Short communication

Technical note: Examining ozone deposition over seawater

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ABSTRACT

Surface layer resistance plays an important role in determining ozone deposition velocity over sea-water and can be influenced by chemical interactions at the air-water interface. Here, we examine the effect of chemical interactions of iodide, dimethylsulfide, dissolved organic carbon, and bromide in seawater on ozone deposition. We perform a series of simulations using the hemispheric Community Multiscale Air Quality model for summer months in the Northern Hemisphere. Our results suggest that each chemical interaction enhances the ozone deposition velocity and decreases the atmospheric ozone mixing ratio over seawater. Iodide enhances the median deposition velocity over seawater by 0.023 cm s^{-1}, dissolved organic carbon by 0.021 cm s^{-1}, dimethylsulfide by 0.002 cm s^{-1}, and bromide by ~0.0006 cm s^{-1}. Consequently, iodide decreases the median atmospheric ozone mixing ratio over seawater by 0.7 ppb, dissolved organic carbon by 0.8 ppb, dimethylsulfide by 0.1 ppb, and bromide by 0.02 ppb. In a separate model simulation, we account for the effect of dissolved salts in seawater on the Henry's law constant for ozone and find that it reduces the median deposition velocity by 0.007 cm s^{-1} and increases surface ozone mixing ratio by 0.2 ppb. The combined effect of these processes increases the median ozone deposition velocity over seawater by 0.040 cm s^{-1}, lowers the atmospheric ozone mixing ratio by 5%, and slightly improves model performance relative to observations.

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1. Introduction

The geographic extent for air quality studies has expanded from regional to hemispheric/global scales in order to simulate the long-range transport and global interaction of atmospheric pollutants. The expanded use of large-scale modeling domains containing substantial oceanic regions has made the inclusion of atmosphere-ocean interactions increasingly important. Deposition of pollutants to the Earth's surface is an important pathway for atmospheric removal and the vast sea surface plays a critical role in regulating the budget of atmospheric pollutants at the hemispheric/global scales.

Dry deposition to the sea-water surface can be an important sink for atmospheric ozone (O_3) in the marine boundary layer. Ganzeveld et al. (2009) reported that many atmospheric chemistry models use a constant dry deposition velocity of 0.05 cm s^{-1} for O_3 over the ocean that does not consider any chemical interactions

with seawater constituents (Chang et al., 2004; Ganzeveld et al., 2009). Seawater contains numerous chemical constituents that can react with dissolved O_3 in seawater. Such chemical reactions deplete O_3 at the sea surface which leads to additional transfer of atmospheric O_3 into seawater as dictated by Henry's law constant. This enhances O_3 deposition velocity (v_d) and decreases atmospheric O_3 in marine regions. Several modeling studies (Oh et al., 2008; Sarwar et al., 2015) have reported that iodide can enhance O_3 deposition velocity and subsequently decrease surface O_3 mixing ratios.

In addition to iodide, dimethyl sulfide (DMS) (Stefels et al., 2007), dissolved organic carbon (DOC) (Kepkay and Wells, 1992), and bromide (Sander et al., 2003) are abundantly present in seawater and can react with dissolved O_3. DMS is the most abundant biological sulfur compound emitted to the atmosphere (Simpson et al., 2014), and is oxidized in the marine atmosphere to various sulfur-containing compounds (Lucas and Prinn, 2005). Significant progress has been made in measuring the seawater DMS concentrations and a global database of sea surface DMS measurements is available (Kettle et al., 1999; Kettle and Andreae,

2000; Lana et al., 2011, 2012). DOC in marine environments represents a large organic carbon pool and plays a central role in biogeochemistry (Farrington, 1992). DOC is not a single chemical species but a mixture of many chemical species and balanced by its biogenic and chemical production, removal, and transport into the deep ocean. Transport from rivers and lakes also affects DOC concentrations in coastal water. Many investigators have reported measurements of DOC in seawater. Though it is still the least understood organic reservoir, the amount of information on DOC has increased dramatically, supported by progress in field measurements and modeling studies (Hansell et al., 2009; Ogawa and Tanoue, 2003). Laboratory experiments (Shaw and Carpenter, 2013; Martino et al., 2012) involving DOC in seawater and O_3 have shown that DOC also contributes to the enhancement of O_3 v_d over seawater. Bromide is present in seawater at higher concentration than iodide, DMS, or DOC and can potentially also react with O_3 dissolved in seawater. The O_3-bromide reaction has been studied for many years in the context of using O_3 for water treatment. In addition to the chemical reactivity of seawater components and O_3, it has long been recognized that the salinity of seawater has an impact on the Henry's law constants of water soluble substances (Dacey et al., 1984) and in turn may decrease the deposition velocity of atmospheric O_3 onto seawater. The correction factor of Henry's law constants for seawater compared to fresh water can exceed 20% for VOC species (Dewulf et al., 1995). This work is an extension of our previous study (Sarwar et al., 2015) that examined the impacts of enhanced O_3 deposition due to the interaction of O_3 with iodide in seawater and atmospheric halogen chemistry using a comprehensive atmospheric modeling system. Here, we investigate the impacts of iodide, DMS, DOC, bromide, and seawater salinity on O_3 deposition over seawater.

