Multi-scale modeling study of the source contributions to near-surface ozone and sulfur oxides levels over California during the ARCTAS-CARB period

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Abstract. Chronic high surface ozone (O3) levels and the increasing sulfur oxides (SOx = SO2+SO4) ambient concentrations over South Coast (SC) and other areas of California (CA) are affected by both local emissions and long-range transport. In this paper, multi-scale tracer, full-chemistry and adjoint simulations using the STEM atmospheric chemistry model are conducted to assess the contribution of local emissions to SC O3 and to evaluate the impacts of transported sulfur and local emissions on the SC sulfur budget during the ARCTAS-CARB experiment period in 2008. Sensitivity simulations quantify contributions of biogenic and fire emissions to SC O3 levels. California biogenic and fire emissions contribute 3–4 ppb to near-surface O3 over SC, with larger contributions to other regions in CA. During a long-range transport event from Asia starting from 22 June, high SOx levels (up to ~0.7 ppb of SO2 and ~1.3 ppb of SO4) is observed above ~6 km, but they did not affect CA surface air quality. The elevated SOx observed at 1–4 km is estimated to enhance surface SOx over SC by ~0.25 ppb (upper limit) on ~24 June. The near-surface SOx levels over SC during the flight week are attributed mostly to local emissions. Two anthropogenic SOx emission inventories (EIs) from the California Air Resources Board (CARB) and the US Environmental Protection Agency (EPA) are compared and applied in 60 km and 12 km chemical transport simulations, and the results are compared with observations. The CARB EI shows improvements over the National Emission Inventory (NEI) by EPA, but generally underestimates surface SC SOx by about a factor of two. Adjoint sensitivity analysis indicated that SO2 levels at 00:00 UTC (17:00 local time) at six SC surface sites were influenced by previous day maritime emissions over the ocean, the terrestrial emissions over nearby urban areas, and by transported SO2 from the north through both terrestrial and maritime areas. Overall maritime emissions contribute

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10–70% of SO\textsubscript{2} and 20–60% fine SO\textsubscript{4} on-shore and over the most terrestrial areas, with contributions decreasing with inland distance from the coast. Maritime emissions also modify the photochemical environment, shifting O\textsubscript{3} production over coastal SC to more VOC-limited conditions. These suggest an important role for shipping emission controls in reducing fine particle and O\textsubscript{3} concentrations in SC.

1 Introduction

In the past 20 years, California population has increased by 33% and the economy has grown rapidly (Cox et al., 2009). In the meanwhile, California has taken good efforts to reduce the emissions of most primary pollutants and the entire state has met the state and national standards for most of these pollutants except tropospheric ozone (O\textsubscript{3}) and particulate matter (PM). Nearly all Californians live in areas that are designated as nonattainment for the state (about 99%) and national (about 93%) health-based O\textsubscript{3} and/or PM standards.

O\textsubscript{3} is an atmospheric pollutant harmful to human health and agriculture, and is also one of the most important short-lived green-house gases (GHG). The US National Ambient Air Quality Standard (NAAQS) for daily maximum 8-h average O\textsubscript{3} has recently been lowered to 75 ppb, and is likely to be lowered further to between 60 ppb and 70 ppb in future regulatory reviews of its direct impacts on human health. The California Air Resource Board (CARB) currently sets more stringent state 1-h and 8-h O\textsubscript{3} standards at 90 ppb and 70 ppb to better address long-standing urban and regional O\textsubscript{3} problems. Despite the continued precursors emission reductions, limited improvement in O\textsubscript{3} has been achieved over the last decade. Local production from both natural and anthropogenic emission sources, together with inter-continental and in-state transport contributes to the O\textsubscript{3} levels over both urban and rural areas.

Aerosols play an important role in the climate system causing both direct and indirect effects (IPCC report, 2007). They can be transported thousands of kilometers due to their lifetimes of about a week, and adversely affect human health and visibility. Sulfate (SO\textsubscript{4}) is an important component of ambient aerosols, and it hasa cooling effect on climate. Sulfur compounds emitted into the atmosphere are ultimately oxidized into SO\textsubscript{4}, by a variety of oxidants such as hydroxyl radical (OH) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) in gas and/or liquid phases. Among various sulfur compounds, SO\textsubscript{2} remains an important primary atmospheric pollutant. It is a highly reactive gas harmful to human respiratory system. It can be emitted from both anthropogenic and natural sources, and can be produced from oxidation of other chemicals such as hydrogen sulfide (H\textsubscript{2}S) by OH. SO\textsubscript{2} emissions from anthropogenic sources are generally thought to be better known than other species such as non-methane volatile organic compounds (NMVOCs). The documented largest sources of SO\textsubscript{2} emissions in the US are from fossil fuel combustion at power plants (66%) and other industrial facilities (29%) (US EPA, http://www.epa.gov/air/sulfurdioxide/). Various techniques have been used to control SO\textsubscript{2} emissions from these large sources. However, the major SO\textsubscript{2} emission sources over California vary with location. Unlike the continuous decreasing trend in statewide NO\textsubscript{x}, VOC, and CO emissions through the past decades, anthropogenic SO\textsubscript{x} emissions started to increase from 2005 and this trend is estimated to continue for the next 10 years. This increasing trend is mainly due to the emissions from the “other mobiles” categories, including the significant growth in shipping activities and the high-sulfur fuels that ocean-going vessels typically use, especially around the coastal areas such as San Francisco (SF) and Los Angeles (LA) counties (Cox et al., 2009). Although shipping emission control regulations are in action since 2009, the SO\textsubscript{2} levels over some South Coast (SC) surface sites are still increasing. In addition, SO\textsubscript{2} emitted from terrestrial industrial processes, certain modes of surface transport, and area sources contribute to the SO\textsubscript{x} concentrations over southern California. Similar as for O\textsubscript{3} and its precursors, the long-range transport of SO\textsubscript{4} affects the California sulfur budget. Because of various health concerns, the US EPA has recently tightened the primary standard for 1-h SO\textsubscript{2} to 75 ppb and changed the SO\textsubscript{2} monitoring requirements. The design of effective emission reduction strategies requires estimates of the factors that influence the regional background pollution levels and the local enhancements. A number of observational and modeling studies have been conducted to quantify the effects of sector emissions on near-surface O\textsubscript{3} and SO\textsubscript{x} levels. It has been concluded that less than 40 ppb of O\textsubscript{3} are contributed by natural sources (Fiore et al., 2003; Wang et al., 2009; Koo et al., 2010). For anthropogenic emissions, the effects of shipping emissions on regional air quality have been shown important since 1997 (Corbett et al., 1997) over different regions. For example, Vutukuru et al. (2008) focused their studies on the emissions from the LA – Long Beach area, where one-third of the cargo containers to the US arrive (BST associates, 2007). They estimated the impacts of shipping emissions on surface 1-h and 8-h O\textsubscript{3} to be up to >20 ppb, and the SO\textsubscript{2} emissions from shipping to cause a rise in-on-shore SO\textsubscript{2} concentrations by 2–4 ppb in 2002, and is projected to grow to 8–10 ppb by 2020.

