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Regional and global modeling estimates of policy relevant background ozone over the United States

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ABSTRACT

Policy Relevant Background (PRB) ozone, as defined by the US Environmental Protection Agency (EPA), refers to ozone concentrations that would occur in the absence of all North American anthropogenic emissions. PRB enters into the calculation of health risk benefits, and as the US ozone standard approaches background levels, PRB is increasingly important in determining the feasibility and cost of compliance. As PRB is a hypothetical construct, modeling is a necessary tool. Since 2006 EPA has relied on global modeling to establish PRB for their regulatory analyses. Recent assessments with higher resolution global models exhibit improved agreement with remote observations and modest upward shifts in PRB estimates. This paper shifts the paradigm to a regional model (CAMx) run at 12 km resolution, for which North American boundary conditions were provided by a low-resolution version of the GEOS-Chem global model. We conducted a comprehensive model inter-comparison, from which we elucidate differences in predictive performance against ozone observations and differences in temporal and spatial background variability over the US. In general, CAMx performed better in replicating observations at remote monitoring sites, and performance remained better at higher concentrations. While spring and summer mean PRB predicted by GEOS-Chem ranged 20–45 ppb, CAMx predicted PRB ranged 25–50 ppb and reached well over 60 ppb in the west due to event-oriented phenomena such as stratospheric intrusion and wildfires. CAMx showed a higher correlation between modeled PRB and total observed ozone, which is significant for health risk assessments. A case study during April 2006 suggests that stratospheric exchange of ozone is underestimated in both models on an event basis. We conclude that wildfires, lightning NO_x and stratospheric intrusions contribute a significant level of uncertainty in estimating PRB, and that PRB will require careful consideration in the ozone standard setting process.
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1. Introduction

Policy Relevant Background (PRB) ozone is the metric that the US Environmental Protection Agency (EPA) uses in its standard setting process to define uncontrollable "background" concentrations (EPA, 2006, 2007). Specifically, PRB is the surface ozone concentration that would be present across the US in the absence of all anthropogenic emissions from North America (US, Canada and Mexico). It includes contributions from natural sources globally (e.g., biogenic, wildfires, lightning NO_x, and stratosphere-troposphere exchange) and from anthropogenic emissions outside of North America.

In 2008, EPA promulgated a reduction in the 8-h ozone National Ambient Air Quality Standard (NAAQS) from 0.08 ppm to 0.075 ppm (Federal Register, 2008), and has begun the next review for the 2013 ozone standard. PRB is critically important in the standard setting process because it establishes the baseline in the comparison of health risks at alternate ozone levels being evaluated for the NAAQS. Health benefits derived for different levels of the ozone standard can be overestimated when PRB is set too low, as outlined by Lefohn (2007) using data from the EPA's Risk Assessment Technical Support Document (Abt Associates, 2007). PRB also has a significant impact on the feasibility and cost of compliance; as the ozone standard approaches the zero emission PRB level, the probability of practicably achieving the NAAQS is greatly diminished.

Prior to 2006, EPA based estimates of background ozone on observational evidence from data at remote monitoring sites on

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"clean" days. EPA first considered global modeling as a means to establish the range of PRB over the US when preparing for the 2008 ozone NAAQS. EPA (2006) specifically cited the work of Fiore et al. (2003), who applied the GEOS-Chem global model at $2 \times 2.5^{\circ}$ grid size (>200 km) for the year 2001. GEOS-Chem estimated a mean PRB range of 15–35 ppb, with a 2–7 ppb mean stratospheric influence and a 4–12 ppb global anthropogenic contribution. While GEOS-Chem performed well in replicating seasonal mean rural ozone observations, it did not replicate the frequency of the highest western US ozone events (>60 ppb) in winter and spring when global transport and stratospheric–tropospheric exchange (STE) peak (Yienger et al., 1999; Lefohn et al., 2001). EPA (2006) discusses the technical issues associated with global models, including coarse spatial/temporal resolution, highly uncertain global emission inventories (most notably for Asia), and simplifications of some important processes such as STE.

Observational research by Lefohn et al. (2001) suggests higher background ozone (often exceeding 50 ppb) with more natural short-term variability and more evidence of transport from the stratosphere (points which were directly countered by Fiore et al., 2003). Subsequent observational studies have continued to present evidence for higher background ozone, particularly with respect to STE influences (e.g., Cooper et al., 2005; Hocking et al., 2007; Oltmans et al., 2008; Langford et al., 2009). Lefohn et al. (2011) describe statistical and trajectory modeling analyses over 2006–2008 that suggest spring and summer STE events are well correlated with multi-day surface ozone enhancements reaching 50–65 ppb at remote sites in the western and northern US. Furthermore, Parrish et al. (2009) present compelling evidence that ozone entering the US west coast between 1980 and 2008 is increasing at 3–5 ppb per decade, signifying that long-term PRB ozone trends need to be addressed.

As a hypothetical construct, PRB is not directly measureable and so modeling is a necessary tool, but modeled estimates must be informed by and evaluated based on measurement data from remote sites. More recently, Wang et al. (2009) re-estimated 2001 PRB levels using GEOS-Chem with 1° (~100 km) resolution over North America and reported little difference from PRB estimates of Fiore et al. (2003). Mueller and Mallard (2011) evaluated 2002 North American background ozone at 36 km resolution using EPA's regional Community Multiscale Air Quality (CMAQ) model, with lateral boundary conditions provided by a $2 \times 2.5^{\circ}$ degree GEOS-Chem run. Most recently, Zhang et al. (2011) employed GEOS-Chem with improved estimates of Asian emissions, a revised stratospheric ozone treatment, and North American resolution of $0.5 \times 0.625^{\circ}$ (~50 km) to simulate PRB over 2006–2008. These enhancements incrementally improved model performance in replicating the high end of the observed ozone frequency distribution, particularly at high elevation sites, while marginally increasing PRB estimates. However, Zhang et al. (2011) state that GEOS-Chem is unable to replicate event-oriented phenomena such as wildfires and STE. Global models continue to be driven by meteorological analyses of low temporal resolution (6 h), which can severely limit the models' capacity to replicate rapid deep circulations at relatively small scales, such as often occur in the intermountain western US.

Whereas the majority of PRB modeling in the literature to date has employed global models, this paper summarizes a comprehensive ozone modeling analysis for the year 2006 using both low-resolution global ($2 \times 2.5^{\circ}$) and very high-resolution regional (12 km) chemical transport models. We compare differences in model predictive performance against ozone observations and differences in temporal and spatial background variability over the US. Regional modeling over the North American continent was conducted using the Comprehensive Air quality Model with extensions (CAMx; ENVIRON, 2010). Following the nesting approach of Mueller and Mallard (2011), lateral boundary conditions were determined from the global modeling component using a contemporary version of GEOS-Chem.

2. Methodology

2.1. Global modeling

GEOS-Chem version 8-03-01 was used to derive ozone estimates over the US and to provide boundary condition inputs for CAMx. This version of GEOS-CHEM includes several important updates as described by Zhang et al. (2011), including several chemistry and solver updates, revised treatment of stratospheric chemistry and stratosphere–troposphere exchange ("LINOZ"), and global emission updates. GEOS-Chem was run on a $2 \times 2.5^{\circ}$ latitude/longitude grid with 47 vertical layers, 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 43 chemical species, and LINOZ was invoked. Additional information on GEOS-Chem structure, inputs and algorithms is available at http://acmg.seas.harvard.edu/geos/index.html.

