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Chemical Transport Model Simulations of Organic Aerosol in Southern California: Model Evaluation and Gasoline and Diesel Source Contributions

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Abstract. Gasoline- and diesel-fueled engines are ubiquitous sources of air pollution in urban environments. They emit both primary particulate matter and precursor gases that react to form secondary particulate matter in the atmosphere. In this work, we use experimentally derived inputs and parameterizations to predict concentrations and properties of organic aerosol (OA) from mobile sources in southern California using a three-dimensional chemical transport model, the Community Multiscale Air Quality Model (CMAQ). The updated model includes secondary organic aerosol (SOA) formation from unspeciated intermediate volatility organic compounds (IVOC). Compared to the treatment of OA in the traditional version of CMAQ, which is commonly used for regulatory applications, the updated model did not significantly alter the predicted OA mass concentrations but it did substantially improve predictions of OA sources and composition (e.g., POA-SOA split), and ambient IVOC concentrations. The updated model, despite substantial differences in emissions and chemistry, performs similar to a recently released research version of CMAQ. Mobile sources are predicted to contribute about 30-40% of the OA in southern California (half of which is SOA), making mobile sources the single largest source contributor to OA in southern California. The remainder of the OA is attributed to non-mobile anthropogenic sources (e.g., cooking, biomass burning) with biogenic sources contributing less than 5% to the total OA. Gasoline sources are predicted to contribute about thirteen times more OA than diesel sources; this difference is driven by differences in SOA production. Model predictions highlight the need to better constrain multi-generational oxidation reactions in chemical transport models.

1 Introduction

Organic aerosol (OA) is a major component of atmospheric fine particulate matter (Jimenez et al., 2009). Source apportionment studies have historically attributed the majority of ambient OA in urban areas to motor vehicles emissions (Schauer et al., 1996), but analysis of data from the California Research at the Nexus of Air Quality and Climate Change (CalNex) study has led to conflicting conclusions about the overall contribution of motor vehicles to OA in southern California and the relative importance of gasoline versus diesel sources. Bahreini et al. (2012) hypothesized that the majority of OA in southern California was secondary organic aerosol (SOA) formed from emissions from gasoline powered-sources based on differences in weekday and weekend concentrations; Hayes et al. (2013) and Zotter et al. (2014) have come to the same conclusion based on an analysis of mass spectrometer and radiocarbon data respectively. In contrast, Gentner et al. (2012) concluded that diesel vehicles contributed more OA than gasoline vehicles based on a comprehensive speciation of SOA precursors present in gasoline and diesel fuels. Ensberg et al. (2014) proposed that observed levels of OA could be explained only if vehicle emissions were a minor source of SOA or that the SOA formation potential of vehicle emissions was significantly higher than that measured in laboratory studies.

Finally, source-resolved chemical transport model (CTM) simulations predict that gasoline sources contribute approximately twice as much POA as diesel sources in southern California (Woody et al., 2016).

Research and regulatory efforts have historically focused on emissions of primary organic aerosol (POA) but recently the attention has shifted to secondary organic aerosol (SOA) since it is believed to dominate OA mass concentrations even in urban areas. Typical CTM treatments of OA include emissions of non-volatile POA and formation of SOA from "traditional" precursors (Carlton et al., 2010), which are speciated volatile organic compounds (VOCs) such as alkanes and aromatics, isoprene and mono- and sesquiterpenes. Robinson et al. (2007) proposed a new conceptual model for emissions and evolution of OA from combustion sources. Robinson et al. (2007) and a lot of subsequent work has demonstrated that: (1) POA emissions are semi-volatile and reactive (Grieshop et al., 2009;Huffman et al., 2009;May et al., 2013a;May et al., 2013c, b), (2) combustion sources emit substantial amounts of intermediate volatility organic compounds (IVOCs) that are efficient SOA precursors (IVOCs are higher carbon number species (C_{12+}) that are difficult to speciate using gas chromatography mass spectrometry techniques as a result of the large number of constitutional isomers and/or polarity of partially oxidized species (Jathar et al., 2014;Presto et al., 2011;Zhao et al., 2015;Hatch et al., 2015)) and (3) semi-volatile organic vapors in equilibrium with OA photo-chemically react or "age" in the atmosphere to form additional SOA (Miracolo et al., 2010). Recent state-of-the-science OA model treatments have included these three processes, which can be linked to improvements in model performance (Murphy and Pandis, 2009;Koo et al., 2014). These improvements, however, require simultaneous inclusion of all the above-mentioned processes; for example, inclusion of semi-volatile POA without the addition of SOA formation from IVOCs and aging reactions actually degrades model performance vis-à-vis total OA mass. The inputs used to represent these three processes in models remain poorly constrained. For example, IVOC emissions from all sources are assumed to be 1.5 times the POA emissions (Robinson et al., 2007;Shrivastava et al., 2008;Koo et al., 2014;Woody et al., 2016), based on measurements from two medium duty diesel vehicles (Schauer et al., 1999). New experimental data are needed to better constrain these processes.