However, the accuracy of observational-based studies of estimating natural O\textsubscript{3} levels relies on the representativeness of measurement sites and the methods to filter out the local anthropogenic contributions (Fiore et al., 2003), and the studies of fire impacts on O\textsubscript{3} are mostly conducted by comparing O\textsubscript{3} levels during fire and non-fire periods, in which way daily variations due to other factors cannot be completely excluded (Viswanathan et al., 2006; Bytnerowicz et al., 2010). Model-based estimations are also uncertain as they are highly dependent on model resolutions, key inputs (such as emission inventories (EIs) and meteorology conditions), chemical mechanisms, and the study periods (Plister et al., 2008; Wang et al., 2009).
al., 2009; Koo et al., 2010). Many of these modeling studies use coarse grids (from 36 km to several degrees horizontally), and the O$_3$ enhancement resulting from biogenic and fire sources are estimated either by tracer calculations (Pfister et al., 2008), or from simulations using purely natural emissions (Koo et al., 2010).

As one of the most important model inputs that affect the uncertainties of source contribution studies, EIs have been developed based on various data sources and assumptions, with different spatial and temporal variability. Their reliability needs to be validated. A previous field experiment, the Intercontinental Transport and Chemical Transformation of Anthropogenic Pollution (ITCT), conducted by NOAA in 2002 discovered the potential underestimation in sulfur species emissions (2010 CalNex science and implementation plan, 2008). The uncertainties imported from EIs in source contribution studies need to be quantified. By using two natural Els (SMOKE and MEGAN), natural O$_3$ backgrounds differed by 4 ppb in a 2002 study and were close in a 2018 case (Koo et al., 2010). Model simulations with different EIs and the comparisons with various three-dimensional observational datasets are important methods to complement the EI validation and provide better understanding of uncertainties of source contribution studies.

In this paper we estimate various source contributions to the regional background O$_3$ levels and local enhancements of SO$_x$ by analyzing observations obtained during the California portion of the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS-CARB) field experiment period (18–24 June 2008) using the STEM regional-scale modeling system. The system used includes tracer and full-chemistry models at two different spatial and temporal resolutions. Based on the modeled pollutant spatial patterns and the quantity of flight observational data, we mainly focus this study on California’s South Coast (SC) region. We look at the near-surface O$_3$ and SO$_x$ distributions over SC (and other regions) and identify the effects of long-range transport and local contributions. The long-range transport of SO$_x$ during a specific period is discussed in this paper (O$_3$ transport during this period was discussed in Huang et al. (2010)). We quantify the effects of the local emissions from natural sources (i.e., biogenic and wildfires) on O$_3$ levels with two different EIs in two resolutions, and estimate the impacts of maritime emissions on on-shore air quality in the finer grids. We also compare results using two SO$_x$ EIs with observations and identify areas where further improvements are needed. Adjoint sensitivities are calculated and used to study the impacts of daytime and nighttime terrestrial and maritime SO$_2$ emissions on surface SC SO$_2$ levels.

2 Methods

2.1 Mission and source data

The ARCTAS-CARB field experiment was conducted in June 2008 by the National Aeronautics and Space Administration (NASA). The NASA DC-8 aircraft platform sampled trace gas and aerosol concentrations through four scientific flights over California on 18, 20, 22 and 24 June 2008 and the flight paths are shown together in Fig. 1b. Three (18, 22, 24 June) out of the four flights took measurements over the SC area during the daytime (~15:00–24:00 UTC (08:00–17:00 local time)). This mission had multiple scientific objectives, including improving the state emission inventories, characterizing off-shore shipping emissions, and quantifying the import of pollution from Asia (Jacob et al., 2010). Ozone was measured by the NCAR team using the Chemiluminescence method. Two SO$_2$ measurement teams (CIT and GIT) and two SO$_4$ measurement teams (UNH and CU–Boulder) were on board for all the flights. (http://www-air.larc.nasa.gov/cgi-bin/arctstat-c). The CIT and GIT teams both used chemical ionization mass spectroscopy (CIMS), and UNH and CU-Boulder (CUB) used Soluble Acidic Gases and Aerosol (SAGA) and Aerosol Mass Spectrometry (AMS), respectively (Weinheimer et al., 1994; Scheuer et al., 2003;
McNaughton et al., 2007; Slusher et al., 2004; Crounse et al., 2009; Dunlea et al., 2009). These data were averaged every one minute for use in this study.

We focus this study on the SC area because it had the largest number of flight-collected air samples, although analysis was also done over the SF and the Central Valley (CV) area. The SC, SF and CV domains are defined in boxes in Fig. 1b. The latitude/longitude ranges that the three regions cover are \(33^\circ\)N–34.5\(^\circ\)N, 121\(^\circ\)W–117\(^\circ\)W; \(37^\circ\)N–39\(^\circ\)N, 123\(^\circ\)W–121\(^\circ\)W; \(36^\circ\)N–37\(^\circ\)N, 119\(^\circ\)W–121\(^\circ\)W, respectively.

In addition to the airborne measurements, surface measurements were analyzed. The data analyzed included continuous hourly \(\text{SO}_2\) measurements with low instrument sensitivity and hourly \(\text{O}_3\) concentrations from six CARB surface sites. The locations of these sites are shown in Fig. 1a and more detailed descriptions are provided in the supplementary material (http://www.arb.ca.gov/qaweb/siteinfo.php). Sulfate aerosol data used included: EPA Air Quality System (AQS) daily-averaged fine PM (diameter 0–2.5 \(\mu\)m) specification data (including \(\text{SO}_4\)) at a variety of California urban sites on 20 and 23 June (http://www.epa.gov/tnn/airsaqs/detaildata/downloadaqsdata.htm, referred as “STN” in this paper); daily-averaged fine \(\text{SO}_4\) mass from Interagency Monitoring of Protected Visual Environments (IMPROVE) sites on 20 and 23 June (http://views.cira.colostate.edu/web/DataWizard/); and weekly-averaged \(\text{SO}_4\) mass at six Californian Clean Air Status and Trends Network (CASTNET) surface sites over the remote areas (http://java.epa.gov/castnet/index.jsp). Several CASTNET and IMPROVE sites are co-located.

2.2 Model, meteorology and boundary conditions

We simulated the ARCTAS – CARB period (18–24 June) using the Sulfur Transport and dEposition Model (STEM) – Version 2K3. The modeling system applied here included three components: (1) a hemisphere tracer model in 60 km polar stereographic grids (http://www.cgrer.uiowa.edu/ARCTAS/arctas-2k8.html); (2) a continental scale gas-phase and aerosol chemical transport simulation in 60 km grids on a subset of (1) (http://www.cgrer.uiowa.edu/ARCTAS2/arctas2-2k8.html), and (3) a regional-scale gas-phase and aerosol chemical transport domain centered over California in a 12 km Lambert conformal conic grid, covering Nevada and part of Mexico. The SAPRC-99 chemical mechanism was used (Carter, 2000). This mechanism has been applied to many US cases and compared with several other mechanisms (Chen et al., 2010; Luecken et al., 2008). Meteorology fields for all three grids were generated by the Advanced Research Weather Research & Forecasting Model (WRF-ARW) Version 2.2.1 (Skamarock et al., 2007) with forecast and reanalyzed meteorological inputs (Mesinger et al., 2006) for the 60 km and 12 km simulations, respectively. Different boundary conditions were used in this study for the 60 km and 12 km simulations. In the 60 km base case, lateral boundary conditions (LBC) for thirty gaseous species and top boundary conditions for ten gaseous species were obtained from the archived RAQMS global model predictions. The LBCs for BC, OC, dust, sea salt and \(\text{SO}_4\) were taken from the 60 km STEM tracer results. Boundary conditions for the 12 km simulations came from the 60 km full-chemistry simulations. The details of the model configuration are described in Huang et al. (2010) and in Table 1.

