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# Naphthalene distributions and human exposure in Southern California

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# Abstract

The regional distribution of, and human exposure to, naphthalene are investigated for Southern California. A comprehensive approach is taken in which advanced models are linked for the first time to quantify population exposure to the emissions of naphthalene throughout Southern California. Naphthalene is the simplest and most abundant of the polycyclic aromatic hydrocarbons found in polluted urban environments, and has been detected in both outdoor and indoor air samples. Exposure to high concentrations of naphthalene may have adverse health effects, possibly causing cancer in humans. Among the significant emission sources are volatilization from naphthalene-containing products, petroleum refining, and combustion of fossil fuels and wood. Gasoline and diesel engine exhaust, with related vaporization from fuels, are found to contribute roughly half of the daily total naphthalene burden in Southern California. As part of this study, the emission inventory for naphthalene has been verified against new field measurements of the naphthalene-to-benzene ratio in a busy traffic tunnel in Los Angeles, supporting the modeling work carried out here.

The Surface Meteorology and Ozone Generation (SMOG) airshed model is used to compute the spatial and temporal distributions of naphthalene and its photooxidation products in Southern California. The present simulations reveal a high degree of spatial variability in the concentrations of naphthalene-related species, with large diurnal and seasonal variations as well. Peak naphthalene concentrations are estimated to occur in the early morning hours in the winter season. The naphthalene concentration estimates obtained from the SMOG model are employed in the Regional Human Exposure (REHEX) model to calculate population exposure statistics. Results show average hourly naphthalene exposures in Southern California under summer and winter conditions of 270 and 430 ng m<sup>-3</sup>, respectively. Exposure to significantly higher concentrations may occur for individuals close to local sources, or in naphthalene "hotspots" revealed by simulations and observations. Such levels of naphthalene exposure may be used to gauge the

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potential health impacts of long-term naphthalene exposure. Results are also given for the distributions of 1,4-naphthoquinone, a naphthalene reaction product that may have significant health effects. © 2004 Elsevier Ltd. All rights reserved.

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# 1. Introduction



Naphthalene (I) is the simplest and most abundant of the polycyclic aromatic hydrocarbons (PAHs) in polluted urban atmospheres (Atkinson et al., 1988; Arey et al., 1989; Fraser et al., 1998). Naphthalene is present primarily in the gas-phase under typical atmospheric conditions, and has been detected in both outdoor and indoor air samples (e.g., Arey et al., 1987, 1989; Atkinson et al., 1988; Chuang et al., 1991, 1999).

Naphthalene is defined as a hazardous air pollutant by the US Environmental Protection Agency (USEPA), and was identified as a toxic air contaminant under California's air toxics "Hot Spot" Assembly Bill (AB) 2728. Naphthalene fumes can irritate the eyes, skin and the respiratory tract. If inhaled over a long period of time, naphthalene may cause kidney and liver damage, skin allergy and dermatitis, cataracts and retinal damage, and may attack the central nervous system (USEPA, 2003). Naphthalene is also a blood toxicant: exposure to high concentrations can damage or destroy red blood cells, causing hemolytic anemia (USEPA, 2003). In animal tests, naphthalene has caused cancer as a result of inhalation (USEPA, 2003). Based on results from animal studies, the US Department of Health and Human Services concluded that naphthalene is reasonably anticipated to be a human carcinogen (Agency for Toxic Substances and Disease Registry (ATSDR), 2004) and the International Agency for Research on Cancer (IARC) has classified naphthalene as possibly carcinogenic to humans (International Agency for Research on Cancer (IARC), 2002). In April, 2002 the State of California's Proposition 65 program listed naphthalene as a substance known to cause cancer. The US EPA has adopted a Reference Concentration for Chronic Inhalation Exposure of  $3 \,\mu g \,m^{-3}$  in its Integrated Risk Information System (USEPA, 1998).

Naphthoquinones are among the atmospheric photooxidation products of naphthalene (Sasaki et al., 1997). The potential health effects of exposure to quinones are a current focus of research (e.g., Nel et al., 2001; Li et al., 2000, 2002, 2003; Cho et al., 2004). The quinones express their toxicity through both electrophilic addition and oxidation-reduction reactions. It has been shown that one equivalent of quinone can generate multiple equivalents of reactive oxygen species and thus overwhelm the protective effects of antioxidant enzymes and other reducing agents (Li et al., 2000).

Fuel combustion and industrial discharges raise the levels of naphthalene and its photochemical products in polluted environments. To date, these compounds have not been extensively studied in Southern California, or other large metropolitan airsheds, where millions of individuals may be exposed. For the present study, we focus on the California South Coast Air Basin (SoCAB) that encompasses Orange County and portions of Los Angeles, San Bernardino and Riverside Counties. However, our modeling region encompasses portions of the South Central Air Basin (Ventura and Santa Barbara Counties), the Mojave Desert Air Basin (Los Angeles and San Bernardino Counties), the Salton Sea Air Basin (Riverside County), and San Diego Air Basin (San Diego County). For simplicity, this region is referred to below as Southern California.

We have linked the Surface Meteorology and Ozone Generation (SMOG) airshed model and the Regional Human Exposure (REHEX) model to assess human exposure to air pollutants in Southern California (Fig. 1). Our approach incorporates regional information on primary pollutant emissions, simulates the transformation and dispersion of pollutants, and calculates the statistics of total population exposure to primary and secondary species, including particulates. Ultimately, such an approach will aid in the design of cost-effective and optimally health-protective emission control strategies.

The present investigation focuses on naphthalene. We discuss emissions in the following section, after which SMOG simulations of naphthalene spatial distributions and diurnal and seasonal variations are analyzed. Finally, the detailed concentration profiles are used in the REHEX model to calculate population exposure to naphthalene in Southern California.

