Impacts of transported background pollutants on summertime western US air quality: model evaluation, sensitivity analysis and data assimilation

M. Huang1,6, G. R. Carmichael1, T. Chai2, R. B. Pierce3, S. J. Oltmans4, D. A. Jaffe5, K. W. Bowman6, A. Kaduwela7, C. Cai7, S. N. Spak1,8, A. J. Weinheimer9, L. G. Huey10, and G. S. Diskin11

1Center for Global and Regional Environmental Research, University of Iowa, Iowa City, IA 52242, USA
2NOAA/OAR/ARL, College Park, MD 20740, USA
3NOAA/NESDIS, Madison, WI 53706, USA
4NOAA/ESRL, Boulder, CO 80305, USA
5University of Washington, Bothell, WA 98011, USA
6Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA
7California Air Resources Board, Sacramento, CA 95812, USA
8Public Policy Center, University of Iowa, Iowa City, IA 52242, USA
9National Center for Atmospheric Research, Boulder, CO 80305, USA
10School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA
11NASA Langley Research Center, Hampton, VA 23681, USA

Correspondence to: M. Huang (mhuang1@engineering.uiowa.edu)

Abstract. The impacts of transported background (TBG) pollutants on western US ozone (O₃) distributions in summer 2008 are studied using the multi-scale Sulfur Transport and dEposition Modeling system. Forward sensitivity simulations show that TBG contributes ~30–35 ppb to the surface Monthly mean Daily maximum 8-h Average O₃ (MDA8) over Pacific Southwest (US Environmental Protection Agency (EPA) Region 9, including California, Nevada and Arizona) and Pacific Northwest (EPA Region 10, including Washington, Oregon and Idaho), and ~10–17 ppm-h to the secondary standard metric “W126 monthly index” over EPA Region 9 and ~3–4 ppm-h over Region 10. The strongest TBG impacts on W126 occur over the grass/shrub-covered regions. Among TBG pollutants, O₃ is the major contributor to surface O₃, while peroxyacetyl nitrate is the most important O₃ precursor species. W126 shows larger responses than MDA8 to perturbations in TBG and stronger non-linearity to the magnitude of perturbations. The TBG impacts on both metrics overall negatively correlate to model vertical resolution and positively correlate to the horizontal resolution.

The mechanisms that determine TBG contributions and their variation are analyzed using trajectories and the receptor-based adjoint sensitivity analysis, which demonstrate the connection between the surface O₃ and O₃ aloft (at ~1–4 km) 1–2 days earlier. The probabilities of airmasses originating from Mt. Bachelor (2.7 km) and 2.5 km above Trinidad Head (THD) entraining into the boundary layer reach daily maxima of 66% and 34% at ~03:00 p.m. Pacific Daylight Time (PDT), respectively, and stay above 50% during 09:00 a.m.–04:00 p.m. PDT for those originating 1.5 km above California’s South Coast.

Assimilation of the surface in-situ measurements significantly reduced the errors in the modeled surface O₃ during a long-range transport episode by ~5 ppb on average (up to ~17 ppb) and increased the estimated TBG contributions by ~3 ppb. Available O₃ vertical profiles from Tropospheric Emission Spectrometer (TES), Ozone Monitoring Instrument (OMI) and THD sonde identified this transport caused by...
event, but assimilation of these observations in this case did not efficiently improve the O\(_3\) distributions except near the sampling locations, due to their limited spatiotemporal resolution and/or possible uncertainties.

1 Introduction

Transported background (TBG) ozone (O\(_3\)) and its precursors from the eastern Pacific and the lower stratosphere, together with the locally-formed O\(_3\) from anthropogenic and natural (e.g., biogenic/geogenic, lightning and biomass burning) emissions, affect the O\(_3\) variability over the western United States (US). The contribution from TBG indicates the strength of influences from extra-regional emission sources and the stratospheric O\(_3\), and accounts for a significant part of the background O\(_3\), defined as the concentration that is not affected by recent locally-emitted/produced anthropogenic emissions. The magnitude of TBG is expected to increase as the international emission sources grow (Task Force on Hemispheric Transport of Air Pollution (HTAP), 2010; National Research Council (NRC), 2009; Cooper et al., 2012). This trend is especially important in the context of US air quality standards, which tend to be tightened over time to further protect human health and ecosystems. The US Environmental Protection Agency (EPA) proposed to lower the federal 8-h primary O\(_3\) standard to a level within 60-70 ppb, and to establish a seasonal “secondary” standard to protect sensitive vegetation and ecosystems, in the form of “cumulative peak-weighted index” (W126) within 7–15 ppm-h (US EPA, 2010). The proposal was withdrawn in 2011 and the next revision is expected to occur in 2013 based on the most recent scientific findings (The White House Office of the Press Secretary, 2011).

Observational and modeling studies have been conducted to evaluate the impacts of extra-regional sources on western North America (NA) O\(_3\) variability and to estimate the background O\(_3\) levels. They have shown that trans-Pacific transport episodes are frequent and intense during the spring time (Cooper et al., 2010; HTAP, 2010). There is growing recognition that the extra-regional contributions in summer are also important (Bertschi et al., 2004; Jaffe et al., 2004; Parrish et al., 2010; Pfister et al., 2008, 2011a,b; Huang et al., 2010a). In addition to impacts of TBG O\(_3\) itself, O\(_3\) precursors (e.g., peroxyacetyl nitrate (PAN)) in the extra-regional plumes can generate O\(_3\) during the transport and subsidence processes (Alvarado et al., 2010; Zhang et al., 2008; Fischer et al., 2010, 2011; Mena-Carrasco et al., 2007; Walker et al., 2010).

Observations over three dimensions are available to characterize pollutant distributions and their evolution, and the capabilities for observational-based estimates of extra-regional/TBG influences are also increasing (Ambrose et al., 2011; Cooper et al., 2011; Parrish et al., 2009; Langford et al., 2011; Wigder et al., 2012). These include: surface observations from monitoring programs and research sites at remote locations which provide valuable information for identifying inflow characteristics; aircraft in-situ measurements and sondes, which provide information on pollutant vertical structures and can be extensive during field campaigns; and satellite measurements that routinely provide broad geographic coverage, and which are taking efforts to improve the near-surface sensitivity of the retrievals (e.g., combined retrieval of the ultraviolet (UV), infrared (IR) and visible (Vis) spectral ranges, Worden et al., 2007; Zoogman et al., 2011; Fu et al., 2012), and to better characterize/represent the upper troposphere vertical structures (Moody et al., 2012).

To date, most of the modeling studies that estimate background O\(_3\) levels and the contributions from extra-regional sources to US pollution levels have used global models with horizontal resolution ranging from several degrees to ~half degree, and they typically perturb emissions from various source regions/sectors by 20 % or 100 % (HTAP, 2010; Zhang et al., 2011; Lin et al., 2012a). However, there remain large uncertainties in these estimates. One source of uncertainty derives from the model resolution. The advantages of using finer model resolution in representing the pollutant import/export processes have been demonstrated (Lin et al., 2010; Wild and Prather, 2006), especially over urban areas and the regions with complex terrain. Increasing model horizontal resolution may result in higher estimates of extra-regional contributions to the western US (Zhang et al., 2011; Lin et al., 2012a). Model vertical resolution is also critical for representing boundary layer structure and vertical mixing, key processes associated with inflow subsidence (Saide et al., 2011). The impacts of model vertical resolution on the sensitivity of NA O\(_3\) distributions to extra-regional pollutants have not been well characterized. Another source of uncertainty is that due to the extrapolation of emission perturbation results to estimate source attribution. Using global models, Fiore et al. (2009) and Wild et al. (2012) have studied the contribution from European NO\(_x\) emissions to NA O\(_3\) levels and found that the estimates that were linearly extrapolated from 20 % perturbations were lower than those based on 100 % perturbations, and the extent of the differences depended on season. A better understanding of the non-linear effects of NA surface O\(_3\) in response to perturbations of various species in extra-regional plumes is needed, especially in light of the fact that future emission scenarios indicate a wide range of possible emission changes.

Reducing the uncertainties in modeling pollutant distributions and estimating the contributions of extra-regional sources to local air quality require a closer integration of the observations and models. Sensitivity analysis and data assimilation (DA) (cf. Boustier and Courtier, 1999; Carmichael et al., 2008; Sandu and Chai, 2011) are important techniques to: (1) help understand the chemical and physical processes associated with the transport/subsidence processes; (2) assess the degree to which the current observations can detect/represent long-range transport (LRT) airmasses and help
reduce model uncertainties; and (3) provide suggestions for future observing systems, such as measurements by extended O$_3$ sonde networks, regional airlines, and geostationary satellites that are expected to have higher spatiotemporal resolution (Committee on Earth Observation Satellites (CEOS), 2011; Geostationary Coastal and Air Pollution Events (GEOPCAPE), http://geo-cape.larc.nasa.gov).

In this paper, the regional scale Sulfur Transport and deposition Model (STEM) is used to address the issues raised above. Specifically we study the impacts of TBG pollutants on western US surface O$_3$ during summer (mid-June to mid-July) 2008 when the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) field campaign was conducted (http://www.espo.nasa.gov/arctas/) by National Aeronautics and Space Administration (NASA). This study extends the analysis period in Huang et al. (2010a), which focused exclusively on O$_3$ during a one-week period over California (CA), and expands the study domain to the western US. For this region, we estimate the contributions of various TBG pollutants to two policy-relevant O$_3$ metrics over different geographical locations and land types. We also compare the bias-corrected TBG contributions with those from other contributors to background O$_3$ (Sect. 3.1). We then evaluate the effects of model resolution and NA anthropogenic emissions on the uncertainties in estimated TBG contributions (Sect. 3.2). To better understand the mechanisms that determine the TBG contributions and their variation, we analyze in detail the sources of O$_3$ at three selected sites, and how the surface O$_3$ levels are connected to the airmasses aloft at these sites (Sect. 3.3). Finally, we investigate the effectiveness of currently available O$_3$ observations in identifying a LRT episode and reducing the errors in modeled total O$_3$ and the estimated TBG contributions (Sect. 3.4).

2 Data and methods

2.1 Study period, meteorological conditions and fire activities

The study period spans from 16 June to 14 July, 2008, during which the NASA ARCTAS-CARB and ARCTAS-B field experiments were conducted (Jacob et al., 2010).

