Dear Editor and Reviewers,

Thank you for the comments to help improve the quality of the paper. We have revised the manuscript to address your comments and a detailed response to each comment is provided in this file.

The comments are in regular font, the responses are in red, and the changes in the manuscript are in blue.

Anonymous Referee #1

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The authors discussed the concentrations and sources of primary and secondary organic aerosols in PM0.1 over California for 2000-2008 using the source-oriented UCD/CIT model. The article is overall well-written. I will suggest the paper accepted by ACP after the authors address my following questions/suggestions:

1. SOA module

The SOA module used in this study is based on the two-product method. Different SOA formation treatments could result in different results. It would be meaningful if an alternate SOA module (e.g., VBS) is applied in the future study of POA and SOA.

Responses: Thanks for the comment. Atmospheric SOA formation pathways and processes are the focus of intense research which leads to continuous evolution in our understanding about accurate SOA modeling approaches. Part of our research team has recently developed a new statistical oxidation model to simulate SOA (Cappa et al. 2013; Cappa et al. 2016; Jathar et al. 2016) that is able to study the effects of multi-generational chemistry, evaporation of SOA fragments, wall loss effects, etc. Many of these issues are also the focus of VBS modeling efforts, and so we feel that we are capturing the essence of the scientific questions even if we have not directly applied the VBS model itself. The results of the statistical oxidation modeling studies are described in Section 3.3 of the manuscript. Future applications of long-term modeling in California will improve on the 2-product model to capture the latest scientific findings, but this issue is beyond the scope of the current paper. As a result, no changes were made in the current manuscript based on this comment.

2. OC/Mass ratios

The authors discussed the underpredictions of OC/Mass ratios shown in Figure 2, which could be due to the overestimation of dust emissions. Are dust emissions affected by wind speed from WRF? Did the authors evaluate the meteorology provided by WRF? What about seasalt, since some sites are along the coast? Although most of seasalt are coarse particles, they may contribute a little bit to PM2.5?

Responses: In reality the dust emissions are affected by the wind speed and soil moisture. However, the dust emissions in our study were developed by California Air Resources Board based on average wind speeds. Therefore the WRF wind speed was not used in the dust emissions. This point has been clarified on lines 234-236 of the revised manuscript.

The WRF predictions have been evaluated against meteorological observations. The results were described in the Part I paper. We have clarified the sentence on lines 164-165 of the revised manuscript to clarify this point.

The seasalt emissions were included in the simulations. The seasalt emissions were calculated online using the WRF wind speed. The detailed description of the emissions was also provided in the Part I paper. This point has been clarified on lines 154-155 of the revised manuscript.

Some other comments:
1. Page 6, line 78, UCD/CIT has been defined in page 4 line 52
Responses: Corrected.
2. Page 8, line 136-137, do you mean BENZ (i.e., ABNZ1_X1, ABNZ1_X2, ABNZ2_X1, and ABNZ2_X2)?
Responses: Yes, we corrected the sentence.
3. Page 9, line 155, change “meteorology fields” to “meteorological fields”
Responses: Changed.
4. Page 13, line 246, “Condensation of SOA”, do you mean the condensation of volatile VOCs?
Responses: We changed the sentence to “Condensation of the semi-volatile products to form SOA”.
5. Page 15, line 277, “some important sources”, could you please provide some specific sources that for Riverside case?
Responses: We speculate the missing sources are mostly likely some area sources, such as residential and/or agricultural waste emissions. With no solid evidence, we are not sure what exactly the sources are, so we don’t want to give specific names in the manuscript to avoid providing misleading information to readers. No changes were made for this comment.
6. Page 15, line 287, do you mean less POA converted to SOA in ultrafine size range?
Responses: No, we mean PM0.1 OA is more of POA and less of SOA, compared to PM2.5 OA. The sentence has been clarified in the revised manuscript on line 295.
7. Page 16, line 311, You may want to switch the order of supplementary figures.
Responses: Accepted. The order of figures in the supplemental materials was changed to follow when they are mentioned in the paper.

8. Page 31, Figure 4b, why are PM0.1 SOA/TOA ratios very high over the southeastern corner? Is that partly due to boundary conditions?
Responses: That is because very low POA concentrations (as can be seen in Figure 7), i.e., very low anthropogenic emissions, in that region. No changes were made for this comment.

Anonymous Referee #2

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The authors provided a long-term analysis for the spatial distribution of PM0.1, and

its components including POA and SOA. By using the source apportionment method, the authors further discussed the contribution of different sources on PM0.1 and its components. The article is generally well-written, and has clearly expressed the conclusions clearly by showing convincing data analysis. I will suggest the paper published on ACP, after the authors address my following suggestions:
Pg 10: define the metric used for the evaluation: MFB and MFE. Can put the equation into the Supporting.
Responses: Accepted. We put the definitions in the Supplemental Materials and referred to the definition in the main text.

Pg 10: "in the first paper in the series": if the authors claimed this paper as "the fourth in the series" (Pg 5 line 70), then I suggest the authors change "the first paper" to "the third : : :." to avoid confusion, or do the other way.
Responses: We changed to "Part I paper" to avoid confusion.

Pg 11, line 189-190: I assume the authors were still talking about the winter when they say "Wood smoke is predicted to be : : :."?
Responses: To be more accurate, we changed to "Wood smoke is predicted to be the dominant OC source in winter….".

Pg 11, line 192-193: the authors implied that the overestimation of the PM2.5 in the San Jose site was due to the overestimated emission inventory. So how did the authors make that conclusion? Was the emission inventory data significant different from the other places, or more uncertain compared with others?
Responses: The PM2.5 OC was consistently over-predicted at San Jose in all winter seasons during the 9 year period (Figure 1b). While at other sites, wintertime PM2.5 OC was not always over-predicted in all winters. Considering that wood burning is the dominant source of winter PM2.5 OC in California, and similar meteorological performance among these sites, we attributed the consistent over-prediction of PM2.5 OC at San Jose more likely to overestimated wood burning emissions at this location.

Surveys of home heating methods conducted by the Bay Area Air Quality Management District (BAAQMD) found that wood smoke emissions inventories were over-estimated in San Jose for the years 2012 and 2013. While these years are outside of the analysis window in the current manuscript, these findings support the hypothesis that wood smoke emissions in San Jose are over-estimated in the years 2000-2009.

This has been explained on lines 200-202 of the revised manuscript.

Pg 12: line 217-219: I suggest the authors move the brief introduction of the 6 Obs sites into Pg 10 to Pg 10 in front of Fig. 1. Also can the authors comment why they didn't use the EI Cajon site to evaluate the model's performance of simulating in PM2.5 in Fig. 1?

Responses: We moved the brief introduction of the observation sties to Pg10 in front of Fig.1. We kept six sites in Fig. 1 to make the figure clearer, but in the revised manuscript, we added El Cajon in Fig. 1.

Pg 15, line 287: change “PM2.5” to “PM2.5-SOA fraction” or “that in PM2.5”. Also the authors concluded that the SOA fraction in PM0.1 lower than that in PM2.5, but in Figure 4, we can see the fractions are higher in PM0.1 than PM2.5 in rural areas. Can the authors explain why?
Responses: We changed to “that in PM2.5” and we added “in urban areas” to be more accurate.

The SOA/TOA fractions in PM0.1 are generally low at all locations where primary combustion emissions are significant. This includes all major urban areas or locations with major transportation corridors. The PM0.1 SOA/TOA fraction increases in regions with very low primary combustion emissions because few natural sources emit primary OA in this size range. Natural sources including windblown dust contribute more to the PM2.5 size fraction than the PM0.1 size fraction in these remote regions, which explains the different behavior illustrated in Figure 4 and Figure S1. All concentrations are very low in these remote regions, and so the points have minor importance for health effects analysis. We feel that the extended discussion would risk confusing the reader, and so we have made these points in the Figure caption for S1 rather than in the main text.

Pg 34, in Figure 7 and others, also in the supplementary, I am confused about the meaning of colorbar. I thought it stands for the fractions from each source category in the total PM0.1 POA, but it seems not. What is the “maximum concentration value”, maximum of the monthly mean or maximum of the yearly mean? Also how the authors made the conclusion that the dominant regional sources are “wood smoke, meat cooking : : :”? Looking at the map, most of the data are in the range of “0-10” %, and you can’t tell which regions are in the 1% and which regions are in the 9%. For sources with a Max value of 900 but fractions around 1% may not be larger than the source with a Max value of 120 and fractions around 9%. Please quantify the fractions from each source before making conclusion. Also consider doing this for other similar plots.
Responses: The maximum concentration value is the maximum 9-year average concentrations. We made the changes in the figure captions to be clearer.

The dominant sources were determined based on the total contributions of the sources region wide. We added the fraction values in the discussion and we did the same changes for the discussion of Figure 8.

Pg 43 & 44: Switch the order S4 and S5 to follow when they are mentioned in the paper.
Responses: The order of figures in the supplemental materials was changed to follow

when they are mentioned in the paper.

Anonymous Referee #3

Received and published: 27 December 2016

General Comments: This manuscript presents results of concentrations and sources Ultrafine Organic Aerosols from 9 years chemical transport model simulations, which is important for health effects studies. The presentation quality is excellent and no major scientific problems with the presentation. I only have some minor concerns, which are listed below.

Specific comments:

1. In model evaluation, the authors claim that their calculated monthly MFB and MFE meet Boylan and Russel (2006) standard. It is better to point out the standard in manuscript.

Responses: The PM model performance criteria of MFB and MFE, suggested by Boylan and Russell (2006), are a function of PM concentration as follows,

MFB (%) $\leqslant \pm 140e^{-(Co+Cm)} + 60$

MFE (%) $\leqslant 125e^{-2(Co+Cm)/3} + 75$

where Co and Cm represent the observed and predicted PM concentrations, respectively.

We added above criteria equations in the Supplemental Materials.

2. Emission inventory is a key part in air quality modeling, but the authors do not write much about emission inventory (based on which year, what the sectors are, and etc.). Besides, the simulation period is as long as 9 years. It is better if the authors can consider the changes in emissions over this period.

Responses: The details of emission inventory were provided in the Part I paper, so we didn’t repeat in this paper. This is clarified on lines 144-146 of the revised manuscript. A few additional details are provided below to help the reviewer understand what was done.

The emission inventory base year was 2000. We did consider the changes in emissions over the modeling period when information is available. The EMFAC 2007 model (CARB 2008) was used to scale the mobile emissions using predicted temperature and relative humidity fields through the entire nine-year modeling episode. Biogenic emissions were generated using the Biogenic Emissions Inventory System v3.14 (BEIS3.14), which includes a 1-km resolution land cover database with 230 different vegetation types (Vukovich and Pierce 2002). Sea-salt emissions were generated on-line based on the formulation described by de Leeuw et al. (de Leeuw et al. 2000) for the surf zone and the formulation described by Gong (Gong 2003) for the open ocean. Emissions from wildfires and open burning at 1 km × 1 km resolution were obtained from the Fire INventory from NCAR (FINN) (Hodzic et al. 2007; Wiedinmyer et al. 2011). These emissions included the changes over the model period. However, for other emissions, for example, stationary sources and residential wood burning emissions were kept unchanged due to unavailable information to scale the emissions.

3. The authors compared ratio from model to CMB derived ratio. Are the CMB derived ratios 100% reliable? How is its uncertainty? And it is also better to introduce the CMB method in the manuscript.
Responses: The uncertainties of CMB derived SOA range from 1% - 22% (Daher et al. 2012). The information was added in the caption of Figure 3.

We used the CMB results to evaluate the model performance of SOA and POA predicted by the UCD/CIT model. Because the CMB method is not the focus of this study, we think it is not necessary to introduce the CMB method in the manuscript. The references on the CMB method were provided in the original manuscript.

4. The authors discuss the impact of vapor wall losses on SOA concentrations. How will it affect model evaluation? In Figure 1, model overpredicts OA at some sites. After vapor wall losses correction, model may mismatch with observations.
Responses: The vapor wall losses correction didn't significantly affect the model evaluation results for total OA. The predicted SOA/TOA fractions in the base model is very low (generally < 10%) at the observation sites located in urban areas (Figure 4 and Figure S1). Even though the vapor wall loss correction led to substantial increase of SOA concentrations, the total OA concentrations didn't increase much.

A sentence was added in the manuscript in the lines 363-366:
"Due to low SOA/TOA fractions (< 10%) at the observation sites located in urban areas (Figure 4 and Figure S1), the substantial increase of SOA by the vapor wall loss corrections does not strongly change the total OA concentrations and therefore does not significantly affect the model evaluation results shown in Figure 1."

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Long-term Particulate Matter Modeling for Health Effects Studies in California – Part II: Concentrations and Sources of Ultrafine Organic Aerosols

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Abstract

Organic aerosol (OA) is a major constituent of ultrafine particulate matter ($PM_{0.1}$). Recent epidemiological studies have identified associations between $PM_{0.1}$ OA and premature mortality and low birth weight. In this study, the source-oriented UCD/CIT model was used to simulate the concentrations and sources of primary organic aerosols (POA) and secondary organic aerosols (SOA) in $PM_{0.1}$ in California for a 9-year (2000 - 2008) modeling period with 4 km horizontal resolution to provide more insights about $PM_{0.1}$ OA for health effects studies. As a related quality control, predicted monthly average concentrations of fine particulate matter ($PM_{2.5}$) total organic carbon at six major urban sites had mean fractional bias of -0.31 to 0.19 and mean fractional errors of 0.4 to 0.59. The predicted ratio of $PM_{2.5}$ SOA/OA was lower than estimates derived from chemical mass balance (CMB) calculations by a factor of 2~3, which suggests the potential effects of processes such as POA volatility, additional SOA formation mechanism, and missing sources. OA in $PM_{0.1}$, the focus size fraction of this study, is dominated by POA. Wood smoke is found to be the single biggest source of $PM_{0.1}$ OA in winter in California, while meat cooking, mobile emissions (gasoline and diesel engines), and other anthropogenic sources (mainly solvent usage and waste disposal) are the most important sources in summer. Biogenic emissions are predicted to be the largest $PM_{0.1}$ SOA source, followed by mobile sources and other anthropogenic sources, but these rankings are sensitive to the SOA model used in the calculation. Air pollution control programs aiming to reduce the $PM_{0.1}$ OA concentrations should consider controlling solvent usage, waste disposal, and mobile emissions in California, but these findings should be revisited after the latest science is incorporated into the SOA exposure calculations. The spatial distributions of SOA associated with different sources are not sensitive to the choice of SOA model, although the absolute amount of SOA can change significantly. Therefore, the spatial distributions of $PM_{0.1}$ POA and SOA over the 9-year study period provide useful information for epidemiological studies to further investigate the associations with health outcomes.

Key Words: Primary organic aerosols, secondary organic aerosols, California, sources, UCD/CIT model.

1. Introduction

Organic aerosol (OA) is a significant constituent of fine particulate matter ($PM_{2.5}$) (Zhang et al. 2007) and a dominant constituent of ultrafine particulate matter ($PM_{0.1}$) (Kleeman et al. 2009; Sardar et al. 2005b). Epidemiology studies carried out over the past 20 years link $PM_{2.5}$ to severe short-term and long-term health effects such as asthma, cardio-respiratory disease, and lung cancer (Dockery 2001; Dockery and Pope 1994; Dockery et al. 1993; Franklin et al. 2007; Le Tertre et al. 2002; Pope and Dockery 2006; Pope et al. 2002). Epidemiological studies for $PM_{0.1}$ mass are in the early stages of development but preliminary results show associations with premature mortality (Ostro et al. 2015) and low birth weight (Laurent et al. 2014). OA is an important species due to its contribution to $PM_{2.5}$ and $PM_{0.1}$ mass, and the toxicity of some compounds within OA has motivated even greater scrutiny in health studies (Mauderly and Chow 2008). A few $PM_{2.5}$ epidemiology studies have investigated the associations between exposure to OA and health effects with mixed results (Cao et al. 2012; Krall et al. 2013; Levy et al. 2012; Mar et al. 2000; Ostro et al. 2006; Ostro et al. 2010). The early epidemiological studies conducted for $PM_{0.1}$ have identified subcategories of OA that are highly associated with negative health effects (Laurent et al. 2014; Laurent et al. 2016a; Laurent et al. 2016b; Ostro et al. 2015) and these results merit further investigation to identify the exact sources and compound classes that may be related to $PM_{0.1}$ OA toxicity.

