the hourly predicted and observed ozone pairs by dividing by the observed value. This works fine when using the 60 ppb filter, however when using no filter there is a possibility of dividing by zero or a small observed value. Thus, we will present

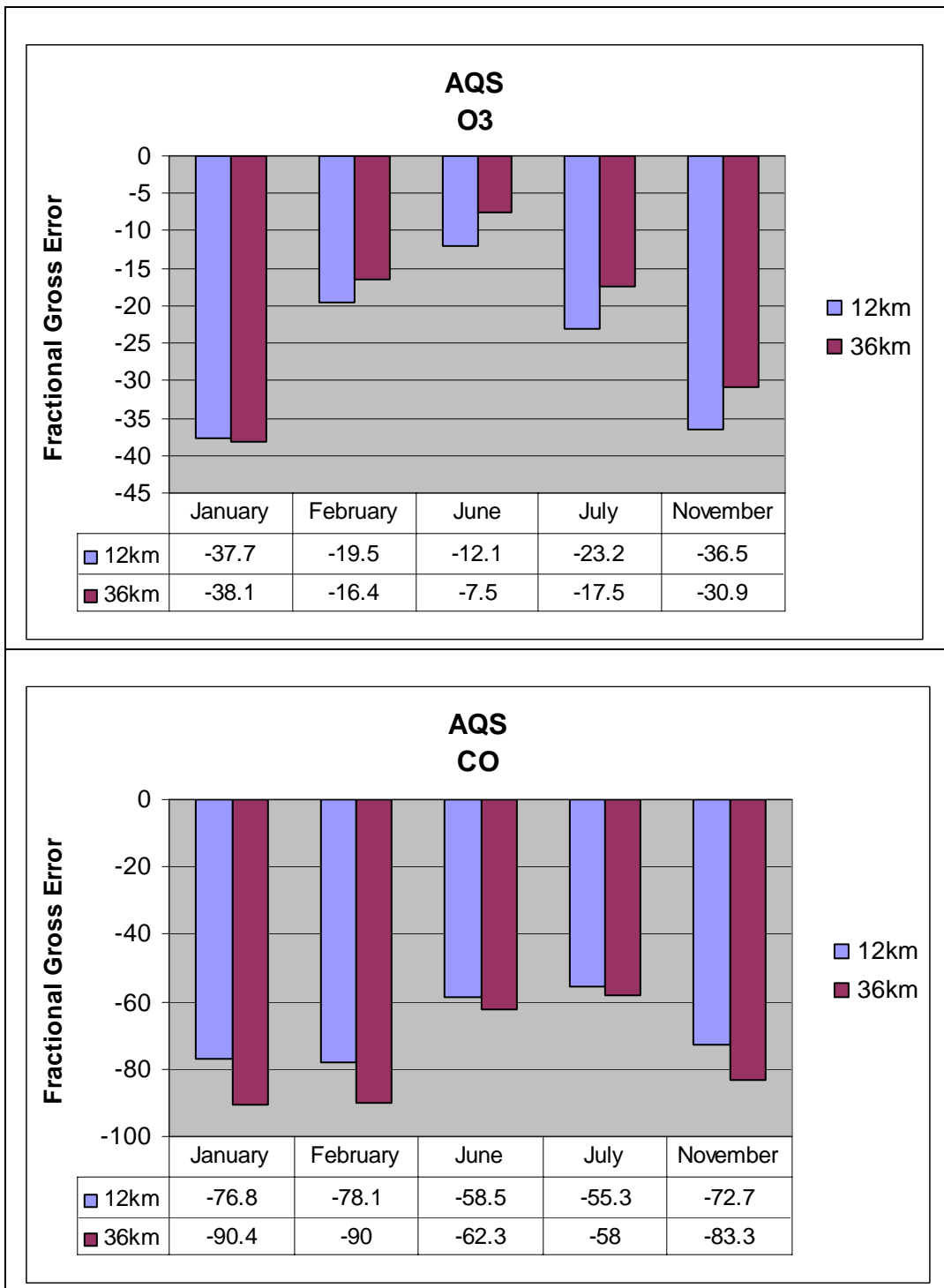
performance metrics using the Mean Fractional Bias and Error (MFB and MFE) metrics that divide by the average of the predicted and observed ozone and are therefore bounded and won't blow up like the MFB and MNGE can.

Figure 3-2 compares the ozone performance for CMAQ v4.4 and v4.5 for the AQS data. Following traditional ozone model performance guidance, we excluded all ambient data for which the measured concentration was less than 60 ppb. As a result, the comparison was weighted toward those days with high ambient ozone, and this tended to cause the model to under-predict the data, especially for the winter months during which there were few days with measured ozone greater than 60 ppb. We also performed this analysis without the filter on the ambient data so that all ozone data were included in the comparison. In that comparison (not shown here) the model tended to over predict ozone, with larger over predictions occurring during the winter months. Overall, we expect CMAQ to over predict total oxidant and to slightly over predict formation of SOA for low ambient ozone conditions, and to slightly under predict formation of SOA for high ambient ozone conditions.



**Figure 3-2. Ozone monthly MFB for the 36-km results for CMAQ versions 4.4 and 4.5 compared to the AQS hourly average ozone data, using a filter to exclude all hours with data less than 60 ppb.**

Figure 3-3 shows the CMAQ 12-km and 36-km model MFB compared to the AQS gas-phase ambient data for ozone and CO, where the ozone MFB is calculated using the ambient data filter to exclude measured ozone values less than 60 ppb, as described earlier. Each of these plots shows the same general result: although there are small differences between the MFBs calculated for the 12-km and the 36-km models, their performance is quite similar. It is not apparent that one version of the model is in any way superior to the other. These results indicate that there would be no advantage in terms of our MPE to running the more resource-intensive 12 km model instead of the 36-km model.