The following anthropogenic emission inventories were employed and internally adjusted to the 2006 simulation year:

- Europe: 2005 European Monitoring and Evaluation Programme (EMEP, 2011);
- Asia: Streets 2006 Inventory (Zhang et al., 2009);
- Mexico: 1999 Big Bend Regional Aerosol and Visibility Observation Study (BRAVO; Kuhns et al., 2005);
- Canada: 2002 Criteria Air Contaminants (CAC) inventory (Environment Canada, 2011);
- US: 2005 National Emission Inventory (NEI; EPA, 2010);
- Remaining world: Emissions Database for Global Atmospheric Research (EDGAR, 2011).

The 2006 Streets inventory for Asia reflects a doubling of anthropogenic NO_x 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). To be consistent with satellite evidence, and following the approach from Zhang et al. (2011), we scaled NO_x emissions in Japan and Korea upward by a factor of two. 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 2 (GFED2, 2005), internally calculated lightning NO_x according to GEOS-5 meteorology, and soil NO_x from both natural bacterial activity and agricultural fertilizer application.

GEOS-Chem was first run for the year 2006 in two ways: (1) with all global anthropogenic emissions included for the purposes of assessing model performance against US observational data (the "Base Case"); and (2) with North American anthropogenic emissions from US, Mexico, and Canada removed (the "PRB Case").

2.2. North American regional modeling

CAMx version 5.30 was run for the entire year of 2006 on a single large North American domain with 36 km grid spacing. CAMx was subsequently run on two smaller nested domains with 12 km grid spacing that split the US into western and eastern halves

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(Fig. 1). All three CAMx grids possessed identical 34 vertical layer structures spanning the entire troposphere and lower stratosphere up to a pressure altitude of 50 mb. Gas-phase photochemistry was treated with the Carbon Bond 2005 mechanism (CB05; Yarwood et al., 2005) but particulate matter (PM) was ignored. Standard and default transport, diffusion and removal algorithms were employed. Additional information on CAMx structure, inputs, and algorithms is documented by ENVIRON (2010).

Chemical boundary conditions for the 36 km grid were defined from three-hourly GEOS-Chem concentration output fields using an interface program documented by Morris et al. (2007) and employed for CMAQ by Mueller and Mallard (2011). This processor interpolates three-dimensional concentration fields horizontally and vertically to the CAMx boundary grid definition. It then maps GEOS-Chem gas species to the CB05 compounds required by CAMx. Boundary concentrations were held constant (not time-interpolated) between each three-hour GEOS-Chem output interval. Boundary conditions for each CAMx 12 km simulation were subsequently extracted from the CAMx 36 km simulation results on an hourly basis.

Meteorological and emission datasets for the year 2006 were derived by the EPA Office of Research and Development (ORD) as part of the Air Quality Model Evaluation International Initiative (AQMEII) program (Rao et al., 2011). Datasets were generated for a single large domain aligning with the CAMx 36 km grid but at 12 km grid spacing. EPA/ORD employed the Weather Research and Forecast (WRF) model (Skamarock et al., 2008) to generate 1-hour meteorological fields with 34 vertical layers from which the CAMx vertical structure was defined. Matching CAMx to WRF's map projection and grid structure minimized the manipulation of the meteorological data that drives the separate (or "offline") photochemical model simulation. This was an important design objective so that hourly resolved three-dimensional transport patterns derived by WRF were faithfully transferred to, and preserved by CAMx to the maximum extent possible.

The EPA/AQMEII hourly point and 12 km gridded emissions datasets included contributions from the following inventories and models:

- Version 3 of the 2005 NEI, grown to 2006;
- 2006 Continuous Emissions Monitoring (CEM) data for major NO_x/SO_2 point sources;
- 2006 Environment Canada CAC inventory;
- 1999 BRAVO inventory for Mexico, grown to 2006;
- Biogenic emissions from the Biogenic Emission Inventory System (BEIS v3.14; Vukovich and Pierce, 2002);
- 2006 event-specific fire emissions from the SmartFire algorithm (Coe-Sullivan et al., 2008).

These emission estimates were further augmented with recently updated 2005/2006 emission inventories for the oil and gas development sector in the western US according to work directed in part by the Western Regional Air Partnership (WRAP) and the Independent Petroleum Association of Mountain States (IPAMS, 2008). These updates reflect the latest information on ozone precursor emissions from oil and gas activities in the central Rocky Mountains, including several of the most actively producing basins in Wyoming, Utah, Colorado, and New Mexico. Finally, we generated estimates of lightning NO_x emissions following the approach of Koo et al. (2010). In this approach, information on hourly convective activity (precipitation rate, convective cloud depth, and pressure) from the 12 km WRF meteorological dataset was used as a surrogate to spatially and temporally allocate annual estimates of total lightning NO (1.06 Tg) over North America. The annual estimate was obtained by assuming an intra-cloud to cloud-to-ground flash ratio of 2.8, and multiplying the annual North

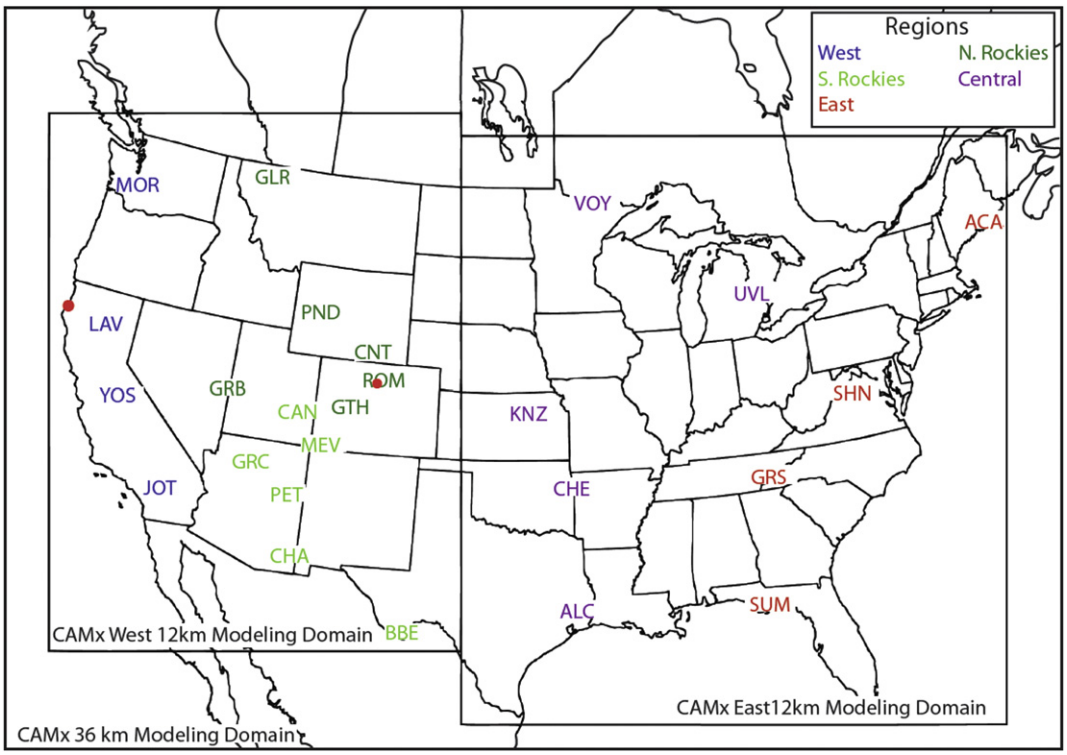

Fig. 1. Depiction of the CAMx 36 km modeling grid (full extent of figure), 12 km western and eastern US modeling grids (insets), with locations of ozonesonde sites (red dots) and Clean Air Status and Trends Network (CASTNET) surface ozone sites (given by site name abbreviations, analysis regions are grouped by color).