Climatologically, the central and eastern Pacific during summertime is dominated by a surface high-pressure system, while Asia and the western Pacific experience a low-pressure system associated with the seasonal monsoon. Fue1berg et al. (2010) generalized synoptic conditions during 18 June–13 July, 2008, and found no major departures from climatology. Cyclones were frequent and intense, mostly forming over Northern Russia and Canada, but had little impact on CA. The jet stream at 300 hPa was located over central China (close to climatology) and northern Asia (with strong positive anomaly).

Fire activity was overall high during summer 2008 over CA, Canada, and Eurasia. Rapid PAN conversion from fire-emitted NO$_x$ was indicated, and the lifting of emissions above the boundary layer due to buoyancy led to LRT events (Jacob et al., 2010). LRT and NA fire plumes were frequently sampled by the DC-8 aircraft (http://www.espo.nasa.gov/arctas/flightDocs.php) during ARCTAS. Compared with previous years fire records (Table S1), the 2008 Siberia fire counts and total radiative power were higher, but with a lower value of radiative power per plume (RPPP) than those in 2002–2003 (Bertschi et al., 2004 and Jaffe et al., 2004 showed the strong impacts of summer 2003 Siberia fires on northwestern US air quality).

A record lack of rainfall, severely dry vegetation and uncharacteristically windy weather combined to cause the strong fire activity over CA and Oregon (OR), the majority of which started from 20–21 June due to lightning and dry thunderstorms over northern and central CA. The areas burned in 2008 (∼1.47 million acres) far exceeded previous years (2003–2007 average: 729 986 acres, http://www.fire.ca.gov/downloads/redbooks/2008/02-wildland-statistic-all-agencies/11-2008-FIRE-SUMMARY.pdf). Fires can result in O$_3$ enhancements, which can be intensified when interacting with urban smog over CA (Singh et al., 2012).

2.2 Observation data

The observations used as model inputs and to evaluate/improve the model performance are summarized in Table 1. They include:

1. Surface O$_3$ measurements: Hourly O$_3$ at all US EPA Air Quality System (AQS) and Clean Air Status and Trends Network (CASTNET) sites in CA, OR, Nevada (NV), Washington (WA) and Idaho (ID) (multiple measurement methods described in Table 1); and hourly O$_3$ measurements by UV Photometric Ozone Analyzer at Mt. Bachelor Observatory (MBO, topography ∼2.7 km a.s.l.). This high-altitude site has been demonstrated to represent LRT of pollution into the northwestern US (e.g., Fischer et al., 2010, 2011; Weiss-Penzias et al., 2007; Ambrose et al., 2011);

2. Ozone sondes: Twenty O$_3$ sondes launched (8 in June, 12 in July) at Trinidad Head (THD, ∼20 m a.s.l.), mostly at ∼19:00–22:00 UTC (noon-03:00 p.m. Pacific Daylight Time (PDT)) in support of ARCTAS. THD is a coastal remote air quality measurement site located in northern CA, which is thought to well represent the properties of airmasses entering the US (Oltmans et al., 2008);

3. Aircraft measurements: CO, O$_3$, total oxides of nitrogen (NO$_x$), and PAN sampled on the 22 June DC-8 flight off shore of CA were used to evaluate the
Table 1. Description of observational datasets used in this study.

<table>
<thead>
<tr>
<th>Observational data</th>
<th>Location</th>
<th>Dates of the observations</th>
<th>Spatiotemporal resolution</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground O$_3$</td>
<td>U.S. EPA AQS sites in CA, NV, OR, WA, and ID</td>
<td>16 June–14 July</td>
<td>1 h</td>
<td>Multiple methods: UV; UV absorption; UV radiation absorption; UV 2B Model 202</td>
</tr>
<tr>
<td>Ground O$_3$</td>
<td>Eight CASTNET sites in CA, NV, OR, WA, and ID</td>
<td>16 June–14 July</td>
<td>1 h</td>
<td>UV absorbance</td>
</tr>
<tr>
<td>Site O$_3$</td>
<td>MBO (44° N, −121.7° W, ~2.7 km a.s.l.)</td>
<td>16 June–14 July</td>
<td>1 h</td>
<td>Ultraviolet (UV) Photometric Ozone Analyzer</td>
</tr>
<tr>
<td>O$_3$ sondes</td>
<td>THD (40.8° N, −124.2° W, ~20 m a.s.l.)</td>
<td>20 June–12 July</td>
<td>mostly ~19:00 UTC, 20 days</td>
<td>Electrochemical detection methods through the reaction of O$_3$ in an aqueous potassium iodide solution in an electrochemical cell</td>
</tr>
<tr>
<td>DC-8 CO</td>
<td>Eastern Pacific (flight track in Fig. 1g)</td>
<td>22 June</td>
<td>1 min (DC-8 speed: ~14 km min$^{-1}$)</td>
<td>Diode laser spectrometer</td>
</tr>
<tr>
<td>DC-8 O$_3$ &amp; NO$_x$</td>
<td>Northern Hemisphere</td>
<td>30 June and 2, 4, 6 July</td>
<td>every other day, 2° × 4°</td>
<td>Measures the infrared-light energy (radiance) emitted by Earth’s surface and by gases and particles in Earth’s atmosphere</td>
</tr>
<tr>
<td>DC-8 PAN</td>
<td>Eastern Pacific (150–120° W, 30–60° N)</td>
<td>16 June–14 July</td>
<td>See sampling density plot in Fig. 1g</td>
<td>Tropospheric Emission Spectrometer (TES) Level 3 carbon monoxide (CO) and tropospheric O$_3$ columns on multiple days were used to locate the movement of transported pollutants from Asia to the western US, and the Level 2 V004 nadir O$_3$ vertical profiles from special observations (in the “step-and-stare” mode where the separation between observations is ~35 km along the orbit, Beer, 2006) were used for evaluating the model performance over the eastern Pacific and for DA on 5 July. TES Level 2 data does not have the capability</td>
</tr>
</tbody>
</table>
of resolving the boundary layer \(O_3\) distribution except in summertime when there is strong thermal contrast between ground and air, and has \(\sim 5\% - 15\%\) positive biases over LIDAR and sonde profiles (Nassar et al., 2008; Richards et al., 2008; Boxe et al., 2010); OMI Level 2 V003 \(O_3\) vertical profiles where cloud fraction = 0 (selected by Moderate Resolution Imaging Spectroradiometer (MODIS) MOD06_L2 cloud products (Platnick et al., 2003) as suggested by Russell et al., 2011) were also assimilated on 5 July. The OMI vertical profiles have larger horizontal coverage but much lower vertical resolution than TES, showing overall positive biases ranging from \(<10\%\) to \(\sim 30\%\) for mid-latitude regions, with lower sensitivity at lower and upper troposphere (Wang et al., 2011; Kroon et al., 2011; Veeckind et al., 2009); Daily total \(O_3\) columns from OMI were used in the online Tropospheric Ultraviolet-Visible (TUV) radiation model (Madronich, 2002) to generate the photolysis rates for STEM.

2.3 STEM model experiments and input data

We simulated the study period using the full-chemistry version of STEM (2K3) modeling system, including its forward and adjoint versions, which have been used and evaluated in a number of field campaigns in the past decade (e.g., Carmichael et al., 2003a, b; Tang et al., 2004, 2007; Adhikary et al., 2010; Stith et al., 2009). The full-chemistry version of STEM calculates gas-phase chemistry reactions based on the SAPRC 99 gaseous chemical mechanism (Carter, 2000) with thirty photolysis rates calculated online by the TUV model.

A set of simulations were performed using a continental scale \(60 \times 60\) km polar stereographic grid with 18 vertical layers in the troposphere. The re-analyzed tropopause (http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.tropopause.html) for this study period ranged from 120–220 hPa, increasing with latitude. The STEM model top is placed at \(\sim 170–210\) hPa. These simulations were analyzed to characterize the general picture of pollutant distributions over the eastern Pacific and continental US. A set of simulations were also conducted using a \(12 \times 12\) km Lambert conformal conic grid over the western US, with 32 vertical layers in the troposphere. They were used to study in greater detail the processes that link the airmasses aloft to the surface. The 18 layer grid had \(\sim 7\) layers below 1 km and \(\sim 10–11\) layers below 4 km. The 32 layer grid had \(\sim 11\) layers below 1 km and \(\sim 20–21\) layers below 4 km.

2.3.1 Model inputs

We conducted base simulations in both the \(60\) km and \(12\) km grids (C0 and F0 in Table 2, respectively). Meteorology fields for both grids were generated by the Advanced Research Weather Research & Forecasting Model (WRF-ARW) (Skamarock et al., 2008), driven by Global Forecast System and North American Regional Reanalysis data (Mesinger et al., 2006), respectively. The same physics options were used as in Huang et al. (2010a). In the \(60\) km/18 layer base case C0, lateral boundary conditions (LBCs) for thirty gaseous species and top boundary conditions (TBCs) for ten gaseous species (\(O_3\), \(CO\), \(NO\), \(NO_2\), \(NO_3\), \(HNO_3\), \(HNO_4\), \(PAN\), \(N_2O_5\), and \(H_2O_2\)) were downscaled from archived (\(2^\circ \times 2^\circ\) horizontal and 6-h temporal resolution) Real-time Air Quality Modeling System (RAQMS) (Pierce et al., 2007) global real-time chemical analyses which assimilated the OMI \(O_3\) columns and Microwave Limb Sounder (MLS) stratospheric \(O_3\) profiles. The \(60\) km LBCs for black carbon, organic carbon, dust, sea salt and sulfate were taken from the \(60\) km hemispheric tracer results (Huang et al., 2012). The \(12\) km BCs came from the \(60\) km STEM full-chemistry simulations for both gas and aerosol species.

Since time-varying BCs downscaled from results in a coarser grid may significantly affect the regional model results (Tang et al., 2007; Huang et al., 2010a; Pfister et al., 2011a), we evaluated the BCs used in this study by comparing RAQMS and \(60\) km STEM results with: (1) \(O_3\), \(CO\), \(PAN\) and \(NO_2\) sampled by the 22 June DC-8 flight over the eastern Pacific, and (2) TES nadir \(O_3\) vertical profiles for the days that “step and stare” observations were available over the eastern Pacific (150–120\(^\circ\) W, 30–60\(^\circ\) N) (Fig. 1). Unlike the flight-observed vertical structures over the terrestrial polluted regions such as southern CA (Huang et al., 2011) and the Central Valley, the elevated concentrations for these species over the eastern Pacific are seen in the middle and upper troposphere. The RAQMS-modeled PAN, \(NO_2\), and \(O_3\) agree well with the aircraft observations, with slight overprediction \(<4\) km, while \(CO\) shows 40–50 ppb bias below 4 km, and low variability at higher altitudes. The \(60\) km STEM simulations are similar to RAQMS with slight improvement (e.g., for \(NO_3\) below 4 km). Both mean RAQMS and STEM \(60\) km \(O_3\) profiles (with the TES observation operator (Sect. 2.4) applied) generally show good agreement with the TES retrieval.

