

Semivolatile POA and parameterized total combustion SOA in CMAQv5.2: impacts on source strength and partitioning

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Supporting Information

SVOC aging mechanism formulation

The theory of Donahue et al. (2012) was used both to determine the properties of the SVOC compounds used in this study and to populate the SVOC aging mechanism.

Box model analysis of SVOC aging mechanism

A box model was constructed to examine differences between the mechanism developed for this study (CMAQ52) and ones used in previous literature. The 2D-VBS formulation for low-NO_x conditions used by Chuang and Donahue (2016) was chosen for reference (REF). Alternative mechanisms included that of Koo et al. (2014) (KOO), Grieshop et al. (2009) (GRI), and the POA particle-phase aging mechanism found in CMAQv5.1 (Simon and Bhave, 2012) (CMAQ51). The CMAQ51 mechanism included nonvolatile POA but experienced mass growth as the particles age. The box model enforced a constant OH mixing ratio of 1×10^6 molec cm⁻³ and particles and vapors equilibrated between every time step (1 min). The initial OA (gas + particle = $10 \mu\text{g m}^{-3}$) was given a volatility distribution equal to that of the primary emissions in CMAQv5.2, hence the semivolatile configurations decrease dramatically in aerosol concentration in the first time step. A background concentration of $5 \mu\text{g m}^{-3}$ OA was assumed.

The CMAQ52 aging mechanism produced SOA at nearly the same rate as the REF mechanism for the first half hour at this loading and OH concentration (Fig. 1a). After an hour, the CMAQ52 underpredicts by about 10%, whereas the KOO case underpredicts throughout the time series. The GRI case produces SOA at the same rate as the KOO case for the first hour but then continues producing SOA, eventually overtaking the REF case. In general the SOA aging mechanism recovers to about 80% of the original POA mass concentration, and about 55% of the potential POA formed from oxidation. Similar relationships are seen at lower and higher initial concentrations and higher OH concentrations.

Figure 1b shows that the KOO and GRI do a better job predicting O:C of the REF case than does the CMAQ52 mechanism, which overpredicts by about 0.1 in O:C. This is a result of the relatively high O:C chosen for the oxygenated OA species. In the future, the model may treat this SOA production pathway with source-specific model species, allowing the O:C of those species to be more individually tailored to observations of that pollution source.

Tables S1. Background CO values (ppbV) from observations and CMAQ predictions

Site	Observed	Reference	Predicted
Pasadena	110	Hayes et al. (2013)	85
Bakersfield	90	Gentner et al. (2012)	70
Cool	85	Setyan et al. (2012)	75

*Predicted background CO is calculated as the average of the bottom 5% of predicted CO concentrations.

