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The influence of ocean halogen and sulfur emissions in the air quality of a coastal megacity: The case of Los Angeles

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Abstract

The oceans are the main source of natural halogen and sulfur compounds, which have a significant influence on the oxidizing capacity of the marine atmosphere; however, their impact on the air quality of coastal cities is currently unknown. We explore the effect of marine halogens (Cl, Br and I) and dimethyl sulfide (DMS) on the air quality of a large coastal city through a set of high-resolution (4-km) air quality simulations for the urban area of Los Angeles, US, using the Community Multiscale Air Quality (CMAQ model). The results indicate that marine halogen emissions decrease ozone and nitrogen dioxide levels up to 5 ppbv and 2.5 ppbv, respectively, in the city of Los Angeles. Previous studies suggested that the inclusion of chlorine in air quality models leads to the generation of ozone in urban areas through photolysis of nitryl chloride (ClNO₂). However, we find that when considering the chemistry of Cl, Br and I together the net effect is a reduction of surface ozone concentrations. Furthermore, combined ocean emissions of halogens and DMS cause substantial changes in the levels of key urban atmospheric oxidants such as OH, HO₂ and NO₃, and in the composition and mass of fine particles. Although the levels of ozone, NO₃ and HO_x are reduced, we find a 10% increase in secondary organic aerosol (SOA) mean concentration, attributed to the increase in aerosol acidity and sulfate aerosol formation when combining DMS and bromine. Therefore, this new pathway for enhanced SOA formation may potentially help with current model under predictions of urban SOA. Although further observations and research are needed to establish these preliminary conclusions, this first city-scale investigation suggests that the inclusion of oceanic halogens and DMS in air quality models may improve regional air quality predictions over coastal cities around the world.

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Appendix A. Supplementary data

Keywords

Marine natural emissions Halogens; DMS; CMAQ; Los Angeles; Urban air quality

1. Introduction

The world's population and urbanization rates are increasing, and with it the number of megacities – cities with over 10 million inhabitants. Many megacities such as Los Angeles, California in the United States are located in coastal regions (Fig. 1). Due to its large urban population and meteorological and geographic conditions, California has historically suffered from severe air quality problems, especially in regard to high ozone concentrations (Neuman et al., 2012). The urban area of Los Angeles is part of the South Coast Air Basin (SoCAB), which is surrounded by mountainous terrain and the Pacific Ocean (Fig. 1). These geographical features cause pollution to be trapped in the basin, leading to increased pollution levels that can negatively affect human health and ecosystems (Kim et al., 2016). Since the early 1960s, a tightening of ambient quality standards has led to strong air pollution controls in SoCAB in order to reduce anthropogenic emissions of nitrogen oxides ($\text{NO}_x = \text{NO}_2 + \text{NO}$) and volatile organic compounds (VOCs) that are the main precursors of tropospheric ozone (Pollack et al., 2013). Despite significant anthropogenic emission reduction during the last decades (Fujita et al., 2013), the concentrations of ozone and particulate matter (PM) in Los Angeles in 2015 still exceeded the corresponding air quality standards.

Nonetheless, urban air quality can also be influenced by natural emissions as marine air masses confluence with polluted urban air. Halogenated species produced in the oceans by biological and photochemical processes are emitted to the marine atmosphere where they undergo photolysis and reaction with atmospheric oxidants to release reactive iodine, bromine and chlorine radicals, which can then catalytically destroy tropospheric O_3 in the troposphere (Simpson et al., 2015) and in the stratosphere (Fernandez et al., 2017; Hossaini et al., 2015; Oman et al., 2016). Halogenated compounds can also alter the oxidative capacity of the marine troposphere by changing the budget and balance of important atmospheric oxidants such as NO_x and HO_x ($\text{HO}_x = \text{HO}_2 + \text{OH}$) (Saiz-Lopez and von Glasow, 2012). Previous global modelling studies have shown that combined chlorine-bromine-iodine chemistries can deplete up to 20% of ozone in remote and clean marine environments (Saiz-Lopez et al., 2012a; Sherwen et al., 2016). Conversely, chlorine compounds released via heterogeneous reaction on marine aerosols can increase ground-level O_3 concentration in coastal polluted regions (Hossaini et al., 2016; Osthoff et al., 2008; Tham et al., 2016), that in turn, affect PM concentration (Chan et al., 2017). An increase of 1.0–6.0 ppbv in 8-h daily maximum O_3 concentration due to chlorine activation on marine aerosols was estimated for the North Hemisphere (Sarwar et al., 2014) and across the United States (Sarwar et al., 2012). However, multi-model assessments using global and regional chemical transport models have still found systematic overpredictions of surface ozone concentrations at representative coastal sites over North America and South East Asia (Han et al., 2008; Reidmiller et al., 2009).