**Figure 3-3. Mean fractional bias for the 12-km and 36-km CMAQ compared to AQS gas-phase ozone and CO data.**

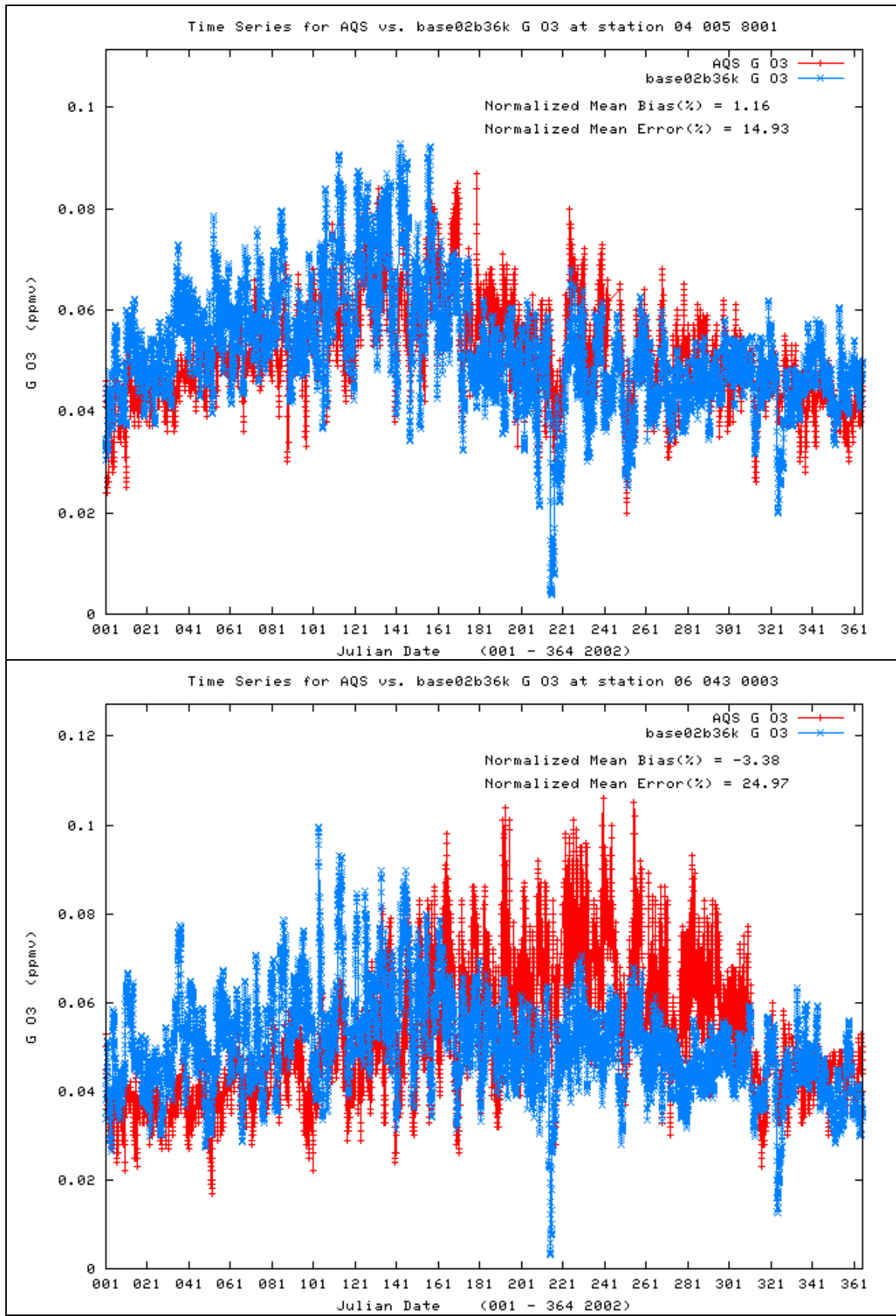
### 3.2 Ozone Time-series Plots

Time-series plots comparing modeled and observed ozone is another useful approach for evaluating the ozone model performance. We selected those sites that are in or near Class I areas, and these results are shown in Figures 3-4 to 3-6. The plots also show the calculated normalized mean error and bias for all 365 days at each sites.

