FINAL REPORT

Using Global and Regional Models to Represent Background Ozone Entering Texas

AQRP Project 12-011

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CONTENTS

ACKNOWLEDGMENT ..................................................................................................................I

EXECUTIVE SUMMARY .......................................................................................................... 1

1.0 INTRODUCTION ............................................................................................................. 4
  1.1 Background ...................................................................................................................... 4
  1.2 Objectives ........................................................................................................................ 5
  1.3 Report Organization ........................................................................................................ 5

2.0 GLOBAL AND REGIONAL PHOTOCHEMICAL MODELING ........................................... 6
  2.1 Global Models .................................................................................................................. 6
    2.1.1 MOZART ................................................................................................................ 6
    2.1.2 GEOS-Chem ........................................................................................................... 6
    2.1.3 AM3 ....................................................................................................................... 7
  2.2 CAMx Regional Modeling .............................................................................................. 8

3.0 MODEL PERFORMANCE ASSESSMENT ..................................................................... 11
  3.1 Global Models ................................................................................................................ 11
  3.2 CAMx Regional Modeling .............................................................................................. 14

4.0 CONCLUSION AND RECOMMENDATION ................................................................ 27
  4.1 Summary ........................................................................................................................ 27
  4.2 Recommendation .......................................................................................................... 29

5.0 REFERENCES ................................................................................................................ 30

APPENDICES

Appendix A: April-October Monthly Mean Ozone Profile Comparisons; AM3, MOZART, GOES-Chem Global Models
Appendix B: April-October Monthly Mean Ozone Profile Comparisons CAMx with Boundary Conditions from Global Models
TABLES
Table 1: Species mapping between AM3 and CAMx for CB05 and CB6 chemistry mechanisms with PM. .................................................................9
Table 2. CAMx model configuration and sources of input data for the 2008 modeling dataset.................................................................10
Table 3. Species concentrations set for the simple constant boundary condition case. CB05 species not listed were set to lower bound values (typically on the order of 10^{-7} ppb) within CAMx..........................18

FIGURES
Figure 1. CAMx modeling grids: outer 36 km grid (full extent of map), 12 km nest (red), 4 km nest (green; not used). .........................................................10
Figure 2. CASTNET sites used to assess global and regional model performance for ozone. Sites are grouped into three regions according to color........12
Figure 3. Monthly fractional bias (left) and error (right) for 6-hourly ozone from three global models (colors) against CASTNET ozone data in the southwest (top), south-center (center), and southeast (bottom) US............13
Figure 4. Measured (black) and predicted (red) monthly mean ozone vertical profiles (MSL) at the Houston ozonesonde site for April through October 2008. Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the vertical grids for each model........15
Figure 5. Monthly fractional bias (left) and error (right) for 6-hourly ozone from three global models (solid lines) and three corresponding CAMx runs (dashed lines) against CASTNET ozone data in the southwest (top), south-center (center), and southeast (bottom) US.............................................17
Figure 6. Monthly fractional bias (left) and error (right) for hourly ozone from four CAMx runs against CASTNET ozone data in the southwest (top), south-center (center), and southeast (bottom) US.............................................19
Figure 7. Measured (black) and predicted (red) monthly mean ozone vertical profiles (MSL) at the Boulder, Colorado ozonesonde site for April and May 2008. Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the vertical grids for each model........20
Figure 8. Monthly fractional bias (left) and error (right) for MDA8 ozone from four CAMx runs against CASTNET ozone data in the southwest (top), south-center (center), and southeast (bottom) US.............................................21
Figure 9. AQS and CASTNET sites used to assess regional model performance for ozone along the Gulf of Mexico.................................22
Figure 10. Monthly fractional bias (left) and error (right) from four CAMx runs against hourly ozone data along the Gulf Coast at Galveston (top), Sabine Pass (top middle), Padre Island (bottom middle), and Sumatra (bottom).

Figure 11. Time series of hourly observed (black) and simulated (colors) ozone at the Padre Island AQS site during July 2008.

Figure 12. Measured (black) and CAMx-predicted (red) monthly mean ozone vertical profiles (MSL) at the Houston ozonesonde site for April through October 2008. Results are shown for cases with boundary conditions generated from MOZART (left), AM3 (middle), and GEOS-Chem (right). Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the CAMx vertical grid.
EXECUTIVE SUMMARY

The production, transport, and fate of tropospheric ozone are highly dynamic processes with contributions from a multitude of anthropogenic and natural sources spanning spatial scales from local to global. Regional models used for regulatory assessments now routinely address worldwide contributions by deriving chemical boundary conditions from global models. As global models continue to emerge and improve, their contributions to background ozone as represented in regional models need to be evaluated.

The Texas Commission on Environmental Quality (TCEQ) uses the Comprehensive Air quality Model with extensions (CAMx) for research and regulatory photochemical modeling. Two popular global models have been routinely coupled to CAMx to provide chemical boundary conditions for its continental-scale grid system: the Goddard Earth Observing System - Chemistry model (GEOS-Chem); and the Model for OZone and Related chemical Tracers (MOZART-4). A newer global model called AM3 has gained attention lately from recent applications to quantify Asian and stratospheric influences on springtime high surface ozone events in the western US.

We developed boundary condition inputs for CAMx utilizing output from three global models (GEOS-Chem, MOZART, and AM3) and analyzed the sensitivity of simulated ozone in and around Texas to the source of regional boundary conditions. The April-October 2008 CAMx database employed in this study was developed independently and was used in several concurrent AQRP modeling projects. We performed quantitative performance comparisons of the global and CAMx models against available rural ozone measurements throughout the southern US and assessed their ability to provide reasonable boundary conditions for regional downscaling, particularly with respect to state-wide regulatory ozone modeling in Texas.