Anthropogenic emissions in the \(60\) km simulations were taken from the 2001 National Emissions Estimate Version 3 (NEI 2001), an update of the 1999 US National Emissions Inventory with growth factors applied by source classification code, and augmented with national inventories for Canada (2000) and Mexico (1999). Biogenic emissions of monoterpenes and isoprene were from twelve-year-averaged values from the OrChidee model (Lathiere et al., 2006). Daily biomass burning emissions were provided by RAQMS (the Cooperative Institute for Meteorological Satellite Studies). The total emissions were then unevenly distributed vertically from the surface to \(\sim 4–5\) km with nonlinear factors decreasing from 0.12 to 0.013 as the model height increased (Adhikary et al., 2010). For the \(12\) km simulations over CA and during the ARCTAS-CARB mission period, we used daily-varying anthropogenic and biogenic emissions re-gridded from a recent California Air Resources Board (CARB) 4 km emission inventory (received in July 2009, by personal contact with A. Kaduwela and C. Cai in CARB). For the time
Fig. 1. Observed and modeled (RAQMS and STEM 60 km) vertical profiles along the outbound part of the 22 June DC-8 flight, for (a) PAN; (b) NO$_y$; (c) CO; and (d) O$_3$. Comparison between TES and (e) RAQMS and (f) STEM 60 km modeled O$_3$ over the eastern Pacific. TES observational operator was applied. (g) TES special observation sampling density in the compared domain for STEM. Sampling density = number of samples in each $1^\circ \times 1^\circ$/total number of samples. The outbound part of the 22 June DC-8 flight path is shown as purple line.

period outside of the ARCTAS-CARB mission, we used the averaged CARB emissions without daily variation. Anthropogenic and biogenic emissions outside of the CARB domain were same as those used in 60 km. Biomass burning total emissions were generated with PREP-CHEM-SRC (Freitas et al., 2011) by processing the MODIS-detected point fire information at 1 km ground resolution (Giglio et al., 2003; Davies et al., 2009). The total emissions were then unevenly distributed from surface to $\sim$1.5--2 km, with the same nonlinear curve used in the 60 km. The injection heights were closer to the analyzed satellite (i.e., Multi-angle Imaging Spectro-Radiometer (MISR)) wildfire plume injection heights during previous years over various regions, Table S1).

2.3.2 Forward sensitivity simulations

Eleven forward sensitivity simulations (Table 2, Cases C1--C11) were conducted in the 60 km/18 layer grid to study the TBG impacts on O$_3$ distributions. To estimate the effects of the UTLS airmasses, the O$_3$ concentrations at the TBC were perturbed by 50% in Case C1. Three simulations (Cases C2--C4) were conducted to study the surface O$_3$ response curve to perturbations in BCs, where O$_3$ concentrations at both TBC and LBC were reduced by 75%, 50%, and 25%, respectively. To investigate the influence of TBG precursor species, another three simulations were performed in which eight non-O$_3$ species (CO, NO, NO$_2$, NO$_3$, HNO$_3$, PAN, and N$_2$O$_5$) in the LBCs and TBCs were perturbed by 75%, 50%, and 25%, respectively (Cases C5-C7). With specific interest in the impacts of TBG PAN on O$_3$ levels, two simulations with PAN in TBC and LBC reduced by 50% and 25% were conducted (Cases C8-C9). In addition, PAN chemistry was partially (Case C10) and completely (Case C11) blocked in separate simulations, and the differences in PAN and O$_3$ levels between these two cases represent the amounts of decomposed transported PAN, and its contributions to O$_3$.

Forward sensitivity simulations with TBC and LBC O$_3$ perturbed by 50% were also conducted: (1) under scaled US anthropogenic emissions (Case CR1) to compare with
the sensitivities generated between Cases C0 and C3 in the 60 km/18 layer grid; and (2) in a 60 km/32 layer (Cases CL0/CL1) and the 12 km (Cases F0/F1) configurations to discuss the impacts of model resolution on the sensitivities.

Biomass burning and biogenic emissions were turned off in two additional emission sensitivity simulations (Cases CBB and CBG) to compare their contributions to background O3 with the TBG at surface and selected sites (Sects. 3.1.4 and 3.3.2).

2.3.3 Four-dimensional variational (4D-Var) DA and adjoint sensitivity analysis

The performance of contemporary models is highly dependent on parameterizations, the quality of model inputs (e.g., emissions and meteorological fields), chemical mechanisms, and resolution (Stevenson et al., 2006; Shindell et al., 2006; Fiore et al., 2009; Hakami et al., 2005, 2006). Accurately modeling of air pollutants distributions still remains a challenge, especially for O3 which is involved in complex chemical processes. DA is an efficient mathematical method to improve the model performance by integrating observations, and the 4D-Var method has shown moderate/strong capabilities of improving modeled O3, compared to other DA techniques (e.g., Singh et al., 2011; Wu et al., 2008). This method seeks the optimal solution to minimize the cost functional in Eq. (1):

$$ J(c_0, p) = \frac{1}{2} \left( c_0 - c_0^b \right)^T \mathbf{B}^{-1} \left( c_0 - c_0^b \right) + \frac{1}{2} \left( p - p^b \right)^T \mathbf{P}^{-1} \left( p - p^b \right) + \frac{1}{2} \sum_{i=0}^{N} (h(c_i) - y_i)^T \mathbf{O}_i^{-1} $$

where \( \mathbf{B} \), \( \mathbf{P} \), and \( \mathbf{O} \) are error covariance matrices for the a priori model forecast (background), for any model parameters (such as emissions), and for available observations at any instant time \( t = t_i \) within the assimilation window, respectively. The \( h \) operator calculates the observation vector \( y = y(x, t) \) from the model space \( c = c(x, t) \).

The 4D-Var method minimizes Eq. (1) by applying minimization routines (in this study we use Quasi-Newton limited memory-Broyden-Fletcher-Goldfarb-Shanno (L-BFGS), a limited-memory quasi-Newton code for bound-constrained optimization as introduced by Zhu et al. (1997) and applied by Chai et al. (2006, 2007) in STEM 4D-Var) through iterations, and requires a model and its adjoint. The evolution of the adjoint variable vector \( \lambda \) reads as

$$ \frac{\partial \lambda}{\partial t} + \nabla \cdot (u \lambda) = -\nabla \cdot \left( \frac{\rho K \cdot \nabla \lambda}{\rho} \right) - (F \cdot \lambda) - \phi $$

where \( u \) is the wind field vector, \( \rho \) the air density, \( K \) the turbulent diffusivity tensor, and \( \phi \) is a forcing functional vector which will be defined in Sect. 2.3. The backward integration of equation (2) gives adjoint variables at any time, and the variation of the cost functional due to small changes in initial conditions is

$$ \delta J = \left[ \lambda_0^T + (c_0 - c_0^b)^T \mathbf{B}^{-1} \right] \cdot \delta c_0 $$

where \( \lambda_0^T + (c_0 - c_0^b)^T \mathbf{B}^{-1} \) is the gradient information needed for the minimization. In contrast to the model forward sensitivity studies which quantify the response of chemical distributions in all grids at future times to the perturbation of model inputs/parameters, the distributions of the adjoint variable \( \lambda_n \) in the entire computational domain, named as “instantaneous areas of influence” (Sandu et al., 2005), reflect backward in time the change of chemical distributions of the species \( n \) in grids that influence the response function (e.g., O3 concentrations at given receptor at a specific time). The adjoint values can: (1) help understand the specific processes that lead to a state of the atmosphere; (2) identify areas where perturbations/uncertainties in the concentration of the chemical species of interest at earlier times will result in significant changes in O3 levels at the receptor site at future time; and (3) help explain the 4D-Var DA efficiency. Adjoint sensitivity analysis and the 4D-Var DA have been applied in a number of previous studies from global to regional scales for gases and aerosols (e.g., Zhang et al., 2009; Kopacz et al., 2010; Zoogman et al., 2011; Henze et al., 2009; Carmichael et al., 2008; Chai et al., 2006, 2007, 2009; Hakami et al., 2005, 2006).

This study used STEM adjoint sensitivity simulations to understand the surface O3 sensitivities at two selected receptor regions (i.e., northern CA and OR (NWR) and southern CA (SCR)) with respect to concentrations of O3 backward in time during the study period (Cases FA1/FA2 and CA1/CA2 for the 12 km and 60 km/18 layer configurations, respectively, in Table 2). These cases help interpret the linkages between O3 at surface and at upwind measurement sites, as well as the effect of model resolution on the forward sensitivities in Sect. 3.2.2. The adjoint simulations require completion of forward model simulations, and they used the same model inputs as in the forward simulations. In each case, 27 adjoint sensitivity simulations (spanning the period of 16 June–14 July) were conducted, with 00:00 UTC of each day during 18 June–14 July as the final time, and an interval for each simulation of 49 h.

Several types of observations (i.e., hourly surface O3, and the vertical profiles on 5 July from THD sonde, TES and OMI) were assimilated into the 12 km grid from 5 July, 18:00 UTC to 7 July, 00:00 UTC, a LRT episode detected by satellite and in-situ measurements (Ambroise et al., 2011).