Recently, a series of experiments investigated the SOA formation from gasoline vehicles, diesel vehicles and small off-road engines recruited from the California in-use fleet (Gordon et al., 2014a;Gordon et al., 2014b;Gordon et al., 2013). Jathar et al. (2014) analyzed these data to derive quantitative estimates of the emissions of IVOCs and their potential to form SOA after several hours of atmospheric oxidation. Here, we use the term IVOCs, to represent the class of intermediate-volatility SOA precursors that remain unresolved at the molecular level using conventional GC-MS techniques; Jathar et al. (2014) have referred to these as unspeciated organic compounds. We use the term VOCs, to include the class of SOA precursors typically speciated using conventional GC-MS techniques (e.g., alkanes smaller than C_{12}, single ring-aromatics). Separate parameterizations were derived to account for SOA formation from IVOC emissions from gasoline and diesel sources for use in CTMs. This paper builds upon recent work by Baker et al. (2015) and Woody et al. (2016) who used different versions of CMAQ to simulate OA in California during May and June 2010. In this work, we update emissions profiles for VOCs (based on May et al. (2013c) and May et al. (2013b)) and include emissions and parameterizations for SOA production from IVOCs (based on Jathar et al. (2014)) in a CTM to simulate ambient OA from gasoline and diesel sources in southern California. Model predictions are evaluated using data collected during CalNex, compared to predictions of other models, and used to investigate the contribution of gasoline and diesel sources to ambient OA concentrations. We note that this is the first time that a comprehensive set of gasoline and diesel source data have been used to develop source-specific inputs for a CTM. Earlier modeling efforts have relied on data that are almost a decade old (e.g., Koo et al. (2014)) and/or have used box models that do not accurately simulate horizontal and vertical transport and deposition (e.g., Hayes et al. (2015)). Hence, our work presents a step forward in improving the representation of sources, emissions and photochemical production of OA in large-scale models.

2 Methods

In this section, we provide a brief overview of CMAQ followed by more detailed descriptions of the OA model and emissions.

2.1 Chemical Transport Model

The CMAQ model version 5.0.2 was used to simulate air quality in California from May 4 to June 30, 2010, which coincides with the CalNex campaign (May–July 2010). Details about the application of this version to CalNex can be found in Baker et al. (2015) and Woody et al. (2016). Briefly, the model domain covered California and Nevada with a 4-km (317 x 236) grid resolution (Figure S.1). The vertical domain included 34 layers and extended to 50 mbar. Atmospheric _ENREF_60gas-phase chemistry was simulated with the Carbon Bond 2005 (TUCL05) chemical mechanism (Yarwood et al., 2005;Whitten et al., 2010;Sarwar et al., 2012). Aerosol chemistry and partitioning was simulated using the aerosols 6 (AERO6) module with different models to represent OA (described below). United States anthropogenic emissions were based on the EPA's 2011v1 modeling platform (http://www.epa.gov/ttnchie1/net/2011inventory.html) and biogenic emissions were estimated using the Biogenic Emission Inventory (BEIS) version 3.14 model (Carlton and Baker, 2011). Gridded meteorological variables used for input to CMAQ and SMOKE were generated using version 3.1 of the WRF model (Skamarock et al., 2008). The first 11 days of the simulation were excluded from the analysis to minimize the influence of initial conditions. Boundary conditions were provided by a 36-km continental U.S. CMAQ simulation from the same time period.

2.2 OA Model

The OA model used here builds on the volatility basis set (VBS) implementation in CMAQ (Koo et al., 2014) and is referred to as the VBS-IVOC model. The novel aspects of this work are the implementation of updated gas-phase emissions profiles that explicitly account for IVOC emissions from gasoline and diesel sources and experimentally constrained parameterizations of Jathar et al. (2014) for the SOA production from these emissions.

In the VBS-IVOC model, we extend the work of Baker et al. (2015) and Woody et al. (2016), both of which evaluated different OA models in CMAQ using the CalNex data. Baker et al. (2015) evaluated the standard OA module in CMAQ (Carlton et al., 2010). Woody et al. (2016) evaluated the VBS version of CMAQ as implemented by Koo et al. (2014), which allows for a semi-volatile and reactive treatment of POA and SOA contributions from VOCs and IVOCs and their multigenerational oxidation or aged products. The VBS-IVOC model is the same as the VBS model of Woody et al. (2016) except for the treatment of gasoline and diesel sources. To facilitate direct comparison between the different models, all three studies (this work, Baker et al. (2015) and Woody et al. (2016)) use the same CTM (CMAQ v5.02), emissions inventory (except for the modifications described below) and meteorology inputs; we note that Baker et al. (2015) used a different gas-phase chemical mechanism (SAPRC07b). We refer to the Baker et al. (2015) treatment of OA and the model results as the 'Traditional' model and we refer to the Woody et al. (2016) treatment of OA and the model results as the 'VBS' model.

The VBS model includes four distinct volatility basis sets to separately track different classes of OA: anthropogenic POA, anthropogenic SOA, biogenic SOA, and biomass burning POA (Koo et al., 2014). The VBS-IVOC model includes an extended version of CMAQ that has three more additional basis sets for POA from gasoline sources, diesel sources, and cooking activities to provide POA source apportionment (Woody et al., 2016). Each basis set has five volatility bins with different effective saturation concentrations (C*): non-volatile and logarithmically distributed bins from 10^0 to 10^3 μg m^{-3} at 298 K. The gas-particle partitioning of semi-volatile organic compounds in each basis set is calculated assuming they form a quasi-ideal solution with all of the OA.

Emissions: In the VBS-IVOC model, we use emission inventories developed by Baker et al. (2015) and modified by Woody et al. (2016) for use with the VBS model. In this section we briefly describe the VBS inventory of Woody et al. (2016), focusing on the updates to gasoline and diesel organic emissions used in the VBS-IVOC model.

We (in the VBS-IVOC model) and Woody et al. (2016) use the same semi-volatile POA emissions. These were estimated by redistributing the non-volatile POA emissions of Baker et al. (2015) into the VBS. For gasoline and diesel exhaust and biomass burning, this redistribution is done using the source-specific volatility distributions of May and coworkers (May et al., 2013c, b;May et al., 2013a). Cooking emissions were redistributed using an approximation developed by Woody et al. (2016) based on thermodenuder measurements made with cooking emissions and ambient measurements made during MILAGRO (Huffman et al., 2009). For all other sources, the volatility distribution of Robinson et al.(Robinson et al., 2007) was used to map the existing POA emissions into the VBS.

