

This is a repository copy of *Comparing the Importance of Iodine and Isoprene on Tropospheric Photochemistry*.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/198640/>

Version: Published Version

---

**Article:**

Pound, R. J. [orcid.org/0000-0003-1547-6565](https://orcid.org/0000-0003-1547-6565), Durcan, D. P., Evans, M. J. [orcid.org/0000-0003-4775-032X](https://orcid.org/0000-0003-4775-032X) et al. (1 more author) (2023) Comparing the Importance of Iodine and Isoprene on Tropospheric Photochemistry. *Geophysical Research Letters*. e2022GL100997. ISSN 0094-8276

<https://doi.org/10.1029/2022GL100997>

---

**Reuse**

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:

<https://creativecommons.org/licenses/>

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.

# Geophysical Research Letters®



## RESEARCH LETTER

10.1029/2022GL100997

## Comparing the Importance of Iodine and Isoprene on Tropospheric Photochemistry

R. J. Pound<sup>1</sup> , D. P. Durcan<sup>1</sup>, M. J. Evans<sup>1,2</sup> , and L. J. Carpenter<sup>1</sup> 

<sup>1</sup>Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, UK, <sup>2</sup>National Centre for Atmospheric Science, University of York, York, UK

### Key Points:

- Present-day inorganic iodine emissions decrease tropospheric O<sub>3</sub> substantially more than biogenic isoprene emissions increase it
- At the surface, the impact of iodine on O<sub>3</sub> exceeds that for isoprene, and is larger in defining the background for Europe and North America
- Iodine has a negligible impact on OH concentrations and CH<sub>4</sub> lifetimes compared to isoprene

### Supporting Information:

Supporting Information may be found in the online version of this article.

### Correspondence to:

R. J. Pound,  
ryan.pound@york.ac.uk

### Citation:

Pound, R. J., Durcan, D. P., Evans, M. J., & Carpenter, L. J. (2023). Comparing the importance of iodine and isoprene on tropospheric photochemistry. *Geophysical Research Letters*, 50, e2022GL100997. <https://doi.org/10.1029/2022GL100997>

Received 31 AUG 2022

Accepted 16 APR 2023

### Author Contributions:

**Conceptualization:** R. J. Pound, M. J. Evans, L. J. Carpenter  
**Formal analysis:** R. J. Pound  
**Funding acquisition:** L. J. Carpenter  
**Investigation:** R. J. Pound  
**Methodology:** R. J. Pound  
**Software:** R. J. Pound  
**Supervision:** M. J. Evans, L. J. Carpenter  
**Writing – original draft:** R. J. Pound  
**Writing – review & editing:** M. J. Evans, L. J. Carpenter

**Abstract** Isoprene, arguably the most studied biogenically emitted gas, is thought to have a large impact on tropospheric composition. Other naturally emitted species have been considered 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 3.4% decrease in tropospheric O<sub>3</sub> burden, a smaller absolute change than the 5.9% increase from removing iodine emissions. Iodine has a negligible impact on global mean OH concentrations and methane lifetime (+0.6% and +0.05%) whereas isoprene has a substantial impact on both (−4.3% and −4.2%). Isoprene emissions and chemistry are seen as essential for tropospheric chemistry models, but iodine is often not. We suggest that iodine should receive greater attention in model development and experimental research to allow improved predictions of past, present, and future tropospheric O<sub>3</sub>.

**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<sub>3</sub>, 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<sub>3</sub> concentrations) emissions 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 embedding this information into our simulations 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, marine air (Sinha et al., 2007; Yang et al., 2011). The resulting sulfur aerosol directly scatters solar radiation as well as acting as cloud condensation nuclei and thus these emissions play an important role in global climate (Andreae & Crutzen, 1997; Ayers & Gillett, 2000; Shaw, 1983).

