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The impact of marine organics on the air quality of the western United States

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Abstract

The impact of marine organic emissions to the air quality in coastal areas of the western United States is studied using the latest version of the US Environmental Protection Agency (EPA) regional-scale Community Multiscale Air Quality (CMAQv4.7) modeling system. Emissions of marine isoprene, monoterpenes, and primary organic matter (POM) from the ocean are implemented into the model to provide a comprehensive view of the connection between ocean biology and atmospheric chemistry and air pollution. Model simulations show that marine organics can increase the concentration of $PM_{2.5}$ by 0.1–0.3 $\mu g\,m^{-3}$ (up to 5%) in coastal cities. This increase in the $PM_{2.5}$ concentration is primarily attributed to the POM emissions, with small contributions from the marine isoprene and monoterpenes. When marine organic emissions are included, organic carbon (OC) concentrations over the remote ocean are increased by up to 50% (25% in coastal areas), values consistent with recent observational findings. This study is the first to quantify the air quality impacts from marine POM and monoterpenes for the United States, and highlights the need for inclusion of marine organic emissions in air quality models.

1 Introduction

It is has been well established that organic emissions from marine sources have the potential to affect the atmospheric chemistry of coastal areas. Observations of aerosol composition show that these emissions, which include both biogenic trace gases and particles, are strongly tied to the seasonal cycles in ocean biology (O'Dowd et al., 2004). Organic aerosols, whose contribution to marine aerosol composition increases with decreasing aerosol size (Keene et al. 2007; Facchini et al., 2008a), have been divided into two distinct categories depending on source: primary and secondary. Primary organic matter (POM) is emitted into the atmosphere through bubble bursting processes from the sea surface microlayer that is enriched in organic matter relative to the sub-surface water. These aerosols have elevated emission rates in areas with high surface chlorophyll-a concentrations ([Chl-*a*]) and wind speed and are thought to be largely water insoluble (O'Dowd et al., 2008), or have carbohydrate-like composition (Russell et al., 2009). There is accumulated evidence suggesting that over the productive waters of the ocean the majority (up to 80% of submicron mass) of sea spray aerosols could be organic in nature (O'Dowd et al., 2004; Keene et al., 2007; Facchini et al., 2008a). Bigg and Leck (2008) further argue that all marine aerosols below 200nm in diameter have non-sea salt origin and are primarily composed of sulfate and organics.

While the source of marine primary organic aerosols is generally agreed upon, production of secondary organic aerosols (SOA) from phytoplankton-generated reactive trace gases is a topic of considerable debates in the recent literature. Formation of SOA with a marine source begins with the oxidation of biogenic volatile organic compounds (VOCs) emitted by phytoplankton. After oxidation through gas and aqueous-phase reactions, the lower volatility products can condense on pre-existing particles or form new particles over marine areas (O'Dowd et al., 2007 and references therein). Several VOCs with the potential to form aerosols have been measured in the marine boundary layer, including dimethyl sulfide (DMS), iodine species, isoprene, monoterpenes, and amines (Shaw et al., 1983; O'Dowd et al., 2002; Bonsang et al., 1992; Yassaa et al., 2008; Facchini et al., 2008b). While the sources of water soluble and insoluble marine organic aerosols have been elucidated using gradient measurements (Ceburnis et al., 2008), recent studies have argued that in addition to phytoplankton-emitted VOCs, the source of the water soluble component of marine organic aerosols may be attributed to the oxidation of phytoplankton biomass (Claeys et al., 2010).