We also used the adjoint of STEM (Sandu et al., 2005; Chai et al., 2009) to study the \(\text{SO}_2\) sensitivity with respect to receptor (the SC surface sites in this case) \(\text{SO}_2\) concentration during the flight week (Sect. 3.7) in the 12 km regional simulation. This adjoint approach has been applied in previous studies for source attribution and for data assimilation (Carmichael et al., 2008). Model forward sensitivity studies quantify the change of chemical distributions in all grids at future times in response to the perturbation of model inputs. In contrast, adjoint sensitivities represent backward in time the change of chemical distributions in those grids that influence a given receptor at a specific time.

2.3 Emissions

Emission inputs for each of the three modeling components differed slightly, based on respective demands for resolution and completeness. In the hemispheric tracer model, we used a bottom-up global gridded inventory developed for the ARCTAS mission (developed by David Streets, Qiang Zhang et al., received in 2008, http://mic.greenresource.cn/arctas-premission). This inventory is driven by regional-specific information on fuels and activity from various economic sectors, and includes anthropogenic, biomass and global shipping contributions. In the 60 km continental model, anthropogenic emissions for North America 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). The NEI 2001 includes emission around the port area, but misses the shipping emissions over the open ocean. Daily biomass burning emissions from the Real-time Air Quality Modeling System (RAQMS) (Pierce et al., 2007) were provided by the Cooperative Institute for Meteorological Satellite Studies (CIMSS). Biogenic emissions of monoterpene and isoprene were taken from twelve-year-averaged values from the Orchidee model (Lathiere et al., 2006). For the 12 km model the anthropogenic and biogenic emissions were re-gridded from a contemporary CARB 4 km emission inventory. The anthropogenic emissions outside of the CARB domain (including Mexico, states of Nevada, Washington and Idaho) were taken from NEI 2001, same as in the 60 km base simulation. Biomass burning emissions were generated by the prep-chem-source model (WRF/Chem Version 3.1 users’ guide, 2009), which used
Table 1. Summary of STEM model inputs for base cases in two resolutions.

| Inputs                                         | Source Data                        | Resolutions                |
|------------------------------------------------|------------------------------------|----------------------------|
| Meteorology, WRF 2.2.1                         | GFS + one time step SST            | 60 km/18 layers/6h base case| 12 km/32 layers/1h base case |
| Ozone column, required by the TUV model        | Measured by Ozone Mapping Spectrometer (OMI) instrument on board the NASA Aura spacecraft, daily | 1° × 1°, 1 day             |

Anthropogenic Emissions (point and mobile)         NEI 2001, weekday varied from weekends | CARB 2005, projected from 2002, daily varied. Out of CARB domain filled with NEI 2001 | 1° × 1°, 1 h | 4 km × 4 km, 1 h |

Biogenic Emissions                                   Orchidee                          | CARB 2005 projected from 2002, daily varied | 1° × 1°, monthly averaged | 4 km × 4 km, 1 h |

Biomass burning Emissions                            RAQMS real time                   | MODIS-detected hot spots, processed by prep-chem-source model; mass-conserved normalization | 1° × 1°, 12 h | 1 km × 1 km, 24 h |

Top and Lateral Boundary Conditions                  RAQMS real time (gases) + STEM tracer (several aerosols) | STEM 60 km base case | 2° × 2°, 6 h and | 60 km × 60 km, 6 h | 60 km × 60 km, 18 layers, 6 h |

MODIS – detected point fire information at 1 km ground resolution (Giglio et al., 2003; Davies et al., 2009) and was adjusted at each time step to match total emissions rates from RAQMS. H₂S and dimethyl sulfide (DMS) emissions were not included in these cases.

3 Results and discussions

3.1 General conditions and O₃ levels in base cases

The California summer climate in 2008 was hot and dry, influenced by the Pacific high pressure system. Wildfire events broke out on 21 June at various locations over both northern and southern California. On 18–20 June, fires were detected along the California-Mexico border. The 12 km average WRF-modeled 10 m winds at multiple times (00:00, 06:00, 12:00 and 18:00 UTC → 17:00, 23:00, 05:00, 11:00 local time, respectively) over California during the experiment week are shown in Fig. 2. The northwesterly winds along the coast and through the Central Valley, together with the sea-land breezes, determined the regional transport of pollutants during this period. The wind vectors are overlaid on the WRF-predicted mixing layer height (PBLHT). The PBLHT over the ocean stayed below ~600 m, while the PBLHT over parts of the SC terrestrial areas reached up to ~1500 m during daytime. These are consistent with the vertical structures of short-lived chemicals observed by the aircraft measurements (shown in Fig. 7, to be discussed).

The observed O₃ concentrations along all DC8 flights (Sect. 2.1 and Fig. 1) below 1000 m are shown in Fig. 1a and 3e horizontally and vertically, respectively. Observed O₃ ranged from less than 40 ppb to ~120 ppb with large variability. The highest O₃ levels (≥120 ppb) were found around Riverside. The O₃ levels over the ocean were typically below 80 ppb.

The modeled O₃ concentrations from the 12 km simulations are shown in Fig. 3a and b, for the 15:00–24:00 UTC averaged O₃, and for the daily averaged maximum O₃, respectively. The predicted O₃ concentrations over the Central Valley and southern California are over 70 ppb during the flight times. The averaged O₃ levels during the flight times over northern California, southern California urban areas are 5–10 ppb lower. The predicted average daily maximum O₃ levels occur in the Central Valley and a large part of southern California (>90 ppb).

Finer grid simulations are usually expected to better capture local features. However, coarser grids (in this study, the 60 km) simulations (typically used in global models and in forecast-mode regional model simulations) with different model inputs are also valuable to evaluate the uncertainties of model sensitivity to sector emissions, which will be described in detail in Sect. 3.2. The base case simulations are shown in this section first. The modeled O₃ concentrations from the 60 km simulations are presented in Fig. 3c and d, for the averaged 15:00–24:00 UTC O₃, and for the averaged daily maximum O₃, respectively. Overall the 60 km simulations show similar spatial patterns over CA compared with the 12 km results, but lower O₃ concentrations over the Central Valley and southern California.

Figure 3e compares the predicted O₃ for the two model resolutions with all flight observations below 1000 m vertically. The 12 km simulations captured the observed variability fairly well, with the correlation of 0.62. It generally overpredicted the O₃ concentrations, but captured the higher observed concentrations (>75% quantile, mostly over terrestrial regions) better, with mean bias 11.6 ppb and root mean square error 13.9 ppb. The 60 km simulations showed less
vertical variability, but similar correlation with observations ($r = 0.58$) as the 12 km simulations. Its extent of overprediction of O$_3$ was lower than the 12 km case, but the simulations for the higher-observed concentrations (>75% quantile) showed higher biases, with mean bias of 15.9 ppb and root mean square error of 19.8 ppb.

Figure 3f compares the observed and modeled O$_3$ time series averaged over the six CARB surface sites (Fig. 1a) during the flight week. No significant weekday-weekend variations (21 and 22 June are Sat. and Sun.) are found. The 12 km simulation results were well correlated with the observations ($r = 0.73$), and captured the daytime variations fairly well. Nighttime O$_3$ concentrations were over-predicted by 10–30 ppb, due to the under prediction of nighttime NO$_x$ and uncertainties in the transport of upwind O$_3$ concentrations. The 60 km results showed lower correlations ($r = 0.6$) and weaker diurnal variations, with higher overpredictions during the night time. It is harder for the coarser grids to capture the night time titration processes and the transport of background O$_3$ from the upwind locations.

