FINAL REPORT

Air Quality Impacts of Ship Emissions in the South Coast Air Basin of California

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Principal Investigator:
Donald Dabdub, UC Irvine

Co-Researchers:
Satish Vutukuru

Prepared for:
State of California Air Resources Board
Planning and Technical Support Division
PO Box 2815
Sacramento CA 95812

Contact Information:
Donald Dabdub
Department of Mechanical Engineering
University of California, Irvine
Irvine, CA 92697
(949) 824-6126

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1. INTRODUCTION

Ship emissions are becoming a significant source of air pollution in cities near major ports. Recent estimates of global sulfur and nitrogen oxide emissions from international shipping are 6.49 Tg S and 6.87 Tg N respectively (Corbett and Koehler, 2003). Emission containing oxides of nitrogen (NO_x) and sulfur (SO_x), are processed by atmospheric chemical and physical mechanisms resulting in the formation of secondary pollutants such as ozone and particulate matter (PM). Although ship emissions currently constitute only a small fraction of total global emissions, they could have important environmental effects on coastal areas near ports with heavy ship traffic as shown in studies for regions in Europe, Asia and North America (Dore et al., 2007; Derwent et al., 2005; Endresen et al., 2003; Lu et al., 2006; Streets et al., 2000).

According to the International Maritime Organization (International Maritime Organization, 2000), 80% of shipping traffic occurs in the Northern Hemisphere of which 75% occurs within 400 km from coast. Emissions from such shipping activities undergo atmospheric transport and may affect coastal air quality. Environmental regulation over past two decades led to the reduction of emissions from land-based sources. However, today ships represent a major unregulated source category. Furthermore, emissions from shipping activities are growing. Ship emissions will increase significantly in next 10 to 40 years owing to expanding international commerce (Eyring et al., 2005). As a result, it is necessary to understand atmospheric impacts of these emissions, especially on regional air quality.

This study evaluates the impacts of ship emissions on ambient ozone and particulate matter concentrations in the South Coast Air Basin of California (SoCAB). The South Coast air basin contains Los Angeles and Long Beach ports. The Los Angeles port is the busiest port in United

States, followed by the neighboring Long Beach port, in terms of cargo volume processed (BST Associates, 2007). The two port complexes combined form the fifth-largest port complex in the world, bringing in about one-third of total container cargo arriving to the United States. Ships that visit these ports are mostly ocean-going vessels carrying containerized cargo and liquid fuels.

Ocean-going vessels are propelled by two-stroke diesel engines with power ranging from 10 to 70 MW. These engines run on residual fuel, emitting high levels of NO_x, SO_x and particulate matter. Further, such marine fuels contain high levels of sulfur, resulting in particularly high levels of SO_x emissions. For instance, the world-wide average sulfur content in marine fuels is 2.7% (27,000 ppm) (Entec 2002), while the state of California's sulfur limit for on-road diesel is 1800 times less at 0.0015% (15 ppm). Therefore, contribution of ship emissions to ambient sulfates is of particular interest.

Previous studies evaluated the impact of ship emissions focusing on global issues. Lawrence et al., (1999) showed increase in surface ozone and OH radical concentrations when NO_x emissions from ships are included in a global chemistry-transport model. Similarly, Capaldo et al., (1999) calculated an increase of SO_2 concentrations as high as 60% when sulfur emissions from ships are included in a global model. Ship emissions also lead to increase in aerosol production through enhancement of OH radical concentration. A 30% increase in sulfate aerosol is predicted due to sulfur emission from ships (Capaldo et al., 1999). Streets et al., (2000) concluded that parts of Southeast Asia receive significant amounts of sulfur deposition due to ship emissions. More recently, studies with updated emission inventories show a maximum perturbation of 12 ppb for tropospheric ozone concentrations (Endresen et al., 2003). Derwent et al., (2005) applied a Lagrangian chemistry-transport model and showed that contribution of ships

to sulfur deposition is as high as 55% for some locations in Europe. Although global and continental scale modeling studies established the importance of ship emissions, there are only few studies available that quantify the impact of ship emissions on smaller scales using high-resolution models.

Section 2 describes the methodology in detail, which is followed by Section 3 containing results for the base year. Impacts for future year using projected emission inventories are presented in Section 4.

2. METHODOLOGY

In Southern California, high levels of ozone occur during the summertime due to high temperatures and stagnant conditions. High ozone enhances the formation of secondary particulate matter, also leading to high levels of PM (Meng et al., 1997). Therefore, a summer episode is selected for this study. Air quality impacts of ship emissions are quantified by analyzing the difference between model-predicted ambient concentrations that include ship emissions and those that do not include ship emissions. Eight-hour and one-hour average concentrations are used to analyze ozone impacts and 24-hour average concentrations are used for PM impacts.

Air quality simulations are performed using the UCI-CIT model. The UCI-CIT model was developed at the California Institute of Technology (Harley et al., 1994) and is now under continuous development at the University of California, Irvine. The model incorporates state-of-science modules to simulate the atmospheric chemistry, transport and aerosol formation processes to predict spatial and temporal distribution of atmospheric trace gases and particles. The UCI-CIT model has been applied extensively for atmospheric studies for the southern

California region: investigation of chlorine chemistry (Knipping and Dabdub, 2003); study of the coupling between particulate matter and NO_x and VOC emission controls (Nguyen and Dabdub, 2002a); calculation of incremental aerosol reactivity (Carreras-Sospedra et al., 2005); assessment of air quality impacts from distributed power generation (Rodriguez et al., 2006, 2007); and dynamics of secondary organic aerosol (Vutukuru et al., 2006).

The UCI-CIT model solves numerically mass conservation equations for modeled species on a computational grid to obtain spatially and temporally resolved concentrations of gas and aerosol species of interest. Atmospheric gas-phase chemistry is modeled using the Caltech Atmospheric Chemical Mechanism (CACM) (Griffin et al., 2002). The CACM mechanism is a lumped species mechanism that includes detailed chemistry of organic compounds in air quality simulations. CACM includes a total of 191 species, of which chemistry of 120 species is tracked explicitly, 67 species are assumed to be pseudo-steady-state and 4 species are constant.

Inorganic aerosol calculations are performed using Simulating Atmospheric Equilibrium 2 (SCAPE2) (Meng et al., 1998). Aerosol concentrations are resolved into eight size bins and are obtained by solving the condensation/evaporation equation in a fully dynamic fashion (Meng et al., 1998). An operator-splitting technique (McRae and Seinfeld, 1982) is implemented to decouple the individual processes and obtain a numerical solution. This technique provides flexibility to use different numerical schemes for each numerical operator (i.e. atmospheric mechanism that affects concentration of modeled species). For this study, the Quintic Splines Taylor Series Expansion (QSTSE) algorithm is used to solve the advection equation (Nguyen and Dabdub, 2001). The condensation/evaporation equation associated with inorganic aerosol dynamics is solved by the Partitioned Flux Integrated Semi-Lagrangian Method (PFISLM) (Nguyen and Dabdub, 2002b).

The UCI-CIT model has been evaluated in previous studies using data from extensive field campaigns. Meng et al., (1998) compared aerosol calculations with observations from the 1987 summer campaign. Similarly, the performance of the model with respect to ozone predictions is presented by Griffin et al., (2002). In addition to model validation, extensive sensitivity studies are also conducted for the model. Carreras-Sospedra et al., (2005) evaluated model sensitivity to input meteorological parameters (temperature, UV radiation, mixing height, and wind speed), boundary and initial conditions, and model components (chemical mechanism and advection solvers). Rodriguez et al., (2005) used Monte Carlo methods to study uncertainty and sensitivity of CACM mechanism to chemical rate parameters.

2.1. Model Configuration

Modeling domain for this study is shown in Figure 1 and covers the south coast air basin (SoCAB) of California. The modeling domain includes port complexes of Los Angeles and Long Beach, part of Pacific Ocean that contain shipping lanes traversed by ships visiting these ports along the coasts of Santa Barbara and Ventura. The model domain is divided in to a computational grid of 80 X 30 cells in the horizontal direction of 5 km X 5 km resolution. In the vertical dimension, the model domain is resolved in to 5 layers up to 1100 m using terrain following coordinates. The heights of individual layers are 38.5, 154, 308, 671 and 1100 m.

The UCI-CIT model requires gridded fields of hourly meteorological parameters (temperature, wind and relative humidity) and basin-wide emission inventories. Meteorological data are used from a field campaign conducted in 1987 that enables to simulate a three-day air quality episode. This dataset was collected during the Southern California air Quality Study (SCAQS), an extensive campaign of atmospheric measurements that occurred in the SoCAB during August 27–29, 1987. This dataset was used to validate the UCI-CIT model in several air

quality studies (Meng et al., 1998, Griffin et al., 2002). Furthermore, the South Coast Air Quality Management District (SCAQMD) of California used this dataset to develop air pollution control strategies in order to attain ozone attainment by 2010. Zeldin et al., (1990) showed that this episode is statistically within top 10% of severe ozone-forming metrological conditions.

In the SoCAB, dominant direction of wind is from west (Pacific Ocean) to east (inland locations) resulting from onshore pressure gradients. The meteorological conditions during the SCAQS episode are representative of this pattern, resulting in emissions from urban areas around Los Angeles being transported to inland areas around Riverside in the eastern part of the domain. During the SCAQS episode, temperatures ranged from moderate (15 – 20 ^{o}C) in the night to high (40 – 42 ^{o}C) at inland locations in the afternoon. Further, a well-defined diurnal inversion layer formed at the top of neutral/unstable layers near the surface and a slightly stable boundary layer during the night led to low mixing heights (~50 to 1100 m) during the episode. Low mixing heights lead to limited vertical mixing, and thus causing high concentration of pollutants due to accumulation. Carreras-Sospedra et al., (2006) provides further description on meteorological aspects of this episode.

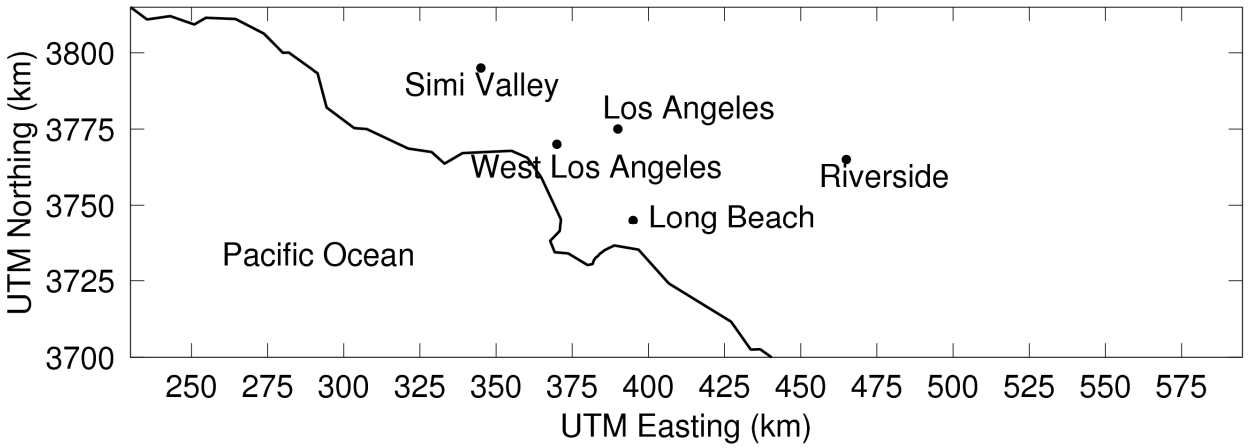

Figure 1: Modeling Domain of the study that covers most of the South Coast air basin of

California.