Ozone initial conditions were controlled in all DA cases (Table 3). The background error correlation matrix was prepared through the NMC (National Meteorological Center, now National Centers for Environmental Prediction) method using the 3-day, 2-day and same-day forecasts, and was inverted using the truncated singular value decomposition (TSVD) (Chai et al., 2007). The construction of background variances followed the method in Singh et al. (2011). Observation error
Table 2. Description of STEM base and sensitivity (forward and adjoint) simulations a.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Model grid used</th>
<th>Description of model inputs and perturbations</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>Base case 12 km/32 L</td>
<td>CARB anthropogenic and biogenic emissions, MODIS/PREC-CHEM-SRC biomass burning emissions, WRF meteorology, TBCs and LBCs from the Case C0 results</td>
</tr>
<tr>
<td>F1</td>
<td>50% BC O₃</td>
<td>TBCs and LBCs from the Case C3 results</td>
</tr>
<tr>
<td>FA1/FA2</td>
<td>Adjoint NWR/SCR cases 12 km/32 L</td>
<td>Northern California and Oregon/ Southern California as receptors, control surface O₃ at 00:00 UTC; simulation window for each day is 49 h.</td>
</tr>
<tr>
<td>C0</td>
<td>Base case 60 km/18 L</td>
<td>NEI 2001 anthropogenic emissions, Orchidee biogenic emissions, RAQMS biomass burning emissions, WRF meteorology, RAQMS and 60 km tracer results (Huang et al., 2012) as gases and aerosol boundary conditions, respectively.</td>
</tr>
<tr>
<td>C1</td>
<td>50% TBC O₃ 60 km/18 L</td>
<td>TBC O₃ reduced by 50%</td>
</tr>
<tr>
<td>C2/C3/C4</td>
<td>25%, 50% and 75% BC O₃ 60 km/18 L</td>
<td>TBC and LBC O₃ reduced by 75%, 50% and 25%</td>
</tr>
<tr>
<td>C5/C6/C7</td>
<td>25%, 50% and 75% BCs for multiple species b 60 km/18 L</td>
<td>TBCs and LBCs for multiple species reduced by 75%, 50% and 25%</td>
</tr>
<tr>
<td>C8/C9</td>
<td>50% and 75% BC PAN 60 km/18 L</td>
<td>TBC and LBC PAN reduced by 50% and 25%</td>
</tr>
<tr>
<td>C10/C11</td>
<td>PAN composition/ composition and decomposition off 60 km/18 L</td>
<td>Reaction(s) of PAN composition/composition and decomposition are blocked</td>
</tr>
<tr>
<td>CA1/CA2</td>
<td>Adjoint NWR/SCR cases 60 km/18 L</td>
<td>Northern California and Oregon/ Southern California as receptors, control surface O₃ at 00:00 UTC; simulation window for each day is 49 h.</td>
</tr>
<tr>
<td>CL0</td>
<td>Base case 60 km/32 L</td>
<td>Same as C0, but using 32 vertical layers.</td>
</tr>
<tr>
<td>CL1</td>
<td>50% BC O₃ 60 km/32 L</td>
<td>Same as C3, but using 32 vertical layers.</td>
</tr>
<tr>
<td>CR0</td>
<td>scaled emissions 60 km/18 L</td>
<td>Same as C0, but scaled the US anthropogenic CO, NOₓ and VOCs emissions based on EPA emission trend.</td>
</tr>
<tr>
<td>CR1</td>
<td>50% BC O₃ and scaled emissions 60 km/18 L</td>
<td>Same as C3, but scaled the US anthropogenic CO, NOₓ and VOCs emissions based on EPA emission trend.</td>
</tr>
<tr>
<td>CBB</td>
<td>biomass burning emissions off 60 km/18 L</td>
<td>Same as C0, but not including the biomass burning emissions</td>
</tr>
<tr>
<td>CBG</td>
<td>biogenic emissions off 60 km/18 L</td>
<td>Same as C0, but not including the biogenic emissions</td>
</tr>
</tbody>
</table>

a The studied period for each simulation case in this table was 16 June–14 July, 2008.

b Multiple species in cases C5–C7 refer to the shared non-O₃ gaseous species in TBCs/LBCs, including: CO, NO, NO₂, NO₃, HNO₂, HNO₃, PAN and N₂O₅.

c L: Layers

Abbreviations
CARB: California Air Resources Board; NEI: National Emission Inventory; PAN: Peroxyacetyl nitrate; RAQMS: Real-time Air Quality Modeling System; TBCs/LBCs: Top/Lateral Boundary Conditions; WRF: Weather Research and Forecasting Model

covariance matrices are diagonal, and the selection of observation errors for each case (Table 3) accounted the instrument uncertainties and the representative errors (due to the gap of spatial resolution between measurements and model). Upper-limits of each chemical species (useful for the optimization routine, as described in Chai et al., 2006) varied vertically,
and for O₃ they were set at 200 ppb from surface to mid-troposphere, and 400 ppb in the upper troposphere reflected by satellite retrievals on 5 July (Sect. 3.4). All cases used 25 iterations, and the cost function decreased significantly after ~12–15 iterations (e.g., >~40 %, Fig. S6).

2.4 Observation operator and the forcing term

The observation operator h(c), which can vary for different types of observations, enables the comparison of modeled O₃ fields with the observations. It is critical for (1) evaluating model performance; and (2) calculating cost function and the forcing term for DA. For surface measurements and sondes, h(c) is linearly-interpolated model output to observations locations.

The TES retrieval follows (4) (Chapter 8, TES L2 data user’s guide, Version 5.0, 2011):

\[ \hat{z} = z_c + A_{\text{TES}}(z - z_c) + \varepsilon \]  

(4)

where \( \hat{z} \), \( z \) and \( z_c \) are the natural log form of the estimated state, true state, and constraint vectors for O₃ concentrations (in volume mixing ratio (vmr) units), respectively. \( \varepsilon \) is the TES observation error that assumed to have mean zero and covariance \( S \) (Bowman et al., 2006), and \( A_{\text{TES}} \) is the averaging kernel matrix (usually non-symmetric) reflecting the sensitivity of retrieval to changes in the true state (Rogers, 2000). Retrieval in vmr is \( y = \exp(\hat{z}) \). The TES observation operator \( h_z \) for O₃ is written in (5):

\[ h_z = z_c + A_{\text{TES}}(\ln(F_{\text{TES}}(c)) - z_c) \]  

(5)

where \( F_{\text{TES}} \) projects the modeled O₃ fields \( c \) to the TES grid using spatial and temporal interpolation. The resulting mismatches in vmr between TES retrieval and the model state are the differences of the exponential form of (4) and (5) (i.e., \( \exp(\hat{z})-\exp(h_z) \)) at each location along the orbit, which is used to calculate the cost functional in Eq. (1). Usually \( \varepsilon \) is much lower than the mismatches between model and satellite retrieval.

The OMI observation operator is built upon the similar function of constraint vectors and averaging kernels as for TES, except that the O₃ concentrations in retrievals are in Dobson Units (DU) per layer, and should be converted to layer average by using (6):

\[ \langle \text{vmr} \rangle_i \text{(ppb)} = 1.2672 \times 10^3 \times \frac{N_i}{dP_i} \]  

(6)

where \( N_i \) is partial column in DU in the layer, and \( dP_i \) is the pressure difference between the bottom and the top of the layer in hPa. Accordingly, the OMI averaging kernel for the profiles in DU should be converted for the profiles in vmr using Eq. (7) (Veefkind et al., 2009):

\[ A_{\text{OMI}}^\text{vmr} = A_{\text{OMI}}^\text{DU} \times \frac{dP_j}{dP_i} \]  

(7)

The forcing term \( \phi \) in Eq. (2) appears as in Eq. (8):

\[ \phi = H^T O^{-1} (h(c) - y) \]  

(8)

where \( H = \partial h(c)/\partial c \) and \( y \) is the observation.

For assimilating surface observations, \( h(c) = H \cdot c \), where \( H \) reflects interpolation in space and time when constructing model counterparts of the observations. For assimilating TES and OMI profiles, \( H^T \) follows Eqs. (9) and (9), respectively.

\[ H^T = \left( \frac{\partial [\exp(\hat{h}_z)]}{\partial c} \right)^T = \left( \frac{\partial [\exp(z_c + A_{\text{TES}}(\ln(F_{\text{TES}}(c)) - z_c))]}{\partial c} \right)^T \]  

(9)

\[ H^T = \frac{F_{\text{OMI}}^\text{TES}}{A_{\text{OMI}}} \cdot \frac{A_{\text{OMI}}^\text{vmr}}{} \]  

(10)

3 Results and discussions

3.1 Forward sensitivity of surface O₃ to BCs

3.1.1 Model evaluation for base case surface O₃

Figure 2 compares two O₃ regulatory metrics at surface sites (225 AQS sites and 8 CASTNET sites that had data available for \( > = 75 \% \) of the daytime through the study period and were located inside of both 60 km and 12 km model domains) with the model results generated in 60 km and 12 km grids. The two metrics are Monthly mean Daily maximum 8-h Average O₃ (MDA8) and W126 Monthly Index (MI, calculation followed the method: http://www.epa.gov/tn/analysis/w126.htm) for primary and secondary O₃ standards, which set limits to protect human health and public welfare, respectively. Both observed and modeled O₃ show highest concentrations over the Central Valley and southern CA (with MDA8 > 75 ppb and W126 > 15 ppm-h). Ozone levels over most areas of NV, OR and WA are lower (with MDA8 < 60 ppb and W126 < 7 ppm-h). The 60 km and 12 km simulations present similar gradients, and the 12 km results capture more accurately the local features. The predictions show higher positive biases along the coast, larger in the 60 km grid, which may be caused by uncertainties in emissions (especially the biomass burning emissions) and the BCs, as well as the inaccuracies in predicted meteorology associated with complicated land-sea breezes and topography.

Statistical comparisons between the observed and modeled MDA8 and W126 were calculated at these AQS (Table 4a) and CASTNET sites (Table 4b), including root mean square error (RMSE), mean bias (bias = modeled-observed), mean error (error = |modeled-observed|), mean fractional bias (fractional bias = 2 × (modeled-observed)/(modeled + observed)) and mean fractional error (fractional error = 2 × |(modeled-observed)/(modeled + observed)|) (suggested by Boylan and Russell, 2006). The model performance is generally good for MDA8, similar to the contemporary community chemical.

weather forecast model evaluations (e.g., McKeen et al., 2009), and the model performs better at CASTNET sites than at AQS sites, due to the fewer number of CASTNET sites and weaker anthropogenic influences on O$_3$ over these rural/remote locations. The 12 km results show better performance with lower bias, error and RMSE.

### 3.1.2 Impacts of multiple TBG species on surface O$_3$

The sensitivities of surface MDA8 and W126 metrics to various species in BCs were evaluated by a number of forward sensitivity simulations (Sect. 2.3.2), and the results were averaged over ten EPA regions (Fig. 3a–b). The largest sensitivities are found in the west (Regions 8, 9, and 10), which is less populated (text below Fig. 3c) and has larger grass/shrub coverage (barplot in Fig. 3c, grouped from the US Geological Survey (USGS) 24 land types used in the model simulations, Table S2). The eastern US has a higher population density and larger forest coverage, and shows $\sim$1/3 of the sensitivity to TBG pollutants as that for the west. For all EPA regions, surface MDA8 and W126 are most sensitive to TBG O$_3$, followed by PAN.