Several recent studies have implemented emission of marine isoprene and primary organic aerosols into 3-dimensional photochemical models to determine the air quality impacts. O'Dowd et al. (2008) implemented North Atlantic primary emissions into the REMOTE climate model by using a relationship between the organic fraction of submicron sea spray and [Chl-*a*]. The model-predicted aerosol concentration of between

0.2–0.3 $\mu g\,m^{-3}$ were similar to observations at Mace Head, Ireland for both the summer and winter months. Marine isoprene emissions were implemented in the Community Multiscale Air Quality (CMAQ) model to determine the impacts on air quality in the United States (Gantt et al., 2010). They show that marine isoprene can add up to 0.004 $\mu g\,m^{-3}$ to the SOA concentration in coastal areas, a minor contribution (<0.5%) when compared to the terrestrial sources (Gantt et al., 2010). The effect of marine isoprene on ozone (O_3) formation in urban coastal areas was also small, with enhancement of maximum 8 h average O_3 only by 0.2 ppb. In this study, we expand upon Gantt et al. (2010) by examining the impact of both POM and SOA from marine sources on the air quality of the western US.

2 Method

2.1 CMAQ model description

We have conducted three summertime simulations with CMAQ model (Version 4.7) using a $12\times12\,km^2$ spatial resolution in a domain comprising the western US and parts of the Pacific Ocean. The model simulations are conducted using meteorological data generated offline by the Pennsylvania State University/National Center for Atmospheric Research Mesoscale Modeling System Generation 5 (MM5) version 3.7.4 (Grell et al., 1994). Simulations start on 1st June 2005 using the initial conditions from the 31st May output from year-long CMAQ simulations performed by the EPA. The boundary conditions are set every hour from a global chemical transport model, the Goddard Earth Observing System (GEOS)-Chem (Park et al., 2004). Emissions of anthropogenic gaseous and aerosol species are based on the 2005 National Emissions Inventory (NEI) version 1, while biogenic emissions are based on the Biogenic Emissions Inventory System (BEIS) version 3.13. Gas-phase chemistry is computed using the Carbon-Bond Mechanism version 5 (CB05) reactions, with SOA formation simulated using an advanced module including processes such as acid catylization, oligomerization, and in-cloud processing (Carlton et al., 2010).

Using this model configuration, three different summertime simulations were performed. The first is a baseline simulation in which no marine emissions are added. The second, referred hereto as the “bottom-up” simulation, includes emissions of marine isoprene based on laboratory measurements of Gantt et al. (2009) and marine POM based on O’Dowd et al. (2008). Marine monoterpenes were not included in bottom-up simulations due to extremely low emission rates from diatoms (∼100 times lower compared to isoprene) reported in laboratory incubation experiments of Yassaa et al. (2008). The third simulation, referred as the “top-down”, is similar to the bottom-up approach except both marine isoprene and monoterpene emissions are calculated based on marine boundary layer (MBL) concentration measurements reported for the Southern Ocean (Columb et al., 2009). Marine monoterpenes are included in the top-down approach due to reported ambient concentrations comparable to phytoplankton-produced isoprene (Yassaa et al., 2008; Colomb et al., 2009). A detailed description of the method used to create these emissions is found in Sects. 2.2 and 2.3.

2.2 Marine VOC emissions

In both the bottom-up and top-down simulations, marine VOC emissions were added offline to the existing terrestrial emissions files. For the bottom-up simulations, marine isoprene emissions were created based on laboratory measurements of isoprene production from diatoms under a range of light conditions from Gantt et al. (2009). The creation and implementation of marine isoprene emissions followed the same method of Gantt et al. (2010), with the main difference being the use of monthly-averaged Level 3 MODIS/Aqua-derived [Chl-*a*] and k_{490} coefficient at ∼4 km for the three months of simulations. These data were regridded to the 12×12 km^2 spatial resolution and projected into the Lambert Conformal Conic coordinates of the model domain. The ambient solar radiation, 10 m winds, and skin temperature (a proxy for sea surface temperature (SST)) were obtained from the MM5 meteorological fields to calculate the emission rates. Detailed description of the bottom-up marine isoprene emission calculations and implementation into the CMAQ model are given in Gantt et al. (2009) and Gantt et al. (2010), respectively.