The surface evaluation focused on the southwest, south-central, and southeast regions of the US surrounding Texas and the Gulf of Mexico. In general, the models’ performance tracked each other throughout the 2008 simulation, with very large over prediction biases in the warm seasons (May – October) and lower positive bias in the cool seasons (November - April). Poor global model performance during the summer in the south-central and southeast regions was likely the result of coarse resolution that increases ozone production efficiency. Other factors likely include uncertainties in biogenic emissions and the chemistry of isoprene nitrate, and may include transport of over predicted ozone from the Gulf and Atlantic to coastal states, and a misrepresentation of tropospheric convection that would impact boundary layer venting, photolysis rates, and estimates of nitrogen oxides (NOx) generated by lightning.

All three global models performed the best in the southwest region, where MOZART and AM3 performed particularly well year-round. GEOS-Chem exhibited significantly larger over prediction bias during the warm season, which has been attributed to over estimates of lightning NOx. AM3 performed the best in the spring, which has been attributed to its better representation of stratospheric intrusions.
CAMx fractional bias and error in the south-central and southeast regions tended to be better than all three global models by about 10-20\% during the summer months. The similarity in fractional bias and error trends in these two regions among the three CAMx runs indicated a fairly insensitive response to the choice of boundary conditions. Analyses with various statistical performance measures suggest that the rural diurnal ozone wave in these regions was not well simulated, which is more likely related to limitations in the regional model. The use of simple time/space-constant boundary conditions led to only minor differences in statistical performance in the south-central and southeast regions during most months. There was no clearly superior source of boundary conditions according to performance in the south-central and southeast regions.

Conversely, the three CAMx cases performed best year-round in the southwest region, paralleling the respective global model results. The southwest region is highly influenced by deep vertical transport of ozone from the upper troposphere and lower stratosphere to the higher terrain elevations of the inter-mountain west. MOZART, GEOS-Chem, and the associated CAMx runs tended to under estimate ozone in the spring months. AM3 and its associated CAMx run performed better than the other models in the spring, but CAMx bias patterns suggested deleterious effects from coarse vertical resolution toward the top of the modeling domain. The use of simple boundary conditions was clearly invalid for the southwest region, as the influence of higher ozone concentrations in the upper troposphere and lower stratosphere, as provided by the global models, plays a substantial role in the springtime regional surface ozone pattern in the western US. In this case, AM3 provided a superior source of boundary conditions for the southwest region.

A separate ozone performance analysis was conducted for a small set of coastal sites along the Gulf of Mexico that routinely measure very low ozone concentrations entering Texas during onshore flow conditions. These sites are often influenced by modeled boundary conditions as there are only minor source impacts between the boundaries and the Texas coastline. Over predictions peaked at nearly 100\% at two sites during mid-summer, with nearly identical bias among all CAMx and global model runs. There is growing evidence that current modeling systems (global and regional) are missing an important ozone destruction mechanism associated with oceanic halogen emissions, which is potentially far more effective at removing ozone over the Gulf than deposition processes alone.

We compared monthly-mean global and regional model predictions of vertical ozone profiles against ozonesonde measurements at four sites across the US. Simulated profiles over Houston from all models were generally very consistent with the measured profiles and with each other throughout the year, with less variability in the summer months. The largest variability exhibited by each model, and across all models, occurred during the non-summer months in the upper troposphere and stratosphere. All three global models tended to under predict mid-summer tropospheric ozone (particularly in the boundary layer) over Houston, most likely because of their inability to resolve the Houston ozone plume. CAMx tropospheric ozone profiles over Houston exhibited little sensitivity to choice of boundary conditions. CAMx
runs matched the ozonesonde data in the boundary layer much better in the mid-summer months than the global models. However, the stratospheric profiles (>12 km) were not well reproduced by CAMx, which were related to coarse layer resolution toward the top of the CAMx domain. Performance issues aloft would mostly impact lower tropospheric ozone over the western US, including west Texas.

In the conclusion section of this report, we suggest additional work to address model performance issues that will have direct relevance for future statewide regulatory ozone modeling in Texas.
1.0 INTRODUCTION

1.1 Background

The production, transport, and fate of tropospheric ozone are highly dynamic processes with contributions from a multitude of anthropogenic and natural sources spanning spatial scales from local to global. The US Environmental Protection Agency (EPA) requires the use of regional photochemical models to demonstrate that local emission control plans will achieve the federal standard for ground-level ozone (EPA, 2007). As the ozone standard is lowered, sources contributing to uncontrollable “background” ozone become more significant and must be more accurately accounted. In response, regulatory modeling applications have employed continuously larger domains to explicitly include sources over broader portions of the continent. Regional models now include worldwide contributions by deriving chemical boundary conditions from global models (e.g., Lin et al., 2010; Pfister et al., 2011; Emery et al., 2012). As global models continue to emerge and improve, their contributions to background ozone as represented in regional models need to be evaluated.

The Texas Commission on Environmental Quality (TCEQ) uses the Comprehensive Air quality Model with extensions (CAMx; ENVIRON, 2011; www.camx.com) for research and regulatory photochemical modeling. Two popular global models have been routinely coupled to CAMx to provide chemical boundary conditions for its continental-scale grid system:

- The Goddard Earth Observing System - Chemistry model (GEOS-Chem; Bey et al., 2001), developed and distributed by Harvard University (http://acmg.seas.harvard.edu/geos/index.html);
- The Model for OZone and Related chemical Tracers (MOZART-4; Emmons et al., 2010), developed by the National Center for Atmospheric Research (NCAR), the Max Planck Institute for Meteorology, and the National Oceanic and Atmospheric Administration’s Geophysical Fluid Dynamics Laboratory (GFDL), and distributed by NCAR (http://www.acd.ucar.edu/gctm).

A newer global model called AM3 (Donner et al., 2011) is the atmospheric chemical transport component of the CM3 coupled atmosphere-oceans-land-sea ice climate model developed by Princeton University and the GFDL (http://www.gfdl.noaa.gov/atmospheric-model). This particular model has gained attention lately from recent applications to quantify Asian and stratospheric influences on springtime high surface ozone events in the western US (Lin et al., 2012a,b). Unlike GEOS-Chem and MOZART, which employ parameterizations to treat stratospheric ozone, the AM3 model includes fully coupled stratospheric-tropospheric chemistry and dynamics, described more fully by Lin et al. (2012a) and Naik et al. (2013). Analyses of daily ozonesonde and surface measurements during the CalNex field campaign in May-June 2010 indicate that AM3 captures key features of inter-daily ozone variability in the free troposphere and at surface sites over the western US, and thus is a suitable tool for quantifying “episodic background”.
Summaries of each model are provided at their respective web pages, while a multitude of model descriptions and application results are published in the articles cited throughout this report.

