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Supplement of

Gas and aerosol carbon in California: comparison of measurements and model predictions in Pasadena and Bakersfield

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Organization of the Supporting Information

Table S1a. Episode total emissions (tons) of primarily emitted PM2.5 organic carbon by area delineated by source classification code (SCC). The Los Angeles (LA) total includes Los Angeles and Orange counties. The southern San Joaquin Valley (SSJV) total includes Kern, Fresno, Kings, and Tulare counties. Only categories above 1% contribution shown.

Area	Tons	Percent	SCC7	SCC7 Description
SSJV	72.0	17.4	2302002	Industrial Processes;Food and Kindred Products: SIC 20;Commercial Cooking - Charbroiling
SSJV	54.1	13.1	2104008	Stationary Source Fuel Combustion;Residential;Wood
SSJV	49.3	11.9	2801500	Miscellaneous Area Sources;Agriculture Production - Crops;Agricultural Field Burning - whole field set on fire
SSJV	28.4	6.9	310004	Industrial Processes;Oil and Gas Production;Process Heaters
SSJV	25.4	6.1	2230074	Mobile Sources;Highway Vehicles - Diesel;Heavy Duty Diesel Vehicles (HDDV) Class 8A & 8B
SSJV	14.7	3.5	2201001	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Vehicles (LDGV)
SSJV	13.5	3.3	2294000	Mobile Sources;Paved Roads;All Paved Roads
SSJV	12.9	3.1	2282005	Mobile Sources;Pleasure Craft;Gasoline 2-Stroke
SSJV	12.9	3.1	101009	External Combustion Boilers;Electric Generation;Wood/Bark Waste
SSJV	11.3	2.7	202002	Internal Combustion Engines;Industrial;Natural Gas
SSJV	10.5	2.5	2201020	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Trucks 1 & 2 (M6) = LDGT1 (M5)
SSJV	8.9	2.1	305006	Industrial Processes;Mineral Products;Cement Manufacturing (Dry Process)
SSJV	8.8	2.1	2230073	Mobile Sources;Highway Vehicles - Diesel;Heavy Duty Diesel Vehicles (HDDV) Class 6 & 7
SSJV	6.2	1.5	2265003	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Industrial Equipment
SSJV	6.0	1.4	2610000	Waste Disposal, Treatment, and Recovery;Open Burning;All Categories
SSJV	5.4	1.3	2296000	Mobile Sources;Unpaved Roads;All Unpaved Roads
SSJV	5.4	1.3	2201040	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5)
LA	269.4	26.8	2302002	Industrial Processes;Food and Kindred Products: SIC 20;Commercial Cooking - Charbroiling
LA	95.9	9.5	2282005	Mobile Sources;Pleasure Craft;Gasoline 2-Stroke
LA	94.0	9.4	2201001	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Vehicles (LDGV)
LA	82.7	8.2	2104008	Stationary Source Fuel Combustion;Residential;Wood
LA	66.6	6.6	2307000	Industrial Processes;Wood Products: SIC 24;All Processes
LA	58.0	5.8	2201020	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Trucks 1 & 2 (M6) = LDGT1 (M5)
LA	38.4	3.8	2230074	Mobile Sources;Highway Vehicles - Diesel;Heavy Duty Diesel Vehicles (HDDV) Class 8A & 8B
LA	29.9	3.0	2201040	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5)
LA	23.8	2.4	2104006	Stationary Source Fuel Combustion;Residential;Natural Gas
LA	17.5	1.7	2103008	Stationary Source Fuel Combustion;Commercial/Institutional;Wood
LA	15.0	1.5	2230073	Mobile Sources;Highway Vehicles - Diesel;Heavy Duty Diesel Vehicles (HDDV) Class 6 & 7
LA	13.6	1.4	2294000	Mobile Sources;Paved Roads;All Paved Roads
LA	12.0	1.2	2302080	Industrial Processes;Food and Kindred Products: SIC 20;Miscellaneous Food and Kindred Products
LA	10.8	1.1	2265004	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Lawn and Garden Equipment
LA	10.7	1.1	2265006	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Commercial Equipment

Table S1b. Episode total emissions (tons) of the sum of benzene, toluene, and xylenes by area delineated by source classification code (SCC). The Los Angeles (LA) total includes Los Angeles and Orange counties. The southern San Joaquin Valley (SSJV) total includes Kern, Fresno, Kings, and Tulare counties. Only categories above 1% contribution shown.

Area	Tons	Percent	SCC7	SCC7 Description
SSJV	112.3	12.8	2201001	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Vehicles (LDGV)
SSJV	81.1	9.2	2201020	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Trucks 1 & 2 (M6) = LDGT1 (M5)
SSJV	71.3	8.1	2680001	Waste Disposal, Treatment, and Recovery;Composting;100% Biosolids (e.g., sewage sludge, manure, mixtures of these matls)
SSJV	44.2	5.0	2440000	Solvent Utilization;Miscellaneous Industrial;All Processes
SSJV	41.8	4.8	2201040	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5)
SSJV	35.7	4.1	2460000	Solvent Utilization;Miscellaneous Non-industrial: Consumer and Commercial;All Processes
SSJV	32.5	3.7	2282005	Mobile Sources;Pleasure Craft;Gasoline 2-Stroke
SSJV	31.9	3.6	2265004	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Lawn and Garden Equipment
SSJV	31.5	3.6	2310010	Industrial Processes;Oil and Gas Production: SIC 13;Crude Petroleum
SSJV	30.6	3.5	2620030	Waste Disposal, Treatment, and Recovery;Landfills;Municipal
SSJV	27.6	3.1	2265001	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Recreational Equipment
SSJV	25.6	2.9	309010	Industrial Processes;Fabricated Metal Products;Electroplating Operations
SSJV	20.6	2.4	2282010	Mobile Sources;Pleasure Craft;Gasoline 4-Stroke
SSJV	16.5	1.9	2401002	Solvent Utilization;Surface Coating;Architectural Coatings - Solvent-based
SSJV	15.1	1.7	2201070	Mobile Sources;Highway Vehicles - Gasoline;Heavy Duty Gasoline Vehicles 2B thru 8B & Buses (HDGV)
SSJV	14.8	1.7	2265005	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Agricultural Equipment
SSJV	14.7	1.7	2401005	Solvent Utilization;Surface Coating;Auto Refinishing: SIC 7532
SSJV	14.6	1.7	2401020	Solvent Utilization;Surface Coating;Wood Furniture: SIC 25
SSJV	12.0	1.4	2801500	Miscellaneous Area Sources;Agriculture Production - Crops;Agricultural Field Burning - whole field set on fire
SSJV	11.3	1.3	2265003	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Industrial Equipment
SSJV	10.9	1.2	2260004	Mobile Sources;Off-highway Vehicle Gasoline, 2-Stroke;Lawn and Garden Equipment
SSJV	10.6	1.2	2230074	Mobile Sources;Highway Vehicles - Diesel;Heavy Duty Diesel Vehicles (HDDV) Class 8A & 8B
SSJV	10.3	1.2	2415300	Solvent Utilization;Degreasing;All Industries: Cold Cleaning
SSJV	10.1	1.2	2265006	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Commercial Equipment
SSJV	10.1	1.2	2460500	Solvent Utilization;Miscellaneous Non-industrial: Consumer and Commercial;All Coatings and Related Products
SSJV	9.5	1.1	2501011	Storage and Transport;Petroleum and Petroleum Product Storage;Residential Portable Gas Cans
SSJV	9.2	1.0	2201080	Mobile Sources;Highway Vehicles - Gasoline;Motorcycles (MC)
LA	546.0	15.9	2201001	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Vehicles (LDGV)
LA	345.8	10.1	2201020	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Trucks 1 & 2 (M6) = LDGT1 (M5)
LA	244.8	7.1	2265004	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Lawn and Garden Equipment
LA	207.7	6.0	2282005	Mobile Sources;Pleasure Craft;Gasoline 2-Stroke
LA	201.2	5.9	2460000	Solvent Utilization;Miscellaneous Non-industrial: Consumer and Commercial;All Processes
LA	178.1	5.2	2201040	Mobile Sources;Highway Vehicles - Gasoline;Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5)
LA	114.0	3.3	2401050	Solvent Utilization;Surface Coating;Miscellaneous Finished Metals: SIC 34 - (341 + 3498)
LA	106.8	3.1	2282010	Mobile Sources;Pleasure Craft;Gasoline 4-Stroke
LA	104.9	3.0	2620030	Waste Disposal, Treatment, and Recovery;Landfills;Municipal
LA	88.2	2.6	2260004	Mobile Sources;Off-highway Vehicle Gasoline, 2-Stroke;Lawn and Garden Equipment
LA	84.1	2.4	2401005	Solvent Utilization;Surface Coating;Auto Refinishing: SIC 7532
LA	74.4	2.2	2265006	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Commercial Equipment
LA	70.6	2.1	2401090	Solvent Utilization;Surface Coating;Miscellaneous Manufacturing
LA	70.1	2.0	2460500	Solvent Utilization;Miscellaneous Non-industrial: Consumer and Commercial;All Coatings and Related Products
LA	69.1	2.0	2415300	Solvent Utilization;Degreasing;All Industries: Cold Cleaning
LA	63.3	1.8	2201070	Mobile Sources;Highway Vehicles - Gasoline;Heavy Duty Gasoline Vehicles 2B thru 8B & Buses (HDGV)
LA	58.7	1.7	306888	Industrial Processes;Petroleum Industry;Fugitive Emissions
LA	56.5	1.6	2401025	Solvent Utilization;Surface Coating;Metal Furniture: SIC 25
LA	55.9	1.6	2501011	Storage and Transport;Petroleum and Petroleum Product Storage;Residential Portable Gas Cans
LA	41.8	1.2	2440000	Solvent Utilization;Miscellaneous Industrial;All Processes
LA	40.4	1.2	2401040	Solvent Utilization;Surface Coating;Metal Cans: SIC 341
LA	39.8	1.2	2265003	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Industrial Equipment
LA	39.5	1.1	2401070	Solvent Utilization;Surface Coating;Motor Vehicles: SIC 371
LA	38.7	1.1	2201080	Mobile Sources;Highway Vehicles - Gasoline;Motorcycles (MC)
LA	36.9	1.1	2265001	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Recreational Equipment

Table S2a. Matching grouped measured and modeled PM2.5 species. Measured SOC contributions estimated by dividing the total tracer concentration by group with a photochemical reaction chamber derived SOC mass fraction for the same group.

