

Abstract

Naturally emitted reactive trace gases are thought to impact tropospheric composition, predominantly through the emission and chemistry of isoprene (C_5H_8). Other species are thought to play a less important role. Here the GEOS-Chem model is used to compare the impacts of isoprene and iodine emissions on present-day tropospheric composition. Removing isoprene emissions leads to a 4.4% decrease in tropospheric O_3 burden, a smaller absolute change than the 5.7% increase from removing iodine emissions. Iodine has a negligible impact on global mean OH concentrations and methane lifetime (-0.2% and +0.1%). Isoprene has a substantial impact on both (-7% and +6.5%). Isoprene emissions and chemistry are seen as essential for tropospheric chemistry models, but iodine is often not. We suggest iodine should receive greater attention in model development and experimental research to allow improved predictions of past, present and future tropospheric O_3 .

Plain Language Summary

Natural emissions from the Earth's surface play a large role in determining the chemistry of the atmosphere, influencing air quality and climate change. Considerable attention is given to land based emissions, notably of isoprene, which are emitted in vast quantities by trees and other vegetation and can impact the concentration of O_3 , aerosols and the hydroxyl radical. Historically less emphasis has been on the influence of emissions of other compounds. We show that for one aspect of atmospheric composition (the globally averaged O_3 concentrations) emission of iodine from the ocean are likely at least as important as isoprene emissions and may be more so. As such, there should be an increased focus on better understanding the emissions and chemistry of iodine species (and other halogens) and embed this information into our understanding of the Earth system.

1 Introduction

Gaseous emissions arising from terrestrial and marine ecosystems play important roles in regulating tropospheric photochemistry, in turn influencing climate and air quality. For example, oceanic emissions of dimethyl sulfide (DMS) are the dominant source of sulfur into clean background marine air (Yang et al., 2011; Sinha et al., 2007). The resulting sulfur aerosol directly scatters solar radiation as well as acting as cloud con-

44 densation nuclei and thus these emissions play an important role in global climate (Shaw,
45 1983; Andreae & Crutzen, 1997; Ayers & Gillett, 2000).

46 Natural terrestrial biogenic emissions of volatile organic compounds (VOCs) have
47 significant impacts on atmospheric oxidants (Trainer et al., 1987). Isoprene (C_5H_8) forms
48 the largest of these emissions ($500Tg\ yr^{-1}$ (Guenther et al., 2012, 2006)), and has been
49 the focus of a large body of research in terms of both the rate and controlling factors of
50 its emission and its subsequent atmospheric degradation chemistry. Isoprene emissions
51 come from plants and are dependent on temperature, rainfall, leaf area and other fac-
52 tors, exhibiting large variability both geographically and seasonally (Fuentes & Wang,
53 1999; Schnitzler et al., 1997; Guenther et al., 2006). Tropical broadleaf trees contribute
54 approximately half of all global isoprene emissions (Guenther et al., 2006), thus the largest
55 isoprene emissions come from areas with the greatest concentration of this plant type,
56 in particular the Amazon rainforest.

57 The oxidation chemistry of isoprene has been extensively studied in the field (Wiedinmyer
58 et al., 2001; Roberts et al., 1998; Starn et al., 1998; Biesenthal & Shepson, 1997) and in
59 laboratory experiments (Atkinson et al., 1989; Paulson et al., 1992; Paulson & Seinfeld,
60 1992; Grosjean et al., 1993). Numerical models have been developed to incorporate known
61 degradation chemistry (Trainer et al., 1987; Jenkin et al., 2015; Saunders et al., 2003;
62 Bates & Jacob, 2019). Oxidation of isoprene is typically initiated by the hydroxyl rad-
63 ical (OH) and thus isoprene represents a large, natural, global sink for OH (Lelieveld et
64 al., 2008). It can also react with ozone (O_3) and other oxidants (nitrate radical (NO_3),
65 chlorine radical (Cl)) (Wennberg et al., 2018). The subsequent photo-chemistry is com-
66 plex, with a large number of long and short lived species (Wennberg et al., 2018). If iso-
67 prene oxidation occurs in the presence of suitable NO_x concentrations, the production
68 of peroxy radicals (RO_2) can lead to net O_3 production. At lower NO_x concentrations
69 the primary reaction between O_3 and isoprene, together with its ability to produce NO_y
70 reservoir species and so reduce NO_x concentrations, can lead to net O_3 loss (Paulot et
71 al., 2012; Horowitz et al., 2007). Transport of NO_y species produced during isoprene ox-
72 idation can increase NO_x concentrations in remote downwind regions, increasing O_3 pro-
73 duction many thousands of kilometers from the isoprene source (Bates & Jacob, 2019).
74 Overall, isoprene is calculated to be a net source of O_3 into the global troposphere (Pierce
75 et al., 1998; Fiore et al., 2011; Squire et al., 2015; Bates & Jacob, 2019).

