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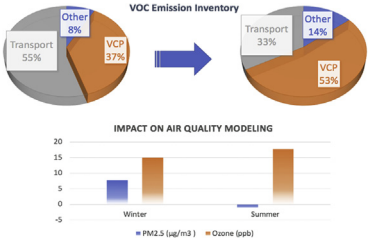
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An uncertainty for clean air: Air quality modeling implications of underestimating VOC emissions in urban inventories

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GRAPHICAL ABSTRACT



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ABSTRACT

Recent literature has shown that volatile organic compound (VOC) emission inventories for urban regions may be substantially underestimated. In particular, non-transportation sources including volatile chemical products (VCP) are increasing in relative importance due to both the current and historical focus on controlling transportation emissions. These findings have major implications for photo-chemical air quality modeling used to determine appropriate and effective regulatory controls to meet limits for primary and secondary pollutants. Using a regional air quality model, we quantify the changes in ozone and fine particulate matter ($PM_{2.5}$) simulated for updated VOC emissions reported in the recent literature relative to a baseline inventory for California. Results show that simulated maximum 8-hr ozone concentrations could increase by 17.4 ppb in summer and by 15.6 ppb in winter, and the 24-hr maximum $PM_{2.5}$ could increase by 7.8 μg/m^3 in winter. Impacts reflect differences in the spatial location of VCP source emissions relative to those for transportation. However, compared to measurement data, model performance is not substantially improved by the adjustment of VOC emissions of current sources. In brief, augmented VOC emission inventories impact simulated concentrations of pollutants, but may not improve the performance of models used for the design of emission control policy without more refined representation of missing VCPs sources in the inventory.

1. Introduction

Volatile organic compounds (VOC) are associated with atmospheric processes including the abundance and distribution of trace gases and secondary organic aerosols (SOA) which directly impact regional air quality burdens (Seinfeld and Pandis, 2016). In a recent study, McDonald and colleagues concluded that (1) VOC emissions from the use of volatile chemical products (VCP) in urban regions are increasing in relative contribution to overall emission budgets, and (2) current emission inventories for urban regions in California substantially

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underestimate VCP, and VOC emissions overall (McDonald et al., 2018). Such underestimation can be attributed to various factors including a lack of atmospheric measurement studies of oxygenated VOCs common in household products. Additionally, available ambient VOC measurement studies typically focus on compounds present in fossil fuels, while excluding many species found in chemical products.

The findings by McDonald et al. could have important implications for the design of control strategies to reduce urban air pollution. Emission inventories compiled by various entities, including the federal and state agencies responsible for ensuring compliance with the National Ambient Air Quality Standards (NAAQS), are a crucial input to air quality models. For regulatory planning purposes, photochemical models are used to predict compliance with NAAQS in future years by quantifying atmospheric concentrations in response to prescribed reductions in precursor emissions accounting for atmospheric chemistry and transport (Foley et al., 2015; Simon et al., 2013). In California, this approach has increased importance given the challenges in ensuring compliance with NAAQS for both ozone and fine particulate matter ($PM_{2.5}$), which requires comprehensive planning and execution of emission control regulation (CARB, 2018). Accurate modeling as a guidance tool for policy development is necessary to ensure clean air in the future. Therefore, further study of the impacts of VOC underestimation within urban inventories on air quality model performance is warranted. Although, other emission uncertainties such as biogenic NO_x/VOCs emissions would also have notable impact on model performance (Almaraz et al., 2018; Sartelet et al., 2012).

The role of VOC in atmospheric chemical reactions yielding increases in concentrations of ground-level ozone and aerosols is well-known. Along with nitrogen oxides (NO_x) and sunlight, VOC provide the third reactant necessary for photochemical smog formation in urban regions characterized by high concentrations of ozone, peroxyacetyl nitrate, and other species harmful to human health (Finlayson-Pitts, 1997). Additionally, VOC serve as precursors to the formation of SOA which comprise an important fraction of $PM_{2.5}$ in urban regions (Volkamer et al., 2006). VOC initiated $PM_{2.5}$ form via gas-to-particle conversion processes including nucleation, condensation and heterogeneous and multiphase chemical reactions.

Control strategies for ozone have focused on reducing NO_x and VOC emissions (Bachmann, 2007). Similarly, the control of VOC emissions has been considered a mechanism to reduce PM concentrations in some regions of California (Nguyen and Dabdub, 2002). However, the non-linear complexity of the formation pathways for ozone and $PM_{2.5}$ makes it impossible to estimate in a quick calculation the responses to precursor emission reductions (Atkinson, 2000). Furthermore, the relationship between ozone and emissions of VOC and NO_x is of particular importance to control strategy development (National Research Council, 1991; Farrell et al., 1999). Some regions in the United States (US) experience NO_x-limited conditions, while others are VOC-limited with implications for ozone formation (Sillman et al., 1997). Based on previous observation and modeling studies, metropolitan regions in California largely experience VOC-limited conditions (Kleinman et al., 2005; Murphy et al., 2007; Pollack et al., 2012), especially in the South Coast Air Basin (SoCAB) encompassing the greater Los Angeles area. However, rural regions including the San Joaquin Valley (SJV) are more likely to experience NO_x-limited conditions in the summer (Buysse et al., 2018; Pusede and Cohen, 2012). If, as McDonald et al. suggest, VOC emissions exceed current estimates that serve as the basis for regulatory planning purposes, regional ozone and $PM_{2.5}$ burdens in California may not decline as expected even if emission reduction targets are met. This is particularly important for the SoCAB since it experiences the poorest ozone air quality in the U.S. The SoCAB is a complex air basin comprised of a large variety of anthropogenic and biogenic sources of NO_x and VOC (Chinkin et al., 2003; Fujita et al., 1992; Taha, 1996). Additional regions of California that would benefit from a greater understanding of this phenomena include the SJV, Greater Sacramento and the San Francisco Bay Area as these areas experiences episodes of degraded air quality and contain large populations. Therefore, further information on the dynamics between precursor species relating to regional pollutant burdens is needed, given the new insight on VOC emissions.

This work uses a photochemical air quality model to quantify the impact of VOC emission inventory underestimations reported by McDonald et al. on ozone and $PM_{2.5}$ concentrations in California. Relative to a baseline emissions inventory, scenarios are developed for enhanced emissions from both VCP and other source categories, and resolved for both a summer and winter episode to capture seasonal effects from meteorology, emission source signatures, etc. We then compare model performance between the baseline and adjusted VOC inventories to measurement data to quantify the impact of VOC emission augmentation. Namely, this work provides insight into the potential implications of VOC inventory underestimation from an air quality modeling perspective. From the results of the assessment conclusions can be drawn which help support the development of effective control regulations in California. Furthermore, insights can be gained regarding VCP relative to transportation VOC, including which regions of California may benefit most from targeted VCP reductions.

2. Materials and methods

2.1. Baseline and adjusted VOC emissions inventory

McDonald et al. (2018) report a consistent underestimation of petrochemical VOC emissions within current emission inventories in the US. For the SoCAB, VOC emissions are underestimated by a factor of 1.5–2 in current inventory, in particular, VOC emissions from VCP sources are underestimated by a factor of 3. McDonald et al. define VCP as including pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products that release VOC emissions because of presence of organic solvents. While a central finding in McDonald et al. is the relative importance of VCP related VOC emissions, the authors also note an underestimation of VOC emissions by a factor of 2–3 from upstream sources including petroleum fuel production. This phenomenon has been noted consistently in the literature including emissions from large industrial facilities (Li et al., 2017) and petroleum refineries (Cuclis, 2012; Hoyt and Raun, 2015; Ryerson, 2003). Therefore, the main objective of this work is to perturb both VCP, and other VOC source emissions including vehicles and fuel production activities to determine the impacts of underestimation of VOC emissions both from VCP alone, and from all major sources.