Species	Measured Species	CMAQ Model Species
PM2.5 Elemental Carbon	EC	AECI + AECJ
PM2.5 Organic Carbon	OC	(AXYL1J + AXYL2J + AXYL3J)/2.0 + (ATOL1J + ATOL2J + ATOL3J)/2.0 + (ABNZ1J + ABNZ2J + ABNZ3J)/2.0 + (AISO1J + AISO2J)/1.6 + AISO3J/2.7 + (ATRP1J + ATRP2J)/1.4 + ASQTJ/2.1 + 0.64*AALKJ + AORGCJ/2.0 + (AOLGBJ + AOLGAJ)/2.1 + APOCJ + APOCI
Isoprene	(2-methyl erythritol + 2-methyl trietol + 2-methylglyceric acid) * (1/0.063)	(AISO1J + AISO2J)/1.6 + AISO3J/2.7 + (AOLGBJ/2.1 * iso_fraction)
Monoterpenes	(3-acetyl hexanedioic acid + 3-hydroxyglutaric acid + 3-methyl-1,2,3 buanetricarboxylic acid + 3-acetyl pentanedioic acid + Pinic acid + 2-hydroxy-4,4-dimethylglutaric acid) * (1/0.231)	(ATRP1J + ATRP2J)/1.4 + (AOLGBJ/2.1 * trp_fraction)
Sesquiterpenes	(b-caryophellinic acid) * (1/0.023)	ASQT/2.1 + (AOLGB/2.1 * (1-trp_fraction-iso_fraction))
Toluenes + Xylenes	(2-3-dihydroxy-4-oxo-pentanioc acid) * (1/0.0079)	(ATOL1J + ATOL2J + ATOL3J + AXYL1J + AXYL2J + AXYL3J)/2 + (AOLGAJ/2.1 * (tol+xyl_fraction))
Benzenes	n/a	(ABNZ1J + ABNZ2J + ABNZ3J)/2 + (AOLGAJ/2.1 * bnz_fraction)
Alkanes	n/a	AALKJ/1.56 + (AOLGAJ/2.1 * alk_fraction)
Methylgloxal + glyoxal	n/a	AORGCJ/2
Napthhalene	(phthlaic acid + isophthalic acid) * (1/0.0357)	n/a

iso_fraction = (AISO1J +AISO2J +AISO3J) / (AISO1J +AISO2J +AISO3J +ATRP1J ATRP2J +ASQT)
trp_fraction = (ATRP1J +ATRPJ) / (AISO1J +AISO2J +AISO3J +ATRP1J ATRP2J +ASQT)
bnz_fraction = (ABNZ1J +ABNZ2J +ABNZ3J) / (ATOL1J +ATOL2J +ATOL3J +AXYL1J +AXYL2J +AXYL3J +ABNZ1J +ABNZ2J +ABNZ3J +AALKJ)
alk_fraction = (AALKJ) / (ATOL1J +ATOL2J +ATOL3J +AXYL1J +AXYL2J +AXYL3J +ABNZ1J +ABNZ2J +ABNZ3J +AALKJ)
tol+xyl_fraction = (ATOL1J +ATOL2J +ATOL3J +AXYL1J +AXYL2J +AXYL3J) / (ATOL1J +ATOL2J +ATOL3J +AXYL1J +AXYL2J +AXYL3J +ABNZ1J +ABNZ2J +ABNZ3J +AALKJ)

Table S2b. Matching grouped measured and modeled VOC species.

Species	Measured Species	CMAQ Model Species
Isoprene	Isoprene	5*ISOPRENE
Benzenes	Benzene	6*BENZENE
Monoterpenes	beta-pinene + alpha-pinene + 2-carene + limonene	10*TERP
Sesquiterpenes	n/a	15*SESQ
Toluenes	Toluene + Ethylbenzene + Isopropylbenzene*0.78 + n-	7*TOLUENE
Xylenes	m-p xylene + o-xylene + m-ethyltoluene*0.89 + p-ethyltoluene*0.89 + 1,3,5-trimethylbenzene*0.89 + o-ethyltoluene*0.89 + 1,2,4-trimethylbenzene*0.89 + p-diethylbenzene*0.80	8*(MXYL + OXYL + PXYL)
Ethane	Ethane	2*ALK1
Ethene	Ethene	2*ETHENE
Formaldehyde	Formaldehyde	HCHO
Methanol	Methanol	MEOH
Ethanol	Ethanol	2*ETOH
Total VOC (non-methane)	Sum of all measured non-methane VOC species	(3.*ACETONE + 2.*ACETYLENE + 3.*ACROLEIN + 2.*ALK1 + 3.*ALK2 + 4.*ALK3 + 5.*ALK4 + 8.*ALK5 + 8.*ARO1 + 9.*ARO2 + 4.*BACL + 7.*BALD + 6.*BENZENE + 4.*BUTADIENE13 + 2.*CCHO + 2.*CCOOH + 7.*CRES + 2.*ETHENE + 2.*ETOH + 2*GLY + HCHO + HCOOH + 5.*ISOPRENE + 5.*IPRD + 4.*MEK + MEOH + 4.*MACR + 3.*MGLY + 4.*MVK + 5.*OLE1 + 5.*OLE2 + 8.*(PXYL + MXYL + OXYL) + 6.*PRD2 + 3.*PROPENE + 3.*RCHO + 3.*RCOOH + 7.*TOLUENE + 9.*TRIMETH_BENZ124 + 6.0*RNO3)

Figure S1. Model domain and CALNEX monitor locations.

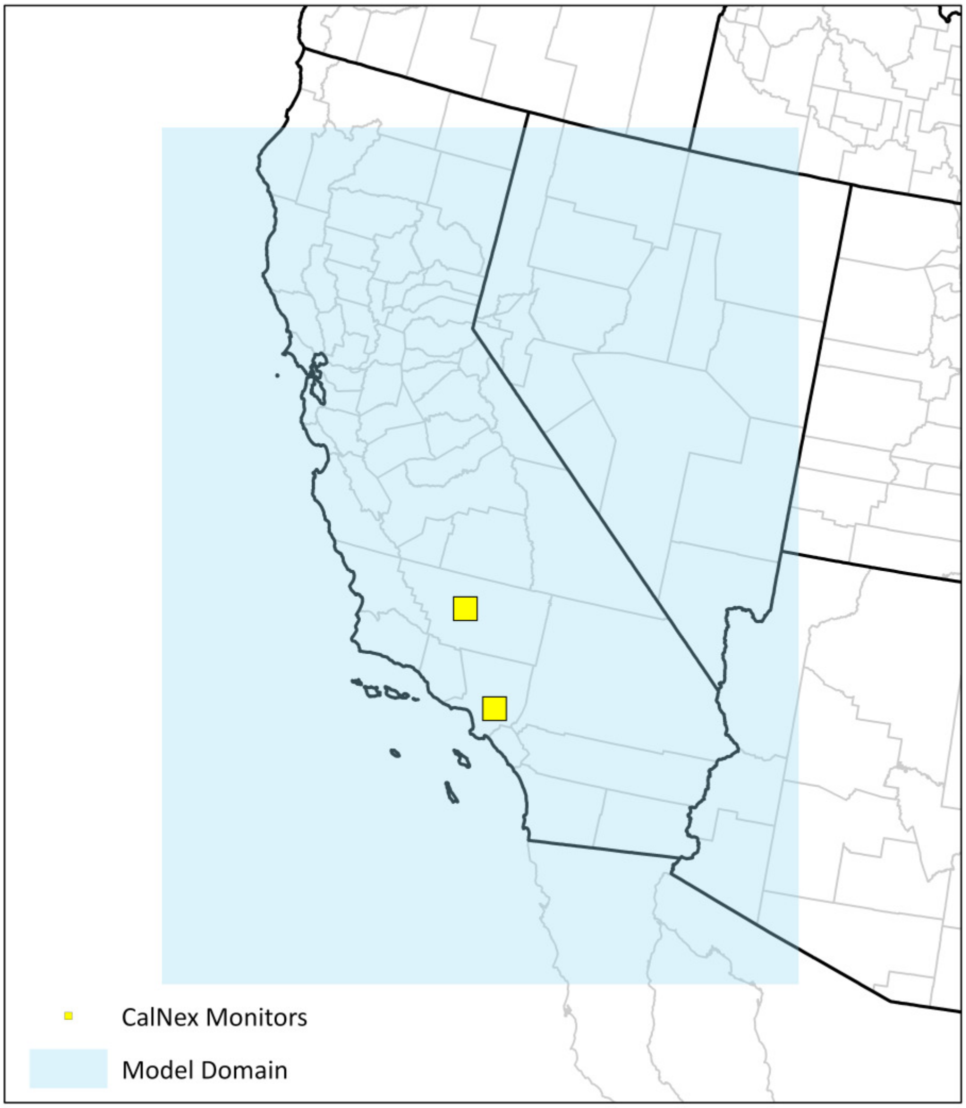


Figure S2. CMAQ SOA schematic diagram. Reproduced from Carlton et al., 2010: Carlton, A.G., Bhave, P.V., Napelenok, S.L., Edney, E.O., Sarwar, G., Pinder, R.W., Pouliot, G.A., Houyoux, M., 2010. Treatment of secondary organic aerosol in CMAQv4.7. Environmental Science and Technology 44, 8553-8560.

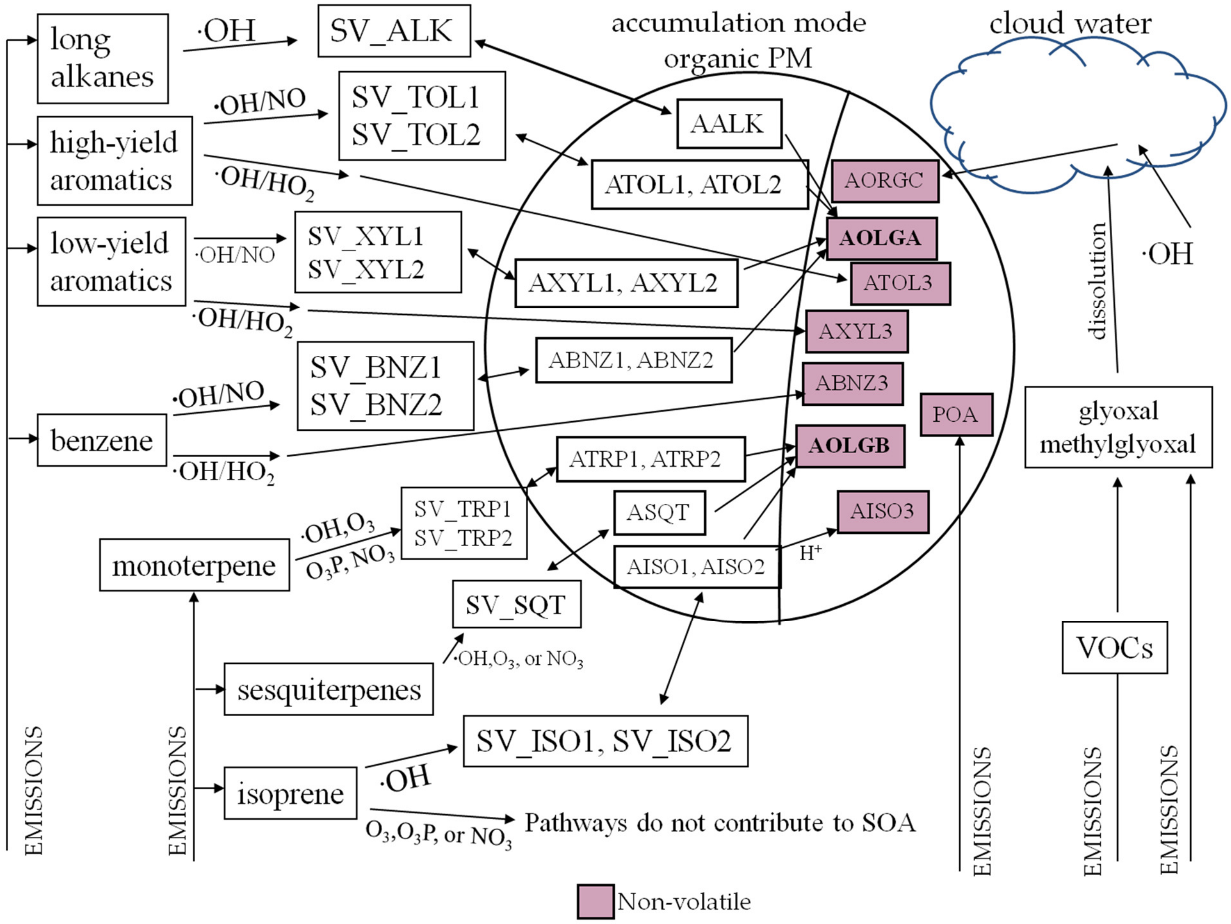


Figure S3a. Bakersfield CALNEX site and nearby CSN location.