Remarkably, observations made at the Californian coast (La Jolla) have reported significant and highly variable levels of dihalogens (Cl_2 , Br_2 and I_2) in polluted coastal air, suggesting a possible role of this chemistry in coastal urban air quality (Finley and Saltzman, 2008). However, despite their detection in polluted coastal air and their demonstrated ability to alter the oxidative capacity of the marine atmosphere (Simpson et al., 2015), the omission of natural halogen sources altogether (Cl , Br and I) and their combined chemistry in air quality models has so far prevented a comprehensive evaluation of their effect on air quality within and around coastal megacities through high-resolution simulations.

Dimethyl sulfide (DMS) is produced by many species of phytoplankton in the oceans and emitted to the atmosphere (Stefels et al., 2007) where, following reactions with oxidants (OH , NO_3 and BrO) (Boucher et al., 2003; Breider et al., 2010), represents the primary source of sulfate aerosol over remote ocean regions. Sulfate aerosols can impact climate via direct and indirect effects on radiation and clouds (Haywood and Boucher, 2000). Hence, DMS plays an important role in the Earth's global climate system, although its influence on urban aerosol formation on coastal cities remains poorly assessed. Here, we investigate the potential of marine halogens (Cl , Br and I) and DMS to influence the levels of key pollutants with relevant health impacts (Delamater et al., 2012) in the megacity of Los Angeles, and surrounding areas, through a set of city-scale air quality simulations. We explore the resulting implications for air quality policies relevant to coastal urban areas.

2. Methods

2.1. Model

High-resolution simulations were performed using the Community Multiscale Air Quality (CMAQ v5.1) regional model (Appel et al., 2017), with the Carbon Bond chemical mechanism (Whitten et al., 2010) and the chlorine chemistry scheme (Sarwar et al., 2015; Sarwar et al., 2014). The model is used to assess the impact of ocean emissions and combined chemical processes of halogens (iodine, bromine and chlorine) and DMS on air quality levels of Los Angeles and SoCAB using a horizontal grid resolution of 4 km and 35 vertical levels. Simulations were completed for August (used as a spin up period) and September of 2006. The Community Multiscale Air Quality (CMAQ) model (<https://github.com/USEPA/CMAQ>) is a chemical transport model containing comprehensive treatment of all important atmospheric processes related to air pollution. It has been widely used throughout the world in a variety of applications. The skill of the model has been demonstrated by evaluating the model predictions against numerous observational datasets (Appel et al., 2007; Appel et al., 2017; Appel et al., 2013; Foley et al., 2010; Appel et al., 2008). The chlorine implementation in CMAQ was previously evaluated using, among others, the ClNO_2 observations made during the CALNEX campaign that took place in California in 2010 (Mielke et al., 2013; Riedel et al., 2012). However, the chemistry was modified to include iodine and bromine (further details can be found in (Gantt et al., 2017; Sarwar et al., 2015)) and DMS reactions.

2.2. Emissions and meteorological data

Marine emissions of halogen species are divided into halocarbons, inorganic bromine and inorganic iodine, according to (Gantt et al., 2017) and references therein. (Sarwar et al., 2015) and (Xing et al., 2015) described the emissions and meteorological datasets for the outermost domain while (Appel et al., 2017) and (Hogrefe et al., 2015) described the emissions and meteorological datasets for the intermediate domain. The Sparse Matrix Operator Kernel Emissions (SMOKE) system (Houyoux et al., 2000) was used to prepare model-ready emissions for the innermost domain. Anthropogenic emission datasets were taken from the 2005 Version 4.2 US EPA emission modelling platform, based on the National Emission Inventory (NEI) version 3 and harmonized with emissions submitted by California Air Resources Board (CARB) inventory. Biogenic emissions were calculated in-line using the Biogenic Emissions Inventory System version 3.14 (Schwede et al. 2005). Halogen (Sarwar et al., 2015) and DMS (Lana et al., 2011) emissions were calculated in-line.

