Secondary organic aerosol formation from naphthalene roadway emissions in the South Coast Air Basin of California

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Abstract: Naphthalene is the simplest and most abundant polycyclic aromatic hydrocarbon (PAH) in California fuels, with concentrations of up to 2,600 mg L^{-1} in gasoline and 1,600 mg L^{-1} in diesel fuel. In this work, naphthalene emission factors for gasoline and diesel vehicles are combined with an activity-based automobile inventory to characterise anthropogenic naphthalene emissions in the South Coast Air Basin of California (SoCAB). A three-dimensional air quality model is used to examine transport and chemical reaction losses of naphthalene in the SoCAB. Inclusion of naphthalene emissions from on-road gasoline and diesel vehicles was found to increase modelled SOA growth by up to 10%. Hence, reductions of naphthalene from both gasoline and diesel fuels may be an effective means of reducing the emissions of an important SOA-forming precursor to the atmosphere of large urban centres with characteristics similar to the SoCAB. The implications of these findings are discussed.

Keywords: air quality modelling; environmental pollution; naphthalene; photochemistry; secondary organic aerosol; SOA; gasoline and diesel emissions factors.

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1 Introduction

Atmospheric aerosols produce severe health effects, affect radiative forcing making them important to climate change, and influence environmental chemistry through uptake and transport of ambient trace gases and through augmentation of photolysis (IPCC, 2001, 2007). Secondary organic aerosols (SOAs) can comprise a significant fraction of the total atmospheric organic particulate mass (Jimenez et al., 2009; Kroll and Seinfeld, 2008). Additionally, inhalation of SOAs has been associated with adverse health effects (Baltensperger et al., 2008).

There has been extensive development in models of SOA formation which is comprehensively summarised in Kroll and Seinfeld (2008) and Kanakidou et al. (2005). In short, atmospheric oxidants such as ozone (O_3), hydroxyl radical (OH), and nitrate radical (NO_3^-) react with volatile organic compounds (VOCs) to form reduced volatility products. The semivolatile and non-volatile products further react through multiple steps producing oxidised products with decreased volatility and/or increased solubility. The decreased volatility process leads to gas-to-particle partitioning which has been verified with a wide range of experimental results (Odum et al., 1996; Seinfeld and Pankow, 2003). Phase partitioning depends on a number of atmospheric conditions including relative humidity, temperature, and local aerosol composition (Chang et al., 2010). However, SOA measurements are typically one to ten times larger than model predictions (Volkamer et al., 2006), indicating additional SOA formation pathways that remain unaccounted in current models (Kroll and Seinfeld, 2008). More recently Ahmadov et al. (2012) implemented a new SOA parameterisation based on the volatility basis set (VBS) in a regional air quality model WRF-CHEM which reduced the uncertainty of SOA model predictions. Donahue et al. (2012) discussed the use of a two-dimensional volatility-oxidation space (2-D-VBS) to describe SOA formation from wood smoke and dilute diesel-engine emissions.

Several studies have suggested the importance of polycyclic aromatic hydrocarbons (PAHs) in the production of SOAs (Chan et al., 2009; Kautzman et al., 2010; Odum et al., 1997). The most abundant atmospheric PAH in the SoCAB is naphthalene (Eiguren-Fernandez et al., 2004; Lu et al., 2005). Furthermore, it has been shown that naphthalene is highly reactive with atmospheric oxidants forming reduced-volatility products (Sasaki et al., 1997). Based on extensive studies performed in the Caltech dual chambers, Chan et al. (2009) reported that SOA yields from naphthalene, 1-methylnaphthalene (1-MN), 2-methylnaphthalene (2-MN), and 1,2-dimethylnaphthalene (1,2-DMN) are on the order of 25%–45% under high-NO_X conditions, and 58%–73% under low-NO_X conditions ($NO_X = NO + NO_2$). Naphthalene is a health concern because exposure can cause hemolytic anemia that can be passed from a pregnant woman to her unborn child, tumours, and damage to the respiratory system (ATSDR, 2005). As a result, the US Department of Health and Human Services classifies naphthalene as a carcinogen.

Currently, there is significant uncertainty associated with naphthalene emission factors of gasoline and diesel vehicles. Emissions factors tend to vary with season due to changes in temperature and relative humidity, fuel composition, and vehicle fleet composition. This study presents a first step at examining on-road vehicular emissions of naphthalene that considers the best estimates of averaged emissions factors to date. The total naphthalene emissions used in this study compare well with those reported by Lu et al. (2005) (Table 1). Nevertheless, uncertainty in naphthalene emissions from diesel sources can be as high as a factor of two.