2.2. Ship and Land-based Emissions in Southern California

Estimation of emissions from shipping activities is a challenging exercise; as such task requires extensive data on ship traffic, characteristics of ships such as engine size, fuel and power usage and finally estimates of emission factors. A global geographically-resolved emission inventory developed by Corbett and Fishbeck (1997) was used in early global modeling studies that showed the importance of ship emissions (Capaldo et al., 1999). In the following years, several estimates of ship emissions were developed using various assumptions and data sources. They include studies that derive emission estimates from global fuel-consumption statistics (Corbett et al., 1999), from satellite observations (Richter et al., 2004), and activity-based estimates that use operation profile of ship traffic (Endresen et al., 2003; Corbett et al., 2003).

This work uses the ships emission inventory recently developed by Corbett et al., (2007). The new inventory represents the most recent estimate currently available for ship emissions from ocean-going commercial and passenger vessels in the North American region (Wang et al., 2007). The inventory was developed using a bottom-up methodology to obtain a spatially-resolved inventory using historical ship movements, ship attributes and ship emission factors. Aggregated estimates of monthly emissions for North American region are available for years 2002, 2010 and 2020. August estimates are used in order to evaluate the impact of ship emissions during summer months.

Air quality models simulate episodes of few days using emissions data that is resolved in spatial and temporal dimensions and chemical speciation. The UCI-CIT model requires hourly and speciated emissions data over the modeling region. Two assumptions are made in order to

develop emission inventories using aggregated data from Corbett et al., (2007). First, daily emissions for summertime are obtained from aggregated geographically-resolved August month emissions by dividing by 31, i.e. assuming that total emissions do not differ significantly on daily basis for a given month. The hourly-resolved emissions are obtained by assuming uniform distribution during the day. . However, ship emissions are expected to show some diurnal and weekly variation as port operations occur mostly during the day on weekdays. Therefore, a parametric analysis is conducted to evaluate the effect of temporal profile of ship emissions. In the first scenario that accounts for diurnal variation, 70% of total daily ship emissions occur between 8 AM to 8 PM and 30% occur between 8 PM to 8 AM. In the second scenario, the first day of the three-day episode is assumed to be a weekend day or a holiday, followed by two weekday emissions. Ship emissions during the weekend day are assumed to be at 50% of weekday emissions, keeping the total emissions during the month as estimated by Corbett et al., (2007). Model results from air quality simulation of these scenarios show that although impacts of ship emissions depend on temporal profile, only small differences are observed in comparison with the case that assumes uniform emissions. Therefore, the assumption of uniform rate of emissions serves well in the absence of high-resolution ship emissions data.

Second assumption relates to speciation of hydrocarbon and PM emission from ships as such data is currently not available. This study uses the California Air Resources Board (CARB) profile of internal combustion engine using distillate fuel that closely represents engines used to power ocean-going vessels (Table 1). Similarly, speciation and size-distribution of particulate matter emissions is obtained from CARB speciation profile for the combustion of distillate fuel (Table 2). As per CARB size-distribution profile, 95% of particles are in PM2.5 size range and 97% are in PM10 size range.

Land-based emissions include gridded fields of both surface and elevated emissions. These emissions are developed using the SoCAB emission inventory for the year 1997, which was used in the development of South Coast air quality management plan adopted in 2003 by SCAQMD. The 1997 inventory is scaled to the level of year 2002 emissions using countywide aggregate data available from CARB. The summary of domain-wide emissions for the year 2002 with and without ship emissions is shown in Table 3. Daily NO_x and SO_x emissions from ships in the modeling domain are 38.4 and 22.8 tons respectively. Ships contribute up to 25% of total SO_x emissions in the modeling domain. As mentioned before, this is due to the use of fuel with high sulfur content. NO_x emissions are at about 7% of total domain-wide emissions. VOC and PM emissions are less than one percent. Figures 2 - 5 show geographic distribution of total NO_x and SO_x emissions in the domain and from ships only. Emissions of NO_x and SO_x are concentrated in urban areas along the coast. Ship emissions occur along the coast of Los Angeles and Ventura counties. Ship emissions are treated as area sources in the first layer. As seen in Figures 2 - 5, most of the ship emissions (approximately 90%) occur within 45 km (24 nautical miles) from the coast.

Table 1: Speciation of VOC Emissions.*

Specie	Fraction
Methane	0.116
Ethane	0.028
Ethylene	0.287
Propylene	0.173
Acetylene	0.113
1-Butene	0.134
1,3-Butadiene	0.070
Benzene	0.079

* Source: Speciation profile data from California Air Resources Board. Available at: http://www.arb.ca.gov/ei/speciate/dnldopt.htm#specprof

Table 2: Speciation and size distribution of particulate matter from ships.*

Specie	Weight % of total	Weight % of PM 2.5	Weight % of PM 10
Arsenic	0.03	0.04	0.05
Barium	0.05	0.05	0.05
Calcium	0.55	0.55	0.55
Chromium	0.55	0.55	0.55
Cobalt	0.05	0.05	0.05
Copper	0.05	0.05	0.05
Elemental Carbon	22.76	20.18	6.0
Iron	2.83	3.17	4.0
Manganese	0.05	0.05	0.05
Molybdenum	0.05	0.05	0.05
Nickel	0.55	0.55	0.55
Nitrates	0.05	0.05	0.05
Potassium	0.36	0.42	0.55
Selenium	0.04	0.05	0.05
Strontium	0.05	0.05	0.05

Sulfates	44.12	50.26	65.0
Titanium	0.05	0.05	0.05
Vanadium	0.55	0.55	0.55
Other	27.25	23.28	21.75

* Source: Particulate matter speciation profile data from California Air Resources Board. Available at http://www.arb.ca.gov/ei/speciate/dnldopt.htm#specprof

Table 3: Summary of daily domain-wide emissions for year 2002.

	Without ship emissions (tons/day)	With ship emissions (tons/day)	Emissions from Ships (tons/day)	Ship emissions as percentage of total basin-wide emissions (%)
NO_x	874.5	912.9	38.4	4.2
SO_x	72.0	94.8	22.8	24.1
VOC	580.0	582.9	2.9	0.50
PM	1215.5	1216.4	0.9	0.07

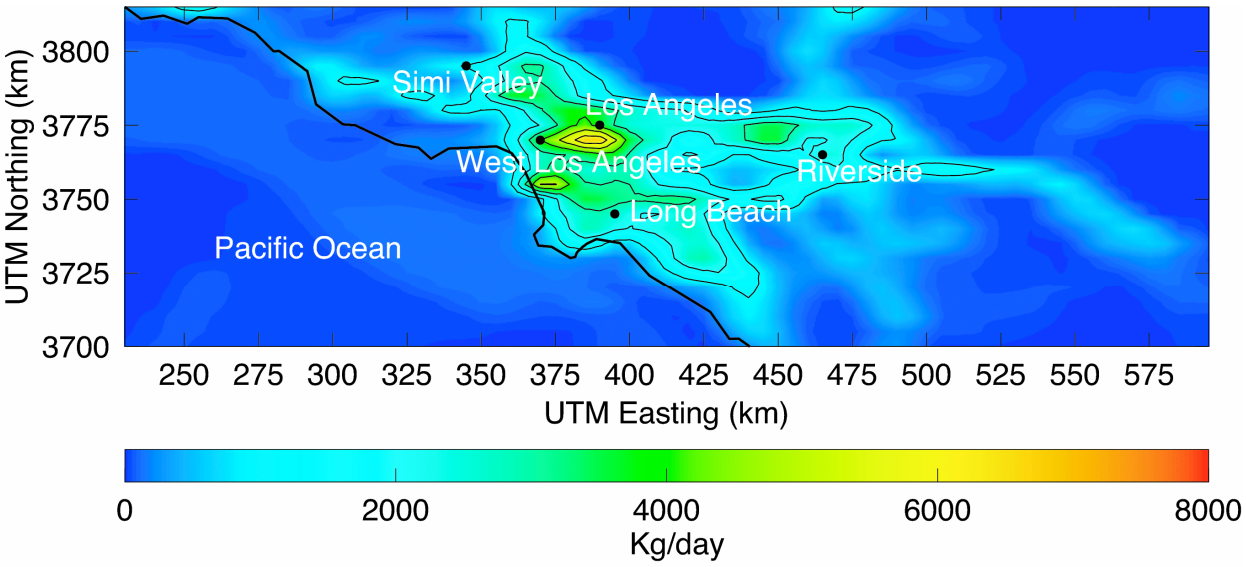

Figure 2: Spatial distribution of NO_x emissions for year 2002 in the South Coast air basin of California in Kg/day.

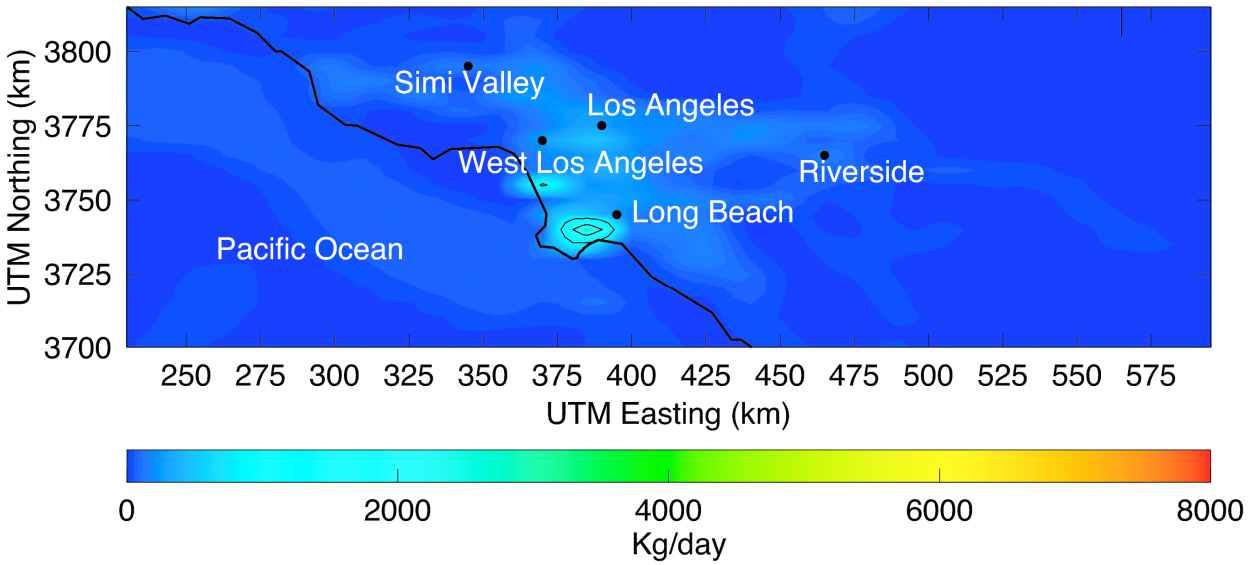

Figure 3: Spatial distribution of SO_x emissions for year 2002 in the South Coast air basin of California in Kg/day.