The exposure fields used in the published $PM_{0.1}$ epidemiology studies to date have been generated with chemical transport models (CTMs) because $PM_{0.1}$ measurements with sufficient spatial or temporal resolution are not widely available. In these studies, predictions using the UCD/CIT (University of California Davis/California Institute of Technology) model were evaluated against $PM_{2.5}$ and $PM_{0.1}$ point measurements as a confidence building exercise and the model predictions were then used to estimate exposure fields with ~4km and ~24hr resolution over the state of California (Hu et al. 2014a; Hu et al. 2014b; Hu et al. 2015). The OA exposure fields generated through this approach reflect the state-of-the-science predictions from CTMs at the time they were done, but they may not capture the full complexity of atmospheric OA. OA consists of primary organic aerosol (POA) and secondary organic aerosol (SOA). POA is directly emitted to the atmosphere in the particle phase and SOA is formed in the atmosphere from the oxidation of volatile or semi-volatile organic compounds (Seinfeld and Pankow 2003). Both POA and the precursors of SOA can be emitted from anthropogenic and biogenic sources (Mauderly and Chow 2008). Numerous theories have been put forward about the volatility of POA (Robinson et al. 2007), the conversion of intermediate volatility compounds to SOA (Jathar et al. 2014; Zhao et al. 2014), and the role of water in SOA formation (Jathar et al. 2016; Pankow et al. 2015). A comprehensive model for OA that has been fully constrained by measurements has not been demonstrated to date, which makes it difficult to estimate $PM_{2.5}$ OA exposure using CTMs. However, measurements indicate the OA in the $PM_{0.1}$ size fraction is more heavily influenced by POA (Ham and Kleeman 2011; Kleeman et al. 2009), which makes estimating exposure to $PM_{0.1}$ using CTMs more feasible.

The current paper, as the fourth in the series (Hu et al. 2014a; Hu et al. 2014b; Hu et al. 2015), investigates the UCD/CIT model capability in predicting the concentrations and sources of POA and SOA in $PM_{0.1}$. The objective of this study is to identify the features of the CTM POA and SOA results that could add skill to the exposure assessment for epidemiological studies and to discuss the potential problems in modeling POA and SOA for use in health effects studies.

2. Methods

2.1 Model Description

The source-oriented UCD/CIT air quality model was used to predict OA concentrations in the current study. The UCD/CIT model tracks primary particles and SOA formation from different sources separately through the calculation of all major aerosol processes such as emissions, transport, deposition, gas-to-particle conversion, and coagulation. The standard algorithms of these processes used in the current study are provided in a companion paper (Hu et al. 2015) and references therein, therefore only the details of the algorithms for POA and SOA source apportionment calculation are described here.

The UCD/CIT source-oriented air quality model tracks primary particles emitted from different sources by adding artificial tracers to represent total primary mass contributions from different sources in each particle size bin (Ying et al. 2008). The emissions of tracers are empirically set to be 1% of the total mass of primary particles emitted from each source category, thus the particle radius and the dry deposition rate are not significantly changed. The primary PM total mass concentrations from a given source then are directly correlated with the simulated artificial tracer concentrations from that source. Source specific emission profiles are used to estimate the POA concentrations in the primary PM total mass using the equation (1):

$$POA_{i,j} = C_{i,j} \times A_{i,j} \qquad \text{(eq. 1)}$$

where $POA_{i,j}$ and $C_{i,j}$ represent POA concentration and primary PM total mass concentration in size bin i from jth source, respectively. $A_{i,j}$ represents OA fraction per unit mass of PM emitted from the jth emission source in size bin i. More details describing the POA source apportionment technique and the emission profiles are provided in the previous studies (Ying and Kleeman 2004; Ying et al. 2008).

The SOA module used in the current study follows the two-product method described by Carlton et al. (2010). SOA formation is considered from seven precursors: isoprene, monoterpenes, sesquiterpenes, long-chain alkanes, high-yield aromatics, low-yield aromatics, and benzene. The seven precursors form twelve semi-volatile products and seven nonvolatile products. The calculations consider dynamic gas-particle conversion of the semi-volatile and nonvolatile products. A more detailed description of the SOA module and parameters used in gas-to-particle transfer calculation is provided in the part I paper (Hu et al. 2015) and references therein.

The original SOA module described above was modified to have the source apportionment capability inherent in the UCD/CIT model. SOA source apportionment is predicted by tracking the SOA precursor emissions from different sources individually through all atmospheric processes as they react to form low-volatility products that can partition to the particle phase based on the SOA module described above. This approach was initially developed for source apportionment of secondary inorganic aerosols, such as nitrate, sulfate, and ammonium (Mysliwiec and Kleeman 2002; Ying and Kleeman 2006). Later, this approach was applied for SOA source apportionment in California using the Caltech Atmospheric Chemistry Mechanism (Chen et al. 2010; Kleeman et al. 2007) and in Texas using the SAPRC99 mechanism (Zhang and Ying 2011, 2012). In the current study, the SAPRC11 mechanism was used and expanded to track the reactions of SOA precursors emitted from different sources. Chemical reaction products leading to SOA formation are labeled with the source-identity of the reactant so that source attribution information is preserved. For the example of benzene (BENZ) reaction with OH forming benzene derived SOA,

BENZ + OH → SV.BNZ1 + SV.BNZ2 (rx. 1)
SV.BNZ1 ↔ ABNZ1 (rx. 2)
SV.BNZ2 ↔ ABNZ2 (rx. 3)

where SV.BNZ1 and SV.BNZ2 represents the two semi-volatile products that partition between gas and particle phase, and ABNZ1 and ABNZ2 represent the particle phase SOA products from SV.BNZ1 and SV.BNZ2, respectively. If there are two sources for BENZ, then BENZ is expanded into two species BENZ_X1 and BENZ_X2 in the model. The above pathways (rx1 – rx3) are then expanded as:

BENZ_X1 + OH → SV.BNZ1_X1 + SV.BNZ2_X1 (rx. 4)
SV.BNZ1_X1 ↔ ABNZ1_X1 (rx. 5)
SV.BNZ2_X1 ↔ ABNZ2_X1 (rx. 6)
BENZ_X2 + OH → SV.BNZ1_X2 + SV.BNZ2_X2 (rx. 7)
SV.BNZ1_X2 ↔ ABNZ1_X2 (rx. 8)
SV.BNZ2_X2 ↔ ABNZ2_X2 (rx. 9)

Thus, the SOA products from BENZ (i.e., ABNZ1_X1, ABNZ1_X2, ABNZ2_X1 and ABNZ2_X2) contain the information needed to calculate source contributions to the SOA concentrations.

2.2 Model Application

The UCD/CIT model was applied to simulate the concentrations and sources of POA and SOA during ~ a decadal period (9 years from 2000 January 1st to 2008 December 31st) over

California using a one-way nesting technique added to the UCD/CIT model (Zhang and Ying 2010). The parent domain covers the entire state of California using a 24km horizontal grid resolution and two nested domains cover the most populated areas (> 92% of California total population) using a 4km horizontal grid resolution. A detailed description of the emissions inventory used for the analysis has been presented previously (Hu et al. 2015) and so only a brief summary is discussed in the current manuscript. Emissions of the seven SOA precursors were grouped into nine source categories: on-road gasoline engines, off-road gasoline engines, on-road diesel engines, off-road diesel engines, wood smoke, meat cooking, high sulfur fuel combustion, other anthropogenic sources (including solvent usage, waste disposal emissions etc.), and the natural/biogenic sources. Primary PM emissions were also grouped into these 9 source categories. Particulate composition, number and mass concentrations in the range between 0.01 and 10 μm in diameter were represented in 15 size bins with the first 5 bins for $PM_{0.1}$ (0.01 to 0.1 μm) in the model. Biogenic emissions were generated using the U.S. EPA's biogenic emission inventory system (BEIS3.14). Sea salt emissions were estimated based on wind speed as described in the Part I paper (Hu et al. 2015). The Weather Research and Forecasting model (WRF) v3.1.1 (William C. Skamarock June 2008) was used to simulate the 24 km and 4 km hourly meteorological fields (wind, temperature, humidity, precipitation, radiation, air density, and mixing layer height) that drove the UCD/CIT model simulations. WRF simulations were initialized and bounded by the North American Regional Reanalysis (NARR) data with 32 km resolution and 3-hour time resolution. The four-dimensional data assimilation (FDDA) (Liu et al. 2005) technique was used and the surface friction velocity (u*) in the WRF model was increased by 50% to improve the surface wind predictions as suggested by previous studies (Hu et al. 2012; Hu et al. 2010; Mass 2010). Details of the modeling domains, vertical cell spacing, preparation of emissions and meteorological inputs (including a full comparison to meteorological measurements) are provided in the Part I paper in the series (Hu et al. 2015).

3. Results

3.1 Concentrations of POA and SOA

Hourly POA and SOA concentrations in multiple size fractions were calculated throughout the 9-year simulation period, and then averaged to daily and monthly average concentrations. Although the focus of the current study is $PM_{0.1}$ POA and SOA, the predicted $PM_{2.5}$ OA concentrations were also calculated and compared to measurements as a confidence building exercise (since $PM_{0.1}$ measurements are not routinely available). Model calculations predict organic matter (OM) concentrations while ambient measurements quantify organic carbon (OC) concentrations. Simulated OM concentrations are converted to OC concentrations using an OM/OC ratio of 1.6 for POA (Turpin and Lim 2010) and species-specific OM/OC ratios for SOA species taken from Table 1 in Carlton et al. (2010). Detailed evaluation of the model performance for $PM_{2.5}$ OC (and other PM / gaseous species) has been presented in the first paper in the series (Hu et al. 2015). In summary, predicted monthly average $PM_{2.5}$ OC has a mean fractional bias of -0.32 and a mean fractional error of 0.43. Monthly mean fractional bias (MFB) and mean fractional errors (MFE) (equations E1 and E2 in the Supplemental Materials) calculated using daily average OC generally meet the model performance criteria proposed by Boylan and Russell (2006) (equations E3 and E4 in the Supplemental Materials).

Figure 1 illustrates the time series of the predicted and measured monthly-average total $PM_{2.5}$ OC concentrations at seven major urban locations (a) Sacramento, (b) San Jose, (c) Fresno,

(d) Bakersfield, (e) Los Angeles, (f) Riverside, and (g) El Cajon. At each site, daily average measured concentrations of the $PM_{2.5}$ total mass and OC were obtained from California Air Resources Board (CARB) (CARB 2011) "1 in 3" sampling network and averaged over the 9 year period. Measured $PM_{2.5}$ OC concentrations at all sites show strong seasonal variation with higher concentrations in winter months and lower concentrations in summer months. OC concentrations predicted by the UCD/CIT model generally capture the monthly average concentrations and seasonal variations with MFB ranging from -0.31 to 0.19 and MFE ranging from 0.4 to 0.59. However, the model predicts much weaker trends of $PM_{2.5}$ OC over the 9 years at Los Angeles and Riverside, indicating that the declining emission trends might not be well represented in the inventory. At Sacramento and Fresno, the measured monthly average OC concentrations frequently exceeded 10 $\mu g/m^3$ in winter and the maximum monthly OC concentrations reached or exceeded ~25 $\mu g/m^3$. Wood smoke is predicted to be the dominant OC source in winter at the two locations, contributing over 70% of the total OC concentrations on average. Wood smoke is also predicted to be the dominant OC source in winter at San Jose and Bakersfield. Model calculations tend to over-predict the winter OC concentrations at San Jose, indicating the wood smoke emissions are likely over-estimated in this area. This is consistent with more recent surveys of home heating fuels conducted by the Bay Area Air Quality Management District (BAAQMD). Model calculations generally under-predict OC in summer when concentrations are lower. Meat cooking and other anthropogenic sources are predicted to be the largest sources in summer at Sacramento, San Jose, Fresno, and Bakersfield. Together these two categories contribute over 86% of the total predicted OC in summer. Both measured and predicted seasonal variation is weaker at Los Angeles and Riverside than in Northern California due to smaller wood smoke contributions. Meat cooking and other anthropogenic sources make the largest predicted contributions to OA at these two Southern California locations. Mobile sources (gasoline and diesel engines) also contribute approximately 30% of the total $PM_{2.5}$ OC at Los Angeles. Model calculations tend to under-predict $PM_{2.5}$ OC concentrations in all seasons in 2000-2006 at Riverside (approximately 80 km downwind of the Los Angeles urban center). Intense emissions transported from the upwind Los Angeles areas along with the meteorology and topography enhances photo-oxidation of volatile organic compounds (VOCs) and formation of SOA at this location. A measurement study of organic aerosols at Riverside in summer indicated high SOA fraction of the total OA with an average SOA/OA ratio of 0.74 (Docherty et al. 2008). The $PM_{2.5}$ OC under-prediction at Riverside during summer and the general under-prediction in summer at other sites may indicate that some important precursors and pathways of $PM_{2.5}$ SOA are missing or only partially included in the current SOA module, such as SOA formation from glyoxal and methylglyoxal (Ervens and Volkamer 2010; Fu et al. 2008; Ying et al. 2015) and from aerosol aqueous phase chemistry (Volkamer et al. 2009), the conversion of intermediate volatility compounds to SOA (Jathar et al. 2014; Zhao et al. 2014), or SOA forming with higher yields than included in the module (Zhang et al., 2014; Cappa et al., 2016).

Figure 2a compares the average $PM_{2.5}$ OC/mass ratios estimated from ambient measurements and the values predicted by the UCD/CIT model over the 9-year study period at seven representative urban locations. Predicted concentrations on the corresponding days were extracted and averaged for the comparison. The average OC/mass ratios were then calculated. The observed average OC/mass ratios vary in the range of 0.24 (at Riverside) to 0.45 (at Sacramento). The predicted average OC/mass ratios are in relatively good agreement with measured values at Los Angeles, Riverside, and Bakersfield (difference < 20%), but not at Sacramento, San Jose, Fresno, and El Cajon (difference > 35%). The predicted average OC/mass ratios are consistently lower than observed ratios, by 0.01 (3% at Los Angeles) to 0.22 (48% at Sacramento). This under-prediction is partly attributed to the under-prediction of OC concentrations, especially the SOA concentrations, but also to the over-prediction of total mass concentrations due to over-estimated dust emissions (Hu et al. 2014a; Hu et al. 2015). The seasonal average dust emissions used in the current study were not adjusted based on wind speed and soil moisture. A sensitivity analysis was conducted by removing the dust concentrations from the predicted $PM_{2.5}$ mass (Figure 2a). The average predicted OC/mass ratio increased from 0.22 to 0.29 (average across the seven sites), compared to the observed ratio of 0.33. Omission of dust from the model predictions improves agreement with OC/mass measurements at all sites except central Los Angeles, although OC/mass without dust is still lower than measurements at four sites (Sacramento, San Jose, Fresno, and El Cajon) indicating OC predictions are likely biased low at these locations.