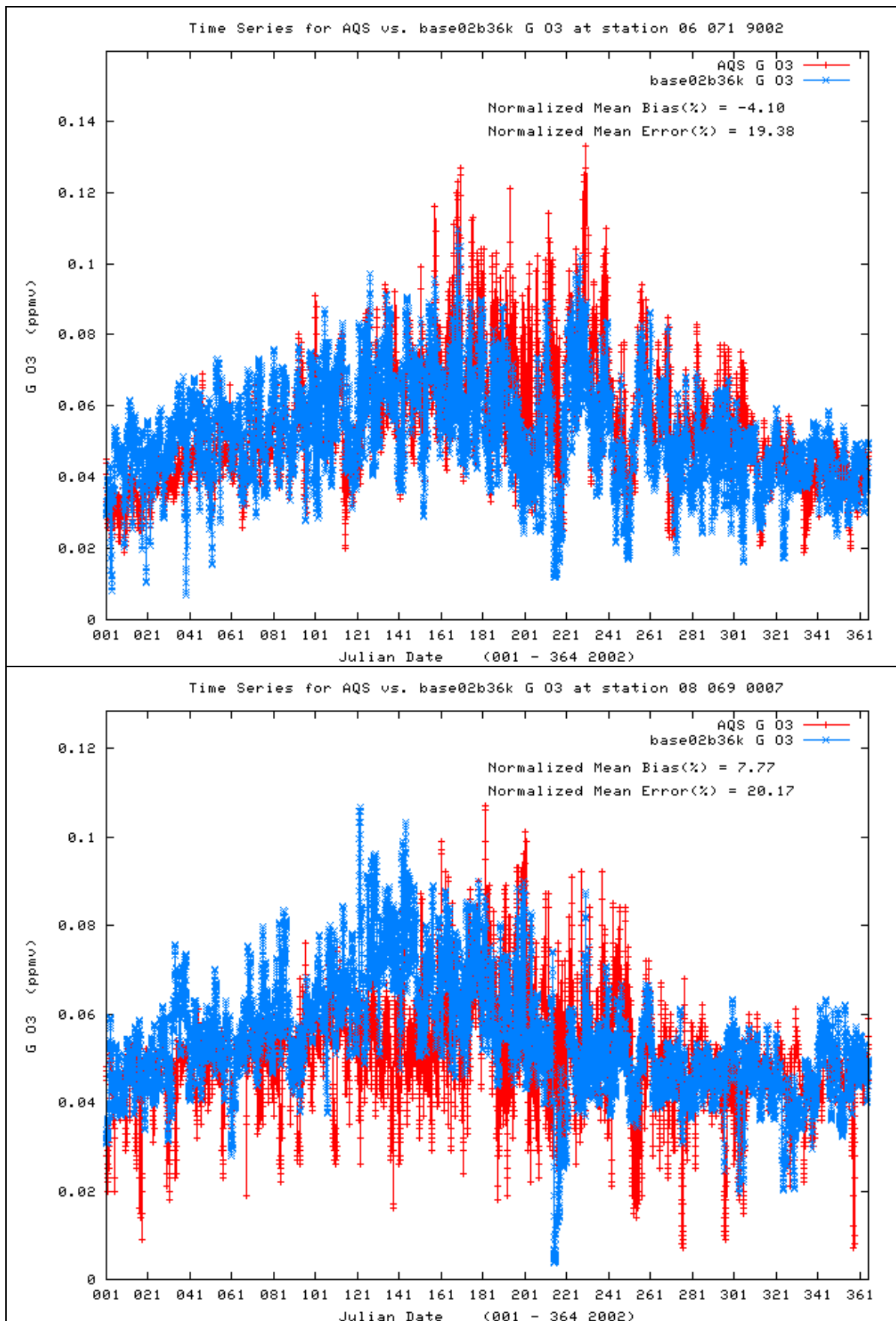
The model performs quite well for most of these rural sites, with the exception of Glacier National Park (see Figure 3-6, top plot) for which ozone frequently approaches minimum values near zero during the nighttime. This is indicative of nearby NO<sub>x</sub> emissions sources at this site that titrate the surface ozone concentration in the surface layer. At the other sites, the model reproduces the daily maxima and minima and the diurnal profile for ozone. The model also matches the seasonal trends in the data at most of the sites, except for site Yosemite National Park (see Figure 3-4, bottom plot) for which the model over-predicts ozone in the spring and under-predicts ozone in the summer.

It would be valuable to screen the complete set of AQS gas species monitoring sites to select additional rural sites and to perform a more comprehensive model evaluation for these site. This task would require collaboration with state and local staff who are familiar with the characteristics of each monitoring site.

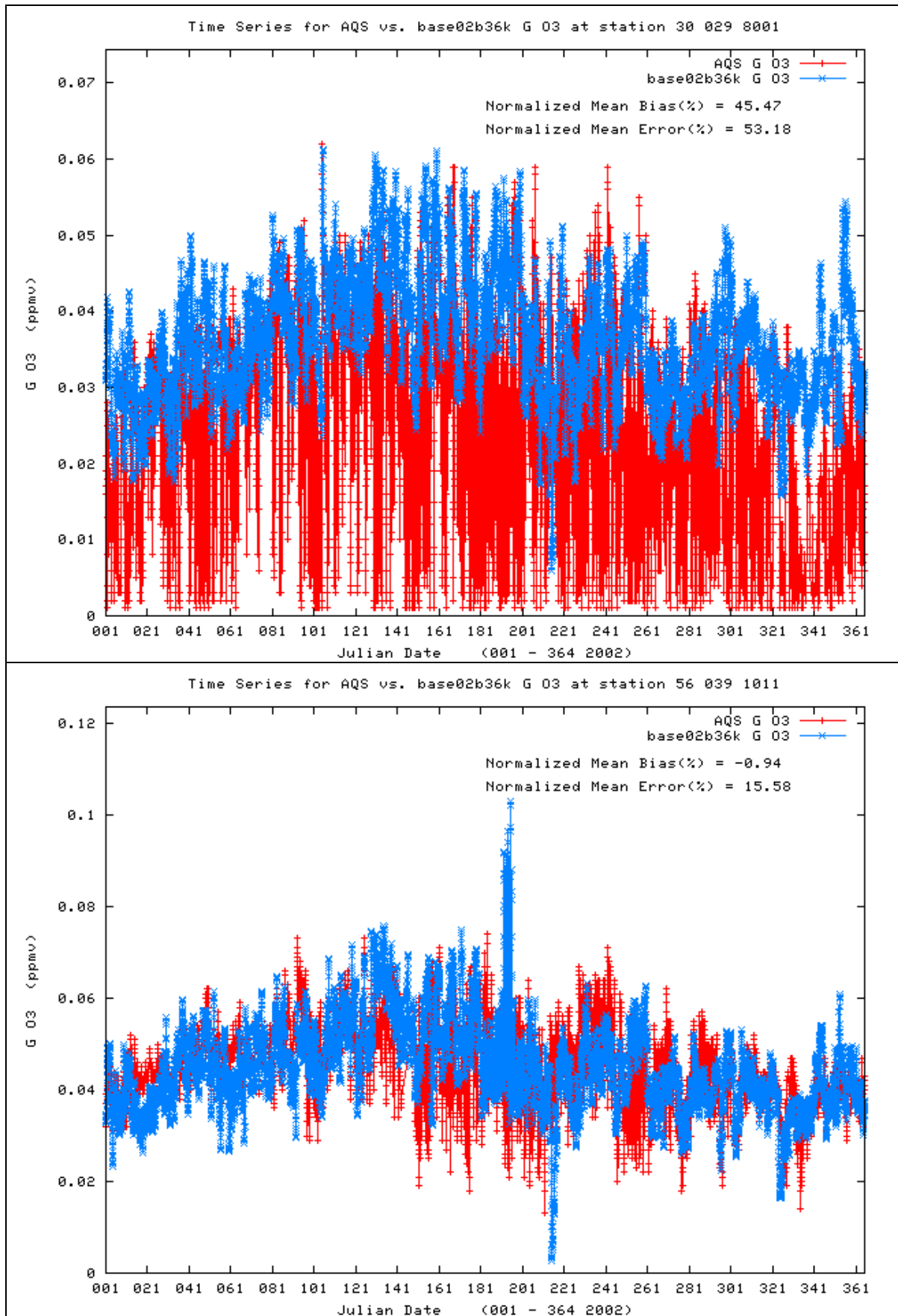
As discussed in Section 3-5, we do not recommend using urban or urban influenced sites in the 36-km model MPE because the coarse grid resolution does not sufficiently resolve local scale concentration gradients in ozone, VOC and NO<sub>x</sub>. Therefore, we would expect poor model performance for these urban sites. Nevertheless, the evaluation of the rural sites suggests that the 36-km model does simulate regional ozone levels quite well.