Meteorology and non-oceanic biogenic emissions are identical for all the simulations presented. The Meteorology from the Weather Research and Forecasting (WRFv3.7.1) model (Skamarock, 2008) was used to drive the chemical transport model in all three nested domains. WRF was initialized from global NCEP FNL Operational Model Global Tropospheric Analyses with a spatial resolution of $1^\circ \times 1^\circ$ and a temporal resolution of 6 h (<http://dx.doi.org/10.5065/D6M043C6>) while sea surface temperature is updated daily from NCEP SST global analyses with 0.5° resolution (http://polar.ncep.noaa.gov/sst/rtg_low_res).

2.3. Observation data

Observed data was retrieved from the Environmental Protection Agency (EPA) Air Quality System (AQS) database for September 2006 (http://aqsdrl.epa.gov/aqsweb/aqstmp/airdata/download_files.html). Eight monitoring sites located in the area of Los Angeles were selected in order to compare modeled ozone concentration to observed data (Table 1).

2.4. Simulation cases

Simulations were performed for three nested model domains (Fig. 2). The outermost domain covers the Northern Hemisphere using 108-km horizontal grid-resolution, the intermediate domain covers the continental United States using 12-km horizontal grid-resolution, and the innermost domain covers the South Coast Air Basin using 4-km horizontal grid-resolution. Results from the outermost domain provided boundary conditions for the intermediate domain while the results from the intermediate domain provided boundary conditions for the innermost domain. The analysis focuses on the innermost domain. Three simulations were completed for each domain. The first simulation used the Carbon Bond chemical mechanism without any halogen or DMS chemistry (Baseline simulation). The second simulation (Case B or full-halogen simulation) used the Carbon Bond chemical mechanism with chlorine, bromine, iodine, and DMS chemistry (Tables S1–S3). This setup allows assessing the sensitivity of ambient air concentration levels of criteria pollutants such as O_3 , NO_2 or $PM_{2.5}$ to marine emissions (halogens and DMS simultaneously) at city-scale for the first

time. One sensitivity simulation is run to assess the individual role of chlorine chemistry for which we used the Carbon Bond chemical mechanism and the chlorine chemistry alone.

3. Results and discussion

3.1. Effect on O₃, NO₂, secondary organic aerosols and HO₂/OH and NO₂/NO ratios

Model results are compared with surface ozone observations (at the sites listed in Table 1) to understand whether observed changes contribute to improve model predictions (Fig. 3) and thus, support the validity of the additions being tested. In the whole domain, normalized mean bias is reduced from 13.5% to 4.9% when marine halogen and DMS emissions are considered in the simulation.

A noticeable impact on monthly mean surface ozone concentrations relative to the Baseline is found when marine halogen emissions are included in the simulation (Fig. 4). Surface ozone levels are reduced all over the modelling domain. This impact is higher closer to the Californian coast and decreases into the interior of continental US. The combined chemistry of the three halogen species destroys surface ozone by 2 ppbv (3%) on average over most inland regions, while 2.5–5 ppbv (5–10%) are reduced in coastal areas (Fig. 5). The effect on NO₂ ambient concentration levels (panel B) is strongly conditioned by the distribution of emission sources. While concentrations increase over non-urbanized areas (up to 15% over the ocean), the effect of halogens over the urban areas is the opposite, with a maximum reduction of nearly 5% in NO₂ concentrations for downtown Los Angeles (around 3 ppb). In polluted areas halogen chemistry shifts the NO_x partitioning to NO, while in non-polluted areas with high concentrations of halogens the reaction between XO and NO shifts the balance to NO₂ (Fig. 7) (Mahajan et al., 2009; Saiz-Lopez et al., 2012b). Finally, panel C shows how the inclusion of DMS and halogens brings about a clear increase of regional levels of secondary organic aerosol (SOA). Although maximum relative increments are found over the sea and non-urbanized inland areas, the increase over Los Angeles is as high as 10%, which leads to a net SOA fraction increase of 0.2 µg·m⁻³ (Fig. 5).