#### 2. Naphthalene loading in Southern California

#### 2.1. Measured concentrations

Observations of naphthalene in Southern California are very limited. In February 1986, Arey et al. (1987)



Fig. 1. The MM5–SMOG–REHEX modeling system. SMOG model includes treatments of mesoscale meteorology, tracer transport and dispersion, gas-phase photochemistry, aerosol microphysics and aqueous-phase chemistry, as well as solar and terrestrial radiative transfer. The REHEX model assesses population exposures based on pollutant concentrations with detailed spatial and temporal distributions predicted by the SMOG model.

measured ambient concentrations of 2875 and  $3315 \text{ ng m}^{-3}$  for nighttime (1800–0600 h) and daytime (0600-1800 h) conditions, respectively, in Torrance, CA during a high- $NO_x$  episode. In a 9-day period in August 1986 at Glendora, CA, Arey et al. (1989) found average daytime and nighttime concentrations of 3100 and  $4300 \text{ ng m}^{-3}$ , respectively, with a range from 2000 to  $6100 \text{ ng m}^{-3}$ . Nighttime and daytime 12-h averages of naphthalene at Reseda, CA in May 1987 were measured to be 1300 and  $750 \text{ ng m}^{-3}$  (Atkinson et al., 1988). During a severe Los Angeles photochemical smog episode in 8-9 September 1993, the ambient concentration of naphthalene was measured at four urban sites and on one offshore island by Fraser et al. (1998), yielding an average concentration of  $6000 \text{ ng m}^{-3}$  within a wide range from 0 to  $22,600 \text{ ng m}^{-3}$ . Gupta (1995) collected seven 12-h daytime and six 12-h nighttime ambient air samples in Redlands, California from 19 October to 28 October 1994. The observed 12 h average ambient concentrations of naphthalene ranged from 348 to  $715 \text{ ng m}^{-3}$  (Gupta, 1995).

These measurements represent polluted concentrations observed prior to the introduction of California Phase II reformulated gasoline (RFG) in the first half of 1996, which required extensive changes to gasoline properties, including an increase in oxygen content, decreases in alkene, aromatic, benzene, and sulfur contents, a reduction in volatility, and decreases in distillation temperatures (CARB, 1994). Kirchstetter et al. (1999) determined that from 1995 to 1996, the RFG program resulted in 70-75% reductions in the benzene and naphthalene weight fractions in gasoline samples collected at Berkeley, CA. Moreover, the weight fraction of benzene in non-methane organic carbon emissions measured in the Caldecott tunnel in the San Francisco Bay Area was reduced by 38% from summer 1995 to summer 1996; a change in naphthalene emissions was not reported from that study.

More recent measurements indicate naphthalene concentrations are now significantly lower in Southern California. Table 1 summarizes the average concentrations and variations of naphthalene measured by Southern California Particle Center and Supersite (SCPCS) researchers (Eiguren-Fernandez et al., 2004) at several sites where the University of Southern California (USC) carried out the Southern California Children's Health Study (CHS). Between May 2001 and September 2002, 24-h samples were made every 8th day using the PUF/XAD-4/PUF collection method. Samples were extracted by Soxhlet for two periods of 8 h with quantification by HPLC with selective fluorescence (Eiguren-Fernandez et al., 2004). Measured concentrations ranged from below detection limit to  $1035 \,\mathrm{ng}\,\mathrm{m}^{-3}$ , except for three episodic samples with much higher concentrations, reported as about  $6340 \text{ ng m}^{-3}$  at Riverside (8 May 2002),  $5620 \text{ ng m}^{-3}$  at San Dimas (8 May 2002), and  $4290 \text{ ng m}^{-3}$  at Mira Loma (30 June 2002). Excluding these three anomalous samples, average naphthalene concentrations at different sites ranged from 91 to  $445 \text{ ng m}^{-3}$  (Table 1).

Reisen and Arey (2005) also measured naphthalene more recently with Tenax adsorbent tubes at USC, a location near downtown Los Angeles influenced by emissions from heavy traffic, and at the University of California, Riverside (UCR), a downwind site less directly impacted by traffic. Samples were collected four times daily over five-day measurement periods in August 2002 and January 2003 at USC and UCR, and the data are summarized in Table 2 (Reisen, 2003; Reisen and Arey, 2005). Naphthalene concentrations were much higher in Los Angeles than Riverside, and winter concentrations were about three times or more than those in summer, presumably due in part to lower mixing heights in the winter. A peak concentration of 1600 ng m<sup>-3</sup> was measured in Los Angeles in the morning in the winter samples, consistent with emissions from rush-hour traffic.

Table 1

Naphthalene concentrations measured by the Southern California Particle Center and Supersite in the California South Coast Air Basin (data from Eiguren-Fernandez et al., 2004)

Site location	Measurement period	Average conc. $(ng m^{-3})$	Ranges $(ng m^{-3})$
Riverside, CA	31/5/01-29/7/01	323	92-650
Riverside, CA	28/10/01-23/12/01	277	131-513
Riverside, CA	21/3/02-30/4/02	396	328-449
San Dimas, CA	31/5/01-29/7/01	252	118-550
San Dimas, CA	28/10/01-23/12/01	360	41-652
San Dimas, CA	21/3/02-30/4/02	182	83-361
Mira Loma, CA	20/8/01-7/10/01	143	27-325
Mira Loma, CA	8/1/02-24/2/02	445	224-1035
Mira Loma, CA	21/5/02-8/7/02	160	152-168
Upland, CA	12/8/01-7/10/01	142	26-197
Upland, CA	8/1/02-4/3/02	216	124-306
Upland, CA	21/5/02-14/6/02	263	222-295
Long Beach, CA	15/8/02-23/9/02	91	46-178

Three episodic samples have been excluded from the data. See text for detail.

# Table 2 Naphthalene concentrations measured at USC in Los Angeles and UCR in Riverside (data from Reisen, 2003 and Reisen and Arey, 2005)

Site location	Measurement period	Times	Average conc. $(ng m^{-3})$	Ranges $(ng m^{-3})$
Los Angeles, CA	12/8/02-16/8/02	0700-1030 PDT	389	256-605
Los Angeles, CA	12/8/02-16/8/02	1100-1430 PDT	152	109-173
Los Angeles, CA	12/8/02-16/8/02	1500-1830 PDT	127	94-179
Los Angeles, CA	12/8/02-16/8/02	1900-0630 PDT	202	124-290
Riverside, CA	26/8/02-30/8/02	0700-1030 PDT	301	118-429
Riverside, CA	26/8/02-30/8/02	1100-1430 PDT	55	27-79
Riverside, CA	26/8/02-30/8/02	1500-1830 PDT	22	13-31
Riverside, CA	26/8/02-30/8/02	1900-0630 PDT	148	79-260
Los Angeles, CA	13/1/03-17/1/03	0700-1030 PST	1589	851-2223
Los Angeles, CA	13/1/03-17/1/03	1100-1430 PST	758	532-1060
Los Angeles, CA	13/1/03-17/1/03	1500–1830 PST	1211	595-2543
Los Angeles, CA	13/1/03-17/1/03	1900–0630 PST	1149	727-1477
Riverside, CA	27/1/03-31/1/03	0700-1030 PST	535	418-767
Riverside, CA	27/1/03-31/1/03	1100–1430 PST	110	29-324
Riverside, CA	27/1/03-31/1/03	1500-1830 PST	183	65-275
Riverside, CA	27/1/03-31/1/03	1900–0630 PST	499	204–636