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American cloud-to-ground flash rate (30 million; Orville et al., 2002) by emissions rate per flash (665 moles N per flash, Holler and Schumann, 2000).

PRB ozone was simulated by removing all anthropogenic emissions from the US, Mexico, and Canada, as well as using the corresponding GEOS-Chem PRB run to supply boundary conditions for the 36 km CAMx grid.

2.3. Model evaluation

We conducted an ozone performance evaluation of the 2006 global and regional Base Case simulations. Model performance was gauged against surface measurement data reported by the rural Clean Air Status and Trends Network (CASTNET) for the 25 individual sites displayed in Fig. 1. These sites were chosen to represent various regions of the US, with particular emphasis on high altitude sites throughout the intermountain west. Observation-prediction statistics were calculated from GEOS-Chem three-hourly ozone and CAMx hourly ozone.

The form of the US 8-hour ozone standard is rooted in the fourth highest concentrations occurring each year at a given monitoring site. Therefore, our performance evaluation for surface ozone focused on the upper end of the ozone frequency distributions of daily maximum 8-hour average (MDA8) ozone. Further, we analyzed overall performance in terms of standard linear regression and correlation of MDA8 at individual sites, rather than relying on bulk ensemble statistics (e.g., bias and error) that can mask performance issues when averaging over large spatial and temporal scales.

Ozone performance aloft was assessed against routine ozonesonde data in California and Colorado (Fig. 1), which were included as part of the spring/summer 2006 INTEX-B Ozonesonde Network Study (IONS-06, 2006). Given the limited number of soundings launched each month, seasonally-averaged observed and predicted ozone profiles were compared.

3. Results

3.1. Model performance

Fig. 2 presents the spatial distribution of 2006 annual fourth highest MDA8 ozone concentrations over North America in the GEOS-Chem and CAMx Base Cases. When presented in this fashion, each grid cell reports an independent annual fourth highest MDA8 value, which can occur on a different date from neighboring cells. Besides the obvious difference in grid resolution between the two models, the overall patterns of fourth highest MDA8 ozone are

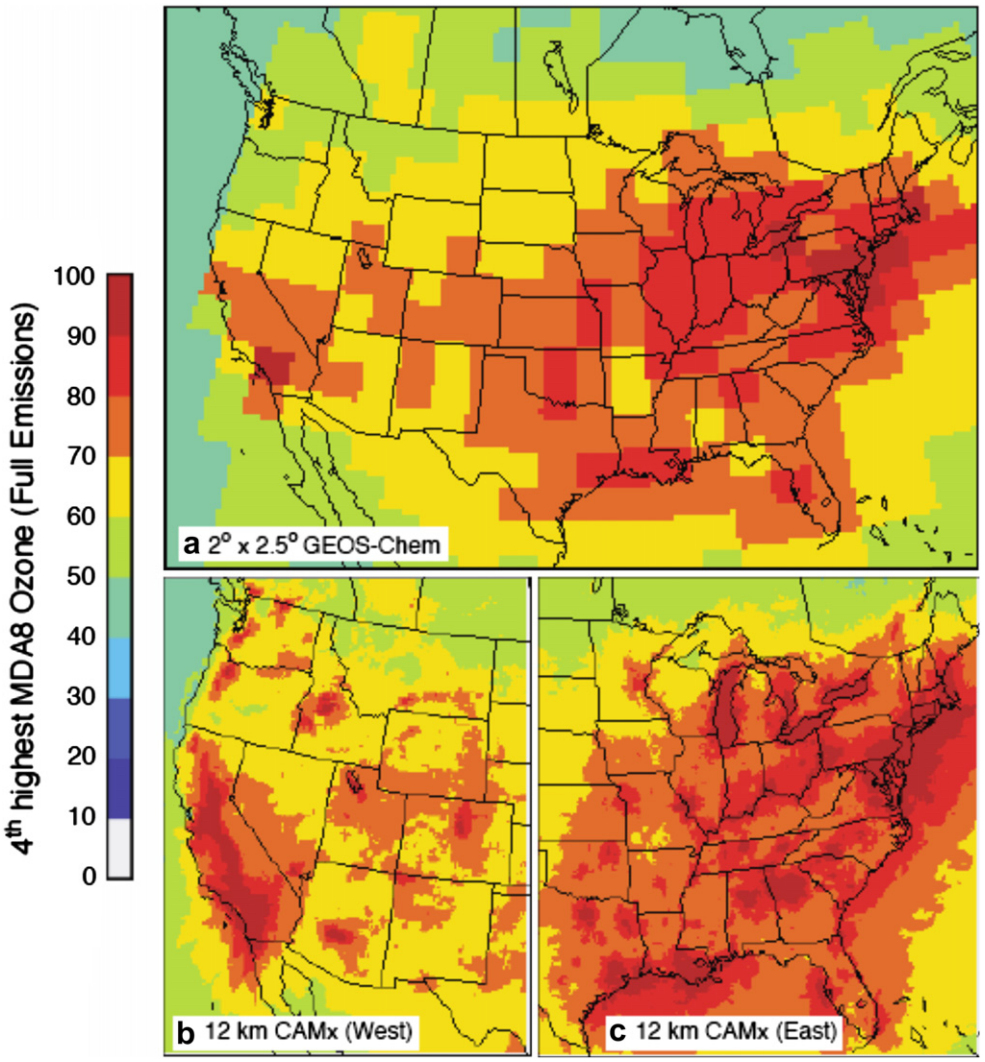

Fig. 2. Annual fourth-highest maximum daily 8-hour average (MDA8) surface ozone patterns (ppb) for 2006 predicted by GEOS-Chem (a) and by CAMx (b, c) using full emission inventories.

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similar. CAMx predicted higher peak ozone values in the vicinity of large source areas, as would be expected with higher resolution. Given the well-known temperature dependence of many types of emission sources and ozone kinetics, both models also generally agreed in the timing of the fourth highest MDA8 ozone (not shown), with a majority of the US reaching maximum values between late spring (rural western US) and early autumn (central and eastern US).

The left side of Fig. 3 compares GEOS-Chem and CAMx predictions of spring and summer (March–August) MDA8 ozone against CASTNET observations at all 25 sites, grouped into the five regions defined in Fig. 1. Similar figures for each individual site are presented in Supplemental Information (Fig. S6). Both models performed generally well (and similarly) for median ozone, with a tendency for under predictions in the west and over prediction in the central and eastern US. Both models tended to over predict low ozone and under predict high ozone. Performance for both models was similarly the least skilled in the southern Rocky Mountains based on the degree of scatter as quantified by minimum correlation. CAMx exhibited somewhat better standard linear regression