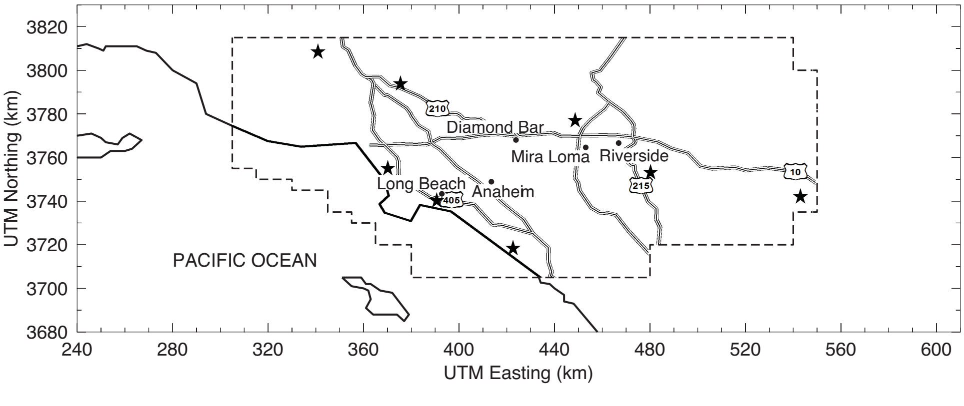
Table 1 Daily outdoor naphthalene mobile emissions (kg) in the SoCAB

	Current study	*Lu et al. (2005)*
Light-duty gasoline activity	790 (42%)	745 (43%)
Heavy-duty diesel activity	289 (15%)	160 (9%)
Slow cure asphalt		230
Consumer products		254
Mineral spirit and industrial sources		331

Naphthalene is produced primarily by incomplete combustion processes (Lu et al., 2005; ATSDR, 2005). Additionally, Lin et al. (2007) found naphthalene to be one of the most prominent PAHs emitted from gasoline automobiles. Aromatic hydrocarbons, including PAHs, are released into the atmosphere principally during incomplete combustion and account for approximately 20% of non-methane organic hydrocarbons in urban air (Nishino et al., 2008). Engine exhaust has been suggested to be an important missing source of SOAs (Bahreini et al., 2012).

Bahreini et al. (2012) concluded that gasoline emissions dominate over diesel emissions in the formation of SOA mass, and suggested that a decrease in the naphthalene content of gasoline may reduce SOA formation in the SoCAB. Contrasting with these conclusions, Gentner et al. (2012) suggested that diesel exhaust is seven times more efficient at forming organic aerosol than gasoline exhaust, and that, while both sources are important for air quality, diesel is responsible for 65% to 90% of vehicular-derived SOA, with substantial contributions from aromatic and aliphatic hydrocarbons, depending on a region's fuel use.

Figure 1 Map of the SoCAB showing the 5 km × 5 km UCI-CIT air quality model domain as dashed line



Notes: NOAA weather sites shown with stars. Circles show ambient air sample sites (Eiguren-Fernandez et al., 2008). Highways, interstates, and coastlines shown with solid lines.

This study applies a computational approach to predict the SOA production from roadway (on-read vehicles only, off-road sources not included) naphthalene emissions. An activity-based inventory of on-road naphthalene emissions is spatially and temporally allocated within the South Coast Air Basin of California (SoCAB). Atmospheric transport is predicted with the University of California, Irvine-California Institute of Technology (UCI-CIT) model which includes the latest SOA modules (Chang et al., 2010). Partitioning of naphthalene from vapour to particle phase is modelled using absorptive partitioning theory (Pankow, 1994) with partitioning parameters derived from chamber measurements (Shakya and Griffin, 2010). The study domain is shown in Figure 1. Vapour-phase and particle-phase naphthalene atmospheric samples from Eiguren-Fernandez et al. (2008) are used as ground-truth, to evaluate model predictions of May 29 through June 6, 2005. The following sections describe the methodology of modeling the meteorological period, atmospheric transport, and phase partitioning, followed by a presentation and discussion of results.

2 Methods

2.1 *Meteorological modeling*

The complex photochemistry naturally occurring in the troposphere is driven largely by prevalent meteorological conditions. The advanced research weather research and forecasting model (WRF-ARW; Skamarock et al., 2005) is used to generate the meteorological variables wind speed, relative humidity and temperature, pressure, mixing height and cloud cover. The National Centres for Environmental Prediction (NCEP) final operational global analysis 1° × 1° grids data are used for WRF initial and boundary conditions. Land use data is taken from the United States geological survey (USGS). WRF is currently the primary mesoscale model used to drive air quality simulations (Klausmann et al., 2003).

Summer in Southern California is hot with temperatures reaching 38°C (100°F). During the day, winds are predominantly west-east from the ocean towards inland, with reverse nightly winds moving east-west. WRF meteorological predictions are evaluated with the US Environmental Protection Agency (EPA) atmospheric model evaluation tool (AMET). AMET evaluates the WRF meteorological predictions using observational data from eight National Oceanic and Atmospheric Administration (NOAA) administered sites in SoCAB, shown in Figure 1.

2.2 *Photochemical modeling*

The UCI-CIT regional photochemical model (Cohan et al., 2008; McRae and Seinfeld, 1982) is used to predict atmospheric transport of naphthalene in the SoCAB during May 29 through June 6, 2005. The model characterises the domain (Figure 1) with 5 × 5 km grid cells which spans 0 to 1100 m in height over five terrain-following vertical layers. Ground layer (0–38 m) results are the focus of the present investigation. The UCI-CIT model employs an expanded version of the Caltech atmospheric chemical mechanism (Griffin et al., 2002). The chemical mechanism has been thoroughly tested to model urban and rural photochemistry as well as daytime and night-time reactions (Griffin et al., 2002; Jiminez et al., 2003).