Figure 2b compares the predicted and observed OC/mass ratios in the ultrafine ($PM_{0.1}$) or quasi-ultrafine ($PM_{0.18}$, $PM_{0.25}$) particles. The ultrafine/quasi-ultrafine measurement data were compiled in a previous study (Hu et al. 2014a) from published literature (Herner et al. 2005; Kim et al. 2002; Krudysz et al. 2008; Sardar et al. 2005a; Sardar et al. 2005b). The ultrafine or quasi-ultrafine data are more sparse than the $PM_{2.5}$ data, but still cover a sufficient total number of days to allow for robust comparison. The observed OC/mass ratios in ultrafine/quasi-ultrafine sizes vary from 0.43 (at Modesto) to 0.71 (at USC). The predicted ultrafine/quasi-ultrafine OC/mass ratios generally agree well with observed values at all sites. The generally better agreement of OC/mass ratios in the ultrafine/quasi-ultrafine size range compared to the $PM_{2.5}$ size range reflects the fact that SOA formation and dust emissions make limited contributions to ultrafine/quasi-ultrafine concentrations. Condensation of the semi-volatile products to form SOA mostly takes place in the particle accumulation mode, and is generally not dominant in the ultrafine size range due to the increase in the saturation vapor pressure above small particles (Kelvin effect). Dust components mainly contribute to coarse and fine particles, but make little contribution to the ultrafine particles.

The primary and secondary fraction of total OA cannot be directly measured in ambient OA samples. A few indirect methods have been developed to estimate the POA and SOA concentrations, such as molecular marker-based method (Daher et al. 2011; Daher et al. 2012; Ham and Kleeman 2011; Kleindienst et al. 2007), elemental carbon (EC) tracer method (Cabada et al. 2004; Lim et al. 2003; Polidori et al. 2007; Polidori et al. 2006; Turpin and Huntzicker 1995), water soluble organic carbon content method (Weber et al. 2007), aerosol mass spectrometry factorization method (Aiken et al. 2008; Lanz et al. 2007; Ulbrich et al. 2009), and the un-explained fraction of OA by tracers for major POA categories (Chen et al. 2010; Schauer and Cass 2000). In the current study, $PM_{2.5}$ SOA concentrations were estimated by the molecular marker Chemical Mass Balance (CMB) method (Daher et al. 2012) during sampling periods in 2005-2007 at four locations. $PM_{2.5}$ POA concentrations were then estimated by subtracting $PM_{2.5}$ SOA concentrations estimated by the CMB method from the total measured OA concentrations. Figure 3 shows the $PM_{2.5}$ POA and SOA concentrations predicted by the UCD/CIT model (right dark columns) compared to the $PM_{2.5}$ POA and SOA concentrations estimated using the CMB method (left gray columns). Error bars represent the standard deviation of concentrations estimated during the sampling periods. The total $PM_{2.5}$ OA (i.e., POA + SOA) concentrations predicted by the UCD/CIT model generally agree with measured values (with fractional bias within ±35%) except at the Riverside site (with a fraction bias of -63%). But the $PM_{2.5}$ SOA concentrations predicted by the UCD/CIT model appear to be a factor of 2~3 lower than the

SOA concentrations estimated by the CMB method (ratio ranging from 2.2 at Riverside to 2.8 at WSanG). The $PM_{2.5}$ POA concentrations predicted by the UCD/CIT model are higher than those estimated by the CMB method at WSanG and ESanG1. This may reflect the effects of POA volatility. Studies have indicated that some fraction of POA emissions will evaporate, and this material may undergo photo-oxidation and condense back to particle phase (Robinson et al., 2007). In the current model, POA is treated as non-volatile. Thus, no such evaporation occurs. However, the substantial under-prediction of $PM_{2.5}$ SOA at all sites suggests that some SOA precursors and pathways are likely missing from the current SOA mechanism. Both $PM_{2.5}$ POA and SOA are under-predicted at Riverside, indicating that some important sources are likely missing in that area.

Figure 4 illustrates the predicted total $PM_{0.1}$ OA concentrations (Figure 4a) and the predicted ratios of SOA to total OA averaged over the 9 year modeling period (Figure 4b). High total $PM_{0.1}$ OA concentrations with maximum concentrations > 2 $\mu g/m^3$ are located in urban areas where the POA emissions are large due to human activities. Predicted $PM_{0.1}$ SOA generally accounts for less than 10% of total $PM_{2.5}$ OA at urban areas, but predicted SOA contribute to 10~20% of total OA in suburban areas, and contribute to 20~50% in rural areas. The spatial distribution of $PM_{2.5}$ SOA concentrations and the SOA to total OA ratios (shown in Figure S1) are generally similar to those of $PM_{0.1}$, but $PM_{0.1}$ OA has sharper spatial gradients and the $PM_{0.1}$ SOA fraction is lower than that in $PM_{2.5}$ in urban areas, indicating POA contributes more in the ultrafine size range.

Figure 5 shows the contributions from the 9 precursor species to the $PM_{0.1}$ SOA concentrations (results of $PM_{2.5}$ SOA are shown in Figure S2). Maximum SOA concentrations are located in southern part of the SJV. Monoterpenes, sesquiterpenes, oligomers, and long alkanes are the most important precursors, contributing over 90% of the total SOA in most areas, while other precursors (xylene, toluene, and benzene) in total contribute less than 10 ng/m^3 to SOA concentrations. These finding are very dependent on the treatment of vapor wall losses during the formulation of the SOA model. The contributions from different precursors to SOA concentrations have very different spatial distributions. Long chain alkanes form SOA mainly in the urban areas of Southern California and in the middle-southern portion of the SJV. Isoprene, monoterpenes, and sesquiterpenes form SOA at coastal and foothill locations where the biogenic emissions are greatest. The longer lifetime of long chain alkanes than isoprene leads to a broader spatial distribution for the SOA derived from alkanes. The spatial distribution of oligomers of anthropogenic SOA (Oligomer_A) and biogenic SOA (Oligomer_B) reflects the patterns of SOA derived from long chain alkanes and the total biogenic species. The relative spatial patterns associated with each precursor are generally not sensitive to the exact formulation of the SOA model (see section 3.3).

3.2 Sources of POA and SOA

Figure 6 displays the time series of monthly average PM$_{0.1}$ SOA source contributions at the six major urban locations. PM$_{0.1}$ SOA concentrations are high in summer (100~300 ng/m^3) and low (20~50 ng/m^3) in winter, reflecting the seasonal variation in photochemistry. PM$_{0.1}$ SOA concentrations are higher at Fresno and Bakersfield than other sites due to larger biogenic source contributions. Biogenic emissions are the largest source of PM$_{0.1}$ SOA across all sites, followed by the other anthropogenic sources (mainly solvent usage and waste disposal emissions, see Figure S3). On-road gasoline engines are an important source of SOA at Los Angeles and

Riverside. Similar source contributions to $PM_{2.5}$ SOA are found and shown in Figure S4 in the Supplemental Materials.

Figure 7 shows the predicted regional source contributions of $PM_{0.1}$ POA averaged over the 9 year modeling period. The important regional sources of $PM_{0.1}$ POA over the entire California are predicted to be other anthropogenic sources (contributing 39.6%), wood smoke (37.1%), on-road gasoline (9.1%), and meat cooking (5.8%). Wood smoke is the dominant POA source especially in Northern California, with the maximum $PM_{0.1}$ POA contribution exceeding 1 $\mu g/m^3$. Meat cooking and mobile (on-road and off-road) sources are the major sources in urban areas, especially in metropolitan areas such as Greater Los Angeles Area and the San Francisco Bay Area. Other anthropogenic sources is another major category in the urban centers in the SJV and also the Los Angeles areas. High sulfur content fuel sources are mainly located around the ports in the Los Angeles and San Francisco Bay areas. The regional source contributions of $PM_{0.1}$ POA are quite different from those of $PM_{2.5}$ POA (shown in Figure S5). The $PM_{2.5}$ POA source contributions are much more widespread than the $PM_{0.1}$ POA sources contributions because $PM_{2.5}$ has a longer lifetime due to slower deposition and coagulation compared to $PM_{0.1}$. For example, the mobile sources and the other anthropogenic sources contribute greatly to $PM_{2.5}$ POA throughout the entire SJV, but only contribute to $PM_{0.1}$ POA in urban centers.

Figure 8 shows the predicted regional source contributions of $PM_{0.1}$ SOA averaged over the 9 year modeling period (and Figure S6 shows the $PM_{2.5}$ SOA results). Biogenic emission is predicted to be the single largest $PM_{0.1}$ SOA source in the present study, contributing 63.7% of the $PM_{0.1}$ SOA over the entire California. The maximum biogenic $PM_{0.1}$ SOA concentration is up to 0.1 $\mu g/m^3$ around Bakersfield in the southern SJV. Other anthropogenic sources (22.2%), and on-road gasoline engines (10.8%) are predicted to be the most important anthropogenic sources of $PM_{0.1}$ SOA in California. The spatial distribution of $PM_{0.1}$ SOA concentrations from these anthropogenic sources are similar (but different from the spatial distribution of SOA from biogenic sources) with high concentrations in Southern California. $PM_{0.1}$ SOA formation from on-road diesel engines, off-road diesel engines, wood smoke, meat cooking and high sulfur fuel combustion are small, with $PM_{0.1}$ SOA contributions generally less than a few ng/m^3. A recent epidemiological study has revealed that anthropogenic $PM_{0.1}$ SOA is highly associated with ischemic heart disease mortality (Ostro et al. 2015). Therefore, the results in this study suggest that control of solvent usage, waste disposal, and mobile emissions should be considered to protect public health in California, but the exact determination of source controls will need to be evaluated after the SOA formation mechanism is updated.

3.3 Influence of vapor wall losses on SOA exposure in California

The SOA concentrations predicted in the current study are based on the SOA yield data measured in chamber experiments. A recent study has demonstrated that organic vapors can be lost to chamber walls during SOA formation experiments resulting in SOA yields that are biased low (Zhang et al. 2014). Efforts have been carried out to parameterize the effect of vapor wall losses on SOA formation in the UCD/CIT air quality model to account for this effect when predicting ambient SOA concentrations in Southern California (Cappa et al. 2015). SOA concentrations are predicted to increases by factors of 2-5 with low vapor wall loss rates, and by factors of 5-10 with high vapor wall loss rates, compared to the concentrations in the simulations with no consideration of vapor wall losses. Due to low SOA/TOA fractions (< 10%) at the observation sites located in urban areas (Figure 4 and Figure S1), the substantial increase of SOA by the vapor wall loss corrections does not strongly change the total OA concentrations and therefore does not significantly affect the model evaluation results shown in Figure 1. Here we further analyzed the changes in the population weighted concentrations (PWCs) of SOA when vapor wall losses are accounted for. Two sets of simulations (scenarios) conducted by Cappa et al (2015) are considered, one with the low-NO_x, high-yield parameters (denoted as “highyield”) and the other with high-NO_x, low-yield parameters (denoted as “lowyield”). Each set of simulations included three vapor wall loss cases, i.e., no consideration of vapor wall losses (denoted as “base”), low vapor wall loss rates (denoted as “lowwallloss”), and high vapor wall loss rates (denoted as “highwallloss”). PWCs of SOA are calculated for six counties in the Southern California for the six scenarios, respectively. Spatial difference in exposure is important in cohort studies, therefore the relative changes of PWCs among counties are examined. Figure 9 shows the PWCs of SOA and their relative changes in different scenarios in the six counties. The results indicate that PWCs of SOA increase substantially by accounting for vapor wall losses in all counties (panel a). However, the spatial pattern of SOA PWC, as characterized by normalizing the PWC for each location by the PWC in Orange County, is very similar in all scenarios (panel b). Consequently, accounting for vapor wall losses changes the SOA exposure ratio in different counties by only a small extent of < 15% for most scenarios/counties (panel c). These results suggest that future simulations that account for vapor wall losses in SOA simulations will yield increased absolute values of concentrations but will have spatial patterns that are similar to the basecase results in the current paper when used for epidemiology studies.

Figure 9 suggests that associations between anthropogenic SOA and health effects identified in previous epidemiological studies will prove robust to future updates in SOA models. This finding also extends to the spatial pattern of individual SOA precursors. The influence of vapor wall losses on exposure to SOA formed from different precursors (i.e., long alkanes, aromatics, isoprene, sesquiterpenes, and monoterpenes) is shown in Figures S7-S11. In all cases, the spatial pattern of PWC for SOA derived from each precursor is similar under all treatments of wall losses. Long alkanes and aromatics are mainly from anthropogenic sources, and isoprene, sesquiterpenes, and monoterpenes are mostly from biogenic sources. Further detailed interpretation of source contributions to SOA and associated health effects should only be carried out after new exposure fields are calculated using the latest SOA models.

4. Conclusions

The source-oriented UCD/CIT model was applied to predict the concentrations and sources of $PM_{0.1}$ POA and SOA in California for a 9 year (2000 - 2008) modeling period with 4 km horizontal resolution to provide data for health effects studies. As a confidence building measure, predicted total $PM_{2.5}$ OC concentrations (primary + secondary) and the $PM_{2.5}$ and $PM_{0.1}$ OC/mass ratios generally agree with measured values at fixed point locations. Compared to the POA and SOA concentrations estimated from measurements at 4 sites using the CMB method, the $PM_{2.5}$ total OA concentrations predicted by the UCD/CIT model have a fractional bias within ±35% except at the Riverside site. The CMB model estimated $PM_{2.5}$ SOA concentrations accounted for 13-37% of total OA while the UCD/CIT SOA concentrations accounted for 4-11% of total OA. POA volatility, incomplete SOA formation mechanism, and/or missing sources may account for the discrepancy. For these reasons, the current study focuses on the $PM_{0.1}$ size fraction.

$PM_{0.1}$ OA has larger contributions from primary sources than the $PM_{2.5}$ size fraction. Wood smoke is found to be the single biggest source of $PM_{0.1}$ OA in winter in California, and meat cooking, mobile sources and other anthropogenic sources (mainly solvent usage, and waste disposal) are the most important sources in summer, but these rankings are sensitive to the SOA model used in the calculation. Biogenic emissions are predicted to be the largest $PM_{0.1}$ SOA source, followed by the other anthropogenic sources, and mobile sources. A recent epidemiological study has revealed that anthropogenic $PM_{0.1}$ SOA is highly associated with ischemic heart disease mortality (Ostro et al. 2015). Therefore, the results in the present study suggest that control of solvent usage, waste disposal, and mobile emissions should be considered to protect public health in California, but detailed source control programs can only be carried out after revised calculations are performed using updated SOA models. The predicted spatial distributions of the concentrations and sources of POA and SOA in $PM_{0.1}$ over the 9-year periods provide detailed information for epidemiological studies to further investigate the associations with other health outcomes, and these spatial patterns are generally not sensitive to the treatment of wall losses in the SOA model formulation. All model results included in the current manuscript can be downloaded free of charge at http://faculty.engineering.ucdavis.edu/kleeman/.