In the VBS-IVOC model, we use new VOC speciation profiles for tailpipe emissions from gasoline and diesel sources (Table S.1). These speciation profiles are applied to the emissions inventory of Baker et al. (2015). Therefore, the VBS-IVOC model has the same mobile source emission rates as Baker et al. (2015) but with different speciation. For all gasoline sources (on and non-road), the VOC speciation is based on fleet-averaged data from May et al. (2014), which reports emissions of 202 unique species measured during chassis dynamometer testing of 68 light-duty gasoline vehicles operated over the Cold Unified Cycle (UC) using gasoline that met California summertime specifications (five of the vehicles were also run on the Freeway, Arterial and Hot UC cycles). For on-road and off-road diesel vehicles, the VOC speciation is derived from the EPA SPECIATE profile for on-road heavy-duty diesel vehicles (Profile number 8774); the same emissions profile is used in Baker et al. (2015) and Woody et al. (2016). All VOCs are mapped to CB05 model species using EPA's speciation tool, which lumps unique organic compounds to a representative model species that are similar in terms of reactivity and reaction chemistry(Eyth et al., 2006;Carter, 2008).

For gasoline and diesel sources, in the VBS-IVOC model we estimate the IVOC emissions based on the gas-phase carbon-balance analysis of Jathar et al. (2014), who found that unspeciated organic compounds (assumed to be mainly IVOCs) constituted, on average, 25% and 20% of the non-methane organic gas (NMOG) emissions from gasoline and diesel vehicles respectively. IVOCs are included in the VBS-IVOC model by reapportioning the existing emissions between VOCs and IVOCs (effectively renormalizing the VOCs described above). Therefore, unlike previous VBS models such as Woody et al. (2016) where IVOC emissions are added on top of the NMOG emissions, no new NMOG emissions are added to the model for the gasoline and diesel sources. In addition, gasoline and diesel POA emissions in the C* bins of 10^3 and 10^4 μg m^{-3} (organic compounds that, in the atmosphere, exist in the vapor phase; 32% of gasoline and 35% of diesel POA emissions) are reclassified as IVOCs, consistent with the parameterization of Jathar et al. (2014).

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Following Robinson et al. (2007), IVOCs for all other sources (non-gasoline and diesel) were assumed to be 1.5 times the POA emissions (Woody et al. (2016) assumed this for all sources). Some of the IVOCs, as defined here, may already be included in the original emissions profile as ALK5 and UNK, however, as Pye and Pouliot (2012) show these emissions are very likely underestimated and, therefore, do not pose a serious problem of double counting SOA precursors.

To illustrate the effects of these changes, Figure 1 plots the POA and SOA precursor emissions (BTEX (all aromatics), ALK5 (long alkanes) and IVOCs) from gasoline and diesel sources in Los Angeles and Orange counties aggregated over the simulation period (May 4 to June 30, 2010). Table S.2 in the supplementary material lists the emissions for on- and off-road gasoline and diesel use, all other sources, and biogenic sources. Here, gasoline and diesel sources include both on- and off-road applications.

The magnitude of the POA emissions is identical between all three models with the exception that some of the POA emissions are reclassified as IVOCs in the VBS-IVOC model as mentioned earlier. The BTEX emissions are identical between the Traditional and VBS models, but lower in the VBS-IVOC model because we have renormalized the NMOG emissions to account for IVOCs. The Traditional model does not include IVOC emissions. The IVOC emissions in the VBS-IVOC model are a factor of four higher for gasoline sources than in the VBS model, but 20% lower for diesel sources. Taken together, the BTEX, ALK5 and IVOC emissions (sum of all anthropogenic SOA precursors) are somewhat higher (40%) in the VBS-IVOC model compared to the VBS model for gasoline sources and slightly lower (5%) for diesel sources. Therefore, discounting for differences in reaction rate constants and SOA mass yields, we expect roughly similar SOA production from gasoline and diesel sources between the VBS and VBS-IVOC simulations. In all models, gasoline sources have substantially larger organic emissions than diesel sources (e.g. 3.7, 42, 35 and 16 times more POA, BTEX, ALK5 and IVOC for the VBS-IVOC model, respectively); therefore we anticipate much higher SOA production from gasoline sources over diesel sources.

SOA formation: SOA production from VOCs is simulated using the parameterizations of Murphy and Pandis (2009) except for toluene (Hildebrandt et al., 2009). SOA production from aromatics (toluene, xylene, and benzene), isoprene, and monoterpenenes have high- and low-NO_x yields; there is no NO_x dependence in the SOA yield from sesquiterpenes and IVOCs. Emissions profiles that include VOCs, IVOCs and their SOA yields, specific to gasoline and diesel tailpipe emissions, are presented in Table S.1.

IVOC emissions from gasoline and diesel sources are represented separately using two (one for gasoline and one for diesel) gas-phase species in the chemical mechanism (CB05-TUCL) and the parameterizations of Jathar et al. (2014) are used to estimate the SOA production from the IVOC oxidation. _ENREF_20The IVOCs react with the OH to form a set of semi-volatile products distributed in the VBS (Table S.1). The stoichiometric mass yields for each product were determined by fitting the SOA production measured in smog chamber experiments performed with diluted vehicle exhaust (Jathar et al., 2014). Following Woody et al. (2016), for all other sources (i.e. not gasoline and diesel) SOA production from IVOCs is based on the published yields for the SAPRC ARO2 model species from Murphy and Pandis (2009).