Marine isoprene and monoterpene emissions in our top-down approach are based on average surface concentration measurements of Colomb et al. (2009) in the remote MBL of the Southern Indian Ocean using a method similar to Luo and Yu (2010). In this approach, surface VOC concentration measurements from a region of maximum biological activity and little influence from terrestrial emissions are used to estimate the surface fluxes. The averaged VOC emissions over the Southern Indian Ocean (normalized by chlorophyll abundance, surface wind speed and SST) are then used to calculate marine isoprene and monoterpene emissions over the model domain. The emissions of marine isoprene and monoterpenes are estimated using the following equation of Guenther et al. (1996), suggested for terrestrial isoprene emissions calculations:

$$E_{\mathrm{SIO}} = C \cdot H \cdot \tau^{-1}$$

In this formulation, E_{SIO} is the emission rate (molecules cm^{-2} s^{-1}) at the Southern Indian Ocean site, C is the average MBL concentration (molecules cm^{-3}), H is the MBL height (cm), and τ is the lifetime of the gas (s). We assume a τ of 2 h (7200 sec) for isoprene and 3.75 h (13 500 s) for monoterpenes, values adapted from Atkinson and Arey (1998) and Galbally et al. (2007). The lifetime of monoterpenes is based on the lifetime of α-pinene, the most common monoterpene measured in the MBL (Yassaa et al., 2008). Because Colomb et al. (2009) report the surface VOC concentrations and meteorological/ocean measurements as ~12 h averages over the surface ocean waters of variable biological productivity, the flux footprint is very complex and hard to interpret. Parameters affecting VOC emission rates/ambient concentrations such as phytoplankton abundance and speciation, surface solar radiation, and wind speed/direction are not well constrained. The very short atmospheric lifetime of isoprene also leads to strongly decaying vertical mixing ratios that further complicate emission rate calculations. As a result of these uncertainties, to convert the reported surface concentrations to C values used in the above equation, we employ MBL vertical profiles of isoprene predicted by the bottom-up CMAQ simulation in remote ocean regions off the coast of Baja California, northern California, and Washington. Isoprene and monoterpene emissions derived for the Southern Indian Ocean are then normalized by gas exchange coefficients and [Chl-*a*] values and applied to the CMAQ domain. The emission rate in CMAQ (E_{CMAQ}) can be calculated using the following equation:

$$E_{\mathrm{CMAQ}} = \frac{k_{\mathrm{CMAQ}}}{k_{\mathrm{SIO}}} \cdot E_{\mathrm{SIO}} \cdot \frac{[\mathrm{Chl}-a]_{\mathrm{CMAQ}}}{[\mathrm{Chl}-a]_{\mathrm{SIO}}} \cdot SA \quad (1)$$

where E_{CMAQ} is in units of moles s^{-1}, SA denotes 12×12 km^2 CMAQ grid, k_{SIO}, k_{CMAQ} and [Chl-*a*]$_{\mathrm{SIO}}$, [Chl-*a*]$_{\mathrm{CMAQ}}$ are the gas exchange coefficients (m s^{-1}) and surface chlorophyll concentration (mg m^{-3}) at the Southern Indian Ocean measurement site and CMAQ domain, respectively. The gas exchange coefficient is given by the equation:

$$k = 0.31 U_{10}^2 \cdot \left(\frac{660}{Sc}\right)^{0.5}$$

(Wanninkhof, 1992), with U_{10} taken from the measurements of Colomb et al. (2009) and the MM5 hourly 10 m wind speed for Southern Indian Ocean and CMAQ domain, respectively. Schmidt number (Sc) is calculated using De Bruyn and Saltzman (1997) formulation.