1.2 Objectives

The objective of this project was to develop boundary condition inputs for CAMx utilizing output from all three global models (GEOS-Chem, MOZART, and AM3) and to analyze the sensitivity of simulated ozone in and around Texas to the source of regional boundary conditions. We developed quantitative performance comparisons of these global models against available rural ozone measurements throughout the southern US and assessed their ability to provide reasonable boundary conditions for regional downscaling, particularly with respect to state-wide regulatory ozone modeling in Texas.

The CAMx regional modeling database for this work was developed independently and was used for several concurrent AQRP modeling projects. The modeling spans the period of April-October 2008 with a continental US (CONUS) grid at 36 km resolution and a large nested grid over the central US at 12 km resolution. The database supports simulation for both ozone and particulate matter (PM).

1.3 Report Organization

Section 2 describes the global and regional photochemical modeling conducted in this study. Section 3 present analyses and results of the model inter-comparisons. Section 4 summarizes results from this study and presents our recommendations.
2.0 GLOBAL AND REGIONAL PHOTOCHEMICAL MODELING

2.1 Global Models

Pre-existing MOZART global data for 2008 were downloaded from NCAR. ENVIRON ran GEOS-Chem for the entire year of 2008. MOZART and GOES-Chem data were processed to CAMx boundary condition input formats using the pre-existing interface programs. Princeton ran AM3 for the entire year of 2008 and post-processed raw output fields into formats needed for a new CAMx boundary condition interface program. To maximize consistency among the data products from all three global models, 6-hourly concentration fields were output from GEOS-Chem and AM3 to match the frequency of pre-existing MOZART data from NCAR. Concentration fields of ozone generated by GEOS-Chem, MOZART, and AM3 were inter-compared for the period spanning April-October 2008, which is the period covered by the CAMx modeling database employed in this study.

2.1.1 MOZART

MOZART 6-hourly model output fields for the entire globe are available from NCAR spanning 2003 through early 2013. The spatial resolution is 2.8 degrees with 28 vertical levels resolving the troposphere and the lower stratosphere up to an altitude of about 40 km. This source of MOZART data has been routinely accessed to generate CAMx boundary conditions for several projects in Texas. ENVIRON downloaded 6-hourly global MOZART data for 2008 from http://www.acd.ucar.edu/wrf-chem/mozart.shtml. The particular MOZART database that we obtained was generated using GEOS-5 global meteorological analyses similar to GEOS-Chem. The raw data were mapped to species comprising the Carbon Bond 2005 (CB05; Yarwood et al., 2005) gas-phase chemistry mechanism and processed to CAMx boundary condition file formats using the pre-existing MOZART2CAMx interface program.

2.1.2 GEOS-Chem

GEOS-Chem version 9-01-02 (released Nov 28, 2011) was run by ENVIRON for the entirety of 2008 to derive ozone estimates over the US and to provide boundary condition inputs for CAMx. This version of GEOS-CHEM includes several important updates, including aerosol dry deposition over ice and snow, and new treatments or datasets for global ammonia, volatile organic compounds (VOC) and biomass burning emissions. GEOS-Chem was run on its standard 2x2.5° latitude/longitude grid with 47 vertical levels from the surface to 80 km, using 3-hourly surface and 6-hourly aloft GEOS-5 global meteorological analyses produced and distributed by the National Aeronautics and Space Administration (NASA) Global Modeling and Assimilation Office (GMAO, 2011). Standard and default settings, solvers, algorithms, and datasets were used to treat emissions, chemistry, transport, and removal. Gases and aerosols were resolved with 59 chemical species, and the LINOZ stratospheric ozone parameterization was invoked. Additional information on GEOS-Chem structure, inputs and algorithms is available at http://acmg.seas.harvard.edu/geos/doc/archive/man.v9-01-02/index.html.

The following anthropogenic emission inventories were employed and internally adjusted to the 2008 simulation year:
The 2006 Streets inventory for Asia reflects a doubling of anthropogenic NOx emissions in China relative to the previous 2001 Streets inventory, based on comparisons of earlier GEOS-Chem results against satellite measurements (Zhang et al., 2009; Zhang et al., 2011; Emery et al., 2012). Natural sources include biogenic emissions derived from the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2006), monthly fire emissions from the Global Fire Emissions Database, version 3 (GFED3; http://www.globalfiredata.org/References/index.html; Giglio et al., 2010), internally calculated lightning NOx according to GEOS-5 meteorology, and soil NOx from both natural bacterial activity and agricultural fertilizer application.

GEOS-Chem v9-01-02 is distributed with a default restart file valid on January 1, 2004. It is recommended that this file is used if the LINOZ option is invoked. Therefore, GEOS-Chem was configured as outlined above, and first run for one year spin-up period from January 1 to December 31, 2007 using the January 1, 2004 restart file for 2007. Subsequently the model was run for the entire year of 2008 and output three-dimensional concentration fields at 6-hourly intervals. The raw data were mapped to CB05 species and processed to CAMx boundary condition file formats using the GEOS2CAMx interface program.