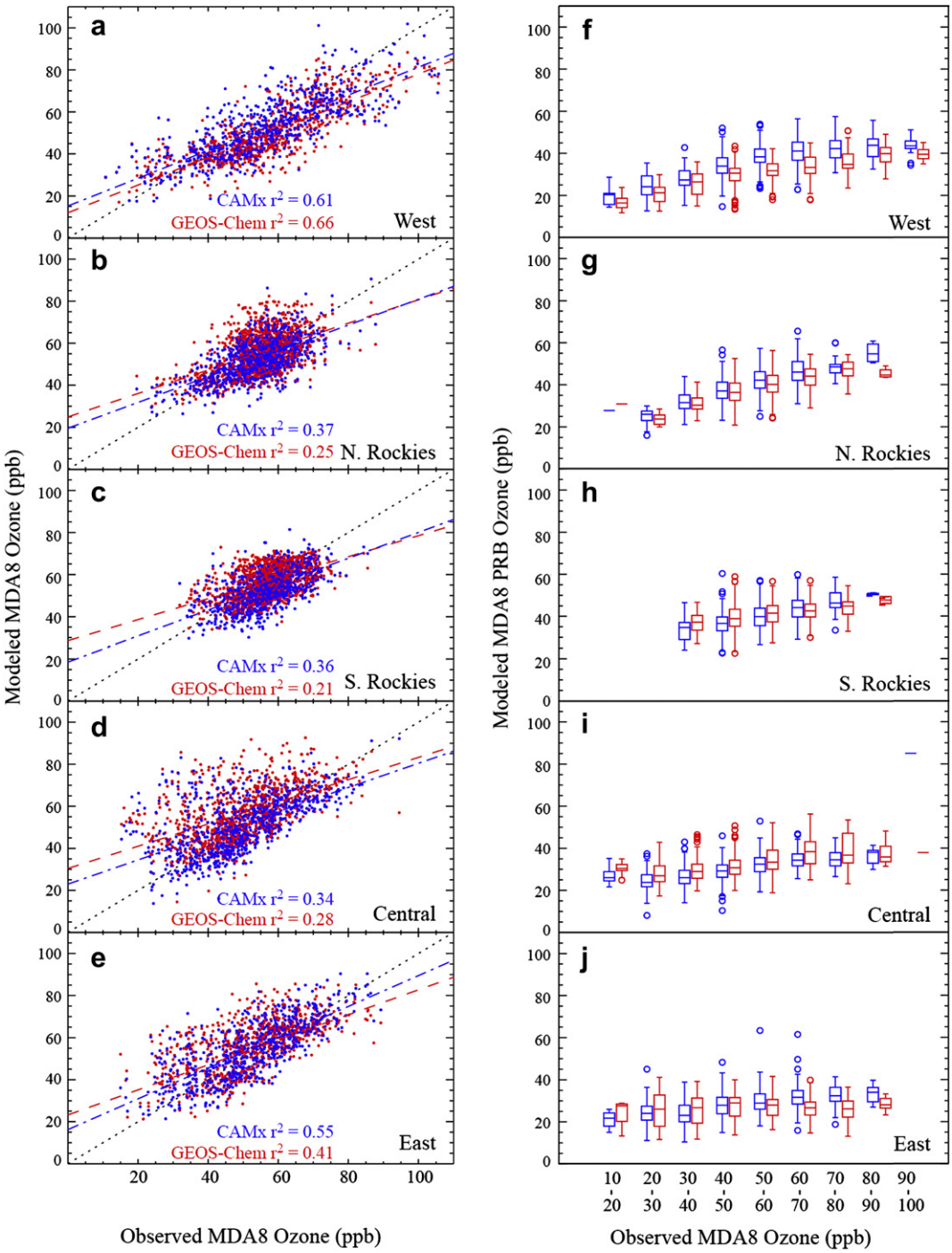

Fig. 3. Scatter plot and standard linear regression fit of predicted vs. observed MDA8 surface ozone (ppb) at CASTNET sites in five regions of the United States (a–e) for CAMx (blue) and GEOS-Chem (red). Panels f–j show the relationship between modeled MDA8 PRB and observed MDA8 (in 10 ppb intervals) for each region. Data in all figures is for spring and summer only. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

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and correlation in all regions except the west, mostly because of its performance at either end of the observed ozone distribution. As we discuss later (and exemplified in Supplemental Information), we have verified that some of the highest observed and CAMx-predicted ozone in the western US was related to stratospheric intrusion events that impinge on elevated sites. CAMx performed better than GEOS-Chem during these events, but neither model predicted the full magnitude of surface ozone enhancement.

GEOS-Chem tended to over predict ozone during the summer in the eastern US. Model resolution and the peaking of natural emissions likely play stronger roles in the model performance characteristics during the summer months. For example, the coarse resolution in GEOS-Chem contributes to immediate mixing of a variety of point and urban emissions with biogenic precursors, heightening the efficiency of ozone chemistry and leading to ozone over predictions. In contrast, the finer CAMx grid more correctly separates urban and point source emissions from biogenic sources, limiting ozone efficiency. We have often seen similarly strong resolution-dependent ozone performance tendencies with CAMx in the eastern US.

Lightning NO_x peaks in the summer months in the southwestern and southeastern US, and according to Zhang et al. (2011) lightning could be driving ozone over predictions in the Southern Rocky Mountain regions as well as potentially contributing to ozone differences between the two models. This source presents a very large and potentially important uncertainty in both models, and further research is needed to improve methodologies to estimate lightning emissions.

To better illustrate model differences at the upper end of the observed ozone range, Fig. 4 presents the fraction of days throughout 2006 in which observed and predicted MDA8 ozone exceeded 60, 65, and 70 ppb at each of the 25 CASTNET sites. GEOS-Chem tended to over predict the frequency of days above each of the three MDA8 values in the central and eastern US, while both models tended to under predict frequencies in the west. CAMx generally performed better in replicating frequencies for all three values. The CAMx results for the Northern and Southern Rocky regions compare well with those in Fig. 4 of Zhang et al. (2011), suggesting that the high resolution version of GEOS-Chem is performing significantly better than its low-resolution counterpart in this region.

Spring- and summer-average vertical ozone profiles at Trinidad Head, California and Boulder, Colorado are shown in Fig. 5. On the west coast, CAMx closely tracked GEOS-Chem ozone during both seasons, which is expected given that CAMx ozone was dominated by western boundary conditions from GEOS-Chem. It is also important to note that all stratospheric ozone in CAMx was entirely driven by GEOS-Chem via boundary conditions (as a tropospheric chemistry model, CAMx is incapable of chemically maintaining a stratosphere). GEOS-Chem under predicted the entire mean springtime profile, by roughly 10 ppb in the troposphere and up to 100 ppb in the stratosphere. The summer-mean profile was better replicated except in the lowest 3 km where the global model continued to under predict by up to 10 ppb. Over the Rocky Mountains, predicted spring-mean ozone profiles were also similar among the two models but they continued to under predict much of the troposphere by 10 ppb and the lower stratosphere by 100 ppb. While CAMx replicated the observed summer-mean troposphere ozone profile well, GEOS-Chem over predicted by 5–10 ppb through the lowest 4 km, likely because this grid column contained the Denver metropolitan area. Like Trinidad Head, GEOS-Chem performed better in replicating the mean summertime stratospheric profile above Boulder. The consistent springtime stratospheric under prediction bias in GEOS-Chem is related to an inadequate representation of STE activity that peaks in spring.

CAMx tended to over predict summer stratospheric ozone above Boulder, and we tracked its source to the topmost layer. This behavior was related to a combination of two factors: (1) the vertical advection solver, while second-order accurate, possesses numerical diffusion that is enhanced for large gradients as seen in the stratosphere; and (2) relatively coarse vertical resolution above the tropopause amplifies the diffusive effect (in this case the upper layers are 1–3 km deep at altitudes above 10 km). We investigated the sensitivity of tropospheric ozone to this stratospheric bias by running CAMx with fewer layers and coarser vertical resolution above 10 km. This increased the CAMx summertime stratospheric ozone bias but resulted in only marginal impacts to seasonal-mean ozone profiles in the low to mid troposphere and 1–5 ppb surface ozone differences.