#### 2.2. Naphthalene emissions

Naphthalene has a number of significant emission sources, including combustion of fossil fuels and wood, evaporation from naphthalene-containing products, and refining operations (ATSDR, 2004). Naphthalene is a natural constituent of coal tar and crude oil, and is used in manufacturing dyes, plastics, leather tanning agents, carbonyls used in insecticides, and many other products (Howard, 1990; Lewis, 1997). Naphthalene was the predominant PAH in both gasoline and diesel fuels studied by Marr et al. (1999). Unburned fuels and the conversion of 2-methylnaphthalene in the fuel to naphthalene are the main sources of naphthalene in motor vehicle exhaust (Rhead and Pemberton, 1996).

# 2.2.1. Naphthalene emission inventory

The latest emission inventory developed for the South coast air quality management district's (SCAQMD) 2003 air quantity management plan (AQMP) is adopted here to estimate naphthalene emissions in Southern California (SCAQMD, 2003). The AQMP base year 1997 emission inventory (SCAQMD, 2003) covers point, area, off-road and on-road sources, and includes contributions from gasoline dispensing, industrial coatings, consumer products and residential wood combustion. On-road emissions were estimated using the California air resources board (CARB) EMFAC-2002 emission factors, and transportation activity data developed by the Southern California Association of Governments (SCAG) in their 2001 Regional Transportation Plan. Emissions from off-road vehicles, including trains, ships, construction equipment, and utility engines, were constructed using estimated activity levels and emission factors (SCAQMD, 2003). The inventory was spatially distributed over a grid system composed of 5-km by 5-km grid cells spanning Southern California.

The latest CARB organic gas speciation profiles (i.e., the emission factors for specific organic compounds and groups of compounds) have been used to estimate naphthalene emissions from each source category. The naphthalene emission factor for diesel exhaust was updated using more recent information from Schauer et al. (1999). The resulting estimated naphthalene emission rates from major sources in the study area are listed in Table 3. On this basis, about  $745 \text{ kg day}^{-1}$  is due to gasoline evaporation and engine exhaust, accounting for 44% of the total emission, with diesel exhaust contributing another 9% of the total. Asphalt products on paved roads are estimated to release  $230 \,\mathrm{kg} \,\mathrm{day}^{-1}$  of naphthalene into the atmosphere. Naphthalene is present in many consumer products; for example, multipurpose solvents, insecticides, lubricants, herbicides, charcoal lighter, and degreasers, as well as hair spray, all of which contribute about 15% of the total daily emissions. Emissions from certain episodic events, such as forest fires, have not been carefully evaluated and are not included here. Total emissions for Southern California are then estimated to be about  $1700 \text{ kg } \text{day}^{-1}$ , with emissions from gasoline and diesel motor vehicle exhaust and fuel vaporization contributing more than half of the total.

The spatial distribution of naphthalene emissions over Southern California is shown in Fig. 2. As expected, high emission rates are found in populated urban areas with peaks in city centers, such as downtown Los Angeles. The spatial distribution patterns are highly

Table 3 Naphthalene emission in the California South Coast Air Basin

	Emission rates (kg day <sup>-1</sup> )	Percent of total
Gasoline engine exhaust and evaporation	745	44
Diesel engine exhaust	160	9
Slow cure asphalt	230	13
Consumer products	254	15
Mineral spirit and industrial sources	331	19

correlated with major roadways in the region owing to the importance of vehicle exhaust as a naphthalene source. Naphthalene emissions in remote areas are estimated to be relatively small.

# 2.2.2. Naphthalene-to-benzene ratio

Uncertainties exist in mobile source emission factors for naphthalene, in part due to sampling difficulties. For example, naphthalene can be lost to walls when exhaust gases are collected and stored in bags. Since naphthalene is too volatile for complete collection on a denuder, it is also necessary to back up denuders with PUF cartridges (Schauer et al., 1999). In addition, mobile source emission factors are usually determined by sampling exhaust from a small number of vehicles under conditions that may not be representative of vehicles in use.

In contrast, benzene can be reliably measured in both vehicle exhaust and ambient air, and the ratio of naphthalene to benzene may be used to assess the reliability of naphthalene emission factors. Hence, to verify mobile source emission factors for naphthalene, we conducted a sampling experiment at the Sepulveda tunnel near the Los Angeles International Airport (LAX) with high traffic volume. By observing the vehicle mix, we confirmed that gasoline-powered passenger cars dominated the traffic through the tunnel, accounting for more than 95% of the trips. Hence, it was concluded our measurements were representative of automotive emissions.

Samples were collected on 11 December and 12 December 2003 at the south exit of the tunnel, from 2:00 pm to 6:30 pm at approximately 1-h intervals. Benzene was collected in 6-l air canisters. Naphthalene was collected with a new LS-TM-XAD sampling system (L. Sheetz Enterprises, Reno, NV) using 20 g of XAD-4 resin as a collection matrix, and was extracted by sonication with dichloromethane:acetonitrile (2:1 v/v) for 24 min. The extracts were filtered using a Millipore filtration system (0.45  $\mu$ m membrane), and injected into an HPLC-FL detector. The detailed chromatographic conditions are summarized elsewhere (Eiguren-Fernandez and Miguel, 2003). Gas chromatographic (GC) analyses of benzene collected in canisters was carried out by the SCAQMD.

The overall average naphthalene-to-benzene mass ratio determined for the tunnel samples is  $0.033 \pm 0.004$ . This value is identical to the ratio (0.033) corresponding to averaged gasoline vehicle emissions based on the CARB emissions inventory. Accordingly, the tunnel results provide strong support for the naphthalene emission rates used in the air quality simulations discussed below.

To further verify emission factors using the ratio technique, ambient air samples were collected at the California Institute of Technology, Pasadena CA, roughly 20 km northeast of downtown Los Angeles.



Fig. 2. Spatial distributions of naphthalene emissions over Southern California. The emission distribution pattern is highly correlated with city centers and major road ways. Black lines represent coastal and county boundaries. Gray lines represent major highways in the region.