2.3 Marine primary organic emissions

Emissions of marine primary organic aerosols were added to the model online in both the bottom-up and top-down simulations. The emission rate of marine primary organic aerosols was determined using the relationship between [Chl-*a*] and the sub-micron organic mass fraction of sea spray mass concentration from O'Dowd et al. (2008). The marine primary organic aerosol emissions in CMAQ are added to the existing Aitken (0.01% by mass) and accumulation mode (99.9% by mass) primary organic carbon emissions, which were previously restricted exclusively to terrestrial regions. Using the sub-micron sea spray function to calculate the organic fraction of the CMAQ accumulation mode sea spray mass is justified, as the majority of the CMAQ accumulation mode particle mass is less than 1 µm in diameter. The [Chl-*a*] for each model grid is determined from the monthly-averaged Level 3 MODIS/Aqua-derived [Chl-*a*], and the sea spray mass emissions are calculated from the existing accumulation mode CMAQ sea salt emissions. The CMAQ sea salt fluxes are driven by the MM5 meteorological variables using the Gong-Monahan (Gong, 2003) and the deLeeuw (deLeeuw et al., 2000) emission functions for the open ocean and the surf zone, respectively. A complete description of the sea salt emission model in this version of CMAQ, including relative humidity and white cap coverage dependence, is found in Kelly et al. (2009). The sea salt emissions were converted into sea spray emissions by calculating the apparent density of the sea spray aerosol as a function of organic fraction. In the model results, the sum of the Aitken and accumulation mode constitutes particles with an aerodynamic diameter less than 2.5 µm. For model-predicted changes in $PM_{2.5}$ concentrations due to marine organics, an OM/OC mass ratio of 1.4 is used for marine primary organic aerosols (Decesari et al., 2007).

3 Results

3.1 Comparison with observations

To test the effect of the marine emissions on model-predicted atmospheric concentrations of OC, the simulated values were compared to ambient measurements at several different monitoring stations on the coast of California. OC concentration observations were obtained from Point Reyes National Seashore (38.12° N, 122.91° W) and Redwood National Park (41.56° N, 124.09° W) as part of the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (http://vista.cira.colostate.edu/improve/). Both IMPROVE stations are less than 4 km distance from the ocean, and typically experience onshore winds. The IMPROVE stations sample organic carbon particles <2.5 µm in aerodynamic diameter ($OC_{2.5}$) on filters for 24 h every 3 days to give the average daily concentration in µg m^{-3}. In the model, $OC_{2.5}$ is the sum of the accumulation mode secondary organic carbon from biogenic and anthropogenic VOCs and the Aitken/accumulation mode primary OC. Table 1 shows that for the entire simulation period (1 June to 31 August 2005) the model tends to overpredict surface $OC_{2.5}$ concentration for the two coastal sites, and the addition of marine $OC_{2.5}$ aerosol brings the simulated mean further from the observations. However, careful examination of time series revealed considerable differences between roughly two halves of the simulation period where the first half (1 June to 15 July) was characterized by stronger onshore winds (Fig. S1, http://www.atmos-chem-phys-discuss.net/10/6257/2010/acpd-10-6257-2010-supplement.pdf) and lower elemental carbon (EC) concentration (Fig. S2, http://www.atmos-chem-phys-discuss.net/10/6257/2010/acpd-10-6257-2010-supplement.pdf). Table 1 shows that during this period with little anthropogenic influence, the inclusion of marine organic emissions improves magnitude and correlation (Redwood only) of the model-predicted $OC_{2.5}$ concentration for the Point Reyes and Redwood sites.

To assess the effect of marine isoprene emissions, the model-predicted ambient isoprene concentrations were compared to observations taken from Photochemical Assessment Monitoring Stations (PAMS) network (http://www.epa.gov/air/oaqps/pams/index.html) located in Ventura, CA (34.28° N, 119.31° W) and Oceanside, CA (33.22° N, 117.40° W) on the southern California coast. The PAMS stations use gas chromatography-flame ionization detector (GC-FID) to measure the instantaneous isoprene concentrations in units of ppb every 6 days several times during the day. The two PAMS stations used for comparison are within 1 km of the Pacific Ocean. The bottom-up and top-down approaches slightly improve the dramatic underpredictions of isoprene concentrations in the baseline simulation at both sites shown in Table 2. However, the addition of marine isoprene and monoterpene emissions does not improve correlations between model predicted and observed concentrations. This is expected as marine emissions of these trace gases are dwarfed by terrestrial sources (Palmer and Shaw, 2005) and it has been previously noticed that there is consistent disagreement between CMAQ predictions and the PAMS network measurements (Carlton and Reff, 2009).