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Figures and Tables

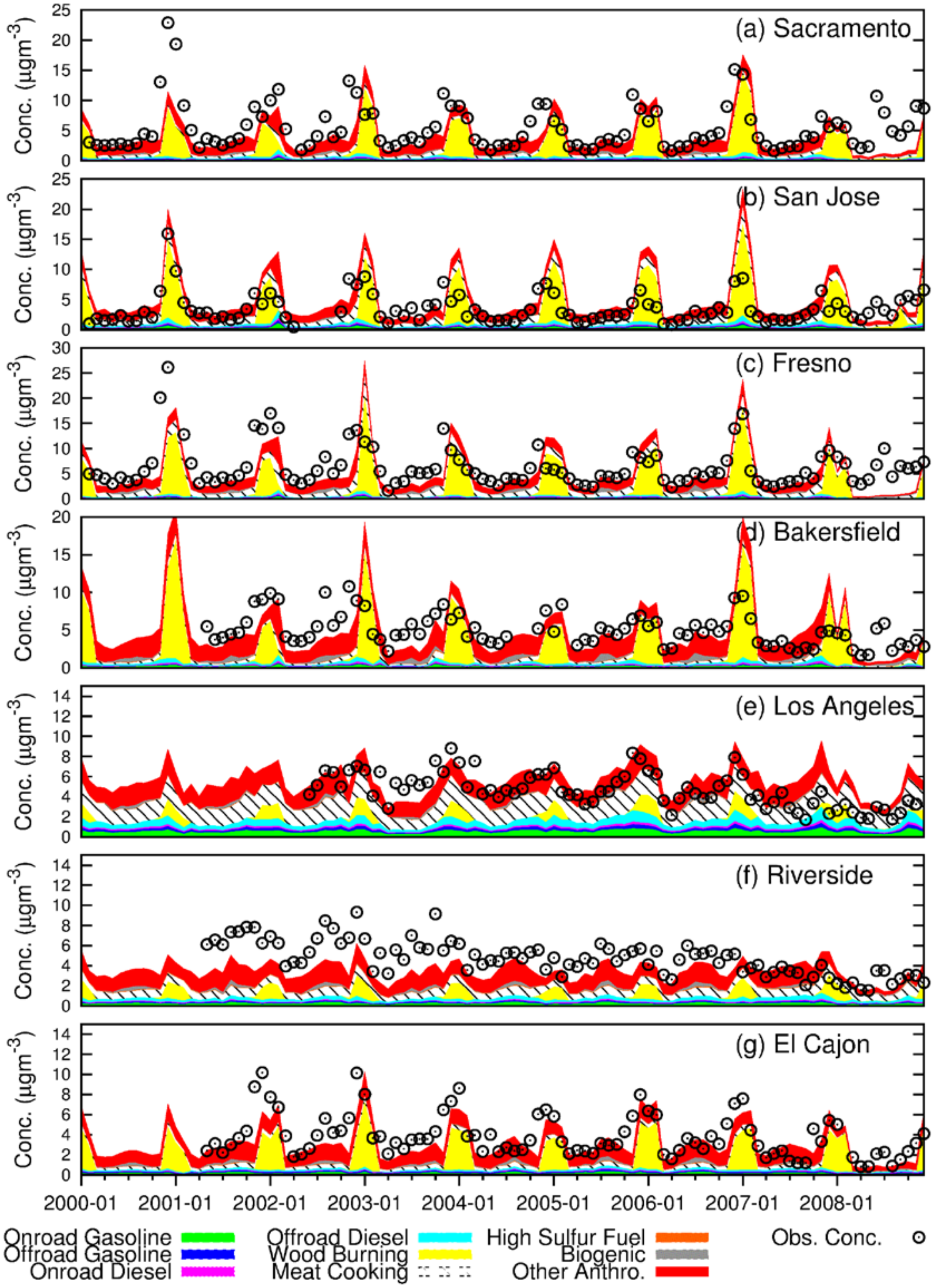

Figure 1. Monthly source contributions to $PM_{2.5}$ total OC at 7 urban sites. Observed total OC concentrations are indicated by the dot-circles, and predicted OC concentrations from different sources are indicated by the colored areas.

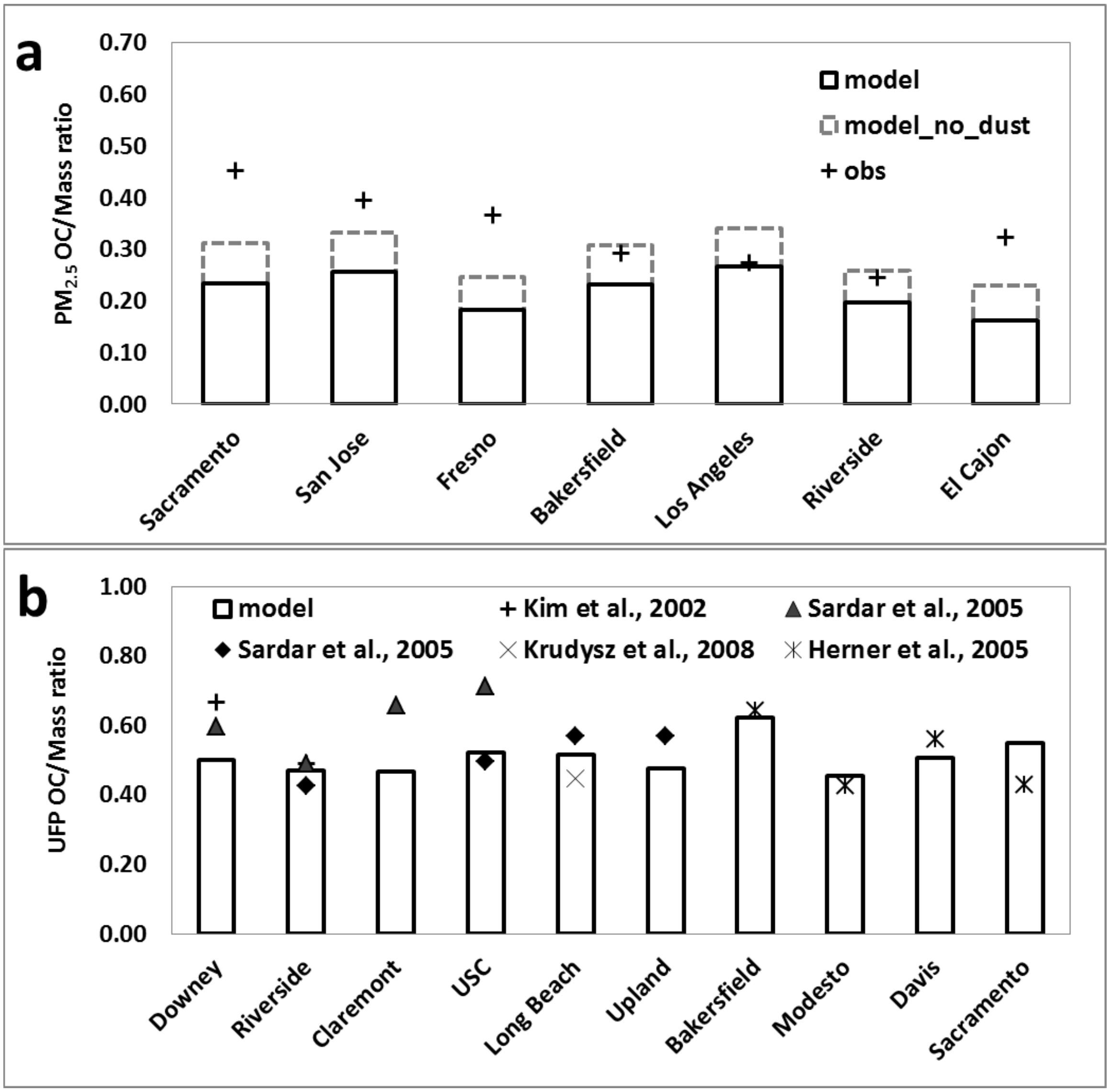

Figure 2. Observed (obs) and predicted (model) OC/Mass ratios in (a) $PM_{2.5}$ and (b) ultrafine and quasi-ultrafine PM. In (a), a sensitivity analysis is conducted by removing the dust concentration from the $PM_{2.5}$ total mass (model_no_dust).The ultrafine and quasi-ultrafine data in (b) are extracted from published literature as indicated in the figure.

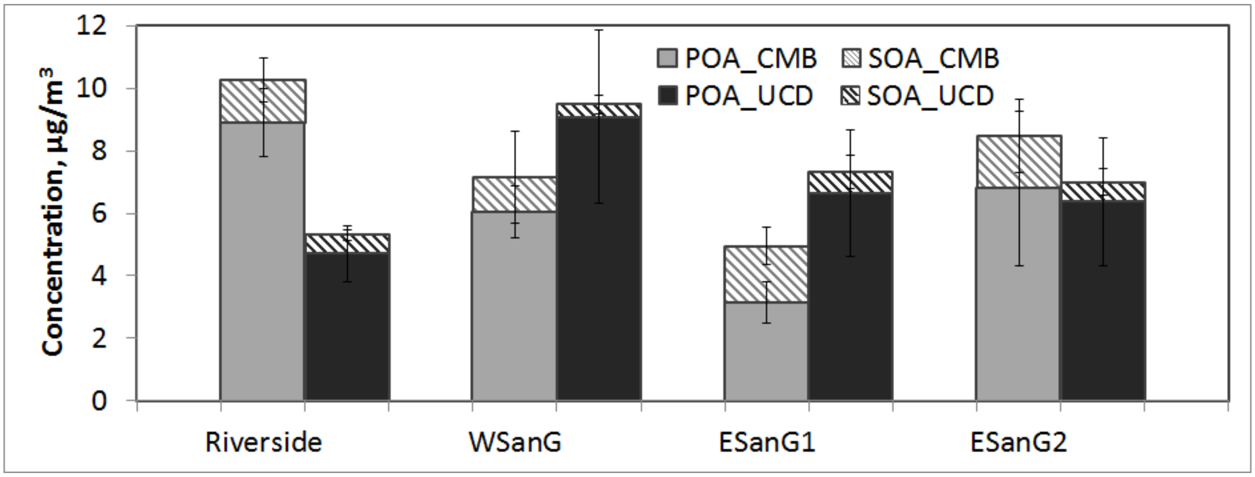

Figure 3. POA and SOA concentrations estimated by the CMB method (left gray columns) and predicted by the UCD/CIT model (right dark columns). Error bars represent the standard deviation of concentrations estimated during the sampling periods by both methods. The uncertainties of CMB derived SOA range from 1% - 22% (Daher et al., 2012). The data are for sampling periods in 2005-2007 at four sites in Southern California.

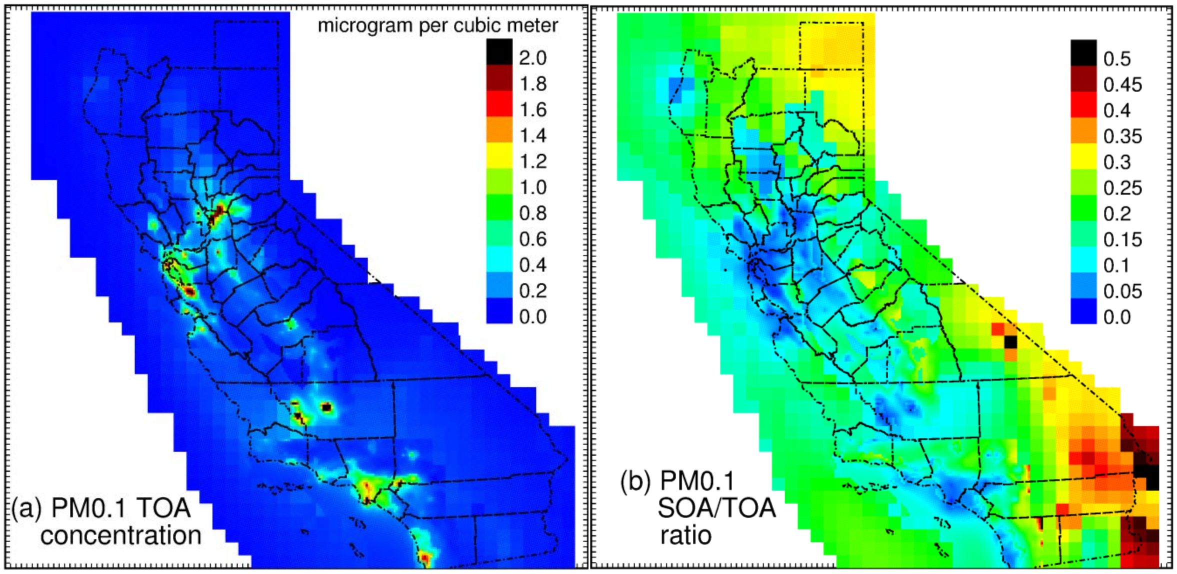

Figure 4. Predicted 9-year average (a) $PM_{0.1}$ Total OA (TOA) concentration and (b) $PM_{0.1}$ SOA/TOA ratio in California.

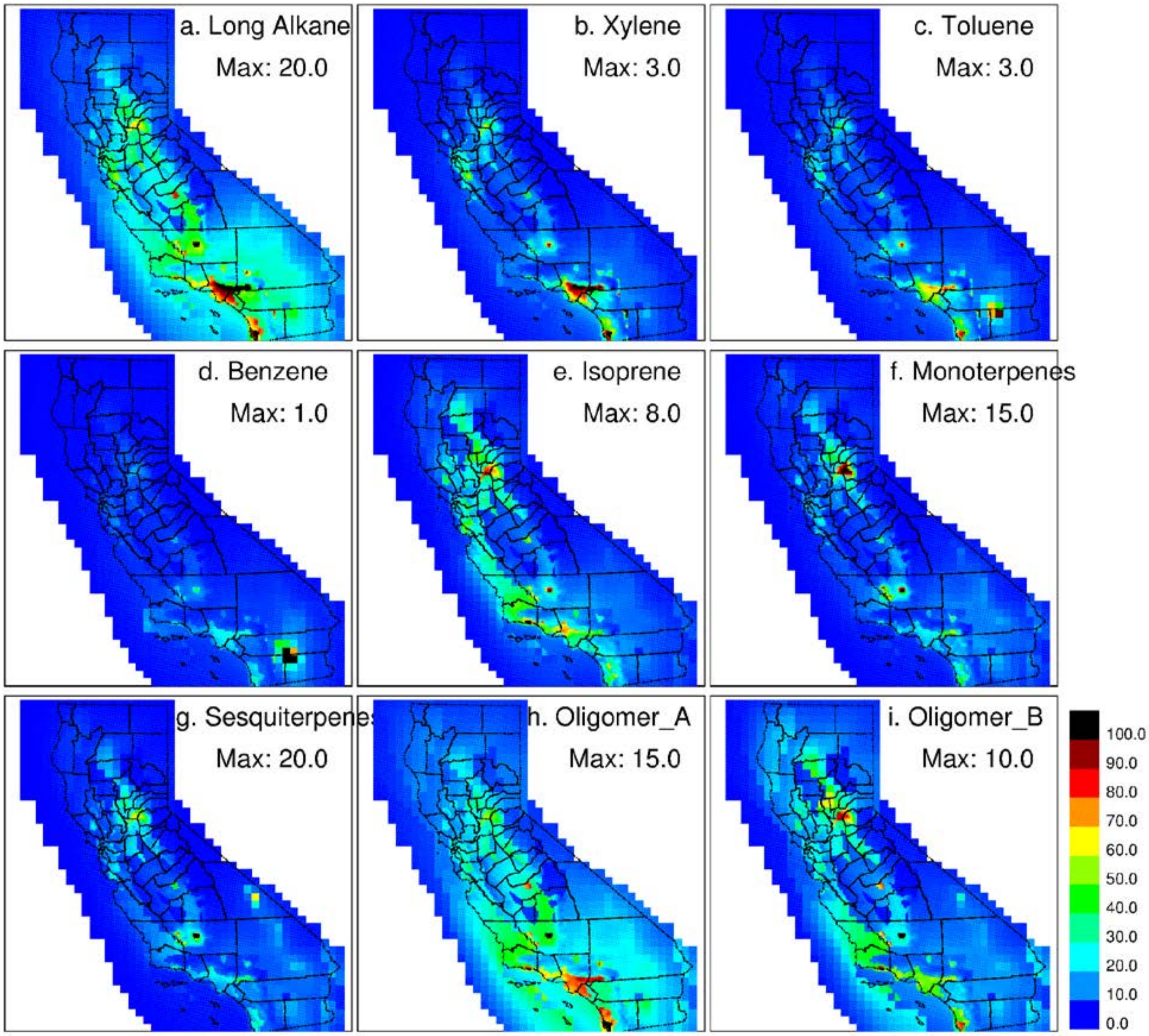

Figure 5. The 9-year average $PM_{0.1}$ SOA concentrations derived from (a) AALK, b) AXYL, c) ATOL, d) ABNZ, e) AISO, f) ATRP, g) ASQT, h) AOLGA, and i) AOLGB. Note AXYL and ATOL are actually derived from lumped aromatics species ARO2 (groups of aromatics with kOH > 2×10^4 ppm^{-1} min^{-1}, including xylenes and other di- and polyalkylbenzenes) and ARO1 (groups of aromatics with kOH < $\times10^4$ ppm^{-1} min^{-1}, including toluene and monoalkylbenzenes). The color scales (shown in the last panel in unit of %) indicate the ratios of the concentrations to the maximum 9-year average values, which are shown in the panels under species names with a unit of ng/m^3.