**Figure 3.4. Model and observed ozone for (top) Grand Canyon National Park; and (bottom) Turtleback Dome, Yosemite National Park.**



**Figure 3.5. Model and observed ozone for (top) Joshua Tree National Monument; and (bottom) Rocky Mountain National Park.**



**Figure 3.6. Model and observed ozone for (top) Glacier National Park; and (bottom) Yellowstone National Park.**

### **3.5 Model performance issues for regional and urban ozone modeling.**

Different approaches may be used for evaluating model performance for urban versus rural or remote locations. Urban influenced areas have much greater emissions density of the ozone precursors VOC and NO<sub>x</sub> along with large spatial variability in emissions and large concentration gradients of VOC and NO<sub>x</sub>. As a result, high resolution grids are required to model urban ozone, with typical applications using grid resolutions of 4 km or finer. Even with a high resolution grid, it may not be possible to adequately resolve sharp concentrations gradients of VOC, NO<sub>x</sub> and ozone near urban areas. Because ozone monitors are located at a specific point, and model predicted ozone is averaged over the area of an entire grid cell (typically 16 square km for a 4 km grid), there is the possibility of significant discrepancies between ambient data and model grid cell averages for urban influenced locations. Error or bias in wind speed and direction may also have a more profound effect on model uncertainty for urban ozone. By contrast, rural location tend to have much lower emissions of VOC and NO<sub>x</sub> with more uniform concentration distributions, large contributions from transported ozone instead of locally produced ozone, and lower concentrations of ozone. For all of these reasons, a coarser resolution model may perform better for rural ozone than it does for urban conditions.

Ambient ozone monitoring data is available from the AIRS database, however, most ozone monitors are located in urban or urban influenced areas, and we do not necessarily expect good model performance on the 36 km or even the 12 km grid for those sites because the coarse grid resolution limits the model skill in simulating extreme high and low ozone concentrations. However, we do expect better performance for rural or remote sites.

### **3.6 New approaches to ozone MPE**

As described above, only a limited MPE was completed for ozone because the large majority of gas phase monitoring sites were located in areas influenced by urban emissions, and the 36-km model was not expected to perform well for these sites because of the inability to resolve high concentration gradients of ozone and its precursors in or near urban areas. Because the primary focus of WRAP was on visibility and PM<sub>2.5</sub>, and because errors or bias in modeled ambient ozone were expected to have smaller effect on modeled PM<sub>2.5</sub> than errors or bias in emissions and meteorology, WRAP did not pursue a more comprehensive ozone model performance evaluation. However, there are some approaches which could be used to further evaluate the ozone performance. These include the following:

1. Stratifying monitoring data by site characteristics.
2. Implementing new ozone monitoring sites at remote locations to better characterize ozone transport.
3. Performing additional aloft measurements of ozone to better characterize vertical ozone profiles.

4. Adding additional gas species measurements to better characterize conditions for which ozone production is VOC sensitive or NO<sub>x</sub> sensitive.

**Stratifying monitoring data by site characteristics:** To evaluate the ozone model performance for the rural regions in the coarse grid model, it will be necessary to characterize the site conditions, topography and location relative to emissions source for each monitoring site, and then to perform model to data comparisons for groups of different sites. Types of monitoring sites will include the following:

- a) Urban sites in areas with emissions of NO<sub>x</sub> and high concentrations of NO for which ozone concentrations frequently approach zero because of ozone titration by NO.
- b) Near urban sites which have large gradients in concentrations of ozone and its precursors, and for which the model may correctly predict high ozone concentrations but for which it may not reliably match the ambient data because of errors or bias in wind speed, wind direction, and planetary boundary layer height.
- c) Downwind sites from urban areas that may typically have lower peak ozone levels and smaller concentration gradients in ozone and its precursors, and for which the model might more accurately predict ozone maxima and diurnal profiles.
- d) Upwind urban sites for which transport is the primary source of ozone with a smaller contribution from ozone formation from local sources.
- e) Remote sites for which transport is the primary source of ozone.

To the extent that all monitoring sites can be stratified according to these categories, it may be possible to compile statistical model performance metrics for groups of similar sites. However, it may be difficult to stratify monitoring sites because of unique conditions at each site. For example, some “remote” sites in Class I areas might be influenced by local mobile source emissions from tourism activity, and these sites might be more similar to rural sites. Ultimately, it might be necessary to evaluate unique conditions for each individual site to gain the best insight into the model performance at that site.

Implementing new monitoring sites and new gas species measurements will be a long term activity and will not be useful for ozone model performance evaluations in the near term. Additional monitoring of ozone at remote sites and aloft will be useful for better characterizing long range transport and stratospheric intrusion of ozone. Measurements of additional precursor species will be useful for better evaluating local formation of ozone. One of the most useful sets of measurement will be for the species HCHO and NO<sub>x</sub> because these species are important ozone precursors, and the ratio of HCHO/NO<sub>x</sub> has shown some promise as useful indicator of whether ozone formation occurs in either VOC sensitive or NO<sub>x</sub> sensitive conditions .