SOA formed from VOCs and IVOCs is aged via reactions of the organic vapors with OH using a rate constant of 2 x 10^{-11} cm^3 $molecules^{-1}$ s^{-1}. These aging reactions form products with a vapor pressure reduced by one order of magnitude. Biogenic SOA is not aged. Semi-volatile POA vapors from all sources are aged using the scheme of Robinson et al. (2007) – gas-phase reactions with the hydroxyl radical (OH) using a rate constant of 4 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, which lowers volatility by an order of magnitude (Robinson et al., 2007). We note that the rate constant used for the aging reactions is not well constrained and it could potential vary with C* and O:C of the OA. A portion (~10%) of the POA mass is shifted from the POA to the anthropogenic SOA basis set to maintain O:C ratios (Koo et al., 2014). OH is artificially recycled in the IVOC oxidation and all aging reactions to prevent double counting and impacts to the gas-phase chemistry of the underlying chemical mechanism (Koo et al., 2014).

3 Results

Although the simulation domain covers the entire state of California, we focus our analysis on model predictions over southern California and the metropolitan area of Los Angeles. This region is the second most populated area in the US, has historically had severe air pollution problems, and was the focus of a major air quality campaign (CalNex) during the simulation period.

3.1 Spatial distribution of OA

Figure 2 shows maps of episode-average concentrations of predicted total OA (POA+SOA) from the following sources: (a) all, (d) gasoline, (e) diesel, (f) biogenic and (g) other from the VBS-IVOC simulation. In addition, Figure 2 also plots the ratio of (b) POA to OA and (c) SOA to OA. Episode-average concentrations of OA in southern California range between 1.5 and 3 $\mu g\ m^{-3}$ where POA accounts for slightly more than half of the OA in source regions such as downtown Los Angeles (a 'source' region is defined where one encounters high anthropogenic emissions of species such as POA) and SOA dominates in non-source regions and off the coast.

Gasoline sources contribute ~35% of the inland OA while diesel sources contribute less than 3% (for details see Section 5). Gasoline OA exhibits a slightly different spatial pattern than total OA, with higher downwind concentrations near Riverside than those near central Los Angeles, reflecting the importance of atmospheric production of SOA. As expected, biogenic SOA is more important outside of the urban areas contributing 5% of total OA in urban areas versus 10-20% in non-urban. Other OA contributes slightly more than half of all OA in the urban areas. Other OA is dominated by cooking POA, biomass burning POA and other anthropogenic SOA (see Figure 4 for contributions of these sources in Pasadena).

3.2 Model Evaluation Using OA Mass and Composition Measurements

The VBS-IVOC model was evaluated using measurements made at the Chemical Speciation Network (CSN) and the CalNex Pasadena ground sites. Figure 3(a) compares predicted daily-averaged OA mass concentration to measurements of organic carbon (OC) made at six CSN sites in California (Fresno, Bakersfield, Central Los Angeles, Riverside, El Cajon and Simi Valley). Figure 3(b) compares predictions of daily-averaged OA concentrations to measurements made using a high-resolution aerosol mass spectrometer (HR-AMS) (Hayes et al., 2013). The CSN measurements have been multiplied by an OA-to-OC ratio of 1.6 to account for the non-carbon species associated with organic carbon (Turpin and Lim, 2001).

Predictions from the VBS-IVOC model are slightly lower than the filter-based OC measurements at the CSN sites, similar to other studies (Simon et al., 2012). The fractional bias and error versus CSN sites are -23% and 43%, respectively. At the CSN sites, predictions from the VBS-IVOC model are marginally better at the southern California sites (Central LA, Riverside, El Cajon, Simi Valley, Pasadena) than the central California sites (Fresno, Bakersfield). This may be due to sources related to oil and gas production and agricultural activity being more important in central California (Gentner et al., 2014).

Figure 3(b) indicates predictions from the VBS-IVOC model are a factor of three lower than the HR-AMS OA data at the Pasadena site. It is unclear why the model performs much better at numerous CSN sites than the Pasadena site. One possibility is that the Pasadena site is influenced by local sources and transport that is not captured by the model at 4 km resolution.

OA mass concentrations are only one measure for evaluating model performance. Given the myriad sources of and complexity in SOA production, a model can predict the right absolute OA concentration for the wrong reason. Therefore, it is important to evaluate the model against OA composition. Figure 4 compares predicted POA and SOA mass concentrations to results from a positive matrix factorization (PMF) analysis of HR-AMS measurements made in Pasadena (Hayes et al., 2013). Since the absolute OA concentrations as measured with the HR-AMS are under-predicted (Figure 3(b)), we present comparisons of both OA mass fractions and absolute concentrations. Mass fractions only allow for a qualitative comparison of the OA composition and any differences in the modeled and measured mass fractions cannot be interpreted as an under- or over-prediction in the absolute mass concentration.

Figure 4 compares model predictions against hydrocarbon-like OA (HOA), cooking OA (COA) and oxygenated OA (OOA) factors (Hayes et al., 2013). The AMS HOA factor is typically associated with POA from motor vehicles and other fossil fuel sources. Therefore, in this work, it is compared against predictions of POA from gasoline and diesel sources. The AMS COA factor is associated with primary cooking emissions and is compared against predictions of POA from cooking sources. The AMS OOA factor is associated with SOA and is compared against predictions of total SOA; the model did not resolve SOA by degree of oxygenation and hence we have not compared predictions to the individual HR-AMS-derived semi-volatile OOA (SV-OOA) and low-volatility OOA (LV-OOA) factors.

Figure 4 shows that the VBS-IVOC model better predicts the POA-SOA split than the Traditional model. For the VBS-IVOC model, the POA-SOA split is 1:1 versus ~20:1 for the traditional model. The measurement-based factor analysis estimates a POA-SOA split of 1:2. For the Traditional model, SOA is less than 3% of the total OA.