The coastal side of Los Angeles has reductions in monthly mean surface ozone concentration around 3–4 ppbv, and up to 5 ppbv in downtown Los Angeles, which represents a decrease of 10% relative to the Baseline simulation without halogens (Fig. 6). The impact of halogen chemistry gradually decreases inland, where surface ozone concentrations are depleted by 2–2.5 ppbv or less, such as in San Bernardino where ozone is reduced by 1 ppbv (around 4%). Although the net effect clearly diminishes inland, the distribution of ozone variations throughout the day at both locations is similar. Maximum reductions (3–5 ppbv) occur during the afternoon (from 13 to 17 h local time) when maximum concentrations are typically observed (this is why reductions relative to the baseline scenario are small, less than 5% as an average). Conversely, small variations during the low ozone concentration period (nighttime and early morning) result in large relative reductions, 30% and 40% as an average over downtown Los Angeles and San Bernardino, respectively. These variations however show a considerable spread pointing out that ozone destruction is affected by local factors such as meteorological conditions and variations on emission patterns.

It is well known that the inclusion of chlorine in air quality models leads to the generation of ozone in urban areas through the heterogeneous production and subsequent photolysis of nitryl chloride (Sarwar et al., 2012). We therefore ran a sensitivity simulation with the heterogeneous production of nitryl chloride and gas phase chlorine only. In agreement with previous studies (Sarwar et al., 2014), our simulation indicates that chlorine chemistry alone increases monthly mean ozone concentrations by approximately 1–2 ppbv in the city of Los Angeles. However, the results from the Case B simulation, where full halogen chemistry is considered, shows that the net effect is the destruction of ozone dominated by iodine and bromine chemistry, which prevails over the ozone production by chlorine. Ozone is depleted directly with catalytic cycles involving the self-reactions of XO radicals (where X = Br, I) as rate determining (reactions 1–5). Indirect reduction in ozone also occurs as halogens decrease the HO₂/OH ratio (reactions 4–5) (Saiz-Lopez and von Glasow, 2012) (Fig. 7, Tables S1 – S3):

Baseline and Case B model predictions are compared to observed data retrieved from the Environmental Protection Agency (EPA) Air Quality System (AQS) database. For this, we use measurements from 8 representative sites located in Los Angeles (Table 1). This comparison indicates that in general our Baseline CMAQ simulation overpredicted the monthly average ozone concentrations by 3–10 ppbv across the city of Los Angeles during September 2006 (Fig. 3). The monthly mean ozone concentration predictions from the Baseline simulation have a normalized mean bias of 13.5%, a normalized mean error of 15.8% and a correlation coefficient of 0.79. Case B simulation (full halogen) improves model performance by reducing ozone concentrations around 2–5 ppbv at most sites. The simulation with halogens clearly improves statistics relative to the Baseline simulation, producing a normalized mean bias of 4.9%, normalized mean error of 11.7% and correlation coefficient of 0.81.

In coastal urban areas, halogen chemistry reactions involving criteria pollutants such as NO_2 can also be important for air quality. Fig. 5 shows a reduction of up to 2.5 ppbv (5%) in the monthly mean NO_2 concentrations over the city of Los Angeles when halogen chemistry is implemented. By contrast, the monthly mean NO concentration is increased around 1–2 ppbv (5–10%). This decrease in the NO_2/NO ratio (Fig. 7) is driven by the halogen-catalyzed reduction in ozone levels which in turn reduces the efficiency of the reaction $\text{O}_3 + \text{NO}$ to yield NO_2 .