As a first step to addressing troposphere transport of naphthalene, this study focuses on modeling the major atmospheric sinks and naphthalene gas-to-particle partitioning. Reaction with OH radicals is the biggest atmospheric loss mechanism for aromatic hydrocarbons (Nishino et al., 2008). Naphthalene and OH react to form over 100 unique products including 1,2-naphthoquinone, oxygenated indenes and benzopyrones (Lee and Lane, 2009). Additionally, NO_3^- and O_3 play an important role in atmospheric reactions of naphthalene (Atkinson, 1994; Sasaki et al., 1997). The reaction rates used to model the major naphthalene atmospheric sinks are shown in Table 2. The oxidants shown in Table 2 react with naphthalene to form a reduced volatility product. The activity-based emission inventory of the year 2005 developed by SCAQMD (SCAQMD, 2007) is used to account for atmospheric oxidant levels.

Table 2 Rate constants (30°C) for reactions with naphthalene

Reactant	*Rate (cm^3 molecule s^{-1})*	*Source*
OH	2.39E-11	Atkinson (1986)
O_3	2.00E-19	Atkinson et al. (1984)
NO_3	3.65E-28 * $[NO_2]^a$	Atkinson (1991)

Note: $^aNO_2$ in molecule cm^{-3}.

Decreased volatility, or increased solubility, allow for the formation of SOA from gas-particle partitioning (Pankow, 1994; Odum et al., 1996). The absorptive partitioning theory developed by Pankow (1994) defines an equilibrium partitioning coefficient:

$$K_P = \frac{P}{GM} \tag{1}$$

where G is the mass concentration of the semivolatile species in the gas phase, P is the mass concentration of the semivolatile species in the particle phase, and M is the mass concentration of the total absorbing particle phase (Kroll and Seinfeld, 2008). Odum et al. (1996) related the SOA yield (mass of aerosol formed per mass of reacted hydrocarbon) with a collection of semivolatile constituents

$$Y = M\sum_i \frac{\alpha_i K_{P,i}}{1 + MK_{P,i}}, \tag{3}$$

where α_i is the mass-based stoichiometric coefficient for product i, and $K_{P,i}$ is its equilibrium absorptive partitioning coefficient between the gas phase and the absorbing condensed organic medium (Pankow, 1994). The UCI-CIT model uses the two-product approach suggested by Odum et al. (1996) where semi-volatile gas-phase species are partitioned into up to two SOA products.

The partitioning of gas-phase naphthalene into the particle-phase was recently measured by Shakya and Griffin (2010) in a chamber study. Their reported equilibrium partitioning ($K_{NAP,1}$ = 0.852, $K_{NAP,2}$ = 0.003 $m^3\mu g^{-1}$) and stoichiometric coefficients (α_1 = 0.167, α_2 = 0.308) are used to predict the partitioning of an oxidised naphthalene product into two distinct naphthalene aerosols. Atmospheric partitioning parameters may vary dynamically as the ratio of parent hydrocarbon to NO_X changes with time and drives the hydrocarbon oxidation. Chan et al. (2009) examined high and low NO_X regimes for SOA yields. However, only high-NO_X partitioning parameters were reported for naphthalene, which were comparable to the values reported by Shakya and Griffin (2010).

2.3 Engine exhaust emissions

VOCs in the SoCAB are mainly emitted by anthropogenic sources with vehicular traffic accounting for about 60% of the total VOC ROG emissions (Cox et al., 2009). Naphthalene emitted from incomplete combustion is predominantly in the vapour phase (Mastral et al., 2000). Lu et al. (2005) examined the influence of naphthalene from vehicle emissions in Southern California using vehicle miles travelled data. Since that first study, there have been few examinations to update naphthalene emissions factors based on current fuel composition and vehicular consumption (Shah et al., 2005; Chen et al., 2006). This study uses measurements obtained in the Caldecott Tunnel of Northern California during the summer of 2004 and winter of 2005 (Eiguren-Fernandez and Miguel, 2012) to compute fuel-based naphthalene vapour emissions factors for gasoline and diesel vehicles.