This area is subject to light and heavy-duty vehicle traffic, as well as point and area sources of naphthalene. The naphthalene-to-benzene mass ratios for the 24-h samples taken on 6 and 7 November 2003 were 0.049 and 0.055, respectively. These ratios are consistent with the naphthalene-to-benzene mass ratio of 0.056 predicted by the SMOG model at Pasadena for the winter case discussed later. Since benzene is emitted mainly from mobile sources, the agreement between the modeled and measured naphthalene-to-benzene ratios indicates the relative contributions to the total naphthalene emissions from mobile sources together with other sources are represented reasonably well in the emission inventory employed here.

#### 3. Modeling naphthalene

While air quality in Southern California has been studied for decades, the regional distributions of naphthalene and its products are not well characterized in Southern California. Accordingly, we employed the SMOG model to estimate the concentrations of naphthalene resulting from the balance between emission, photochemical transformation and dispersion. We explicitly calculate the abundances of the naphthalene atmospheric reaction products, 1- and 2-nitronaphthalene and 1,4-naphthoquinone, including quantities in the vapor and aerosol phases. The present analysis focuses on naphthalene.

# 3.1. The SMOG airshed model

The SMOG airshed model was developed to study the distributions of gaseous and particle-borne pollutants over large metropolitan areas. Details about the structure and algorithms used in the model are discussed elsewhere (e.g., Jacobson et al., 1996; Lu and Turco, 1996; Lu et al., 1997a, b, 2003; Jacobson, 1997). The main components of the SMOG modeling system are summarized in Fig. 1, which includes treatments of mesoscale meteorology, tracer transport and dispersion, gas-phase photochemistry, aerosol microphysics and aqueous-phase chemistry, as well as solar and terrestrial radiative transfer. The meteorological component consists of the NCAR/Penn State Mesoscale Model version 5 (MM5), a limited-area, nonhydrostatic, terrain-following sigma-coordinate model (Anthes and Warner, 1978). SMOG and MM5 are coupled online, using a common MM5 domain to minimize errors arising from interpolations between coordinate systems. In addition, the coupled code utilizes multiple spatial grid nesting, and a four-dimensional data assimilation scheme. Initial and lateral boundary conditions for the MM5 simulations are established on the largest spatial domain by directly linking to the National Centers for Environmental Prediction (NCEP) or the European Centre for Medium-Range Weather Forecasts (ECMWF) analyzed fields available for the dates of interest.

The triply-nested domain used in this study is shown in Fig. 3, and covers the entire Western US. The horizontal resolution for the nested grids identified as D1, D2 and D3 are 45, 15 and 5 km, respectively. To facilitate multi-day simulations, the outer domain, D1, was embedded within the NCEP Eta model analysis products at 40-km resolution, using analyzed fields as time-dependent lateral boundary conditions. Twenty-three vertical layers resolve the troposphere from the surface to 250 hPa, with higher resolution in the boundary layer. The SMOG model is embedded within the highest resolution grid, D3, which covers the Southern California. Background concentrations of key chemical species are used to specify lateral boundary conditions at upwind inflow boundaries (Lu et al., 1997b).

As noted earlier, the AQMP base year 1997 emission inventory (SCAQMD, 2003) was employed here. Emission fluxes of primary criteria pollutants, including NO<sub>x</sub>, SO<sub>x</sub> and CO, as well as non-methane hydrocarbons (NMHC) speciated as carbon bond IV (CB4) surrogates, were determined from the AQMP inventory for each hour at each grid cell of the SMOG computational domain. An extended version of the CB4 photochemical mechanism was used with photochemical reactions and rate coefficients reported previously (Jacobson et al., 1996; Lu et al., 1997a).

# 3.2. Naphthalene atmospheric chemistry

In the gas phase, naphthalene reacts with hydroxyl (OH) and nitrate (NO<sub>3</sub>) radicals through addition to an aromatic ring. In the presence of NO<sub>x</sub>, the OH-naphthalene and NO<sub>3</sub>-naphthalene adducts can further react with NO<sub>2</sub> or O<sub>2</sub> to yield a number of products, competing with the thermal decomposition of adducts to



Fig. 3. A set of three two-way nested domains used for meteorological simulations. The SMOG model predicts pollutant dispersion and transformation on the finest grid, D3, covering Southern California.

reform naphthalene (Atkinson and Arey, 1994; Sasaki et al., 1997). Under tropospheric conditions the reactions with OH and  $NO_3$  radicals, the primary chemical loss processes for naphthalene, lead to formation of naphthoquinones and nitronaphthalenes, together with other products (Sasaki et al., 1997). The specific naphthalene reaction products considered here are listed in Table 4. Of the two main naphthalene reaction pathways, the OH process dominates under most conditions, with the nitrate radical reaction being most effective at night.

The simplified naphthalene photochemical mechanism used for the present simulations is summarized in Table 5. Our principal goal was to include the processes that control naphthalene concentrations in polluted air, while roughly accounting for the fate of the products of naphthalene photooxidation. The gas-phase OH radical reaction with naphthalene yields 1,4-naphthoquinone, naphthols, nitronaphthalenes, hydroxynitronaphthalenes, and a number of ring-opened products. For the OH radical reaction, Sasaki et al. (1997) measured formation yields of 1%, 1.2% and 1.3% for 1,4-naphthoquinone and 1- and 2-nitronaphthalene, respectively. Sasaki et al. (1997) also found that the vield of 1-naphthol from this reaction is  $\sim 7\%$ , when an estimated rate constant of  $2 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the secondary reaction of 1-naphthol with OH was adopted. In the presence of sufficient NO2, as in polluted air, NO3-naphthalene adducts react with NO2 to form 1,4-naphthoquinone and 1- and 2-nitronaphthalenes with yields of 1.9%, 24.4% and 11%, respectively (Sasaki et al., 1997).