In Figure 4, we show that the predicted gasoline+diesel POA fraction compares well with the HR-AMS HOA fraction while the predicted cooking POA fraction is over-predicted compared to the HR-AMS COA fraction; (Woody et al., 2016) note that in the VBS model (which has the same treatment for cooking OA as the VBS-IVOC) likely under-predicts cooking POA emissions based on a comparison of absolute cooking OA concentrations. For the VBS-IVOC model, about 6% of the OA is from biomass burning while Hayes et al. (2013) were unable to determine a biomass burning factor in their PMF analysis. The SOA fraction predicted by the VBS-IVOC model is about 30% lower than the estimated OOA fraction. The SOA under-prediction could be a result of the uncertainty in how the model-predicted anthropogenic (other) POA (defined here as the non-mobile, non-cooking and non-biomass burning POA) needs to be treated when comparing against AMS PMF factors. The anthropogenic (other) category here includes sources such as stationary fuel combustion (e.g., natural gas combustion), surface coatings (e.g., metal coating), mineral processes (e.g., concrete production), road dust and managed burning (e.g., prescribed burns). Unfortunately, the composition of the POA emitted from these sources is not well understood and needs to be investigated by future work.

Although predictions from the VBS-IVOC model are much better than the Traditional model for the POA-SOA split and the fractional source contribution/composition of OA, in Figure 3(b) we show that predictions from the VBS-IVOC model are substantially lower than the absolute concentrations measured by the HR-AMS. Future research should explore higher resolution simulations (<1 km) for the Los Angeles area, in addition to improving estimates of POA emissions (e.g., cooking) and alternative pathways for SOA formation (e.g., higher SOA yields when accounting for vapor wall-losses in chambers).

3.3 Model Evaluation Using IVOC Measurements

A novel aspect of the VBS models (VBS and VBS-IVOC) is that they track IVOCs that are important SOA precursors (Jathar et al., 2014). Campaign-averaged predictions of IVOC concentrations are compared in Figure 5 against IVOC measurements at the Pasadena ground site presented in Zhao et al. (2014); this is the first time 3-D model predictions of IVOCs have been compared against ambient measurements.. The VBS-IVOC model does not represent secondary production of IVOC species (for lack of data) and hence in Figure 5 model predictions only include primary emissions of IVOCs. The IVOC measurements shown in Figure 5 are split into two categories: primary and oxygenated. Zhao et al. (2014) attribute the measured primary IVOCs to emissions from mobile sources (gasoline+diesel) and oxygenated IVOCs to primary sources and those formed in the atmosphere. To correct for differences in atmospheric mixing, we ratio the predictions and measurements with CO.

The predicted concentrations of IVOCs from gasoline and diesel (~ 17 µg m^{-3} ppm-CO^{-1}) compared favorably with the measured primary IVOCs (~20.5 µg m^{-3} ppm-CO^{-1}). The good model-measurement comparison suggests that the VBS-IVOC model reasonably simulates the emissions, transport and chemistry of IVOCs from mobile sources. Coincidentally, the predicted IVOC sum for other anthropogenic sources and biomass burning (~16 µg m^{-3} ppm-CO^{-1}) compared well with the measured oxygenated compounds (~15 µg m^{-3} ppm-CO^{-1}). Given the uncertainty in the model emissions of IVOCs for non-mobile sources (POAx1.5), the comparison with oxygenated IVOCs would need to be explored in future work. We should note that CMAQ predictions of CO in Los Angeles were found to be approximately a factor of 2 too low, which would mean that absolute IVOC concentrations would similarly be approximately a factor of 2 lower than observations.

3.4 Model Inter-comparison for OA

We compared predictions from the VBS-IVOC model to OA predictions from Baker et al. (2015) and Woody et al. (2016) who simulated air quality in California during CalNex. Figure S.2 presents maps of episode-averaged concentrations and ratios of POA, SOA and total OA (POA+SOA) from the Traditional and VBS-IVOC simulations. The results are qualitatively similar to earlier VBS implementations(Fountoukis et al., 2014;Hodzic et al., 2010;Ahmadov et al., 2012;Shrivastava et al., 2011;Tsimpidi et al., 2009) and previous comparisons between VBS and Traditional-like models (Robinson et al., 2007;Shrivastava et al., 2008;Woody et al., 2016;Jathar et al., 2011). In the VBS-IVOC simulation, total OA concentrations are lower in source regions (~50%) but ~20-40% higher away from sources than the Traditional model. The decrease in source regions is due to POA evaporation while an increase away from sources results from enhanced SOA production. The OA predicted by the Traditional model is dominated by POA (1-3 µg m^{-3}) with very little SOA (0.2-0.4 µg m^{-3}) while the OA predicted by the VBS-IVOC model has equal proportions of POA and SOA.

Figure S.3 compares predictions of the VBS and VBS-IVOC models, including episode-averaged concentrations and ratios of POA, SOA and total OA (POA+SOA). The results are surprisingly similar. POA concentrations in the VBS-IVOC model are slightly lower (~10%) in source regions and lower still in non-source regions (~20%) than the VBS model. The SOA concentrations are nearly identical and both models predict a spatially uniform OA concentration in contrast to the Traditional model. The modest differences in POA and SOA likely result from a combination of the following three reasons: (1) the total magnitude of the SOA precursor emissions in the VBS and VBS-IVOC models are roughly similar (see BTEX, ALK5 and IVOC emissions data in Table S.2 for all sources), (2) gasoline and diesel use contributes only 30%-40% of the predicted OA concentrations in southern California (see Section 5 for a detailed discussion) and (3) a majority of the SOA predicted in southern California arises from aging reactions.

Although the VBS and VBS-IVOC models contain very different representations of mobile source emissions, these emissions contribute slightly more than one-third of the total OA in southern California (see Section 5). Therefore, the updates used in the VBS-IVOC model had a limited influence in affecting the overall OA burden. Strict regulations have dramatically reduced emissions from motor vehicles over the past three decades, which has both improved air quality and increased the relative importance of the role played by other sources (McDonald et al., 2015). For example, compared to mobile sources, cooking remains a possibly important, yet understudied, source of fine particle pollution in urban airsheds.