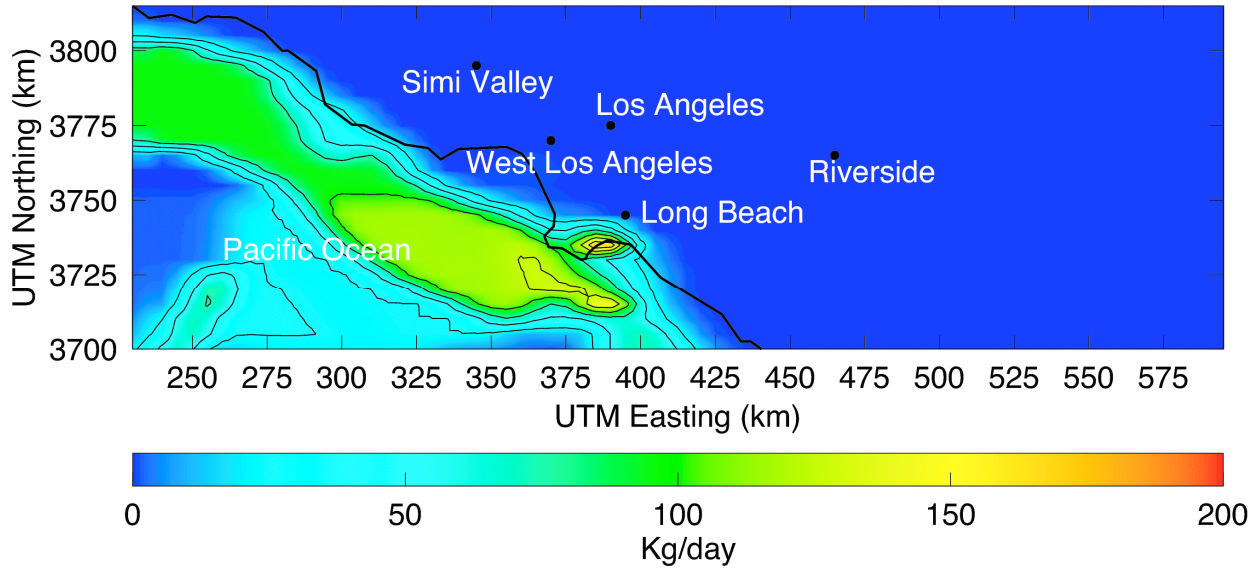

Figure 4: Spatial distribution of NO_x emissions from ships for year 2002 in the South Coast air basin of California in Kg/day.

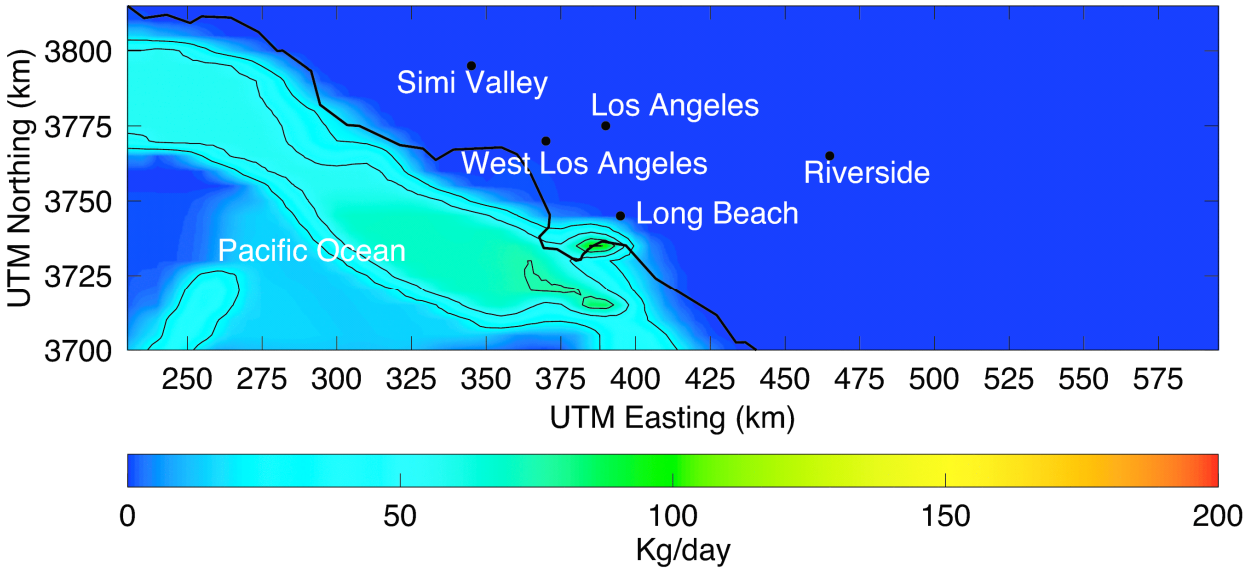

Figure 5: Spatial distribution of SO_x emissions from ships for year 2002 in the South Coast air basin of California in Kg/day.

3. IMPACT OF SHIP EMISSIONS ON AIR QUALITY

3.1. NO_2 and SO_2 Concentrations

Figures 6 and 7 show 24-hour average concentration of NO_2 and SO_2 respectively with ship emissions included in the simulation. Only a small fraction of NO_2 is emitted directly from ships. Most of the NO_2 is formed from the photo-oxidation of NO. The distribution of NO_2 is similar to that of emissions of NO_x as shown in the Figure 2. High concentrations of SO_2 are observed at locations closer to Long Beach where large petroleum refining operations emit high amounts of SO_x. However SO_2 concentrations in the areas of Pacific Ocean with ship emissions are comparable to that of inland locations. This is due to relatively high level of SO_x emissions from ships as shown in the Figure 3.

Figures 8 and 9 show increases in NO_2 and SO_2 concentrations due to ship emissions. Significant increases are observed in the areas of the Pacific Ocean with direct ship emissions. The increase in these areas is as high as 12 ppb for NO_2 and 4 ppb for SO_2. Increases in NO_2 are also predicted to occur at locations downwind of ship emissions, around Los Angeles and Simi Valley. The increases at these locations are comparable to areas in the Pacific Ocean with direct NO_x emissions. In contrast, increases of SO_2 concentrations are less prominent for inland locations and are in the order of 1 ppb. This is due to faster conversion of SO_2 to aerosol sulfate than NO_2 to ozone or aerosol nitrate. Table 4 shows increases in 24-hour average NO_2 and SO_2 concentrations due to ship emissions at five locations in the domain. NO_2 increase ranged from -0.1 to 7.4 ppb at these locations. A negligible decrease is predicted at Simi Valley with relatively low local NO_x emissions (Figure 2a) and therefore higher rates of conversion of excess NO_x from ships to particulate nitrate. NO_2 increase at Central Los Angeles is 7.4 ppb followed by Long

Beach at 5.9 ppb, both locations are close to the ports and contain high local NO_x emissions. Increase in SO_2 ranged from 1.2 to 0.2 ppb. The highest impact is predicted to occur at Long Beach, the location closest to port emissions. The lowest impact occurs at Riverside, the farthest location from the port among considered here.

Table 4 : Increase in 24-hour average NO_2 and SO_2 concentrations due to ship emissions at locations in the South Coast air basin of California.

Location	24-hour average NO_2 concentration (ppb)			24-hour average SO_2 concentration (ppb)		
	Without Ships	With Ships	Contribution From Ships	Without Ships	With Ships	Contribution From Ships
Simi Valley	23.3	23.2	-0.1	2.1	2.4	0.3
West Los Angeles	30.1	33.4	3.3	1.8	2.2	0.4
Central Los Angeles	51.4	58.8	7.4	4.4	4.7	0.3
Long Beach	46.2	52.1	5.9	8.2	9.5	1.3
Riverside	41.4	43.4	2.0	3.9	4.1	0.2

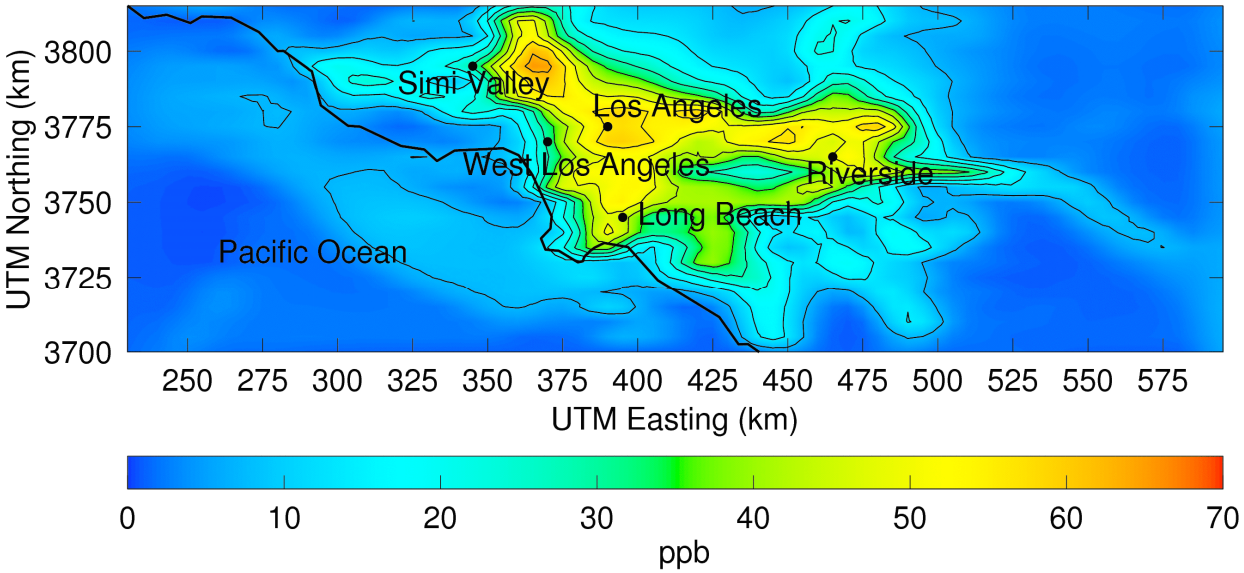

Figure 6: 24-hour average NO_2 concentration (ppb) for year 2002 in the South Coast air basin of California.