The comparison between the California Air Resources Board (CARB) 2010 inventory and McDonald's results (based on measurement for 2010) is shown in Fig. 1. In the CARB 2010 inventory, over half of VOC emissions come from transportation, while emissions from consumer VCP comprise less than 25% of the total. However, the distribution of emissions between sources differs substantially for the McDonald et al. results, with VCP contributing more total emissions than the transport sector. Thus, for the cases here emissions will be adjusted both in total, and proportionally among sources to be representative of the estimates of McDonald et al. The underestimation of VCP is implied in MacDonald et al. to occur due to missing sources in the current inventory. However, the emission differences are accounted here by scaling up existing sources in the current inventory without adding new sources. In this study, four VOC emission scenarios are developed from scaling factors based on the difference between CARB 2010 and the range of estimates by McDonald et al., and applied to a more recent inventory (i.e., CARB, 2012) to generate updated VOC emissions:

- Low Case: VOC emissions of VCP, upstream emissions and transportation are scaled to the 300 Gg estimation
- Medium Case: VOC emissions of VCP, upstream emissions and transportation are scaled to the 350 Gg estimation
- High Case: VOC emissions of VCP, upstream emissions and

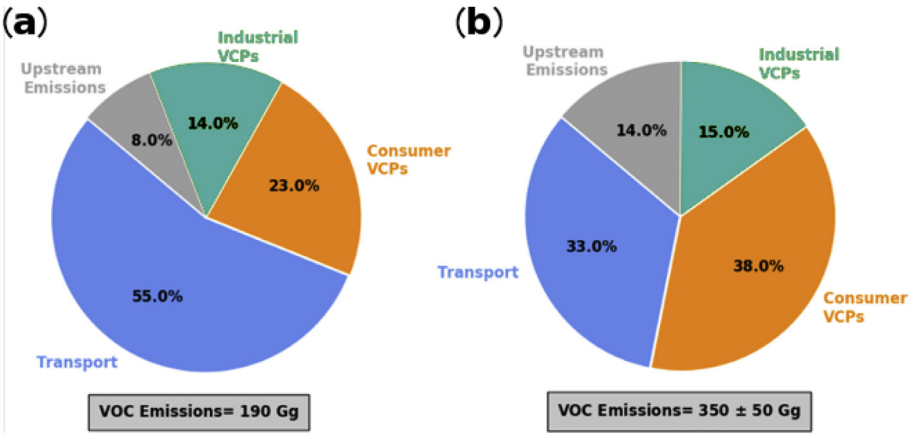


Fig. 1. Contributors to VOC emissions in SOCAB region. Distribution of (a) petrochemical VOC emissions based on the CARB 2010 inventory, (b) petrochemical VOC emissions based on the results of McDonald et al. (2018) (2010 inventory). The annual total emissions are shown on the gray box under each figure, values are obtained from Fig. S2 on the supplementary materials for McDonald et al. (2018).

transportation are scaled to the 400 Gg estimation

- VCP Case: Only the VOC emissions of VCP are scaled based on the 350 Gg estimation

Table 1 shows petrochemical VOC emissions by source category for each Case, as well as the scaling factors used to adjust the baseline emissions for each sector. First, a comparison of the total emissions relative to the baseline inventory (190 Gg) for the Low (300 Gg), Medium (350 Gg), and High (400 Gg) Cases is used to quantify the increase in magnitude. Emissions for each petrochemical source category are then determined based on the relative distributions shown in Fig. 1(b). The scaling factors for each Case are determined based on the ratio between the adjusted VOC emissions of each sector and the Base Case. For the VCP Only Case, only the VOC emissions from consumer and industrial VCP are adjusted. Using this method, VOC emissions from VCP are determined to be underestimated by a factor of 2–3 in the 2012 CARB inventory, which is consistent with the results of McDonald et al.

Scaling factors from Table 1 are applied to the CARB 2012 inventory through the Sparse Matrix Operator Kernel Emission (SMOKE, version 4.0) model (U.S. EPA, 2017) to generate anthropogenic emission fields with updated VOC emissions representative of each Case. One should note that only VOC emissions are adjusted in this study. All other emissions remain at baseline levels, including NO_x. Furthermore, additional VOC emissions are applied to existing sources without changing temporal and spatial patterns and VOC speciation. Moreover, as a preliminary study, potential seasonal difference due to product use and temperature-dependent volatilizations are not considered in the scaling factor calculation. Speciation is based on the SAPRC-07 chemical mechanism (Carter, 2010), and the original speciation profiles from CARB 2012 inventory are used for VCP sources without modification. Next, the files are merged with biogenic emissions obtained from the Model of Emissions of Gases and Aerosols from Nature (MEGAN, version 2.1) (Guenther et al., 2006). Fig. 2 shows emissions of VOC in the Base Case (Fig. 2(a) and (c)), and the difference between the Base Case and High Case (Fig. 2 (b) and (d)). As would be expected given the spatial signature of VCP, important differences are evident in highly populated urban regions including Los Angeles, the San Francisco Bay region (S.F. Bay), and greater Sacramento. In these areas, peak differences could reach 11.68 mol/s per grid (4×4 km^2) in winter and 11.75 mol/s in summer. In general, increases are similar for both winter and summer, except for some coastal areas indicated by blue (Fig. 2 (b)) and black circles (Fig. 2 (d)). Both the increase of VOC emissions within the black circles and the decrease within the blue circle during the summer episode are related to the use of non-methyl bromide pesticides. In Santa Barbara (blue circle), the usage of such pesticides is 3.5 times higher in January than July, while in Ventura County (small black circle) such usage is 19 times higher in July than January, and 15 times higher in the Monterey Bay region (large black circle) (CDPR, 2014).

2.2. Air quality modeling

A chemical transport model is necessary to characterize how changes in VOC emissions impact concentrations of primary and secondary pollutant concentrations, including ozone and $PM_{2.5}$. The Community Multi-scale Air Quality model (CMAQ) version 5.2 is used (US EPA Office of Research and Development, 2017). CMAQ is a state-of-the-art, widely accepted model that is used, for NAAQS attainment demonstration (Carreras-Sospedra et al., 2016) and a wide range of research areas involving atmospheric chemistry and processes (Mac Kinnon et al., 2016; Zhu et al., 2018). The SAPRC-07 chemical mechanism (Carter, 2010) is used for gas phase chemistry and the AERO6 module (Appel et al., 2013) is used for aerosol dynamics with the latest SOA module (Murphy et al., 2017). The modeling domain used is the same as that for Benosa et al. (2018), that covers all of California at a 4 km × 4 km resolution horizontal grid. Simulation data for two

Table 1
Total VOC emissions and scaling factors of petrochemical sources applied to the 2012 CARB Inventory for each scenario.

Cases	Petrochemical Total (Gg/Year)	Consumer VCP (Gg/Year)	Industrial VCP (Gg/Year)	Upstream (Gg/Year)	Transportation (Gg/Year)
Base Case	190	43.7	26.6	15.2	104.5
Low Case	300	114	45	42	99
Medium Case	350	133	53	49	116
High Case	400	152	60	56	132
VCP Case	306	133	53	15.2	104.5
	Scaling factor	**Scaling factor**	**Scaling factor**	**Scaling factor**	**Scaling factor**
Low Case	1.58	2.61	1.69	2.76	0.95
Medium Case	1.84	3.04	1.99	3.22	1.10
High Case	2.11	3.48	2.26	3.68	1.26
VCP Case	1.61	3.04	1.99	1.00	1.00