3.2. Effect on NO_3 and HNO_3

Our results show that the combined inclusion of marine halogens and DMS can also exert an impact on the modeled levels of the main urban atmospheric oxidants, HO_x and nitrate (NO_3) radicals. We find that the main nocturnal oxidant, NO_3 , formed by the reaction of $\text{O}_3 + \text{NO}_2$, decreases by 20–50% (2–4 pptv) in Los Angeles (Fig. 8). The reduction of NO_3 in Case B is driven by *i*) direct reaction with DMS, which represents a major sink for marine and coastal NO_3 (Andreae et al., 1985) and *ii*) indirectly due to the reduction of O_3 and NO_2 in the presence of halogens. This decreased oxidation capacity in the nocturnal atmosphere of Los Angeles has important air quality implications since NO_3 -mediated oxidation of VOCs proceeds to form organic aerosol. The diurnal OH mean concentration is minimally altered (increase of 1–2%) by halogen chemistry; however, the levels of HO_2 are reduced by about 4% (Fig. 8) through reactions 4–5, leading to an overall decrease in the levels of HO_x radicals over Los Angeles. The other important pollutant affected by the inclusion of halogens is nitric acid (HNO_3), which forms through daytime reaction of $\text{OH} + \text{NO}_2$, and nighttime heterogeneous hydrolysis of N_2O_5 . Monthly mean HNO_3 concentration (Fig. 8) over the city decreases 6–10%, due to the halogen-driven reduction in NO_2 and subsequently N_2O_5 . However, HNO_3 concentration is increased over the ocean due to the increase in OH and NO_2 levels in that region. All this highlights that marine natural halogens have the potential to significantly impact the oxidative capacity of the urban atmosphere of coastal megacities.

3.3. Effect on aerosol composition

Fig. 9 shows that the implementation of ocean emissions of halogen and DMS in the model has a non-negligible impact on aerosol total mass and composition over the Los Angeles area. For instance, in downtown Los Angeles, the composition of secondary inorganic aerosols is modified, showing an increment of aerosol sulfate mass around 10%, mainly due to a oxidation of DMS, and a decrease of aerosol nitrates of 14%. While the increase of the sulfates is quite consistent throughout the area modeled, the influence of marine emissions on nitrate levels, associated with the reduction in the concentrations of HNO_3 , decreases inland to a modeled aerosol nitrate reduction of 7% at San Bernardino. The increase in the sulfate fraction is driven by the oxidation of DMS, the most important oceanic gaseous precursor for sulfate aerosol over the ocean. The combined chemistry of NO_3 , OH and BrO oxidants increases the oxidation of DMS and consequently the total sulfate fraction in the Case B simulation. The resulting effect is an increase in the aerosol acidity which has important atmospheric implications for secondary aerosol formation. According to our simulations, the concentration of hydronium ion (H_3O^+), used for the computation of acid-

catalyzed uptake of isoprene epoxydiols (IEPOX) onto aqueous aerosol, is increased by 15–30% in the Los Angeles area.

We now turn to the effect of marine emissions of DMS and halogens in the formation of additional aerosol mass from secondary organic aerosol (SOA). SOA forms when VOCs, mainly isoprene, react with oxidants such as ozone, NO_3 and HO_x radicals, to form low-volatility compounds that can partition to the aerosol phase (Ortega et al., 2016). Surprisingly, even though the concentration of ozone, NO_3 and HO_x is lower (Fig. 8), Fig. 4 shows an increment over the modelling domain between 0.12 and 0.22 $\mu\text{g}/\text{m}^3$ (10%) of monthly mean SOA concentration when DMS and halogens are considered. Over Los Angeles, the increase ranges from 10% (Downtown) to 8% in the surrounding areas such as San Bernardino. According to our simulation, aged isoprene-derived compounds constitute the predominant fraction of SOA which is consistent with previous studies in this area (Hayes et al., 2015; Hayes et al., 2013). We estimate an increase of oligomerization reactions of biogenic species although the largest difference in modeled SOA in Case B is due to a larger production of IEPOX from isoprene peroxy radicals (RO_2) related to aerosol-phase aqueous processes. We find that the inclusion of DMS and halogen chemistry results in an increase in aerosol acidity due to DMS oxidation by NO_3 , OH and BrO leading to more sulfate formation. The BrO impact on DMS oxidation is comparable to that of NO_3 , but less than OH, and is particularly large over the ocean and much less inland. Aerosol acidity has been shown to increase substantially the SOA mass yields from isoprene (Pye et al., 2013; Surratt et al., 2010; Surratt et al., 2007). Therefore, DMS-mediated increase in aerosol sulfate represents a pathway for enhanced SOA formation that may help to some extent with the discrepancy, at least over coastal megacities, between observed and predicted SOA that indicates there is still a significant amount of “missing urban SOA” currently not included in atmospheric models (Pye et al., 2013; de Gouw et al., 2005; Heald et al., 2005; Volkamer et al., 2006; Woody et al., 2016).