2.1.3 AM3
Princeton/GFDL has run AM3 for the years 1980-2012 with ~200 km resolution, however only daily-averaged fields of a few key long-lived species (e.g., ozone, peroxyacetyl nitrate, carbon monoxide, particulate matter, etc.) have been archived at GFDL. Therefore, AM3 was run by Princeton specifically for this project over the entire year of 2008 at ~200x200 km² horizontal resolution and with 48 vertical levels from the surface to 86 km. The AM3 simulation was nudged to reanalysis winds from the National Center for Atmospheric Research (NCAR) and the National Centers for Environmental Prediction (NCEP), as described by (Lin et al., 2013). The simulation used anthropogenic emissions from the Representative Concentration Pathways 8.5 (RCP8.5), one of the high emission scenarios used in the Fifth Intergovernmental Panel on Climate Change (IPCC) Assessment Report (Moss et al., 2010; Riahi et al., 2011). RCP8.5 emissions from the period 2005-2010 were interpolated to 2008, and monthly mean biomass burning emissions for 2008 were estimated from GFED3 (van der Werf et al., 2010). The model applies climatological soil NOx emissions. Biogenic isoprene emissions are tied to the model
meteorology based on MEGAN2.1 (Guenther et al., 2006; Rasmussen et al., 2012). Lightning NOx is calculated from a mean 1981-2000 global production rate of 4.5 ± 0.2 Tg N (as NO) per year with diurnal, seasonal, and inter-annual variability based on sub-grid convection parameterized in AM3 (Donner et al., 2011; Naik et al., 2013). Methane (CH4) concentrations for chemistry are nudged to observed global annual mean values below 800 hPa as a lower boundary condition.

AM3 generated 6-hourly three-dimensional output fields containing speciated nitrogen oxides (both NOx and NOy), volatile organic compounds (VOC), carbon monoxide (CO), and ozone concentrations. The raw output fields were translated from the native AM3 grid system to a standard latitude/longitude grid similar to that of GEOS-Chem and MOZART. With assistance from Princeton University, ENVIRON developed a new interface tool to translate AM3 output to the boundary condition inputs required by CAMx. Special considerations were given to the chemical mapping of AM3 NOx, NOy, and VOC species to CB05 and Carbon Bond version 6 (CB6; Yarwood et al., 2010) photochemical mechanisms employed in CAMx. Although this project did not address particulate matter, the AM3-CAMx interface was developed to include PM as well. Table 1 presents the species mapping between AM3 and CAMx.

2.2 CAMx Regional Modeling

CAMx v5.41 (ENVIRON, 2011) was run using an April-October 2008 CAMx dataset developed by Alpine Geophysics for the Eight Hour Coalition (a cooperative of Houston petrochemical and refining companies). This dataset is configured with a continental US (CONUS) 36 km grid and a large 12 km nested grid over the central US (Figure 1), includes both ozone and PM precursor emissions chemically speciated for the CB05 chemical mechanism, and uses emissions data from both the TCEQ and EPA (Table 2). Biogenic emissions were available from both MEGAN and GloBEIS, but only GloBEIS emissions were used in this project. The 36 and 12 km grids were run in 2-way interactive nested mode; the 4-km grid shown in Figure 1 was not used. Boundary conditions were developed for the 36 km CONUS grid shown in Figure 1 using the 6-hourly output from GEOS-Chem, MOZART, and AM3.
Table 1: Species mapping between AM3 and CAMx for CB05 and CB6 chemistry mechanisms with PM.

<table>
<thead>
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<th>CAMx CB05</th>
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<th>CAMx CB6</th>
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</tr>
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<tbody>
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<td>CO</td>
<td>CO</td>
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<td>PAR</td>
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<td>ISOPOOH</td>
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<td>ONIT + ONITR + ISOPNO3</td>
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<td>ONIT</td>
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<td>lg_dust</td>
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Table 2. CAMx model configuration and sources of input data for the 2008 modeling dataset.

<table>
<thead>
<tr>
<th>Model Component</th>
<th>Description</th>
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<tr>
<td>Modeling Period</td>
<td>April 1 - October 18, 2008</td>
</tr>
<tr>
<td>Modeling Domain</td>
<td>36/12 km resolution (4 km not used)</td>
</tr>
<tr>
<td>Vertical Structure</td>
<td>30 Vertical Layers</td>
</tr>
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<td>Meteorological Model</td>
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<td>CB05</td>
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<td>Zhang</td>
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<td>GloBEIS</td>
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<tr>
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<td>MOVES</td>
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<td>Off Road Mobile</td>
<td>EPA NEI</td>
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<tr>
<td>Shipping</td>
<td>EPA NEI</td>
</tr>
<tr>
<td>Area Source</td>
<td>EPA NEI</td>
</tr>
<tr>
<td>Point Source</td>
<td>TCEQ</td>
</tr>
<tr>
<td>Wildfire</td>
<td>BlueSky/EPA SMARTFIRE 2</td>
</tr>
</tbody>
</table>

Figure 1. CAMx modeling grids: outer 36 km grid (full extent of map), 12 km nest (red), 4 km nest (green; not used).
3.0 MODEL PERFORMANCE ASSESSMENT

3.1 Global Models

Surface ozone predictions from all three global models were analyzed against available rural surface measurements from the EPA Clean Air Status and Trends Network (CASTNET; http://epa.gov/castnet/javaweb/index.html). Evaluation against urban-oriented Air Quality System (AQS) sites was not performed because: (1) our analysis focused on regional background ozone levels, and (2) grid resolution employed in the global and regional models was too coarse to adequately simulate urban photochemistry. Furthermore, ozone at urban monitors is dominated by influences from local emissions, which interact with background ozone and thus obscure differences among the three global models and the respective CAMx simulations.

The surface evaluation focused on the southwest, south-central, and southeast regions of the US surrounding Texas and the Gulf of Mexico (Figure 2). Statistics included fractional bias (FB) and error (FE) as described in EPA modeling guidance (EPA, 2007):

\[
FB = \frac{2}{N} \sum_{i=1}^{N} \frac{P_i - O_i}{P_i + O_i}
\]

\[
FE = \frac{2}{N} \sum_{i=1}^{N} \frac{|P_i - O_i|}{P_i + O_i}
\]

where \(P_i\) and \(O_i\) are model predictions and observations, respectively, for each prediction-observation pairing \(i\), and \(N\) is the total number of pairings. Fractional metrics were selected over traditional metrics like normalized bias and error because they are less skewed by over predictions of very low observed concentrations. For the global model assessment, 6-hourly global model output was paired with hourly ozone measurements every 6-hours to match the global model output frequency. Global model performance statistics for fractional bias and error were tabulated on a monthly basis.