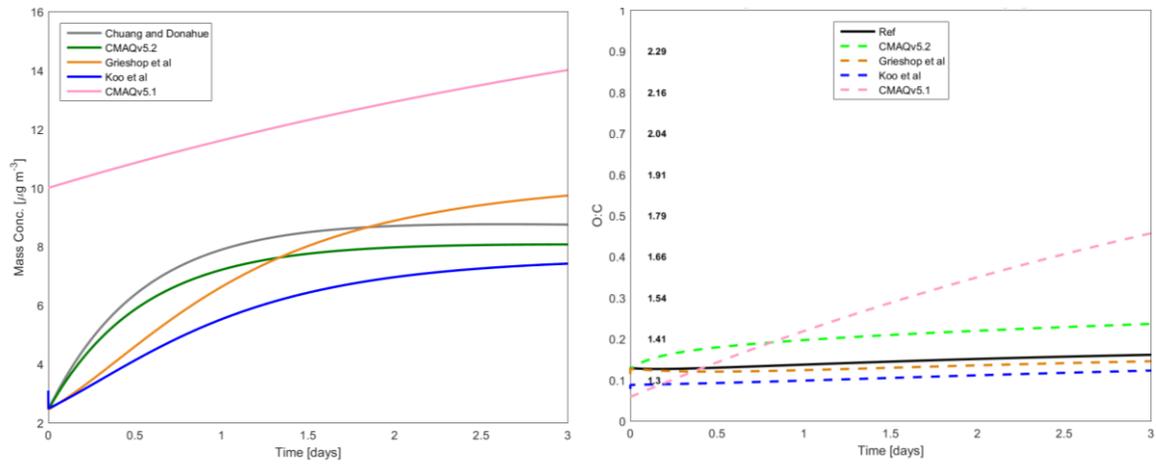


Figure S1. Box model OA concentrations (a) and O:C (b) with an assumed constant OH concentration equal to $1 \times 10^6 \text{ molec cm}^{-3}$, an initial loading of $10 \mu\text{g m}^{-3}$ and a background OA concentration of $5 \mu\text{g m}^{-3}$. In plot (b) the numbers on the inside of the left axis quantify OM:OC as a function of O:C using the method of Simon and Bhawe (2012).

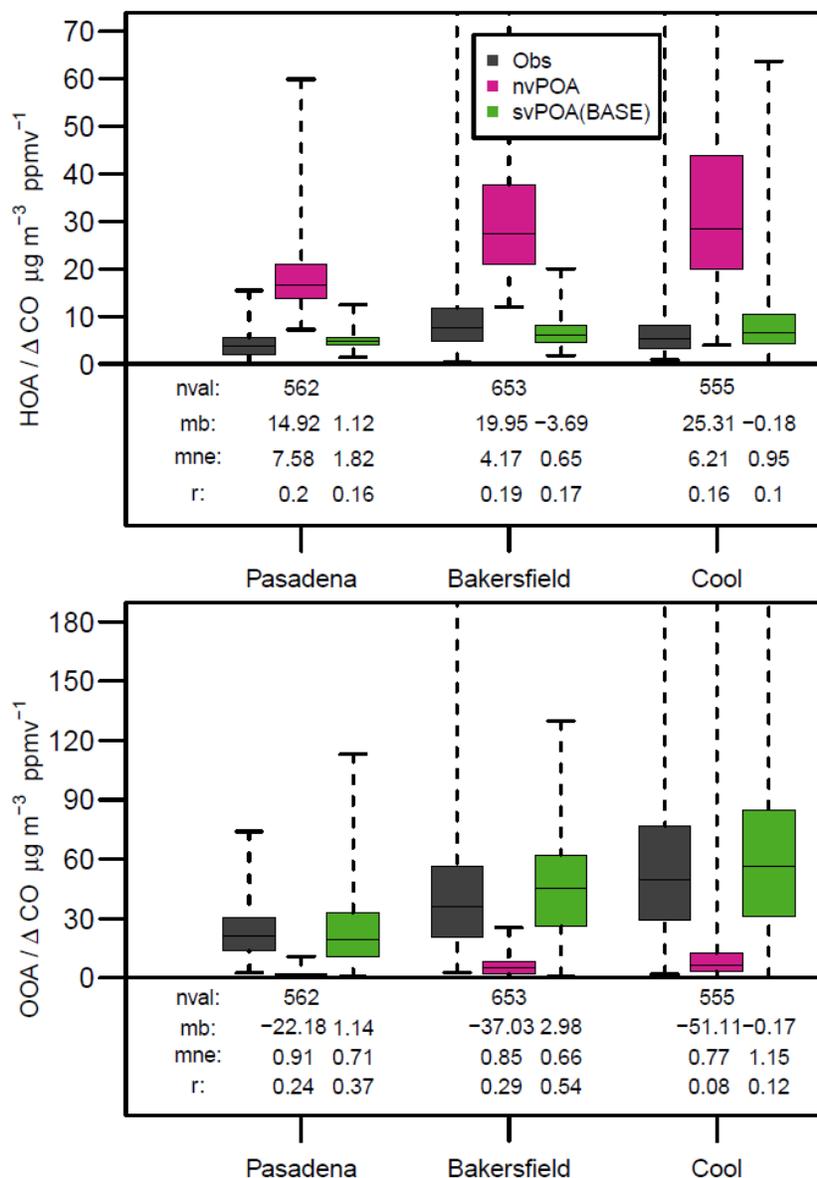


Figure S2. Evaluation of CMAQ-predicted hydrocarbon-like and oxygenated organic aerosol at 2 urban sites during CalNex (Pasadena and Bakersfield) and one urban downwind site during CARES (Cool). HOA and OOA from CMAQ are approximated by summing primary and secondary organic aerosol species, respectively, consistent with table 4. Here, all observed and predicted OA concentrations are normalized by the corresponding observed or predicted CO enhancement. The site-dependent background CO values applied to the observations are informed by existing literature while those applied to the CMAQ-predicted CO are calculated as the mean of the bottom 5% of the timeseries at each site. The background values are reported in table S1.