The Caldecott Tunnel samples were analysed by HPLC-fluorescence, a technique that does not allow quantification of alkylnaphthalenes. Emission factors are calculated by relating total carbon emissions in the tunnel to the carbon content of fuels (Kirchstetter et al., 1999; Miguel et al., 1998; Marr et al., 1999):

$$E_{NAP} = 10^6 \left(\frac{\Delta NAP}{\Delta CO + \Delta CO_2} \right) \omega_C \tag{3}$$

where E_{NAP} is the mobile naphthalene emission rate in µg per kg of fuel burned, ΔNAP is the change in naphthalene concentration measured in the tunnel above background levels (ng m^{-3}), ΔCO_2 and ΔCO are the increases in the concentrations of CO_2 and CO, respectively, above background levels (µg of C per m^3), and ω_C is the carbon weight fraction of the fuel. To calculate the diesel emission factors, it is necessary to exclude light-duty vehicle contributions to total pollutant concentrations. The naphthalene diesel vehicle contribution is calculated by subtracting the gasoline vehicle contribution assuming gasoline and diesel vehicles emit comparable amounts of CO per unit distance travelled (Kirchstetter et al., 1999; Miguel et al., 1998; Pierson et al., 1996):

$$\Delta NAP_D = \Delta NAP - \Delta CO(1 - f_D)\left(\frac{\Delta NAP}{\Delta CO}\right)_2 \tag{4}$$

where ΔNAP_D is the diesel naphthalene contribution, f_D is the fraction of diesel traffic, and $\left(\frac{\Delta NAP}{\Delta CO}\right)_2$ is the ratio of gasoline contributed naphthalene to CO measured from a tunnel bore that

is restricted to gasoline vehicles (bore 2 of the Caldecott tunnel, in Berkeley) (0.06 ∓ 0.02). The diesel CO_2 contribution is calculated using traffic counts and the fuel economies of light-duty gasoline vehicles and heavy-duty diesel trucks

$$\frac{\Delta CO_{2,D}}{\Delta CO_2} = \frac{f_D U_D \rho_D \omega_D}{f_D U_D \rho_D \omega_D + (1 - f_D) U_G \rho_G \omega_G} \tag{5}$$

where $CO_{2,D}$ is CO_2 from diesel traffic, U is the fuel consumption rate, and the subscripts D and G denote diesel and gasoline, respectively. Equations (3) through (5) are used to calculate naphthalene vapour mobile emission factors for gasoline and diesel vehicles of 1,200 ± 375 and 3,357 ± 3,618 (μg of naphthalene vapour per kg of fuel), respectively. Additional discussion about the data and methodology used to estimate naphthalene roadway emission factors is presented in Eiguren-Fernandez and Miguel (2012) and Kirchstetter et al. (1999).

Total mobile naphthalene emissions, $EMIS_{NAP}$, within SoCAB are calculated by summing the diesel and gasoline contribution

$$EMIS_{NAP} = E_G FC_G + E_D FC_D, \tag{6}$$

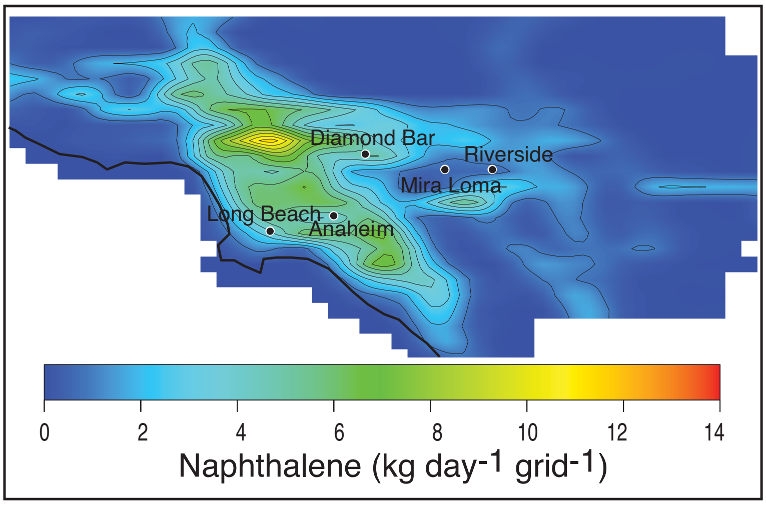
where FC is the fuel consumption. California vehicle fuel consumption for gasoline and diesel vehicles is obtained from the US Department of Transportation Federal Highway Administration (FHA, 2012). The California Air Resources Board (CARB) Emission Factor Model (EMFAC) is used to separate county fuel consumption from state fuel consumption. Daily naphthalene emissions within the (SoCAB) are shown in Table 1.

This study uses an activity-based emission inventory from the year 2005 developed by the South Coast Air Quality Management District (SCAQMD) (SCAQMD, 2007) in order to allocate spatially and temporally naphthalene mobile emissions. This emissions inventory was used by Ensberg et al. (2010) to evaluate the impact of electronically photo-excited NO_2 on air pollution in SoCAB. Mobile CO gasoline and diesel emissions from the SCAQMD inventory are used as a surrogate to determine roadway activity

$$\begin{aligned} EMIS_{NAP}(\vec{x}, t) = {} & E_G FC_G \left(\frac{EMIS_{CO,G}(\vec{x}, t)}{DailyCO_G}\right) \\ & + E_D FC_D \left(\frac{EMIS_{CO,D}(\vec{x}, t)}{DailyCO_D}\right) \end{aligned} \tag{7}$$