3.2 Changes in $OC_{2.5}$ and $PM_{2.5}$

The most substantial air quality effect of marine organic emissions was the increase in $OC_{2.5}$ concentration. Figure 1 shows that over the remote ocean up to 50% of the $OC_{2.5}$ concentration can be attributed to the marine sources. This value is consistent with the findings of Russell et al. (2009) who show that 50% of the Northern Atlantic MBL OM_1 mass has a marine origin. Figure 1 also demonstrates that at the coastal areas a considerable fraction (up to 25% in certain locations) of $OC_{2.5}$ aerosol mass can have marine origin. This is important because the age and chemical evolution of organic aerosols affects their reactivity, hygroscopicity, volatility, and optical properties, parameters that are important for climate forcing and human health (Andreae et al., 2009; Jimenez et al., 2009). However, even with such large contribution to MBL $OC_{2.5}$ aerosol mass, marine organic emissions seem to have modest influence on marine $PM_{2.5}$ concentration which is primarily determined by sea salt and sulfate aerosol mass. Figure 2a shows that the greatest change in $PM_{2.5}$ occurs over the ocean near the northern California coast with increases over $0.3\,\mu g\,m^{-3}$. The spatial distribution in percentage changes of average surface $PM_{2.5}$ concentration (Fig. 2b) is similar to that of the total change in $PM_{2.5}$ (Fig. 2a). Despite little (up to 5%) contribution to $PM_{2.5}$, marine organic aerosol emissions may be important for regulatory purposes in coastal cities like San Francisco, CA and Los Angeles, CA that are in nonattainment for the 2006 $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) (http://www.epa.gov/air/oaqps/greenbk/pm25_2006_designations_20091113.pdf).

The estimated increase in $PM_{2.5}$ concentrations over the ocean (due to marine sources of OC) is considerably higher than that over the land. Figure 2b shows that the percentage changes in $PM_{2.5}$ are over 10% off the northern California coast. Our model predicted OC values over the ocean agree relatively well with summertime OC measurements in areas strongly affected by marine aerosols such as Amsterdam Island (Scaire et al., 2009), Mace Head, Ireland (Yoon et al., 2007), the Azores (Pio et al., 2007), and the Northern Atlantic (Russell et al., 2009) which have reported average concentrations of ∼0.2, 0.4, 0.5, and 0.25 µg m^{-3}, respectively.

3.3 Comparison of bottom-up and top-down simulations

The primary difference between the bottom-up and top-down simulation is the introduction of marine terpenes into the model and increased emissions of marine isoprene. These additional emissions result in substantial changes in the O_3 concentration when compared to the bottom-up simulation. Figure 3a shows that for the top-down approach model simulations predict moderate enhancement (0.5%) of average surface O_3 concentration in coastal urban areas and slight decrease (−0.1%) in concentration over the remote ocean. The differences between top-down and bottom-up simulations shown on Fig. 3a and b can be viewed as the high and low estimates of the potential role that marine isoprene and monoterpenes can play in O_3 formation near coastal areas. Figure 3c and d display surface SOA concentration changes due to emissions of marine isoprene and monoterpenes for the top-down and bottom-up simulations, respectively. These figures show that while the simulated SOA change in top-down approach is considerably higher than that of the bottom-up, contribution of marine sources of SOA to the total $PM_{2.5}$ concentrations is an order of magnitude lower compared to the primary emission of OC aerosol from marine biogenic sources. Therefore, our model simulations suggest that marine isoprene and terpenes contribute a minor fraction of model predicted OC aerosol mass concentration in near coastal regions. This result is consistent with the modeling and observational studies of Arnold et al. (2009) and Claeys et al. (2009) who show that marine isoprene-SOA makes up a minor portion of fine mode marine OC aerosol mass.