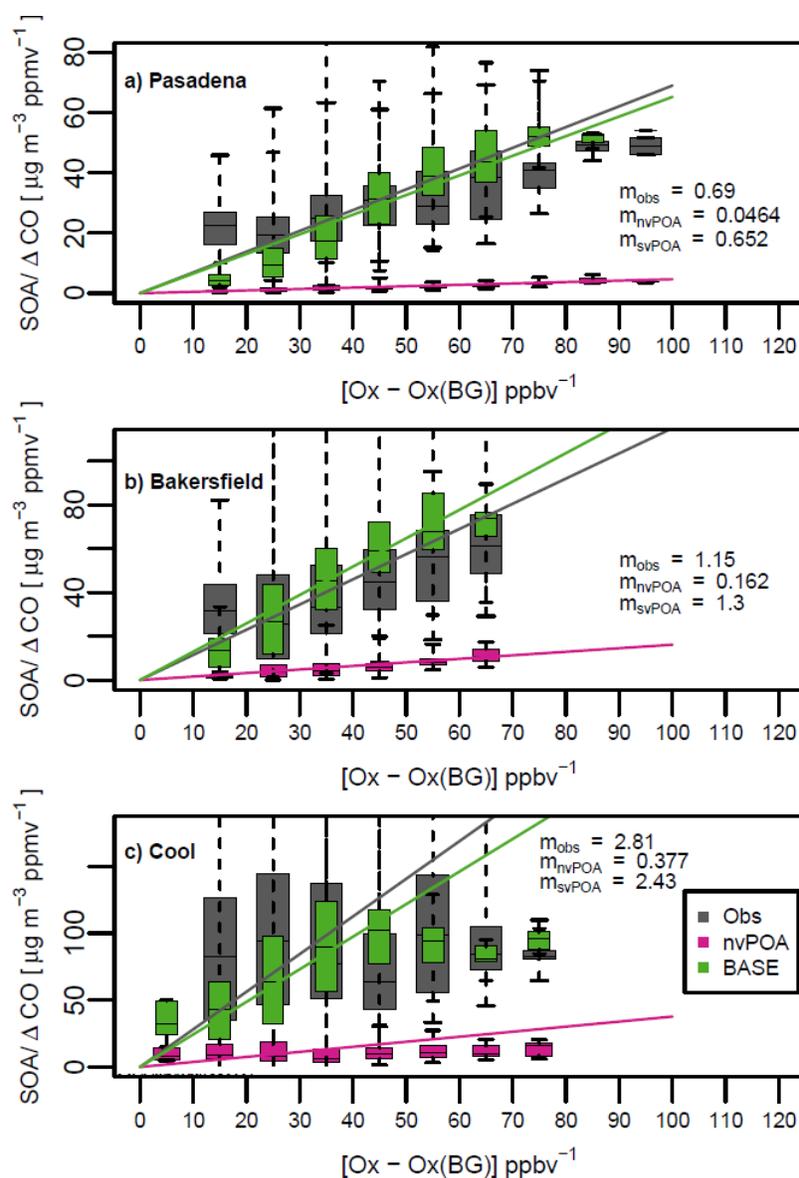


Figure S3. OOA observed and predicted enhancement as a function of oxidant loading at two urban sites during CalNex (Pasadena and Bakersfield) and one urban downwind sites during CARES (Cool). Ox concentrations are calculated as the sum of O_3 and NO_2 for Pasadena and Bakersfield. For Cool, the observed NO_2 concentrations are approximated as the difference between NO_y and NO . Here the OOA (observed) and SOA (predicted) concentrations are normalized by the CO enhancement (ΔCO) consistent with Fig. S2.