Another reason for the similarity between predictions from the VBS and VBS-IVOC models is the role of aging reactions. Both models use the same aging scheme where aged SOA is a combination of oxidation products arising from both the POA and SOA basis sets (for more details, see Koo et al. (2014)) To quantify its contribution to predicted SOA concentrations, we ran the VBS-IVOC model with aging reactions turned off; these results are plotted in Figure S.4.. Without aging, total predicted OA is nearly halved and SOA concentrations are significantly reduced (more than a factor of five in source regions, factor of 10 to 20 in terrestrial non-source regions and up to a factor of 40 over the ocean). Given that mobile sources contribute only about one-third of the total OA and that aging reactions significantly enhance OA concentrations, it appears that modest differences in the emissions and yield potential of SOA precursors between the VBS and VBS-IVOC models have a limited effect the OA burden.

The aging reactions simulate the multigenerational gas-phase oxidation of vapors in equilibrium with OA. The aging mechanism used here is conceptually based on the work of Robinson et al. (2007) and only allows for the formation of functionalized, lower-volatility products. In essence, aging reactions, with enough time, will convert all semi-volatile vapors into particles. However, the mechanism assumes a constant reaction rate constant, which may vary with C* and O:C of the OA and does not account for fragmentation reactions, which should become increasingly important at longer time scales(Kroll et al., 2011). The reaction rate for aging and the effects of aging at longer time scales have not been constrained against laboratory data. This implies that the OA predictions, despite the substantial new data, become poorly constrained as one moves downwind of source regions. Murphy and Pandis (2009) have found that model predictions agree better with measurements when aging reactions are turned off for biogenic SOA. Recently, Jathar et al. (2016) have shown that aging reactions similar to those suggested in Robinson et al. (2007) might not be necessary since the laboratory chamber experiments that are used to parameterize SOA production already include products from the aging reactions happening inside the chamber. The work of Murphy and Pandis (2009) (for biogenics) and Jathar et al. (2016) suggests that including aging reactions in CTMs may double count SOA production and over-predict the importance of multigenerational gas-phase chemistry in the atmosphere. Although some work has been done to understand the aging of biogenic SOA (Donahue et al., 2012;Henry and Donahue, 2012), future laboratory work needs to be directed in understanding the role of aging of OA vapors formed from anthropogenic sources on the mass and properties of OA.

4 Discussion on Gasoline versus Diesel OA

Recent analyses of the CalNex data have led to conflicting conclusions about the contribution of gasoline and diesel sources to OA in southern California (Bahreini et al., 2012;Gentner et al., 2012;Ensberg et al., 2014;Hayes et al., 2013;Zotter et al., 2014;Hayes et al., 2015). The source-resolution implemented in the VBS-IVOC model allows for an assessment of the absolute and relative importance of gasoline and diesel sources to OA in southern California. In Figure 6, we plot the campaign-averaged OA concentrations attributable to gasoline and diesel use. The SOA production from VOCs for gasoline and diesel sources was not tracked separately in the model. Here, the SOA from VOCs is estimated based on the contribution of gasoline and diesel sources to the emissions of VOC precursors (BTEX and ALK5) in the Los Angeles and Orange counties.

In Pasadena, predictions from both VBS models show that gasoline sources contribute ~7-8 times more OA than diesel sources (Figure 6(a)), which is somewhat lower than other inland locations in southern California (Figure 6(b)). Domain-wide, the gasoline contribution to OA is 10 to 20 times that of diesel. At Pasadena, predictions from the VBS-IVOC model show that gasoline contributes 20 times more SOA than diesel. Both VBS models predict that the combined (gasoline and diesel) POA-to-SOA split is ~1:3 implying that the contribution of gasoline and diesel sources to ambient OA strongly depends on SOA production and not directly-emitted POA. Based on results from the VBS-IVOC model, gasoline sources produce more SOA than POA (SOA~3.6xPOA) while diesel sources produce less SOA than POA (SOA~0.5xPOA).

Our predictions are consistent with the weekday/weekend analysis of Bahreini et al. (2012) that do not detect a diesel contribution to SOA in the LA basin and qualitatively with the findings of Zotter et al. (2014) and Hayes et al. (2013). However, Hayes et al. (2015) predict a much larger contribution of diesel sources to SOA than this work (approximately 1.5 to 2 times lower than gasoline), which can mostly be attributed to the differences in emissions inputs for S/IVOC emissions (Hayes et al. (2015) estimate that 44-92% of the SOA arises from S/IVOCs). Hayes et al. (2015) estimated S/IVOC emissions by scaling POA emissions based on Schauer et al. (1999) and using the volatility distribution from Robinson et al. (2007). The POA scaling data are from two medium duty vehicles from nearly two decades ago and the volatility data are from a single diesel engine from a decade ago. These data sources make the S/IVOC estimates of Hayes et al. (2015) quite uncertain. In contrast, our work uses a much more comprehensive dataset to determine S/IVOC emissions from gasoline and diesel sources. Finally, we should note that a Traditional model (with a non-volatile POA and small SOA prediction), based on the emissions inventory (see Table S.1), would have predicted that gasoline use contributed four times more OA than diesel use.