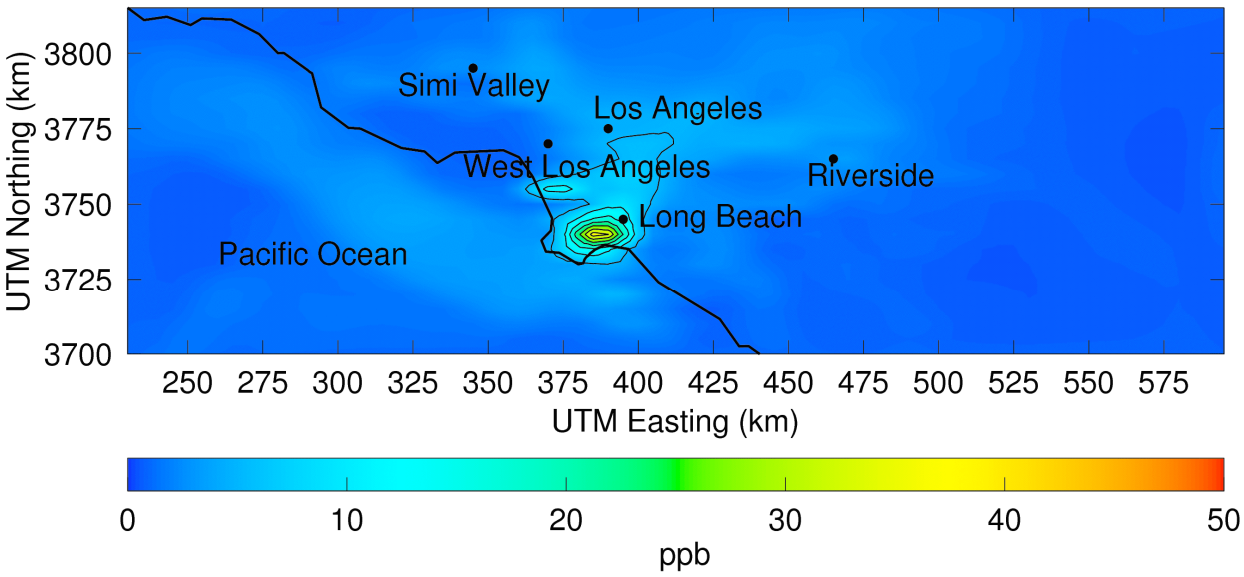

Figure 7: 24-hour average SO_2 concentration (ppb) for year 2002 in the South Coast air basin of California.

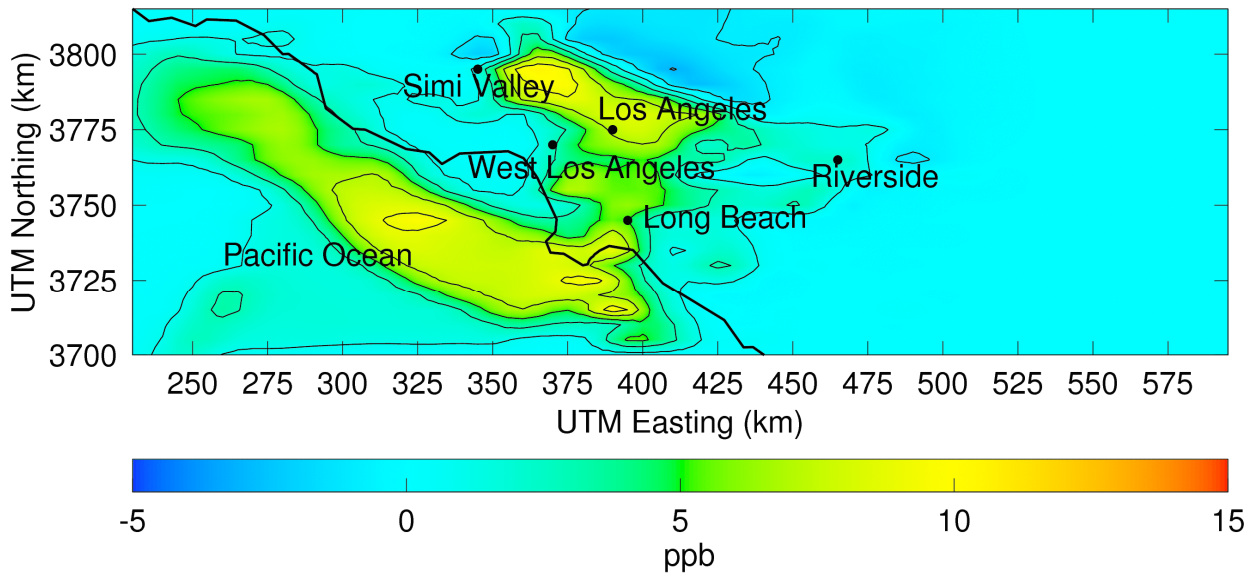

Figure 8: Difference between 24-hour average NO_2 concentration (ppb) for year 2002 in the South Coast air basin of California between cases with and without ship emissions. A positive value indicates an increase in the concentration due to ship emissions.

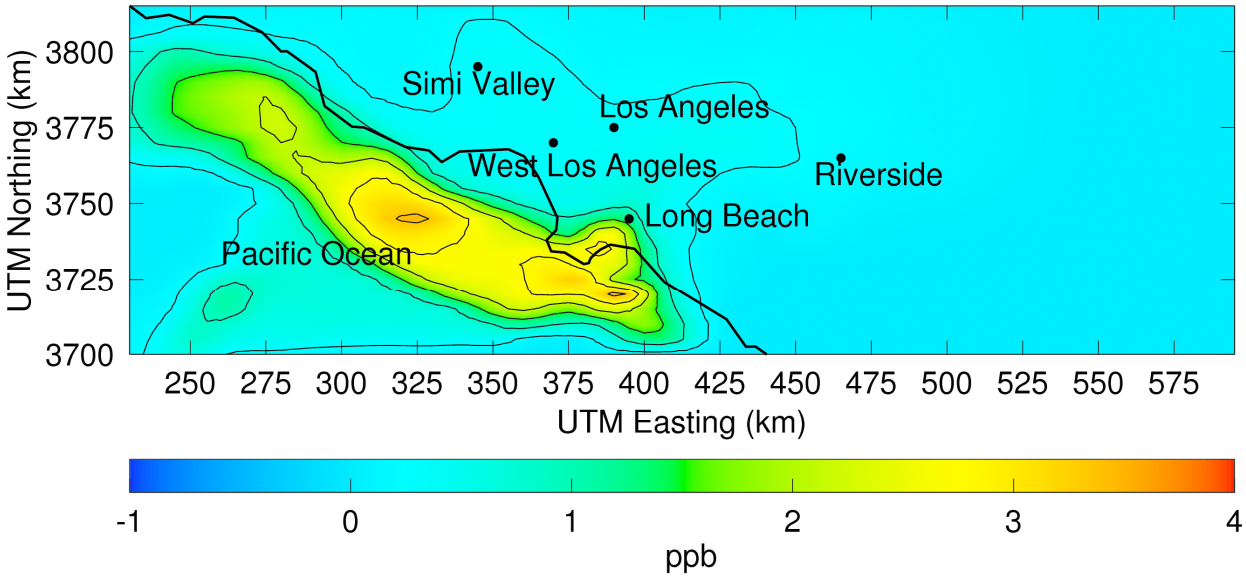

Figure 9: Difference between 24-hour average SO_2 concentration (ppb) for year 2002 in the South Coast air basin of California between cases with and without ship emissions. A positive value indicates an increase in the concentration due to ship emissions.

3.2. Ambient Ozone Concentrations

Ambient ozone, formed from the photochemistry of NO_x and volatile organic compounds, is known to pose health risk to the exposed population. The SoCAB region experiences some of the highest ozone concentrations in the United States, especially during summer months. Ambient ozone concentrations are regulated by United States federal and California state air quality standards. While the California ozone standard is based on peak one-hour and eight-hour average ozone concentrations, federal ozone standard is based upon eight-hour average ozone concentration. The SoCAB is currently designated as a severe non-attainment area towards the compliance with federal eight-hour ozone standard and as non-attainment with respect to state standards. During the year 2006, ambient ozone concentrations in the SoCAB are exceeded on 85 and 102 days against federal eight-hour standard and the state one-hour standard respectively (CARB, 2007). This section presents analysis of increases in predicted maximum one-hour and eight-hour average ozone concentrations due to ship emissions.

Figures 10 and 11 show maximum one-hour average and eight-hour average ozone concentrations on the final day of the simulation that includes ship emissions. High ozone concentrations are predicted in eastern part of the domain, downwind of urban coastal areas. In the SoCAB, emissions from coastal urban areas are transported to inland areas, leading to high levels of pollution in the eastern parts of the domain. This trend is in qualitative agreement with previous studies (Griffin et al., 2002a; Chock et al., 1999). However, the measured peak is closer to the coast than predicted by the model.

Figures 12 and 13 show the difference between maximum one-hour average concentrations for cases with ship emissions and without ship emissions. Positive values indicate increase in concentrations due to ship emissions. Significant increases, up to 25 ppb, are observed along the

coasts of Los Angeles and Ventura counties, which have relatively clean air without ship emissions. Ship emissions are major local sources of ozone precursors in this part of the domain. Under these conditions when background NO_x levels are low, the number of ozone molecules produced per nitric oxide molecule is higher than typical urban conditions due to non-linearity of ozone formation process (Liu et al., 1987). Large increases, up to 29 ppb, are predicted in the region northwest of Los Angeles, downwind of Simi Valley, with already high ozone levels. This is due to daytime sea breeze that moves north of Los Angeles and transports pollutants from coastal regions. Similar trends are observed for increases in maximum eight-hour average ozone concentrations as shown in Figure 13. However, in this case the impact of ship emissions has smaller spatial gradients as compared to impact on one-hour ozone concentration. Maximum domain-wide increase in eight-hour ozone concentration is 24 ppb and occurs along the coast of Los Angeles.

Increases or decreases in ozone concentrations due to ship emissions are both due to transport of ozone itself from the region of ship traffic, and transport of precursor species (NO_x and VOCs) which may increase or decrease ozone formation locally. However, the production of ozone is a highly non-linear function of precursor concentrations (Kleinman et al, 1997; Sillman, 1999). Hence the contribution of ship emissions depends upon the intensity of local precursor emissions, especially NO_x to VOC ratio, and other factors such as temperature. This explains why relatively small increases in ozone from ship emissions are predicted in the Los Angeles area. Region around Los Angeles is NO_x rich (Griffin et al. 2004) and further increase in NO_2 due to ship emissions leads to a decrease in ozone concentration. Therefore, the combined effect of transport of ozone and ozone precursors from the region of ship traffic leads to an overall smaller effect from ship emissions in that area as compared to other coastal locations.