3.2. PRB simulations

Fig. 6(a–c) displays the spatial distribution of GEOS-Chem and CAMx annual fourth highest MDA8 ozone in the PRB Case. The most striking difference among these models is the local impact from wildfires in Idaho and the Pacific Northwest, which push CAMx MDA8 ozone to 60–100 ppb in the immediate vicinity of the fires. These differences are largely driven by the spatial and temporal

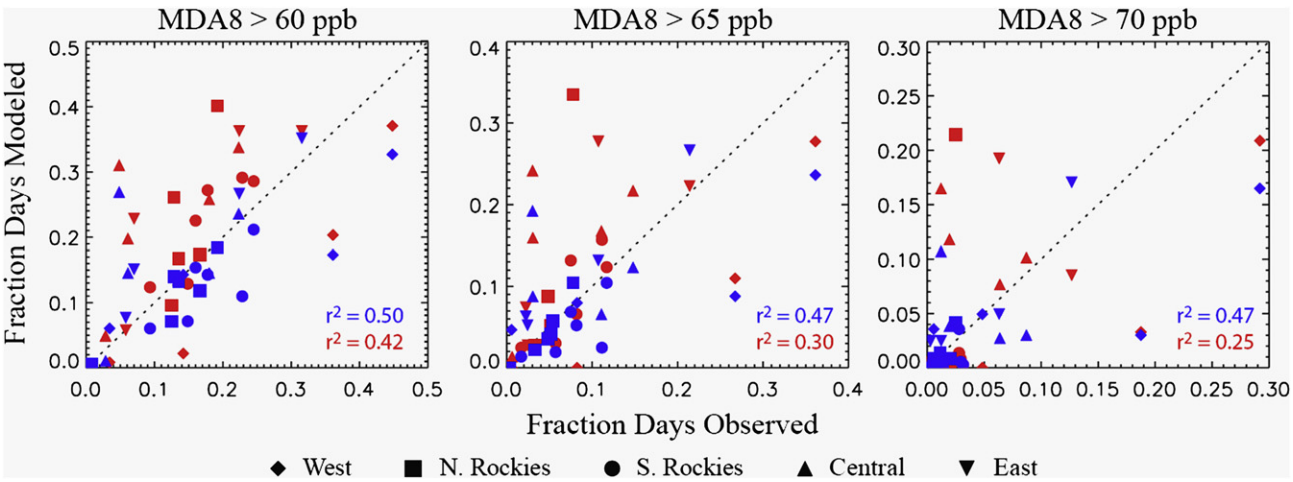

Fig. 4. Comparison of the modeled vs. observed fraction of days in 2006 with MDA8 ozone greater than 60 (a), 65 (b) and 70 ppb for CAMx (blue) and GEOS-Chem (red). Each symbol represents a different region of the United States. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

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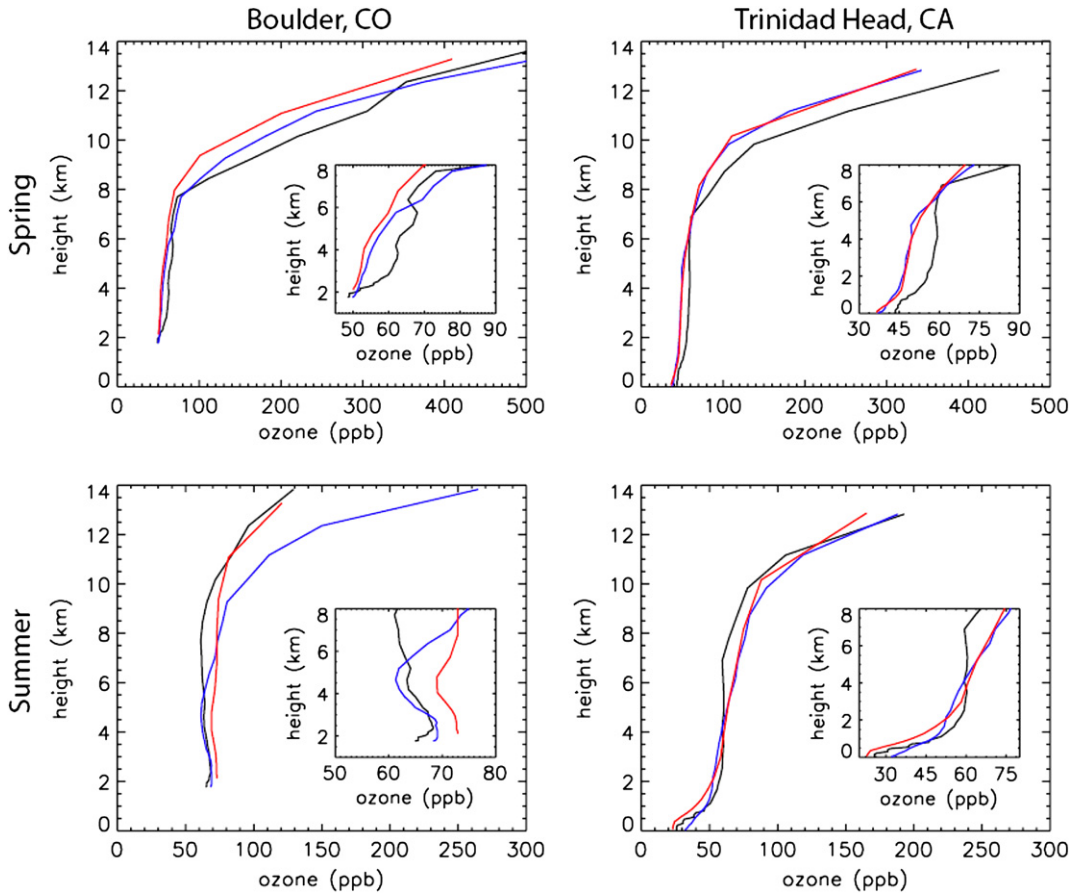

Fig. 5. Comparison of season-averaged observed ozonesonde profiles at Boulder, CO and Trinidad Head, CA with modeled profiles. Inset panels show the bottom 8 km of the atmosphere. Observations are black, CAMx is blue, and GEOS-Chem is red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

resolution of fire emissions, while variations in chemistry have secondary effects. The SmartFire emissions used in CAMx include hourly variations applied to day-specific fires estimates, whereas monthly-total GFED2 fire emissions are supplied to GEOS-Chem at a constant rate each hour of the month.

These CAMx fire impacts are consistent with the findings of Mueller and Mallard (2011), who used CMAQ with 2002 event-specific fire estimates and reported typical contributions of 30–50 ppb, often exceeding 100 ppb. McKeen et al. (2002) modeled 10–30 ppb ozone enhancements over large areas of central and eastern US due to multi-day transport from large Canadian wildfires, but there is little evidence in the literature that such large enhancements are seen for surface ozone in the immediate area of wildfires except possibly when mixed with urban pollution (e.g., Singh et al., 2010). Commonly used fire speciation profiles derived from the literature (e.g., Andreae and Merlet, 2001; Karl et al., 2007) possess large quantities of reactive biogenic and oxygenated VOC that would be expected to generate locally high ozone concentrations when mixed with fire NO_x. Whereas the CAMx CB05 gas chemistry accounts for radical production from these primary and secondary VOCs, GEOS-Chem does not include oxygenated VOCs formed from fast-reacting VOCs (Daniel Jacob, personal communication). In reality, surface ozone production may be limited to factors that current models do not consider, such as fire-induced deep convection that lofts the bulk of emissions into the upper troposphere, and smoke shading that would reduce photochemistry. A CAMx test was conducted in which all fire emissions were removed; the resulting spatial distribution of the fourth highest MDA8 PRB ozone is shown in Fig. 6(d–e). In the west, removal of fires resulted in a dramatic reduction of the PRB estimate in Idaho, Oregon and areas of California by 10–50 ppb – all areas where the largest fires were recorded in 2006. Other more subtle differences occurred throughout the US, where fire contributions remained within a few ppb.