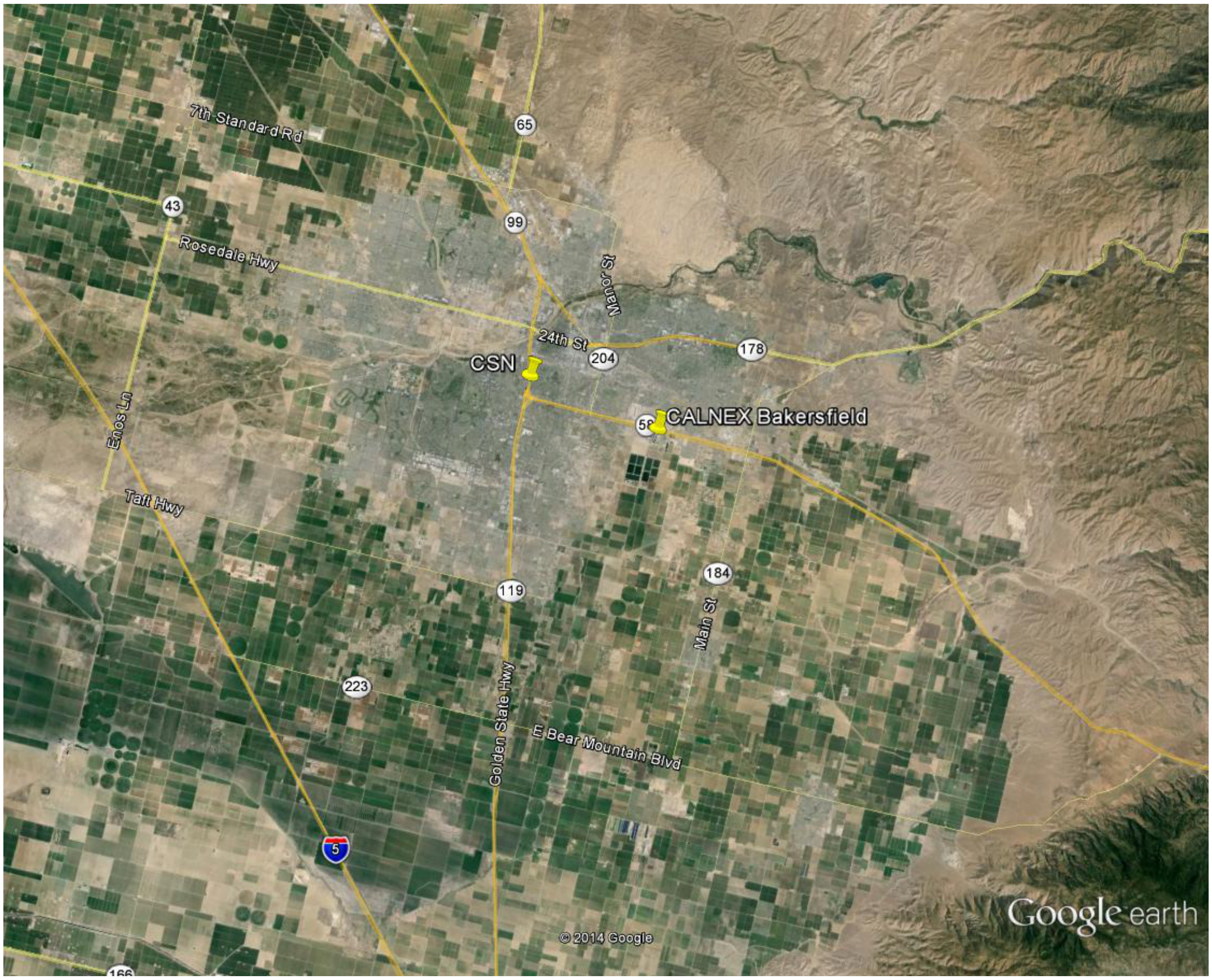


Figure S3b. Pasadena CALNEX site and nearby CSN location.

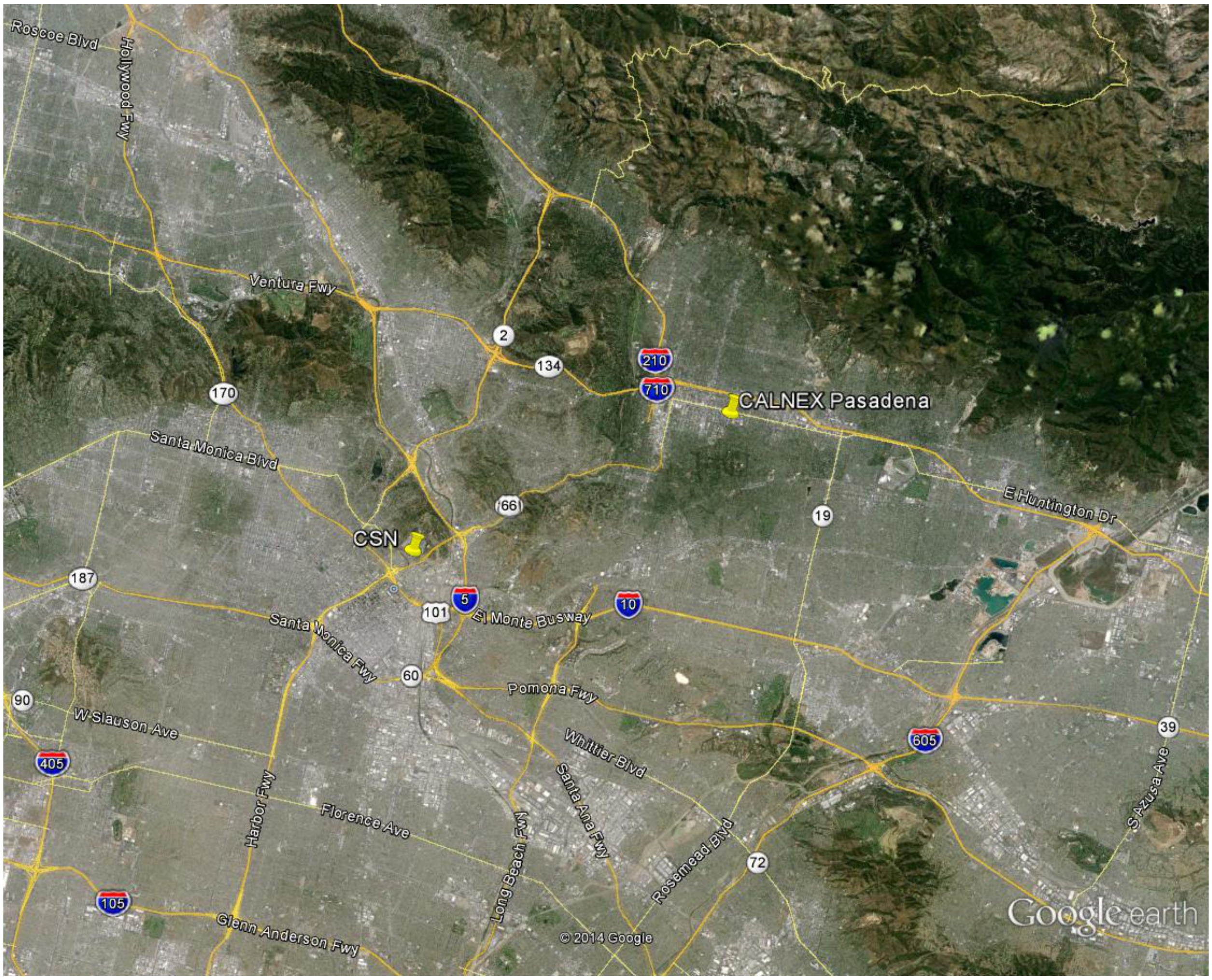


Figure S4a. Observed daily average temperature (F) compared with daily average PM2.5 fossil carbon, PM2.5 contemporary carbon, PM2.5 organic carbon, and PM2.5 elemental carbon at Pasadena. Concentrations shown are in units µgC/m^3.

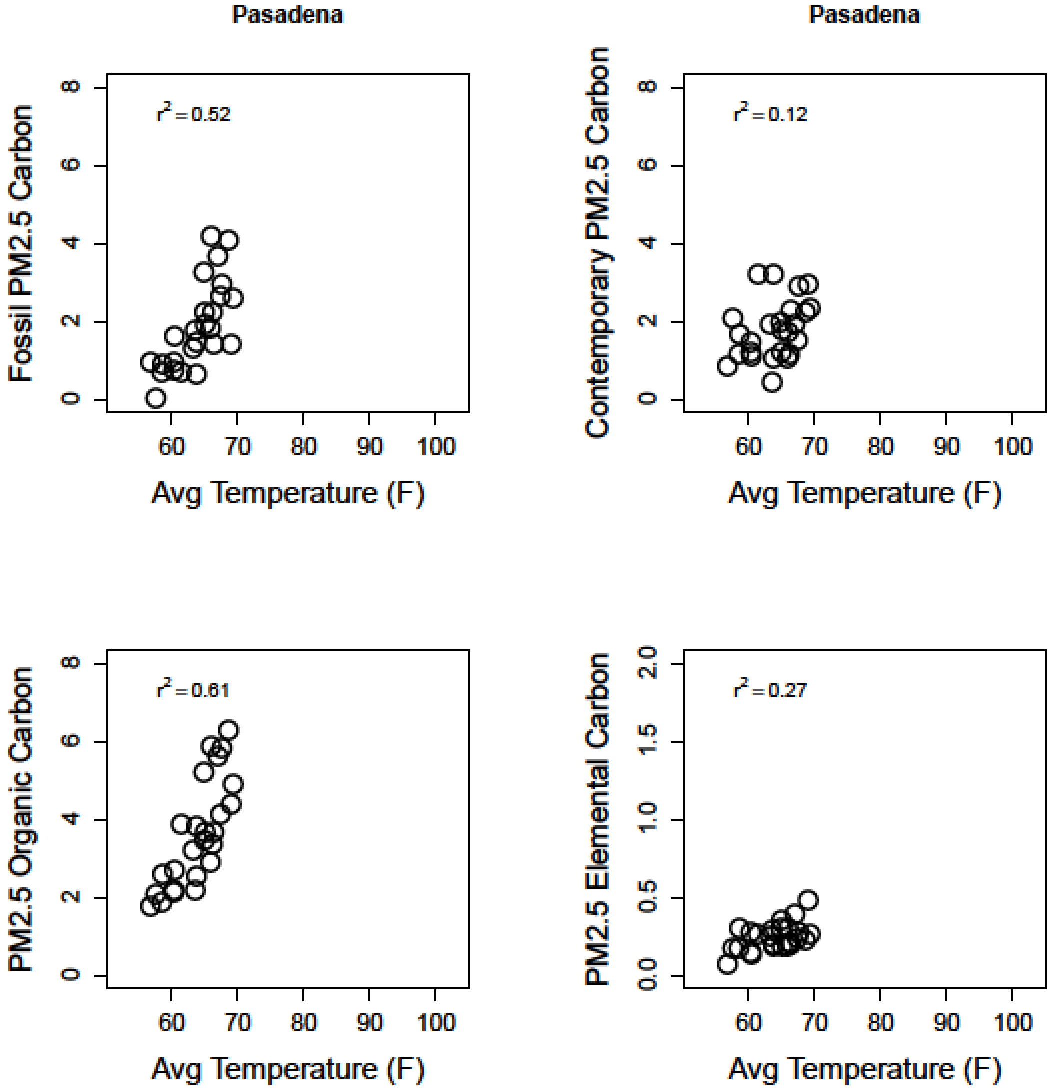


Figure S4b. Observed daily average temperature (F) compared with daily average PM2.5 fossil carbon, PM2.5 contemporary carbon, PM2.5 organic carbon, and PM2.5 elemental carbon at Bakersfield. Concentrations shown are in units µgC/m^3.