Sonde-based studies have shown that the impacts of stratospheric O$_3$ may be the main reason for modifying the O$_3$ vertical structures in summer (Cooper et al., 2007). The stratospheric O$_3$ impacts on tropospheric O$_3$ distributions in regional chemical transport models can be affected by O$_3$ variability in model TBCs, the location(s) of the model top boundary, and the model vertical resolutions. The period-mean O$_3$ TBC taken from RAQMS ranged from 80–220 ppb, decreasing from June to July. The sensitivities of MDA8 and W126 to 50 % perturbation in the O$_3$ TBCs in the western US are below 1 ppb and 1 ppm-h, respectively (Fig. 3a–b), with higher values over the high topography regions of eastern ID, Wyoming (WY) and Colorado. This method ignores the impacts of stratospheric-origin O$_3$ included in LBC O$_3$.

We further analyzed the sensitivity of MDA8 and W126 in Regions 9 and 10 over different geographical regions/land types to the magnitude of BC perturbations for multiple species (Fig. 3e–f). The TBG impact is largest on grass/shrub
Fig. 3. Surface (a) MDA8 and (b) W126 responses to perturbations in boundary conditions in the 60 km/18 layer grid, shown by ten EPA regions. (c) Fractions of the grouped USGS land types (bar) and population densities (text below the bar) in ten EPA regions. (d) The ten EPA regions; Surface (e) MDA8 and (f) W126 responses to perturbations of various species in boundary conditions in the 60 km/18 layer grid, shown by geographical regions (EPA Regions 9 and 10) and grouped USGS land types, respectively (“precursors” in legends: the cases in which CO, NO, NO₂, NO₃, HNO₃, HNO₄, PAN, N₂O₅ in BCs were perturbed).
Table 3. Description of 4-D Var data assimilation cases in the 12 km model grid.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Descriptions</th>
<th>Observation error (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>Assimilate observations from AQS, CASTNET and MBO sites</td>
<td>constant 3 ppb: maximum representative error</td>
</tr>
<tr>
<td></td>
<td>Assimilate available observations at all times in the assimilation window.</td>
<td>(defined by Chai et al., 2007) in each grid</td>
</tr>
<tr>
<td></td>
<td>CASTNET and MBO observations were assimilated at actual altitudes. AQS</td>
<td>&amp; ~10 % of mean observations in the assimilation window</td>
</tr>
<tr>
<td></td>
<td>observations were assimilated from the surface level.</td>
<td></td>
</tr>
<tr>
<td>AT</td>
<td>Assimilate O\textsubscript{3} vertical profiles from TES special observations</td>
<td>constant 6 ppb for TES (~7 % of mean 84 ppb):</td>
</tr>
<tr>
<td></td>
<td>TES special observations were assimilated at Aura overpass time (~22:00 UTC,</td>
<td>Nassar et al., 2008, and Boxe et al., 2010</td>
</tr>
<tr>
<td></td>
<td>5 July). Only the observations with quality flag = 1 and cloud optical</td>
<td></td>
</tr>
<tr>
<td></td>
<td>depth &lt;= 2.0 were used.</td>
<td></td>
</tr>
<tr>
<td>AO</td>
<td>Assimilate OMI O\textsubscript{3} vertical profiles</td>
<td>constant 11 ppb for OMI: 10 % of mean ~110 ppb</td>
</tr>
<tr>
<td></td>
<td>OMI observations were assimilated at Aura overpass time (~22:00 UTC, 5 July).</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Only the observations at places where MODIS cloud fraction = 0 were used</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(suggested by Russell et al., 2011).</td>
<td></td>
</tr>
<tr>
<td>AD</td>
<td>Assimilate THD O\textsubscript{3} sonde</td>
<td>constant 5 ppb: ~10 % (Thompson et al., 2010;</td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{3} sondes at THD were binned into model levels and</td>
<td>Liu et al., 2009) of mean observations at all</td>
</tr>
<tr>
<td></td>
<td>assimilated at the launch time (~19:00 UTC, 5 July).</td>
<td>levels in the troposphere</td>
</tr>
<tr>
<td>AST</td>
<td>Assimilate site &amp; TES O\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>ASO</td>
<td>Assimilate site &amp; OMI O\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>ASD</td>
<td>Assimilate site &amp; THD O\textsubscript{3} ozoneonde</td>
<td></td>
</tr>
</tbody>
</table>

* All cases used the same background error correlation matrix calculated by the NMC method as introduced by Chai et al. (2007). Assimilation window was 18:00 UTC, 5 July–00:00 UTC, 7 July 2008 (30 h).

and smallest on forest for all sensitivity cases. Both MDA8 and W126 show close-to-linear response to perturbations in several non-\textsubscript{O3} species in BCs, but non-linear responses to perturbations in BC O\textsubscript{3} and PAN. MDA8 sensitivity over Region 9 shows stronger non-linearity to BC PAN perturbations than over Region 10, reflecting stronger local impacts.

### 3.1.3 TBG contributions with bias corrections

We estimated the absolute TBG contributions to surface MDA8 and W126 by summing up the contributions from TBG O\textsubscript{3} and its precursors, extrapolated from their sensitivity curves to the BC perturbations. The extrapolation method is described in detail (and for W126 we compared the impact of using four different extrapolation methods on the results) in Section S2 and Figs. S1 and S2. The maximum TBG contributions over the western US occur over northwestern US (e.g., ID and OR) and the Central Valley, respectively (Fig. 4a,d). After exploring the relationships between the model biases in the base simulation and the estimated TBG contributions at surface sites (details in Sect. S3), we concluded that the bias-corrected estimates of TBG contributions to MDA8 are ~30–35 ppb for Regions 9 and 10. The contributions to W126 are ~10–17 ppm-h for Region 9 and ~3–4 ppm-h for Region 10.

Pfister et al. (2011b) concluded that 53 ± 21 % of CO over CA came from model boundary during ARCTAS, close to our estimates of TBG contributions to surface MDA8. They also found that ~1/4 of these (14 ± 6 % of the total) had an Asian origin. Based on this relationship and our estimates of TBG contributions, the upper limits of Asian contribution to MDA8 and W126 are ~9 ppb and ~1–4 ppm-h, respectively. Since O\textsubscript{3} and CO have different lifetimes and sources, a more quantitative estimation of the Asian emissions contribution to...
O$_3$ will require sensitivity simulations or tagging methods in global models.

3.1.4 Comparison with biomass burning and biogenic emissions contributions to background O$_3$

Two other background O$_3$ contributors, biomass burning and biogenic emissions, are compared with the TBG contributions and show more spatially-limited and weaker impacts (Fig. 4). Biomass burning contributes up to 18 ppb and 9 ppm-h to MDA8 and W126, respectively, with the strongest impacts over northern CA. Biogenic emissions have slight negative impacts over most regions in NV, ID, WA and OR, due to the NO$_x$ sensitive regime. The strongest sensitivities occur over northern CA and the Central Valley, up to $\sim$15 ppb and 6–8 ppm-h for MDA8 and W126, respectively.

3.2 Other factors affecting surface O$_3$ sensitivities to BCs

Because of the non-linearity of O$_3$ chemistry and the complex topography over the western US, in addition to the quality of BCs, other factors such as NA anthropogenic emissions and the model resolutions can also affect the model estimated TBG contributions. In this section, we discuss in detail their effects on surface O$_3$ sensitivities to 50% perturbations in BC O$_3$, since TBG O$_3$ is the major contributor among the TBG pollutants.

The spatial distributions of the sensitivities of MDA8 and W126 to 50% reduction in BC O$_3$ are shown in Fig. 5 for several western states. OR and WA show the lowest absolute sensitivity SEN1 (SEN1 = base case-sensitivity case) for W126 but the highest for MDA8, while broad regions in CA and NV show the highest SEN1 to W126 but lowest for
Fig. 5. The O$_3$ sensitivity to 50% reduction in O$_3$ boundary conditions. The surface O$_3$ sensitivity SEN1 (SEN1 = base case-sensitivity case) of (a) W126; (b) MDA8 and (c) ratio of (a)/(b). The surface O$_3$ relative sensitivity SEN2 (SEN2 = (base case-sensitivity case)/base case) of (d) W126; (e) MDA8 and (f) ratio of (d)/(e). Results are from the 60 km/18 layer grid. The mean sensitivities in (a) and (b) are 5.4 ppm-h and 15.5 ppb, respectively, over the plotted domain.

Table 4a. Statistics for observed and modeled surface O$_3$ metrics at EPA AQS sites as shown in Fig. 2 (better performance in bold). Model results were extracted at surface using the linear interpolation method$^{a,b}$.

<table>
<thead>
<tr>
<th>Statistics</th>
<th>MDA8</th>
<th>W126 MI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observation</td>
<td>60 km/18 L</td>
</tr>
<tr>
<td>Mean</td>
<td>57.63</td>
<td>74.08</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>16.75</td>
<td>7.78</td>
</tr>
<tr>
<td>Mean Bias</td>
<td>–</td>
<td>16.45</td>
</tr>
<tr>
<td>Mean Error</td>
<td>–</td>
<td>18.52</td>
</tr>
<tr>
<td>Root Mean Square Error</td>
<td>–</td>
<td>21.55</td>
</tr>
<tr>
<td>Mean Fractional Bias</td>
<td>–</td>
<td>0.28</td>
</tr>
<tr>
<td>Mean Fractional Error</td>
<td>–</td>
<td>0.31</td>
</tr>
</tbody>
</table>

$^{a}$Units (except Mean Fractional Bias/Error are dimensionless) for MDA8 are ppb; for W126 are ppm-h.

$^{b}$L: Layers
MDA8. ID shows strong SEN1 for both MDA8 and W126 due to its high topography. The relative sensitivities SEN2 (SEN2 = (base case-sensitivity case)/base case, dimensionless) of MDA8 and W126 both show maxima over the northwestern US (ID, WA and OR), where O3 in the base case is much lower than over CA. The different features in W126 are due to the non-linear function used in the calculation that gives greater weights for high hourly O3 concentrations. The ratio of W126/MDA8 sensitivities indicates regions where W126 levels are more sensitive to extra-regional sources than MDA8. Regions of high SEN1 ratios (>0.6) appear over the Central Valley and southern CA where regional photochemical production is strong. The SEN2 ratios are overall higher than those of SEN1, with the higher values in NV, ID and OR (>3).