CAMx predicted maximum (non-fire) PRB ozone over the highest western terrain (up to 60–70 ppb), including the Sierra Nevada range in California, and the Rocky Mountains in Colorado and Wyoming. Evaluation of the timing of these specific maxima revealed that most occurred during the mid to late spring (April and May). The higher CAMx PRB in this region is a result of resolving much higher topography than GEOS-Chem and the fact that background ozone increases with altitude during this season. One exceptionally strong event occurred on April 19–21, resulting in the highest observed (80–90 ppb) and CAMx-predicted MDA8 ozone at sites throughout the northern Rocky Mountains (see Supplemental Information for an analysis of this episode). CAMx generally simulated higher PRB ozone throughout the eastern US by about 5 ppb, especially throughout the southern Appalachian states, while GEOS-Chem PRB was up to 10 ppb higher than CAMx in the Great Lakes region.

The right column of Fig. 3 displays the relationship between modeled PRB and the range in observed MDA8 ozone for each of the five analysis regions. Both models predicted similar PRB ranges as a function of observed MDA8 except in the west where CAMx consistently predicted higher PRB than GEOS-Chem, and in the east where CAMx predicted higher PRB for observations above 60 ppb. Note that both models show a positive PRB slope with observed

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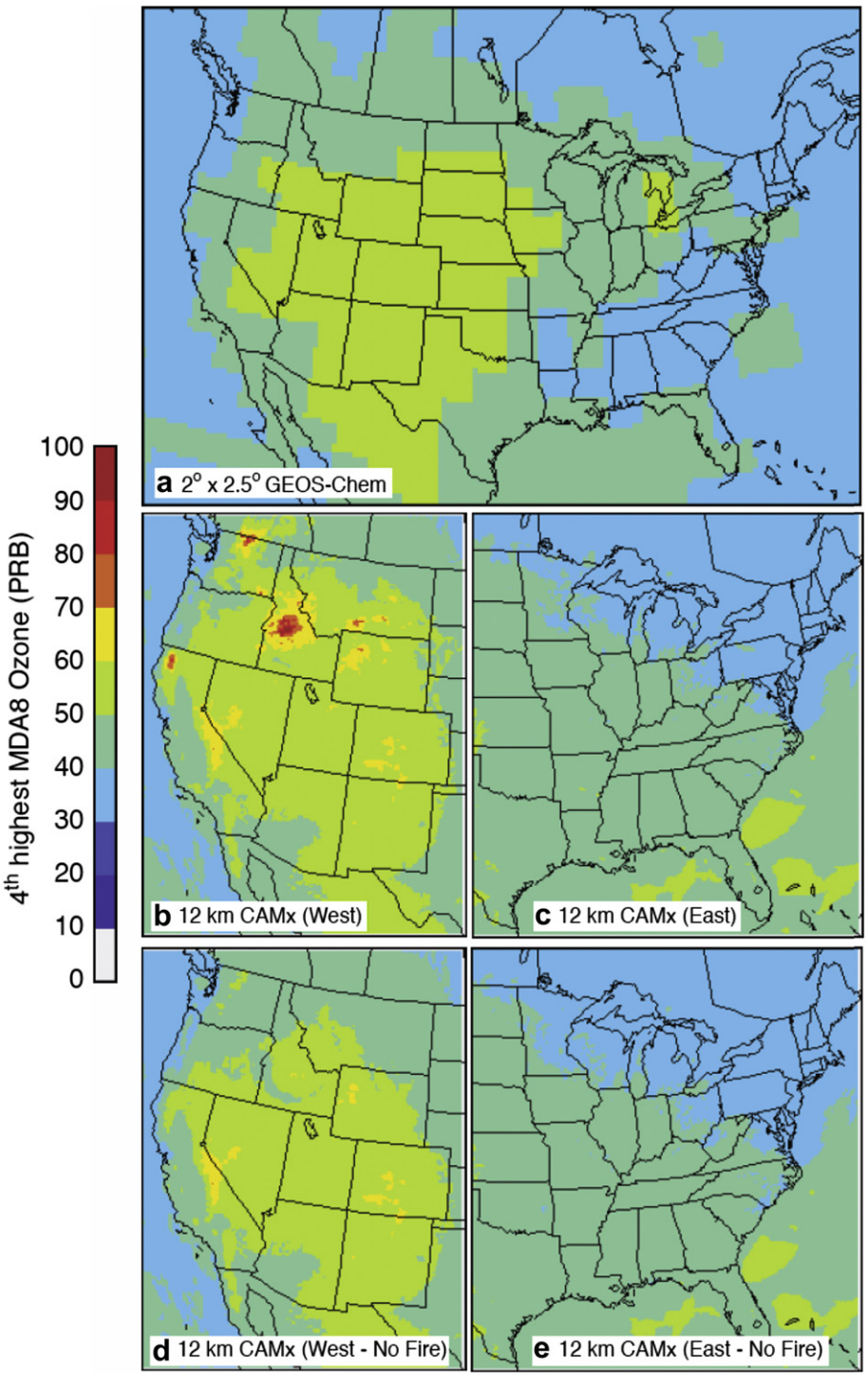

Fig. 6. Annual fourth-highest MDA8 PRB surface ozone (ppb) patterns for 2006 predicted by GEOS-Chem (a) and CAMx (b–d). Panels a–c have all anthropogenic emissions within North America removed. Panels d and e have all anthropogenic emissions within North America and biomass burning removed.

MDA8 in the west and Rocky Mountain regions, consistent with the latest results from Zhang et al. (2011) and observational analyses of Parrish et al. (2010). In the East, CAMx PRB continues to be correlated with total observed ozone (similarly to Zhang et al., 2011), but our coarse resolution GEOS-Chem PRB estimates do not (similarly to Fiore et al., 2003).

Fig. 7 illustrates the spatial distribution of the number of days throughout 2006 that simulated MDA8 PRB ozone (including fires) exceeds 40, 50, and 60 ppb. The frequencies predicted by GEOS-Chem tail off quickly above 40 ppb to zero days above 60 ppb, but consistently show the highest frequencies over the Rocky Mountain and Great Basin states. There are no days predicted above 40 ppb throughout the southeast and along the east coast. CAMx exhibits a similarly sharp reduction in PRB frequency above 40 ppb. However, the western US is predicted to have 200 or more days above the 40 ppb PRB level over large areas of elevated terrain, and over 100