We also investigate the sensitivity of the VBS-IVOC predictions to uncertainty in diesel IVOC emissions. Zhao et al. (2015) recently directly measured the IVOCs from emissions of on-road diesel engines. They found that IVOCs could account for up to 60% of the NMOG emissions, which is much greater than the 20% used here. To explore the implications of the findings of Zhao et al. (2015), we performed two additional simulations where we scale IVOC emissions from diesel sources by a factor of 3 and 5, which are effectively equivalent to IVOC-to-NMOG ratios of 0.6 and 1.0 respectively. For these simulations, additional IVOC mass is added to the inventory. Results from those simulations are also shown in Figure 6(a). We find that increasing the IVOC emissions proportionally increases the OA contribution from diesel sources. However, even if all of the NMOG emissions from diesel are assumed to be IVOCs (an upper bound estimate), gasoline-related OA still dominates OA from diesel sources.

Figure 6(c) shows the cumulative distribution for the contribution of gasoline and diesel sources to total OA across southern California. Gasoline sources contribute much more to the total OA (median contribution of 35%) than diesel sources (median contribution of 2.6%) over southern California (Figure 6(c)). Together, mobile sources (gasoline and diesel use) contribute ~30-40% (10th-90th percentile) of the predicted OA concentration in southern California; the single most important source despite decades of emissions controls. The balance of the OA is from cooking POA (median contribution of 10%), biogenic SOA (median contribution of 10%) and all other anthropogenic sources (median contribution of 40%, which includes SOA from cooking sources). Gasoline sources are still predicted to be the largest source. This finding partially supports the conclusion of Ensberg et al. (2014) that mobile sources are not the dominant source of OA concentrations in southern California and potentially explains why the updates only modestly changed the overall model predictions.

Figure 6(a) resolves the OA contributions based on the precursor class at the Pasadena site. The VBS-IVOC model predicts that IVOCs, particularly from gasoline vehicles, form almost as much SOA as VOCs (long alkanes and single-ring aromatics). This is in contrast to Jathar et al. (2014), who found that unspeciated precursors (or IVOCs) were approximately a factor of 4 larger than VOCs in forming SOA in chamber experiments. There are two possible reasons for this difference. First is the VOC:NO_x dependence on SOA formation. Jathar et al. (2014) parameterized SOA formation from IVOCs at low VOC:NO_x (or high NO_x levels) ratios, which the model applies to both high and low VOC:NO_x ratios. Since SOA yields often increase at high VOC:NO_x ratios (or at low NO_x levels), the transport of emissions from high NO_x to low NO_x regions will serve to reduce differences between VOC and IVOC SOA. This also means that the prediction of IVOC SOA in this work presents a lower bound estimate. Second, Jathar et al. (2014) did not account for the effects of continued aging of IVOC oxidation products on OA concentrations. Simulations with the VBS-IVOC model with aging reactions turned off (discussed in Section 4.4) indicate that aging enhances VOC SOA by a factor of 14 but enhances IVOC SOA only by a factor of 3-5. The different enhancements result from different product distributions for VOC and IVOC SOA in volatility space. This underscores the uncertainty of the treatment of aging (or multigenerational oxidation) in 3-D models. While both laboratory and field evidence indicate that aging is an important atmospheric process, it is unclear if and by how much aging enhances OA over regional scales and whether aging chemistry varies with precursor and source (Jathar et al., 2016). For these reasons, the relative importance of VOC and IVOC SOA precursors and the source apportionment presented here is a first estimate and will likely evolve as we develop better models to simulate the dependence of NO_x and aging on SOA formation.

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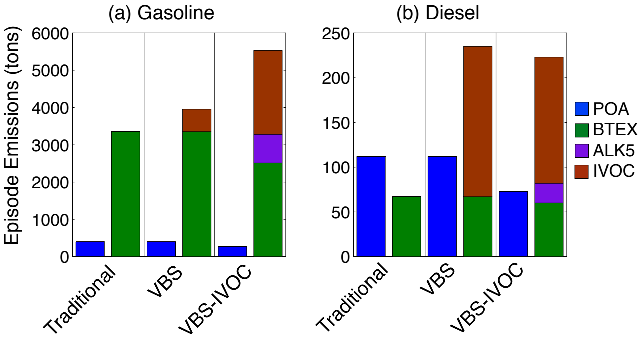

Figure 1: Total episode emissions for POA, BTEX (aromatics), ALK5 (long alkanes) and IVOCs for gasoline and diesel sources in the Los Angeles and Orange Counties for the three OA models: Traditional, VBS and VBS-IVOC.

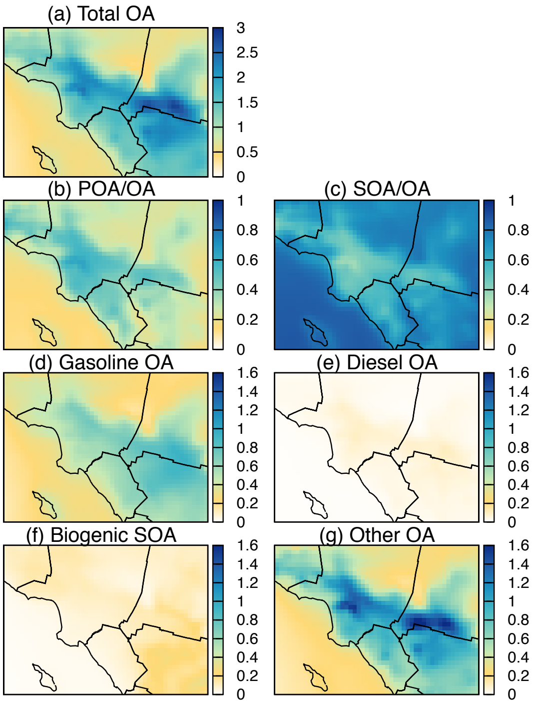

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Figure 2: Episode-averaged model predictions from the VBS-IVOC model for (a) total OA (µg m^{-3}), (b) POA fraction, (c) SOA fraction, (d) total gasoline OA (µg m^{-3}), (e) total diesel OA (µg m^{-3}), (f) biogenic SOA (µg m^{-3}) and (g) other OA (µg m^{-3}) over southern California.