Figure 3 shows fractional bias and error for 6-hourly ozone by month for each of the three global model runs and for each of the three regions noted in Figure 2. In general, the models’ performance tracked each other over the year, with very large over prediction biases in the warm seasons (May – October) and lower positive bias in the cool seasons (November - April). MOZART exhibited larger over prediction tendencies in the south-center and southeast regions all year long, while GEOS-Chem was especially biased high during the autumn in the south-central region. Note that the regions with the largest over predictions have high biogenic emissions. Emery et al. (2012) have attributed such pervasive global model over predictions in the eastern US to coarse resolution employed in these models (~2 degree latitude/longitude), which instantly mixes anthropogenic NOx with biogenic VOC and leads to over estimates of ozone production efficiency. Other likely reasons include uncertainties in biogenic emissions of
Figure 2. CASTNET sites used to assess global and regional model performance for ozone. Sites are grouped into three regions according to color.

isoprene and the chemistry of isoprene nitrate (Horowitz et al., 2007). AM3 uses observationally constrained 8% yield for isoprene nitrate with 40% NOx recycling, while GEOS-Chem uses 18% yield with no NOx recycling (i.e., a permanent sink for NOx). The global models also tend to over predict ozone over the Gulf of Mexico and eastern Atlantic (Yarwood et al., 2012), and as we describe in more detail below, this has direct impacts on model performance in coastal states. Other global model researchers in the past have suggested the cause is possibly related to misrepresentation of tropospheric convection (Fiore et al., 2003), which affects boundary layer venting, photolysis rates, and estimates of lightning NOx (Zhang et al., 2011).

All three global models performed the best in the southwest region, where MOZART and AM3 performed particularly well year-round, but GEOS-Chem exhibited significantly larger over prediction bias during the warm season. Zhang et al. (2013) have attributed GEOS-Chem summertime ozone biases in the inter-mountain western US to over estimates of lightning NOx in convection associated with Mexican monsoonal flow. Note that MOZART and GEOS-Chem
Figure 3. Monthly fractional bias (left) and error (right) for 6-hourly ozone from three global models (colors) against CASTNET ozone data in the southwest (top), south-center (center), and southeast (bottom) US.
tended to under predict ozone in the southwest during the spring, while AM3 exhibited a negligible degree of positive bias. Emery et al. (2012) noted that GEOS-Chem tends to under predict western springtime contributions from the upper troposphere and stratosphere during periods of deep vertical transport, such as typically associated with tropopause folding events triggered by the dynamics of deep and vigorous low pressure systems. Lin et al. (2012a,b) show that AM3 performs better in replicating such events because it contains better representations of stratospheric intrusions. Their episodic analyses demonstrated very good replication of springtime ozone patterns throughout the west, and these same factors are likely reflected in the good AM3 performance exhibited in the results shown in Figure 3.

We graphically compared global model predictions of vertical ozone profiles against ozonesonde measurement data. Routine ozonesonde measurements are available about every 6th day at several sites across the US, including Trinidad Head, California; Boulder, Colorado; and Huntsville, Alabama (ftp://ftp.cmdl.noaa.gov/ozwv/ozone/). Additionally, there were approximately 45 ozonesonde launches from Houston during 2008 as part of the Tropospheric Ozone Pollution Project (TOPP; http://physics.valpo.edu/ozone/ houstondata_2008_2011.htm #2008). Individual observed ozone profiles were first translated to the model vertical grid and paired with simulated profiles at the times closest to the launch. Then monthly-mean observed and simulated ozone profiles were plotted for each ozonesonde site, along with the monthly minimum-to-maximum range among the individual profiles at each vertical grid level.

Such comparisons are shown in Figure 4 for the Houston launches. Monthly profile comparisons at the other ozonesonde sites are provided in Appendix A. Houston profiles of the monthly means and their ranges from all three models were generally very consistent with the measured profiles and with each other throughout the year, with less variability in the summer than in the non-summer months. The largest variability exhibited by each model, and across all three models, occurred during the non-summer months in the upper troposphere and stratosphere. GEOS-Chem tended to over predict stratospheric ozone above Houston in most months whereas AM3 tended to slightly under predict. All models tended to under predict mid-summer tropospheric ozone (particularly in the boundary layer) over Houston with little variability. One potential reason for this may be the inability of these coarse grid models to adequately resolve the Houston ozone plume. Other reasons may include influences from simulated convective activity that ventilates the boundary layer and removes pollutants via wet scavenging.

3.2 CAMx Regional Modeling

We calculated CAMx regional model performance statistics against rural surface ozone measurements from the collection of CASTNET sites shown in Figure 2. Fractional bias and error statistics for ozone are summarized below. To facilitate the comparison between global and CAMx model performance, hourly CAMx ozone predictions and measurements were first paired every 6-hours to generate a consistent set of statistical calculations.
Figure 4. Measured (black) and predicted (red) monthly mean ozone vertical profiles (MSL) at the Houston ozonesonde site for April through October 2008. Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the vertical grids for each model.
Figure 5 shows fractional bias and error by month for each of the three global/regional model combinations and for each of the three regions noted in Figure 2. In general, the models’ performance tracked each other over the year, with very large over prediction biases in the warm seasons (May – October) and lower positive bias in the cool seasons (November - April).

CAMx performance tended to be better than all three global models by about 10-20% in the worst performing months except in the southwest. Note that the CAMx database did not include lightning NOx emissions, which may explain the large reduction of summertime positive bias in the southwest relative to GEOS-Chem alone. All models performed the best year-round in the southwest region, with CAMx paralleling the respective global model results especially during the springtime. Whereas MOZART, GEOS-Chem, and the associated CAMx runs tended
Figure 5. Monthly fractional bias (left) and error (right) for 6-hourly ozone from three global models (solid lines) and three corresponding CAMx runs (dashed lines) against CASTNET ozone data in the southwest (top), south-center (center), and southeast (bottom) US.