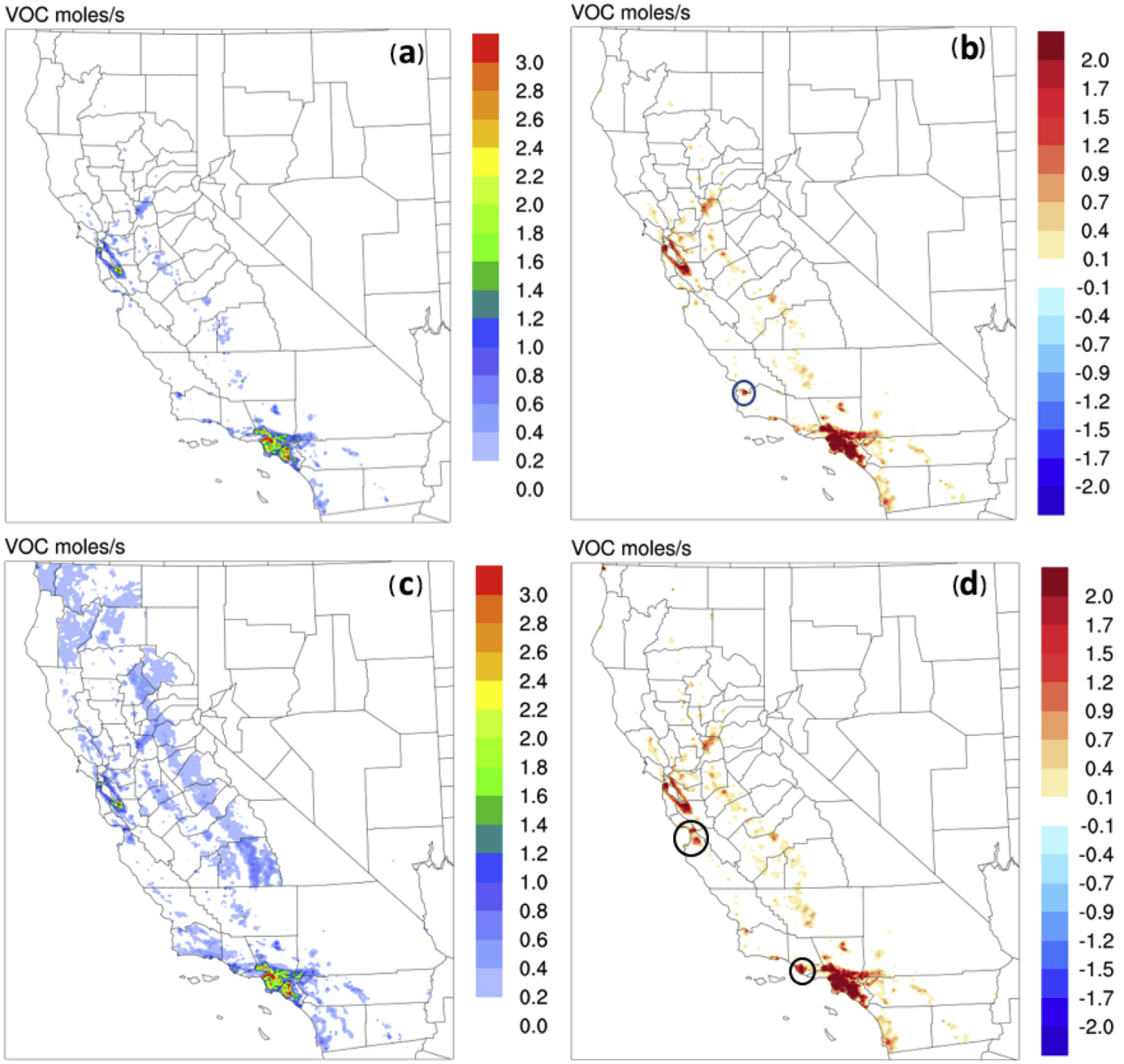


Fig. 2. Weekly averaged VOC emission rate in the Base Case for winter (a) and summer (c). Difference of VOC emission rate between the High and Base Case for winter (b) and summer (d). Areas within circles demonstrate the impact of seasonal pesticide applications which represent the only substantial seasonal difference in emission rates.

subdomains SoCAB and SJV (same resolution), as shown on Fig. S1, are selected for a more detailed analysis as they contain the most severe "designated nonattainment area" for ozone and $PM_{2.5}$ (U.S. EPA, 2018). Initial and boundary conditions are generated from the Model for Ozone and Related Chemical Tracers (Mozart v4.0) (Emmons et al., 2010). Meteorological inputs are downscaled from (Final) Operational Global Analysis data (NECP, 2000) using the Advanced Research Weather Research and Forecasting Model (WRF-ARW, version 3.7), with the MODIS land use database (Friedl et al., 2010) and the YSU parametrization (Hong et al., 2006) for the planetary boundary layer. Simulations are conducted for both a summer (Jul. 8th – Jul. 22nd) and winter episode (Jan. 1st – Jan. 15th) for each emission scenario, with the first 4 days ignored as model spin up.

As the enhancement of VCPs emissions could have notable impact on SOA formation, it is important to consider the implications of the current SOA module (Murphy et al., 2017) used in CMAQ. Specifically, a species called Potential Combustion-origin Secondary Organic Aerosols (PCSOA) species is used within the SOA module to represent the potential missing mechanisms of SOA formation from anthropogenic combustion sources (Murphy et al., 2017). As the nature of this study is to compensate missing sources of SOA precursors, the inclusion of this PCSOA species might lead to a double-counting of those sources. Thus, the predicted PCSOA from the simulation (see Fig. S3) was excluded from SOA and $PM_{2.5}$ analyses in this study.

3. Results and discussion

Utilizing the described modeling methods, impacts on ground-level

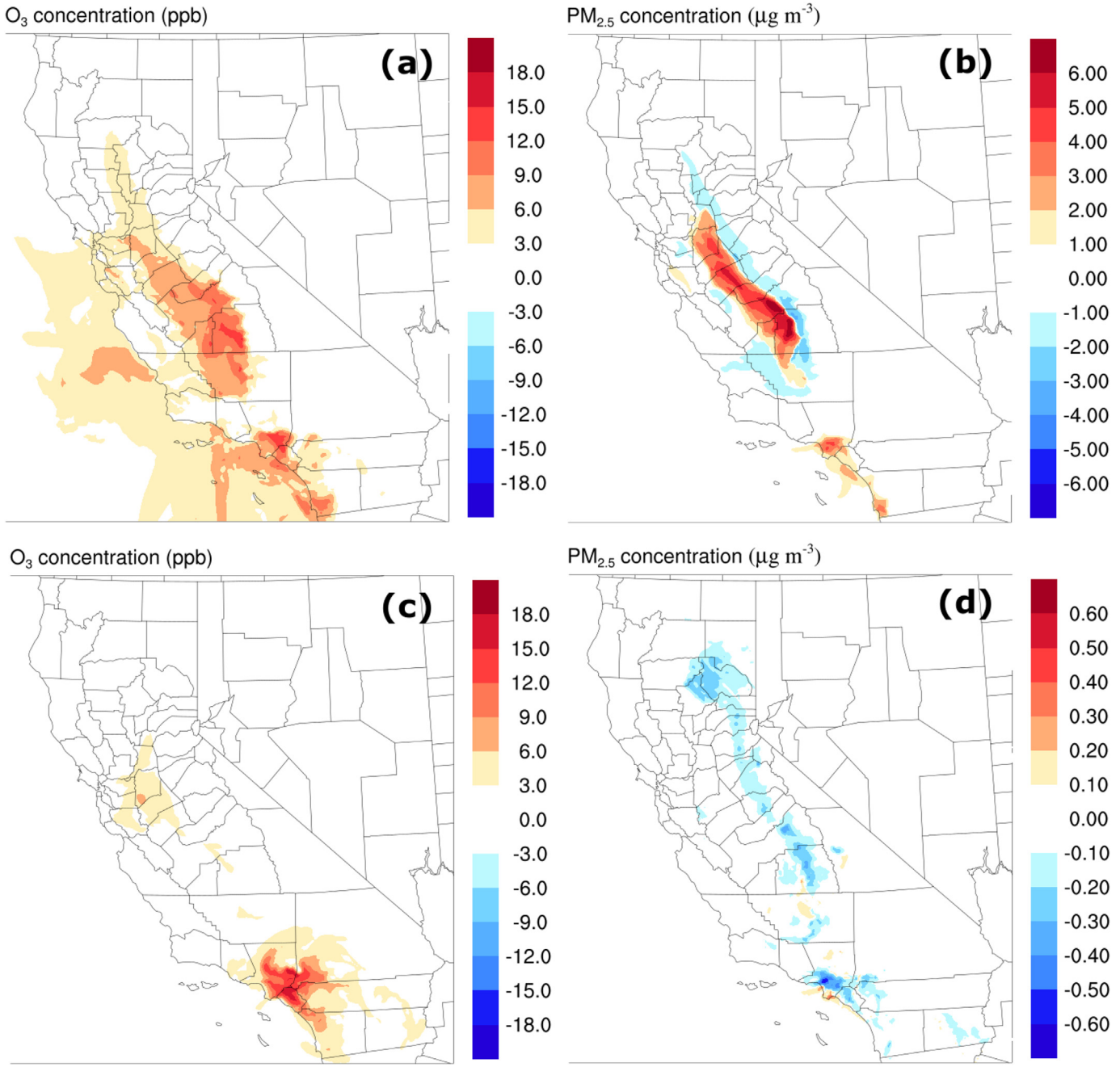


Fig. 3. Peak 8 h daily maximum ozone concentration differences between the High and Base Case for (a) winter period, and (c) summer period. Peak 24 h daily maximum $PM_{2.5}$ concentration differences between the High and Base Case for (b) winter period, and (d) summer period.