3.2 Influences of natural source emissions on SC O$_3$

In order to quantify the impacts of natural emission sources on SC O$_3$ levels, we conducted two sensitivity simulations in the 12 km grids. We turned off the biogenic (isoprene and monoterpene) emissions and wildfire emissions for the two cases, respectively, and analyzed the changes of O$_3$ between the base and each of the sensitivity cases.

Figure 4a shows the 24-h average isoprene and monoterpene emissions from the CARB EI. Their emissions are highly related to the land use type (not shown) and vary over California. Isoprene and monoterpene emission rates are the highest over northern California regions covered by evergreens, and account for 40–60% of total NMVOC emissions over those regions. In contrast, in the Central Valley and south coast urban areas, the emission rates are more than 20 times lower, accounting for less than 2% of the total NMVOC emissions (not shown).

The differences of flight time (15:00–24:00 UTC) and daily maximum surface O$_3$ concentrations during the flight week between the base and no-biogenic emission cases are shown in Fig. 4c, and e, respectively. The largest O$_3$ decreases are found over northern California and the CV, with the flight time O$_3$ changes up to 6 ppb and the average daily maximum changes from 6 to 12 ppb. In contrast, the O$_3$ changes over the SC area are shown smaller, between 2 and 4 ppb.

The impacts of fires on 24-h average surface CO during the flight week are shown in Fig. 4b. The highest differences...
Fig. 3. (a–b) 12 km and (c–d) 60 km modeled (a, c) average 15:00–24:00 UTC (08:00–17:00 local time) and (b, d) daily maximum surface O$_3$; (e) Observed and modeled O$_3$ vertical profiles along all SC flight paths below 1 km; (f) Observed and modeled (60 km base, 12 km base and no-maritime emissions cases) O$_3$ time series at six SC surface sites.

 (>100 ppb) due to California fires occur over northern California, where the wildfires were most intense and durations the longest. Fire locations with changes in CO of 400–800 ppb are shown in northern California and the Monterey Bay areas, and the fire impacts on CO extend to the SC coastal areas (20–50 ppb of delta CO between base and no-fire cases). Analysis of the impacts from wildfires in North Asia and Europe, and South Asia and Africa using the tracer model indicate that the fires that occurred outside of the North America had negligible impacts on surface SC air quality.
Table 2. Modeled O₃ sensitivity along flight paths below 1 km from both resolution cases.

| Flight day | Biogenic | Fire |
|------------|----------|------|
| 12 km      |          |      |
| 18 June SC | Mean (%) | Max (%) | Number of points with sensitivity >10%/total number of points (%) | Mean (%) | Max (%) | Number of points with sensitivity >10%/total number of points (%) |
| 1.36       | 4.98     | 0     | 0.28 0.65 0       |          |      |
| 20 June SC | /        | /     | /     / / /       |          |      |
| 22 June SC | 1.64     | 3.73  | 0     2.81 13.72 5 |          |      |
| 24 June SC | 5.04     | 8.87  | 0     14.47 26.55 62.50 |          |      |
| all SC     | 2.3      | 8.87  | 0     4.26 26.55 16.14 |          |      |
| all CA     | 2.84     | 19.87 | 1.98  4.78 30.2 19.85 |          |      |
| 60 km      |          |      |
| 18 June SC | 6.04     | 26.5  | 15.7  3.19 25.65 5.38 |          |      |
| 20 June SC | /        | /     | /     / / /       |          |      |
| 22 June SC | 1.63     | 5.57  | 0     2.05 6.2 0    |          |      |
| 24 June SC | 1.48     | 3.92  | 0     5.43 17.04 15.38 |          |      |
| all SC     | 3.8      | 26.5  | 7.85  3.41 25.65 6.28 |          |      |
| all CA     | 5        | 26.78 | 9     5.34 26.1 13   |          |      |

(<5% below ~1.5 km, not shown) during this period. The differences of flight time (15:00–24:00 UTC) and daily maximum surface O₃ during the flight week between the base and no-fire emission cases are shown in Fig. 4d and f, respectively. The largest changes in averaged daily maximum O₃ occur over the northern part of the California-Nevada border (9–15 ppb). Negative O₃ changes can be found around the fire locations, indicating the strong influences of aerosol emissions from fires. Over the SC area, the fire impacts on the average surface maximum and flight time O₃ are ~1–3 ppb.

To better understand the impact of biogenic and fire emissions on O₃ concentrations within the boundary layer, we calculated the model sensitivity for each of the one-minute flight data below 1000 m, using Eq. (1).

\[
\text{Sensitivity} (\%) = \left| \frac{\text{base case } O_3 - \text{sensitivity case } O_3}{\text{base case } O_3} \right| \times 100\% \quad (1)
\]

The model sensitivities are plotted in Fig. 5a and b. The sensitivities in both cases are below ~30%, O₃ over the CV area was largely affected by biogenic emissions. The O₃ levels over northern CV, the SF coast, and the central coast were highly impacted by the fire emissions.

The mean and maximum sensitivity for each flight day in SC are summarized in Table 2. The mean 12 km model results show that biogenic and fire emissions contributed 2.3% and 4.3%, respectively, to near surface O₃ over SC (with maximum values reaching contributions of 8.9% and 26.6% for each of these sources, respectively). The contributions of biogenic and fire emissions were higher in regions outside of SC.

To help assess the uncertainties in estimating the role of natural emissions, no-biogenic and no-fire emission sensitivity simulations were also conducted in the 60 km grid domain. The 24-h average Orchidee EI (Fig. 6a) shows a smoother but similar spatial pattern as the 12 km CARB estimates, with the maximum emission rates over northern California, lower than the CARB EI. Moreover, the magnitudes are much lower than the CARB EI along the coastal areas and higher over southeastern California. Delta O₃ between the 60 km base and no-biogenic emission cases are shown in Fig. 6c and e. The changes in average daily maximum O₃ are of similar magnitude as in the 12 km grids over northern California and CV, but are 5–8 ppb over the SC area, higher than the changes in the 12 km grids. The O₃ changes during flight times (15:00–24:00 UTC) also differ from the 12 km cases, with higher magnitudes overall (changes over the SC of 5–6 ppb). The different O₃ changes over SC between the two resolution cases are not only due to the emission differences within California, but also reflect the impacts of model resolution on flow fields, mixing layer height, and the contributions from the Nevada and Mexico biogenic emissions, which the CARB EI does not include.

The differences of daily maximum surface O₃ during the flight week between the base and no-fire emission cases in 60 km grids are shown in Fig. 6f. Same as in the 12 km cases, the highest changes occur over the north part of California-Nevada border (9–15 ppb). Figure 6d shows higher flight time average O₃ changes than in the 12 km cases (approximately doubled magnitudes over most areas). Negative O₃ changes are not found over California because the coarse resolution smooths the intensity of fire emissions, as the CO
Fig. 4. (a) Average surface isoprene and monoterpene emissions from CARB EI (b) 24 h-average differences of CO between base and no-fire cases in 12 km grids; Surface O$_3$ differences between (c, e) base and no-biogenic cases and (d, f) base and no-fire cases of (c–d) averaged 15:00–24:00 UTC (08:00–17:00 local time) and (e–f) average daily maximum O$_3$ in 12 km grids.