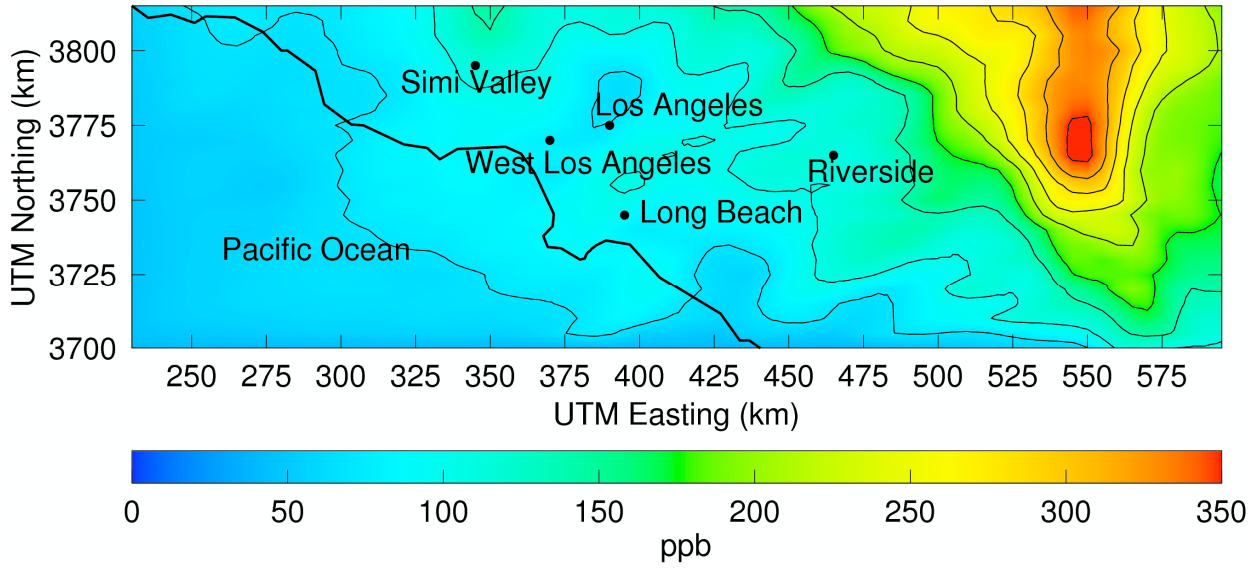

Figure 10: Maximum one-hour ozone concentration (ppb) for year 2002 in the South Coast air basin of California.

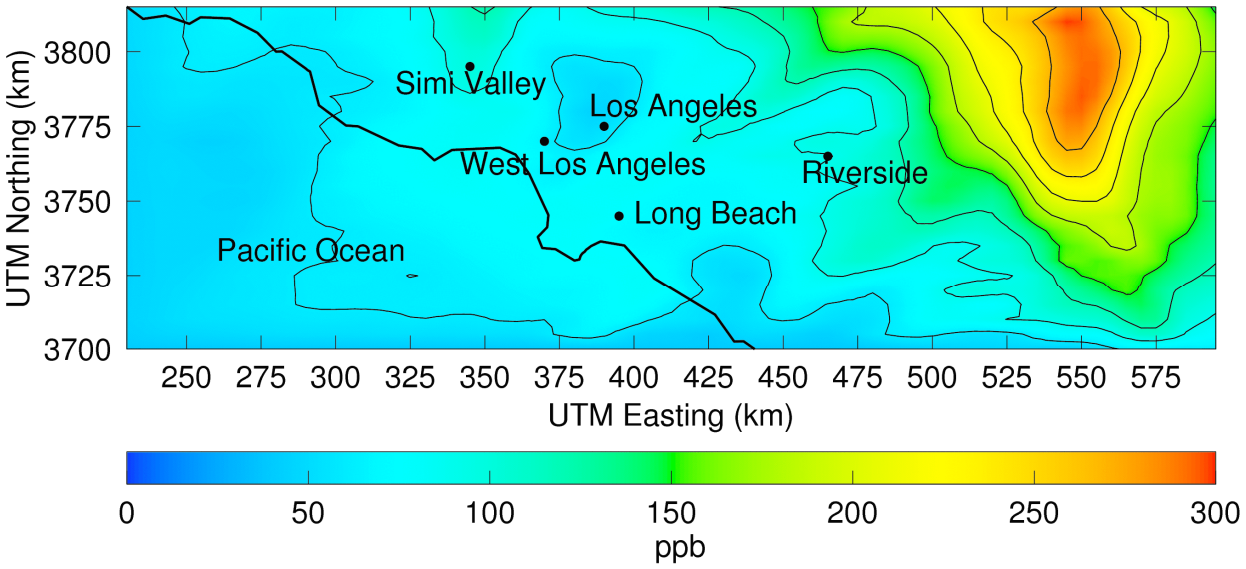

Figure 11: Maximum eight-hour ozone concentration (ppb) for year 2002 in the South Coast air basin of California.

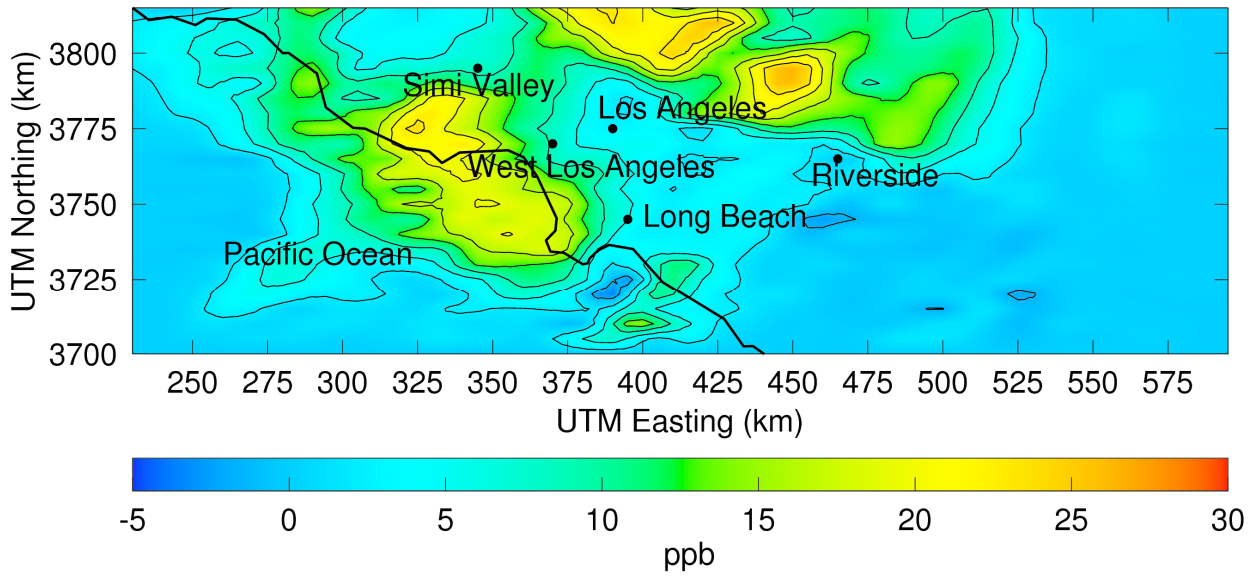

Figure 12: Difference between one-hour ozone concentration between cases with and without ship emissions for the year 2002 in the South Coast air basin of California. A positive value indicates an increase in the concentration due to ship emissions.

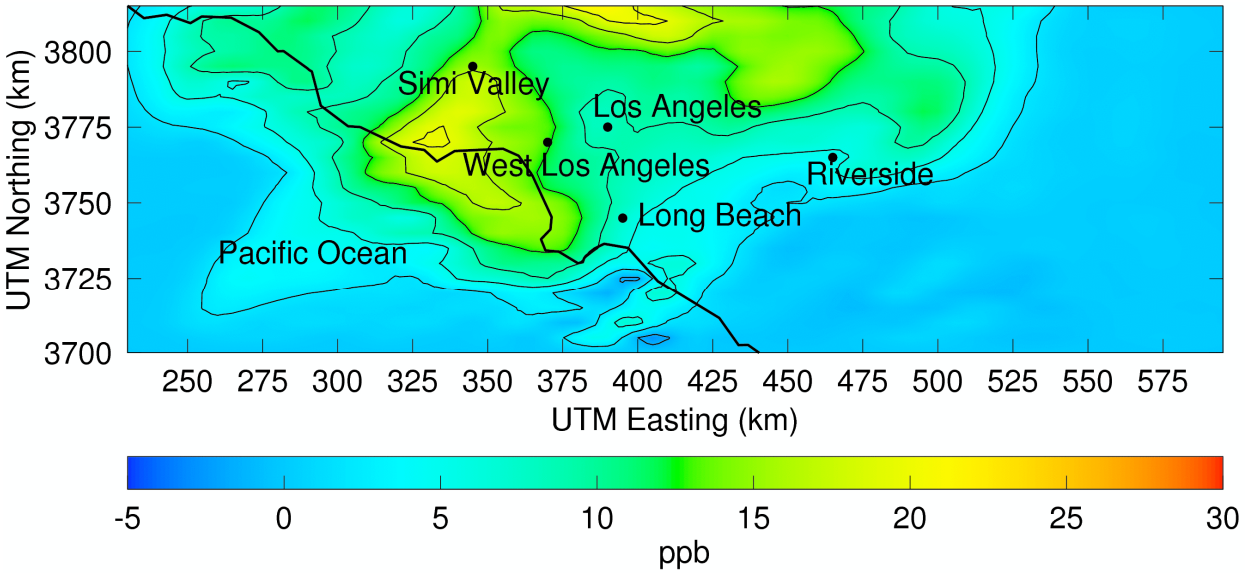

Figure 13: Difference between eight-hour ozone concentration between cases with and without ship emissions for the year 2002 in the South Coast air basin of California. A positive value indicates an increase in the concentration due to ship emissions.

Table 5: Increase in ozone concentrations due to ship emissions at locations in the South Coast air basin of California.

Location	Peak one-hour ozone Concentration (ppb)			Peak eight-hour ozone Concentration (ppb)		
	Without Ships	With Ships	Contribution From Ships	Without Ships	With Ships	Contribution From Ships
Simi Valley	116.0	124.1	8.1	87.8	104.2	16.4
West Los Angeles	60.6	68.8	8.2	45.1	58.2	13.1
Central Los Angeles	56.0	60.5	4.5	37.1	45.0	7.9
Long Beach	86.1	92.4	6.3	69.8	76.2	6.4
Riverside	110.5	110.0	-0.5	82.2	86.5	4.3

Table 5 shows increases in maximum eight-hour and one-hour average ozone concentrations at Simi Valley, West Los Angeles, Central Los Angeles, Long Beach, and Riverside for cases with ship emissions and without ship emissions. For these locations, increases in eight-hour concentrations ranged from 4.3 to 16.4 ppb. The range of impact on one-hour ozone concentrations is -0.5 to 8.1 ppb. For both metrics, the minimum impact is predicted at Riverside – the farthest location from the coast among considered here.

Lawrence et al., (1999) reported the increase in summertime average ozone concentration by 10% in the Southern California region using a global model and 1993 emission inventories on a coarse grid. When 24-hour ozone averages are calculated using results from this study over aggregated cells around the ports with area similar to those in global models (1^o x 1^o), increase in

ozone is 9%. Therefore, the impacts from this regional-scale modeling study are in the same range as coarser scale studies. However, this study shows how individual locations are affected to a varying extent, given much smaller spatial scales and the use of more detailed physical and chemical mechanisms. For instance, the corresponding percentage increase in 24-hour average ozone concentrations due to ship emissions from this work is 35% at Simi Valley, 32% at West Los Angeles, 26% at Central Los Angeles, 13% for Long Beach and 1% for Riverside locations.

3.3. Ambient PM Concentrations

Ambient PM is linked to adverse health effects and hence is designated as a criteria pollutant by United States Environmental Protection Agency. Southern California region exhibits some of the highest levels of ambient particulate matter and experiences large number of days with ambient PM concentrations exceeding the state and federal air quality standards (CARB, 2007). Besides direct emission of particles from combustion and other sources, a significant fraction of this PM is formed through secondary processes from gas-phase emissions. As previous modeling and field studies showed, particulate nitrates and sulfates formed from NO_x and SO_x emissions are major components of PM in the SoCAB (Sawant et al., 2005; Kim et al., 2000). In this section, contribution of ship emissions to ambient PM is quantified by analyzing model-predicted PM concentrations for cases with and without ship emissions.