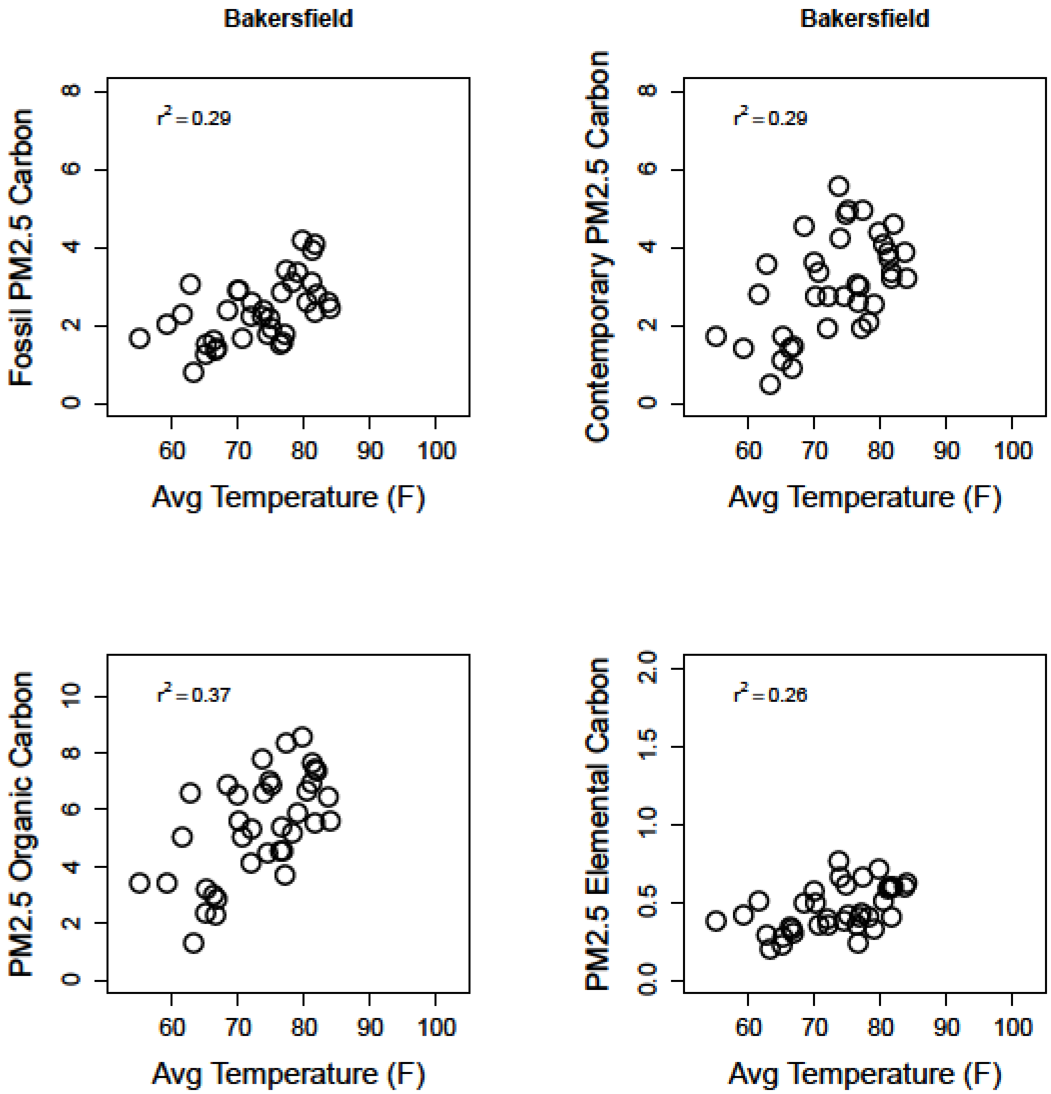


Figure S5. Observed contemporary carbon fraction, PM2.5 contemporary carbon, PM2.5 fossil carbon, and PM2.5 elemental carbon by day of the week for Pasadena and Bakersfield.

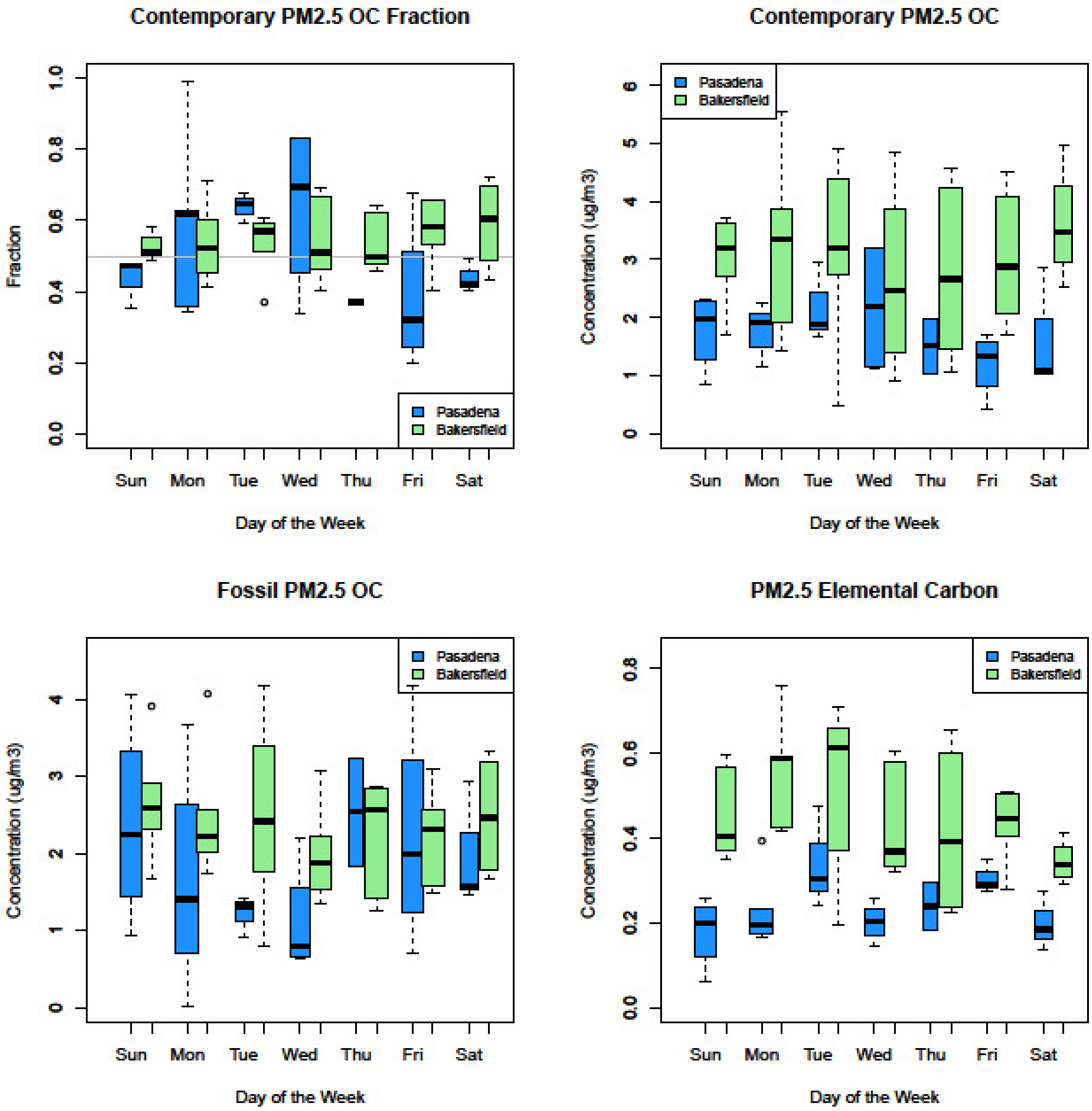


Figure S6. Measured and model estimated contemporary PM2.5 OC fraction at Pasadena and Bakersfield.

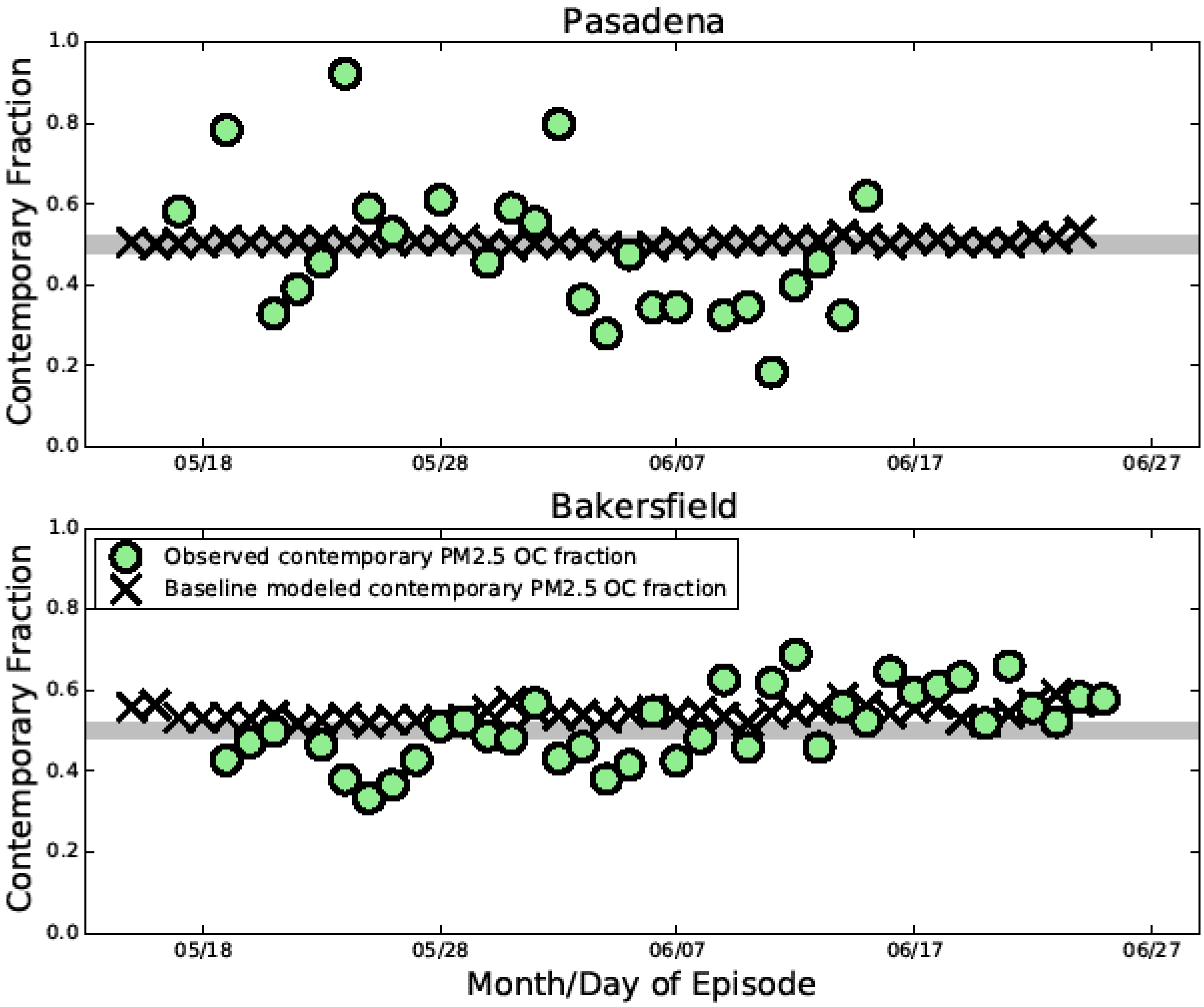


Figure S7. Model predicted and measured $PM_{2.5}$ elemental carbon at Pasadena and Bakersfield.