The OH-radical reactions of the naphthalene products in Table 4 were constructed using relevant laboratory data as well as analogous organic chemical processes (Atkinson et al., 1989; Atkinson and Arey, 1994; Sasaki, et al., 1997). For example, naphthols have been found to react more rapidly with the OH radical than does naphthalene, and 1,4-naphthoquinone is the main observed product of the OH reaction with 1-naphthol (Bunce et al., 1997). However, the yield of 1,4naphthoquinone from 1-naphthol has not been determined experimentally. In the absence of experimental data, we use the measured 10% yield of methylbenzoquinone from the OH radical reaction with *o*-cresol (Olariu et al., 2002) to predict a 10% yield of

Table 4 Naphthalene chemistry species list

NAP	Naphthalene		
G1NN	1-Nitronaphthalene		
G2NN	2-Nitronaphthalene		
G1NOL	1-Naphthol		
G14NQ	1,4-Naphthoquinone		

Table 5						
Naphthalene	chemical	mechanism	used in	the	present	work

Reaction	Rate coefficient <sup>a</sup>	Ref <sup>b</sup>
NAP+OH=0.012 G1NN+0.013 G2NN +0.01 G14NQ+0.067 G1NOL+Products	$2.4 \times 10^{-11}$	1
NAP + NO3 = 0.24 G1NN + 0.11 G2NN + 0.019 G14NQ + Products	$3.6 \times 10^{-28}$ [NO <sub>2</sub> ]	2
G1NOL + OH = 0.10 G14NQ + Products	$2.0 \times 10^{-10}$	3
G1NN + OH = Products	$5.4 \times 10^{-12}$	4
G2NN + OH = Products	$5.6 \times 10^{-12}$	4
G14NQ + OH = Products	$3.1 \times 10^{-12}$	4
G1NN + hv = 0.22 G14NQ + Products	$0.13  imes J_{ m NO_2}$	5
G2NN + hv = Products	$0.018 \times J_{NO_2}$	5
G14NQ + hv = Products	$0.021 \times J_{\mathrm{NO}_2}$	4

<sup>a</sup>Rate coefficients in units of  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> or s<sup>-1</sup>.

<sup>b</sup>Reference: 1: Phousongphouang and Arey (2002); 2: Atkinson and Arey (1994); 3: Sasaki et al., (1997); 4: Atkinson et al. (1989); 5: Phousongphouang and Arey (2003).

1,4-naphthoquinone for use in this study. The photolysis rates of 1- and 2-nitronaphthalene have been measured to be  $0.07 \times J_{NO_2}$  and  $0.005 \times J_{NO_2}$ , respectively, (Feilberg et al., 1999) and  $0.13 \times J_{NO_2}$  and  $0.018 \times J_{NO_2}$ , respectively (Phousongphouang and Arey, 2003). The photolysis of 1-nitronaphthalene generates 1,4-naphthoquinone with a yield of 22% (Atkinson et al., 1989).

# 3.3. Summer and winter meteorological conditions

The local climate in Southern California is controlled to a large extent by the semi-permanent high over the North Pacific Ocean. Moreover, the strength and relative positions of the North Pacific high to the west and a prominent thermal low to the east determine the pressure gradient over the area throughout most of the year. Crucial to the dispersion of air pollution in this region are thermally forced winds, including sea–land breezes and mountain–valley flows, as well as winds channeled by terrain (Lu and Turco, 1994, 1995).

During the summer months, high pressure blankets southern California, leading to light synoptic winds, clear skies and intense sunshine. An elevated temperature inversion is present almost continuously over the summer-half of the year. In the winter months, the Pacific high shifts to the southwest, allowing Pacific storm fronts to penetrate the area. Clear winter skies allow the surface air layer to cool radiatively during longer nights, leading to the formation of shallow ground-based temperature inversions. Transitional, and often less stable, meteorological conditions occur most often between the summer and winter seasons.

The present work focuses on two periods, 15–20 July 1998 and 1–7 November 1999, representing mid-summer and early winter episodic conditions, respectively. During the summer period in 1998, a widespread ozone episode occurred in Southern California. Peak 1-h ozone

concentrations reached 240 ppb, with an 8-h peak of nearly 210 ppb. In the winter case, in which Southern California lay under the northern edge of a low pressure tongue, a high particulate matter episode occurred in Southern California with 24-h averaged PM10 total mass concentrations ranging from 150 to  $200 \,\mu g \,m^{-3}$  measured at Riverside.

The simulated hourly ozone concentrations for these periods are in general agreement with measurements. For example, Fig. 4 compares simulated and measured ozone concentrations for the summer and winter periods at two locations, downtown Los Angeles (CELA) which is a major source region that is located in the western area of the SoCAB, and Riverside (RIVR) which is in the downwind eastern basin. In both cases, simulations have captured the diurnal variations in ozone concentrations and the timing of afternoon ozone peaks. The reported ozone maximum of 190 ppb on 16 August 1998, at RIVR has been predicted within 20%. The peak ozone concentrations at CELA have been underpredicted considerably in the summer case, partially due to the photochemistry calculation with 5-km resolution that does not capture the sub-grid scale variability of emissions in the source region. Both the diurnal and seasonal variations in ozone at Riverside are fairly accurately reproduced with root-mean-square errors of 12 and 31 ppb for the winter and summer cases, respectively.

# 3.4. Simulations of naphthalene and its derivatives in Southern California

Naphthalene concentrations calculated with the SMOG model are generally consistent with recent naphthalene measurements collected by the SCPCS (Table 1). At the five CHS sites—San Dimas, Upland, Mira Loma, Riverside, and Long Beach—the model-predicted 5-day averaged concentrations are 158, 153,



Fig. 4. Comparison of SMOG model prediction of O<sub>3</sub> (blue symbols) with AQMD routine measurements (green symbols) at Downtown Los Angeles (CELA) and Riverside (RIVR) for summer and winter simulation cases.

112, 109 and 120 ng m<sup>-3</sup>, respectively, for the summer case (Fig. 5), and 274, 314, 228, 211, and 181 ng m<sup>-3</sup>, respectively, for the winter case (Fig. 6). These results are within the range of the measured concentrations discussed in Section 2.1 (Table 1). The observations are characterized by large day-to-day variability as shown by the measurement ranges in Table 1, which may indicate that the site measurements were strongly influenced by local emission sources and wind patterns. Since the model averages concentrations over a 5-km grid to capture regional variations, local plumes are not resolved. Accordingly, as noted below, individuals may be exposed to higher concentrations associated with small scale variations, especially in the vicinity of emission sources.

# 3.4.1. Regional distribution

Fig. 5 illustrates the predicted concentrations of naphthalene across Southern California averaged over the last 5 days of the summer simulation. Similar data are given for the winter case in Fig. 6. The regional character of the naphthalene distribution is clearly revealed in these plots, with high concentrations confined largely within the basin defined by mountain ranges to the north and east and coastal ocean to the west and south. Large naphthalene gradients occur along the coast owing to prevailing winds, which transport polluted air masses inland. The peak naphthalene concentrations appear in areas where emissions are greatest; for example, adjacent to downtown Los Angeles. Winter concentrations, on average, exceed those in summer.