Natural terrestrial biogenic emissions of volatile organic compounds (VOCs) have significant impacts on atmospheric oxidants (Trainer et al., 1987). Isoprene (C<sub>5</sub>H<sub>8</sub>) forms the largest of these emissions (500 Tg yr<sup>−1</sup> (Guenther et al., 2006; Guenther et al., 2012)), and has been the focus of a large body of research in terms of both the rate and controlling factors of its emission and its subsequent atmospheric degradation chemistry. Isoprene emissions come from plants and are dependent on temperature, rainfall, leaf area, and other factors, exhibiting large variability both geographically and seasonally (Fuentes & Wang, 1999; Guenther et al., 2006; Schnitzler et al., 1997). Tropical broadleaf trees contribute approximately half of all global isoprene emissions (Guenther et al., 2006), thus the largest isoprene emissions come from areas with the greatest concentration of this plant type, in particular the Amazon rainforest.

The oxidation chemistry of isoprene has been extensively studied in the field (Biesenthal & Shepson, 1997; Roberts et al., 1998; Starn et al., 1998; Wiedinmyer et al., 2001) and in laboratory experiments (Atkinson et al., 1989; Grosjean et al., 1993; Paulson et al., 1992; Paulson & Seinfeld, 1992). Numerical models have been developed to incorporate known degradation chemistry (Bates & Jacob, 2019; Jenkin et al., 2015; Saunders et al., 2003; Trainer et al., 1987). Oxidation of isoprene is typically initiated by the hydroxyl radical (OH) and

© 2023. The Authors.

This is an open access article under the terms of the [Creative Commons Attribution License](https://creativecommons.org/licenses/by/4.0/), which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

thus isoprene represents a large, natural, global sink for OH (Lelieveld et al., 2008). It can also react with ozone ( $O_3$ ) and other oxidants (nitrate radical ( $NO_3$ ), chlorine radical (Cl)) (Wennberg et al., 2018). The subsequent photo-chemistry is complex, involving a large number of long and short lived species (Wennberg et al., 2018). If isoprene oxidation occurs in the presence of suitable  $NO_x$  concentrations, the production of peroxy radicals ( $RO_2$ ) can lead to net  $O_3$  production. At lower  $NO_x$  concentrations the primary reaction between  $O_3$  and isoprene, together with its ability to produce  $NO_y$  reservoir species and so reduce  $NO_x$  concentrations, can lead to local  $O_3$  reductions (Horowitz et al., 2007; Paulot et al., 2012). Transport of  $NO_y$  species produced during isoprene oxidation can increase  $NO_x$  concentrations in remote downwind regions, increasing  $O_3$  production many thousands of kilometers from the isoprene source (Bates & Jacob, 2019). Overall, isoprene is calculated to be a net source of  $O_3$  into the global troposphere (Bates & Jacob, 2019; Fiore et al., 2011; Pierce et al., 1998; Squire et al., 2015).

In contrast to isoprene, iodine emissions lead to the destruction of  $O_3$ . The inclusion of iodine chemistry into box models has been shown to improve the ability to replicate the  $O_3$  loss rate as shown in Read et al. (2008).  $O_3$  from the atmosphere can be transported into the ocean's surface microlayer (SML) where it can react with iodide ( $I^-$ ) to produce HOI and  $I_2$  (Carpenter et al., 2021). These emissions are estimated to supply  $\sim 2$  Tg  $yr^{-1}$  of iodine to the global atmosphere. An additional 0.6 Tg  $yr^{-1}$  of iodine occurs through the emission of iodinated hydrocarbons ( $CH_3I$ ,  $CH_2I_2$ ,  $CH_2IBr$ , and  $CH_2ICl$ ) (Jones et al., 2010; MacDonald et al., 2014; Prados-Roman et al., 2015). This reaction between  $I^-$  and  $O_3$  in the SML is also responsible for a significant fraction of the dry deposition of  $O_3$  to the ocean (Carpenter et al., 2013; Fairall et al., 2007; Luhar et al., 2017; Pound et al., 2020).

Iodide in the SML is formed from the thermodynamically more stable iodate ( $IO_3^-$ ) via biological reduction processes (Amachi, 2008; Chance et al., 2007) and as such could display sensitivity to both seasonal and climate timescales (Carpenter et al., 2021). Ice core samples show that the atmospheric iodine abundance has increased since pre-industrial times and significantly accelerated through the end of the 20th century, which is mainly attributed to increased atmospheric  $O_3$  driving higher HOI and  $I_2$  emissions (Cuevas et al., 2018; Legrand et al., 2018). Tree rings on the Qinghai-Tibet plateau also show this increase in atmospheric iodine ( $I^{127}$ ) through the 20th century, in addition to increases in  $I^{129}$  coinciding with nuclear events (Zhao et al., 2019). No historic iodine trends are yet available for the southern hemisphere.