3.2.1 Impacts of NA anthropogenic emissions

To evaluate the extent to which SEN1 of MDA8 and W126 are dependent on the magnitude of NA anthropogenic emissions, we conducted base and half BC O3 forward sensitivity simulations in the 60 km/18 layer grid, with US anthropogenic emissions for NOx, CO, and VOCs scaled by ~0.7, ~0.7 and ~0.9, respectively (based on the US emission trend from ~2000 to 2008 (http://www.epa.gov/ttnchie1/trends/, using data except wildfires, accessed in December, 2011). The changes in SEN1 of MDA8 and W126 in the scaled emission conditions are generally within ±1.5 ppb and ±1.5 ppm-h, respectively (Fig. 6a–b). The urban regions in CA show lower SEN1 for MDA8 but higher SEN1 for W126, while the remaining areas show the opposite sign for the changes (due to different O3 production regimes).

3.2.2 Impacts of model horizontal and vertical resolution

To assess the impacts of vertical resolution on SEN1 of MDA8 and W126, we conducted base and half BC O3 simulations in a 60 km/32 layer grid to compare with SEN1 in the 60 km/18 layer grid. Adding vertical resolution reduces SEN1 of MDA8 and W126 by up to ~10 ppb (10–40 %) and 6 ppm-h (30–50 %), respectively, and the largest reduction in SEN1 for MDA8 and W126 occur over the OR/ID mountain areas and ID/NV grass/shrub and forest areas, respectively.
The results in Sect. 3.1 show that TBG significantly affects western US surface $O_3$. To better understand the processes that link transported plumes to surface $O_3$, we studied in detail the $O_3$ sources at three sites (MBO, THD and South Coast (SC)) along the western US, and compared how $O_3$ aloft at these sites impacted downwind surface $O_3$ concentrations.

### 3.3.1 Evaluation of model base simulation at sites

Figure 7a compares the observed and modeled $O_3$ time series at MBO. Several high $O_3$ episodes were observed, with hourly maxima over 80 ppb. The model captures most of the observed variability, with major discrepancies at the beginning and end of the study period (18–20 June and 12–14 July), when predicted boundary layer heights (PBLH) were highest (not shown). Erroneously high mixed layer heights, too strong downwind transport, and/or uncertainties in BCs are possible reasons for the overprediction. Statistics for all simulations indicate better performance in the 12 km/layer grid (except correlation $r$): $r$, mean bias, mean error, and RMSE are 0.37, 4.28 ppb, 10.67 ppb, 14.00 ppb, respectively, compared to these in the 60 km/18 layer simulation: 0.56, 9.44 ppb, 12.42 ppb, 14.50 ppb.

The THD sonic data were binned to the 32 model layers and compared with the model simulations (Fig. 7c–e). The 12 km simulation captures much of the observed variability, including the strong episodes that occurred on 22–24 June (Huang et al., 2010a) and 5–7 July, as well as clean periods (e.g., 2–4 July). In the lower free troposphere (~1.5–4 km a.s.l.) mean $O_3$ levels ranged from <40 ppb to ~120 ppb and concentrations >40 ppb are observed 65 %–80 % of the times. Daily model performance statistics show $r$ values >0.5, RMSE <20 ppb, and biases across all levels <15 ppb. The model overpredicts $O_3$ near the surface, consistent with the evaluations at the coastal AQS sites (Sect. 3.1.1), and in the upper troposphere, possibly due to the BCs. The 60 km simulation looks similar in terms of the general temporal variability, but overpredicts some periods (e.g., 28–29 June) due to the uncertainties in biomass burning emissions, and misplaced some vertical features (e.g., 9 July).

Modeled $O_3$ at a CARB surface site SC, (i.e., LA North Main Street: 34.1°N, −118.3°W, elevation 87 m, http://www.arb.ca.gov/qaweb/site.php?s_arb_code=70087) was also compared with the observations (Fig. 7b). The strong $O_3$ diurnal cycle indicates local $O_3$ production, and again the 12 km simulation better captures the temporal variability, with higher correlation (0.61) than 60 km (0.25). The largest model discrepancies occur on 26 June and 10 July when the actual $O_3$ levels were low. The 60 km simulation shows ~20–30 ppb higher positive biases than...
12 km, reflecting its incapability of capturing the nighttime minima due to the smoothed/diluted NOx emissions and uncertain meteorology in the coarse grid over the urban area. The strong diurnal variations seldom modified the simulated O3 vertical structures above ~3 km. Elevated O3 concentrations were predicted above 5–6 km around 24 June and 6–8 July, but they remained decoupled from the lower troposphere (not shown).

3.3.2 O3 sensitivities to BCs and emissions at sites

The time series of O3 sensitivities to: (1) 50 % reduction in BC O3 in three model resolutions; (2) the scaled NA anthropogenic emissions in the 60 km/18 layer grid; and (3) zeroing out biomass burning and biomass burning emissions in the 60 km/18 layer grid are shown at MBO 2.7 km, THD 2.5 km and SC surface level (Fig. 8). Ozone levels at these altitudes are highly connected with downwind surface O3 levels as indicated in Sect. 3.3.3. Ozone sensitivities to BC O3 at THD and MBO show similar temporal variability and magnitude (10–40 ppb, with correlations of 0.6–0.8 depending on resolution), indicating that they are influenced by similar sources/synoptic flow conditions during this period. This supports the findings by Zhang et al. (2009) for spring 2006 when they found that both sites were affected by northern China emissions. The BCs used in analysis correctly reflect when they found that both sites were affected by northern China emissions. The BCs used in analysis correctly reflect the major LRT episodes (22–24 June and 5–7 July), resulting in good model performance at THD and MBO. The uncertainty in the BCs is the major reason causing the O3 overprediction at both locations during 18–20 June and after 12 July. An additional high O3 period (30 June–4 July) at MBO (above the period mean level shown as the thin horizontal red line) is shown to be affected by the NA anthropogenic and biomass burning emissions. Impacts of biogenic emissions are overall slightly negative due to the NOx sensitive condition. THD O3 at 2.5 km was intensively affected by northern CA wildfires, which led to O3 enhancements during ~29–30 June and ~10 July (as indicated from the high sensitivity (up to >50 ppb) to biomass burning emissions). Uncertainties in fire/biogenic emissions possibly caused the overprediction in O3 from the surface to ~4 km (Fig. 7e). The impacts of BC O3 at SC are smaller due to the lower altitude, with a similar diurnal cycle as the total O3 concentrations. SC O3 is less strongly affected by biomass burning than the other two locations, and the varied sensitivities to US anthropogenic emissions indicate the different photochemical regimes and meteorological conditions. The high positive sensitivities to anthropogenic and biogenic emissions after 10 July possibly caused the overprediction in O3 for this period.

3.3.3 Connection of surface O3 and O3 aloft at previous times

Trajectories and the Impacting Probability (IP) metric

The pathways of descending airmasses from MBO 2.7 km, THD 2.5 km and SC 1.5 km (~top of the PBL, based on measurements of daily maximum PBLH at Pasadena in spring 2010 ranging from ~600–1800 m, Newman et al., 2012) were studied by two-day forward trajectories (calculated hourly) based on the 12 km WRF meteorology. The trajectories originating from MBO at all night times (to minimize the local contributions and to study the influences of free troposphere air which typically has higher O3 concentrations) during the 29-day period were calculated, together with the forward trajectories originating from THD 2.5 km and SC 1.5 km at all day times during the studied period. Daytime trajectories were chosen because of the higher O3 and the dominance of on-shore flows during the daytime (Fig. S4).

The IP metric is an indicator of how often the entrainment of transported air occurs at a specific time, and was calculated at all local daytimes (Table 5). The MBO and THD airmasses show the highest chance to be entrained into the boundary layer in the early afternoon (i.e., IP = 0.66 and 0.34, respectively, at ~03:00 p.m. PDT), when the PBL is deep and well mixed over many regions. The overall higher IP for MBO than those for THD is because most of the impacted regions downwind of MBO have higher topography, as explained by Wigder et al. (2012). The IP values for airmasses 1.5 km above SC demonstrate a flatter shape than those for THD and MBO, and are greater than 0.5 during 09:00 a.m.–04:00 p.m. PDT. This reflects that on-shore winds and boundary layer growth quickly connect 1.5 km airmasses above SC with the surface regions.

Adjoint sensitivity: areas of influence

We calculated adjoint sensitivities to surface O3 at receptor regions to further explore the impacts of transport/subsidence of airmasses on surface O3. The STEM adjoint sensitivity
Fig. 7. (a) Observed and STEM modeled O$_3$ time series at the MBO site. The model results were extracted from the layer(s) that matched the actual MBO altitude. (b) Observed and STEM modeled O$_3$ time series at SC surface site. (c) Trinidad Head (THD) daily O$_3$ sonde data during the studied period, binned into 32 model layers; (d) STEM 12 km modeled THD O$_3$ daily vertical profiles at ozonesondes times during the same period; (e) STEM 60 km modeled THD O$_3$ daily vertical profiles at 18:00 UTC during the same period.

analysis has demonstrated advantages over trajectory analysis and previous correlation-based analysis (e.g., Huang et al., 2010a, b) in that it includes horizontal transport, vertical mixing and chemistry processes in the calculations (Sandu et al., 2005). The selected northwestern US receptor (NWR) (4250 grids) and the southern CA receptor (SCR) (1200 grids) (areas in the blue line boxes in Fig. 9a–b) were shown to be affected by the transported airmasses over MBO, THD or SC in the trajectory and correlation analyses (Huang et al., 2010b). The O$_3$ adjoint sensitivities ($\lambda$[O$_3$]) were calculated
Fig. 8. Time series of O$_3$ reductions at (a) MBO 2.7 km a.s.l.; (b) THD 2.5 km a.s.l.; and (c) SC lowest level, in response to 50% perturbations in O$_3$ boundary conditions (dBC), reduction in US anthropogenic emissions (dANemis) and zeroing out the North American biomass burning (BBemis) and biogenic emissions (BIOGemis). Time series of observations at the corresponding altitude and their period mean are drawn as the red thick and horizontal thin lines, respectively.

49 h backward in time from 00:00 UTC of each day, and the areas of influence for each case were averaged to produce the monthly mean areas of influence with 49 time steps, which are used for discussions below.

Figure 9a–b show the vertically-integrated λ[O$_3$] averaged over the previous day daytimes calculated on the 12 km grid. They show the locations that have the biggest impact on next day surface O$_3$ at NWR and SCR, respectively. Surface O$_3$ in the NWR at 00:00 UTC is sensitive to previous day O$_3$ concentrations over a large geographical region that extends over hundreds of kilometers (Fig. 9a). The western extent of the influence area helps identify the multiple transport pathways that bring eastern Pacific airmasses into this region, which are controlled by the moving Pacific-high pressure systems from June to July. Surface O$_3$ over southern CA is shown to be sensitive to O$_3$ in the Central Valley, and the near-shore areas along the central and south coast on the previous day-time, which indicates the impacts of inter-basin transport and sea breezes (Fig. 9b). Returning airmasses from NV to the northern Central Valley in the previous daytime also impact southern CA in the following day.