As noted in Section 2.2, naphthalene emissions are associated with fuel combustion and vaporization. Accordingly, the predicted distributions correlate strongly with transportation corridors in Southern California. For example, high concentrations stretch along the San Gabriel and San Bernardino Mountains in the northern and eastern basin corresponding to the 10 and 210 freeway corridors. Another band of high concentrations extends southeast between the San Fernando Valley and Orange County paralleling the 5 and 405 freeways. Atmospheric dispersion from sources also plays a critical role in controlling the regional distribution of naphthalene, leading to the widespread distributions noted in Figs. 5 and 6.



Fig. 5. Model predicted 5-day average ambient concentrations of naphthalene across Southern California corresponding to July 16–20 1998 summer case (in units of  $ng m^{-3}$ ).



Fig. 6. Model predicted 5-day average ambient concentrations of naphthalene across Southern California corresponding to 2–6 November 1999 winter case (in units of  $ng m^{-3}$ ).

The high degree of spatial variability illustrated in Figs. 5 and 6 suggests one needs a multi-station network like those used to characterize ozone and  $NO_2$  in Southern California to properly characterize naphthalene (and other PAHs) in urbanized regions. As pointed out by Lu et al. (2003) with regard to trace metal distributions in Southern California, concentrations measured within the more urbanized zone are not likely

to represent those in the adjacent suburbs, and vice versa, owing to the large gradients across urban-suburban boundaries.

# 3.4.2. Diurnal and seasonal variations

Fig. 7 shows the mean diurnal variations in naphthalene concentrations at the CELA and RIVR sampling sites for the last 5 days of the simulations. The simulated average hourly concentrations are compared with concentrations measured four times a day (over intervals indicated in the plot) during different time periods by Reisen and Arey (2005). The naphthalene diurnal variations are quite distinctive both in summer and winter. At the source site (CELA), peak concentrations are found in the early morning when the boundary layer is relatively shallow and rush-hour traffic is creating strong emissions. By noontime, the concentrations are greatly reduced because of enhanced boundary layer mixing and lighter traffic. The effect of the broader afternoon and evening traffic peak in boosting naphthalene concentrations depends strongly on the intensity of local boundary layer mixing. The lifetime of naphthalene is about 8 h mainly due to its reaction with OH radicals. As naphthalene is dispersed from major sources, reaction

with OH radicals and vertical mixing reduce the daytime concentrations seen at downwind receptor sites, such as RIVR.

Naphthalene concentrations in winter tend to be considerably higher than in summer due to a more stable boundary layer and a lower mixing height. Similar behavior can be seen in the data of Reisen and Arey (2005). The local measurements at UCR were probably affected to a greater degree by morning traffic patterns than the grid-averaged simulations corresponding to the RIVR site. Although the measurements were made at different times and at adjacent locations, the model predictions appear to be in good agreement regarding naphthalene concentrations and diurnal and seasonal variations.

The diurnal variation in the spatial distribution of naphthalene is illustrated by comparing Figs. 8 and 9,



Fig. 7. Comparison of SMOG model predicted naphthalene concentrations (green symbols) with measured diurnal variations (Reisen and Arey, 2005). Model predictions and measurements are not at the same date periods. Peak concentrations were found in the morning when large emissions occurred while both vertical mixing and photo-oxidation are weak.

which correspond to noon and midnight snapshots, respectively. Most noteworthy is the significantly elevated nighttime level of naphthalene throughout Southern California. A shallow surface inversion traps naphthalene emissions near the ground at this time, leading to higher concentrations in most areas (Fig. 9). Moreover, surface plumes of naphthalene are seen extending more prominently into the high desert regions toward the northeast—and over the coastal waters—during the evening hours.

Naphthalene concentrations near the surface are usually much higher in winter than in summer, although the spatial patterns are quite similar. This can be seen by comparing Figs. 5 and 6 (refer to Section 3.4.1). Higher wintertime naphthalene concentrations are shifted slightly toward the coast as a consequence of weaker sea breezes and stronger land breezes in winter. Regionally, the highest naphthalene concentrations typically occur in the winter night and early morning.

#### 3.4.3. Distributions of 1,4-naphthoquinone

The distribution of 1,4-naphthoquinone in both gaseous and aerosol phases generated by naphthalene photooxidation is shown in Fig. 10 for the summer case. Significant differences can be seen between the concentration patterns of the primary and secondary compounds—naphthalene and naphthoquinone. The 1,4naphthoquinone is concentrated inland along the mountain slopes where air trajectories arrive from the coastal region. The spatial distributions of 1,4-naphthoquinone are generally similar in summer and winter (not shown). However, 1,4-naphthoquinone is distributed over a wider area in summer because naphthalene photooxidation chemistry is more active in summer and mixing is more vigorous. Nevertheless, enhanced naphthalene concentrations in winter can lead to higher 1,4-naphthoquinone concentration in source regions.

The 1.4-naphthoguinone concentrations determined here include contributions from the reactions listed in Table 5. However, other processes not accounted for in this analysis may also contribute to the total burden. For example, the photo-transformation of naphthalene on solid surfaces and fly ash apparently generates naphthoquinones (Guillard et al., 1993). Similar processes may occur on aerosol surfaces in polluted airsheds. Bunce et al. (1997) noted the formation of naphthoquinones in the reaction of naphthalene with OH radicals and subsequent secondary reactions with a peak yield of 6% under their experimental conditions. Moreover, quinones may be emitted in vehicle exhaust (Choudhury, 1982). Further, the toxicities and health impacts of naphthalene oxidation products other than naphthoquinone, including naphthols, formylcinnaldehyde, and other dicarbonyls, are largely unknown. The yield of each of these compounds from the oxidation of naphthalene ranges between  $\sim 3\%$  and 35% (Sasaki et al., 1997). It follows that the sum of these additional compounds could significantly exceed the predicted concentrations of 1,4-naphthoquinone in Fig. 10. Further work is required to quantify the abundances of quinones in urban air, and to characterize their regional distributions and human exposure.



Fig. 8. Model predicted 1-h average ambient concentrations of naphthalene across Southern California corresponding to 12PST, July 17, 1998 (in units of  $ng m^{-3}$ ).



Fig. 9. Model predicted 1-h average ambient concentrations of naphthalene across Southern California corresponding to 00PST, 18 July 1998 (in units of  $ng m^{-3}$ ).