Tropospheric lifetimes of the emitted gaseous iodine compounds are relatively short (on the order of minutes to days), photolyzing to produce atomic iodine (I). The subsequent catalytic iodine cycles are an efficient chemical loss route of  $O_3$ . Iodine atoms are rapidly oxidized by  $O_3$  to form iodine oxide (IO), which can then further self-react to form higher oxides or cycle back to atomic I (Sommariva et al., 2012). Further reactions of IO can impact both  $HO_x$  ( $OH + HO_2$ ) and  $NO_x$  ( $NO + NO_2$ ) concentrations (Sherwen, Evans, et al., 2016; Sommariva et al., 2012). The inclusion of I chemistry in model simulations has been shown to reduce surface  $O_3$  concentrations and lower background  $O_3$  (Sarwar et al., 2019; Sherwen, Evans, et al., 2016).

Recent work suggests that heterogeneous reactions between iodine oxide nanoparticles formed via rapid nucleation of iodic acid ( $HIO_3$ ) (He et al., 2021), and volatile organics can substantially accelerate particle growth in the marine boundary layer (Huang et al., 2022), suggesting a widespread role for iodine in the formation and growth rate of cloud condensation nuclei. Despite the efficient role iodine compounds play in particle formation, new measurements suggest that the recycling of iodine from aerosol is much more efficient than its current representation in models and therefore the impact on gas phase iodine may be small (Huang et al., 2022; Tham et al., 2021). The new proposed roles of iodine in particle formation are not currently represented in models and their impact is uncertain. If increased uptake of iodine to the aerosol phase is mitigated by efficient recycling back to the gas phase, there may be little change to the overall impacts simulated here, although transport of iodine in the aerosol phase may lead to more widespread iodine chemistry and thus change the spatial distribution of its impacts. Future research will be necessary to better understand the impact of aerosol phase iodine on the composition of the atmosphere. Iodine can also be exported from the troposphere into the stratosphere where it may play a role in modulating the concentration of stratospheric  $O_3$  (Cuevas et al., 2022; Koenig et al., 2020), we do not consider this in this study.

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

(X. Wang et al., 2021). Observations have also been made of  $I_2$  (Lawler et al., 2014) and of HOI, IBr, and ICl (Tham et al., 2021), however these are much more limited than those of IO.

Although the mass of isoprene ( $\sim 500 \text{ Tg yr}^{-1}$  (Guenther et al., 2012)) and iodine ( $\sim 2.6 \text{ TgI yr}^{-1}$  (Sherwen, Schmidt, et al., 2016)) emitted into the atmosphere differ significantly, both can have a profound impact on the composition of the troposphere. Assessing the relative impacts on troposphere composition based on previous literature is difficult as these assessments have been made in different models over different timescales and have focused on the impact of only one of these sources at a time. Thus, assessing the relative importance of isoprene and iodine emissions on tropospheric photo-chemistry is difficult. Here we use the GEOS-Chem model to compare the relative impacts of iodine and isoprene on the tropospheric abundance of  $O_3$  and OH, and the impact of both iodine and isoprene on surface  $O_3$  mixing ratios. Thus, we compare the overall impacts of iodine and isoprene on atmospheric composition and present the argument that iodine should be considered, analogously to isoprene, as an important natural control on tropospheric composition.

## 2. Model Description

This work uses the GEOS-Chem model (Bey et al., 2001) version 14.0.2 (GCC14.0.2, 2022) run globally at a spatial resolution of  $2^\circ \times 2.5^\circ$  on the standard vertical grid (72 vertical levels), running with chemistry in both the troposphere and stratosphere. Meteorological data for these runs used MERRA-2 (Gelaro et al., 2017).