#### **4. Input Data Uncertainties in the 2002 Ozone Modeling**

There are several significant uncertainties both in the input data and in the model formulation that limit our confidence in the model predictions for ozone. These include the following:

Uncertainties in anthropogenic emissions: There are varying uncertainties in each source category of anthropogenic emissions. We have the greatest confidence in emissions from CEMS data which are estimated to be accurate within +/- 20%.

Uncertainties in biogenic emissions: There are much larger uncertainties in biogenic emissions of VOC, with uncertainty estimates ranging up to a factor of 3. Biogenic VOC, including isoprene, terpenes and sesquiterpenes can either act as a source of ozone production or as a sink for ozone. For example, regional ozone levels can be depleted in areas with large terpene emissions, and the ozone reaction with terpenes in an important source of secondary particulate organic carbon. In urban areas in the southeastern U.S., including Atlanta and Houston, biogenic VOC can be as important as anthropogenic VOC as a source of ozone formation. Biogenic VOC. Emissions of NO<sub>x</sub> from lightning is a possible source biogenic source of NO<sub>x</sub>, and U.S. emissions of lightning NO<sub>x</sub> are not included in previous WRAP modeling. Globally, lightning NO<sub>x</sub> emissions are estimated to be in the range from 1 to 8 million metric tons per year. Preliminary results from model simulations that include lightning NO<sub>x</sub> show that it may have only a small effect on

Errors and bias in the meteorology data is probably as important as uncertainty in the emissions inventories. WRAP funded a comprehensive evaluation of the MM5 performance with a variety of physics options to optimize the MM5 performance for the western U.S., and the MM5 performance in the WRAP visibility modeling was comparable to that of other modeling studies. Nonetheless, there were limited meteorology available data to evaluate the model, and there were significant errors and bias in wind direction, wind speed that can significantly affect model performance. Data was especially limited for evaluating the MM5 simulated boundary layer height, and the resulting uncertainty in the vertical mixing of ozone and precursors may be the largest uncertainty resulting from the meteorology data. Error introduced by this uncertainty would be most pronounced for nighttime and winter conditions that typically have shallow mixed layer heights, and it is possible that the model could either over-predict or under-predict vertical mixing depending on the specific conditions. Moreover, because the WRAP MM5 simulation was completed for a full year, it was not possible to optimize the MM5 performance of different meteorological conditions during the year, as is typically done for urban scale episodic modeling. Therefore, we expect the WRAP ozone simulations would performance less well compared to typical episodic ozone modeling studies. There was both errors and bias in the MM5 temperature and humidity data, however, the effect of these errors were probably much smaller than errors in wind and vertical mixing. Although temperate and humidity do affect VOC reactivity and ozone

formation, the resulting errors would be small compared to uncertainty in emissions data and in the ozone photochemistry.

Uncertainty and errors in the photochemical mechanism used to simulate ozone formation is another important source of uncertainty. Photochemical mechanisms are described in Section 6.1. There is uncertainty in the accuracy of the VOC oxidation chemistry; however, the photochemical mechanisms perform better in smog chamber studies for low NO<sub>x</sub> rural conditions than they do for urban conditions. Therefore, errors in the VOC reactivity will be smaller for rural and remote areas than for urban ozone modeling. There is a possibility of larger errors in heterogeneous and surface chemistry, especially for sources and sinks of reactive NO<sub>x</sub> that might significantly affect the model simulated production of ozone and the sensitivity of ozone to changes in NO<sub>x</sub>, as discussed in Section 6. However, it is not possible to quantify the uncertainty and any possible bias in the model as result of possible errors is speculative. Nonetheless, this remains an important area of concern for which significant future experimental work is required.

Stratospheric intrusion of ozone into the free troposphere is another possible source of uncertainty in regional ozone modeling. Some studies have suggested that as much as one third of the global tropospheric ozone budget might be from stratospheric intrusion. However, there is large uncertainty in these studies, and the actual contribution is uncertain. To the extent that the GEOS-CHEM simulations include lightning NO<sub>x</sub> and stratospheric intrusion of ozone, these sources are also implicitly included in the WRAP visibility modeling as transport into the lateral boundary conditions. Approaches used in CMAQ and CAMx for treating the flux at the model top are discussed in Section 5.

## **5. Applications of WRAP ozone modeling**

There are several possible uses of the existing WRAP ozone modeling data. The full year model simulated surface ozone results have been archived for the following WRAP simulations: the 2002 MPE case, the 2002 planning case, the 2018 base case, and the 2018 preliminary reasonable progress case. In addition, the modeled 3-d concentrations for ozone and its gas species precursors have also been archived for the 2002 MPE case. These data have not been archived for the other model simulations because of the large disk space required to store the files.

For individual local or state agencies that do not have resources to complete new ozone modeling studies, it is possible that the results of these simulations can be used to evaluate regional ozone conditions for air quality management planning. The primary limitation in using these data sets is that these model simulations were completed using a 36-km resolution grid that does not have sufficient spatial resolution to adequately resolve ozone formation in urban areas. However, for rural and remote areas with low emissions and where transported ozone is the primary source, the 36-km model results may be adequate to evaluate ozone attainment strategies. For example, the existing

model data sets can be easily applied to evaluate ozone sensitivity to VOC and NO<sub>x</sub> emissions. CMAQ simulations can be performed for across the board emissions reductions in VOC and NO<sub>x</sub> without the need for additional processing of emissions, and emissions reductions in VOC and NO<sub>x</sub> can be evaluated for individual source categories with minimal additional effort for emissions processing. These model simulations could be used for evaluation of regional scale ozone attainment strategies using existing WRAP datasets.