4. Summary and conclusions

We have conducted model simulations to explore for the first time at city-scale resolution the effect of halogens and DMS on the air quality of a coastal megacity. The results indicate that natural halogenated and sulfur species emitted from the ocean have a non-negligible impact on the air quality of the megacity of Los Angeles. This includes changes in the concentration of some of the main criteria pollutants and in the composition and mass of fine particles. We therefore suggest that air quality in coastal cities is sensitive to this marine atmospheric chemistry, therefore this chemistry should be included in regional air quality models to accurately reproduce the O_3 , NO_x and particulate matter levels measured by air quality monitoring networks. In-depth diagnostic evaluation of model performance involving observation of relevant species is needed to establish more precisely the role of marine trace gases on urban atmospheres and to review the corresponding gas-phase chemistry as well as formation pathways of secondary aerosols. Additional observations and modelling studies are also needed to understand the overall influence of marine halogen/DMS emissions on air pollution in other coastal megacities around the world.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Representation of population in California per square mile according to Census 2000 in the domain (upper panel), and geographical features of Los Angeles area along with the location of selected monitoring sites (bottom panel).

CMAQ				
Domain	Horizontal resolution (km)	Geographic scope	X-Y dimensions (km)	Vertical levels
D1	108	Northern Hemisphere		44
D2	12	US CONUS	459 x 299	35
D3	4	Los Angeles	324 x 288	35

Fig. 2.
CMAQ modelling domains.

Fig. 3. Distribution of hourly O_3 bias (predicted – observed) for September 2006 for Case B (full halogen and DMS chemistry) and Baseline simulations. Lower bar in the box represents 25th percentile, middle bar represents the median and the upper one 75 percentile values. Maximum and minimum values are shown by error bars.

Fig. 4. Impact of the implementation of marine halogens and DMS on the Los Angeles region. The maps show the relative variation of ground level ozone (A), nitrogen dioxide (B) and secondary organic aerosols (C) relative to the baseline scenario (no halogen/DMS).

Fig. 5. Average monthly variations (absolute values) in predicted surface O_3 , NO_2 and SOA concentrations for September 2006 due to natural marine emissions (halogen/DMS model run – Baseline scenario).

Fig. 6. Detail of surface ozone variations (Case B – Baseline) in Los Angeles urban area (contained by dotted square in Fig. 1). Left and right panels show the average daily concentration pattern during the period simulated (Sept. 2006) in downtown Los Angeles (A) and San Bernardino (B).

Fig. 7.
 NO_2/NO and HO_2/OH modeled daytime ratio changes between Case B (full halogen and DMS chemistry) and Baseline simulations.

Fig. 8. Daytime concentration change between full-halogen and baseline simulation (%) in HO_2 (A), OH (B), monthly variation of HNO_3 (C) and nighttime concentration change for NO_3 (D).

Fig. 9.

Composition of PM_{2.5} in downtown Los Angeles according to the baseline scenario and the incorporation of DMS and halogen chemistry (Marine emissions): PEC – Primary elemental carbon, POA – Primary organic aerosol, SOA – Secondary organic aerosol. Average monthly concentrations are 33.7 µg·m⁻³ and 33.1 µg·m⁻³ respectively.

Table 1

Situation and information of selected monitoring sites from the Environmental Protection Agency (EPA) Air Quality System (AQS) database.

Air quality monitoring station	Site number	Lat (°)	Lon (°)	Elevation (m.a.s.l.)
West Los Angeles	060370113	34.05	-118.46	91
Burbank	060371002	34.18	-118.32	168
Los Angeles-1(LA-1)	060371103	34.07	-118.23	87
Lynwood	060371301	33.93	-118.21	27
Pico Rivera	060371602	34.01	-118.07	75
Pasadena	060372005	34.13	-118.13	250
Long Beach	060374002	33.82	-118.19	6
Los Angeles-2(LA-2)	060375005	33.95	-118.43	21