Isoprene emissions in GEOS-Chem are from MEGAN v2.1 (Guenther et al., 2012) which varies isoprene emissions depending on plant functional type, leaf area index, temperature, and photosynthetically active radiation. Oceanic isoprene emissions are not currently included in the GEOS-Chem. These emissions are three orders of magnitude smaller than that of the terrestrial source (Conte et al., 2020), and are thought to have a minimal impact on atmospheric chemistry and climate (Anttila et al., 2010; Arnold et al., 2009). The subsequent isoprene oxidation chemistry in GEOS-Chem is from Bates and Jacob (2019) which has been used since model version 12.8.

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

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

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

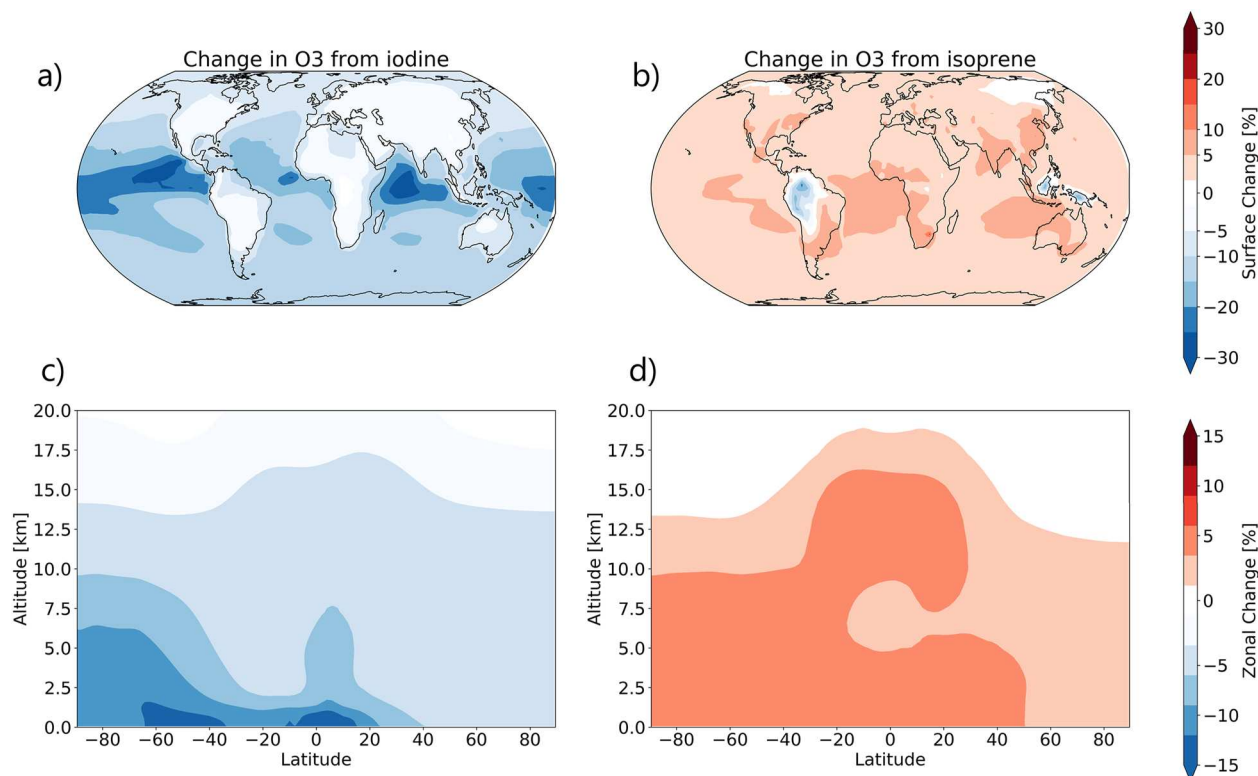
The ocean surface iodide concentration is given by the parameterization of MacDonald et al. (2014), given in Equation 3, where  $T$  is the sea surface temperature [K].

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

Other sources of iodine, for example, coal combustion (Wu et al., 2014), are considered to be negligible and are not currently included in the model.

Three model runs were conducted for the period from 1 January 2016 to 1 January 2018. The first year of each simulation was considered the spin up to allow the composition to reach equilibrium. Analysis was thus performed on the period 1 January 2017 to 1 January 2018. 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 2016-01-01) 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 2016-01-01) 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).