where $\vec{x}$ is position, t is time, $EMIS_{NAP}(\vec{x},t)$ are the spatially and temporally resolved naphthalene vapour emission rate [kg hr^{-1}], DailyCO is the total daily emissions of CO, $EMIS_{CO}(\vec{x},t)$ are the spatially and temporally resolved CO roadway emissions from SCAQMD inventory, and the subscripts G and D indicate the contribution from gasoline and diesel vehicles, respectively. Naphthalene emissions are resolved to a 5 × 5 km spatial and 1-hr temporal resolution for generic summer week and weekend days. Daily naphthalene emissions are shown in Figure 2 with notable emissions along interstate 5 and highway 91. Model resolution is too coarse to discern localised roadway traffic emissions. Diurnal traffic patterns are distinctively different from weekday to weekend. Equation (5) is used to predict naphthalene emissions for a typical weekday and weekend day using CO emissions from a Thursday for weekday emissions calculations, and a Sunday for weekend emissions calculations.

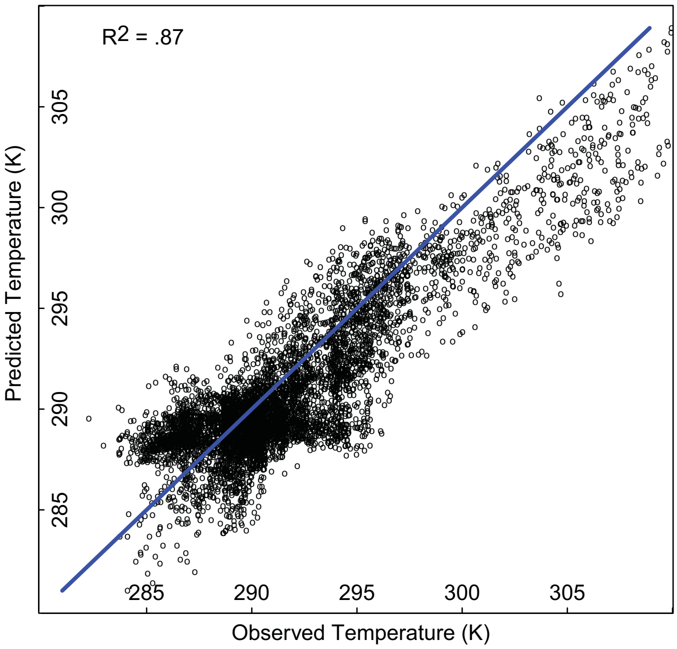
Figure 2 24-hr naphthalene roadway emissions



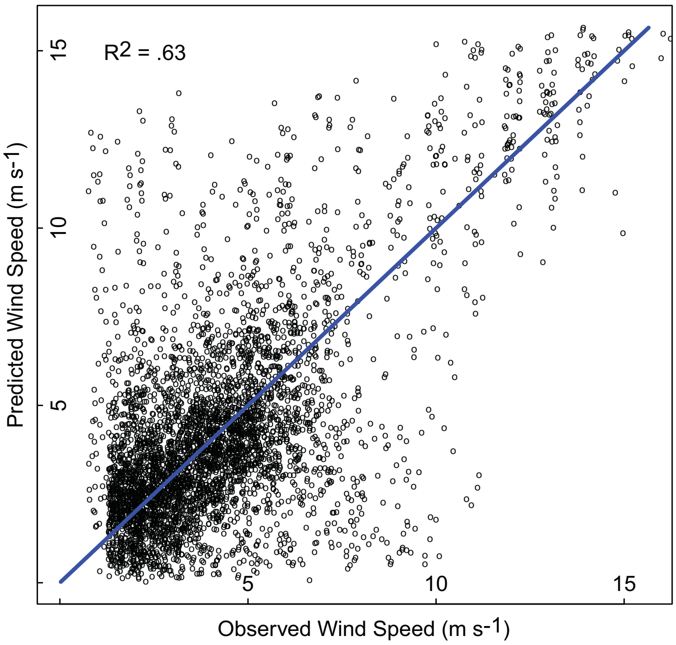
3 Results and discussion

A comparison of WRF-ARW model results and NOAA observations considering 1-hr wind speeds and temperatures is shown in Figure 3. Temperature is well replicated by WRF with a mean absolute error of 1.9 K and a correlation of 87%. Temperature is under-predicted above 27°C (80°F). Wind speed is moderately replicated by WRF with a mean absolute error of 1.7 m/s and a correlation of 63%. WRF predicted high wind speed gusts do not match up as well in space and time with observations at lower speeds. Comparison with NOAA observed wind direction shows a mean absolute error of 460. UCI-CIT model results based on these simulations may tend to over-predict the amount of atmospheric dispersion and under-predict the amount of photochemical production leading to reduced concentrations (Venkatram, 2004).

Figure 3 WRF modelled vs. (a) observed surface temperatures and (b) wind speeds



(a)



(b)

Note: Blue line shows a 1 to 1 correlation.