Fig. 5. Model O$_3$ sensitivity for (a, c) no-biogenic case (b, d) no-fire case from the 12 km (a–b) and 60 km (c–d) cases.

differences in Fig. 6b show. Over the SC area, the fire impacts on the average surface maximum and flight time O$_3$ are less than $\sim$4 ppb.

The model sensitivity along all SC flight paths below 1000 m in 60 km grids are shown in Fig. 5c, d and Table 2. The 60 km simulations show high sensitivity of O$_3$ to biogenic emissions along the southern California-Mexico border. Due to the Mexico biogenic emissions, the 60 km differences between base and no-biogenic emissions cases are higher at SC. Stronger model sensitivity to fire emissions is found over that
region and less strong sensitivity to fire emissions can be seen along the coastal SC areas, indicating the effects of model resolution and fire locations.

The sensitivity studies conducted in two resolutions suggest that fire and biogenic emissions play more important roles in O₃ production over areas outside of SC during the ARCTAS-CARB period. The different model configurations indicate a 3–4 ppb uncertainty due to various factors (such as resolution, ELs, emission injection heights, meteorology fields).

### 3.3 SOₓ spatial distributions and model-observation comparisons

Observed and modeled SOₓ spatial-temporal distributions over SC are discussed in this section. The 60 km domain was used in forecast mode in support of the ARCTAS experiment. The evaluation of the 60 km results found significant negative biases. This motivated the 12 km simulations designed in the post-analysis stage to assess the impacts of model resolution, EL and other factors on model prediction skills.

The model-predicted 24-h surface average total sulfur levels during the experiment week from the 12 km and 60 km simulations are shown in Fig. 7a and c. The corresponding SO₂ contributions to total sulfur (SO₂+SO₄, SO₄ was converted to ppb) are also shown in Fig. 7b, d. Elevated sulfur levels can be seen over SC, SF and Fresno in CV, as well as around the California – Nevada border and the west California – Mexico border, due to the fresh emissions (SO₂% > 60%). The sulfur levels at these areas from the 60 km simulations are generally lower than the 12 km case, especially over the SC area. Due to the lack of the shipping emissions in the NEI 2001, the sulfur levels over the ocean are low in the 60 km case, except the near-shore areas of the central coast. In contrast, the 12 km base case shows more detailed local features over land and the gradients along ship tracks in the ocean.

Figure 7e and f shows the observed total sulfur along all DC-8 flights (below 1 km a.s.l.), together with the SO₂% in the SC area. The observed total sulfur is the sum of averaged SO₂ and SO₄ (units are converted to ppb) measured by different teams. The SO₂% is the ratio of the averaged SO₂ concentrations measured by the two teams over the total sulfur concentrations. Similar to the model simulations, fresh SO₂ (SO₂% > 60%) and higher sulfur levels were observed within the SC domain. Over SC, SOₓ levels were higher at on-shore port areas, such as around Long Beach (up to 5–12 ppb), than over the inland areas (below ~0.5–2 ppb).

The modeled total sulfur concentrations are compared with observations along all SC DC-8 flights (below 5 km a.s.l.), and are shown as vertical profiles in Fig. 7i. The steps used to combine the data from different measurement teams to create average observed values are described here. First, we calculated SO₂ and SO₄ profiles separately. As there were two SO₂ and two SO₄ measurements by different institutional teams, if there are two measurements at any location along the flight paths, we used the average. If there was only one measurement, we used it directly. If there was no data, we treated it as missing value. We then calculated SOₓ = SO₂ + SO₄. For locations with no SO₂ or SO₄ data, we treated it as missing value. The vertical structures constructed by binning data every 500 m and averaging them, show that sulfur was enhanced from the surface to ~3–4 km. The observed average surface sulfur over this region was ~1.8 ppb below 500 m. The predictions show the lowest sulfur (and the highest biases) in the 60 km base case. The 12 km base case also under-predicted total sulfur at all altitudes, but were improved over the 60 km base predictions.

Comparisons of observed and modeled SO₂ and SO₄ along all DC-8 flight paths over the three regions are shown as vertical profiles in Fig. 7g and h. The GIT SO₂ is lower than the CIT SO₂ below 1 km and higher at ~1–3 km. The two sets of measured SO₄ follow the same trend below ~1.5 km, but CU Boulder SO₄ is ~10–20% lower than the UNH SO₄, and both teams observed SO₄ aloft at 2–4 km. The 60 km base case predicted the lowest SO₂ and SO₄. The 12 km base case SO₂ generally followed the CIT SO₂, but was biased low by ~50% at the surface. The general vertical structure of SO₄ was captured, but was more than 50% under-predicted at most altitudes.

The comparisons of observed and modeled SO₂ and SO₄ along all DC-8 flight paths (at all altitudes) are summarized in Table 3. The R values between modeled and observed SOₓ, the Mean Biases (MB) as well as Root Mean Square Error (RMSE) of modeled SO₂ and SO₄ are listed. The higher correlations and lower errors are in bold. The 12 km base case predicted lower SO₂ and SO₄, and showed the weaker correlations with the observations. The 12 km base case improved the modeled SO₂ and SO₄ in magnitudes and correlations. As the partitioning between SO₂ and SO₄ is highly dependent on OH we also compared predicted OH and found that the 12 km base case had higher correlation than the 60 km case (0.47 compared to 0.41, respectively).

In addition to the comparisons of modeled SOₓ along the DC-8 flight tracks, we also compare the predicted SO₂ and SO₄ with surfaces sites. Figure 8a shows the averaged 15:00–24:00 UTC (08:00–17:00 local time) SO₂ at the six SC surface sites (locations shown in Fig. 1a). The 60 km base case under-predicted SO₂ more than 10 times in general (60 km results were multiplied by 10 to be shown in figure). The 12 km base case under-predicts by a factor of two overall, but produce higher maximum, minimum (not shown) and mean SO₂ values than 60 km, and are closer to the observations.

Fine aerosol SO₄ (diameter 0–2.5 µm) mass was measured at multiple AQS (STN) ground sites over California on 20 and 23 June, and at IMPROVE sites on the same days. These sites represent the fine SO₄ distributions over urban and rural areas, respectively. In addition, the total SO₄ mass was measured and analyzed once a week at six California
Fig. 6. (a) Average surface isoprene and monoterpene emissions from the Orchidee EI. (b) 24h-average differences of surface CO between base and no-fire cases in 60 km grids; Surface O$_3$ differences between (c, e) base and no-biogenic cases and (d, f) base and no-fire cases of (c–d) averaged 15:00–24:00 UTC (08:00–17:00 UTC) and (e–f) average daily maximum O$_3$ in 60 km grids.

Table 3. Correlation ($R$), Mean Biases (MB), Root Mean Square Error (RMSE) between modeled and observed SO$_x$ along all SC flight tracks (all altitudes). Higher correlations, lower MB and RMSEs are in bold. Note that model comparisons refer to SC locations where measurements are available for individual teams, and the compared locations differ between teams.

| Measurements | $R$ (observations vs. predictions) | Observed Mean (ppb) | Mean Biases (ppb) | RMSE (ppb) |
|--------------|-----------------------------------|---------------------|-------------------|------------|
|              | 12 km Base                         | 60 km Base          | 12 km Base        | 60 km Base |
| CIT SO$_2$   | 0.36                              | 0.28                | 1.08              | 0.41       |
| GIT SO$_2$   | 0.43                              | 0.20                | 0.62              | 0.13       |
| UNH SO$_4$   | 0.54                              | 0.28                | 0.53              | 0.30       |
| CUB SO$_4$   | 0.50                              | 0.22                | 0.42              | 0.22       |

CASTNET sites, which are located at remote areas. Some CASTNET and IMPROVE sites are co-located. There are several AQS(STN) and IMPROVE sites located in SC domain, as Fig. 8b shows. No CASTNET sites are located in the SC domain (Fig. 8c).