**Figure 1.** Annual average percentage decrease in surface ((a) and (b)) and zonal ((c) and (d))  $O_3$  from iodine emissions ((a) and (c)) and annual average percentage increase in surface and zonal  $O_3$  from isoprene emissions ((b) and (d)).

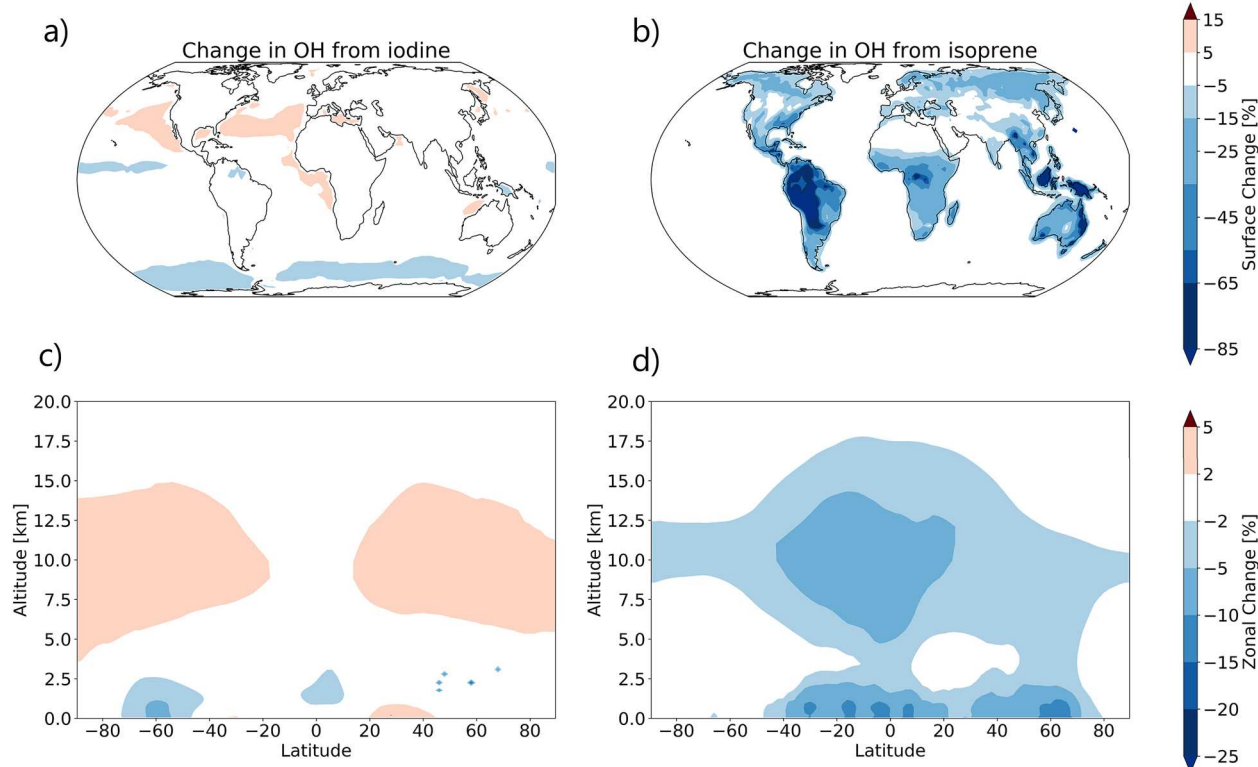
### 3. Results

#### 3.1. Impacts on $O_3$

Figure 1 shows the percentage change in annual mean concentrations of surface and zonal  $O_3$  concentrations from switching off iodine (left) and isoprene emissions (right). Equivalent analyses for  $CO$ ,  $NO_x$  and  $NO_y$  are shown in Figures S1–S3 in Supporting Information S1. Iodine emissions reduce the global tropospheric  $O_3$  burden from 342 Tg/yr to 323 Tg/yr (5.9% 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  $O_3$  extends up to around 6 km altitude. Another region of fractionally significant iodine-initiated  $O_3$  loss is the Southern Ocean where the large ocean surface area provides widespread iodine emission. However due to the comparatively low  $O_3$  concentrations over the Southern Ocean, these large percentage changes do not correspond to large changes in absolute concentration. A percentage decrease of  $\sim 10\%$  at 2 km here translates to  $\sim 2$  ppbv reduction in  $O_3$ .