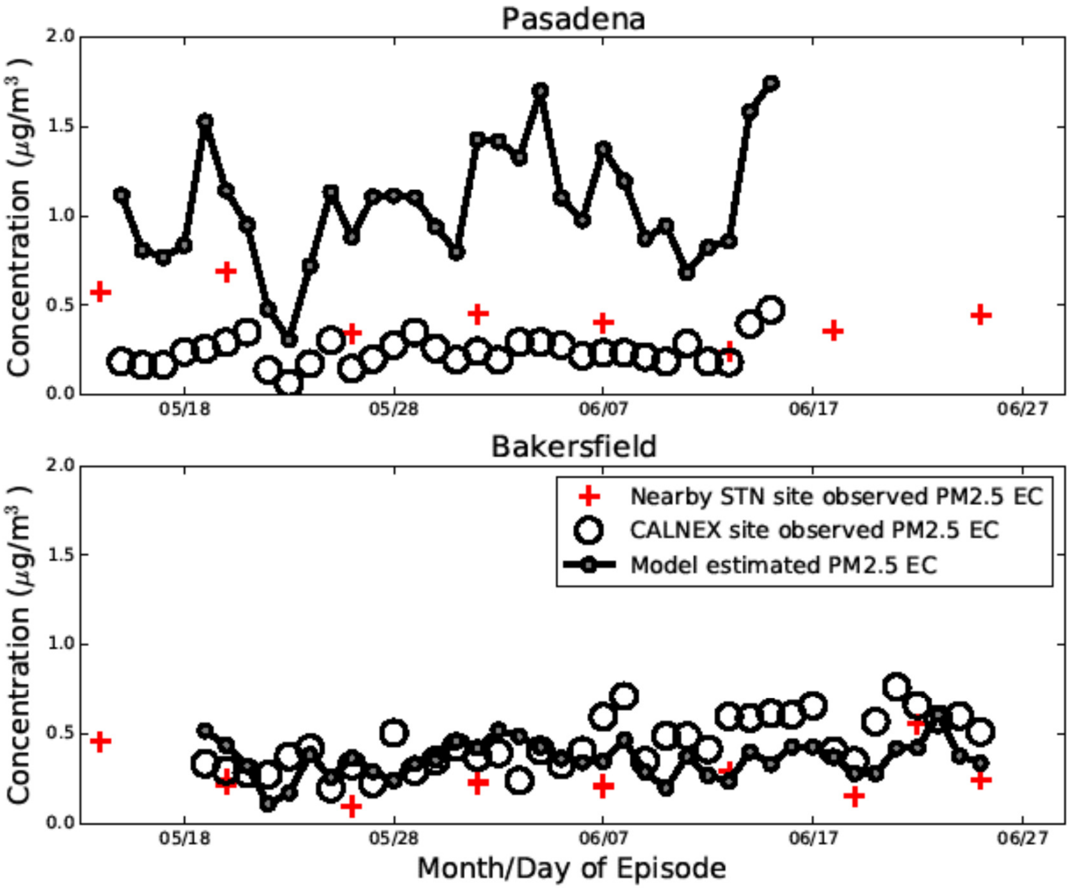


Figure S8. Model and observed hourly VOC (and CO) paired in time and space.

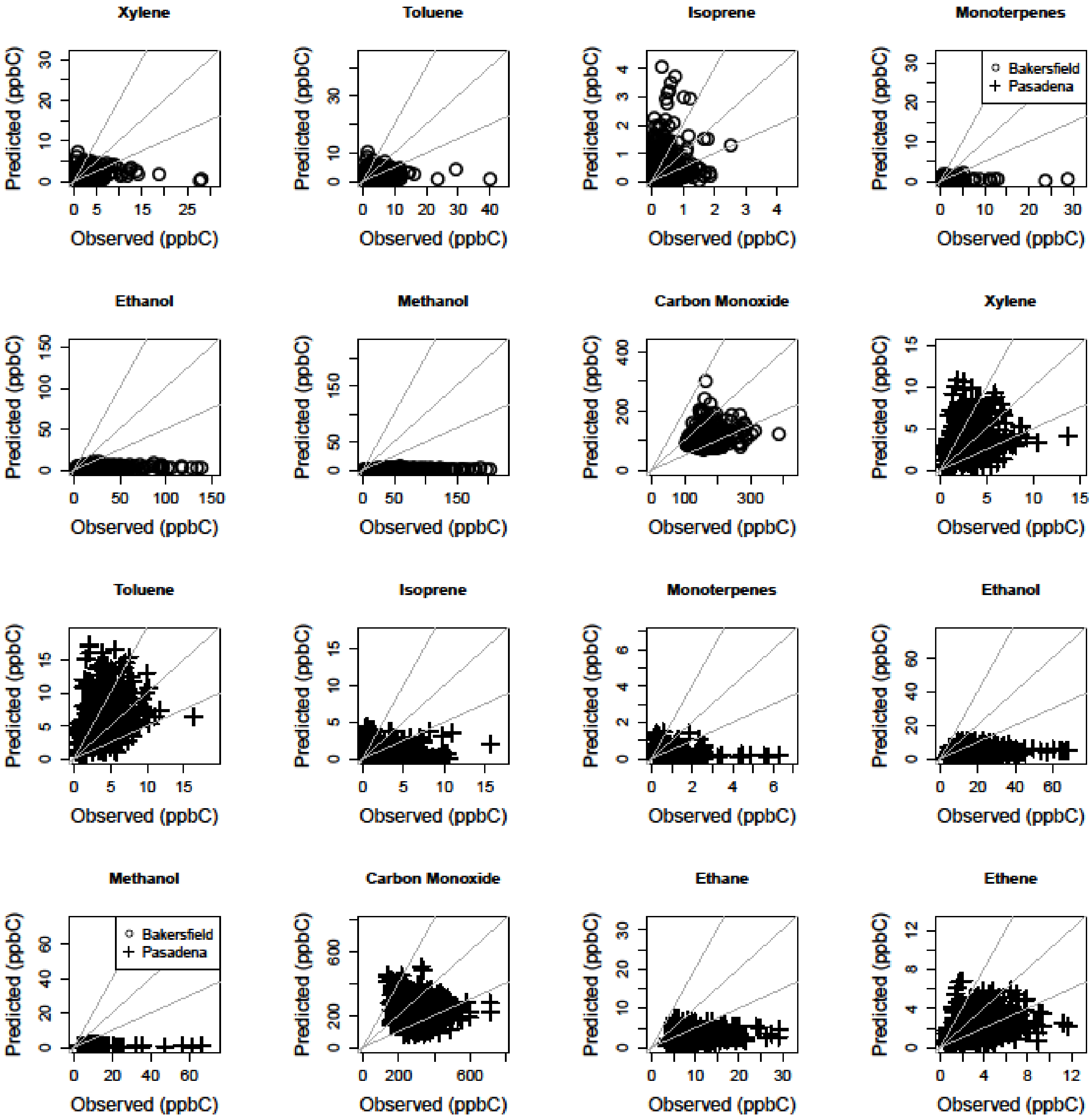


Figure S9. Model and observed mid-morning 3 hour average VOC paired in time and space.