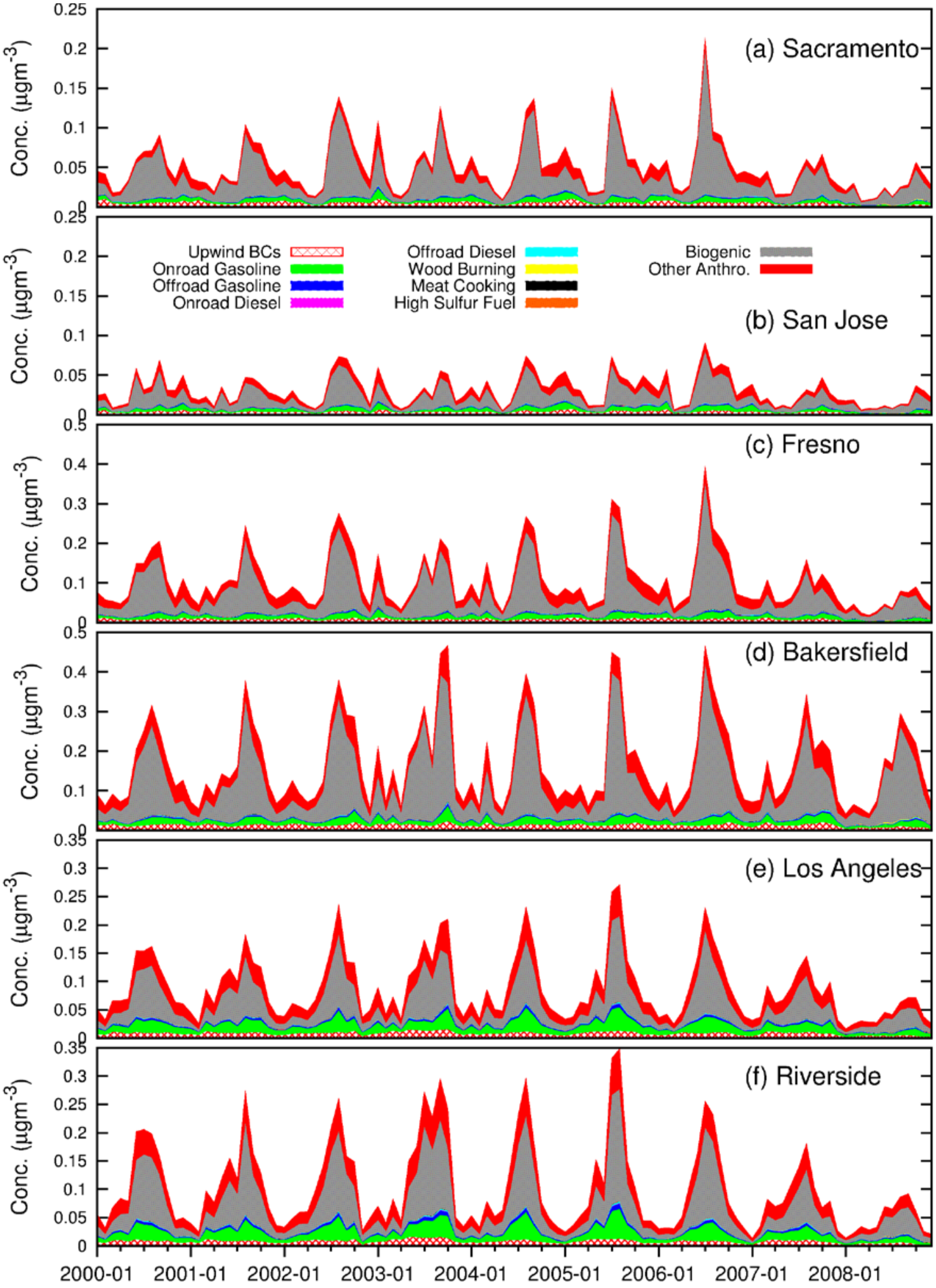

Figure 6. Monthly source contributions to $PM_{0.1}$ SOA at 6 urban sites. Predicted $PM_{0.1}$ SOA concentrations from different sources are indicated by the colored areas.

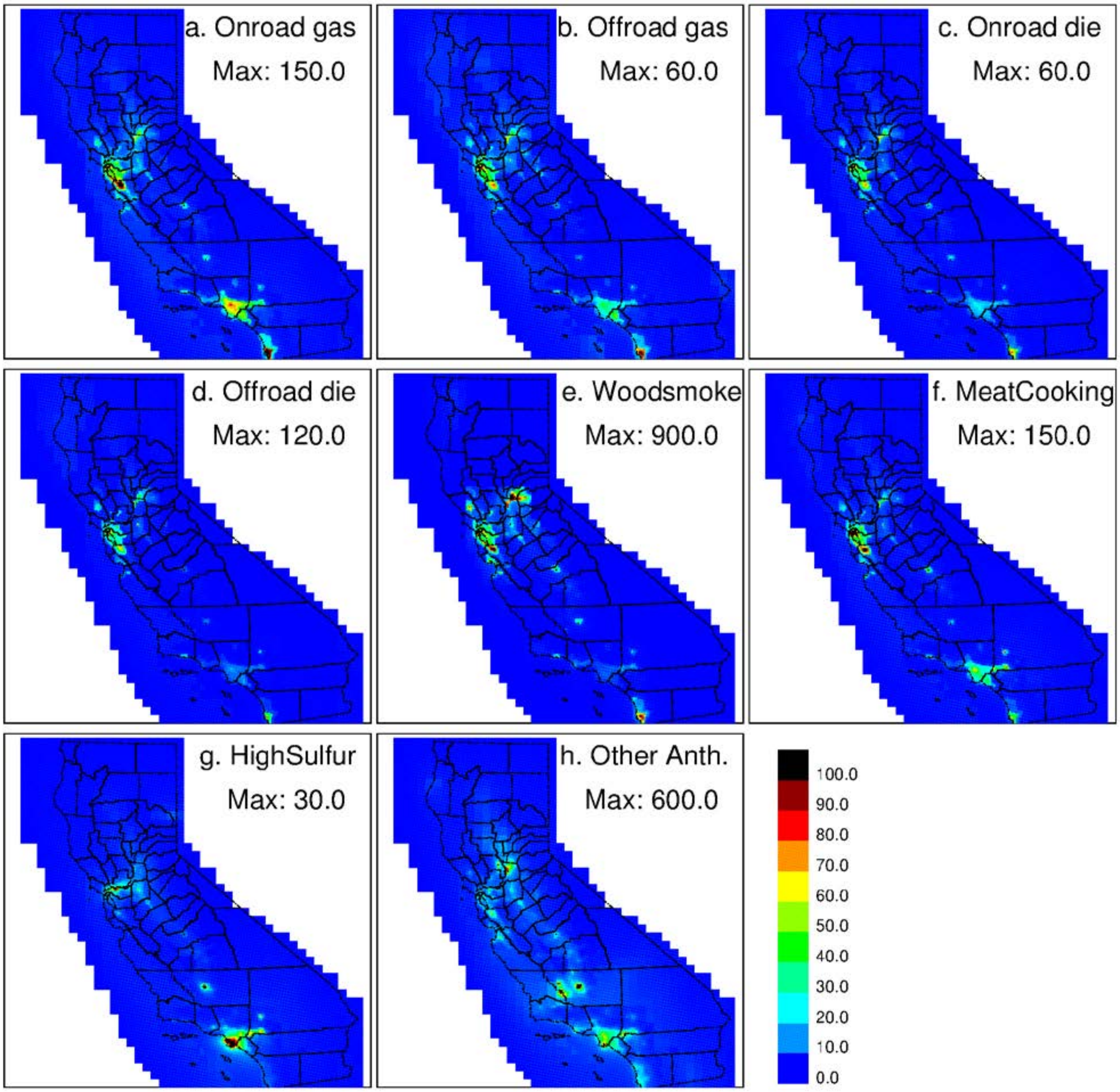

Figure 7. Predicted source contributions to 9-year average $PM_{0.1}$ POA concentrations. The color scales (shown in the last panel in unit of %) indicate the ratio of the concentrations to the maximum 9-year average concentration values, which are shown in the panels under source names with a unit of ng/m^3.

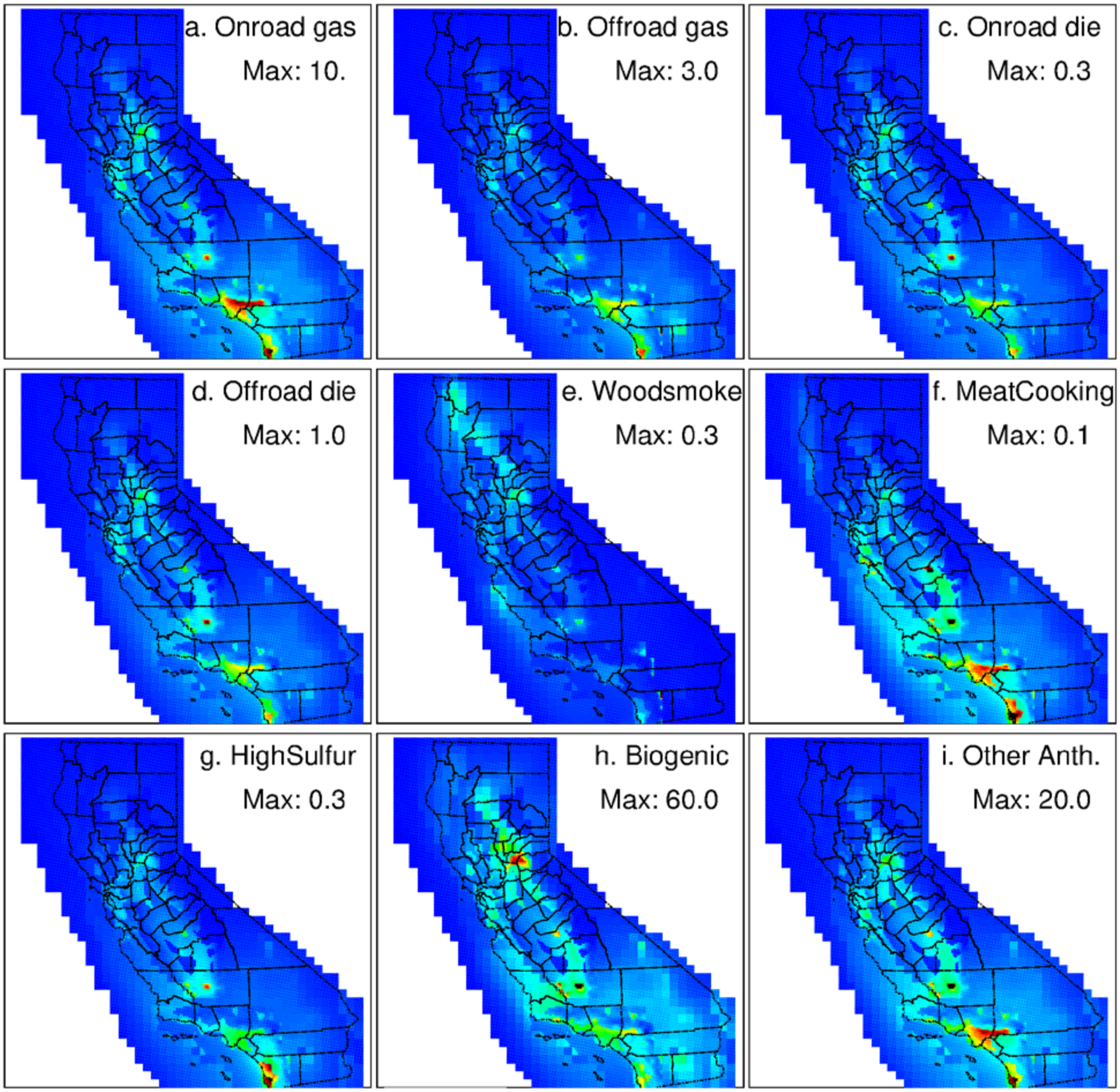

Figure 8. Predicted source contributions to 9-year average $PM_{0.1}$ SOA concentrations. The definition of the color scales are the same as in Figure 7.