ozone and $PM_{2.5}$ as a result of augmented VOC emission inventories are analyzed for all Cases. Each Case is compared to the Base Case to characterize and quantify differences in pollutant concentrations. Both the average and maximum differences are analyses to quantify the general and maximum deviation of the impacts. The absolute difference of individual cells is considered for the peak difference calculations, where the maximum negative difference stands for the largest difference. Section 3.1 presents differences in regional concentrations of ozone. Section 3.2 discusses results associated with changes in averaged $PM_{2.5}$ concentrations. Section 3.3 analyzes model performance by comparing simulated concentrations with observation data for the Base case and augmented Cases.

3.1. Ozone impacts

The introduction of additional VCP emissions leads to a substantial increase in peak ozone concentrations, especially for the High Case as shown on Fig. 3. While the peak impact is higher in summer (17.4 ppb) than winter (15.6 ppb), a more wide-spread impact is observed during the winter (Fig. 3 (a)) relative to summer (Fig. 3 (b)).

In winter, increases in VOC concentrations (Fig. 4 (b)) are prominent over the SoCAB, the SJV extending to Greater Sacramento, and the S.F. Bay Area. Such increases correspond well with VOC emissions increases shown in Fig. 2 (b). In tandem, increases in ozone (Fig. 4 (a)) and decreases in NO_x (Fig. 4 (c)) occur in those regions, indicating the presence of a modeled VOC-limited environments. Averaged ozone increases exceed 6 ppb in the afternoon hours over Visalia, Fresno and Bakersfield County, with peak delta maximum 8-h ozone exceeding

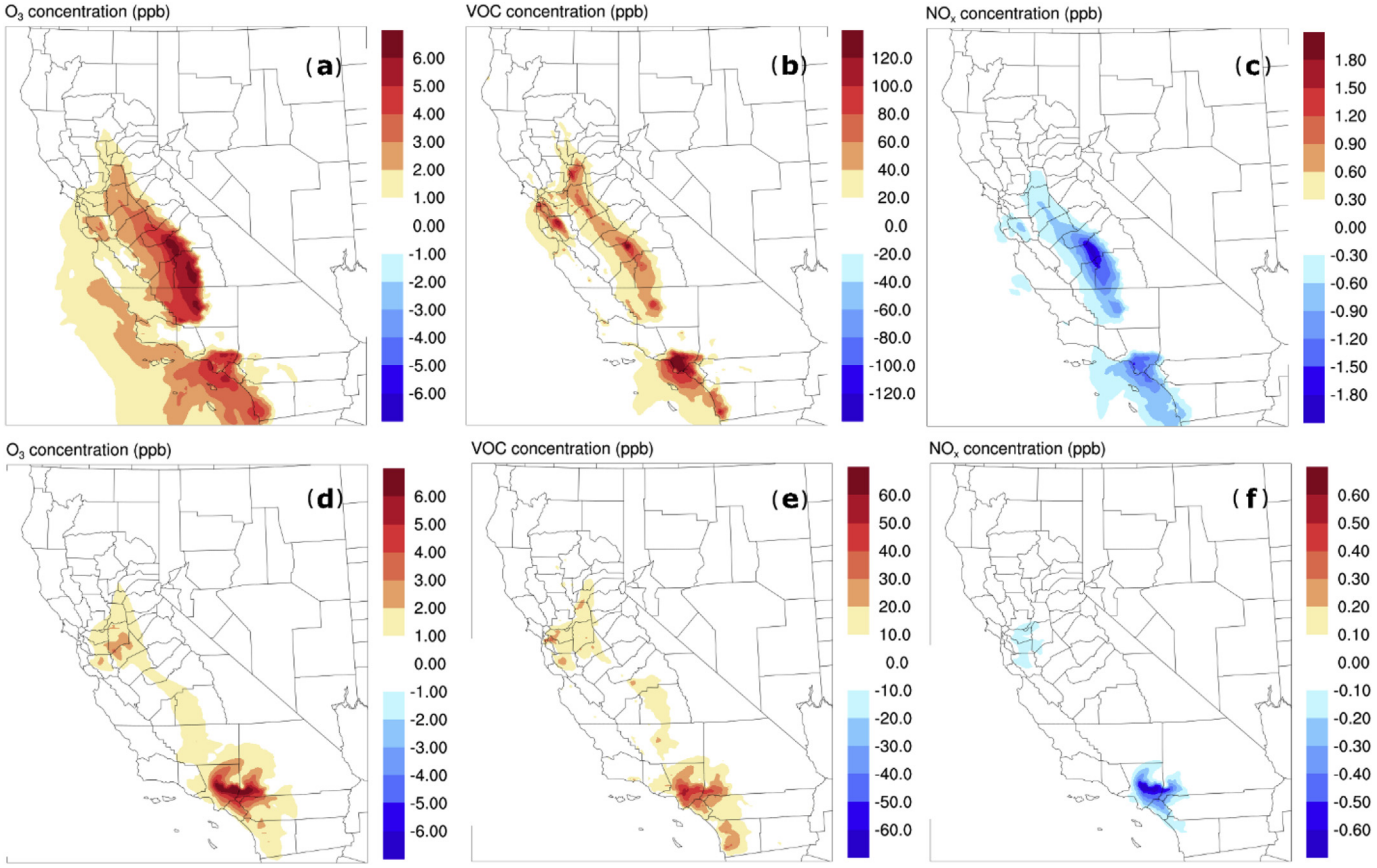


Fig. 4. Averaged concentration differences of afternoon hours (12PM-8PM) between the High and Base case for winter ozone (a), VOC (b), NO_x (c) and summer ozone (d), VOC (e), NO_x (f).