Figures 14 and 15 show 24-hour average concentrations of PM2.5 nitrate and sulfate on the final day of simulation that includes ship emissions. The peak PM2.5 nitrate concentration is approximately 61 $\mu g/m^{-3}$ and occurs in the inland portion of the domain, northeast of Riverside. This regional distribution is in qualitative agreement with previous modeling and measurement studies (Ying et al., 2006; Sawant et al., 2004; Kim et al., 2000). Although NO_x emissions are mainly concentrated in the coastal areas, formation of particulate nitrate as ammonium nitrate

(NH_4NO_3) is limited by the availability of gas-phase ammonia (Nguyen and Dabdub, 2002). Presence of ammonia emissions from dairy operations in the Riverside area and transport of NO_x to inland areas leads to this regional distribution. However, in recent years, ammonia emissions in the Riverside have decreased. Therefore, modeling studies using the latest emission inventories may show a different regional distribution of particulate nitrate in the SoCAB. The peak PM2.5 sulfate concentration is predicted to occur in the Long Beach area, a coastal location. This is due to intense direct sulfate and SO_x emissions from large petroleum refinery operations in the area (Ying et al., 2006). For inland locations, PM2.5 sulfate is more uniformly distributed than PM2.5 nitrate.

Figures 16 and 17 show 24-hour average concentration difference between cases with and without ship emissions for PM2.5 nitrate and sulfate respectively. Positive values indicate increase in concentrations due to ship emissions. The maximum model-predicted increase for PM2.5 nitrate is 12.8 $\mu g/m^3$ and that for PM2.5 sulfates is 1.7 $\mu g/m^3$. Maximum increases for both species are predicted to occur in northern part of the domain, east of Simi Valley. A region of significant increases for both particulate nitrate and sulfate is also predicted to occur between Los Angeles and Riverside. Table 6 shows increase in sulfate and nitrate concentrations at five locations in the basin: Simi Valley, West Los Angeles, Central Los Angeles, Long Beach, and Riverside. The increases range from 1.7 to 6.7 $\mu g/m^3$ for nitrate and 0.4 to 1.0 $\mu g/m^3$ for sulfate concentrations. Riverside, an inland location about 100 km from the coast, is predicted to experience an increase in total PM2.5 concentrations from ships by 4.3 $\mu g/m^3$. As shown in Table 5, 81.4% of this increase is due to increases in PM2.5 nitrate concentrations due to NO_x emissions from ships.

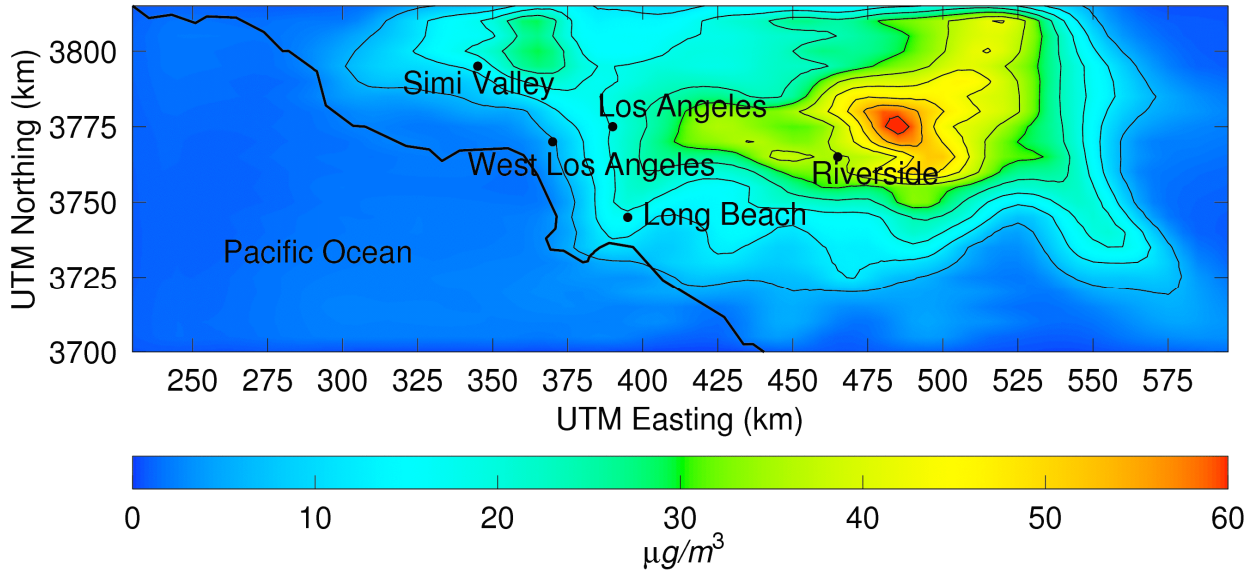

Figure 14: 24-hour average particulate nitrate concentration (μg/m^3) for year 2002 in the South Coast air basin of California with ship emissions.

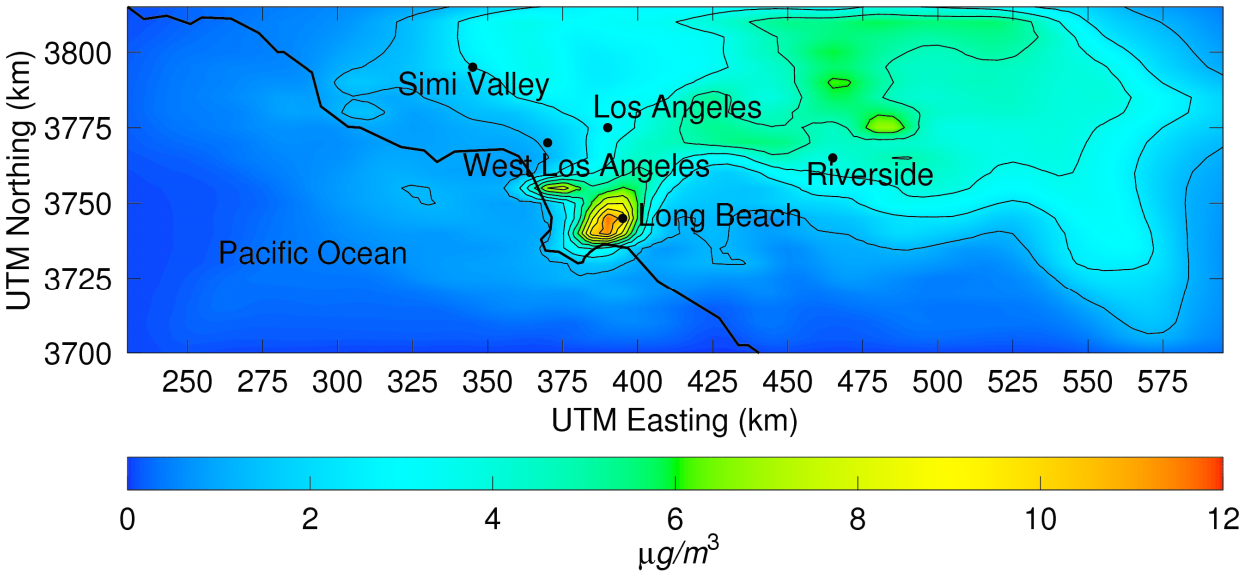

Figure 15: 24-hour average particulate sulfate concentration (μg/m^3) for year 2002 in the South Coast air basin of California with ship emissions.

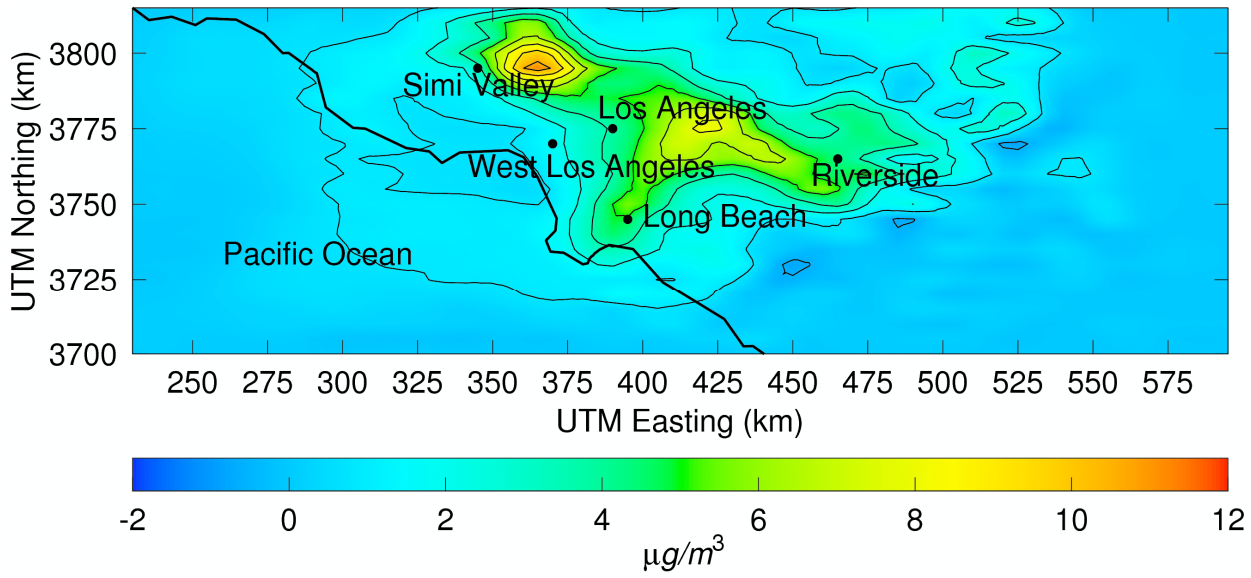

Figure 16: 24-hour average particulate nitrate concentration (μg/m^3) difference for year 2002 between cases with and without ship emissions in the South Coast air basin of California.