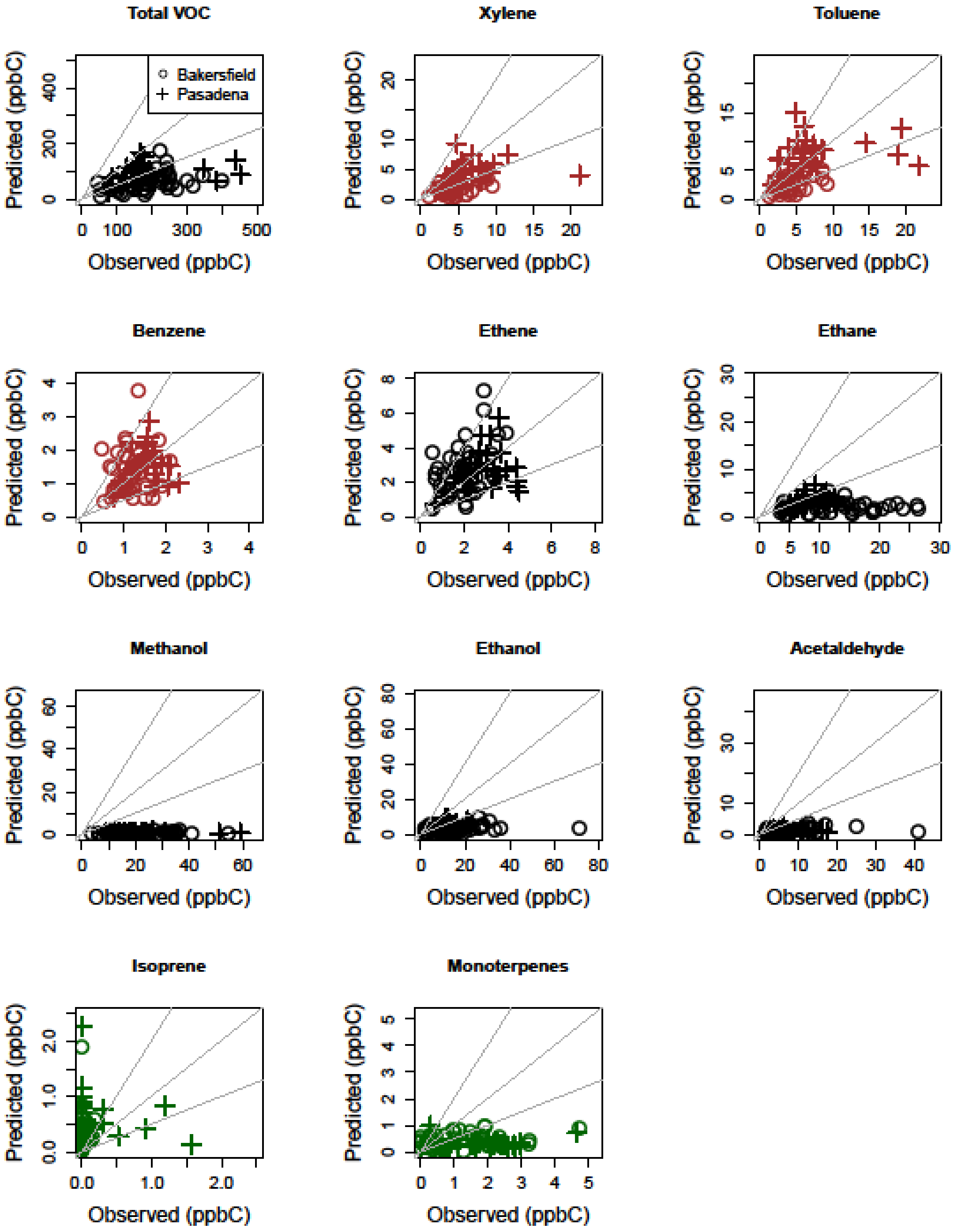
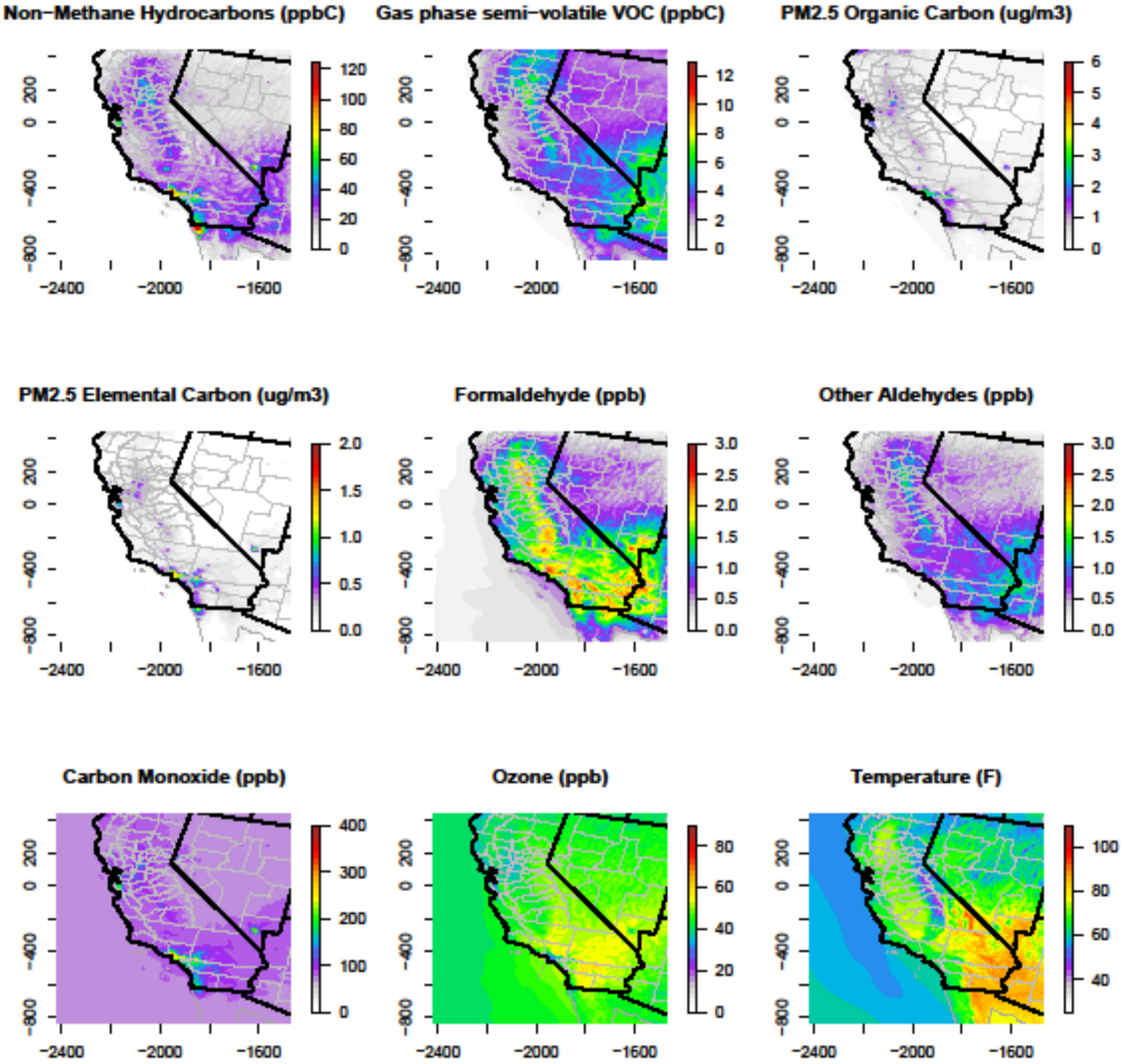


Figure S10a. June average model estimates.


Non−Methane Hydrocarbons (ppbC)

Gas phase semi−volatile VOC (ppbC)

PM2.5 Organic Carbon (ug/m3)

PM2.5 Elemental Carbon (ug/m3)

Formaldehyde (ppb)

Other Aldehydes (ppb)

Carbon Monoxide (ppb)

Ozone (ppb)

Temperature (F)

Figure S10b. June average model estimates. Biogenic VOC, semi-volatile products, and SOA.

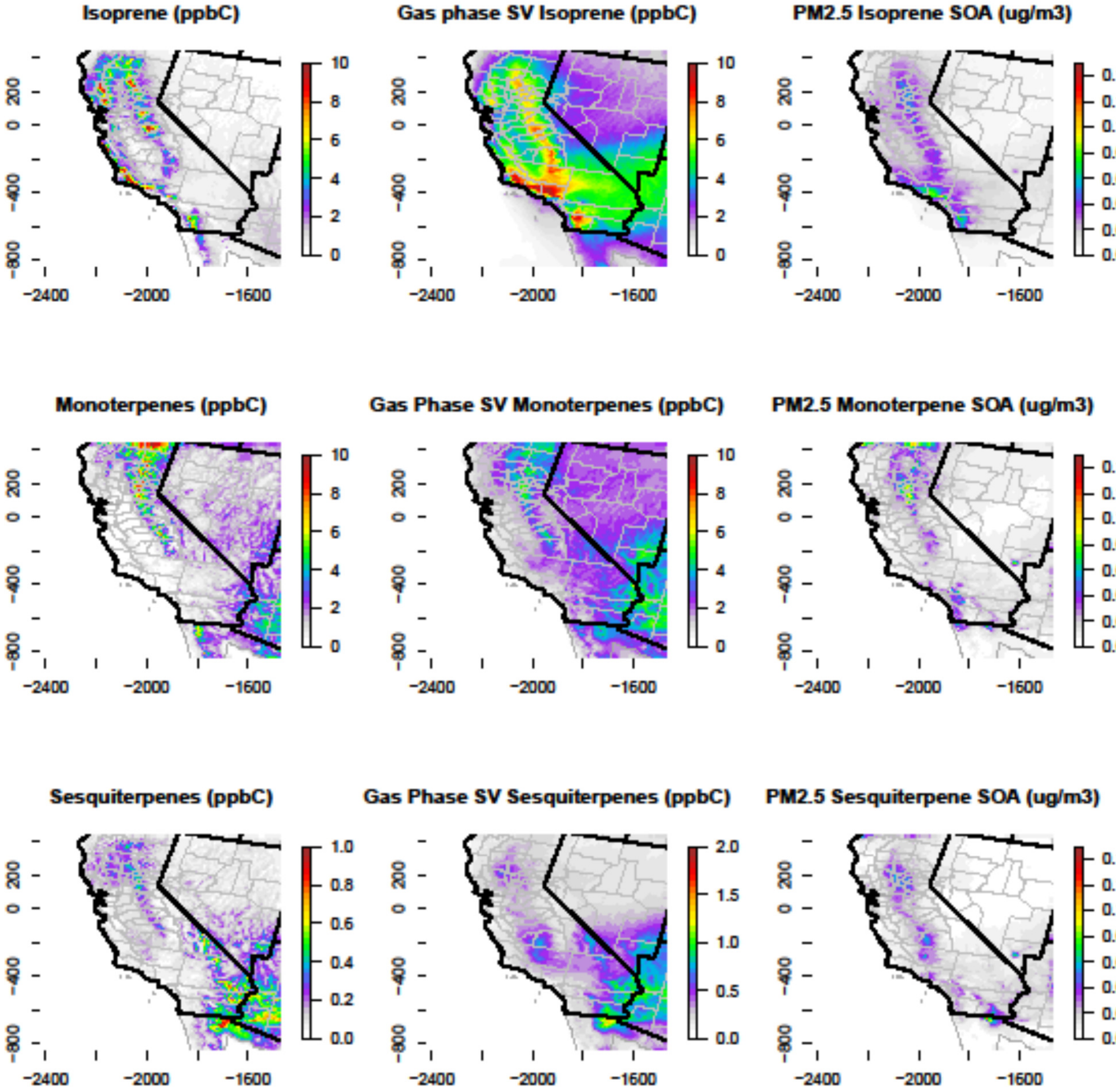


Figure S10c. June average model estimates. Anthropogenic VOC, semi-volatile products, and SOA.