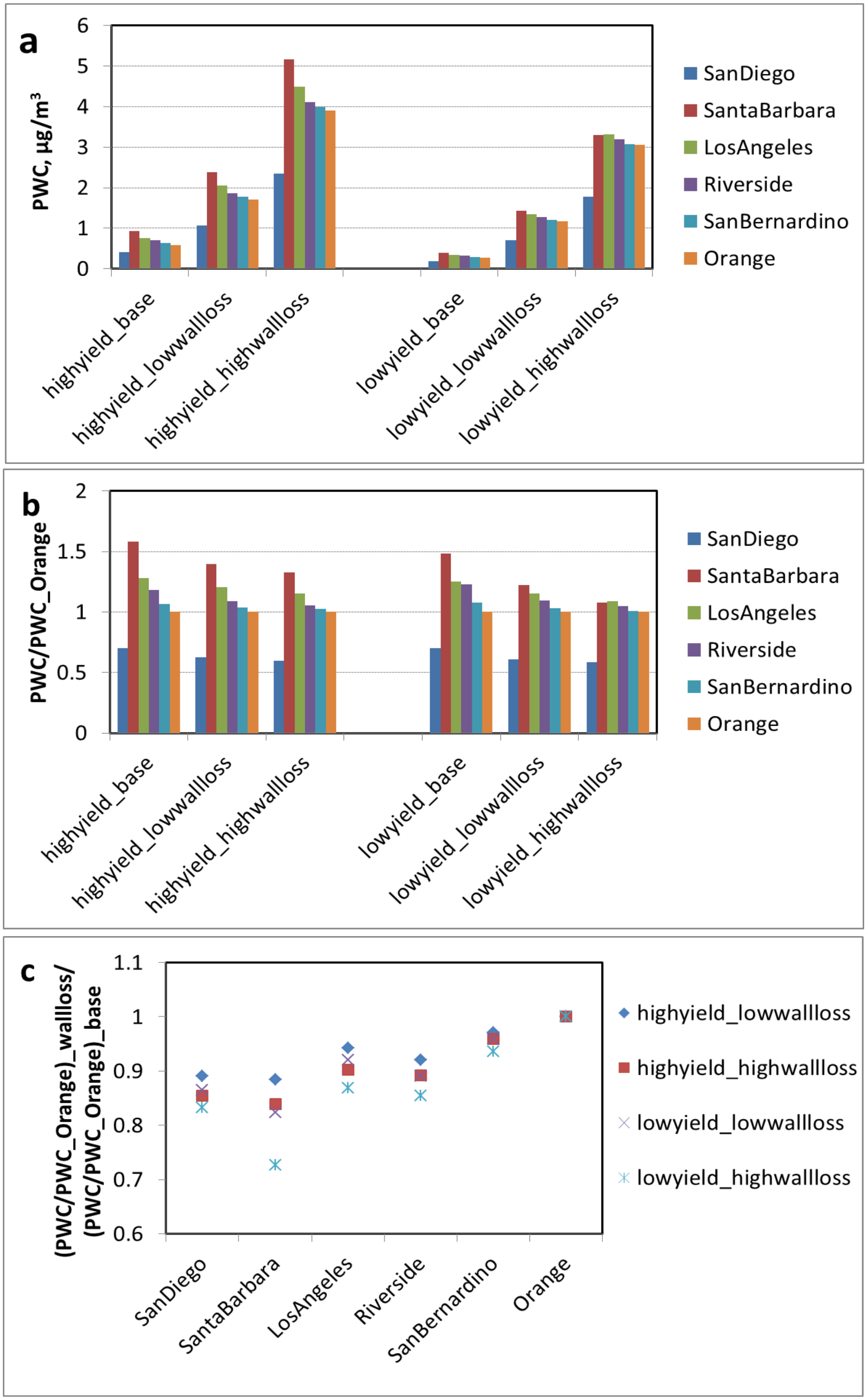
a
PWC, µg/m³
6
5
4
3
2
1
0
highyield_base
highyield_lowwallloss
highyield_highwallloss
lowyield_base
lowyield_lowwallloss
lowyield_highwallloss
SanDiego
SantaBarbara
LosAngeles
Riverside
SanBernardino
Orange
b
PWC/PWC_Orange
2
1.5
1
0.5
0
highyield_base
highyield_lowwallloss
highyield_highwallloss
lowyield_base
lowyield_lowwallloss
lowyield_highwallloss
SanDiego
SantaBarbara
LosAngeles
Riverside
SanBernardino
Orange
c
(PWC/PWC_Orange)_wallloss/
(PWC/PWC_Orange)_base
1.1
1
0.9
0.8
0.7
0.6
SanDiego
SantaBarbara
LosAngeles
Riverside
SanBernardino
Orange
highyield_lowwallloss
highyield_highwallloss
lowyield_lowwallloss
lowyield_highwallloss

Figure 9. (a) Predicted population weighted concentrations (PWCs) of SOA in six counties in Southern California. Two sets of simulations (scenarios) conducted by Cappa et al (2015) were used, one with the low-NO_x, high-yield parameters (denoted as “highyield”) and the other with high-NO_x, low-yield parameters (denoted as “lowyield”), and each set of simulations included three vapor wall loss cases, i.e., no considering of vapor wall losses (denoted as “base”), low vapor wall loss rates (denoted as “lowwallloss”), and high vapor wall loss rates (denoted as “highwallloss”). (b) Normalized PWCs of SOA in all counties to the PWC of SOA in Orange County. (c) Changes in the normalized PWCs of SOA in all counties by accounting for vapor wall losses.

Long-term Particulate Matter Modeling for Health Effects Studies in California – Part II: Concentrations and Sources of Ultrafine Organic Aerosols

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Supplemental Mateirals

Equations:

MFB and MFE are calculated using equation E1 and E2, respectively.

$$MFB = \frac{1}{N}\sum_{i=1}^{N}\frac{\left(C_m - C_o\right)}{\left(\frac{C_o + C_m}{2}\right)} \qquad \text{(E1)}$$

$$MFE = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|C_m - C_o\right|}{\left(\frac{C_o + C_m}{2}\right)} \qquad \text{(E2)}$$

The PM model performance criteria of MFB and MFE, suggested by Boylan and Russell (2006), are a function of PM concentration as follows:

$$\text{MFB (\%)} \leqslant \pm 140e^{-(Co+Cm)} + 60 \qquad \text{(E3)}$$

$$\text{MFE (\%)} \leqslant 125e^{-2(Co+Cm)/3} + 75 \qquad \text{(E4)}$$

Where Co and Cm in E1-E4 represent the observed and predicted PM concentrations, respectively.

Tables and Figures:

Figure S1: Predicted 9 year average $PM_{2.5}$ Total OA concentration and SOA/TOA ratio in California

Figure S2: $PM_{2.5}$ SOA concentrations formed from different precursors.

Figure S3: Emission of different sources of long alkanes and aromatics in the "other anthropogenic" source category.

Figure S4: Monthly source contributions to $PM_{2.5}$ SOA at 6 urban sites.

Figure S5: Predicted source contributions to 9 year average $PM_{2.5}$ POA concentrations.

Figure S6: Predicted source contributions to 9 year average $PM_{2.5}$ SOA concentrations.

Figure S7-S11: Influence of accounting for vapor wall losses on SOA results for SOA derived from long alkanes (S1), aromatics (S2), isoprene (S3), sesquiterpenes (S4), and monoterpenes (S5).

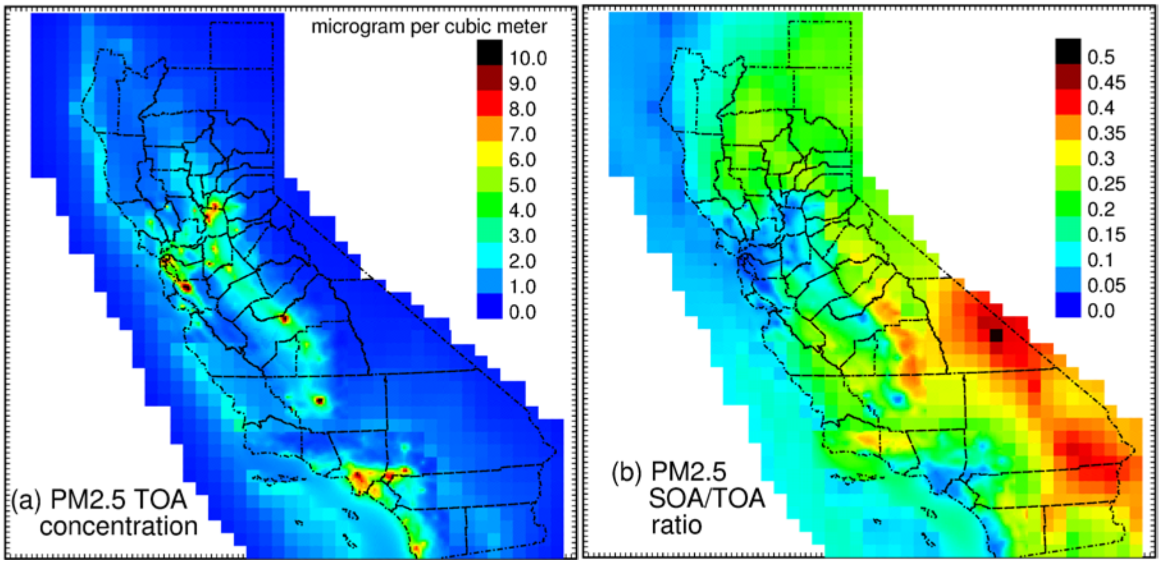

Figure S1. Predicted 9-year average (a) $PM_{2.5}$ Total OA (TOA) concentrations and (b) $PM_{2.5}$ SOA/TOA ratios in California. Natural sources including windblown dust contribute more to the $PM_{2.5}$ size fraction than the $PM_{0.1}$ size fraction in remote regions at the northeast and southeast corners of the state, which explains the different behavior illustrated in Figure 4 and Figure S1.

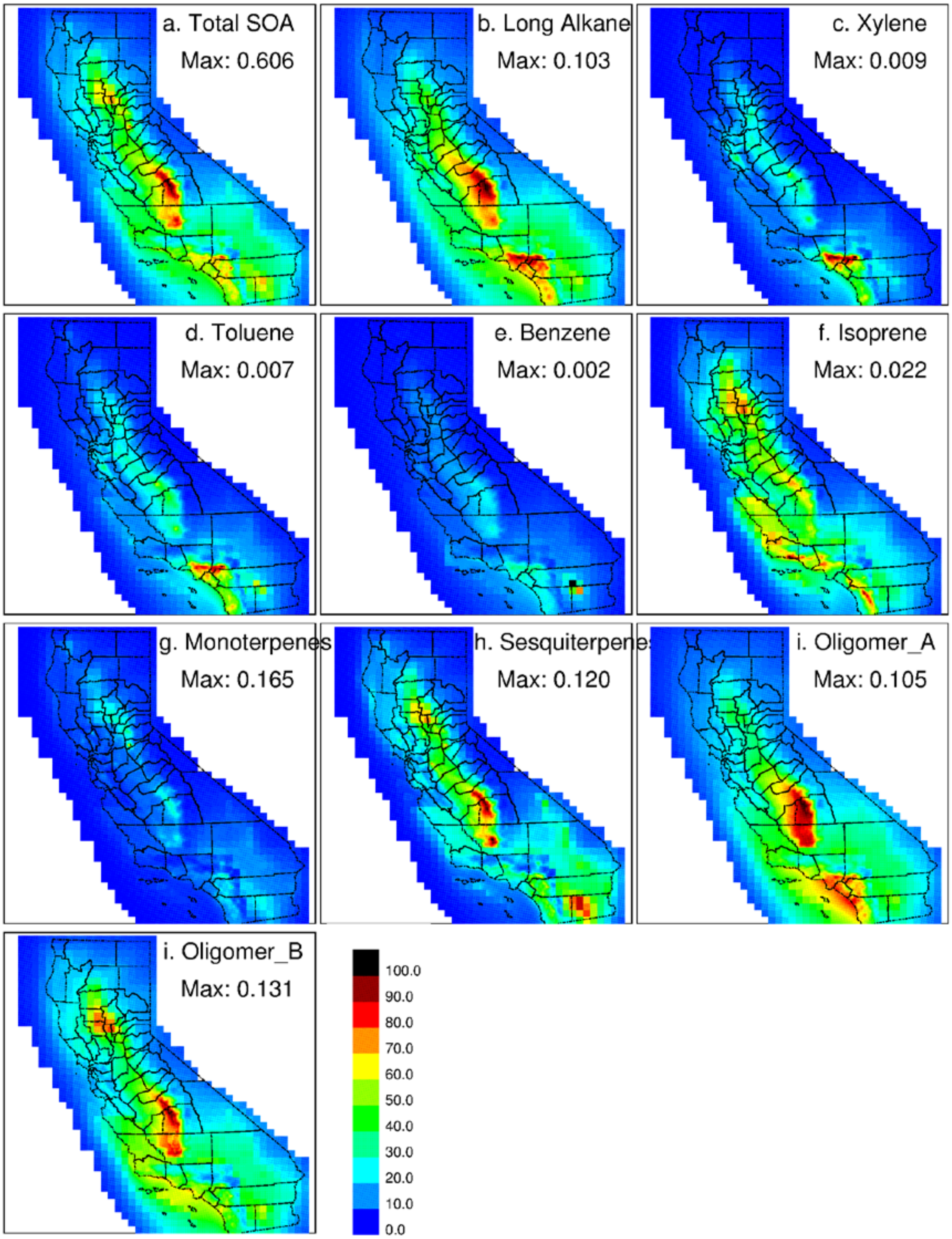

Figure S2. (a) 9-year average SOA concentrations; and SOA formed from (b)AALK, (c) AXYL, (d) ATOL, (e) ABNZ, (f) AISO, (g) ATRP, (h) ASQT, (i) AOLGA, and (j) AOLGB in $PM_{2.5}$. The color scales (shown in the last panel in unit of %) indicate the ratio of the concentrations to the max concentration values. The maximum concentration values are shown in the panels under the names of the species, with a unit of μg/m^3.

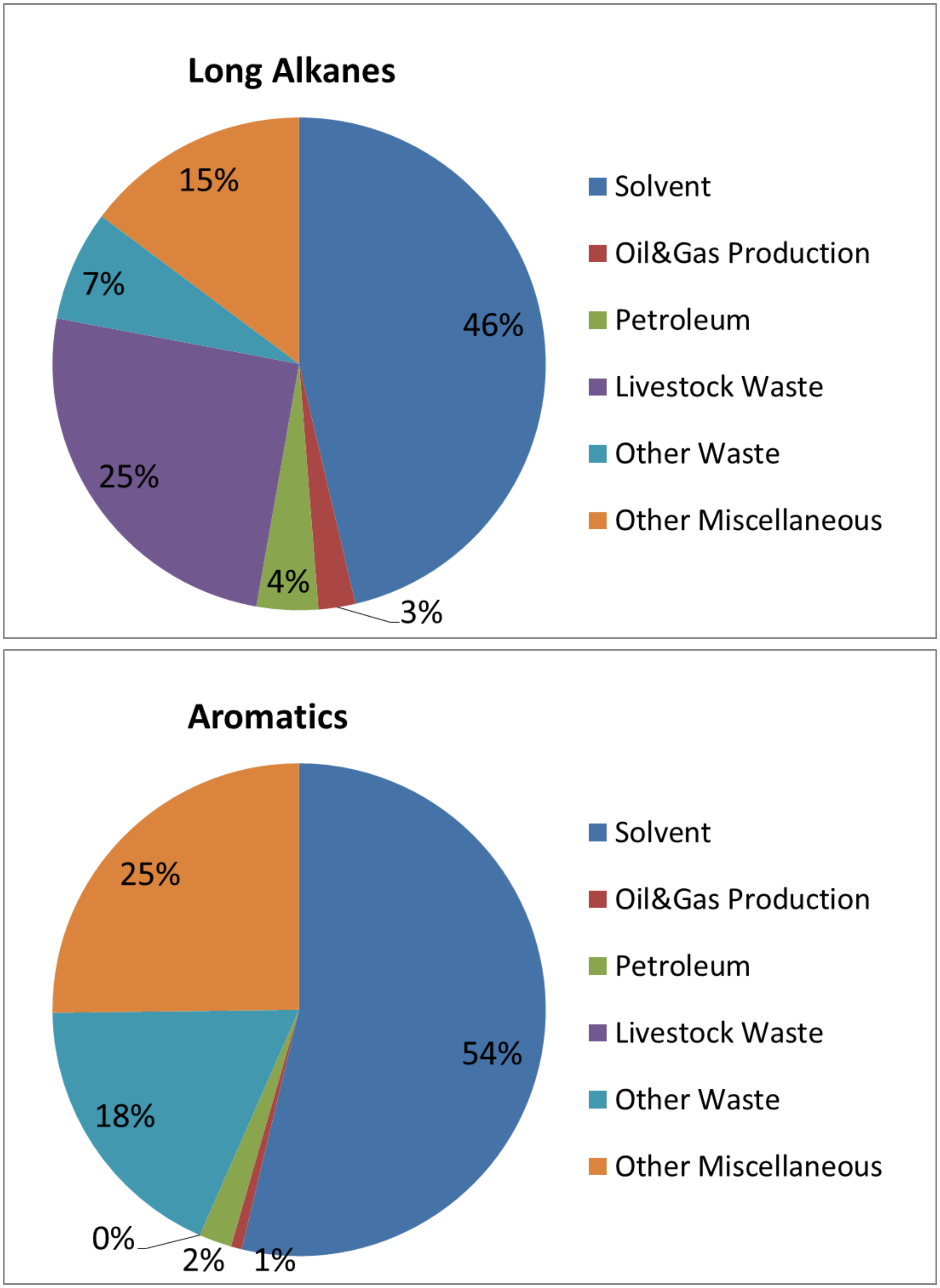

Figure S3. Emission of different sources of long alkanes and aromatics in the “other anthropogenic” source category.