The naphthalene on-road emission inventory is superimposed onto the SCAQMD activity-based emission inventory to produce an updated emissions inventory of SoCAB for spring 2005. Figure 4 shows model predictions of naphthalene from June 2 through June 6. Figure 4 illustrates the spatial variation of predicted naphthalene and naphthalene derived particles, as well as the variation between week and weekend days. Secondary aerosols can be formed from a number of additional gas phase species including NH_3, SO_3, HCl and peroxyacyl nitrates. Therefore, aerosol percent increase from naphthalene-derived SOAs is calculated by comparing 1-hr aerosols from model simulations of the 2005 SCAQMD emission inventory with and without naphthalene roadway emissions.

Figure 4 UCI-CIT model predictions of naphthalene roadway emissions and naphthalene derived particles starting on Thursday June 2, 2005

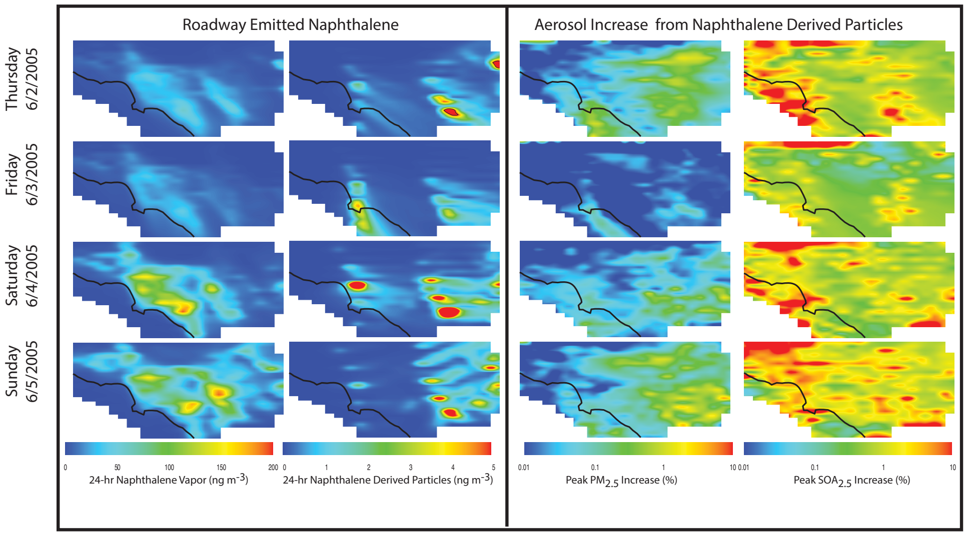
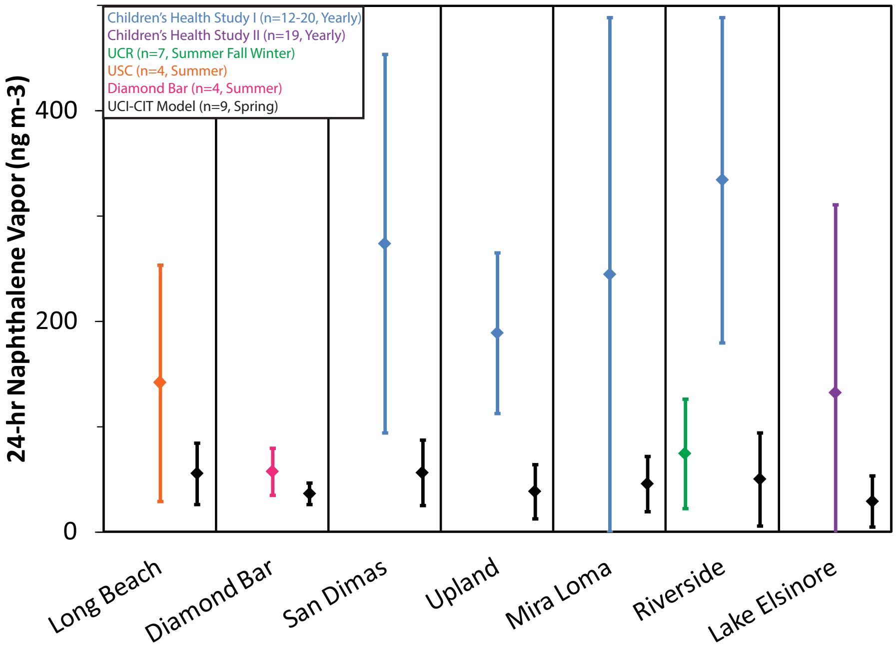


Figure 4 illustrates the sensitivity of model results to meteorology and day of week emissions. While nitric oxide emissions decrease from the weekday to weekend, ozone can increase during the weekend (Cohan et al., 2008) leading to an increase in hydroxy radicals. Generally, there are more naphthalene-derived SOAs during the weekend than during weekdays due an increase in OH-initiated naphthalene vapour oxidation.