4 Conclusion

This is the first study to quantify the combined effect of marine primary organic aerosol, isoprene, and monoterpene emissions on the air quality of coastal areas. Building on a previous modeling study examining the air quality effect of marine isoprene (Gantt et al. 2010), emissions of marine isoprene, monoterpenes, and primary organic aerosols were implemented in the US EPA's CMAQ model with a domain over the Pacific Ocean and western US. The terrestrial impact of marine organic emissions is strongest at the coast, with average surface $PM_{2.5}$ and O_3 concentrations increasing by up to 5% and 0.5%, respectively. Over the remote ocean, marine organics contributed 50% of the surface $OC_{2.5}$ and resulted in a 10% change in $PM_{2.5}$ concentrations. The source of additional $PM_{2.5}$ in the simulations is dominated by POM, with the SOA source from isoprene and monoterpenes making up a much smaller portion of the $PM_{2.5}$ mass. Model calculations indicate that during periods of onshore flow, inclusion of marine organic emissions can yield improved model predictions of surface $OC_{2.5}$ concentration at the California coast. The addition of isoprene and monoterpenes from marine sources did not have considerable effect on O_3 or SOA surface concentration in coastal areas. For surface isoprene concentrations measured at the southern California coast, the large underprediction by the model is slightly improved by the additional marine isoprene emissions. This study suggests that marine organic aerosols account for a considerable portion of the aerosol mass over the remote ocean and some near-coastal regions and, therefore needs to be considered in future air quality models. The subsequent health impacts of marine organics may be underestimated by these results, as studies have shown that the organic mass fraction of marine aerosols is particularly large for particles <0.125 µm in diameter (O'Dowd et al., 2004). Furthermore, organic vapors from marine sources of VOC have been implicated to aid nucleation events and growth of ultrafine particles in coastal environments, potentially producing large numbers of particles at sizes problematic for human health (Vaattovaara et al., 2006; Modini et al., 2009). While this modeling study shows a small contribution of marine isoprene and terpene-SOA to total OC aerosol mass over the ocean, number of important sources of marine-SOA from biogenic amines and methanesulfonate were not included in the current CMAQ simulations. Additional field measurements and model simulations with improved aerosol size/chemical characterization and emission source functions may be necessary to fully explore the significance of marine organic aerosol and biogenic trace gas emissions on coastal air quality and human health.

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Table 1. Comparison between simulated and observed organic carbon aerosol concentrations for two coastal IMPROVE stations during the simulation period and the period from 1 June to 15 July 2005.

Station	Mean Obs.($\mu g\,m^{-3}$)		Simulation	Mean Sim. ($\mu g\,m^{-3}$)		Correlation Coefficient	
	1 June to 31 Aug.	1 June to 15 July		1 June to 31 Aug.	1 June to 15 July	1 June to 31 Aug.	1 June to 15 July
Point Reyes, CA	0.57	0.38	Baseline	0.63	0.15	−0.10	0.07
			Bottom-up	0.80	0.35	−0.10	−0.01
			Top-down	0.80	0.36	−0.10	−0.01
Redwood NP, CA	0.44	0.37	Baseline	1.49	0.20	0.20	0.80
			Bottom-up	1.68	0.35	0.22	0.89
			Top-down	1.69	0.36	0.22	0.89

Table 2. Comparison of isoprene observations and simulations for two coastal PAMS stations from 1 June to 31 August 2005.