Similar adjoint sensitivity analysis was also done on the 60 km/18 layer grid. The results are qualitatively similar, but are much smoother than those for the 12 km analysis (Fig. S5).

Adjoint sensitivity: surface O$_3$ sensitivity to O$_3$ at selected sites at earlier times

To connect the results from forward trajectory analysis conducted for MBO, THD and SC, we plot the time-height curtain of the 12 km-calculated λ[O$_3$] at these sites (i.e., surface O$_3$ sensitivity to O$_3$ at these sites through time), normalized by the number of receptor grids. Figure 9c–d illustrates the temporal evolution of λ[O$_3$] at MBO and THD with respect to the NWR surface O$_3$ at final time. Two hotspots are found in the MBO plot (Fig. 9c): within the boundary layer 1–5 h before the final time; and in the free troposphere 10–15 h backwards in time. The THD plot (Fig. 9d) also shows two hotspots: within the boundary layer 1–5 h backwards in time; and 1.5–2.5 km in free troposphere 25–30 h backwards in time. These results indicate that surface O$_3$ at NWR is affected by both local production (close to the final time) and O$_3$ in the free troposphere at MBO and THD.

The temporal evolution of λ[O$_3$] at SC for SCR is shown in Fig. 9e. The gradients at SC are strongest in the first 10 h before the final time, extend out to 30 h before, and are highest below 2 km a.s.l. These results indicate that the transport of O$_3$ at SC to the SCR surface involve transport above the nocturnal and marine boundary layers and subsequent entrainment into the daytime boundary layer. The transport most
strongly affects O$_3$ over downwind areas in the next 1–2 days. Ozone in the free troposphere over THD also influences the surface O$_3$ levels at SCR (Fig. 9f) with a much weaker intensity (the scale $\times$ 5). The maximum sensitivities are found 30–40 h backward in time at 1–2 km a.s.l., the height at which the plumes enter northern CA, move through the Central Valley, and reach the surface SCR. Again these results are consistent with the trajectory analysis.

Adjoint sensitivities in the 60 km/18 layer grid cannot represent these processes as clearly as in the 12 km grid (Fig. S5).

### 3.4 Case study: DA during a LRT episode

Results from Sects. 3.1–3.3 show that elevated pollution levels over the eastern Pacific can be transported inland and entrained into the PBL in summer. Therefore, improving modeled O$_3$ concentrations over the eastern Pacific can reduce uncertainties in modeled surface pollution levels over the western US. In this section, we explore how well existing O$_3$ observations can constrain modeled surface O$_3$ concentrations using DA and reduce these uncertainties in the estimated TBG contributions. Since model resolution is critical for reflecting the subsidence processes (Sects. 3.2.2 and 3.3.3), all DA cases were performed in the 12 km/32 layer grid.
We selected 5–7 July as a representative LRT episode for a case study, during which time the northwestern US began to be impacted by extra-regional emissions. As indicated in Fig. 7–8, the transported plumes started to influence O$_3$ levels at THD 2.5 km and MBO 2.7 km on 5–6 July. Twelve-day back-trajectories (Fig. 10a) based on the 60 km WRF meteorology from these two locations at 18:00 UTC on 6 July are colored by travelling heights (in km a.g.l.), and they show similar transport pathways. About eleven days before the airmasses were over the Arctic (80° N over Canada) at 9–10 km. Then they were transported over Siberia (where the wildfires occurred as indicated by the overlaid RAQMS fire emissions in grey color scale at 00:00 UTC on 1 July) in the upper troposphere, descended into the mid-troposphere over northeast Asia and across the Pacific, while continuing to descend, and finally reached the western US.

The transport of pollutants during this period was observed by TES. In Fig. 10b–d, we matched the TES total CO and tropospheric O$_3$ columns during this period. Strongly enhanced CO columns (up to 5–6 × 10$^{18}$ molecules cm$^{-2}$) were observed on 30 June–1 July near the fire sources in northeastern Asia. Enhanced O$_3$ tropospheric columns (up to 60–70 DU) were seen during 2–5 July in the middle of the Pacific at 40–50° N. After ~5–7 days of transport from the Russian fire events (4–7 July), enhanced O$_3$ columns were seen over the western US (up to 60–70 DU).

To discuss the impacts of this event on inland air quality, Fig. 10e–f show the 12 km WRF-predicted flow fields (overlaid on WRF-predicted color-shaded surface level pressure (SLP, hPa)) on 5 July and 6 July, 18:00 UTC at ~2.5–3 km a.g.l. On 5 July, winds were mostly westerly, directly bringing the offshore pollution inland. On the following day, the winds shifted towards the south and the on-shore winds affected northern CA.

### 3.4.1 Discrepancies between the model a priori and OMI/TES retrievals

At ~22:00 UTC on 5 July, Aura overpassed the eastern Pacific when the TES special observations and OMI measurements were made (Fig. 11a). The model a priori (without assimilation) at this time is compared with the selected (criteria of selecting TES and OMI data for DA is described in Table 3) satellite retrievals in the DA domain (a subset of the 12 km/32 layer grid covering WA, OR and northern CA, Fig. 11a). The a priori agrees fairly well with the satellite retrievals, and is overall underpredicted compared to OMI, over a wide area of the eastern Pacific north of 42° N. Compared to TES, the a priori overpredicts O$_3$ in the upper troposphere.
and underpredicts in the lower/mid-troposphere. The highest negative biases occur at 500–900 hPa (∼1–5 km) south of 44° N. Note that the discrepancies between satellite and model are determined by both model performance and the retrieval method/quality.

To discuss how the model biases (with respect to the satellite retrievals) over the eastern Pacific might impact surface O\textsubscript{3} over the NWR region (defined in Sect. 3.3.3), we plot the adjoint sensitivities $\lambda[O_3]$ along the TES and OMI sampling locations at the Aura overpass time (Fig. 12a–c). These sensitivities show that surface O\textsubscript{3} over the NWR ∼30 h after the Aura overpass time (00:00 UTC, 7 July) was most sensitive to the O\textsubscript{3} concentrations at ∼2–4 km at TES and OMI sampling locations. The magnitudes of $\lambda[O_3]$ at the OMI sampling locations are overall higher than those at TES, possibly due to the wider horizontal coverage of samples and the wind fields on this day. These findings are different from the conclusions by Zoogman et al. (2011) over urban regions, where the local production dominates and the O\textsubscript{3} production efficiency is most sensitive to PBL O\textsubscript{3}. The two-day forward trajectories originating at the Aura overpass time from TES sampling locations at 4 km (colored by traveling heights) demonstrate that airmasses originating south of 44° N, where the highest discrepancies between the a priori and TES retrievals occur, rarely reached inland areas. In contrast, two-day forward trajectories originating at the same time from OMI sampling locations at ∼2 km impacted broad inland areas.

Similar analyses were conducted at THD (Fig. 12e–f), which indicates that airmasses at ∼2–5 km at the sonde
launch time (∼19:00 UTC on 5 July) had the strongest impacts on O3 over downwind areas in northern Central Valley on the following day, with the maximum λ[O3] close to the magnitude of the monthly mean (Fig. 9d, the hot spot ∼30 h before the final time).

### 3.4.2 Data assimilation results

**Assimilation impacts at the surface**

Figure 13a–b show the modeled daytime-mean surface O3 during the 30-h assimilation window, before and after assimilating the available surface (AQS, CASTNET and MBO)
observations (Case AS). A 54-h assimilation window (ending at 00:00 UTC on 8 July) was also tested but did not show significant differences for the first 30 h from Case AS. The AQS observations were assimilated from the model surface level, while CASTNET and MBO (located at higher altitudes) observations were assimilated from the model layer(s) that matched their actual altitudes. These observations are overlaid on the plots, most of which are located in northern CA. The a priori generally captures the observed O\textsubscript{3} magnitudes over WA and OR, and underestimates O\textsubscript{3} over most northern CA regions, where active biomass burning occurred during this time. In another case, we assimilated the available surface AQS NO\textsubscript{2} measurements and controlled NO\textsubscript{x} emissions by using a 24-h assimilation window (method details are described in Chai et al., 2009). Largest adjustment in NO\textsubscript{x} emissions occurred in northern CA (Fig. S6), reflecting the high uncertainties in biomass burning emissions that may lead to the O\textsubscript{3} biases in the a priori. After assimilating surface observations, surface O\textsubscript{3} over northern CA increases substantially (mostly by 5–10 ppb, but up to 10–20 ppb, Fig. 13c). Errors (error = modeled-observed) at these observational sites are overall reduced after the assimilation (Table 6), with highest improvement over northern CA due to the largest discrepancies of the a priori and the dense number of observations.

Figure 13d–f show the differences of daytime-mean surface O\textsubscript{3} before and after assimilating vertical profiles from TES (Case AT), OMI (Case AO) and THD sonde (Case AD), respectively. The effects of assimilating vertical profiles modified daytime-mean surface O\textsubscript{3} by < ± 0.5 ppb, with the major differences over WA and OR as well as near the sampling locations. The errors for daytime-mean O\textsubscript{3} at the available surface sites were overall slightly reduced (<±0.2 ppb, Table 6). The limited changes in surface O\textsubscript{3} compared to those in Case AS reflect the lack of spatiotemporal resolution for the assimilated vertical profiles.

We also assimilated surface observations and vertical profiles together (Cases AST, ASO and ASD for adding TES, OMI, and THD sonde, respectively). The differences of daytime-mean surface O\textsubscript{3} between these cases and Case AS reflect the effects of adding O\textsubscript{3} vertical profiles into the assimilation (Fig. 13g–i). Daytime-mean surface O\textsubscript{3} over WA and OR increase slightly due to the underestimated O\textsubscript{3} in mid-altitude offshore, and drop by up to 2–3 ppb in northern CA, different from the features shown in Fig. 13d–f. The changes in errors for these cases are within ∼ ± 2 ppb and are overall positive (Table 6), indicating the competing/conflicting effects of assimilating the observations taken from different platforms/regions that may be due to retrieval uncertainties and model vertical structure (details in a following section of “Estimation of the uncertainties in satellite retrievals”).

Assimilation impacts in the vertical

To demonstrate how the assimilation cases modified the O\textsubscript{3} vertical distributions, we plotted the O\textsubscript{3} changes (assimilation case-the a priori) at the TES (Fig. 14), OMI (Fig. 15a–d) sampling locations and at THD (Fig. 15e–f) for Cases AS, AT, AO, and AD. These compare the consistency in the information provided by these observations.