Fig. 10. Model predicted 5-day average ambient concentrations of 1,4-naphthoquinone across Southern California corresponding to 16-20 July 1998 (in units of ng m<sup>-3</sup>).

# 4. Naphthalene exposure assessment

In estimating human exposure to airborne pollutants, and setting standards for exposure levels, regional simulations can provide crucial information that would otherwise be difficult to obtain from ground-based measurements alone. In addition, the distributions of a range of co-pollutants can be obtained in a selfconsistent manner for multicomponent exposure analysis. In the present work, however, we focus on naphthalene, which has never been assessed comprehensively in Southern California. Exposures to naphthoquinones are not explicitly addressed owing to the greater uncertainty in their distributions and effects, as noted earlier.

#### 4.1. Regional human exposure (REHEX) model

The REHEX model is a semi-physical stochastic exposure model originally developed by Winer et al. (1989). Details about applications and features of the model can be found elsewhere (Fruin et al., 2001; Hall et al., 2001; Lurmann and Korc 1994). The REHEX model calculates personal exposure by weighting pollutant concentrations in various microenvironments by the fraction of time people spend in these locations.

#### 4.1.1. Time-activity sequence database generation

The time-activity patterns for California residents were obtained from the Consolidated Human Activity Database (CHAD) developed by the USEPA, which provides 24-h time-activity patterns based on recall diaries (USEPA, 1997). There are 3950 sequence profiles available for California residents, including the time-activity surveys conducted for California adolescents and adults in 1987 and 1988 (Wiley et al., 1991); for California children in 1989 and 1990 (Wiley, 1991); and the National Human Activity Pattern Survey conducted between 1992–1994 (Klepeis et al., 2001). Diary data were transformed into time-activity sequences by assigning each 15-min interval into three microenvironments (indoor, outdoor and in-vehicle).

# 4.1.2. Demographic groups

Population data for California residents by age, gender and race were obtained from the US Census 2000 at the census block level (US Census Bureau, 2002). Block-level population was allocated to the 5km by 5km SMOG modeling grid using ArcGIS 8.2 (ESRI Inc.). For small blocks ( $< 0.5 \text{ km}^2$ ), we used an area allocation method, assuming a uniform population distribution in each block. For large blocks  $(\geq 0.5 \text{ km}^2)$ , we used a street-segment allocation method, assuming a population distribution proportional to total length of streets within any sub-area of a block. The Tiger 2000 streets (ESRI, 2002) were used in the street-segment allocation, excluding major freeways with speed limits equal or greater than 65 mile/h (Paul Ong, personal communication, 2002). Compared to the uniform distribution method, the street-segment allocation improved population interpolation in large blocks. For example, a block (No. 061110073001019) located in Ventura County had 138 persons in a 27 km<sup>2</sup> area with several small streets. If we used the area allocation method alone, a majority of the population in that block would have been assigned to areas with no streets, which is unrealistic.

# 4.1.3. Outdoor concentrations from the SMOG model

Regional ambient naphthalene distributions calculated with the SMOG model, as described above, provided the 1-h average outdoor concentration inputs for the REHEX model. The gridded model estimates were projected onto appropriate census blocks. The REHEX model utilized the resulting time series of outdoor concentrations in each census block to estimate exposure in outdoor environment.

# 4.1.4. Indoor naphthalene concentrations

Several studies have measured indoor naphthalene concentrations. Chuang et al. (1999) measured mean indoor and outdoor naphthalene concentrations of 2200 and 430 ng m<sup>-3</sup>, respectively, at 24 low-income homes in North Carolina in 1995 (smokers were not excluded). Gold et al. (1991) reported an indoor concentration of  $2200 \text{ ng m}^{-3}$  (with a coincident outdoor concentration of  $300 \text{ ng m}^{-3}$ ) for homes with smokers, and a concentration of  $1000 \text{ ng m}^{-3}$  (with  $100 \text{ ng m}^{-3}$  outdoors) for homes without smokers. Kim et al. (2001) found indoor naphthalene concentrations of  $200-6000 \text{ ng m}^{-3}$ , with a mean and standard deviation of  $1000 \text{ ng m}^{-3}$ , respectively.

However, it is not appropriate to apply these reported indoor naphthalene concentrations or indoor-to-outdoor (I/O) concentration ratios to the current Southern California population. A major concern is that naphthalene usage in mothballs and pesticides in California has been reduced significantly. In addition, the California population had lower smoking rates at residences in recent years compared with the early 1990s or with other states (Pierce et al., 1998). Therefore, present indoor naphthalene concentrations in California homes are likely to be lower than those typically found in the literature.

In our exposure model simulations, ratios of I/O naphthalene concentrations were obtained from recent measurements in Fresno, CA (Paul Roberts, personal communication, 2004). The I/O ratios were based on the distributions of daily naphthalene samples collected inside and outside 47 different homes of non-smokers. The I/O ratios of naphthalene concentrations were calculated and further categorized from 0 to 5 in 0.5 intervals. Distributions of I/O ratios were concentrated around values of 1.0-1.5 but skewed to the higher end up to 5 due to possible indoor sources such as household and personal care products.

#### 4.1.5. In-vehicle naphthalene concentrations

As noted above, motor vehicle emissions are one of the major sources of naphthalene. However, little information has been available for in-vehicle naphthalene concentrations, especially for the current California vehicle fleet. With the use of reformulated gasoline, more stringent emission standards for newer vehicles, and fleet turnover, naphthalene emissions are expected to have declined in the last decade. For example, fuel reformulation, i.e. California Phase I Gasoline in 1992, Federal reformulated gasoline in 1995, and California Phase II Cleaner Burning Gasoline in 1996, dramatically reduced the contents of benzene and other aromatics.

Batterman et al. (2002) found a naphthalene concentration of  $1200 \pm 900 \text{ ng m}^{-3}$  in buses in Detroit, Michigan. This study also indicated BTEX compounds measured in traffic were 2-4 times higher than levels at fixed sites. Benzene, toluene, m-+p-xylene, 1,3-butadiene and formaldehyde concentrations in passenger vehicles were about 2-4, 1-4.5, 2-4, 2.5-6.5, and 1.5-2 times the corresponding ambient concentrations in Los Angeles, depending on the type of roadways traveled (Rodes et al., 1998). Benzene concentrations in school buses in Los Angeles were about 1 (window opened) and 5 (window closed) times nearby ambient concentrations (Jeong et al., 2004), while NO<sub>2</sub> concentrations in school bus cabins (Fitz et al., 2003), and passenger cars (Shikiya et al., 1989) in Los Angeles were found to be 2-4 times nearby ambient concentrations. In the absence of any invehicle naphthalene measurements for Southern California, an average in-vehicle-to-ambient naphthalene ratio of three was assumed for exposure assessment.