Another possible application of the WRAP modeling data sets is to use the results of the WRAP CMAQ simulations to provide the boundary conditions for new air quality modeling studies at finer resolution scales in sub-regions in the WRAP states. Because the WRAP simulations are nested in the results of global scale GEOSCHEM simulations, the WRAP model results include the effects of global emissions and transport. Thus, it would be possible for the western states and tribes to estimate global and regional contributions to local ozone budgets by performing model sensitivity studies using boundary concentrations derived from the WRAP visibility modeling.

## **6. Air Quality Model Formulation and Ozone Photochemistry**

The USEPA developed CMAQ as a “one atmosphere” model that can be used for evaluating the full range of air quality issues, including ozone, PM<sub>2.5</sub>, visibility, mercury and hazardous air pollutants. CMAQ has a modular design that facilitates the implementation of new science algorithms, and it includes two or more user selectable options for many of the sciences processes.

ENVIRON Corporation originally developed the CAMx model in the mid-1990s for simulating ozone air quality, and it has been updated and expanded in parallel with CMAQ to represent all air quality issues as a “one atmosphere” model. Many of the same science algorithms are available in both CMAQ and CAMx, although there are some differences in the implementation of the numerical algorithms. For ozone modeling, the most significant differences between CMAQ and CAMx are in the representation of advection and dispersion. The CAMx horizontal dispersion coefficients are proportional to the square of the horizontal grid resolution, whereas the CMAQ ones are proportional to the inverse of the square of the grid resolution. Consequently, CAMx generally has greater horizontal dispersion than CMAQ with lower peak concentrations of precursors spreading more rapidly over a larger area (i.e., mixed into adjacent grid cells) for coarse (e.g., 36 km) grid resolution, whereas CMAQ has less dispersion with coarse resolution so that precursors are more confined to the grid cell in which emissions occur. The resulting effects on ozone formation and ozone concentrations using coarse grid resolution vary depending on precursor concentrations and on the ratio of VOC to NO<sub>x</sub>, but greater dispersion of precursors should in general produce greater ozone formation

and higher ozone concentrations on a regional level. However, under finer grid resolution (e.g., 4 km) CAMx will have lower horizontal dispersion than CMAQ, which may result in higher peaks in ozone and precursor concentrations and more ozone suppression in high surface NO<sub>x</sub> emission areas. One effect of these differences in the formulation in horizontal dispersions is that the CMAQ model's coarse grid simulations look much more like their fine grid simulations than CAMx does. Another significant difference in the two models is the representation of the boundary conditions at the model top. CMAQ extends from the surface to the lower stratosphere and has a model top at 100 millibars. It uses a zero flux boundary condition at the top, so there is no net transport of species into or out of the model top. With this approach, stratospheric intrusion of ozone into the troposphere is not directly represented in CMAQ. However, stratospheric ozone can be represented indirectly through horizontal transport at the lateral boundaries in the upper layers. Thus, in the WRAP simulations using the GEOS-CHEM derived boundary conditions, a contribution from stratospheric ozone intrusion is included only from the later boundaries and only to the extent that it is included in GEOS-CHEM model. There remains large uncertainty in the contribution of stratospheric ozone to surface ozone, but it is possible that it can be a significant source of surface ozone in the western US (references).

The USEPA maintains and updates CMAQ with updated model science algorithms made available approximately every one to 2 years. The next CMAQ release is scheduled for fall 2008 and is expected to include significant updates to the science algorithms used to represent secondary organic aerosols (SOA) from biogenic emissions. ENVIRON Corporation maintains and updates the CAMx. CAMx Version 4.51 was released in May 2008 ([www.camx.com](http://www.camx.com)) and includes some similar biogenic SOA updates as planned for CMAQ in its fall release.

## 6.1 Photochemical Mechanisms

The major source of ozone in the troposphere is from photochemical formation from precursors VOC and NO<sub>x</sub>, and the primary formation mechanism is the oxidation of VOC by the hydroxyl radical (OH) to form organic peroxy species that react with NO to form NO<sub>2</sub>. The species NO, NO<sub>2</sub> and ozone are in a rapid, photostationary state equilibrium, and the conversion of NO to NO<sub>2</sub> alters that equilibrium to cause an increase in ozone. To simulate ozone formation, air quality models must include a photochemical reaction mechanism that represent the oxidation of VOC. The representation of the inorganic chemistry of the photostationary state is essentially the same for all photochemical mechanisms. However, a number of different approaches have been used to represent the VOC oxidation. There are hundreds of different VOC species emitted to the atmosphere, and thousands of organic intermediate products. The chemistry of many VOC species is uncertain, and because of computational constraints it is not possible to represent explicitly all VOC species in gridded air quality models. Instead, condensed photochemical mechanisms have been developed based on smog chamber experiments to represent the formation of ozone from a simplified mixture of VOC species. There are three different condensed photochemical mechanisms that have

been widely used in air quality modeling: the Carbon Bond Mechanism, the SAPRC mechanism, and the Regional Acid Depositing Mechanism.

The Carbon Bond Mechanism version 4 (CB4) has been the most widely used mechanism for regulatory air quality modeling, and it was used for the WRAP visibility modeling. CB4 uses an approximation of carbon bond types to reduce all explicit VOC species to a set of 7 model species. The CB4 has been recently updated, and the new version, CB-05, is now available in CMAQ. It includes a new carbon bond type (an internal olefin bond) and it includes some important updates in the inorganic chemistry that are expected to make it more reactive for urban conditions. The CB4 was originally designed for use in high NO<sub>x</sub> urban conditions and it did not accurately represent low NO<sub>x</sub> rural ozone chemistry. However, several updates to CB4 during the late 1990s made it more suitable for low NO<sub>x</sub> chemistry.