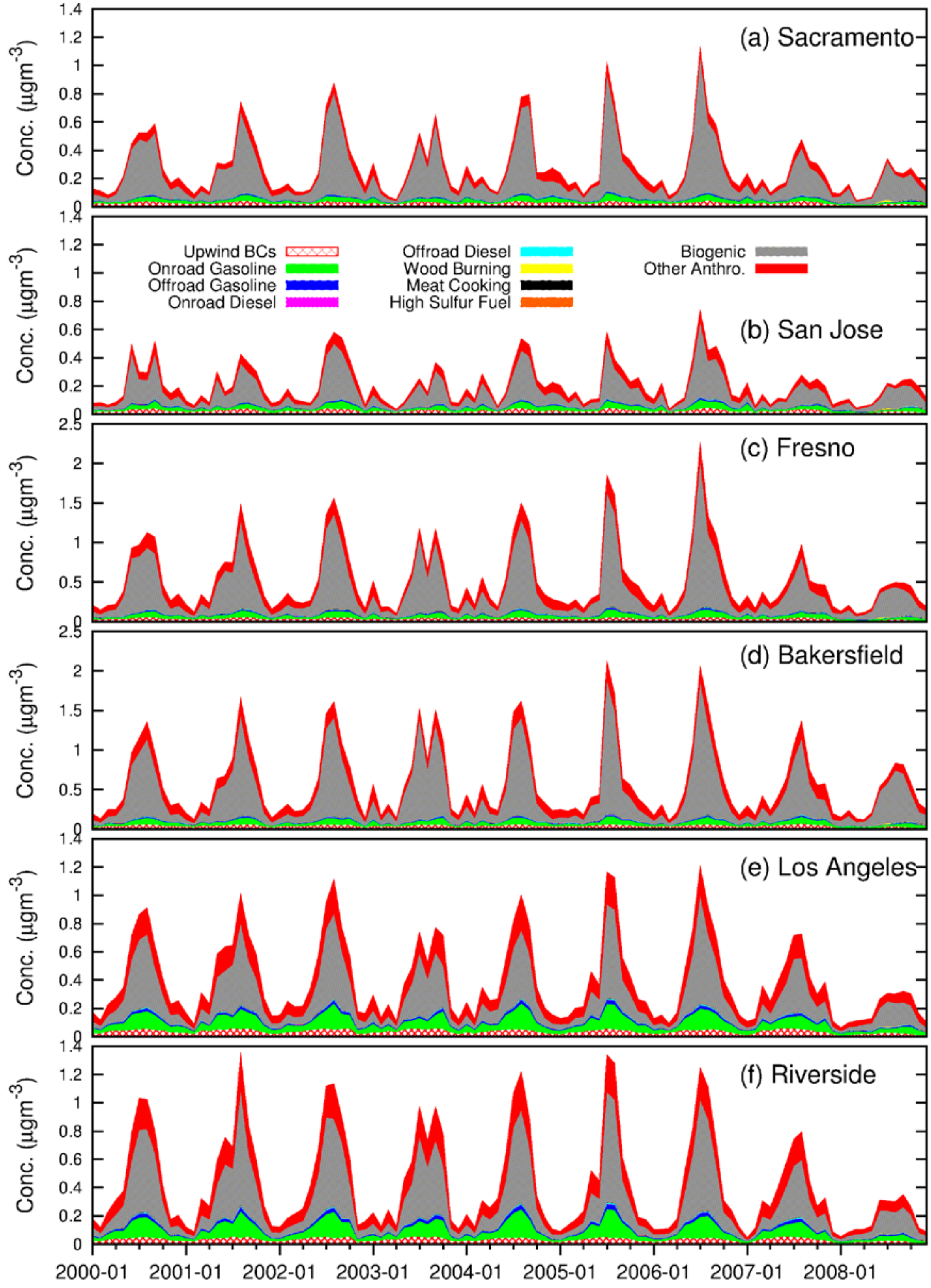

Figure S4. Monthly source contributions to PM$_{2.5}$ SOA at 6 urban sites. Predicted SOA concentrations from different sources are indicated by the colored areas.

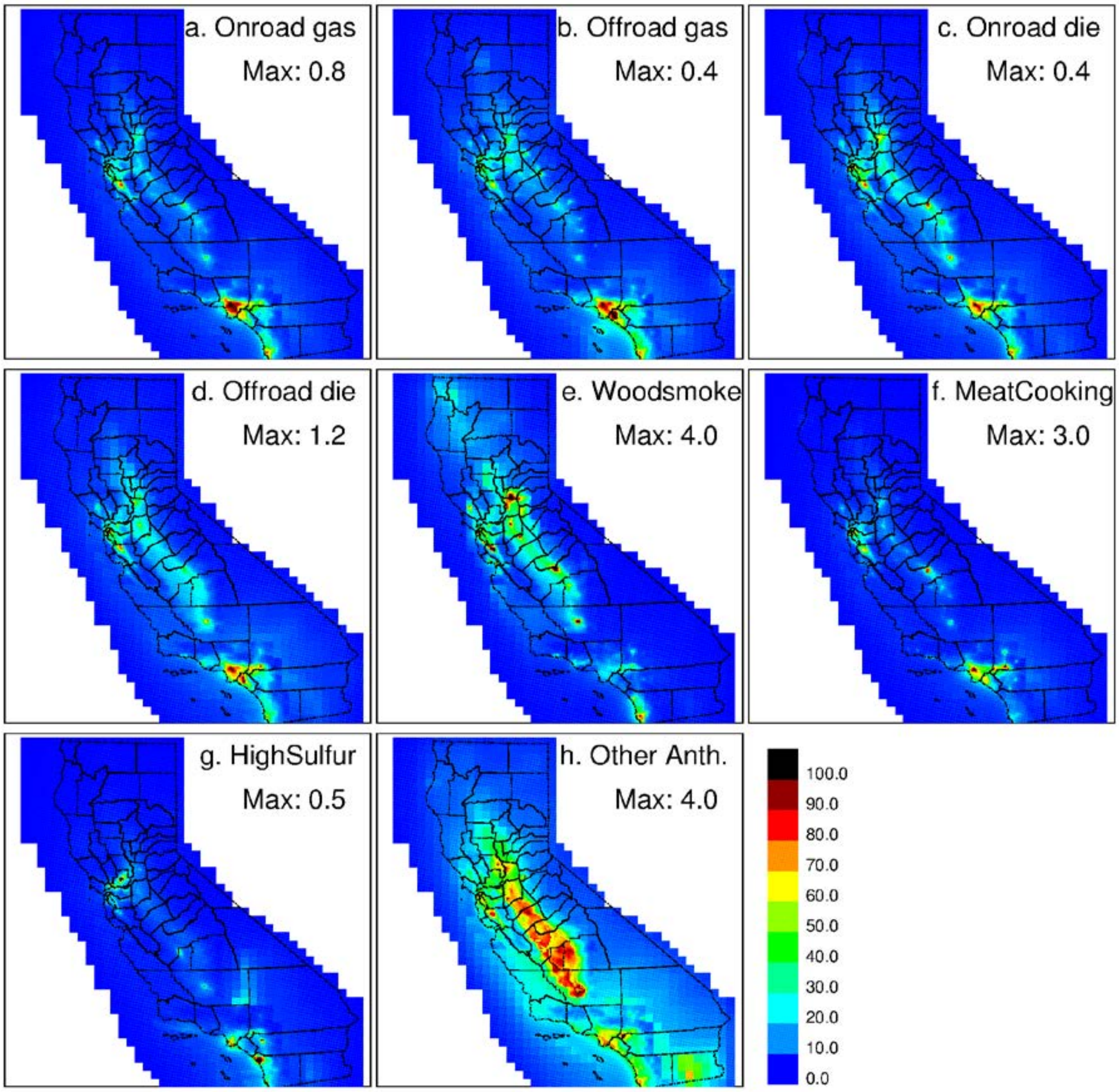

Figure S5. Predicted source contributions to 9 year average $PM_{2.5}$ POA concentrations. The definition of the color scales are the same as in Figure 5.

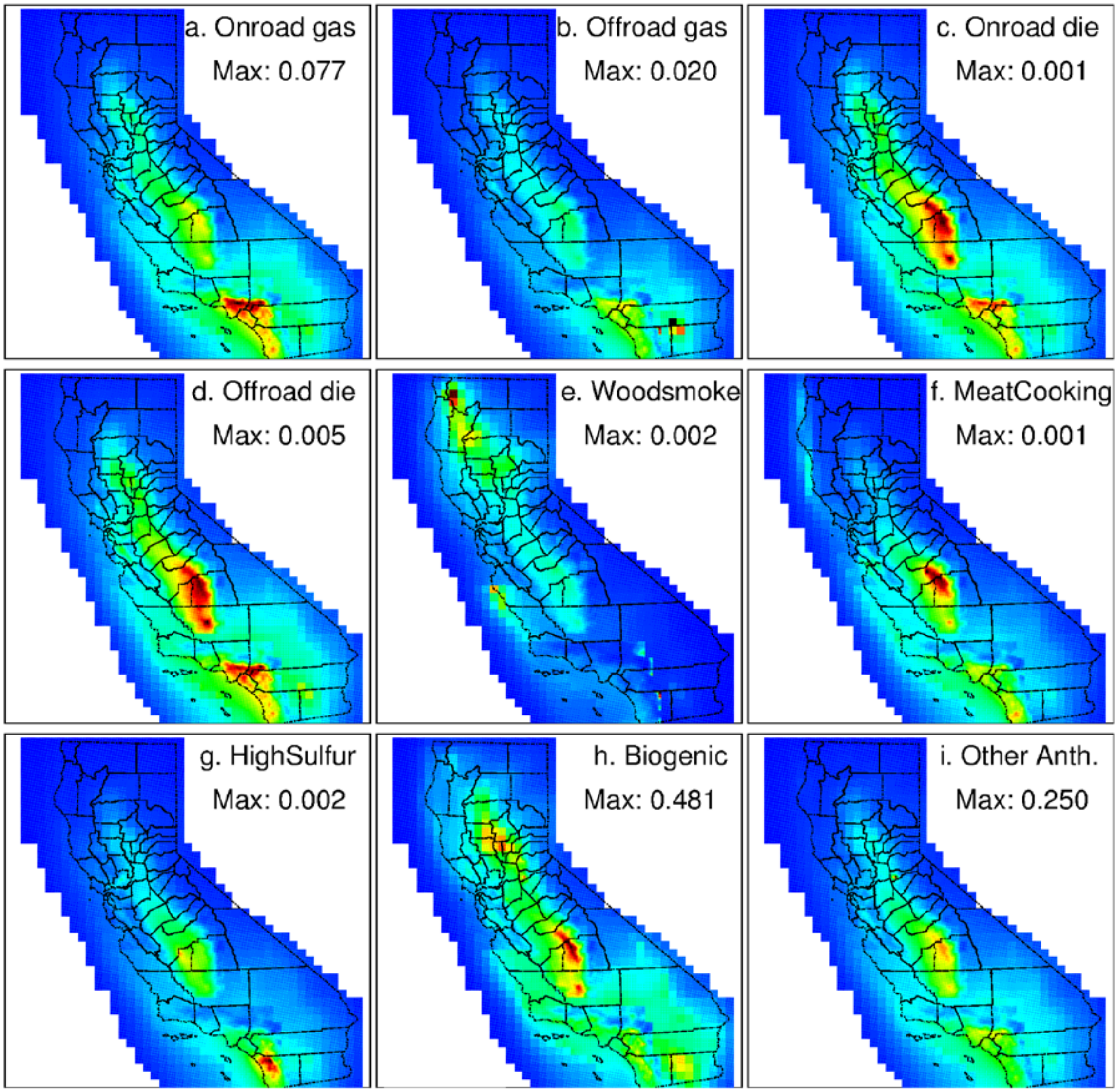

Figure S6. Predicted source contributions to 9 year average $PM_{2.5}$ SOA concentrations. The definition of the color scales are the same as in Figure 5.

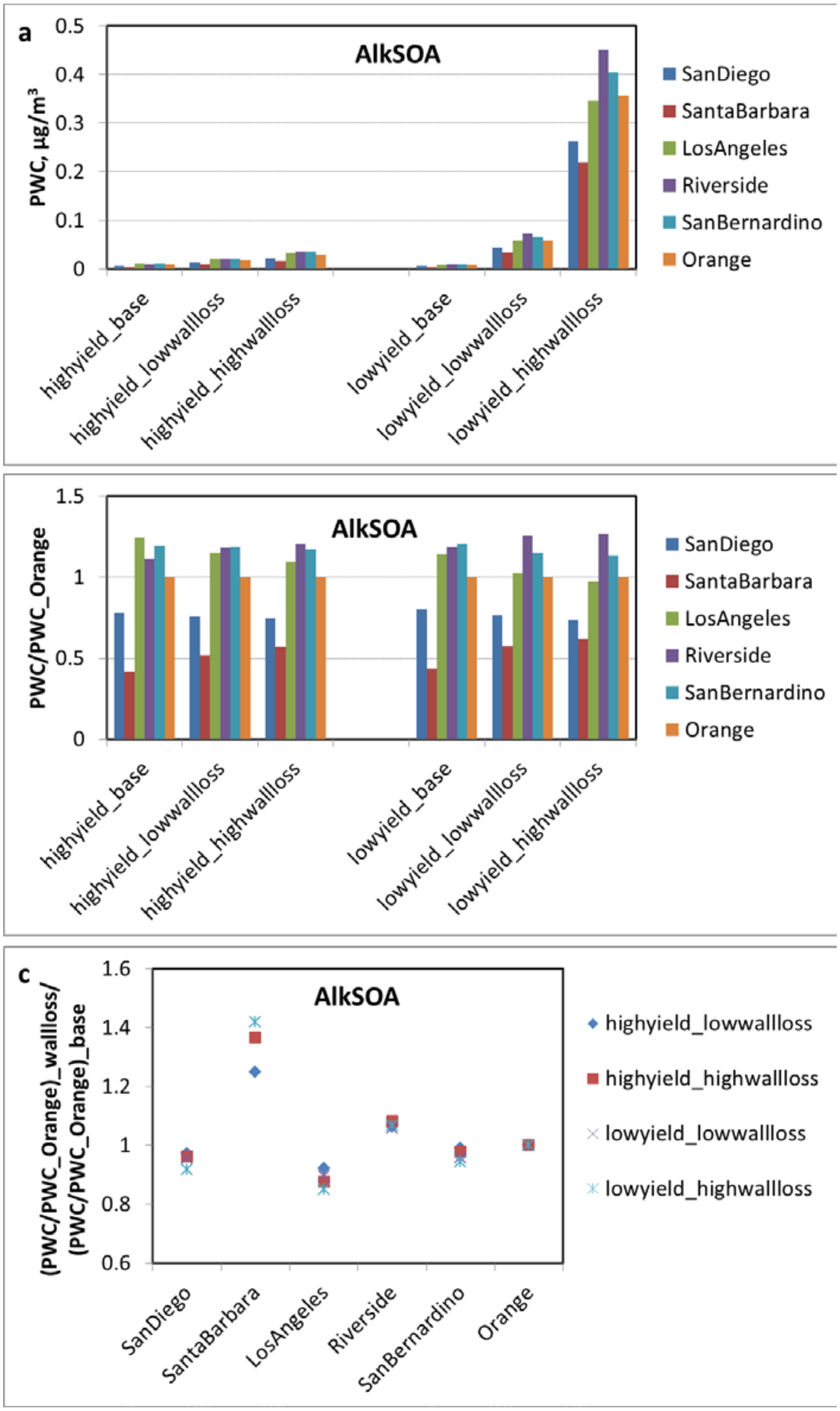

Figure S7 Same as Figure 9, but only for SOA derived from long alkanes (AlkSOA).