These SO$_4$ observations are compared with results from both 12 km and 60 km simulations in Fig. 8b and c. The predictions from both cases are biased low by about a factor of two to three. The 12 km case results are improved over the 60 km predictions by more than a factor of two at the CASTNET and IMPROVE sites statewide and within SC, and slightly improved at STN sites.

From both modeled and observed SO$_4$ masses, it is found that during the flight week the surface values varied spatially according to: urban (AQS-STN) > rural and remote (IMPROVE CASTNET) areas, and both SC urban and rural areas had higher fine SO$_4$ than the statewide average.

Table 4. Ratios of observed and the 12 km simulated SO$_x$.

| (flight time) all SC flight observed/12 km predicted | (24h) surface observed/12 km predicted |
|-----------------------------------------------------|---------------------------------------|
| SO$_2$                                              | 1.71                                  |
| SO$_4$                                              | 2.48                                  |
| Fine SO$_4$                                         | 3.17                                  |

In general, the 12 km results provide closer results to both flight and surface observations during the simulation week. We calculated the ratios of averaged observations over 12 km results along the flight paths and at surface sites in SC (Table 4). In general, the 12 km simulations underestimated SO$_2$ by up to ~1.8 times and SO$_4$ by more than 2.5 times. During the flight periods, the ratios of the under-prediction along
Fig. 7. The 24-h average surface (a, c) total \( \text{SO}_x \) and (b, d) \( \text{SO}_2 \) % from 12 km (a–b) and 60 km (c–d) base simulations during the flight week; Observed (e) total \( \text{SO}_x \) and (f) \( \text{SO}_2 \) % along all SC flights below 1 km. Observed and modeled (g) \( \text{SO}_2 \) (h) \( \text{SO}_4 \) and (i) \( \text{SO}_x \) vertical profiles along all SC flights (averaged every 500 m).
flight paths and at six surface sites were similar (1.71 and 1.79, respectively).

A similar analysis for SO\textsubscript{x} was done over the SF and CV regions (Fig. 1b) and we suggest further improvement on EIs over these regions as well. In general, by using the CARB EI, the model underestimated SO\textsubscript{x} concentrations by a factor of up to 2 in the SF region and more than 10 times around Fresno, and using NEI produced higher negative discrepancies. A more quantitative analysis of model biases for these regions was limited by the fact that many fewer flight observations were made over these regions during the experiment. In order to improve EIs over these regions, further studies are needed.

3.4 The identification of the contributors to the elevated SO\textsubscript{x} concentrations

Figure 7g–i shows that SO\textsubscript{x} was elevated along the SC flight tracks near surface and between 2–4 km. To better understand the possible source contributors to the elevated SO\textsubscript{x} levels near the surface, we summarize the VOC age and CO contributions in Table 5 for flight segments below 1 km using the tracer calculations. VOC age was described in detail by Tang et al. (2004), which represents a combination of transport time, source intensities and diffusion, by using ethane as an indicator that is related to ethane emission and decay rate. During the experiment week, most of the flight-sampled airmasses had anthropogenic China CO% contributions less than 0.5% and North America CO% >99%, except the airmasses on 24 June during 23:00–24:00 UTC (during flight) that had China CO% of ~40%. These airmasses are described in detail in Sect. 3.5.

In order to identify the airmass sources that caused the elevated sulfur aloft over SC between 2–4 km (Fig. 7g–i), we analyzed back-trajectories originating along the three SC DC-8 flight paths at 2–4 km a.s.l. on individual flight days, based on the 12 km meteorological fields. During the flights on 18 and 24 June, the air was lifted and moved from the Central Valley. In contrast, during the other flight day, air masses were from the southwest, and they descended from >3500 m to SC (not shown in figures).
Fig. 9. Vertical profiles for (a) SO$_4$ (with tracer-calculated VOC age) and (b) SO$_2$ and time series (with flight altitudes) for (c) SO$_4$ and (d) SO$_2$ along outbound part of boundary layer flight on June 22; (e) Back trajectories ending at the 22 June flight path (f) Three-day forward trajectories (a.s.l. 2–4 km) and (g) three-day forward trajectories (a.s.l. > 6 km) starting from the outbound of the 22 June flight path.
3.5 Long-range transport events

Long-range transport of pollutants from Asia is typically assumed to be weaker and less frequent during summertime relative to springtime. During the ARCTAS-CARB experiment week, the 22 June flight aimed at characterizing the upwind boundary conditions necessary to model inland O3 and aerosols (Jacob et al., 2010). On this day, the DC-8 took off from Palmdale, CA, flew over the Pacific Ocean to Trinidad Head (a northern California site shown suitable for studying airmass entering the western US), and then circled back to Palmdale along the coast (Fig. 1b). At the outbound part of this flight (approximating 17:00–21:00 UTC), strong Asian inflows were encountered, as indicated from the VOC age (ranging from 200–400 h) shown in Fig. 9a, together with the back trajectories based on the 60 km WRF meteorology fields in Fig. 9e. Vertical profiles and time series of observed and modeled SO2 and SO4 are shown in Fig. 9a–d for this flight. Red circles in figures match elevated SOx concentrations in vertical profiles and time series plots to spatial locations shown in Fig. 9g. The 60 km tracer and 60 km full-chemistry simulated SO4 are compared with the observations in Fig. 9a–b. (The LBCs used in the 60 km full-chemistry simulations were taken from the 60 km tracer SO4 predictions and the 12 km full-chemistry simulations used LBCs from the 60 km full-chemistry results). Both the models captured the magnitudes of SO4 at 2–4 km fairly well. Elevated SO4 was also observed at 6–8 km a.s.l. (up to ~1.3 ppb), mainly at location 2 and partially at location 3, by the CUB team. These airmasses were also high in China CO% based on the tracer model calculations at 6–8 km a.s.l. (23:00–24:00 UTC) (hour) (%) (%) (ppb) (ppb) (ppb) (ppb) foreign sources (ppb) foreign sources (ppb) foreign sources (ppb)

| Flight day | VOC age (hour) | China CO% | North America CO% | SO4-UNH (ppb) | SO4-CUB (ppb) | SO4-CIT (ppb) | SO4-GIT (ppb) | SO4 enhancements by foreign sources (ppb) | SO4 enhancements by foreign sources (ppb) |
|-----------|---------------|-----------|-------------------|--------------|-------------|-------------|-------------|---------------------------------|---------------------------------|
| 18 June SC | 11.26         | 0.01      | 99.94             | 0.6          | 0.44        | 1.31        | 0.87        | 3.1×10^{-4}                      | 6.5×10^{-4}                      |
| 22 June SC | 10.73         | 0.2       | 99.74             | 0.55         | 0.56        | 1.17        | /           | 1.4×10^{-3}                      | 3.6×10^{-3}                      |
| 24 June SC | 15.78         | 16.61 (~40%) | 78.42 (~40%) | 0.63 | 0.58 | / | 0.55 | 0.13 | 0.12 |

Enhancements = (1 – North America CO%) × average SOx by two teams

SOX peaks (<0.7 ppb) were also observed by the CIT team at 6–8 km a.s.l. at flight locations 1 and 2. These were the residuals in Asian plumes, as indicated by similar peaks for a number of observed species and the tracer calculations (not shown). The RAQMS and the 60 km base case results used as boundary conditions missed the SO2 peaks at both locations 1 and 2, but as discussed for SO4, these airmasses containing high SO2 did not affect California surface air quality. Around 0.1 ppb of near-surface SO2 was attributed to foreign sources (Table 5), and the boundary conditions captured SO2 levels at 2–4 km very well (Fig. 9b).