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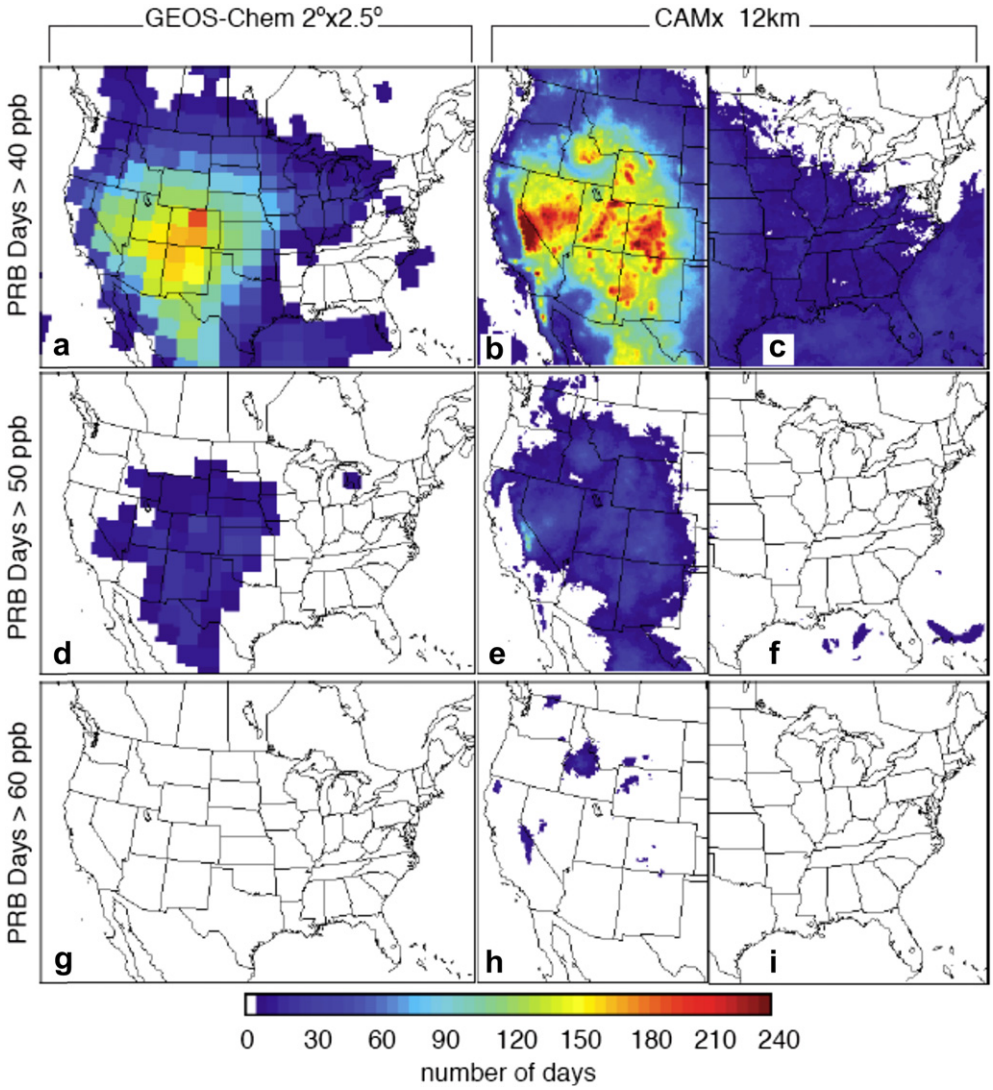

Fig. 7. Number of days in 2006 for which GEOS-Chem (left column) and CAMx (right two columns) predicted MDA8 PRB ozone concentrations above 40 ppb (a–c), 50 ppb (d–f), and 60 ppb (g–i).

days above 50 ppb over the highest terrain. Again, many of these days occur in the winter through late spring months in response to the large frequency and duration of deep low pressure systems that are associated with minimum tropopause heights and STE impacts. The balance of high ozone days occur during the summer with increased biogenic, fire and lightning activity, the latter two of which were very pronounced in late summer of 2006. In the eastern US, CAMx predicts roughly 40 days above 40 ppb nearly everywhere except for the Great Lakes region and the northeast US. Practically zero days are predicted above 50 ppb. Removing fires in CAMx reduced the frequency of days predicted to exceed 60 ppb by 10–20 days.

We compared the range of MDA8 total and PRB ozone over the spring and summer seasons at all 25 CASTNET sites evaluated in this study (Fig. 8). Note that the observation-prediction comparisons shown in Fig. 8, unlike the scatter plots in Fig. 3, are not paired in time and therefore relax the restrictions on the observation-prediction performance assessment. Both models performed generally well in replicating the observed ranges of MDA8 ozone at many sites with respect to the median, quartile, and maximum range of MDA8 ozone. Comparisons are especially favorable at the Rocky Mountain sites, although as we have seen in Fig. 3, time-pairing predictions with observations at these rural elevated sites results in some of the worst correlation among these five regions. With a few exceptions, CAMx performed similarly to or better than GEOS-Chem for the highest ozone, most notably in the west. CAMx-predicted MDA8 PRB ozone ranges were generally higher than GEOS-Chem in the west, northern Rockies, and East by roughly 5–10 ppb. In the southern Rockies, the quartile ranges between GEOS-Chem and CAMx PRB tended to be similar but CAMx resulted in higher maxima. In the central region, CAMx PRB predictions were similar or lower than GEOS-Chem.

4. Discussion and conclusion

We have described a modeling analysis of ozone across the North American continent for the year 2006, using both global and regional chemical transport models for 2006. Results from a low-resolution version of the GEOS-Chem global chemistry model were used in two ways: (1) to generate lateral boundary conditions for the CAMx regional model; and (2) to compare simulated ozone patterns against the regional model predictions.

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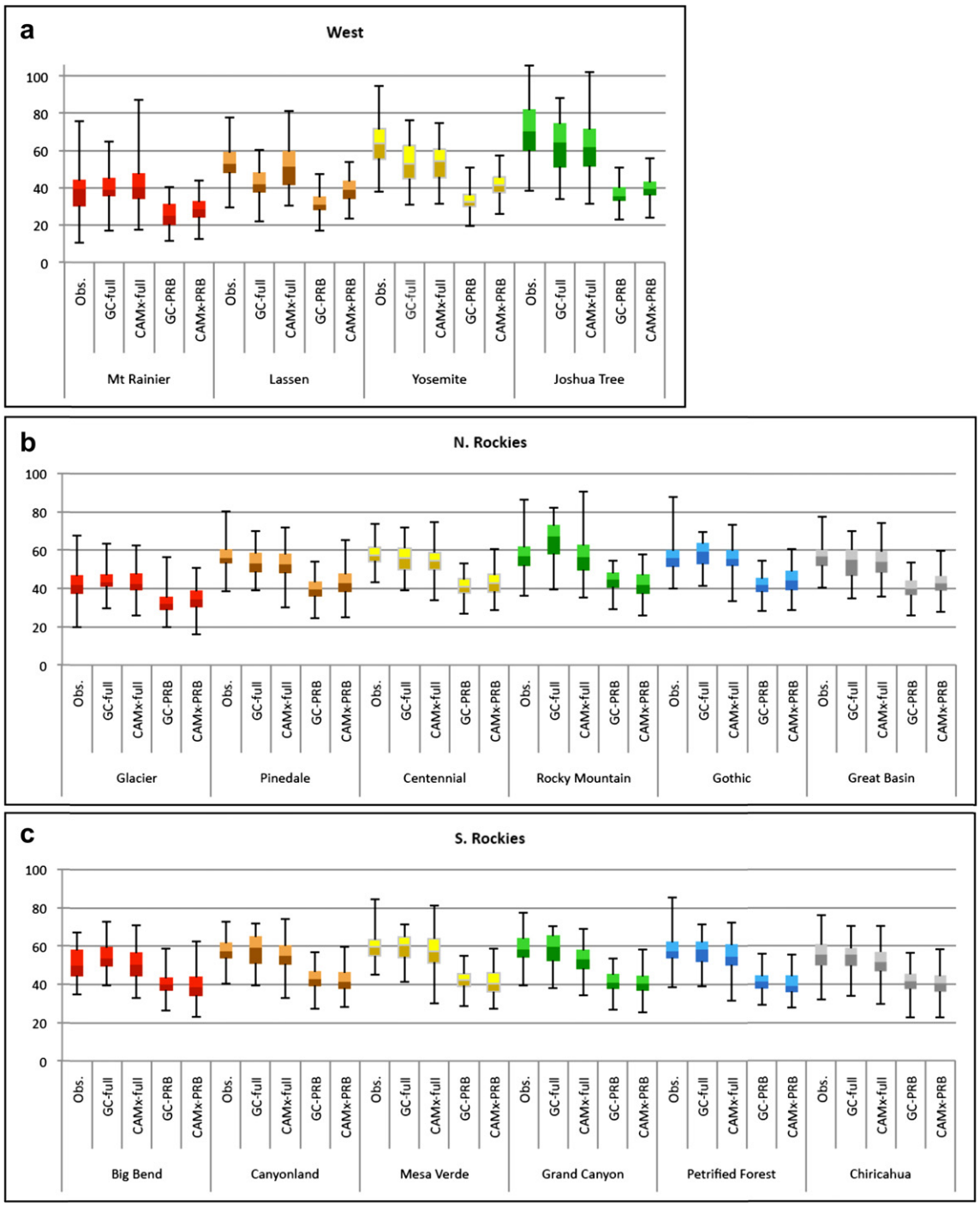

Fig. 8. Box/whisker diagrams of the range in observed and predicted MDA8 surface ozone throughout the spring and summer seasons displayed by region (a–e) as shown in Fig. 1. Ozone predictions with all emissions and predicted PRB are shown for CAMx and GEOS-Chem. Boxes represent the 25th–75th quartile range (median at color shift) and whiskers show the full minimum to maximum range.