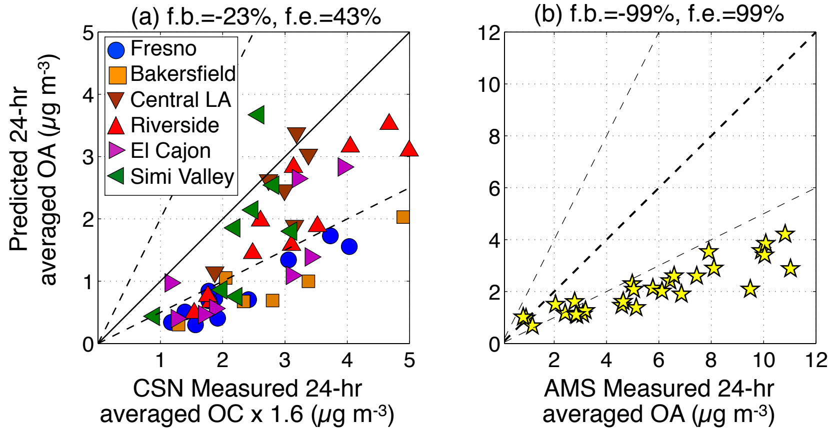

Figure 3: Scatter plot of VBS-IVOC OA predictions versus 24-hr measurements of (a) organic carbon (OC) made at sites operated by the Chemical Speciation Network (CSN) monitoring program and (b) OA made at the Pasadena ground site during the CalNex campaign. In panel (a) the model-measurement comparison is for six sites in California (Fresno, Bakersfield, Central Los Angeles,
5 **Riverside, El Cajon and Simi Valley).**

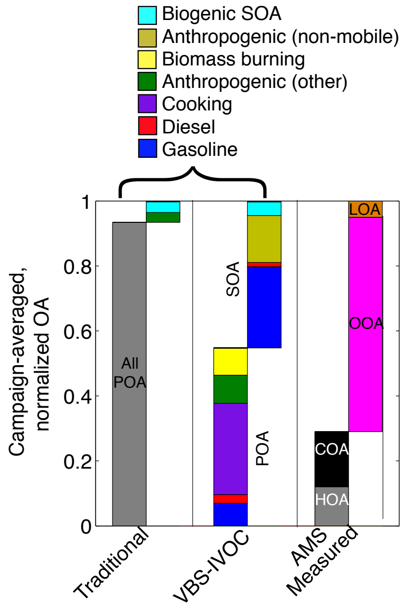

Figure 4: Episode-averaged, normalized composition of OA at the Pasadena ground site as predicted by the Traditional and VBS-IVOC models. Predictions are compared to PMF factors estimated from HR-AMS data from Hayes et al. (2013).

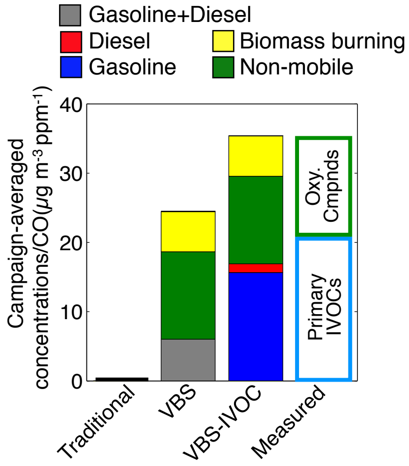

Figure 5: Comparison of predicted and measured campaign-averaged IVOC concentrations at the Pasadena ground site. Measured concentrations are from Zhao et al. (2014). Here, both model predictions and measurements only include primary IVOCs. The predictions of IVOCs also include primary vapors in equilibrium with POA. The data have been normalized by carbon monoxide (CO) concentrations to correct for any differences in mixing.

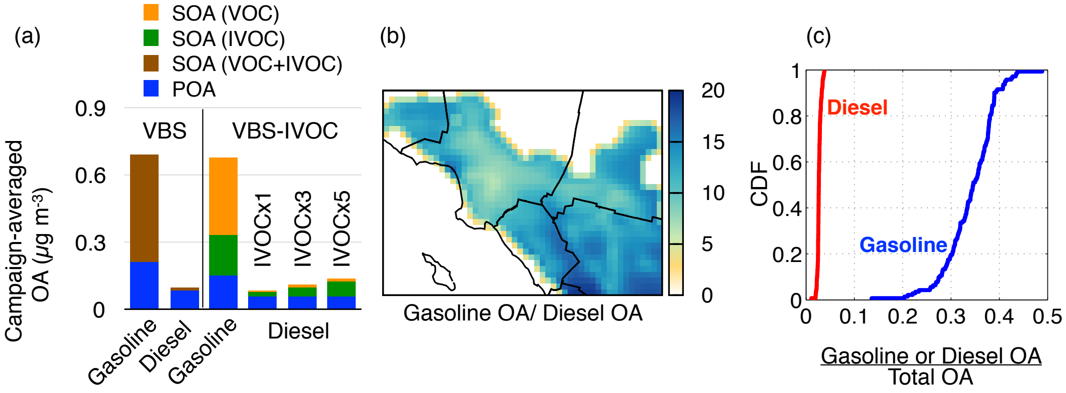

Figure 6: (a) Model predicted campaign-averaged OA concentrations attributable to gasoline and diesel use at the ground site in Pasadena; the IVOCx1 result for diesel use is from the VBS-IVOC simulation, the IVOCx3 and IVOCx5 results are from separate simulations where IVOC emissions from diesel are scaled by a factor of 3 and 5 respectively (b) Ratio of gasoline OA to diesel OA over southern California and (c) cumulative distribution functions that show the contribution of gasoline and diesel OA to total OA in southern California.