Isoprene emissions create a more complex distribution of changes. Over Amazonia and Oceania, the locations of the largest isoprene emission, surface  $O_3$  concentrations are reduced. This is for two reasons. First the direct reaction between  $O_3$  and isoprene increases the chemical loss of  $O_3$  (10% of global isoprene emissions are oxidized by  $O_3$  (Bates & Jacob, 2019)). Second the concentrations of  $NO_x$  in the region decrease due to reactions with isoprene and its products, shifting  $NO_x$  to reservoir species ( $NO_y$ , PeroxyacetylNitrate (PAN) and organic nitrates). This reduction in  $NO_x$  reduces the chemical production of  $O_3$  over the region.  $NO_x$  and  $NO_y$  surface and zonal changes are shown in Figures S2 and S3 in Supporting Information S1. Outside of these regions, the isoprene driven shift of  $NO_x$  to  $NO_y$  species over emission regions contributes to the global picture of increased  $O_3$ ,  $NO_y$  transported from isoprene emitting regions results in an increase of  $NO_x$  concentrations over the remote oceans, increasing  $O_3$  production (Figure 1). This is most noticeable in the southern hemisphere. Globally the increase in  $O_3$  from isoprene emissions is dominated by this increase in  $NO_x$ . Any increase in  $O_3$  due to an increase in





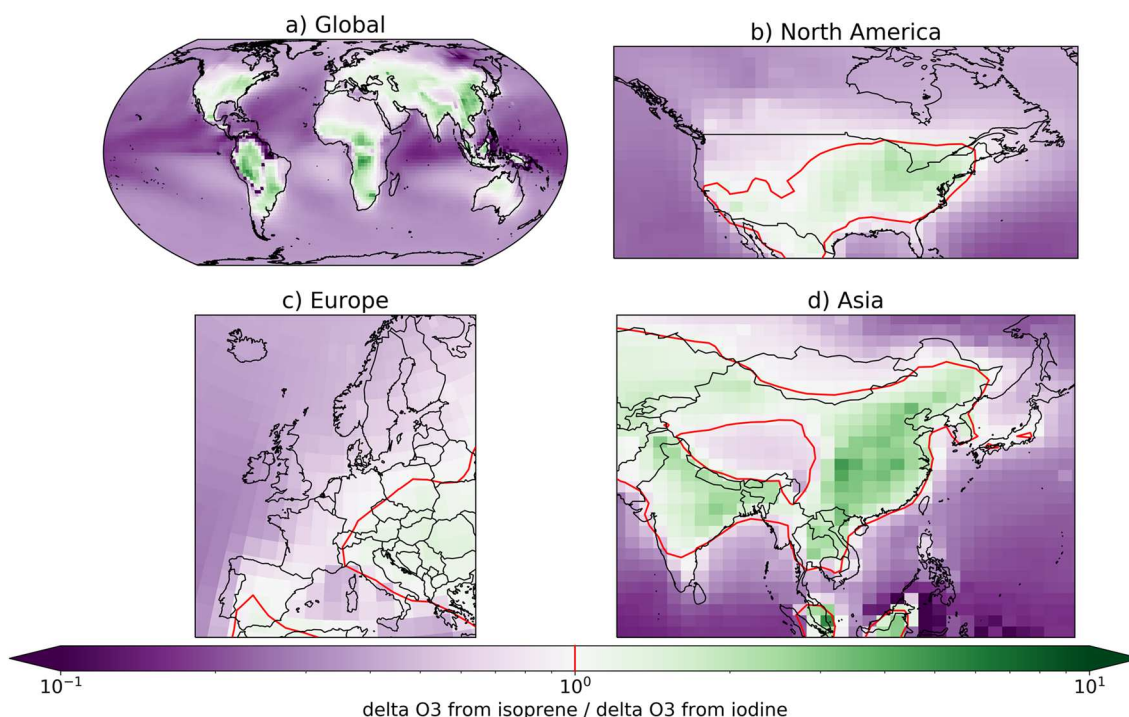
**Figure 2.** Annual average percentage change in surface ((a) and (b)) and zonal ((c) and (d)) OH from iodine emissions ((a) and (c)) and from isoprene emissions ((b) and (d)).