The spatial and temporal distributions of the Base Case fourth highest MDA8 ozone were similar between the two models over broad areas of the US, with obvious differences arising from their vastly different grid resolutions, especially over major sources (urban areas and large fires). Performance metrics at specific rural CASTNET sites consistently showed that CAMx better replicated the highest observed concentrations in the west (greater than 50 ppb) and on a space- and time-paired basis exhibited higher correlation. We attribute the better CAMx performance to the use of higher resolution, which improves the spatial and temporal characterization of emissions, chemistry, and three-dimensional transport (including stratospheric ozone intrusion events). The higher-resolution version of GEOS-Chem (Zhang et al., 2011) similarly performs better in comparison to observations than the low-resolution version presented here. Zhang et al. also suggest that GEOS-Chem may over predict summer ozone in the southwestern US because of too much lightning NO_x, and the same may be true for CAMx. Given its significant role in PRB ozone, further work

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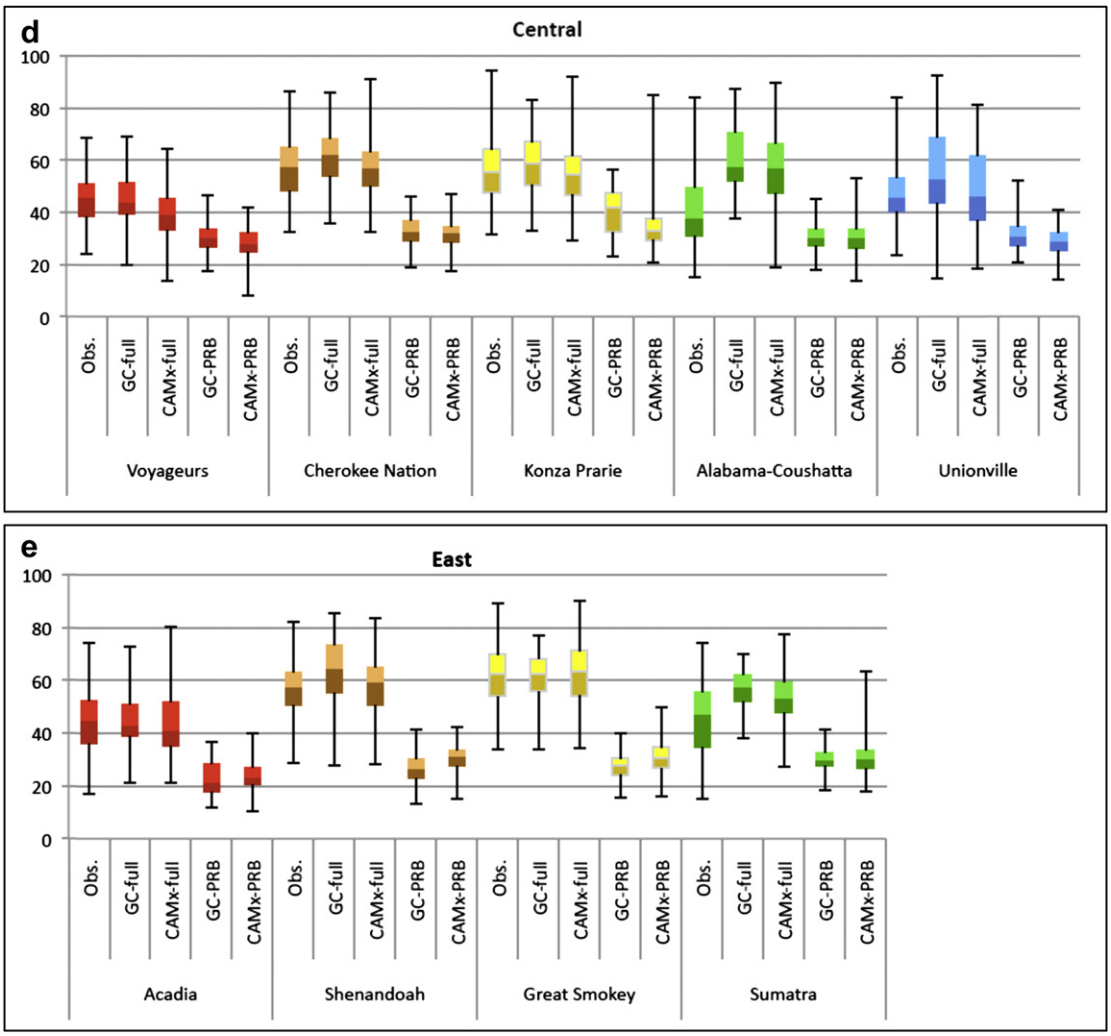

Fig. 8. (*continued*).

refining estimates of the magnitude of lightning NO_x emissions and their temporal and spatial variability is necessary.

Spring-average vertical tropospheric ozone profiles at Trinidad Head, California and Boulder, Colorado were under predicted by both models, and both models systematically under-predicted springtime ozone concentrations at Western US sites (Fig. S6). CAMx performed better at reproducing a stratospheric intrusion event in April 2006 (Fig. S4), but neither model was able to capture the full magnitude of surface ozone observed. The magnitude of stratospheric impacts on surface ozone concentrations remains highly uncertain in these models, and more work needs to be done to improve the temporal and spatial representation of STE events as well as longer-term enhancements of tropospheric ozone.

The two models exhibited significantly more differences in spatial patterns of annual fourth highest MDA8 ozone in the PRB Case than in the Base Case, mostly attributed to the contribution from wildfires. But even with fires removed, CAMx predicted more spatial variation and more days with higher PRB ozone in the complex terrain of the west than GEOS-Chem. This shows that horizontal resolution (a) is a key factor in resolving emissions and chemistry, (b) increases the height of terrain into the mid-troposphere where springtime background ozone increases with altitude, and (c) replicates deep tropospheric circulations that can efficiently transfer ozone aloft to the elevated terrain of the western US, as suggested by observational researchers. In fact, CAMx successfully replicated the timing of certain springtime ozone events that were simultaneously recorded at several monitors in Wyoming and central Colorado but were not captured by GEOS-Chem (see Supplementary Information).

CAMx predictions of PRB ozone ranges were generally higher than GEOS-Chem in most regions of the US and were more positively correlated with ozone observations. The only exception was the central region, where CAMx predicted similar or lower PRB ozone levels. Overall, the CAMx mean PRB ozone ranged between 25–50 ppb throughout the US, whereas the GEOS-Chem mean PRB ranged 20–45 ppb; the fourth highest PRB ranged between 35–100 ppb for CAMx and 35–55 ppb for GEOS-Chem. Outside of areas with wildfire activity, CAMx PRB tended to be roughly 10 ppb higher in the west and 5 ppb higher in the east. When fires were removed, CAMx predicted fourth highest PRB concentrations between 35–65 ppb. Given its significant role in PRB ozone, further work on refining the simulation of wildfires is necessary.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2011.11.012.

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