Station	Mean Obs. (ppb)	Simulation	Mean Sim. (ppb)	Correlation Coefficient
Ventura, CA	0.41	Baseline	0.05	−0.23
		Bottom-up	0.05	−0.23
		Top-down	0.08	−0.24
Oceanside, CA	0.06	Baseline	0.02	−0.12
		Bottom-up	0.03	−0.13
		Top-down	0.03	−0.14

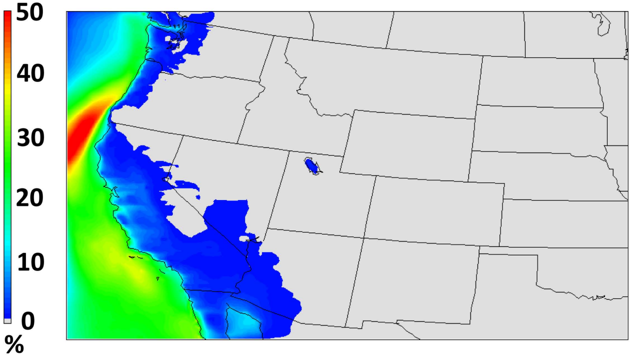

Fig. 1. Average percentage contribution of marine organics to surface $OC_{2.5}$ concentration for the bottom-up simulation from 1 June to 31 August 2005.

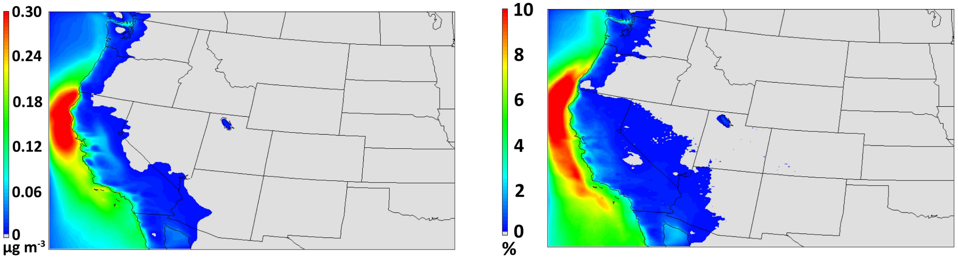

Fig. 2. Average increase **(a)** and percentage change **(b)** in surface $PM_{2.5}$ concentration from marine organics for the bottom-up simulation from 1 June to 31 August 2005.

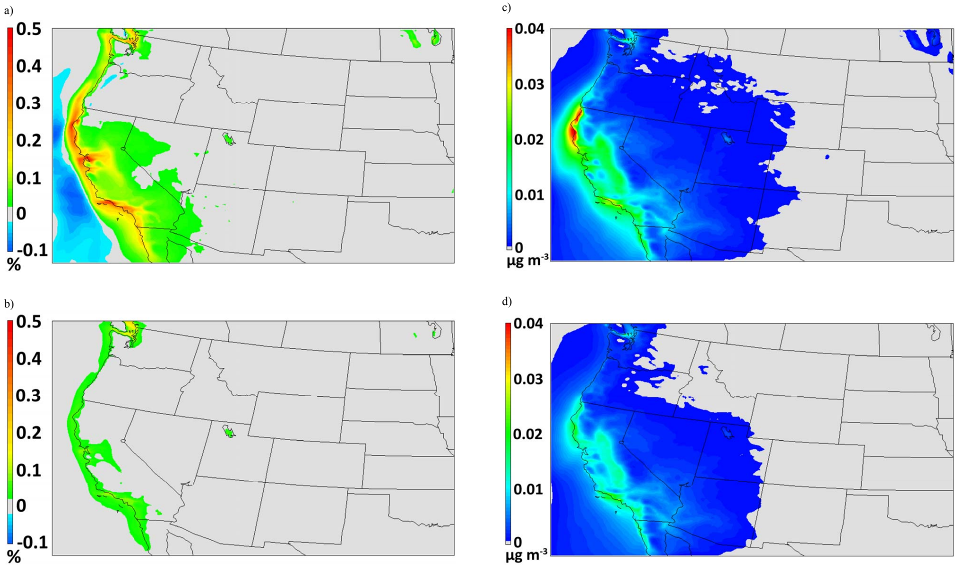

Fig. 3. Average percentage change in surface O_3 for the top-down **(a)** and bottom-up **(b)** simulations and average increase in surface $SOA_{2.5}$ concentrations concentration for the top-down **(c)** and bottom-up **(d)** simulations due to marine emissions from 1 June to 31 August 2005.