VOC concentration is limited because only a small amount of the world is VOC limited (mostly polluted cities in America, Europe and Asia) with the majority of the world's  $O_3$  production being  $NO_x$  limited (Ivatt et al., 2022).

Globally iodine reduces tropospheric  $O_3$  significantly more than isoprene increases it. Isoprene increases the tropospheric  $O_3$  burden by 11.28 Tg (3.4%) whereas iodine decreases it by 19.1 Tg (5.9%). Close to the surface (0–1 km), iodine's impact on  $O_3$  (2.8 Tg, 9.7% decrease) is significantly larger than that of isoprene (1.0 Tg, 3.8% increase). Both are more important in the southern hemisphere than the northern, although iodine reduces the  $O_3$  burden by almost 50% more than isoprene increases it. The relatively larger role of both iodine and isoprene in southern hemispheric  $O_3$  reflects the increased importance of natural processes compared to anthropogenic emissions there.

### 3.2. Impact on OH

The similar magnitude of influence by isoprene and iodine on  $O_3$  is not seen for OH. Figure 2 shows that iodine emissions in the model have negligible changes to tropospheric OH concentration (+0.6%), whereas isoprene emissions decrease tropospheric OH by 4.3%. 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  $O_3$  concentrations from iodine leads to lower primary OH production (from  $O_3$  photolysis in the presence of water), this is however offset by increased conversion of  $HO_2$  to OH cycling via HOI. The global increase in  $O_3$  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 and iodine emissions results in changes in methane lifetimes of similar importance. The reduction in OH concentrations from isoprene emissions increases the methane lifetime by 4.2% (9.25–10.6 years). The negligible changes in OH caused by iodine result in a minimal impact on methane lifetime (0.05% decrease).



**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  $O_3$ ).

### 3.3. Importance of Iodine and Isoprene Emissions on Background $O_3$

Figure 3 shows the ratio of change in surface  $O_3$  from isoprene and iodine emissions. Additional seasonal plots, both global and regional, are shown in Figures S4–S7 in Supporting Information S1. This ratio allows for a comparison of the relative importance of iodine or isoprene emissions to be determined on surface  $O_3$  concentration.

Although isoprene emissions lead to  $O_3$  production in remote regions (from  $NO_y$  being transported from isoprene source regions),  $O_3$  loss due to iodine is more important in the marine environment. Iodine is thus more important than isoprene in determining the background concentration of  $O_3$  at inflow regions (west coast of America and northern Europe). Iodine emissions are less important for Asia as transport of airmasses into this region spend no or negligible amounts of time over the ocean, with inflow coming from Europe.

Northern hemisphere winter  $O_3$  in both terrestrial and oceanic environments has a significantly greater dependence on iodine emissions than isoprene emissions. This is largely due to minimal isoprene emissions and little  $O_3$  production. This is not the case in the southern hemisphere where high isoprene emissions from South America and much of Africa maintain the dependence on isoprene. Changes to wind direction in summer and autumn result in iodine becoming important for  $O_3$  into central Asia as the airmass entering this region switches from continental to oceanic in origin.

An important driver of the seasonal variation in the relative importance of iodine and isoprene is seasonality in their respective emissions. Iodine emissions only have a weak seasonal dependence when compared to isoprene emissions. Monthly averaged iodine emissions in the northern hemisphere increase by 23% from minimum to maximum whereas isoprene increases by  $\sim 270\%$ .