76 In contrast to isoprene, iodine emissions lead to the destruction of O_3 . O_3 from the
77 atmosphere can be transported into the ocean's surface microlayer (SML) where it can
78 react with iodide (I^-) to produce HOI and I_2 (Carpenter et al., 2021). These emissions
79 are estimated to supply 2 Gg yr^{-1} of iodine to the global atmosphere. An additional 0.6
80 Gg yr^{-1} of iodine occurs through the emission of iodinated hydrocarbons (CH_3I , CH_2I_2 ,
81 CH_2IBr and CH_2ICl) (Jones et al., 2010; MacDonald et al., 2014; Prados-Roman et al.,
82 2015). This reaction between I^- and O_3 in the SML is also responsible for a significant
83 fraction of the dry deposition of O_3 to the ocean (Fairall et al., 2007; Carpenter et al.,
84 2013; Luhar et al., 2017; Pound et al., 2020).

85 I^- in the SML is formed from the thermodynamically more stable iodate (IO_3^-) via
86 biological reduction processes (Amachi, 2008; Chance et al., 2007) and as such could dis-
87 play sensitivity to both seasonal and climate timescales (Carpenter et al., 2021). Ice core
88 samples show that the atmospheric iodine abundance has increased since pre-industrial
89 times and significantly accelerated through the end of the 20th century, which is mainly
90 attributed to increased atmospheric O_3 driving higher HOI and I_2 emissions (Cuevas et
91 al., 2018; Legrand et al., 2018).

92 Tropospheric lifetimes of the emitted gaseous iodine compounds are relatively short
93 (on the order of minutes to days), photolyzing to produce atomic iodine (I). The sub-
94 sequent catalytic iodine cycles are an efficient chemical loss route of O_3 . Iodine atoms
95 are rapidly oxidised by O_3 to form iodine oxide (IO), which can then further self-react
96 to form higher oxides or cycle back to atomic I (Sommariva et al., 2012). Further reac-
97 tions of IO can impact both HOx ($OH + HO_2$) and NO_x ($NO + NO_2$) concentrations
98 (Sommariva et al., 2012; Sherwen, Evans, et al., 2016). The inclusion of I chemistry in
99 model simulations has been shown to reduce surface O_3 concentrations and lower back-
100 ground O_3 (Sarwar et al., 2019; Sherwen, Evans, et al., 2016). Recent work also shows
101 that iodine containing trace compounds can be exported from the troposphere into the
102 stratosphere where they may play a role in modulating the concentration of stratospheric
103 O_3 (Koenig et al., 2020; Cuevas et al., 2022).

104 Observations of reactive inorganic iodine compounds in the atmosphere are lim-
105 ited mainly to IO, which has been measured using a number of optical techniques (Prados-
106 Roman et al., 2015; Volkamer et al., 2015; S. Wang et al., 2015; Koenig et al., 2020; Gómez Martín
107 et al., 2013; Großmann et al., 2013; Mahajan et al., 2012, 2010). Although these emis-
108 sions are sparse, model simulations of IO generally compare well to these observations

109 (X. Wang et al., 2021). Observations have also been made of I_2 (Lawler et al., 2014) how-
110 ever these are even more limited in their spatial distribution than those of IO.

111 Although the mass of isoprene (500 Tg yr⁻¹ (Guenther et al., 2012)) and iodine
112 (4 TgI yr⁻¹ (Sherwen, Schmidt, et al., 2016)) emitted into the atmosphere differ sig-
113 nificantly, both can have a profound impact on the composition of the troposphere. As-
114 sessing the relative impacts on troposphere composition based on previous literature is
115 difficult as these assessments have been made in different models over different timescales
116 and have focused on the impact of only one of these sources at a time. Thus, assessing
117 the relatively importance of isoprene and iodine emissions on tropospheric photo-chemistry
118 is difficult. Here we use the GEOS-Chem model to compare the relative impacts of io-
119 dine and isoprene on the tropospheric abundance of O_3 and OH, and the impact of both
120 iodine and isoprene on surface O_3 mixing ratios. Thus, we compare the overall impacts
121 of iodine and isoprene on atmospheric composition and present the argument that io-
122 dine should be considered, analogously to isoprene, as an important natural control on
123 atmospheric composition.