The similarity in the fractional bias and error trends among the three CAMx runs for most months and regions are striking, and indicate a fairly insensitive response to the choice of boundary conditions. An additional CAMx simulation was run with simple boundary conditions that specified constant (time and space) concentrations around the entire 36 km grid boundary. The point of this exercise was to establish the extent to which boundary conditions have any impact on model performance at the mid-continental CASTNET sites for this particular modeling
dataset. These simple boundary conditions were based on “typical” tropospheric continental concentrations for NOx, VOC, and ozone that were established by the EPA in the 1990’s (Table 3). These concentrations were set for the entire horizontal and vertical extent of the modeling domain, which further helped us to assess the influence of upper tropospheric and stratospheric ozone on surface concentrations across the southern tier of the US.

**Table 3. Species concentrations set for the simple constant boundary condition case. CB05 species not listed were set to lower bound values (typically on the order of 10^{-7} ppb) within CAMx.**

<table>
<thead>
<tr>
<th>CB05 Species</th>
<th>Concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>0.010</td>
</tr>
<tr>
<td>NO2</td>
<td>0.100</td>
</tr>
<tr>
<td>O3</td>
<td>30.0</td>
</tr>
<tr>
<td>OLE</td>
<td>0.050</td>
</tr>
<tr>
<td>PAR</td>
<td>5.000</td>
</tr>
<tr>
<td>ETH</td>
<td>0.100</td>
</tr>
<tr>
<td>TOL</td>
<td>0.050</td>
</tr>
<tr>
<td>XYL</td>
<td>0.050</td>
</tr>
<tr>
<td>ISOP</td>
<td>0.001</td>
</tr>
<tr>
<td>FORM</td>
<td>0.050</td>
</tr>
<tr>
<td>ALD2</td>
<td>0.050</td>
</tr>
<tr>
<td>ETOH</td>
<td>0.001</td>
</tr>
<tr>
<td>MEOH</td>
<td>0.001</td>
</tr>
<tr>
<td>CO</td>
<td>100.0</td>
</tr>
<tr>
<td>HONO</td>
<td>0.001</td>
</tr>
<tr>
<td>H2O2</td>
<td>1.000</td>
</tr>
<tr>
<td>HNO3</td>
<td>1.000</td>
</tr>
<tr>
<td>PAN</td>
<td>0.100</td>
</tr>
<tr>
<td>N2O5</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Figure 6 shows fractional bias and error by month for each of the three regional model simulations and for the simple boundary condition run, for each of the three regions noted in Figure 2. In this case, statistics were calculated by pairing all hourly CAMx predictions and measurements. We note that CAMx monthly statistics based on all hourly data in Figure 6 are practically identical (within 1-2%) to the 6-hourly CAMx statistics in Figure 5, indicating that the global-CAMx inter-comparisons using 6-hourly data are robust and are not subject to data aliasing.

In the south-central and southeast regions, CAMx performance was similar among all four runs throughout the year, with very large over prediction biases in the warm seasons (May – October) and lower positive bias in the cool seasons (November - April) when performance metrics tended to diverge. The use of simple boundary conditions led to minor improvements
in statistical performance in these regions during most months, likely because model-based boundary conditions were higher than the 30 ppb specified in the simple case. This suggests that performance issues in the south-central and southeast regions were not primarily dictated by the choice of boundary conditions even though the global models exhibited performance patterns that were very similar to CAMx. Various local factors were driving the CAMx over prediction tendencies in these regions.

The three cases with model-based boundary conditions performed the best year-round in the southwest region, but the simple boundary condition case tended to under predict especially
during the spring. The southwest region is highly influenced by deep vertical transport of ozone from the upper troposphere to the higher terrain elevations of the inter-mountain west. This is clearly evident in the springtime simulated and observed ozone profiles at the Boulder, Colorado ozonesonde site (Figure 7 and Appendix A), where the assumption of 30 ppb background ozone in the upper troposphere is clearly invalid. Therefore, the influence of higher mid- to upper-tropospheric ozone provided by the global models does play a substantial role in the springtime regional surface ozone pattern in the western US, as previously demonstrated by Emery et al. (2011; 2012) using CAMx, by Zhang et al. (2011) using GEOS-Chem, and by Lin et al. (2012a,b) using AM3.

Figure 7. Measured (black) and predicted (red) monthly mean ozone vertical profiles (MSL) at the Boulder, Colorado ozonesonde site for April and May 2008. Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the vertical grids for each model.

CAMx performance statistics were recalculated in each of the three sub-regions for maximum daily 8-hour (MDA8) ozone. The purpose of these additional statistics was to determine if model performance for daytime maximum ozone was any better than the 1-hour statistics that may have been weighted by large over predictions of lower ozone at night (i.e., inability of the model to replicate minima in the diurnal ozone wave). Results are shown in Figure 8 for all four CAMx runs and all three sub-regions.
In the southwest, MDA8 performance was nearly identical to the 1-hour statistics, indicating that both peak ozone and the diurnal wave were generally well replicated. In the south-center and southeast regions, bias and error metrics for MDA8 were improved by typically 20% over the 1-hour statistics during the warm season, but the statistical results among the three model runs remained very similar. These results suggest that the rural diurnal ozone wave in these regions was not well simulated in any case, and this contributed substantially toward the high 1-hour bias. Whereas over predictions of rural MDA8 could be associated with boundary conditions, the lack of diurnal amplitude more likely suggest causes related to limitations in the regional model rather than the source of boundary conditions.

Figure 8. Monthly fractional bias (left) and error (right) for MDA8 ozone from four CAMx runs against CASTNET ozone data in the southwest (top), south-center (center), and southeast (bottom) US.
A separate ozone performance analysis was conducted for a small set of coastal sites along the Gulf of Mexico that routinely measure clean ambient concentrations entering Texas during on-shore flow conditions (Figure 9). These sites are often influenced by modeled boundary conditions as there are only minor source impacts between the boundaries and the Texas coastline. Figure 10 shows monthly fractional bias and error at each of the four sites for all CAMx simulations. Over predictions reached up to 100% at two sites during the peak of summer, yet were much lower in cooler seasons. Ozone performance was consistent among the four CAMx runs with different boundary conditions and practically identical to all three global model runs (not shown). This indicates that all sources of boundary conditions led to similar ozone inflow across the Gulf and into the coastal states, and that probably any cross-coastal ozone recirculation patterns were consistent among all models.