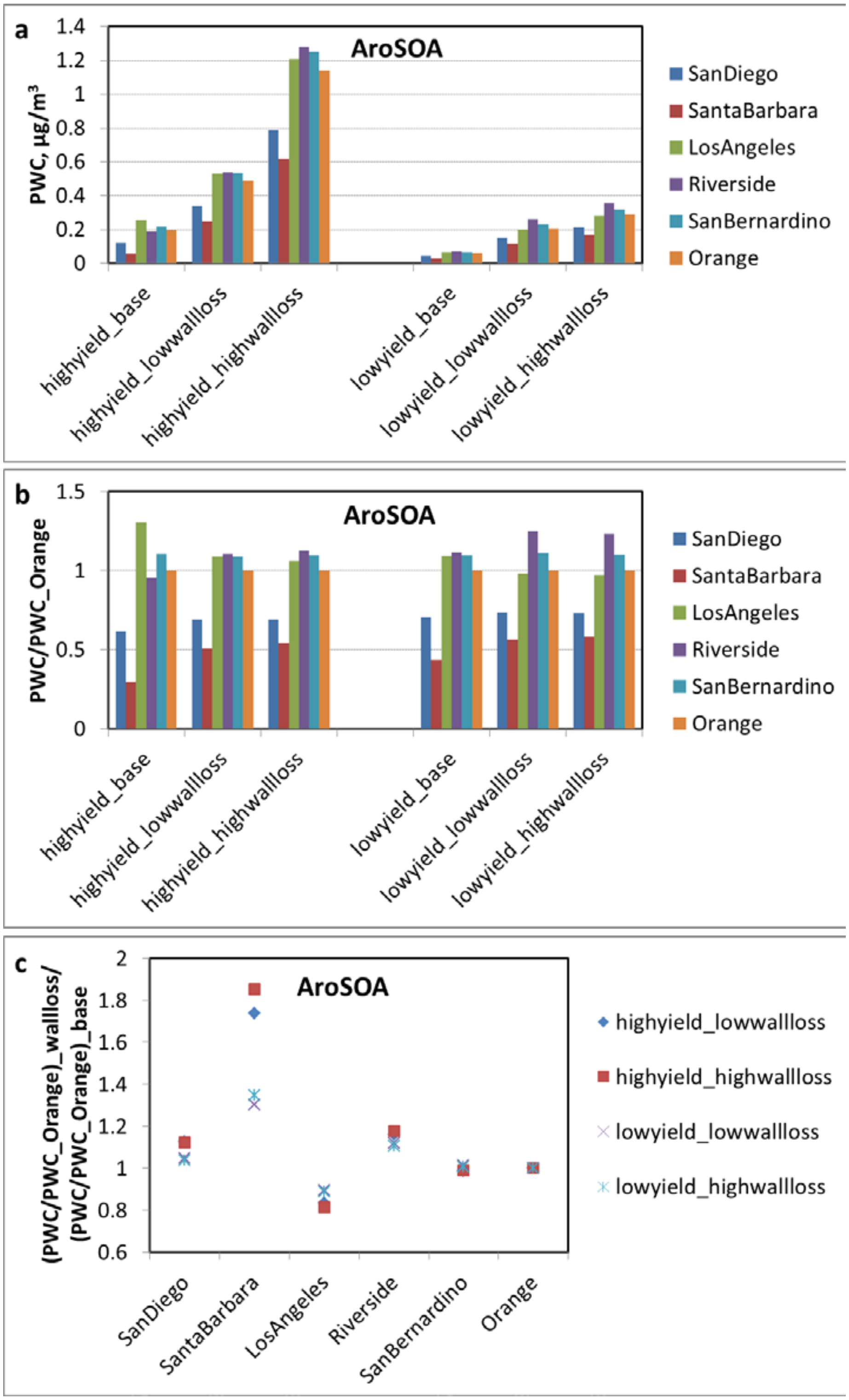

Figure S8. Same as Figure 9, but only for SOA derived from aromatics (AroSOA).

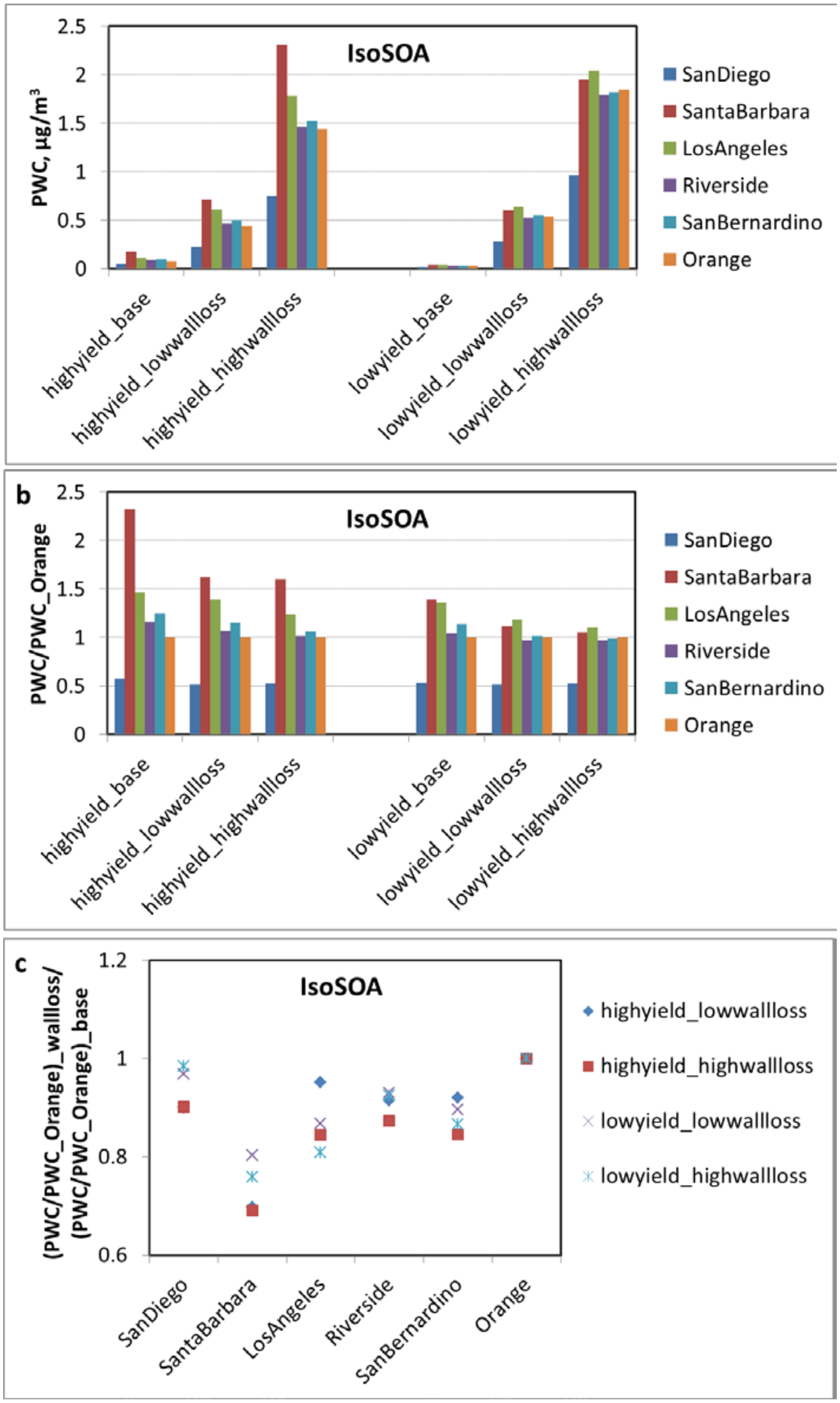

Figure S9. Same as Figure 9, but only for SOA derived from isoprene (IsoSOA).

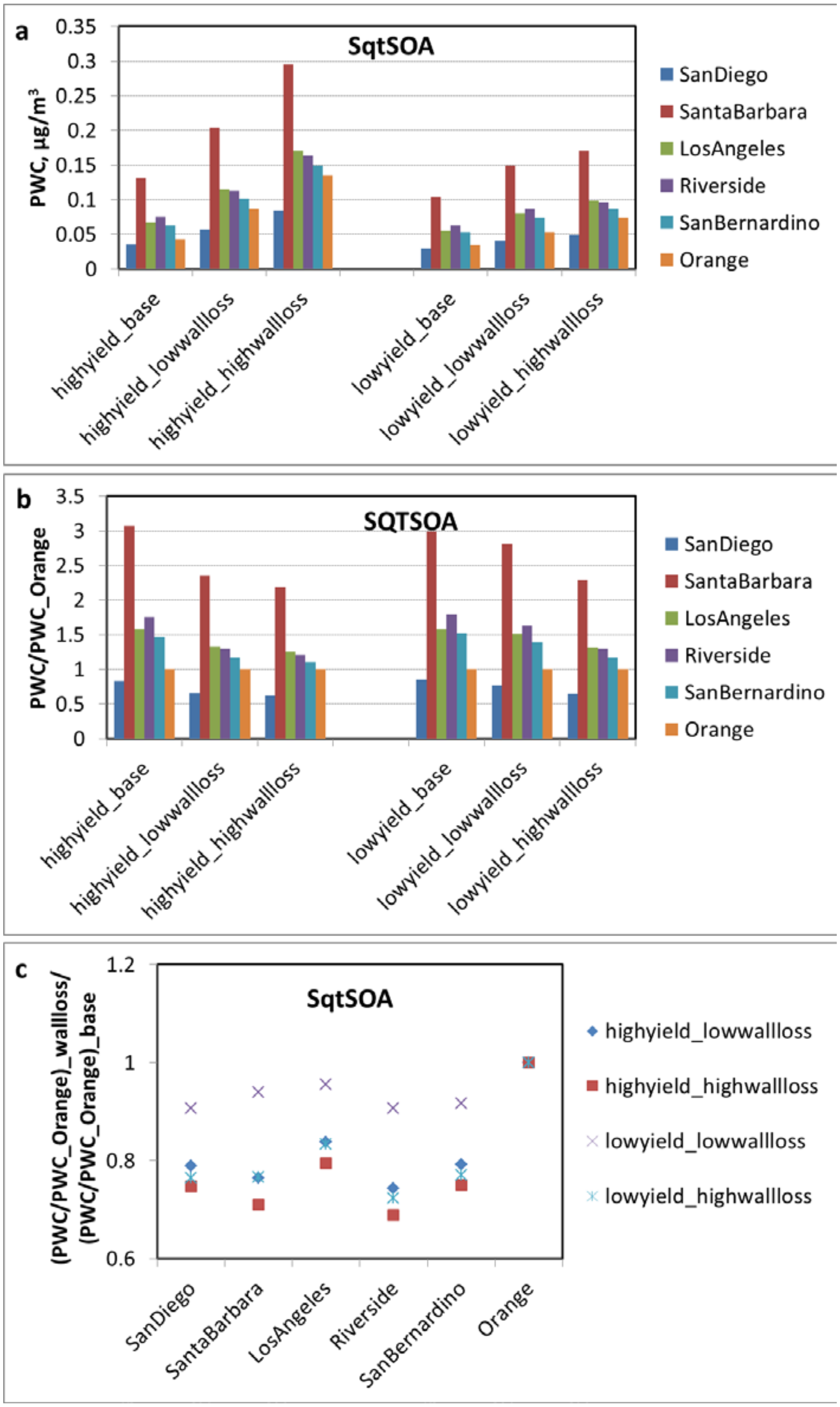

Figure S10. Same as Figure 9, but only for SOA derived from sesquiterpenes (SqtSOA).

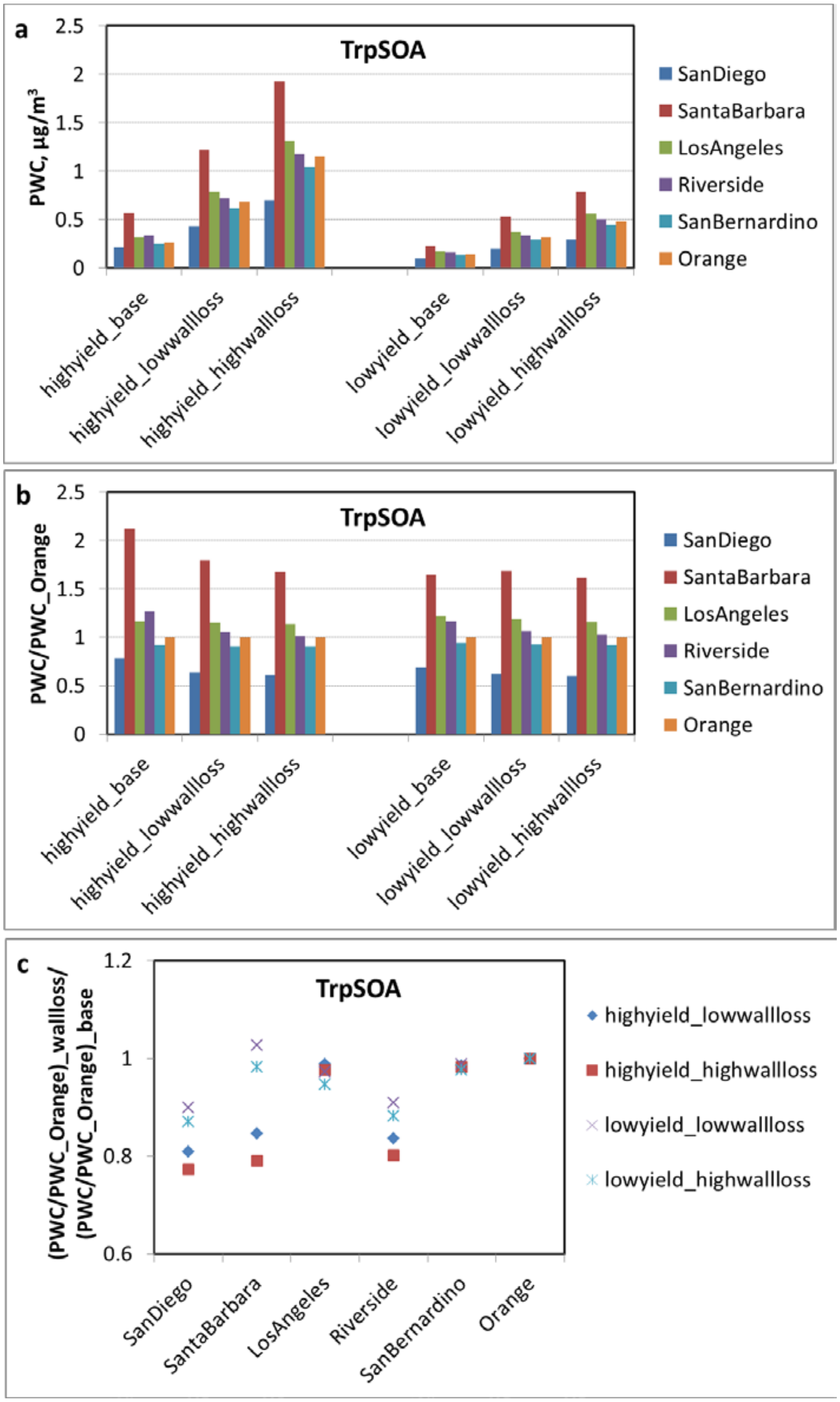

Figure S11. Same as Figure 9, but only for SOA derived from monoterpenes (TrpSOA).