124 2 Model description

125 This work uses the GEOS-Chem model (Bey et al., 2001) version 13.1.1 (GCC13.1.1,
126 2021) run globally at a spatial resolution of $2^\circ \times 2.5^\circ$ on the reduced vertical grid (47 ver-
127 tical levels), running with full chemistry in both the troposphere and stratosphere. Me-
128 teorological data for these runs used MERRA-2 (Gelaro et al., 2017).

129 Isoprene emissions in GEOS-Chem are from MEGAN v2.1 (Guenther et al., 2012)
130 which varies isoprene emissions depending on plant functional type, leaf area index, tem-
131 perature, and photosynthetically active radiation. The subsequent isoprene oxidation chem-
132 istry in GEOS-Chem is from Bates and Jacob (2019) which has been used since model
133 version 12.8.

134 The halogen (Cl, Br, I) chemistry scheme in GEOS-Chem was recently updated
135 in version 12.9 by X. Wang et al. (2021). Organic iodine emissions are from Ordóñez et
136 al. (2012). Inorganic iodine emissions follow Carpenter et al. (2013) as implemented by
137 Sherwen, Evans, et al. (2016) and are given by equations 1 and 2 where ws is the wind
138 speed [m/s], $[O_{3(g)}]$ is the O_3 concentration in the atmosphere at the interface with the
139 surface [ppbv], and $[I_{aq}^-]$ is the oceanic iodide concentration [Mol].

$$F_{HOI} = [O_{3(g)}] \sqrt{[I_{(aq)}^-]} \left(\frac{3.56 \times 10^5}{ws} - 2.16 \times 10^4 \right) \quad (1)$$

$$F_{I_2} = [O_{3(g)}][I_{(aq)}^-]^{1.3} (1.74 \times 10^9 - 6.54 \times 10^8 \ln(ws)) \quad (2)$$

The ocean surface iodide concentration is given by the parameterization of MacDonald et al. (2014), given in equation 3, where T is the sea surface temperature [K].

$$[I_{(aq)}^-] = 1.46 \times 10^6 \times \exp\left(\frac{-9134}{T}\right) \quad (3)$$

Three model runs were conducted from the 1st of January 2015 to the 1st of July 2017. The first year and a half of each simulation was considered the spin up to allow the composition to reach equilibrium. Analysis was thus performed on the period 1st July 2016 to 1st July 2017. For the first simulations no changes were made to the model. For the second simulation iodine emissions from the ocean were set to zero, and the concentration of iodine containing compounds in the model initial condition (for 2015-01-01) were set to zero. In the third simulation, isoprene emissions were set to zero, and the concentration of isoprene derived in the initial condition (for 2015-01-01) were also set to zero.

The model output daily average diagnostics with data processing performed in python using xarray (Hoyer & Hamman, 2017), numpy (Harris et al., 2020), cartopy (Met Office, 2010 - 2015) and matplotlib (Hunter, 2007).

3 Results

3.1 Impacts on O₃

Figure 1 shows the percentage change in annual mean concentrations of surface and zonal O₃ concentrations from switching off iodine (left) and isoprene emissions (right). Equivalent analyses for CO, NO_x and NO_y are shown in the supplementary material (figures S1 to S3). Iodine emissions reduce the global tropospheric O₃ burden from 332 Tg/yr to 315 Tg/yr (5% reduction). The largest decreases occur within the tropical marine boundary layer ($\geq 20\%$) above tropical waters where iodide concentrations are the greatest (Chance et al., 2014), resulting in the highest iodine emissions (Sherwen, Evans, et al., 2016). Due to rapid atmospheric convection over the tropics, this region of depleted O₃ extends up to around 6km altitude. Another region of fractionally significant iodine-initiated O₃ loss

166 is the Southern Ocean where the large ocean surface area provides widespread iodine emis-
167 sion. However due to the comparatively low O_3 concentrations over the Southern Ocean,
168 these large percentage changes do not correspond to large changes in absolute concen-
169 tration. A percentage decrease of 10% at 2km here translates to 2 ppbv reduction in
170 O_3 .