Naphthalene vapour from roadway emissions is concentrated around freeway adjacent urban communities such as Los Angeles, Long Beach and Riverside. Naphthalene-derived SOAs are formed during atmospheric transport and hence increase downwind of major roadway sources, specifically east and south of Riverside in the Inland Empire. The mass of particles derived from naphthalene roadway emissions in SoCAB can be as high as 20% in the riverside area, although it is less than 1% in other areas. As a result, the amount of modelled SOAs produced from naphthalene roadway emissions is more significant in Riverside than in other areas. While the SOA yields from the alkylnaphthalenes 1-MN and 2-MN are higher than from naphthalene (Chan et al., 2009), the concentration of naphthalene alone in California gasoline represents 82% of the content of naphthalenes and alkylnaphthalenes (Gentner et al., 2012). Thus, inclusion of the alkylnaphthalenes precursors would increase the SOA concentrations by less than 20%.

Figure 5 24-hr naphthalene vapour average (diamond) and standard deviation (error bars)



Jia and Batterman (2010) measured outdoor vapour phase naphthalene in the range of 20 to 310 ng m^{-3} for typical urban areas, and lower in rural and remote areas. Figure 5 shows a comparison of 24-hr naphthalene vapour from model predictions for May 29 through June 6, 2005, and observations from a variety of time periods in SoCAB; the Children Health Study I data are from June 2001 through July 2002, the Children Health Study II data are from August 2002 through October 2003, University of California, Riverside (UCR) data are from July 2003 through March 2004, and Diamond Bar data are from August 2004 (Eiguren-Fernandez et al., 2004, 2007, 2008; Miguel et al., 2004, 2005; Lu et al., 2005). Naphthalene vapour follows a seasonal pattern with higher concentrations in winter than summer (Eiguren-Fernandez et al., 2004; Eiguren-Fernandez et al., 2007; Jia and Batterman, 2010). Model results only consider a spring period. Measurements collected during Children Health Study I and II spanned three seasons and hence exhibit a large range. Additionally, naphthalene emissions from on-road gasoline and diesel vehicles account for an estimated 53% (Lu et al., 2005) of the total naphthalene emissions to the SoCAB, leaving 47% of naphthalene outdoor emissions unaccounted in the current study. Naphthalene from moth repellent has been reported as the second largest exposure source after combustion (Jia and Batterman, 2010; National Toxicology Program, 2000). The correlation between observed and modelled naphthalene vapour is poor with model results systematically under predicting observations due to modelling only the spring season and accounting for only part of the entire naphthalene emission inventory in the SoCAB. The modelling predictions presented here represent a lower bound in the SOA production from napththalene.

Figure 6 4-hr concentrations (ng m^{-3}) of modelled naphthalene vapour and secondary aerosol formation from naphthalene vapour are shown in red and blue lines, respectively

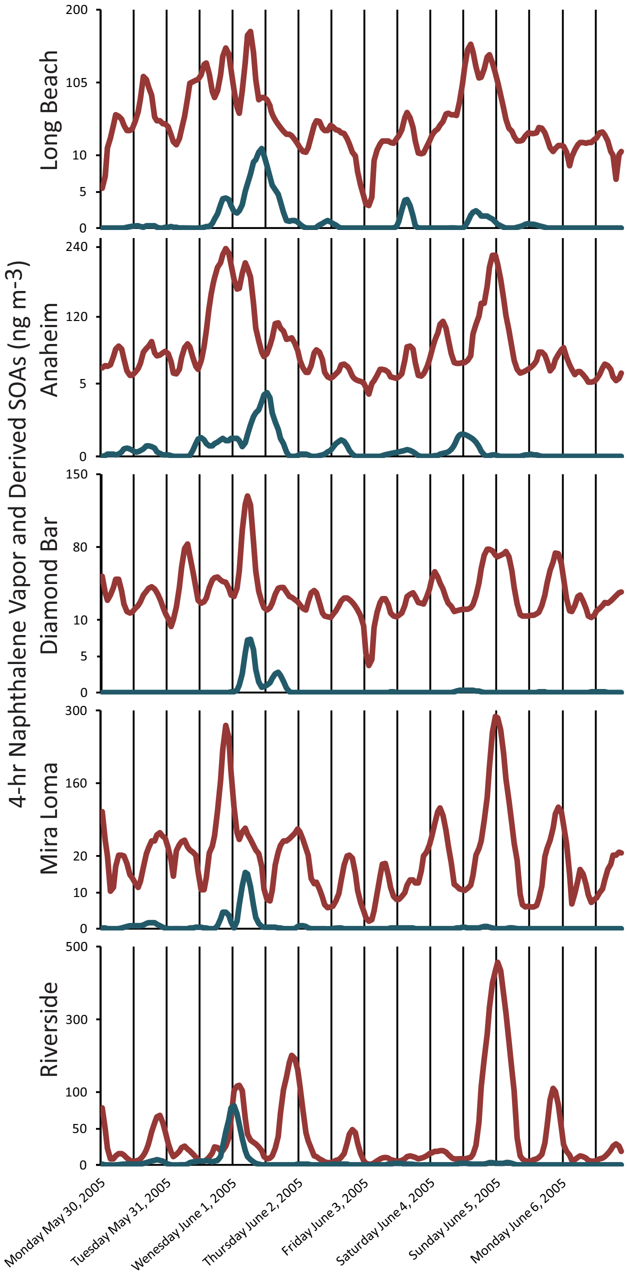


Figure 6 shows the temporal variation of modelled naphthalene and naphthalene derived particles for select locations across SoCAB. Results indicate an increase in naphthalene derived particles moving inland from Diamond Bar to Riverside which is consistent with measurements from Eiguren-Fernandez et al. (2008). Long Beach and Anaheim exhibit similarly low levels of naphthalene derived particle levels. Peaks in vapour phase naphthalene concentration are not paired in space and time with peaks in naphthalene derived particles because of transport occurring as vapour phase naphthalene under goes chemical transformation to produce SOAs. Hence, naphthalene derived particle peaks tend to lag in time and be downwind of vapour phase naphthalene peaks.