2. Methodology

2.1. Model description

The hemispheric Community Multi-scale Air Quality (CMAQv5.0) model (Mathur et al., 2012, 2014) was used for this study (www.cmascenter.org). The model accounts for all major atmospheric processes including advection, chemistry, and dry/wet deposition. It was applied over the Northern Hemisphere using 108-km horizontal grids and 44 vertical layers of varying thickness covering from the surface to 50 mbar. The first layer height was 20 m. Emissions and meteorological fields used here were previously described by Xing et al. (2015) and Sarwar et al. (2015).

2.2. Deposition velocity of O_3 over sea-water

In CMAQ, v_d of gaseous species is parameterized using the resistance analogy approach (Wesley, 1989):

$$v_d = (R_a + R_b + R_s)^{-1} \tag{1}$$

where the aerodynamic resistance (R_a) accounts for the effect of atmospheric turbulence, the boundary layer resistance (R_b) represents diffusion across the quasi-laminar near-surface layer, and the surface resistance (R_s) represents the uptake by the surface. R_a and R_b are calculated using the Pleim-Xiu land surface model (Pleim and Xiu, 1995):

$$R_a = \frac{Pr}{ku_*}\left(\log\left(z_{ref}/z_0\right) - \psi\right) \tag{2}$$

$$R_b = \frac{5}{u_*}\left(\frac{Sc}{Pr}\right)^{2/3} \tag{3}$$

where Pr = Prandtl number (unitless), k = von Karman constant (0.4), u_* = friction velocity (m s^{-1}), z_{ref} = midpoint of the lowest model layer, z_0 = surface roughness (m), Ψ = stability correction function (unitless) and Sc = Schmidt number (unitless). R_S is calculated following the approach of Chang et al. (2004) which accounts for the interaction of O_3 with chemical species present in seawater.

$$R_s = \frac{1}{H_{eff}\left(ak_w + (\lambda D)^{1/2}\right)} = \frac{1}{pk_w + q} \tag{4}$$

where k_w = gas transfer velocity (m s^{-1}), a = chemical enhancement factor, $(\lambda D)^{1/2}$ = chemical loss of O_3, $p = (a)(H_{eff}) = 1.75$, and $q = (\lambda D)^{1/2} (H_{eff})$. The values for k_w and q are calculated as:

$$k_w = \frac{k(\rho_a/\rho_w)^{0.5}(u_*)}{\left(\frac{Sc}{Pr}\right)^{2/3}} \tag{5}$$

$$q = \sum_i q_i = \sum_i \sqrt{k_i C_i d_w}\left(H_{eff}\right) \tag{6}$$

where H_{eff} = dimensionless effective Henry's law constant (ratio of aqueous to gas phase), ρ_a = density of air (g cm^{-3}), ρ_w = density of water (g cm^{-3}), k_i is the rate constant of the reaction of species i in seawater with dissolved O_3 (described in subsequent sections), C_i = concentration of species i in seawater, and d_w = diffusion coefficient of O_3 in water (m^2 s^{-1}). A temperature dependent Henry's law constant (Kosak-Channing and Helz, 1983) is used in the CMAQ model.

Garland et al. (1980) reported that the reaction of O_3 and iodide in seawater can enhance v_d over seawater. Chang et al. (2004) developed a scheme to account for the interaction of dissolved O_3 and iodide in seawater on v_d which was recently implemented into the CMAQ model (Sarwar et al., 2015). In this study, we build upon Sarwar et al. (2015) by modifying the interaction of O_3 with iodide in seawater by also accounting for the interaction of O_3 with DMS, DOC, and bromide in seawater.

2.2.1. Treatment of O_3-iodide interaction

Sarwar et al. (2015) used a fixed O_3-iodide rate constant ($k_{IODIDE} = 2.0 \times 10^9$ M^{-1} s^{-1}) following Garland et al. (1980) and Chang et al. (2004). Magi et al. (1997) performed experiments to study the effect of salinity and water temperature on k_{IODIDE} and reported that both salinity and temperature are positively related to k_{IODIDE}. Using Magi et al. (1997) data, Coleman et al. (2010) developed a correlation for k_{IODIDE} as a function of sea surface temperature (SST) at an ionic strength of 0.7 M as follows.

$$k_{IODIDE} = (0.15 \times SST - 40.85) \times 10^9 \tag{7}$$

While Sarwar et al. (2015) did not include the effect of salinity and water temperature on k_{IODIDE}, we include these effects here. The experiments of Magi et al. (1997) were limited to 273–296 K; thus we limit SST to within this range for calculating k_{IODIDE}. The calculated rate constant at 296 K is 3.6×10^9 M^{-1} s^{-1} which is ~80% larger than the value reported by Garland et al. (1980) while the calculated rate constant at 273 K is an order of magnitude lower than the Garland et al. (1980) reported value.

In their analysis, MacDonald et al. (2014) calculated iodide