171 Isoprene emissions create a more complex distribution of changes. Over Amazo-
172 nia and Oceania, the locations of the largest isoprene emission, O_3 concentrations de-
173 crease at the surface. This is for two reasons. Firstly the direct reaction between O_3 and
174 isoprene increases the chemical loss of O_3 (10% of global isoprene emissions are oxidised
175 by O_3 (Bates & Jacob, 2019)). Secondly the concentrations of NO_x in the region decrease
176 as NO_x is shifted to reservoir species (NO_y , poly-aromatic nitrates (PAN) and organic
177 nitrates) which reduces the chemical production of O_3 over the region (NO_x and NO_y
178 are shown in the supplementary material (figures S2 and S3). Outside of these regions,
179 the isoprene driven shift of NO_x to NO_y species over emission regions contributes to the
180 global picture of increased O_3 . Away from these emission regions, transported NO_y in-
181 crease NO_x concentrations over the remote oceans downwind of high isoprene emissions,
182 increasing O_3 production (figure 1). This is most noticeable in the southern hemisphere.
183 Globally the increase in O_3 from isoprene emissions is dominated by this increase in NO_x .
184 Any increase in O_3 due to an increase in VOC concentration is limited because only a
185 small amount of the world is VOC limited (mostly polluted cities in America, Europe
186 and Asia) with the majority of the worlds O_3 production being NO_x limited (Ivatt et
187 al., 2022).

188 Globally the impact of isoprene and iodine on O_3 are similar but opposite. Isoprene
189 increases the tropospheric O_3 burden by 13.6 Tg (4.1%) whereas iodine decreases it by
190 16.5 Tg (5.4%). Close to the surface (0-1km), iodine's impact on O_3 (2.4 Tg, 8.9% de-
191 crease) is significantly larger than that of isoprene (1.2 Tg, 4.4% increase). Both are more
192 important in the southern hemisphere than the northern, although iodine reduces the
193 O_3 burden by almost 50% more than isoprene increases it. The relatively larger role of
194 both iodine and isoprene in southern hemispheric O_3 reflects the increased importance
195 of natural processes compared to anthropogenic emissions there.

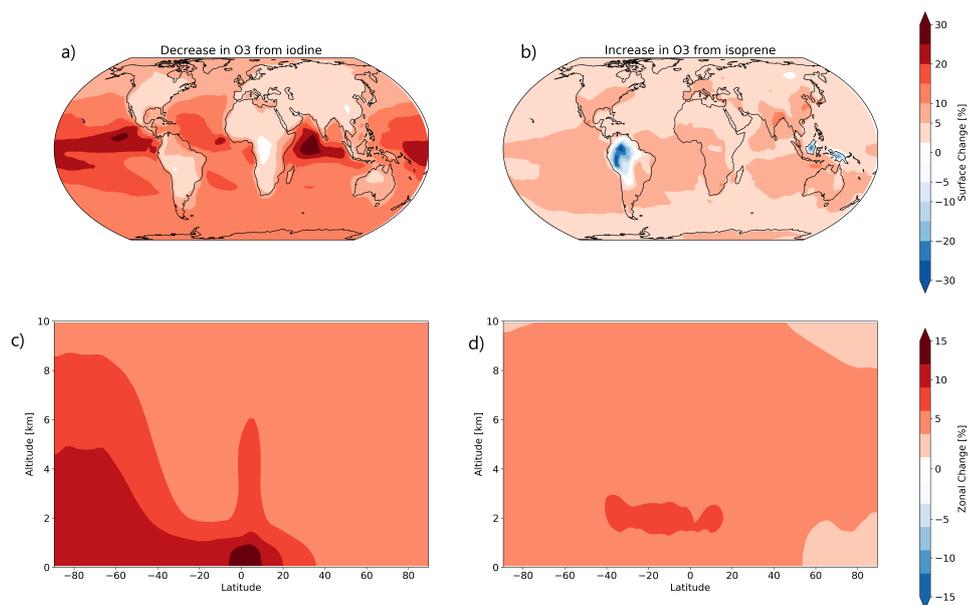


Figure 1. Annual average percentage decrease in surface [a) and b)] and zonal [c) and d)] O₃ from iodine emissions [a) and c)] and annual average percentage increase in surface and zonal O₃ from isoprene emissions [b) and d)].