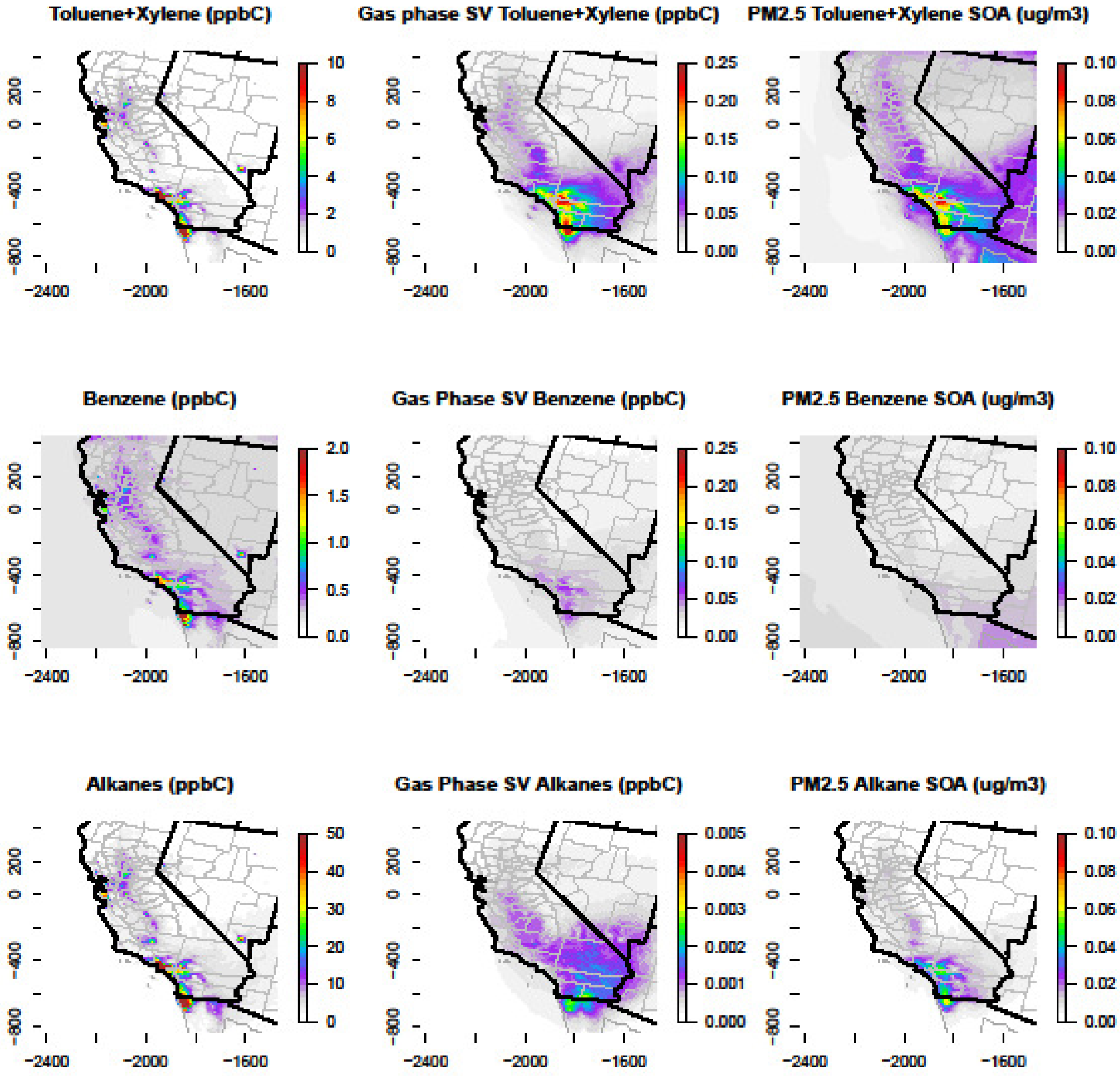
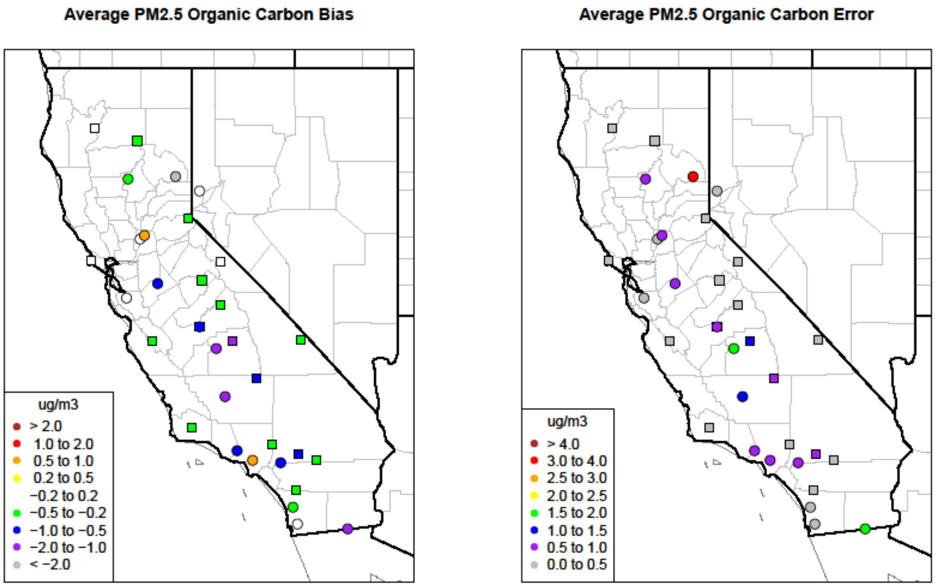
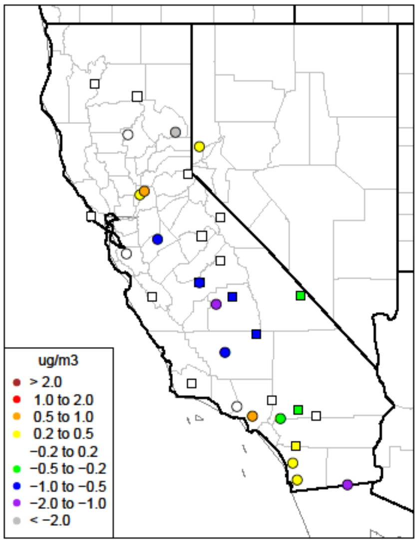
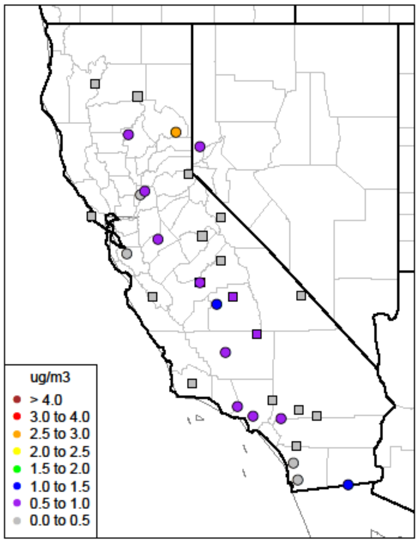


Figure S11. Episode average baseline (top row) and sensitivity (bottom row) model bias and error for PM2.5 organic carbon at CSN (circles) and IMPROVE (squares) sites. The large underestimate at the location in northeast California is related to model underestimates of elevated concentrations during a cold period in this area which may have resulted in increased residential fuel combustion. In general, the model underestimates organic carbon, most notably in urban areas. Rural areas dominated by biogenic sources show minimal bias and error.




Average PM2.5 Organic Carbon Bias


Average PM2.5 Organic Carbon Error

2 ADDITIONAL METHODS INFORMATION

2.1 Additional Information on Sampling and Analysis Methods

CalNex ground measurements took place in Pasadena, CA from 15 May – 15 June 2010 and in Bakersfield, CA from 15 May – 30 June 2010. Filter samples for SOA are integrated for 23-h periods starting at midnight of the designated sampling day. In total, there are 32 filter samples from Pasadena and 36 from the Bakersfield site. The sampling protocols have been described in detail elsewhere (Kleindienst, Lewandowski et al. 2010). $PM_{2.5}$ was collected on quartz filters using high volume $PM_{2.5}$ samplers operated at 0.226 m^3 min^{-1}. Each sampler consists of a $PM_{2.5}$ inlet (Tisch Environmental, Cleves, OH) followed by a 90-mm pre-combusted quartz filter (Pall-Life Sciences, East Hills, NY). Organic carbon denuders were not used in-line for these samples.

For the analysis of the SOA tracer compounds, filters and field blanks were treated using the method described by Kleindienst et al. (Kleindienst, Jaoui et al. 2007). Filters were soxhlet extracted for 24 hours using 125 mL of a 1:1 (v/v) dichloromethane:methanol mixture. Prior to the extraction, cis-ketopinic acid and tetracosane-d_{50} were added as internal standards. Filter extracts were rotary evaporated to a volume of 1 mL, then evaporated to dryness with ultrazero nitrogen. Extracts were derivatized with 250 μL BSTFA (1% TMCS catalyst) and 100 μL pyridine to give a final volume of 350 μL. The silylated extracts were analyzed by GC-ion trap mass spectroscopy (ITMS) in the methane-CI mode. Further detailed aspects of the analytical methodology have been given by Jaoui et al. (Jaoui, Kleindienst et al. 2004).

The mass spectral analysis for the organic compounds used as secondary molecular tracers has been described (Edney, Kleindienst et al. 2003). The tracer compounds are grouped by major ion fragments (Kleindienst, Jaoui et al. 2007). Since standards do not exist for the majority of these compounds, the concentrations of all of the tracers were measured as ketopinic acid (KPA). GC-MS analysis for the tracer compounds was conducted using the total ion chromatogram (TIC) or, in cases where coelution or extremely weak signals occurred, by a selected ion technique. By this method, a factor is determined from laboratory samples of the non-co-eluted peaks that represent the fraction of the five ion intensity to the total ion intensity for each tracer compound. The use of the five-ion-to-TIC calibration factor was found to give more consistent concentration estimates than found using a single ion.

The actual or simulated TIC area was then used to calculate the tracer concentrations as KPA. An assessment of the accuracy of this technique has been estimated as 60% for pinic and norpinic acids (Jaoui, Kleindienst et al. 2005), two compounds for which independent standards were produced. The technique should not introduce major uncertainties into the contribution estimates from the field data, since the same analytical procedures were used to establish the laboratory-based mass fractions, thus, compensating for systematic errors found in laboratory and field samples. For the determination of the total carbon, a 1.45 cm^2 punch was taken from a representative quartz filter and analyzed using the National Institute of Occupational Safety and Health (NIOSH) or thermal-optical transmittance (TOT) method, as described by Birch and Cary (Birch and Cary 1996). Values for OC were corrected for filter background levels. The minimum detect limit for the SOA tracer species is 0.1 ng/m^3.

Canisters for volatile organic compound (VOC) analysis were also collected at the two sites. A total of 41 samples were collected at the Bakersfield site and 31 at Pasadena. Samples were collected in evacuated (ca. 1 atm below ambient pressure) 6-liter canisters using Entech CS1200 samplers. Attached to the CS1200 samplers were Entech TM1100 systems that consisted of a battery operated off/on valve activated by a timer control element. The valve was open for a 3-h collection during the 6:00 – 9:00 a.m. (local daylight time) period. The samples were analyzed by GC-FID and reported compounds were identified by a GC retention time index using a calibration table (CALTABLE) of 402 VOCs developed specifically for GC system. Compounds equal to or less than the detection limit of 0.05 ppbC were defined as zero for comparison presentation of paired experimental and modeled estimates.

2.1.2 References

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2.2 CMAQ AE6 treatment for SOA presented by volatility and O:C ratio

Modeled organic aerosol species, semi-volatile partitioning gas phase analogs, and VOC precursors are matched with a volatility bin assignment based on saturation vapor pressure (C*) (Table S3). C* values for semi-volatile and aerosol species are taken from (Carlton et al., 2010) and calculated for gas-phase VOCs based on (Pankow et al., 1994) (Table S3 and Equation S1). The saturation vapor pressure of sesquiterpenes has not been measured and bin assignment is somewhat arbitrary; sesquiterpenes are placed in the log(C*)=5 bin, two bins lower than monoterpenes and four bins lower than isoprene. Model reference C* values are translated to local conditions at each sampling location by employing the species-specific enthalpy of vaporization (ΔH_{vap}). Mass concentrations of gas-phase species were calculated from the CMAQ reported mixing ratios (ppb_v):

$$C_i\left(\frac{\mu g}{m^3}\right) = X_i \frac{P}{RT} MW_i$$

[1]

Where X_i is the gas phase mixing ratio in ppb_v for species i, P and T are the location specific instantaneous pressure and temperature respectively, R is the ideal gas constant, and MW_i is the species molecular weight.

CMAQ predictions of organic material during CalNex are dominated by gas phase species. This is generally true and consistent with early measurements in California (Fraser et al., 1996). Episode average gas and particle organic carbon estimated by CMAQ for each ground site are shown in Figure S11 by saturation vapor pressure. Most of the carbon mass is either in the gas phase or non-volatile aerosol. Mass in the semi-volatile space is largely in the gas-phase. This suggests the potential exists for additional modeled SOC but this space is difficult to constrain due to limited available gas phase measurements. This Figure also shows gaps in the model representation of $PM_{2.5}$ organic carbon volatility distribution. Additional precursors with a saturation vapor pressure less than 10^8 $\mu g/m^3$ (such as IVOCs) could ameliorate some of the SOC under prediction (Shrivastava et al., 2008).