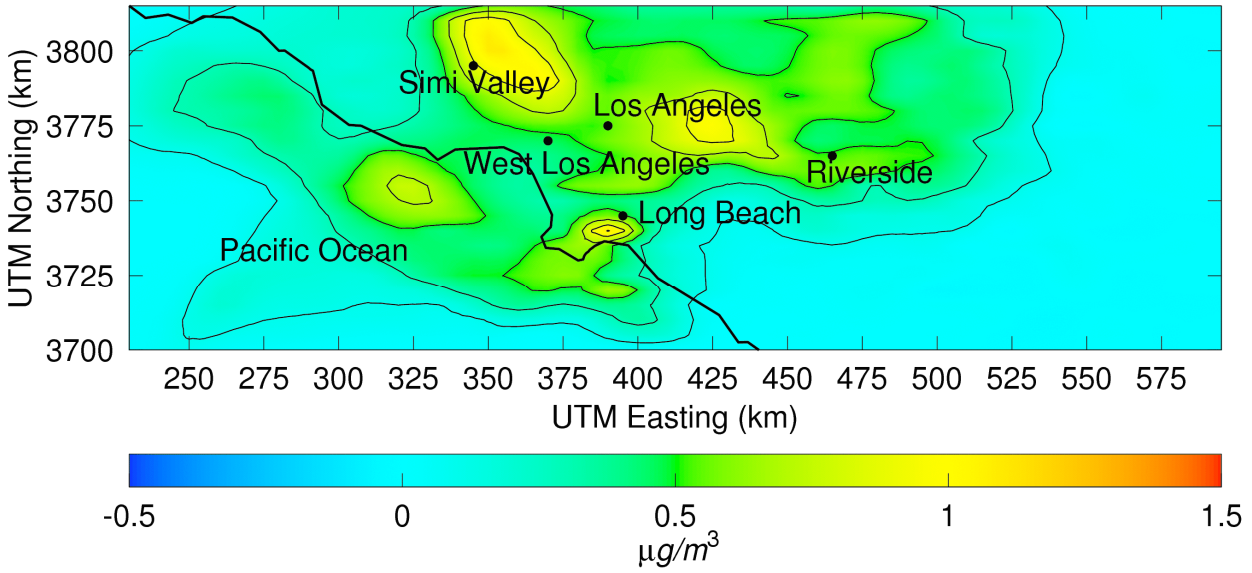

Figure 17: 24-hour average particulate sulfate concentration (μg/m^3) difference for year 2002 between cases with and without ship emissions in the South Coast air basin of California.

Table 6: Increases in 24-hour average nitrate and sulfate concentration at locations in the South Coast air basin of California.

Location	24-hour average particulate nitrate concentration ($\mu g/m^3$)			24-hour average particulate sulfate concentration ($\mu g/m^3$)		
	Without Ships	With Ships	Contribution From Ships	Without Ships	With Ships	Contribution From Ships
Simi Valley	9.1	10.8	1.7	1.4	2.4	1.0
West Los Angeles	2.8	4.8	2.0	0.8	1.3	0.4
Central Los Angeles	14.5	18.2	3.7	2.5	2.9	0.1
Long Beach	14.4	21.1	6.7	10.6	11.2	0.6
Riverside	31.4	35.2	3.8	3.5	4.0	0.5

Direct PM emissions from ships contain a significant amount of sulfate particles due to high sulfur content in marine fuels (Entec, 2002). As discussed in Section 2.2, 45% of total directly emitted PM from ships is in the form of sulfates. However, direct PM mostly affects the region of ship emissions as these particles are deposited rapidly on to the surface. Furthermore, nitrates contribute significantly to total PM2.5 impacts although particulate nitrates in the form of direct PM emissions are negligible (0.01% of direct PM is assumed to be nitrates using the CARB speciation profile). Therefore, most of the contribution from ships to particulate matter at inland locations comes as secondary PM from gas-phase emissions. The formation of secondary particulate matter is heavily influenced by the OH radical concentration. Reaction of OH with NO_2 and SO_2 forms gas-phase HNO_3 and H_2SO_4 respectively. Gas-phase HNO_3 forms NH_4NO_3

in the particulate phase through reaction with NH_3, and H_2SO_4 enters particulate phase through nucleation or condensation on existing aerosol particles. Since ozone is a dominant source of OH radicals in the urban atmosphere, high ozone concentrations in the basin lead to efficient conversion of NO_x and SO_x from ships to particulate nitrate and sulfates. (Meng et al., 1997; Nguyen and Dabdub, 2002). In the presence of clouds and fog, aqueous phase oxidation could play some role. Our study simulates a summertime episode with no cloud cover and fog. Hence, our model does not incorporate any aqueous phase chemistry of SO_2. Southern California experiences cloud cover only on few days during the year. Therefore, it is our sense that aqueous phase chemistry does not play a major role in the conversion of SO_2 to particulate sulfate in the SoCAB.

The impact of ship emissions on annual PM2.5 average concentrations and attainment of PM2.5 standard depends on seasonal variation, spatial extent and distribution of impacts. It is expected that peak impacts occur in the summer due to high levels of secondary PM formation. Therefore, the study, which simulates a summertime episode, can be assumed to predict peak impacts from ships. From the report, summertime simulations show higher increases for particulate nitrate concentrations than sulfate. Therefore, overall PM2.5 concentrations are more affected by nitrate contribution from ships. In the SoCAB, nitrate formation is determined by ammonia and oxidant levels. Consequently, if ammonia emissions are high during Winter and Fall a significant contribution from ships is expected, although not as big as summertime impacts. Secondly it is noted that ozone production from NOx in the area of ship emissions is higher than at coastal and inland locations (which is NOx rich). Therefore, oxidation of NOx and SOx can still occur at considerable levels even in Winter and Fall.

In the SCAB, the eastern portion of the domain (i.e. inland locations such as Riverside)

experiences basin-wide peak levels of PM2.5 and is consistently outside attainment. However, it is observed that ship emissions impact PM2.5 concentrations mostly at coastal and central parts of the domain. Therefore, it is possible that ships impact locations that are in attainment presently. However, increasing ship emissions could lead such locations to PM2.5 levels beyond the attainment limit.

Finally, it is important to consider the magnitude of impact from ships on PM2.5. Figure 18 shows the frequency distribution of impacts from ships in the domain due to total increase in PM2.5 nitrate and sulfate. Model cells with increase in ship concentrations less than 0.1 are excluded in this analysis. As shown in the figure, about 40% and 30% of cells experience increase in concentration between 0 and 1 $\mu g/m^3$ and 1 and 2 $\mu g/m^3$ respectively. Therefore, majority of cells have impacts less than 2 $\mu g/m^3$ PM2.5 concentrations during summer time.

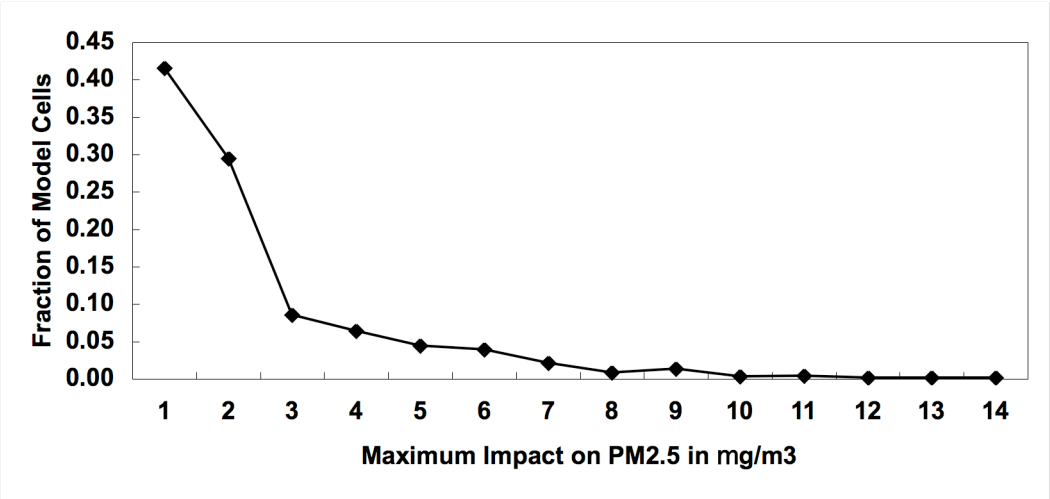

Figure 18: Frequency distribution of PM2.5 impacts from ship emissions

4. FUTURE YEAR IMPACTS

Ship emissions are predicted to increase significantly due to increase in ship traffic (Eyring et al., 2005). Indirect indicators of ship activity such as goods movement, fraction of international trade as a proportion of U.S. gross domestic product are estimated to be growing over 6% per year (Corbett et al., 2007). On the other hand, land-based emissions are projected to decrease due to environmental regulation and the need to comply with air quality standards. Therefore, ship emissions will form a significant portion of regional emission inventories. In this section, the impact of ship emissions for the year 2020 on ozone and particulate matter is quantified using the summer air quality episode described in previous sections.

Corbett et al. (2007) forecasted ship emissions for the year 2020 ("business-as-usual" scenario) by considering potential changes in emission factors, engine sizes, vessel numbers, and fuel quality. Emission forecasts are derived from aggregate installed power of ships after considering such factors. Using these forecasts, ship emissions for a summer day in 2020 are developed as described for the baseline year. Land-based emissions are developed from the 2010 baseline emissions used in the AQMP 2003 plan developed by the South Coast Air Quality Management District. These emissions are scaled to 2020 levels using county-wide factors from emission projections of CARB. Table 7 summarizes estimated total domain-wide and ship emissions for the year 2020. Estimated daily emissions of NO_x and SO_x from ships are 97.9 and 59.1 tons respectively. SO_x emissions from ships contribute almost 40% of total emissions in the basin. NO_x contribution to domain-wide emissions is about 25%, a dramatic increase from 2002 levels.

This is due to both increase in NO_x emissions from ships and anticipated decrease in NO_x emissions from land-based sources in order to achieve air quality standards. Contribution of VOCs is expected to remain less than 2% and that of PM less than 0.5 %.

Table 7: Summary of daily domain-wide emissions for year 2020.

	Without ship emissions (tons/day)	With ship emissions (tons/day)	Emissions from Ships (tons/day)	Ship emissions as percentage of total basin-wide emissions (%)
NO_x	305.8	403.7	97.9	24.2
SO_x	93.6	157.2	59.1	40.5
VOC	662.4	671.2	8.8	1.3
PM	741.9	744.9	3.0	0.40

Figures 19 and 20 show increase in maximum one-hour and 8-hour average concentrations due to ship emissions. Maximum impact is predicted to occur along the coast of Los Angeles County and is around 59 ppb. Ship emissions are the primary source of emissions at these locations and hence high impacts are observed. Some inland sites experience an increase in maximum ozone concentration as high as 30 ppb due to atmospheric transport of precursor species and ozone itself. Impact on maximum 8-hour average concentration is similar to those of one-hour concentrations, however at smaller magnitudes due to longer averaging period. The maximum increase of 45 ppb is predicted to occur along the coast of Los Angeles county, north of Los Angeles and Long Beach port complexes.

Figures 21 and 22 shows differences between 24-hour average concentrations for particulate nitrate and sulfates between cases with and without ship emissions. Maximum impacts are observed at sites downwind of Simi Valley, Los Angeles and Long Beach. The highest impact is predicted to occur downwind of Los Angeles and is about 14 $\mu g/m^3$. Although NO_x emissions from ships increase significantly from 2002 levels, there is no corresponding increase in particulate nitrate concentrations since nitrate formation is limited by the availability of gas-phase NH_3. However, increase of SO_x from ship emissions leads to an increase in particulate sulfates. The maximum increase in particulate sulfates is about 2.5 $\mu g/m^3$ and is predicted to occur downwind of Simi Valley. In contrast to impacts predicted for year 2002, particulate sulfate from ships is observed in eastern portions of the domain in the excess of 1 $\mu g/m^3$.