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3.2 Impact on OH

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The similarity in the influence of isoprene and iodine on O₃ is not seen for OH. Figure 2 shows that iodine emissions in the model have negligible changes to tropospheric OH concentration (-0.24%), whereas isoprene emissions decrease tropospheric OH by around 7%. This difference in the response reflects different chemistry. The impact of iodine on OH has previously been found to be small due to compensating effects (Sherwen, Evans, et al., 2016). The reduction in O₃ concentrations from iodine leads to lower primary OH production, this is however offset by increased conversion of HO₂ to OH cycling via HOI. The global increase in O₃ from isoprene increases the primary chemical production of OH, however globally the increase in the chemical sink from reactions of OH with isoprene and its degradation products, is dominant and OH is decreased. The largest decreases in OH coincide with the regions of greatest isoprene emissions (Amazonia and Oceania). Due to efficient convection over these locations, the reduction in OH is observed throughout the troposphere. The change in model OH concentrations driven by isoprene

210 and iodine emissions results in changes in methane lifetimes of similar importance. The
211 reduction in OH concentrations from isoprene emissions increases the methane lifetime
212 by 6.5% (from 8.7 to 9.3 yrs). The negligible changes in OH caused by iodine result in
213 a minimal impact on methane lifetime (0.1% increase).

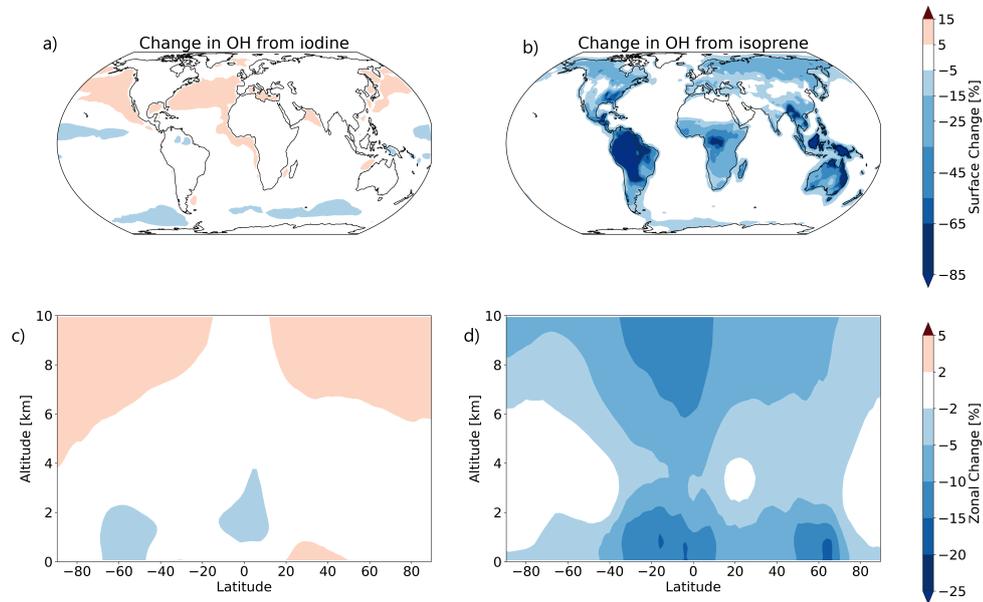


Figure 2. Annual average percentage change in surface [a) and b)] and zonal [c) and d)] OH from iodine emissions [a) and c)] and from isoprene emissions [b) and d)].

214 **3.3 Importance of iodine and isoprene emissions on background O₃**

215 Figure 3 shows the ratio of change in surface O₃ from isoprene and iodine emis-
216 sions. Additional seasonal plots, both global and regional, are shown in figures S4-7 of
217 the supplementary material. This ratio allows for a comparison of the relative impor-
218 tance of iodine or isoprene emissions to be determined on surface O₃ concentration.

219 Although isoprene emissions lead to O₃ production in remote regions via increas-
220 ing NO_y concentration, O₃ loss due to iodine is more important in the marine environ-
221 ment. Iodine is thus more important than isoprene in determining the background con-
222 centration of O₃ at inflow regions (west coast of America and northern Europe). Iodine
223 emissions are less important for Asia as transport of airmasses into this region spend no
224 or negligible amounts of time over the ocean, with inflow coming from Europe.

225 Northern hemisphere winter O₃ in both terrestrial and oceanic environments has
226 a significantly greater dependence on iodine emissions than isoprene emissions. This is
227 largely due to minimal isoprene emissions and little O₃ production. This is not the case
228 in the southern hemisphere where high isoprene emissions from South America and much
229 of Africa maintain the dependence on isoprene. Changes to wind direction in summer
230 and autumn result in iodine becoming important for O₃ into central Asia as the air mass
231 entering this region switches from continental to oceanic in origin.