3.6 SOx local emissions – Emission Inventory comparisons

As the local emissions mainly contributed to the elevated SOx concentrations near the surface during the experiment period, it is important to understand the contributions of the local sources. Therefore the emission inventory is one of the most important model inputs affecting the model-simulated near-surface SOx concentrations. Figure 10 compares the 24-h average surface SOX emissions during 18–24 June from the CARB EI and NEI 2001 EI simulations (12 km and 60 km cases) over SC. Shipping emissions are included in the CARB EI, but are not in the NEI 2001, and the terrestrial SOX emissions in NEI 2001 are generally much lower as shown in Fig. 10a and b. Figure 10c compares the time series of the average emission rates over the six SC surface sites from both EIs. The CARB EI peaks around noon time, while the NEI shows sharper later afternoon peaks (p.m. rush hours). The magnitudes in CARB emission rates are much higher than NEI, ~12 times for the 24 h averaged emission rates at the six sites (6×10^{10} and 5×10^{9} molecules/cm^2/s, respectively).

Table 6 quantifies the mean and maximum surface SOx emission rates in SC and the entire state from both EIs. The statewide mean and maximum emission rates from NEI are much higher than the CARB EI. However, in SC, the situation is opposite. The largest SOx emission sources in SC and California in NEI and CARB EI also differs. In the CARB EI,
Table 6. Maximum and mean SO\textsubscript{x} emission rates over California and SC from both EIs and their top emissions sectors.

|            | Maximum (kg S/km\textsuperscript{2}/day) | Mean (kg S/km\textsuperscript{2}/day) | Top Emission Sector       |
|------------|------------------------------------------|---------------------------------------|---------------------------|
| CARB Statewide | 55.11                                     | 0.09                                  | Ships and commercial boats, 52.1% |
| CARB SC     | 55.11                                     | 0.81 (regional total: 48.5 ton/day)   | Ships and commercial boats, 44.6% |
| NEI Statewide | 173.14                                    | 0.13                                  | Fossil fuel combustion, 51.3%   |
| NEI SC      | 0.70                                      | 0.05 (regional total: 4.91 ton/day)   | Non-road equipment, 40.4%      |

- The sector emissions ranks in CARB and NEI documentations are for summertime South Coast Basin and yearly Los Angeles County, respectively, not the same as our SC domain.
- In their SC domain, CARB documented 2005 and 2010 summer SO\textsubscript{x} emissions are 51.46 ton/day and 38.83 ton/day, respectively.
- Data sources: http://www.epa.gov/air/emissions/so2.htm, http://www.arb.ca.gov/app/emsinv/t25cat/cat_top25.php.

3.7 Effects of maritime emissions on coastal SC air quality

As analyzed in Sect. 3.6, shipping emissions over the SC (and other California coastal areas) account for more than 40–50% of total summertime SO\textsubscript{x} emissions. Therefore, the SO\textsubscript{x} levels at SC are impacted by both terrestrial (highway, port heavy transportations, industry) and maritime emissions (mainly shipping). As for the important O\textsubscript{3} precursors, the maritime emissions account for \sim19% and 14.5% of the total NO\textsubscript{x} emissions in SC and the state, while VOC emissions from ships are negligible.

In order to better understand the model SO\textsubscript{2} sensitivity with respect to SO\textsubscript{2} at receptor sites (the six SC surface sites shown in Fig. 1a), adjoint sensitivity simulations are conducted. Specifically we perturbed SO\textsubscript{2} concentrations at 00:00 UTC of each day during the flight weekend in the four surrounding model grids of all receptor sites. The influence function $\lambda[SO_2]$ represents SO\textsubscript{2} sensitivity at earlier times in various locations in response to the perturbations in SO\textsubscript{2} at the receptors. The sensitivity runs for each day lasted for one day.

Figure 11a shows the weekly-averaged surface $\lambda[SO_2]$ during the time periods (15:00–24:00 UTC), and Fig. 11c depicts the weekly-averaged $\lambda[SO_2]$ vertical structures averaged over maritime and terrestrial grid cells during these
SO$_2$ at the CARB monitoring site receptors is more sensitive to the maritime SO$_2$ levels than the terrestrial levels, especially over the surrounding areas of the ports and along the major shipping tracks, which reflect the impacts of the on-shore daytime transport associated with the sea breeze circulations during these periods. The vertical structures of \( \lambda \) [SO$_2$] reflect the modeled boundary layer structures over the land and ocean. The model level heights vary with location (for example, over the terrestrial regions, model level 10 ranges 730–860 m a.g.l. and over the ocean model level 5 is generally <300 m). Therefore, the integrated \( \lambda \) [SO$_2$] at each level are shown against the median model level height over the maritime and terrestrial regions.

Similarly, Fig. 11b shows the weekly-averaged surface \( \lambda \) [SO$_2$] during the rest of the times (at night and early morning, 01:00–14:00 UTC, 18:00–07:00 LT), after the peak in daytime boundary layer height. Figure 11d depicts the weekly-averaged maritime and terrestrial \( \lambda \) [SO$_2$] vertical structures for these times. At these times, SO$_2$ levels at the six SC sites are more sensitive to the terrestrial SO$_2$ levels than the maritime levels, and the sensitivities are generally lower than during the daytime (15:00–24:00 UTC times), with smaller

Fig. 11. Weekly mean surface SO$_2$ sensitivity for (a) 15:00–24:00 UTC (b) 01:00–14:00 UTC; Vertical profile of integrated mean SO$_2$ sensitivity for (c) 15:00–24:00 UTC (d) 01:00–14:00 UTC; The 24-h averaged surface (e) SO$_4$% and (f) SO$_2$% contributed from maritime emissions over SC, calculated in 12 km grids.
gradients. The sensitivity regions are shown to extend to the San Francisco Bay area, indicating the effects of regional transport. The vertical structures of $\lambda$ [SO$_2$] reflect the transport of SO$_2$ over the ocean during these times, which include the near-surface transport ($<300$ m), and transport at higher altitudes ($\sim3.5$ km), the local contribution over the SC region, and the transport through terrestrial regions along the north and central coast areas. The maximum $\lambda$ [SO$_2$] is found at altitudes $<\sim1.5$ km a.g.l. over land during these times.

To further understand the contributions from terrestrial and maritime emissions to sulfur and O$_3$ concentrations over SC, we conducted an additional model simulation in the 12 km domain with only the terrestrial emissions from the CARB EI for all chemical species. The differences between the base case and the terrestrial-emission-only case provide an estimate of the contribution from maritime emissions.

Figure 11e and f illustrates the 24 h-average contributions of maritime emissions on surface SO$_x$ concentrations during 15:00–24:00 UTC through the flight week. SO$_2$ levels are directly affected by both terrestrial and maritime emissions as shown. The maritime emissions cause high SO$_2$ levels over the ocean and on shore (where SO$_2$ $>60$–70% of the total sulfur), with contributions to total SO$_2$ levels ranging from 10–70%. For SO$_4$, the spatial distribution is highly influenced by reaction rates and the wind fields. SC is heavily under the impact of northwest winds during the daytime in this period. Consequently, the maritime emissions generally contributed 20–60% of fine SO$_4$ along the coastaland inland areas, with the regions of influence extending as far as San Diego and the California – Mexico border area.