At the TES sampling locations (Fig. 14a,c,e,g, raw data: before applying the observation operator), assimilations of all types of observations result in modification of O\textsubscript{3} in the similar location in the mid troposphere (i.e., ∼500–700 hPa), mostly south of 44° N, where the highest biases in the a priori occur. Cases AT, AS and AD result in similar spatial distributions of the O\textsubscript{3} changes, and Case AT shows the biggest changes (∼20 to >40 ppb), while Case AO results in approximately the opposite changes. After applying the TES observation operator (Fig. 14b,d,f,h), the changes between all four cases and the a priori were smoothed (showing decreased magnitudes and extended affected regions as high as to the upper troposphere).

At the OMI sampling locations, assimilating different types of observations all modify the O\textsubscript{3} raw data (Fig. 15a–d black dots) at most altitudes, and Case AO shows the biggest changes (∼20 to 50 ppb), followed by Case AS (∼10 to 40 ppb). Cases AS, AT and AD result in overall negative changes while Case AO caused positive changes. Together with Fig. 14, these indicate a possible high positive bias in OMI measurements. After applying the OMI observation operator (Fig. 15a–d red dots), again the changes between all cases and a priori were smoothed.

Figure 15e–f compare the O\textsubscript{3} vertical profiles at THD from sonde, the a priori and the assimilation cases. The a priori overestimates O\textsubscript{3} at <2 km and >10 km, and underestimates O\textsubscript{3} at 2–3 km. Case AD generates best results, especially the variability at ∼2–3 km and >10 km (Fig. 15e). Assimilating surface measurements modifies O\textsubscript{3} structure at <2 km, and O\textsubscript{3} increases at ∼2–4 km by up to 15 ppb, but fails to capture the sharp variability. The changes made by assimilating TES and OMI measurements at THD are much smaller (<1 ppb), mainly occurring at ∼2–4 km and 6–10 km for TES and OMI, respectively.

Assimilation impacts on the estimated contributions from TBG and local emissions

The 4D-Var approach can provide further insights into the contributions from BCs and local emissions. The assimilation of surface observations (Case AS) changed O\textsubscript{3} along the TES orbit by +(1–6) ppb (∼3 ppb) at 40–42° N (Fig. 14a). This indicates that the inflow over the eastern Pacific for this specific case was underestimated by ∼3 ppb. If we assume the addition of changes in offshore FT to surface O\textsubscript{3} is close to linear everywhere, then this implies that the TBG contribution to surface O\textsubscript{3} after assimilation rises by ∼3 ppb. The
Table 6. Changes of daytime-mean surface O$_3$ errors between different cases, where error = |modeled-observed|.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Min.</th>
<th>1st Qu.</th>
<th>Median</th>
<th>Mean</th>
<th>3rd Qu.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS-a priori</td>
<td>-16.59</td>
<td>-9.15</td>
<td>-4.02</td>
<td>-5.01</td>
<td>-0.21</td>
<td>4.38</td>
</tr>
<tr>
<td>AT-a priori</td>
<td>-6.60E-02</td>
<td>-7.00E-03</td>
<td>-2.00E-03</td>
<td>-4.00E-03</td>
<td>1.00E-03</td>
<td>1.50E-02</td>
</tr>
<tr>
<td>AO-a priori</td>
<td>-8.10E-02</td>
<td>-2.00E-03</td>
<td>~0</td>
<td>8.00E-03</td>
<td>2.40E-02</td>
<td>1.10E-01</td>
</tr>
<tr>
<td>AD-a priori</td>
<td>-1.84E-01</td>
<td>-1.30E-02</td>
<td>-3.00E-03</td>
<td>-1.30E-02</td>
<td>~0</td>
<td>1.60E-02</td>
</tr>
<tr>
<td>AST-AS</td>
<td>-1.15</td>
<td>-0.10</td>
<td>0.13</td>
<td>0.18</td>
<td>0.50</td>
<td>1.01</td>
</tr>
<tr>
<td>ASO-AS</td>
<td>-0.80</td>
<td>-0.15</td>
<td>0.23</td>
<td>0.22</td>
<td>0.50</td>
<td>1.30</td>
</tr>
<tr>
<td>ASD-AS</td>
<td>-0.71</td>
<td>-0.12</td>
<td>0.37</td>
<td>0.35</td>
<td>0.70</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Fig. 13. Impacts of DA at the surface. Daytime-mean surface O$_3$ from (a) STEM a priori; and (b) Case AS. The site measurements were overlaid (only those sites that had all daytime measurements are shown in the plots). (c) Differences of (b)-(a). Daytime-mean surface O$_3$ differences: (d) Case AT-STEM a priori; (e) Case AO-STEM a priori; (f) Case AD-STEM a priori. Daytime-mean surface O$_3$ differences: (g) Case AST-Case AS; (h) Case ASO-Case AS; (i) Case ASD-Case AS. See text and Table 3 for definition of the various cases.
Fig. 14. Impacts of DA in the vertical. O$_3$ differences at the selected TES sampling locations: (a–b) Case AS-STEM a priori; (c–d) Case AO-STEM a priori; (e–f) Case AT-STEM a priori; (g–h) Case AD-STEM a priori. (a,c,e,g) compare the raw data in TES pressure grids and (b,d,f,h) compare the results after applying the TES observation operator.

gross changes in surface O$_3$ after assimilation were $+\left(5–15\right)$ ppb ($\sim+10$ ppb) over northern CA and $-\left(1–3\right)$ ppb ($\sim–2$ ppb) over Region 10. If the rest of errors are assumed to be solely due to local emissions, then the local emissions would need to be adjusted in a manner that would change the surface O$_3$ over Regions 9 and 10 by $\sim7$ ppb and $\sim–5$ ppb, respectively.

Additional DA methods to improve the estimates of TBG/extra-regional contributions in future include: (1) To improve the chemical fields in global models that are used as regional model BCs; and (2) To improve the emissions (e.g., NO$_x$) in extra-regions, and then use the improved emissions to calculate the contributions from extra regions through sensitivity analysis or tagging methods.

Estimation of the uncertainties in satellite retrievals

We determine the upper limits of satellite retrievals from the discrepancies between retrievals and the assimilated fields of Case AS (Fig. 15g). This estimate is based on the assumption that assimilated fields in this case provide the “best” O$_3$ distributions in the lower/mid-troposphere over the domain.

TES shows $5–20\%$ positive biases at 500–900 hPa (the region that surface layer O$_3$ is sensitive to at the overpass time), and OMI has a $5–10\%$ higher bias than TES. This estimation is consistent with conclusions in previous validation studies, but this method needs to be further tested for extended regions and periods.

Discrepancies between THD sonde and assimilated O$_3$ at THD in Case AS are varied, due to much higher vertical resolution and accuracy of the sonde. Case AS is not able to correct the detailed vertical variability due to the coarser model vertical structure.

4 Conclusions and suggestions on future work

In summer 2008, the model-estimated TBG contributions to MDA8 were $\sim30–35$ ppb for EPA Regions 9 and 10. The modeled TBG contributions to W126 were $\sim10–17$ ppm-h for Region 9 and $\sim3–4$ ppm-h for Region 10. The strongest TBG impacts on W126 occurred over the grass/shrub-covered regions. Among the TBG pollutants, O$_3$ is the major contributor to surface O$_3$, while PAN is the most important
O$_3$ precursor species. W126 showed larger responses than MDA8 to TBG perturbations and stronger non-linearity to the magnitude of perturbations. The TBG impacts on both metrics overall negatively correlate to model vertical resolution and positively correlate to the horizontal resolution.

Ozone at MBO and THD was significantly affected by TBG pollutants and occasionally affected by local emissions, while SC O$_3$ was strongly affected by local emissions. The importance of airmasses over the eastern Pacific being transported inland and entrained into the PBL to impact surface O$_3$ was demonstrated by the IP metric and adjoint sensitivities. The IP metric showed that the probabilities of airmasses originating from MBO (2.7 km) and THD (2.5 km) impacting downwind surface air quality reached daily maxima of 66% and 34% at ~03:00 p.m. PDT, respectively, and the IP metric for SC (1.5 km) stayed above 50% during 09:00 a.m.–04:00 p.m. PDT. Receptor-based adjoint sensitivity analysis further highlighted the transport/subsidence processes that link airmasses aloft with the surface, showing that O$_3$ at 1–4 km had the biggest impact on inland surface O$_3$ 1–2 days later.

A case study demonstrated that assimilating surface in-situ observations was successful in constraining modeled O$_3$ spatial distributions in regions where these measurements are dense. Assimilation of the surface in-situ measurements significantly reduced (~5 ppb on average and up to ~17 ppb) the modeled surface O$_3$ errors during a LRT episode, and increased the estimated TBG by ~3 ppb. However, in this case assimilation of existing O$_3$ vertical profiles from satellites and sondes did not efficiently improve the modeled O$_3$ except near the sampling locations.

Suggestions on future work include:

1. A quantitative source attribution requires the use of global models, but the improvement in model predictability and the investigation of the export/import budgets can benefit from nesting with high resolution.
Due to the non-linear function used in calculating W126 to better understand model-based transport/subsidence. This work was supported by NASA awards: http://www.atmos-chem-phys.net/13/359/2013/acp-13-359-2013-supplement.pdf.

Acknowledgements. This work was supported by NASA awards: NNX08AH56G, NNX08AL06G and NNX11AI52G. The authors would like to thank the ARCTAS science team, the people who made the AQS, CASTNET, OMI, TES, MODIS and MISR measurements, and CGRER members who contributed to building the STEM forecast modeling system for ARCTAS. We thank two anonymous referees and Thomas Peters, Charles Stanier and Vicki Grassian (U Iowa) for commenting on previous versions of the paper. We thank Daven Henze (CU-Boulder) for suggesting the W126 calculations. The revision was performed at Jet Propulsion Laboratory, California Institute of Technology, under a contract with NASA. We thank CGRER (U Iowa) and Pleiades (NASA Ames) computational resources and the technical support especially from Jeremie Moen and Johnny Chang. The views, opinions, and findings contained in this paper are those of the authors and should not be construed as an official NOAA or U.S. Government position, policy, or decision.

References


National Research Council (NRC), global sources of local pollution-An Assessment of Long-Range Transport of Key Air Pollutants to and from the United States, 35–66, http://books.nap.edu/openbook.php?record_id=16676, relax=\textprotect\textbackslash ker\textprotect\textbackslash nrelax12743, &page=35, 2009.