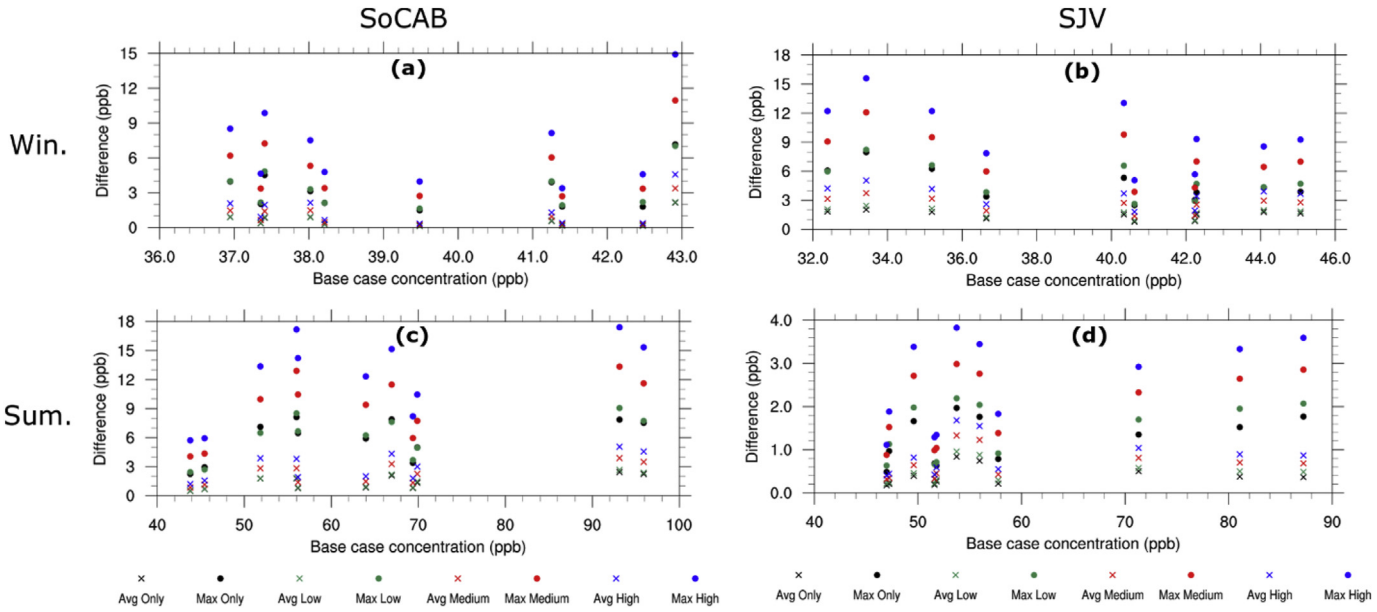


Fig. 5. Relations between daily average Ozone concentration of the base case and average (cross)/peak (dot) differences of each VCPs scenarios for two subdomain (SoCAB winter (a) and summer (c), SJV winter (b) and summer (d)).

15 ppb in Tulare and in the SoCAB (Fig. 3 (a)). Due to low biogenic VOC emissions in the winter, most of the SoCAB and SJV experiences a VOC limited atmospheric chemical condition, that is further supported by the increase of HNO_3 and increase of PANs (Figure S4 (a) and (b)). Under high NO_x conditions, the increase of VOC concentration promotes the conversion of NO to NO_2 with the help of hydroxyl radical ($^{\bullet}OH$). Then, NO_2 molecules could produce more ozone through photolysis ($NO_2 \overset{h\upsilon}{\rightarrow} NO + O$, and $O + O_2 + M \rightarrow O_3 + M$). The increase of VOC also promotes the formation of HNO_3 (Figure S4 (a)) and causes a decrease in total NO_x. It should be noted that the above analysis is based on the comparison between the High Case and Base Case, which

is representative in this study, as other Cases shows similar geographic distribution of impacts at lesser scales.

Relative to winter, areas of increased VOC concentrations in summer are generally reduced. Increases are observed in the SoCAB (Fig. 4 (e)), where VOC-limited condition persist throughout the year as indicated by observation data (Pollack et al., 2012). Similarly, decreases in NO_x concentration are also lesser than winter with the peak decrease over the SoCAB (Fig. 4 (b)). Correspondingly, substantial increases in ozone are limited to the SoCAB, which exceed 7 ppb in average for afternoon hours (Fig. 4 (d)) and almost 18 ppb peak difference in maximum 8-h average for the High Case. In contrast to winter, increases in the SJV are minimal as additional emissions are minor compared to enhanced biogenic VOC emissions in summer from increases in ambient temperatures and more intense periods of sunlight (Figure S2 (b)). Enhanced biogenic emissions alter the atmospheric chemical conditions to NO_x-limited for ozone formation and, as a result, increases in VOC emissions no longer yield large increases in ozone. NO_x-limited conditions in the summer period is consistent with observation data in the SJV (Buysse et al., 2018; Pusede and Cohen, 2012). Thus, the only major area in the study domain that maintains modeled VOC-limited conditions in summer is the SoCAB, which correspondingly experiences peak increases in ozone.

Fig. 5(a) and (b) present the impact of additional VOC emissions on spatially averaged daily maximum 8-hr averaged ozone concentrations over the two subdomains for the winter as a function of base case daily average concentrations. In general, simulated ozone concentrations increase in all Cases proportional to VOC emissions, and the days with larger average differences generally have larger peak difference as well. For the SoCAB, the largest difference happens on the day with highest average concentrations (Jan. 7th), where the peak ozone difference increases from 7 to 15 ppb for the Low and High Cases, respectively (2–4.5 ppb for average difference). For the SJV, ozone increases of a similar magnitude are found in Jan. 5th, where the average concentration is relatively low. For both subdomains, the averaged maximum 8-h concentrations do not exceed the Federal standard of 70 ppb for the winter period. Fig. 4(c) and (d) show the difference in maximum 8-h ozone for those two subdomains in the summer. First, the maximum 8-h concentrations are much higher compared to the winter period. For the SoCAB, one third of the simulation period exceeds the Federal standard. The SJV experiences less total ozone, but it presents three days when spatially averaged concentrations exceed 70 ppb. The addition of VOC emissions results in much higher impacts on maximum 8-h ozone for the SoCAB than the SJV, with the highest increased 17.5 ppb in the SoCAB compared to 3.9 ppb for the SJV. The results correspond well with the difference observed in Fig. 4 (d), and are due to the different nature of chemical regime for ozone formation (NO_x-limited in SJV and VOC-limited in SoCAB) as discussed in the previous paragraph.

In general, the impacts on ozone are more widespread in winter. However, enhanced VOC emissions result in a greater ozone impact in summer for metropolitan areas. As a result, when considering with population density, the implications for health impact assessments caused by the underestimation of VOC emissions is worth noting. Additionally, as maximum 8-h ozone concentration are much higher in the summer, increases make it more difficult to comply with the Federal and State air quality standards.

3.2. Impact on $PM_{2.5}$

Fig. 3 presents the peak impacts of adjusted VOC emissions on simulated 24 h averaged daily maximum $PM_{2.5}$ concentrations in winter (Fig. 3 (b)) and summer (Fig. 3 (d)), and Fig. 6 presents the time averaged concentration differences for winter (Fig. 6 (a)) and summer (Fig. 6 (d)) with results further separated into SOA (b) (e) and ammonia nitrate (c) (f). In general, the peak $PM_{2.5}$ concentrations change most substantially over the SJV (Fig. 3 (b)) ($+7.5\ \mu g/m^3$) in the winter and over the SoCAB (Fig. 3 (d)) ($-0.6\ \mu g/m^3$) in the summer. As with ozone, in average, simulated $PM_{2.5}$ increases substantially over the SJV and the SoCAB in winter (Fig. 6 (a)). When considering SOA (Fig. 6 (b)) and ammonium nitrate (Fig. 6 (c)), most of the difference results from changes in concentrations of ammonium nitrate ($\sim$83% for the SoCAB area and $\sim$88% for the Central Valley) and is consistent with the decreases in NO_x discussed previously. The remainder of enhanced $PM_{2.5}$ occurs from increased SOA formation due to increases in precursor species in tandem with an adequate supply of OH radicals as an oxidizer. As a result, SOA is enhanced over the SJV and SoCAB. Of interest, $PM_{2.5}$ concentrations decrease in regions surrounding the SJV, which is opposite to what happens within the SJV. Further investigation (see Fig. S8) shows a correlation between the change in OH concentration with the change in ammonium nitrate, i.e., OH concentrations decrease in tandem with ammonium nitrate. Those regions are highly vegetated and are likely to experience NO_x limited conditions (Buysse et al., 2018), where OH is limited by NO concentration. As more OH is consumed by the increasing VOC, less available OH for nitrate formation from NO_2 (Seinfeld and Pandis, 2016).

In summer, much smaller impact on $PM_{2.5}$ concentrations are simulated in all areas of the SJV and in the SoCAB relative to the baseline for both peak (Fig. 3 (d)) and average concentrations (Fig. 6 (d)). Overall, impacts are opposite in direction and lower in magnitude than for winter. Considering SOA (Fig. 6 (e)) and ammonium nitrate (Fig. 6 (f)), it is found that the reduction in ammonium nitrate contributes the majority of $PM_{2.5}$ reduction, while SOA concentration increase. Although in the opposite direction, most of the changes in ammonium nitrate and SOA happen throughout SoCAB. As the biogenic VOC is largely increased in the summer (see Fig. 2), most of the state is likely to experience a NO_x-limited condition. As a result, ammonium nitrate decreases when limited OH is consumed by VOC oxidation processes resulting in less available OH for nitrate formation from NO_2 (Seinfeld and Pandis, 2016). The SOA formation is increased as more VOC are oxidized after the VCPs emissions is enhanced, the same as for the winter period.