#### 4.1.6. Environmental tobacco smoke (ETS)

ETS can increase indoor naphthalene concentrations and personal exposure (Gold et al., 1991). However, no quantitative information is available for naphthalene exposures due to ETS for the Southern California population. The impact from ETS was examined in a separate sensitivity test, in which a steady-state mass balance model (Eq. (1)) (Ozkaynak et al., 1996) combined with time-activity sampling was used to estimate the exposure due to the ETS alone

$$C_{\rm indoor} = \frac{paC_{\rm out}}{a+k} + \frac{Q_{\rm is}}{(a+k)V},\tag{1}$$

where p is the penetration coefficient; a is the air exchange rate  $(h^{-1})$ ; k is the decay rate  $(h^{-1})$ ;  $Q_{is}$  is the mass flux generated by indoor ETS sources  $(ng h^{-1})$ ; and V is the house volume  $(m^3)$ .

Adjustments were conducted to the time–activity profiles (1987–94), to account for lower smoking rates among the California population in recent years, as documented in the California Tobacco Survey (Pierce et al., 1998) that reported an overall residential ETS exposure rate of 13%. Naphthalene emission rates of 110  $\mu$ g/cigarette (Guerin et al. 1992) and 40  $\mu$ g/cigarette (Singer et al., 2003) were used as the upper and lower bound of the emission strength. A smoking rate of 20 cigarettes/day (Pierce et al., 1998) was assumed. The average number of smokers in a home including a nonsmoker was taken to be 1.4 (Pirkle et al., 1996). Air exchange rates were sampled from a lognormal distribu-

tion with a geometric mean (GM) of  $0.7 h^{-1}$  and a geometric standard deviation (GSD) of 2.2 (Murray and Burmaster, 1995). House volumes were log-normally distributed with a GM of 320 m<sup>3</sup> and a GSD of 1.8 (Murray, 1997). A unit penetration rate was assumed since our focus is only on gas-phase naphthalene. A decay rate of  $0.06 hr^{-1}$  was assigned for naphthalene in indoor air assuming it had a half-life of 11 h.

#### 4.2. REHEX assessment for naphthalene

The REHEX model yielded mean hourly naphthalene exposures of 270 and  $430 \text{ ng m}^{-3}$  for the Southern California population in summer and winter cases, respectively. These mean hourly exposures are about 80% higher than the population-weighted outdoor concentrations (150 and  $230 \text{ ng m}^{-3}$ ) because of indoor sources and in-vehicle exposures. As indicated in Fig. 11, the model estimates that more than one million people in Southern California are exposed to naphthalene concentrations exceeding  $1000 \text{ ng m}^{-3}$  for one or more hours during the 5-day winter episode. Approximately, 80,000 people are estimated to be exposed to concentrations above  $2000 \text{ ng m}^{-3}$  for one or more hours during the 5-day winter episode. In the summer episode, about 300,000 and 2000 people are estimated to received one or more hours of exposure to concentrations above 1000 and  $2000 \text{ ng m}^{-3}$ , respectively (compare Figs. 11a and b).



Fig. 11. Estimated number of persons exposed to one or more hours of naphthalene exposure above various concentration thresholds in (a) the summer episode, 16–20 July 1998 and (b) the winter episode, 2–6 November 1999.

This result is determined mainly by the predicted seasonal variations in air quality in the region.

No significant differences in exposure are found between demographic groups, partly due to the fact that the distances of indoor and outdoor activities from major roadways were coarsely represented in the regional analysis with 5-km resolution and only three microenvironments were included in this study with the same I/O ratio distribution assigned to all of the demographic groups, reducing possible variances in patterns of consumer product usage.

Indoor sources and travel in vehicles accounted for 40% and 4% of the total exposure, respectively. Exposure due to ETS was  $5-14 \text{ ng m}^{-3}$ , which accounted for only 2-5% and 1-3% of the total exposures in the summer and winter, respectively. This result indicates ETS is not a significant source of population naphthalene exposure, at least for the Southern California population where smoking rates have declined significantly in recent years. However, we did not calculate naphthalene exposures due to direct smoking activities of single individual smokers, whose exposure to naphthalene while smoking should be significantly higher.

# 5. Conclusions

We have applied the SMOG airshed model and the REHEX population exposure model to assess distributions of naphthalene and its photooxidation products and human exposure to naphthalene in Southern California. Naphthalene concentrations and naphthalene-to-benzene ratios predicted as part of this study are broadly consistent with recent measurements in this airshed.

Although naphthalene is emitted by a variety of activities, fuel evaporation and engine exhaust are the major sources in Southern California, accounting for about 50% of daily total naphthalene emissions.

The present simulations of naphthalene and 1,4naphthoquinone provide new detailed information on the basin-wide distributions and behavior of these species. Owing to widespread sources involving motor vehicles, naphthalene is ubiquitous in the region, like many other pollutants having distributed sources. Naphthalene concentrations are found to have a high degree of spatial variability, with large diurnal and seasonal variations as well. On a regional basis, naphthalene exhibits peak concentrations in the early morning hours in the winter season, and in the urban Los Angeles core.

Based on our modeling analysis, the mean hourly naphthalene exposure for the Southern California population is  $270 \text{ ng m}^{-3}$  under the summer synoptic conditions. In a winter setting, the mean exposure is

430 ng m<sup>-3</sup>. There is a substantial uncertainty in these values due to uncertainties in naphthalene emission rates, population activity patterns, and indoor exposure levels. Higher concentrations of naphthalene are experienced by a fraction of the population. For example, more than one million people experienced naphthalene levels greater than 1000 ng m<sup>-3</sup> during the winter episode studied here, and nearly 100,000 were exposed to average concentrations exceeding 2000 ng m<sup>-3</sup>. Such exposures may be significant in terms of health effects and policy responses.

The photooxidation products of naphthalene, including naphthoquinones and nitro-naphthalenes, may be more toxic than the parent species. Our modeling analysis shows naphthoquinones are widely distributed in Southern California. However, the atmospheric concentrations and emission sources of these species are not well quantified at this time. Additional field and laboratory research in support of regional modeling will be needed to characterize naphthoquinone concentrations, distributions and exposures in the Southern California urban environment.

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