Smog chamber experiments conducted at high mass loadings and the SOC parameterizations developed from those experiments, and used in CMAQ, may be a contributing factor to the absence of material in low volatility bins, possibly due to bin mis-assignment (Stanier et al., 2008). It would also seem that some material mapped to the “non-volatile” bin actually exhibit some partitioning and should be elsewhere in the distribution, i.e., $-4<\log_{10}C^*<-1$. Missing SOC from PAHs (the naphthalene tracer) would contribute organic material to bins 0 and 2 with an O:C ratio ~0.5 (Chan et al., 2009b; Pye and Pouliot, 2012) and would not ameliorate the empty gaps. As noted previously, the modeling system does well at replicating total VOC but tends to underestimate aerosol carbon at these sites during this time period. For model applications requiring yields of species with saturation concentrations less than 0.1 $\mu g/m^3$, experiments must be able to measure similarly low concentrations to provide robust parameters (Stanier et al., 2008).

2.2.1 References

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Table S3. Calculation of volatility bin for gas phase organic species.

Species Name	Molecular Weight (g/gmol)	Vapor Pressure (mmHg)	Saturation Vapor Pressure (c*)	log(c*)	Note
ISOP	68.12	550	2.05E+09	9.31	
ALK2,ALK3,ALK4	57.6	100	3.15E+08	8.50	MW=average of 36.7, 58.6, and 77.6
MGLY	108	27	1.60E+08	8.20	Hydrated methylgloxal (higher MW)
MGLY	72.1	27	1.07E+08	8.03	
TOLUENE	92.1	20	1.01E+08	8.00	
GLY	92	18	9.06E+07	7.96	Hydrated glyoxal (higher MW)
BENZENE	78	20	8.54E+07	7.93	
GLY	58.1	18	5.72E+07	7.76	
MXYL,OXYL,PXYL	106.2	7	4.07E+07	7.61	
TERP	136	3.5	2.61E+07	7.42	
Napthalene	128.19	0.087	6.10E+05	5.79	Not included in CMAQv5.0.2
SESQ	204	*0.01*	1.12E+05	5.05	Assumed vapor pressure
ATRP2, SV_TRP2			1.34E+02	2.13	c* from Carlton et al, 2010
AISO1, SV_ISO1			1.16E+02	2.06	c* from Carlton et al, 2010
ABNZ2, SV_BNZ2			1.11E+02	2.05	c* from Carlton et al, 2010
AXYL2, SV_XYL2			3.45E+01	1.54	c* from Carlton et al, 2010
ASQT, SV_SQT			2.50E+01	1.40	c* from Carlton et al, 2010
ATOL2, SV_TOL2			2.13E+01	1.33	c* from Carlton et al, 2010
ATRP1, SV_TRP1			1.48E+01	1.17	c* from Carlton et al, 2010
ATOL1, SV_TOL1			2.33E+00	0.37	c* from Carlton et al, 2010
AXYL1, SV_XYL1			1.31E+00	0.12	c* from Carlton et al, 2010
AISO2, SV_ISO2			6.17E-01	-0.21	c* from Carlton et al, 2010
ABNZ1, SV_BNZ1			3.02E-01	-0.52	c* from Carlton et al, 2010
AALK, SV_ALK			2.00E-02	-1.70	c* from Carlton et al, 2010

Equation S1.

$$C_i^* = \frac{10^6 MW_i \xi_i p_{L,i}^o}{RT} = \frac{10^6 \left(\frac{\mu g}{g}\right) x\ MW_i \left(\frac{g}{gmol}\right)\ x\ \xi_i\ x\ p_{L,i}^o\ (mmHG)}{62.36\left(\frac{L\ mmHG}{K\ mol}\right) x\ 293(K)\ x\ \frac{m^3}{1000L}}$$

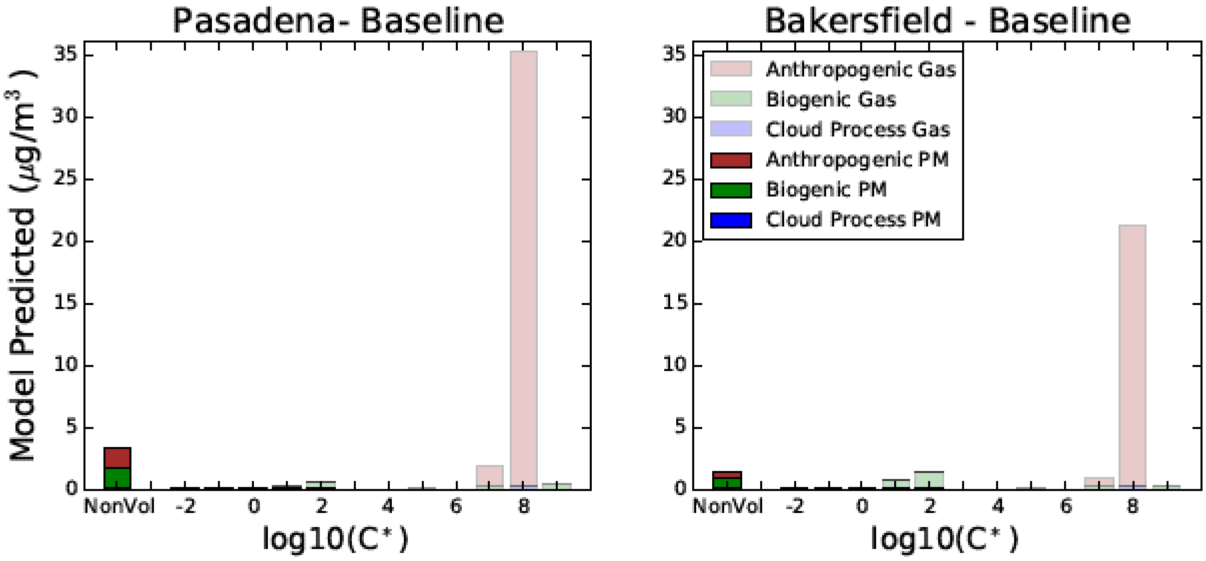
Note that ξ_i is assumed to be 1. This assumption is useful as an index for comparison among species but does not provide a complete description of the partitioning potential of water-soluble organic species.

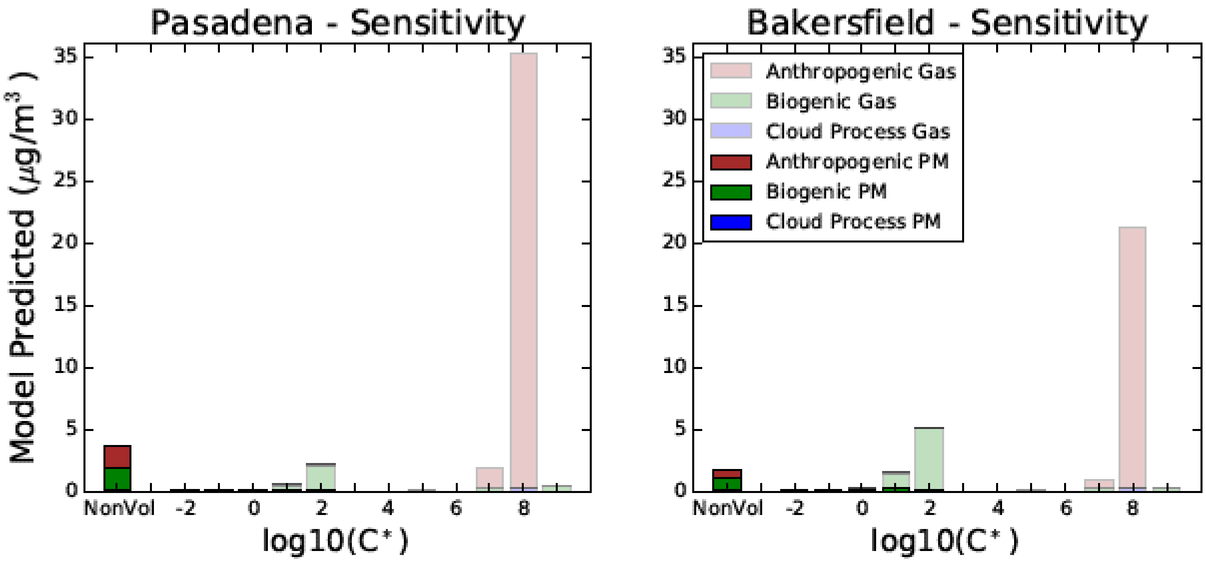
Table S4. Comparison of O:C ratio estimated from the assigned OM:OC ratios and estimated by counting the number of carbon, oxygen and hydrogen atoms.

Species	**MW**	**OM/OC**	**# of C** derived from parent compound	**# of O** integer dervied from MW less carbon mass	**# of H** integer dervied from MW less carbon & oxygen mass	**O:C** calculated from suspected chemical makeup	**O:C** (OM/OC-1)*(3/4)
AISO1	96	1.6	5	2	4	0.40	0.45
AISO2	96	1.6	5	2	4	0.40	0.45
ABNZ1	144	2	6	4	8	0.67	0.75
ABNZ2	144	2	6	4	8	0.67	0.75
ABNZ3	144	2	6	4	8	0.67	0.75
AALK	150	1.56	8	3	6	0.38	0.42
AISO3	162	2.7	5	6	6	1.20	1.28
ATOL1	168	2	7	5	4	0.71	0.75
ATOL2	168	2	7	5	4	0.71	0.75
ATOL3	168	2	7	5	4	0.71	0.75
ATRP1	168	1.4	10	3	0	0.30	0.30
ATRP2	168	1.4	10	3	0	0.30	0.30
AOLGA	176.4	2.1	8	5	0	0.63	0.83
AORGC	177	2	3	8	13	2.00	0.75
AXYL1	192	2	8	6	0	0.75	0.75
AXYL2	192	2	8	6	0	0.75	0.75
AXYL3	192	2	8	6	0	0.75	0.75
AOLGB	252	2.1	10	8	4	0.80	0.83
ASQT	378	2.1	15	12	6	0.80	0.83

NOTE: This analysis is somewhat limited in its application to AOLGA, AOLGB and AORGC. AOLGA and AOLGB represent oligomerization with a potentially changing number of carbon atoms. AORGC represents carboxylic acid and high molecular weight compounds (max O:C of 2). The assigned MW of ATRP1, ATRP2, AXYL1, AXYL2, AXYL3 and AOLGA is not able to accommodate H atoms consistent with the assigned OM:OC ratios.

Figure S12. Episode average CMAQ organic mass plotted by saturation vapor pressure. Gaps in the distribution are associated with chemical properties that potentially provide insight regarding the identity missing organic aerosol mass noted in CMAQ predictions. Model baseline estimates shown on top row and sensitivity simulation on bottom row.




Pasadena - Sensitivity
Bakersfield - Sensitivity
Model Predicted ($\mu g/m^3$)
35
30
25
20
15
10
5
0
NonVol
-2
0
2
4
6
8
log10(C*)
Anthropogenic Gas
Biogenic Gas
Cloud Process Gas
Anthropogenic PM
Biogenic PM
Cloud Process PM