Fig. 7 presents the impact of additional VOC emissions on 24-h averaged $PM_{2.5}$ concentrations over the two subdomains (SoCAB and the SJV) as a function of base case daily average concentration. In general, the peak difference deviates more than the average difference for impacts on ozone concentrations (see Fig. 6), and the impact could occur in opposite directions as the level of VCPs emission enhancement varies, even within the same day. Furthermore, the magnitude of peak differences appears less related to the level of average differences, as days with small average differences may have large peak difference, particularly in the summer (Fig. 7(c) and (d)). For the winter period, consistent with Fig. 6 (a), increasing VOC results in an overall increase in $PM_{2.5}$ concentrations. For the SoCAB, $PM_{2.5}$ increases are proportional to the increase in VOC emissions, with the peak delta on Jan. 7th ranging from 1.8 to 4.5 $\mu g/m^3$. For the SJV region, peak differences occurred in Jan. 5th with higher magnitude (3.5–7.8 $\mu g/m^3$) than SoCAB. However, decreases are noted in $PM_{2.5}$ from Jan. 6th to Jan. 9th in the SJV. It is most likely the wind conditions changed during this period and resulted in the transport of VOCs emitted from the surrounding forested regions into the SJV, thus changing the chemical regime from VOC limited to NO_x limited, and causing a decrease in ammonia nitrate concentration (see Fig. S9). Fig. 7(c) and (d) present the impact for the two subdomains for the summer period. The scale of impacts is much lower relative to the winter period, and the increase of VOC emissions leads to an overall decrease in $PM_{2.5}$ concentration, as expected from Fig. 6 (d).

3.3. Impact on model performance

To determine the impact of adjusted VCP emissions on model performance, simulation results are compared with observation data obtained from U.S. Environmental Protection Agency's Air Quality System

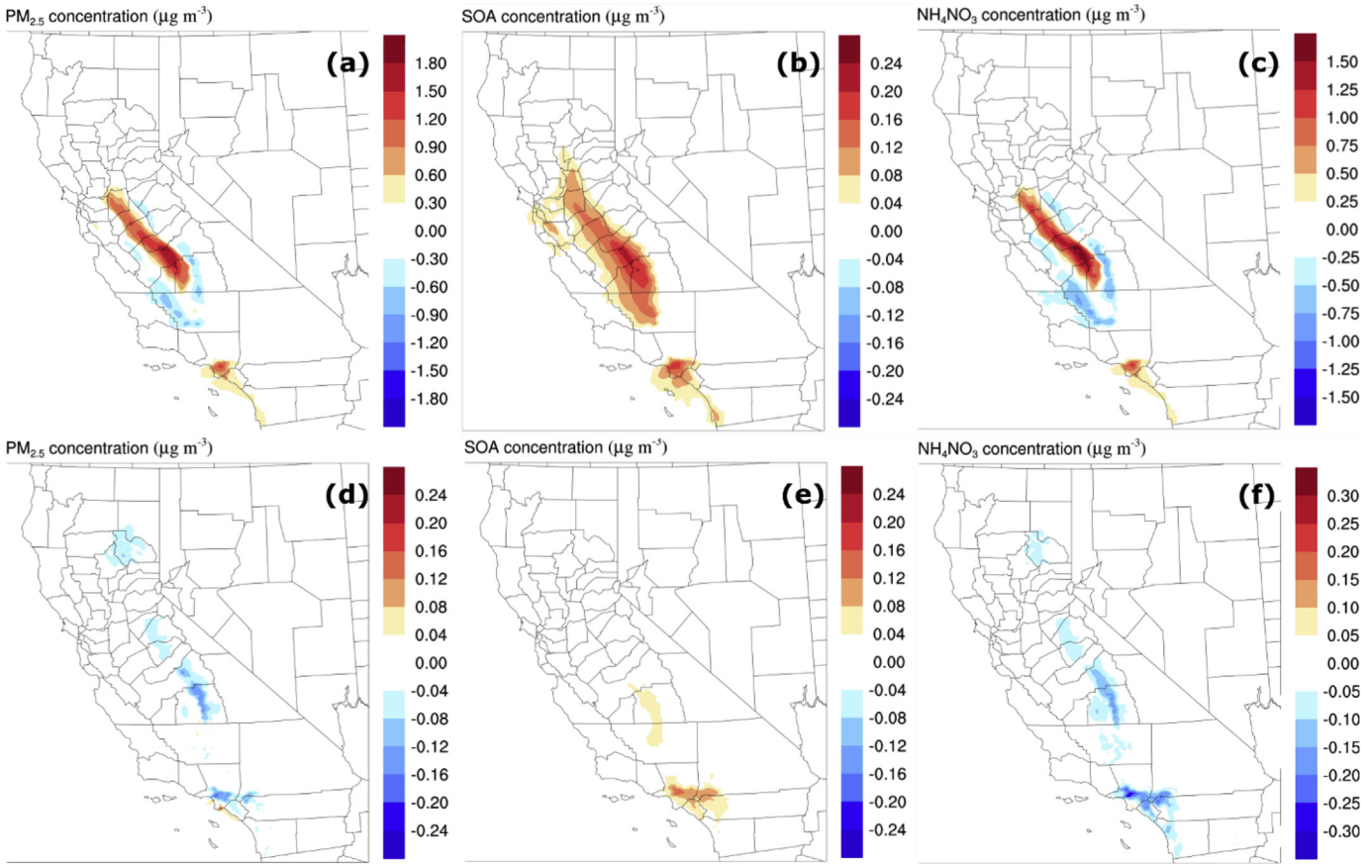


Fig. 6. Time averaged concentration differences between the High and Base case for winter $PM_{2.5}$ (a), SOA (b), Ammonia Nitrate (c) and summer $PM_{2.5}$ (d), SOA (e), Ammonia Nitrate (f).

(AQS). The AQS network (https://www.epa.gov/aqs) provides reliable and verified measurements, with hourly recorded concentrations for $PM_{2.5}$, PM_{10} and ozone, for the entirety of California. The definitions of the statistical parameters used in this study are detailed in the supporting information (SI: Table S1).

Fig. 8 compares ozone (a), (c) and $PM_{2.5}$ (b), (d) between observation data and simulated values for each Case (values averaged across all observation sites). For ozone, in general, model results capture the diurnal patterns as well as peaks and troughs for both simulation periods, with a consistent, moderate over-estimation during the winter period. The overestimation of winter ozone is consistent with previous CMAQ study (Zhu et al., 2018; Figure S2 (a)), where similar