Figure 9. AQS and CASTNET sites used to assess regional model performance for ozone along the Gulf of Mexico.

Time series of observed and simulated 1-hour ozone at the Padre Island site are shown in Figure 11 for the period of July when measurements were available. This site was chosen specifically because of its particularly high error, its relatively remote location and minimal influence from large local urban sources. Time series at the others sites were generally similar (not shown). The over prediction problem at this site is clear: all simulated values varied around 30 ppb for most of the month, while measurements ranged 5-10 ppb for an extended portion of the month. Evidence of an ozone plume impact was simulated on July 19 and a suggestion of that plume occurred in the measurement data one day later.

There is growing evidence that current modeling systems (global and regional) are missing an important ozone destruction mechanism associated with oceanic halogen emissions (Yarwood et al., 2012; Carpenter et al., 2013), which is potentially far more effective at removing ozone
Figure 10. Monthly fractional bias (left) and error (right) from four CAMx runs against hourly ozone data along the Gulf Coast at Galveston (top), Sabine Pass (top middle), Padre Island (bottom middle), and Sumatra (bottom).
Figure 11. Time series of hourly observed (black) and simulated (colors) ozone at the Padre Island AQS site during July 2008.

over the Gulf than deposition processes alone. Therefore, it would be premature to point to global models as the single source of coastal ozone over predictions.

Finally, CAMx results were compared to available Houston ozonesonde data throughout 2008 to evaluate ozone differences above the Houston urban boundary layer arising from the use of the three sets of boundary conditions. Monthly plots of CAMx predicted ozone profiles over Houston are shown in Figure 12; monthly profile comparisons for the other ozonesonde sites are provided in Appendix B.

CAMx tropospheric ozone profiles over Houston exhibited little sensitivity to choice of global model. Generally, the monthly-mean boundary layer and tropospheric profiles were reproduced well. Exceptions include an under prediction tendency in July and August in the mid to upper troposphere (likely a direct linkage to similar under predictions in all three global models), and larger boundary layer variability in August and September than measured. CAMx boundary layer profiles matched the ozonesonde data much better in the mid-summer months than the global models, demonstrating a better ability to resolve and replicate the local Houston ozone plume. However, the stratospheric profiles (>12 km) were not well reproduced by CAMx, showing over predictions just above the tropopause but large under predictions farther aloft. These results are related to coarse layer resolution typically assigned toward the top of the CAMx domain and the model’s simplistic top boundary condition treatment that assumes that concentrations above the model top are identical to the topmost layer concentrations. Both of these issues have been shown by Emery et al. (2011) to contribute toward diffusive spread of the stratospheric ozone gradient.
Figure 12. Measured (black) and CAMx-predicted (red) monthly mean ozone vertical profiles (MSL) at the Houston ozonesonde site for April through October 2008. Results are shown for cases with boundary conditions generated from MOZART (left), AM3 (middle), and GEOS-Chem (right). Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the CAMx vertical grid.
Figure 12 (concluded).
4.0 CONCLUSION AND RECOMMENDATION

4.1 Summary

We developed boundary condition inputs for CAMx utilizing output from three global models (GEOS-Chem, MOZART, and AM3) and analyzed the sensitivity of simulated ozone in and around Texas to the source of regional boundary conditions. MOZART and GEOS-Chem have been used extensively as a source of CAMx boundary conditions in a multitude of Texas modeling projects over the past several years; here we extended this capability to the AM3 global model. The April-October 2008 CAMx database employed in this study was developed independently and was used in several concurrent AQRP modeling projects. We performed quantitative performance comparisons of the global and CAMx models against available rural ozone measurements throughout the southern US and assessed their ability to provide reasonable boundary conditions for regional downscaling, particularly with respect to state-wide regulatory ozone modeling in Texas.

The surface evaluation focused on the southwest, south-central, and southeast regions of the US surrounding Texas and the Gulf of Mexico. In general, the models’ performance tracked each other throughout the 2008 simulation, with very large over prediction biases in the warm seasons (May – October) and lower positive bias in the cool seasons (November - April). Poor global model performance during the summer in the south-central and southeast regions was most likely the result of coarse resolution that increases ozone production efficiency. Other factors likely include uncertainties in biogenic emissions and the chemistry of isoprene nitrate, and may include transport of over predicted ozone from the Gulf and Atlantic to coastal states, and a misrepresentation of tropospheric convection that would impact boundary layer venting, photolysis rates, and lightning NOx estimates.

All three global models performed the best in the southwest region, where MOZART and AM3 performed particularly well year-round. GEOS-Chem exhibited significantly larger over prediction bias during the warm season, which has been attributed to over estimates of lightning NOx. AM3 performed the best in the spring, which has been attributed to its better representation of stratospheric intrusions.

CAMx fractional bias and error in the south-central and southeast regions tended to be better than all three global models by about 10-20% during the summer months. The similarity in fractional bias and error trends in these two regions among the three CAMx runs indicated a fairly insensitive response to the choice of boundary conditions. Warm-season bias and error metrics were further reduced in these regions by an additional 20% when CAMx performance statistics were calculated for MDA8 ozone rather than hourly ozone, but the statistical results among the three model runs remained very similar. These results suggest that the rural diurnal ozone wave in these regions was not well simulated, where nighttime ozone over predictions contributed substantially toward the large 1-hour bias. Whereas over predictions of rural MDA8 could be associated with boundary conditions, the lack of diurnal amplitude more likely suggest causes related to limitations in the regional model.
An additional CAMx simulation was run with simple time- and space-constant boundary conditions (30 ppb ozone) to establish the extent to which boundary conditions have any impact on CAMx model performance. These simple boundary conditions led to only minor improvements in statistical performance in the south-central and southeast regions during most months. Poor CAMx performance in these regions was not primarily dictated by the choice of boundary conditions even though the global models exhibited performance patterns that were very similar to CAMx. Various local factors were driving the CAMx over prediction tendencies in these regions. There was no clearly superior source of boundary conditions according to performance in the south-central and southeast regions.