232 An important driver of the seasonal variation in the relative importance of iodine
233 and isoprene is seasonality in their respective emissions. Iodine emissions only have a
234 weak seasonal dependence when compared to isoprene emissions. Monthly iodine emis-
235 sions in the northern hemisphere increase by 23% from minimum to maximum whereas
236 isoprene increases by 270%.

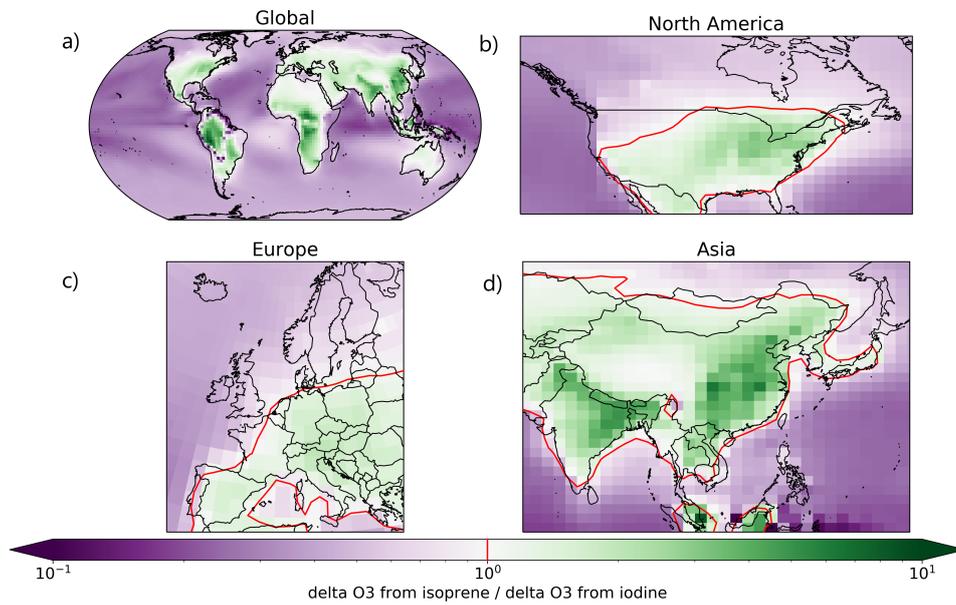


Figure 3. Average surface ratio of fractional change in O_3 from isoprene to fractional change in O_3 from iodine, globally [a)], North America [b)], Europe [c)] and Asia [d)]. Red contour lines on regional plots are drawn based on the value of the ratio being 1 (iodine and isoprene emissions have equal impact on surface O_3)

4 Conclusions

Globally, iodine and isoprene emissions have a similar impact on the tropospheric O_3 burden but in an opposing direction. The relative importance of each depends on location and season. Although iodine has the larger impacts on O_3 , its impact on OH and methane lifetime are negligible compared to isoprene. Iodine has significantly more impact on surface O_3 concentrations than isoprene. This has specific importance when considering background O_3 air quality at inflow regions where the air mass has been transported over the marine environment, such as the western coast of north America and Europe. The emissions and subsequent chemistry of iodine should be considered in the same way as isoprene.

The processes leading to inorganic iodine flux from the ocean surface are complex, much like isoprene, however, the representation of these emissions is currently simplistic. Iodine emissions are dependent on the downward flux of O_3 from the atmosphere into the SML, aqueous iodine chemistry, turbulence and the physical processes in the ocean surface as well as biological factors. Previous experimental constraints of the $O_3 + I^-$ reaction and the role of organic chemistry are poorly constrained due to lack of experimental data and experimental data not reflecting real world SML concentrations. A more advanced representation of oceanic iodine emissions for use in global models should couple the chemical, physical and biological processes in the SML which drive the flux of iodine into the atmosphere. This will more accurately represent the production and subsequent emission of iodine and further improve our understanding of the role ocean atmosphere exchange plays in modulating tropospheric photochemistry.

5 Open Research

GEOS-Chem source code is openly available on GitHub (<https://github.com/geoschem/geos-chem>). This work used model version 13.1.1 (GCC13.1.1, 2021).

Analysis code used to produce statistics and figures in this paper are available at <https://doi.org/10.5281/zenodo.7016985> (Pound, 2022).

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