The SAPRC mechanism was developed at the State Wide Air Pollution Research Center. It uses a surrogate molecule approach in which all explicit VOC species are represented as combinations of 10 surrogate model species. In the older versions, the SAPRC mechanism was more reactive than CB4. However, the reactivity is more similar for SAPRC and CB-05. The third widely used photochemical mechanism is the Regional Acid Deposition mechanism version 2. It uses a surrogate molecule approach similar to SAPRC but uses a different set of surrogate VOC species. More explicit photochemical mechanisms that represent a larger number of VOC species have been developed but computational constraints make it difficult to use larger photochemical mechanisms for long term visibility modeling. Moreover, given the uncertainty in both the organic and inorganic chemistry in all of these mechanisms, it is not certain that a more detailed mechanism would provide better simulation of regional ozone and visibility.

### **Ozone sensitivity to VOC and NO<sub>x</sub>**

Because both VOC and NO<sub>x</sub> are necessary for photochemical formation of ozone, ambient ozone can be reduced by controlled either VOC or NO<sub>x</sub>, or some combination of them. Historically, the primary control strategy for urban ozone has been reduction of VOC. However, NO<sub>x</sub> control strategies in combination with VOC controls have been used in SIPs since the later 1980s in California. The effectiveness of VOC versus NO<sub>x</sub> emissions controls varies depending on the ratio of VOC to NO<sub>x</sub> emissions. At high ratios of VOC to NO<sub>x</sub>, the formation of ozone is primarily sensitive to NO<sub>x</sub> and control of NO<sub>x</sub> emissions is the most effective strategy for reducing ambient ozone. However, at low VOC to NO<sub>x</sub> ratios, NO<sub>x</sub> can inhibit the formation of ozone, both by scavenging of OH radicals ( $\text{OH} + \text{NO}_2 = \text{HNO}_3$ ) and by titration of ozone ( $\text{NO} + \text{O}_3 = \text{NO}_2$ ). Although the latter reaction does not reduce the total oxidant burden, it does reduce the formation of OH radicals from ozone photolysis. Thus, the combination of these two reactions can significantly reduce ozone formation in urban areas with low ratios of VOC to NO<sub>x</sub>. This is the cause of the very low observed ozone levels often observed near urban cores. For many urban areas, initial efforts to control of NO<sub>x</sub> emissions can result in higher concentrations of OH, more rapid reaction of VOC and increased formation of ozone near

the urban center. However, sufficiently large reductions of NO<sub>x</sub> will shift the ambient VOC to NO<sub>x</sub> ratio so that NO<sub>x</sub> control will cause result in reduced urban ozone. Moreover, NO<sub>x</sub> reductions are always effective in reducing ozone at greater distances downwind from the urban area. But to minimize the disbenefit of NO<sub>x</sub> controls in urban areas, a combination of both VOC and NO<sub>x</sub> controls are needed.

In contrast to urban areas, rural areas typically have lower emissions of NO<sub>x</sub>, greater emissions of biogenic VOC, and greater ratios of VOC to NO<sub>x</sub>. As a result, NO<sub>x</sub> control is typically the most effective strategy for reducing rural ozone. This is especially true for areas with large biogenic emissions of isoprene in the southeastern US, where ambient rural ozone may be very insensitive to VOC controls.

It may be possible to assess the relative effectiveness of VOC versus NO<sub>x</sub> control by use indicator of ozone sensitivity. Photochemical indicators are species or combinations of species that assume characteristic values for conditions in which O<sub>3</sub> is primarily either NO<sub>x</sub>-sensitive or VOC-sensitive. Indicators have been derived both for the sensitivity of peak O<sub>3</sub> concentration and for the sensitivity of the instantaneous rate of O<sub>3</sub> or odd oxygen (O<sub>x</sub>) production. The former are useful for investigating the cumulative sensitivity of O<sub>3</sub> production over the history of an air parcel trajectory, while the instantaneous indicators are useful for evaluating local O<sub>3</sub> production sensitivity for air parcels passing over a particular site. There are several limitations to the indicator approach. First, the usefulness of indicators is based on theoretical analyses and model simulations but has not been fully validated by experimental results. Second, the ambient measurements required for indicators are both difficult and expensive to make, and only very limited data is available to evaluate the indicators. Third, indicators only provide an estimate of ozone sensitivity. They do not predict how large a reduction in VOC or NO<sub>x</sub> is necessary to attain an air quality goal or if it is even possible to sufficiently reduce ozone through a particular control strategy. Therefore, although indicators may provide useful information for evaluating ozone sensitivity and the likely effects of emissions controls, they are not a substitute for air quality modeling studies.

### **Urban and regional scale reactivity of VOC and NO<sub>x</sub>**

Reactivity can be thought of as either the rate of ozone formation or the total amount of ozone formed per molecule of VOC or NO<sub>x</sub>. Selective control of high reactivity VOC species dates to the 1970 in southern California in “Rule 66”. Although the USEPA did has historically regulated all VOC species equally on a basis of total mass, it has recognized that some VOC species are less reactive than others and has granted exemptions to VOC regulations for species that are less reactive than ethane. Reactivity scales have been developed for use in California to selectively control high reactivity VOC species through the use of reactivity weighting scales for reformulated fuels. The feasibility of VOC reactivity for regional ozone control is complicated by the consideration of the larger time and spatial scales involved. VOC reactivity may be more effective for urban areas in which slowly reacting VOC species are transported downwind before they can contribute to local ozone formation, however, those species

may then contribute to ozone formation for several days and hundreds of miles downwind from the area emissions. Therefore, the evaluation of reactivity based VOC controls must be considered on a regional basis.