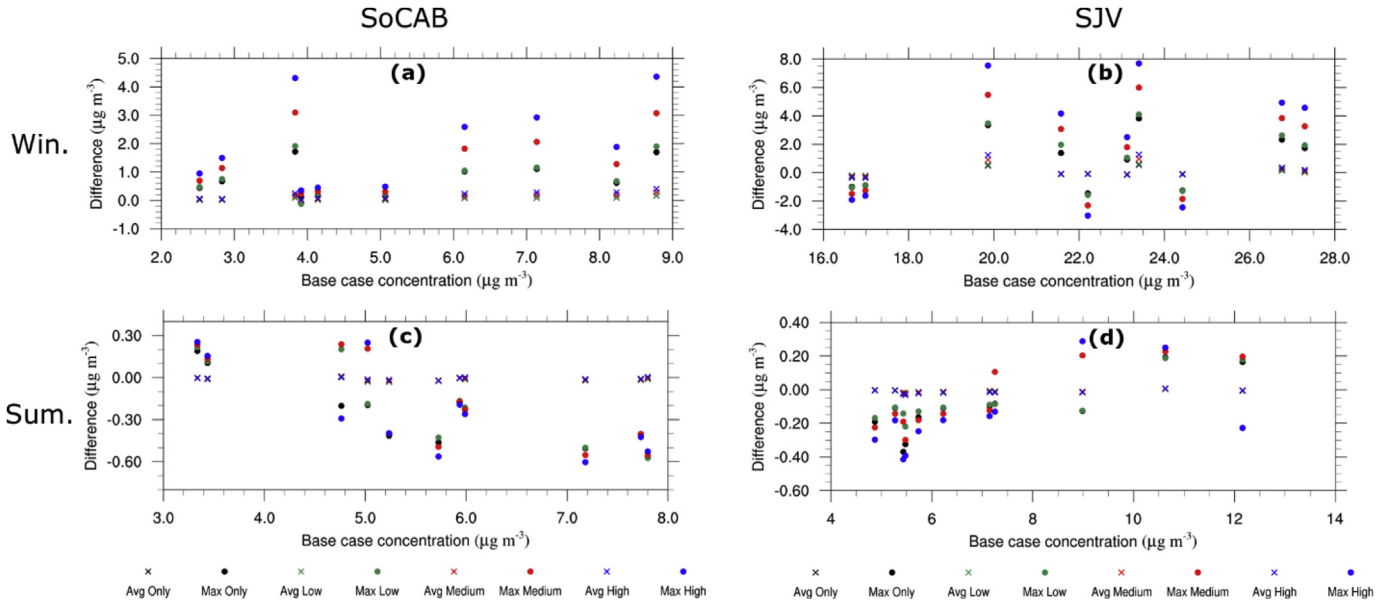


Fig. 7. Relations between daily average $PM_{2.5}$ concentration of the base case and average (cross)/peak (dot) differences of each VCPs scenarios for two subdomain (SoCAB winter (a) and summer (c), SJV winter (b) and summer (d)).

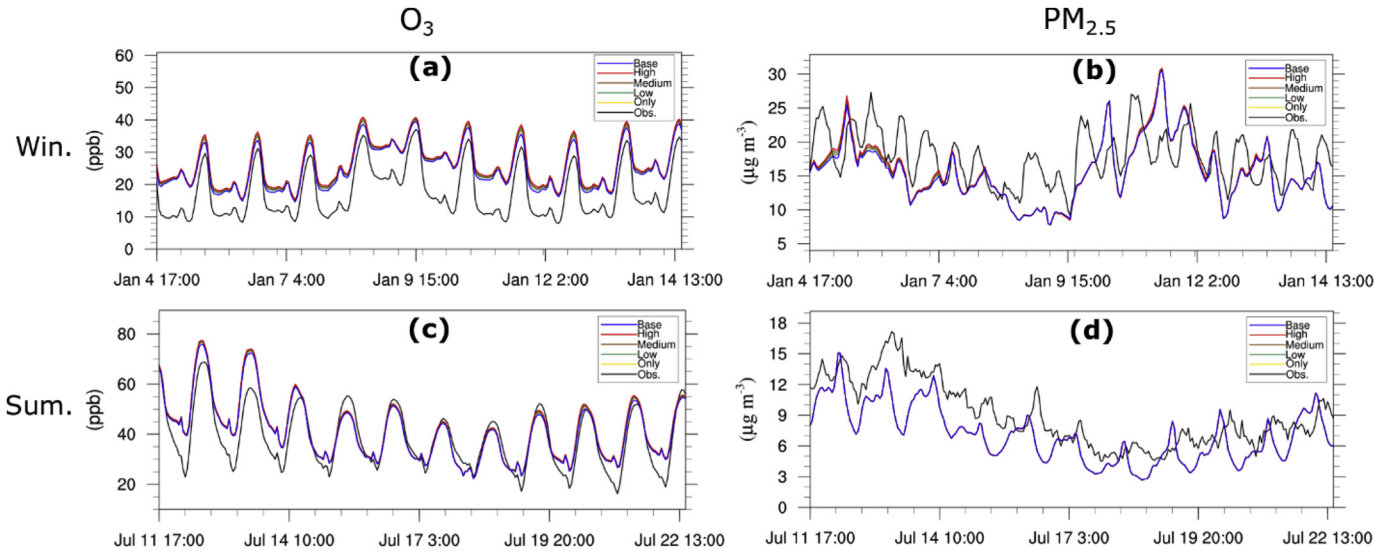


Fig. 8. Time evolution of observation date (averaged over all available sites) and simulation value for each scenario (averaged from corresponding time and location of each observation) for (a): winter ozone, (c): summer ozone, (b): winter $PM_{2.5}$, (d): summer $PM_{2.5}$. (Obs.: ground measurement data; Base: Base case scenario; High: High Case scenario, Medium: Medium Case scenario; Low: Low Case scenario; Only: VCP case scenario; Win.: Winter; Sum.: Summer).

level of overestimation was found throughout California during winter period (The low nighttime ozone mixing ratios of 10 ppb in the winter indicate that ozone is being titrated away by NO_x emissions. To describe this well in the model requires an accurate description of the nighttime boundary layer, which is rather challenging (Haman et al., 2014)). In general, increased VCP slightly increases the simulated ozone concentrations for both winter and summer. However, for individual sites the impacts could be substantial, e.g., the peak difference between the Base and the High Case could reach ~20 ppb in downtown Los Angles as shown on Fig. S6, and most of the impacts occur in the afternoon during peak ozone concentration hours. Consistent with Fig. 3, the overall impact is more pronounced in the winter than in summer. Furthermore, the magnitude of impact increases as more VCP emissions are introduced. Table S2 (a) and (b) presents the model performance statistics for winter and summer period. In general, the overall model performance satisfied the recommended performance criteria with normalized mean bias (NMB) < ±15%, normalized mean error (NME) < 25%) and correlation > 50% (Emery et al., 2017). For both periods, as ozone concentrations are already overestimated, the enhanced VCP emissions leads to higher bias (NMB) and errors (NME), although increases are very slight (≤ 2%).

Similar to ozone, differences in $PM_{2.5}$ are larger for winter than summer, supporting the findings in Fig. 3. The most substantial impact occurs between Jan. 5 and Jan. 7 with the addition of VCP reducing underestimation, with a clear distinction between each Case. Unlike ozone, where enhanced VCP always result in increased concentrations, impacts on $PM_{2.5}$ can either be increasing or decreasing concentrations based on geographical locations as discussed in Section 3.2. For winter, generally slight increases are simulated, although some periods show small decreases (e.g., Jan. 9 -Jan. 10). However, for individual sites the impact could be quite substantial, the peak difference between the Base and the High Case could reach ~20 μg/m^3 as shown on Fig. S7 for one site within the Central Valley. For summer, generally decreases in concentrations are simulated, although with smaller magnitude than those in winter. Table S3 (a) and (b) shows the detailed model performance statistics for $PM_{2.5}$. Model performance meets the recommended performance criteria for both periods and for all scenarios with NMB < ± 30%, MFE < 50% and correlation > 40% (Emery et al., 2017). For the winter period, the performance error (NME) is slightly increased with the enhancement of VCP, while bias (NMB) is reduced along with the improvement of correlation. In general, model performance is improved as the enhancement of VCP emissions reduced the underestimation of $PM_{2.5}$. For the summer, the impact on model performance is very small, a slight deterioration is observed as the enhancement of VCP lower the $PM_{2.5}$ concentration which is already underestimated in the base case.

In addition, model performance impact is investigated for individual observation sites. In winter (Fig. 9 (a)) ozone concentrations are overestimated for most sites. Model performance is degraded in most regions, except for some locations in Kern and San Diego Counties (Fig. 9 (b)). However, model performance of winter ozone is usually not of great concern, as ozone concentrations are generally low in the winter. Model performance for summer ozone is more important as the high ozone pollution episodes happen under the conditions present in summer including higher average temperatures. Here, ozone concentrations are found to be mostly underestimated in Northern California and SJV, while overestimated in Southern California for the summer period (Fig. 9 (e)). As a result, model performance improves in Northern California and SJV as VCP addition increases ozone, reducing underestimation. Conversely, degraded performance is observed in Southern California, particularly in the SoCAB (Fig. 9 (f)). Other emission uncertainties would also have notable impact for the model performance of summer ozone. Model performance might be further improved in Northern California and SJV if the uncertainties of underestimated NO_x emissions from agricultural (Almaraz et al., 2018) are considered. The overestimation of biogenic VOCs of MEGAN in rural regions (Millet et al., 2008) and underestimation in metropolitan regions (Kota et al., 2015) could also impact the VOC or NO_x sensitive chemical regimes, and thus the model performance. Those uncertainties should be considered when evaluating the result of this study and will be investigated in future studies.