The 1-hr naphthalene-derived SOA concentrations are up to 20 times the 24-hr concentrations. Naphthalene concentrations from model prediction show high diurnal activity over the SoCAB. Low nocturnal mixing heights facilitate accumulation of local and regional sources (Pournazeri et al., 2012). Results are consistent with previous studies that found concentrations tend to peak in the night and morning, and are lowest in the afternoon (Lu et al., 2005; Park et al., 2002). Although air quality in California has been improving over the last several years, all major urban areas of California exceed the state annual $PM_{2.5}$ standard of 12 µg per m^3 (ARB 2011). Reduction of the mass concentration of SOA in urban centres, and the attended reduction of $PM_{2.5}$ levels, via reduction of SOA precursors such as fuel naphthalene and alkylated naphthalenes, will have a positive impact on policies to improve the control air quality that protect public health. Recent results (Heald et al., 2008) suggest that SOA will become an increasingly important fraction of the global aerosol burden, affecting both climate and air quality. Therefore, anthropogenic control of SOA formation precursors may constitute an important and effective regulator of global climate.

4 Conclusions

The US EPA recently promulgated a new $PM_{2.5}$ standard that increases public safety by lowering the allowable annual aerosol content from 15 µg/m^3 to 12 µg/m^3. The new stringent regulation will require more state implementation plans for non-attainment areas that may have been previously considered in attainment. The need to well characterise the aerosol environment has increased and this study has confirmed that NAP chemistry plays an important role in the overall SOA budget (Chan et al., 2009; Kautzman et al., 2010; Odum et al., 1997). Additionally, new models are being developed which incorporate a VBS to account for SOA formation (Donahue et al., 2012). Incorporating naphthalene heterogeneous chemistry into a model that uses VBS could have an even bigger impact than predicted in the current study due to increased aerosol production from VBS.

Several experimental studies have found higher aerosol yields for naphthalene than reported by Shakya and Griffin (2002) (Chan et al., 2009; Kleindienst et al., 2012). A higher aerosol yield would lead to more aerosol production from gas-phase naphthalene, indicating this study is likely conservative in its prediction of SOAs formed from on-road naphthalene.

Predicted atmospheric transport of naphthalene vapour from roadway emissions falls within range of concentrations observed. Results indicate that the inclusion of naphthalene increases modelled SOAs in SoCAB by roughly 1%–10%. Diamond Bar is adjacent to considerable roadway traffic from California highways 57 and 60 and interstate 10. Hence, transport of naphthalene roadway emissions correlate better in Diamond Bar than in less highway accessible regions such as riverside.

Atkinson and Arey (2009) estimate the half-life naphthalene with respect to OH is 5.4 hours. Kinetic activity is concurrent with atmospheric transport, fumigating reaction products in the Inland Empire, near Riverside, whose toxicity, and concentration, we can only guess. The effect of air pollution on school children lung development from 10 to 18 years of age was established by the Gaudeman et al. (2004) which found a linear relationship between distance from the ocean (inland towards riverside) and a decrease in the rate of lung growth. There are additional major naphthalene emissions not being accounted for in our model such as slow cure asphalt and moth repellent. Lim et al. (2007) and Marr et al. (1999) found that fuel composition affect PAH engine exhaust emission rates.

Atmospheric NO_X ($NO_X = NO + NO_2$) levels can affect SOA yields (Chan et al., 2009) which vary in modelled atmospheric conditions from high to low. Additionally, in general, smog chamber studies consider the photo-oxidation of single reactive organic gas species while, in the ambient environment, the atmospheric composition includes a large number and variety of reactive organic gases, condensed primary and secondary species.

A novel technique to estimate naphthalene emissions from motor vehicles based on fuel consumption is presented which could be used to predict naphthalene emissions in other regions using different emissions data. Future modeling work should address the influence of SOA boundary conditions, changes in seasonal emission factors, and include SOA producing alkylnaphthalenes. However, there is little empirical evidence to validate naphthalene generated SOA predictions. This works present a first step to characterisation of naphthalene derived aerosol in an environmental model which is needed to understand the implications in human health and climate change.

Considering that naphthalene is the predominant PAH in both fuels, with concentrations of up to 2,600 mg L^{-1} in gasoline and 1,600 mg L^{-1} in diesel fuel, reductions of naphthalene from gasoline and diesel fuels may be an effective means of reducing the emissions of an important SOA-forming precursor to the atmosphere of large urban centres.

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