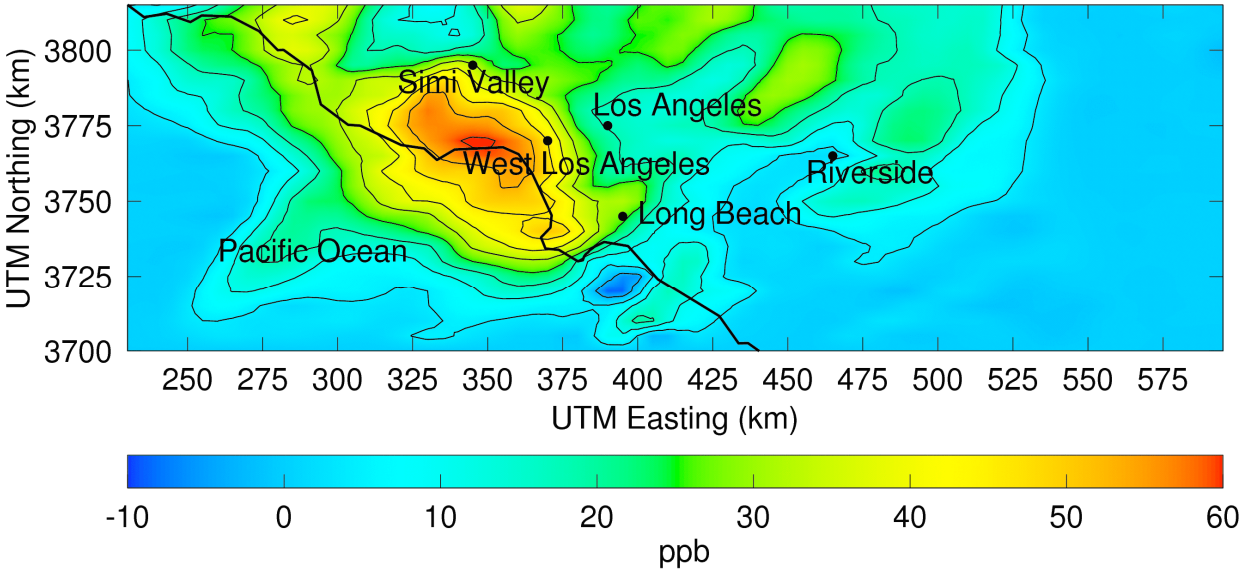

Figure 19: Maximum one-hour ozone concentration (ppb) difference for year 2020 in the South Coast Air Basin of California between cases with and without ship emissions.

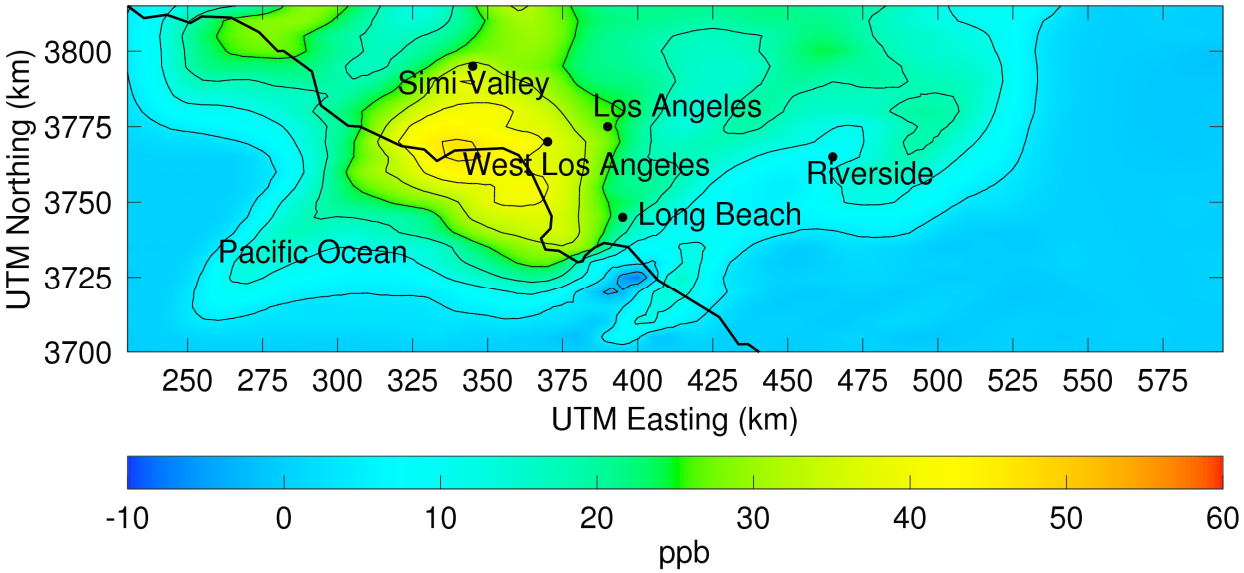

Figure 20: Maximum eight-hour concentration (ppb) difference for year 2020 in the South Coast Air Basin of California between cases with and without ship emissions.

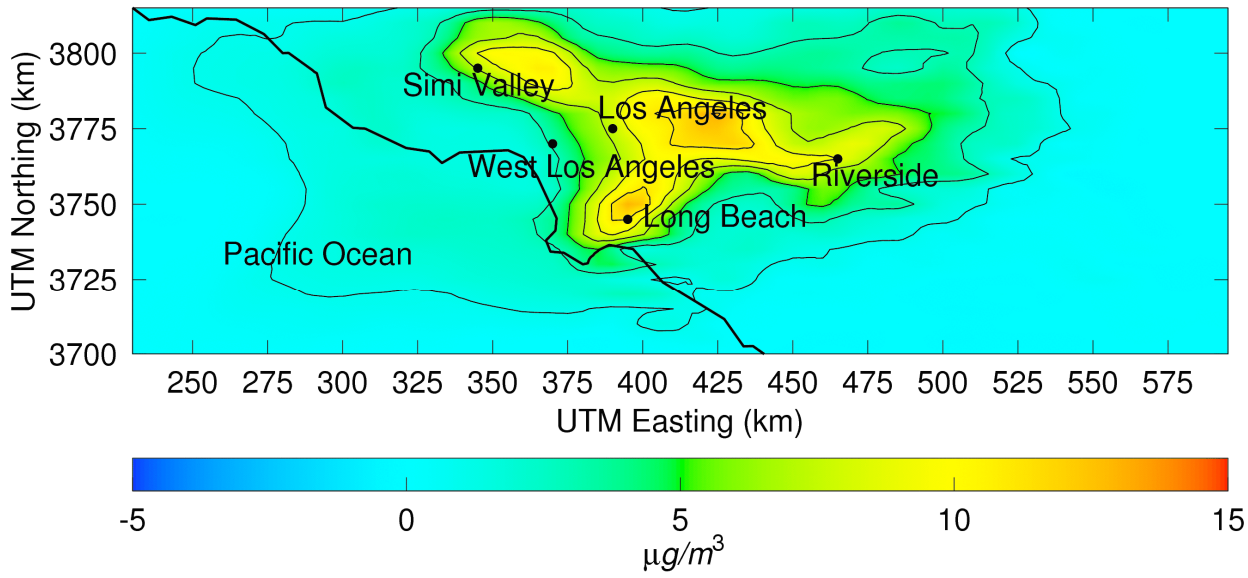

Figure 21: 24-hour average particulate nitrate concentration (μg/m^3) difference for year 2020 in the South Coast Air Basin of California between cases with and without ship emissions.

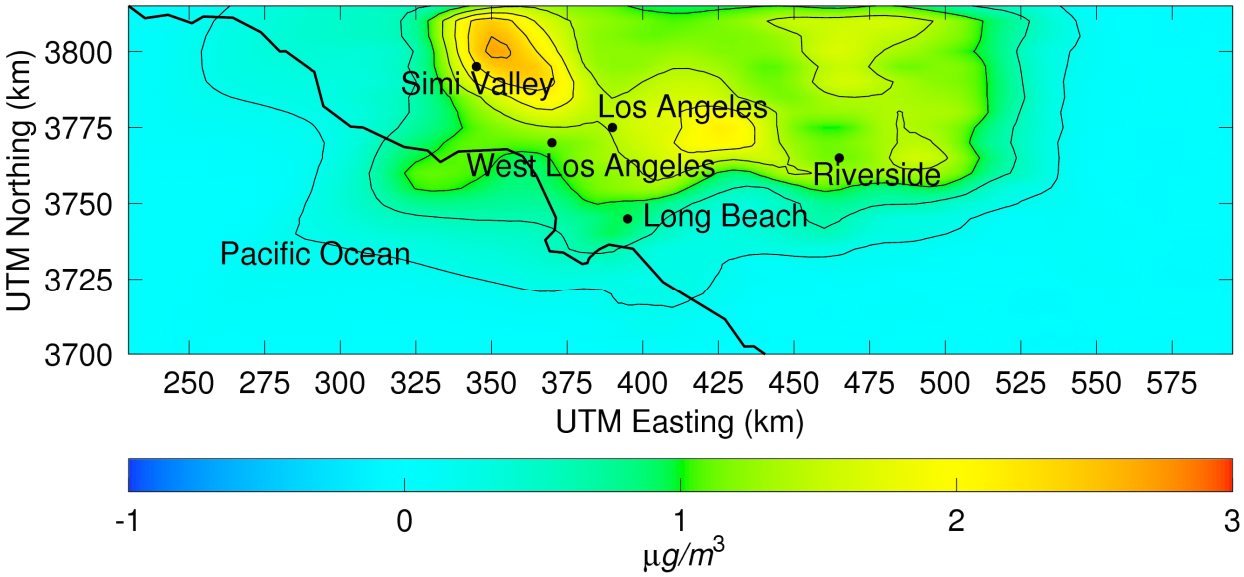

Figure 22: 24-hour average particulate sulfate concentration (μg/m^3) difference for year 2020 in the South Coast Air Basin of California between cases with and without ship emissions.

5. CONCLUSION

This study illustrates the use of regional air quality models to assess the impact of ships at locations close to ports and shipping routes. A comprehensive gas-phase chemical mechanism, such as CACM, enables the prediction of impacts on peak one-hour and eight-hour ozone concentrations that are important from regulatory perspective. Furthermore, a coupled aerosol mode provides an accurate treatment of secondary aerosol formation leading to quantifiable impacts on 24-hour average PM impacts. Results show that individual locations are impacted at different levels depending on local emissions. Results from this study, in combination with population data, are useful in assessing health impacts of ship emissions.

In this study, effects of ship emissions on air quality in southern California are quantified using the UCI-CIT model. Presence of two major ports in the region, coupled with unique topographical and meteorological features lead to increases in ozone, particulate sulfates and nitrates in the region. For the year 2002, ships emitted 38.4 and 22.8 tons/day of NO_x and SO_x emissions respectively in the model domain. Analysis of model runs with and without ship emissions show that ship emissions contribute significantly to ozone and PM concentrations at many coastal locations. Maximum increase of 29 and 24 ppb in peak one-hour and eight-hour average ozone concentration is predicted due to NO_x from ships. Similarly, 24-hour average particulate nitrate and sulfate concentrations increase up to 12 and 1.25 $\mu g/m^3$ due to ship emissions. Inland locations also experience increase in ozone and PM concentrations, although at smaller magnitudes in comparison with coastal locations. As land-based emissions decline in future years due to emission regulations, ship emissions become increasingly important. Model runs using emission estimates for the year 2020 show that ships could become a major source of air pollution in the region.

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