For winter $PM_{2.5}$ (Fig. 9 (d)), model performance is found largely improved around the south of SJV (around Fresno and Madera) where largest increase is found (Fig. 3 (b)). However, model performance deteriorates in most of the remaining observation sites. Notably, the overestimation in the north of SJV is increased with the enhancement of VCP emissions. In the summer, $PM_{2.5}$ concentrations are found to be largely underestimated throughout the state for the base case (Fig. 9 (g)), except for a handful of sites along the central coast. Thus, the model performance is further degraded as the adjusted VCP emissions reduced the $PM_{2.5}$ concentration in most of the state.

Overall, discrepancies in VOC emission inventories have important

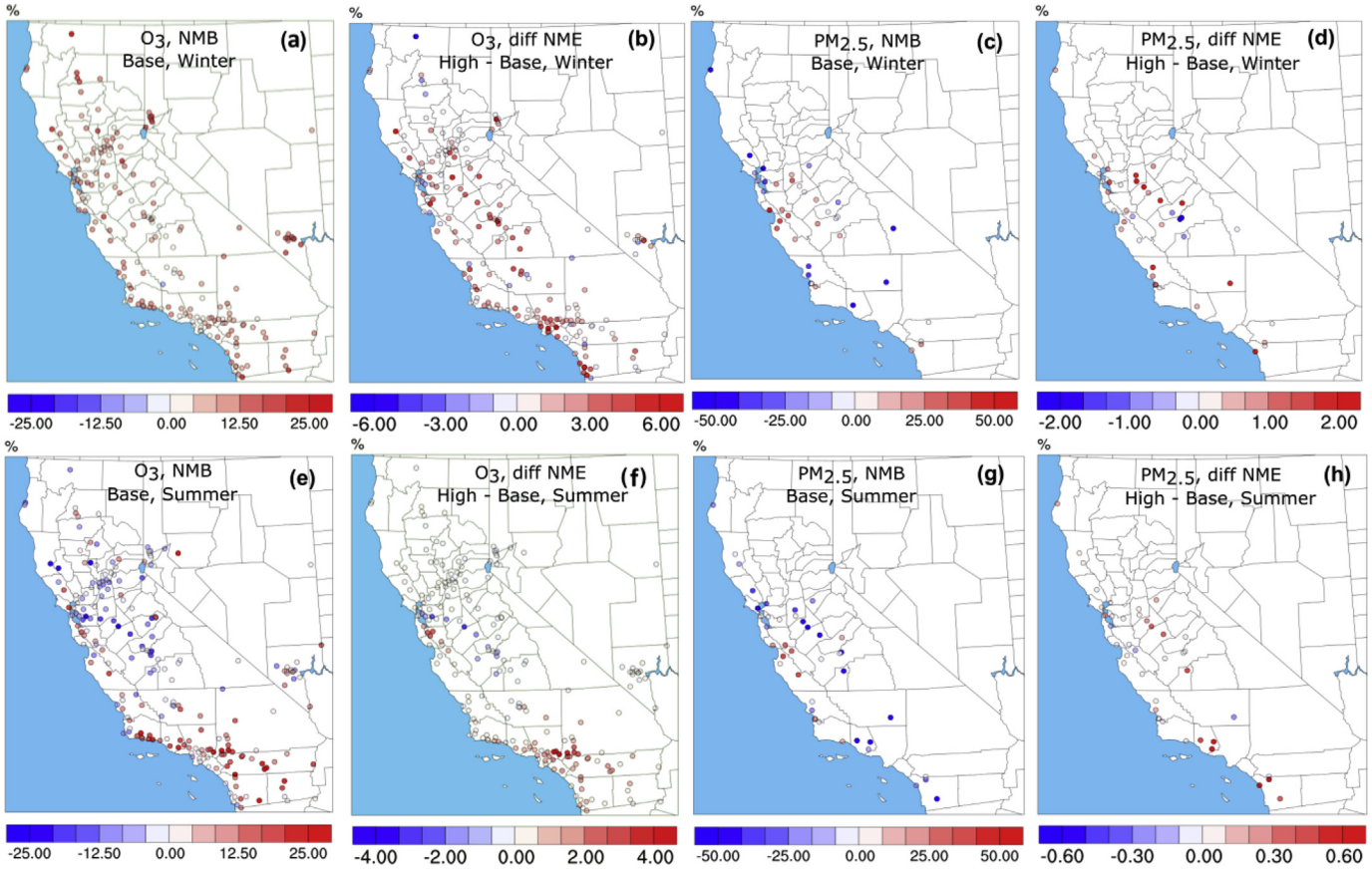


Fig. 9. 1. (a) and (e) are ozone NMB at AQS sites of the Base Case for winter and summer. 2. (c) and (g) are $PM_{2.5}$ NMB at AQS sites of the Base Case for winter and summer. 3. (b) and (f) are difference of ozone NME between the Base Case and the High Case for winter and summer (The difference of NME is indicating whether the High case has larger model errors than the Base case or not, red values indicate deterioration of model performance and blue values indicate an improvement). 4. (d) and (h) are difference of $PM_{2.5}$ NME between the Base Case and the High Case for winter and summer. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

impacts but may not affect the performance of models used for the design of emission control policy.

4. Conclusion

In this work, a baseline VOC emissions inventory based is adjusted based on recent findings reported by McDonald et al. (2018). The study investigates the resulting impacts on air quality simulations using a photochemical model well established on its use for research and regulatory purposes. Four Cases are developed with a range of estimated VOC emissions growth over the baseline from VCP sources, that are underestimated in the baseline inventory according to McDonald et al. Simulations are conducted for California for both a summer and winter period for each Case, and compared to a Base Case assuming the original inventory. In general, predicted ozone concentrations increase in all Cases proportional to VOC emissions. As would be expected, greater impacts on the maximum 8-h average ozone are found for summer (17.4 ppb) than for winter (15.6 ppb), with importance for regulatory modeling as summer ozone levels frequently exceed the NAAQS standards in California. Impacts on $PM_{2.5}$ are more variable relative to ozone. In winter, the most substantial increase in $PM_{2.5}$ (7.5 $\mu g/m^3$) occurs in the SJV, which is associated with the highest baseline concentrations. Concentrations also increase in the SoCAB, although with a lower magnitude (4.5 $\mu g/m^3$), while decreasing in other California regions in winter. In summer, $PM_{2.5}$ concentrations generally decrease, with changes minor in magnitude compared to those from winter ($-0.6\ \mu g/m^3$). Decreases are expected due to the combined effect of reductions in nitric acid as more OH is depleted by VOC. Finally, the impact on model performance is also evaluated using observation data from the AQS network. Generally, model performance for ozone is slightly improved by the adjustment of VOC emissions in northern California and in SJV. For $PM_{2.5}$, only a select few observation sites are found to have improved model performance including sites around Fresno and Madera in the winter where usually has the most polluted $PM_{2.5}$ condition. Although the improvement of model performance is not as expected after the adjustment of VCP emissions in this work, this does not imply that efforts to improve VOC emission inventories do not have benefits to regional air quality modeling. As a preliminary study, there are limitations within this work that could lead to this result, and those limitations need to be further explored in future work. One reason for the lack of improvement in model performance could be that the scaled VOC emissions are only applied to existing sources, which is a major limitation as McDonald et al. implies that new sources should be responsible for those missing emissions with independent time and space distribution. Additionally, there could also be an underestimation of NO_x emission in the base inventory, particularly for the winter period (Oikonomakis et al., 2018). Furthermore, the uncertainty regarding to the speciation of the additional VCPs sources can also impact the model performance, and should also be investigated in future work. Overall, results show that discrepancies in VOC emission inventories have important impacts but its affect for the performance of models used for the design of emission control policy is not straight forward. More effort is needed to construct accurate VCP related emission inventory to better evaluate its impact on model performance.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2019.05.019.

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