The same concerns are relevant to evaluation of NO<sub>x</sub> control strategies, although NO<sub>x</sub> emissions should be considered in terms of their ozone forming potential rather than reactivity. Depending on the ambient concentration and the ratio of VOC to NO<sub>x</sub>, each molecule of NO<sub>x</sub> can contribute to the formation of a number of ozone molecules ranging from 1 to more than 100. For conditions with very low VOC to NO<sub>x</sub> ratios, such as power plant plumes or urban cores, reactive NO<sub>x</sub> emissions can be rapidly converted to inert HNO<sub>3</sub> before significantly contributing to ozone production. By contrast, in rural areas that typically have high VOC to NO<sub>x</sub> ratios, a molecule of NO<sub>x</sub> may contribute to the formation of many molecules of ozone before being converted to relatively inert species of organic nitrate or HNO<sub>3</sub>. Thus, control of widespread area and mobile sources of NO<sub>x</sub> emissions will be more effective, on an equal mass basis, than the control of power plant and urban core emissions. Although there is high confidence in this conclusion regarding the relative ozone forming potential of different NO<sub>x</sub> emissions sources based on our understanding of ozone photochemistry, it is difficult to predict accurately the ozone forming potential for a given source because of uncertainty in NO<sub>x</sub> photochemistry and in the fate of NO<sub>x</sub> reaction products. Factors that create uncertainty in the ozone forming potential of NO<sub>x</sub> include uncertainty in the rate of deposition of N species, uncertainty in the fate of organic nitrates, and uncertainty in the inorganic chemistry that effects the conversion of NO<sub>x</sub> to HNO<sub>3</sub>.

### **Uncertainty in NO<sub>x</sub> budgets**

In addition to the uncertainty in the ozone forming potential per molecule of NO<sub>x</sub>, there is also significant uncertainty in gas phase and heterogeneous chemistry that affects NO<sub>x</sub> budgets. The most significant uncertainty is the conversion of NO<sub>x</sub> to HNO<sub>3</sub> through the nighttime hydrolysis of N<sub>2</sub>O<sub>5</sub>. During the night, NO<sub>2</sub> and NO<sub>3</sub> react to form N<sub>2</sub>O<sub>5</sub> which can then undergo both gas phase and heterogeneous reaction with H<sub>2</sub>O to form HNO<sub>3</sub>. Model simulations estimate that on the order of 30% of total NO<sub>x</sub> emissions can be converted to HNO<sub>3</sub> by N<sub>2</sub>O<sub>5</sub> hydrolysis during the summer, and up to 80% of NO<sub>x</sub> can be converted to HNO<sub>3</sub> by N<sub>2</sub>O<sub>5</sub> hydrolysis during the winter. However, there is large uncertainty in both the gas phase and heterogeneous N<sub>2</sub>O<sub>5</sub> hydrolysis and large uncertainty in the amount of NO<sub>x</sub> lost through this process. This is one of the most critical uncertainties in model simulations of regional ozone.

A second uncertainty involves the possible re-noxification of inert forms of nitrogen species through surface reactions or heterogeneous chemistry (references). This process is well known in smog chamber studies where HNO<sub>3</sub> or organic nitrates deposit to the chamber walls where they are converted back to reactive forms of NO<sub>x</sub> and off gas from the wall. This process is not well understood in ambient air and remains an important area of uncertainty.

## **Use of plume-in-grid and high resolution nested grids**

One source of uncertainty for ozone performance in the WRAP visibility modeling is the effect of the coarse grid resolution in urban areas. It is likely that artificial dispersion and dilution of the VOC and NO<sub>x</sub> precursors in urban areas and in power plant plumes may have resulted in enhanced photochemical production of ozone in the model. Effects of such errors in remote areas would have been mitigated to some degree by subsequent deposition, chemical loss and dispersion of ozone as the air mass was transported from source areas to remote areas. Nonetheless, it would be desirably to treat urban areas and power plant plumes with finer spatial resolution in future modeling studies.

The CMAQ model does not include two-way nesting, so it is not possible to represent high resolution urban areas within a coarse resolution grid. Instead, with CMAQ the only option is to use a high resolution grid for the entire model domain. CMAQ does include a plume-in-grid algorithm that should be used in future model simulation with the 36-km grid. CAMx includes both a plume-in-grid algorithm and two-way nesting, so it is possible to evaluate the effects of high resolution of urban areas in CAMx. It is likely that the result of adopting this approach would better model performance for ozone in urban areas, and slightly reduced export of ozone from urban areas to rural areas.

## **7. Recommendations for Future Ozone Modeling Studies**

There are several recent updates to emissions inventories that could be used in future WRAP ozone modeling studies. There is an alternate biogenic emissions derived from the MEGAN biogenic emissions model that should be compared to the current WRAP biogenic emissions inventory that was prepared using the BEIS3 model.

ENVIRON has developed a new oil and gas emissions inventories for new oil field operations in the western U.S., and this inventory should be used in future WRAP ozone modeling. CRC is currently funding research in natural emissions and air quality modeling sensitivity studies of natural emissions, and it is possible there may be recommended updated to natural emissions based on that work, including a lightning NO<sub>x</sub> emissions inventory. States routinely update their major and minor point source emissions. The next update to the National Emissions Inventory (NEI) will be for the 2008 year.

The most recent update of the CMAQ model includes the CB-05 photochemical mechanism, and although its effects on regional ozone predictions may be small, the updated mechanism should be used in all future modeling studies. The latest CAMx release (V4.51, May 2008) also contains the CB05 chemical mechanism. EPA will also be releasing an updated version of CMAQ in fall 2008, and the most recent CMAQ versions should be used in the next round of modeling studies. We also recommend that

CMAQ and CAMx be compared again with the most recent model versions and data sets for both a base case scenario and for VOC and NO<sub>x</sub> sensitivity cases. Because of differences in the way CAMx and CMAQ represent vertical mixing and horizontal dispersion, and also because of possible differences in N<sub>2</sub>O<sub>5</sub> hydrolysis, it is important to compare the two models. It may not be possible to determine which model is more accurate, especially for VOC and NO<sub>x</sub> sensitivity, but comparison of the two models will help in establishing possible uncertainty in modeled ozone response to reductions in precursor emissions.

If new model simulations performed for both the 2002 base case performance evaluation and for 2018 simulations, the 3-d concentration data should be saved for both models so that it can be used to provide boundary conditions for possible high resolution modeling on smaller, nested domains. Although this data was saved for the previous WRAP 2002 Base Case, it was not saved for 2018 simulations.

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