Figure 7g–i shows the change of the vertical distributions of SO$_x$ in response to cutting off maritime emissions along all SC DC-8 flight paths. During the flight periods, both SO$_2$ and SO$_4$ were reduced in the vertical up to $\sim1500$ m. The maximum reduction of SO$_2$ (by $\sim50\%$) is shown at the lowest 500 m. The differences in simulated SO$_2$ in the 12 km base and terrestrial emission cases are $\sim0.3–0.5$ ppb for each day during the week at the six surface sites (not shown).

The effects of maritime emissions on surface O$_3$ levels are shown in Fig. 12. The average O$_3$ changes during 15:00–24:00 UTC for the flight week are below $\sim4$ ppb, and over the port areas (such as north Long Beach, the flight time average O$_3$ increases by 3–4 ppb after cutting off the maritime emissions. The averaged daily maximum O$_3$ decrease by 3–10 ppb in the domain, and the decreases around north Long Beach are lower ($\sim3–4$ ppb). Figure 3f shows the time series of O$_3$ at the six SC surface sites from the no-maritime emission case, together with observations and 12 km and 60 km base O$_3$ values. The differences in simulated O$_3$ in the 12 km base and terrestrial emission cases are below 5 ppb, and the maximum changes occurred at afternoon peak time on 18 June.

To better understand the reduction of SC O$_3$ caused by maritime emissions, the changes of two O$_3$ production indicator species (NO$_x$ and O$_3$/NO$_x$) are analyzed in Fig. 13. We first evaluate the model-predicted NO$_x$ concentrations
and $O_3/NO_y$ ratios along all DC8 flights. Overall the model captured the main features of the spatial distributions for both of them, and the correlations of model predicted $NO_y$ and $O_3/NO_y$ (<0.5 km) were $R = 0.53$ and 0.71, respectively. The detailed validations of modeled $O_3/NO_y$ and $NO_y$ with flight observations are described in Huang et al. (2011).

Averaged $NO_y$ and $O_3/NO_y$ ratios at 15:00 (22:00 UTC) (the time of peak $O_3$ and PBL height) during the flight week are shown for the base and no-maritime emission cases. When afternoon $NO_y$ <10–25 ppb, or/and $O_3/NO_y >5–10$, the area belongs to the $NO_x$-limited $O_3$ production regime (Milford et al., 1994; Sillman et al., 1995; Jacob et al., 1995). Based on these criteria, the SC urban area in the 12 km base case is estimated to be VOC limited. The removal of maritime emissions leads to flight time average $NO_y$ decreases of up to >10 ppb, over the North Long Beach area, and the $O_3/NO_y$ ratio rises up to 20 over the regions south of Long Beach. This indicates that by cutting off the maritime emissions, some coastal areas can change from VOC-limited to $NO_x$-limited, or more $NO_x$-limited.

Photochemical age (PA) indicators such as $NO_y/NO_z$ help us to evaluate the airmass smog potential. When PA is more than 0.6–0.7, smog potential is exhausted. Figure 13e and f show averaged at 15:00 (22:00 UTC) during the flight week for base and no-maritime emission cases. In both cases, PA are young (<0.6) over terrestrial areas, while the base case shows younger PA along shipping tracks (0.2–0.5), in contrast to PA in the no-maritime emission case (>0.8). Removing maritime emissions leads to old PA over most on-shore areas but slightly younger PA over SC urban areas.

4 Conclusions

The chronic high surface $O_3$ concentrations, as well as the increasing $SO_x$ ambient concentrations over California’s south coast (SC) and other regions, are affected by both long-range transport and local emissions, as shown in previous (Huang et al., 2010) and this study. Asian inflows were shown to be important around 22 June, during which period the $O_3$ concentrations in long-range transported air were 60–80 ppb. The transported air at ~2–4 km contained ~0.1–0.3 ppb of $NO_x$.
SO_{4} (Fig. 9a) in average. Those airmasses descended to the surface and influenced surface concentrations. The contribution from long-range transport occurred first over northern California and then over SC through in-state transport on ~24 June, when up to ~0.25 ppb of surface SO_{4} in SC was attributed to foreign sources (Table 5, upper-limit). During this period SO_{3} and SO_{2} in these long-range transported airmasses were also enhanced at altitudes above 6 km, but were transported at inland at high altitudes and did not influence CA surface air quality. The influence of local emissions from both natural and anthropogenic sources on air quality was evaluated. We conducted sensitivity simulations by turning off biogenic and fire emissions in both 12 km and 60 km model resolutions and compared the modeled O_{3} in base vs. sensitivity cases. We found that both biomass burning and biogenic emissions contribute to regional background O_{3} over SC up to 4 ppb, with larger contributions in other regions of CA (such as in the Central Valley, up to 10–12 and 12–15 ppb from biogenic and fire emissions, respectively). Uncertainties in these estimates due to model resolutions, emissions inventories and other factors are on the order of 3–4 ppb over SC.

The high concentrations of SC surface SO_{x} during the flight week were mostly contributed by local emissions. We compared two anthropogenic SO_{x} EIIs applied in 60 km and 12 km simulations and evaluated the model performance. The EIIs vary temporally and spatially, but the NEI 2001 lacks the shipping emissions, and has lower emissions overall. The resulting predicted SO_{x} concentrations are shown to be significantly underestimated. The CARB 2005 EI improved the magnitudes of emission rates and produced results closer to observations. However, the overall SO_{x} emissions over the SC are found to be underestimated, and estimate that the CARB emissions are low by about factor of two.

Adjoint sensitivity analysis indicated that during the flight week, SO_{2} levels at 00:00 UTC at six SC surface sites were influenced by previous day maritime emissions over the ocean, the terrestrial emissions over nearby urban areas, and by transported SO_{2} from the north, through both terrestrial and maritime areas.

We analyzed the effects of maritime emissions on air quality over SC by conducting a sensitivity simulation without maritime emissions using the CARB EI. The maritime emissions contributed 10–70% of SO_{2} concentrations over on-shore and terrestrial areas, showing apparent negative gradients from the coastal to inland regions. Approximately 20–60% of fine SO_{4} over the terrestrial regions are attributed to the maritime emissions, and the impacts are extended to San Diego areas. The maritime emissions significantly increased the NO_{x} distributions on shore, especially around the port area of North Long Beach. The O_{3} production in downwind areas can be shifted from VOC-limited to NO_{x}-limited after cutting off maritime emissions. Photochemical ages are also modified over on-shore areas as well as urban regions.

These results suggest that further improvements in SO_{x} emission inventories for the studied region as well as its upwind regions (north and central coastal areas) are needed. Optimal methods (such as data assimilation) can provide complete emission scaling factor matrix and reduce the mismatches between observations and model simulations. These methods would benefit from high resolution continuous near-surface measurements over both terrestrial and maritime areas. The impacts of one long-range transport event were analyzed during this one-week study period. Future studies over a longer period of time are needed to determine the frequency and variations in intensity of long range transport events and to identify the impacted regions during summertime. In addition, studies on reducing the uncertainties in estimated contributions from various emission sectors are also needed, which will support the future pollution control policies and regulations.

Supplement related to this article is available online at: http://www.atmos-chem-phys.net/11/3173/2011/acp-11-3173-2011-supplement.pdf.

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