Conversely, the three CAMx cases performed best year-round in the southwest region, paralleling the respective global model results. The southwest region is highly influenced by deep vertical transport of ozone from the upper troposphere and lower stratosphere to the higher terrain elevations of the inter-mountain west. MOZART, GEOS-Chem, and the associated CAMx runs tended to under estimate ozone in the spring months. AM3 and its associated CAMx run performed better than the other models in the spring, but larger CAMx positive bias relative to AM3 was likely due to coarse vertical resolution around the tropopause that led to excessive vertical diffusion of ozone toward the surface. MDA8 performance was nearly identical to the 1-hour statistics in all cases, indicating that both peak ozone and the shallower diurnal wave in the west were generally well replicated.

The simple boundary condition case led to under predictions of ozone in the southwest, especially during the spring. The assumption of 30 ppb background ozone in the upper troposphere was clearly invalid for this area. Therefore, the influence of higher ozone concentrations in the upper troposphere and lower stratosphere, as provided by the global models, does play a substantial role in the springtime regional surface ozone pattern in the western US. In this case, AM3 provided a superior source of boundary conditions for the southwest region.

A separate ozone performance analysis was conducted for a small set of coastal sites along the Gulf of Mexico that routinely measure very low ozone concentrations entering Texas during onshore flow conditions. These sites are often influenced by modeled boundary conditions as there are only minor source impacts between the boundaries and the Texas coastline. Over predictions peaked at nearly 100% at two sites during mid-summer. For example, measurements at Padre Island ranged from 5-10 ppb for extended periods of July while all simulated values varied around 30 ppb. Ozone performance was consistent among all CAMx runs with different boundary conditions and practically identical to all three global model runs. This indicates that all sources of boundary conditions led to similar transport and recirculation patterns in the Gulf area. There is growing evidence that current modeling systems (global and regional) are missing an important ozone destruction mechanism associated with oceanic halogen emissions, which is potentially far more effective at removing ozone over the Gulf than deposition processes alone. Therefore, it would be premature to point to global models as the single source of coastal ozone over predictions.
We compared monthly-mean global and regional model predictions of vertical ozone profiles against ozonesonde measurements at four sites across the US. Simulated profiles over Houston from all models were generally very consistent with the measured profiles and with each other throughout the year, with less variability in the summer months. The largest variability exhibited by each model, and across all models, occurred during the non-summer months in the upper troposphere and stratosphere. All three global models tended to under predict mid-summer tropospheric ozone (particularly in the boundary layer) over Houston, most likely because of their inability to resolve the Houston ozone plume. CAMx tropospheric ozone profiles over Houston exhibited little sensitivity to choice of boundary conditions. CAMx runs tended to under predict mid- to upper-tropospheric ozone profiles in July and August, but matched the ozonesonde data in the boundary layer much better in the mid-summer months than the global models. However, the stratospheric profiles (>12 km) were not well reproduced by CAMx, which were related to coarse layer resolution toward the top of the CAMx domain. Performance issues aloft would mostly impact lower tropospheric ozone over the western US, including west Texas.

4.2 Recommendation

Based on the project results summarized above, we suggest additional work to address model performance issues that will have direct relevance for future statewide regulatory ozone modeling in Texas:

- Review literature on natural halogen emissions from ocean surfaces and their impact on ozone lifetime in marine environments – develop and rigorously test new CAMx model formulations to treat this potentially important removal pathway;
- Implement improved top boundary conditions in CAMx, extending current global model interface programs to provide time/space variable concentration inputs above the model top, and test their impacts with improved vertical resolution above ~10 km.
5.0 REFERENCES


APPENDIX A

April-October Monthly Mean Ozone Profile Comparisons
AM3, MOZART, GOES-Chem Global Models

Huntsville, AL
Boulder, CO
Trinidad Head, CA
Figure A-1. Measured (black) and predicted (red) monthly mean ozone vertical profiles (MSL) at the Huntsville ozonesonde site for April through October 2008. Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the vertical grids for each model.
Figure A-1 (concluded).
Figure A-2. Measured (black) and predicted (red) monthly mean ozone vertical profiles (MSL) at the Boulder ozonesonde site for April through October 2008. Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the vertical grids for each model.
Figure A-2 (concluded).
Figure A-3. Measured (black) and predicted (red) monthly mean ozone vertical profiles (MSL) at the Trinidad Head ozonesonde site for April through October 2008. Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the vertical grids for each model.
Figure A-3 (concluded).
APPENDIX B

April-October Monthly Mean Ozone Profile Comparisons
CAMx with Boundary Conditions from Global Models

Huntsville, AL
Boulder, CO
Trinidad Head, CA
Figure B-1. Measured (black) and CAMx-predicted (red) monthly mean ozone vertical profiles (MSL) at the Huntsville ozonesonde site for April through October 2008. Results are shown for cases with boundary conditions generated from MOZART (left), AM3 (middle), and GEOS-Chem (right). Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the CAMx vertical grid.
Figure B-1 (concluded).
Figure B-2. Measured (black) and CAMx-predicted (red) monthly mean ozone vertical profiles (MSL) at the Boulder ozonesonde site for April through October 2008. Results are shown for cases with boundary conditions generated from MOZART (left), AM3 (middle), and GEOS-Chem (right). Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the CAMx vertical grid.
Figure B-2 (concluded).
Figure B-3. Measured (black) and CAMx-predicted (red) monthly mean ozone vertical profiles (MSL) at the Trinidad Head ozonesonde site for April through October 2008. Results are shown for cases with boundary conditions generated from MOZART (left), AM3 (middle), and GEOS-Chem (right). Minimum to maximum range are shown for measurements (grey shading) and predictions (red whiskers). Measured data were interpolated to the CAMx vertical grid.
Figure B-3 (concluded).