## 4. Comparison to Previous Studies

Table 1 compares the results of this study with previously reported changes in tropospheric  $O_3$  burden, global average OH concentration and methane lifetime due to the inclusion of (a) iodine, (b) all halogens (iodine, bromine, and chlorine), and (c) isoprene. The impact of iodine on the  $O_3$  burden found in this study ( $-5.9\%$ ) is

**Table 1**  
*Comparison of the Results of This Study With Previously Reported Percentage Changes in the Tropospheric O<sub>3</sub> Burden, Average OH Concentration and Methane Lifetime Due to the Inclusion of Iodine, Iodine and Bromine, All Halogens (Iodine + Bromine + Chlorine) and Isoprene Emissions*

Study	O <sub>3</sub>	OH	CH <sub>4</sub> lifetime
<b>Iodine</b>			
Sherwen, Evans, et al. (2016)	−9.9%	+1.8%	–
Iglesias-Suarez et al. (2020) <sup>a</sup>	−10%	–	–
This study	−5.9%	+0.6%	−0.05%
<b>All Halogens</b>			
Sherwen, Evans, et al. (2016) <sup>b</sup>	−14.4%	+1.8%	–
Sherwen, Schmidt, et al. (2016)	−18.6%	−8.2%	+10.8%
Iglesias-Suarez et al. (2020)	−13%	–	–
Badia et al. (2021)	−11%	–	–
X. Wang et al. (2021)	−11%	−4%	–
Li et al. (2022) <sup>c</sup>	–	–	+6.3%
<b>Isoprene</b>			
Houweling et al. (1998)	+17%	–	–
von Kuhlmann et al. (2004)	+9.5%	–	+6%
Pike and Young (2009)	–	–	+23%
Bates and Jacob (2019)	+4.2%	−11%	+12%
This study	+3.4%	−4.3%	+4.2%

<sup>a</sup>Iodine's individual impact estimated based on the assumption that 80% of the halogen-related ozone loss is from iodine. <sup>b</sup>Study considers bromine and iodine but not chlorine. <sup>c</sup>Based on present day values which are averaged between 2000–2019.

lower than that previously reported (−9.9% in Sherwen, Evans, et al. (2016) using GEOS-Chem and −10% for Iglesias-Suarez et al. (2020) using CamChem), with a similar negligible reduction in the impact on OH. The difference between the GEOS-Chem simulations reflects changes in the model's representation of halogens since 2016, including their processing on clouds, role in sulfur oxidation, and the pH dependence of their reactions (X. Wang et al., 2019, 2021; Chen et al., 2017). The global O<sub>3</sub> lifetime has changed little overall between Sherwen, Evans, et al. (2016) and this study (27.6–28.5 days), however, the O<sub>3</sub> chemical lifetime due to iodine has been lengthened substantially from 282 to 391 days. The effect of these changes has been to reduce the importance of iodine chemistry in GEOS-Chem. The chemistry used by Iglesias-Suarez et al. (2020) is substantially different to that used in GEOS-Chem, notably in the representation of heterogeneous processes and the lack of aerosol phase iodine production. These differences may explain the increased sensitivity to iodine found in previous studies compared to the latest version of GEOS-Chem. Li et al. (2022) conclude that halogens have a large impact on the methane lifetime, however whilst the role of chlorine alone is considered, the individual impacts of iodine and bromine are not disentangled and hence a direct comparison to this work cannot be made.

Differences in the sensitivity of models to isoprene emissions are also large, with a general downward trend in the simulated sensitivity over time. The present work shows a similar O<sub>3</sub> response to the GEOS-Chem simulation of Bates and Jacob (2019), which is unsurprising given we use the same chemical mechanism for isoprene oxidation. However, Bates and Jacob (2019) find a substantially larger impact of isoprene on OH. The largest contribution to this is the difference in total biogenic isoprene emissions. Bates and Jacob (2019) scaled the isoprene emissions calculated by MEGANv2.1 to ~535 Tg/yr to match the estimates of (Guenther et al., 2012). Without this scaling, MEGANv2.1 as implemented in GEOS-Chem emits only ~53% of this amount of isoprene (~280 Tg/yr). In addition to this, an increase in the model reactivity will also further reduce the impact of isoprene on OH. Since

Bates and Jacob (2019), a detailed treatment of aromatics (Bates et al., 2021) and ethene and ethyne chemistry (Kwon et al., 2021) has been included in GEOS-Chem. Changes in the emissions of lightning NO<sub>x</sub> between versions can also have a profound impact, particularly over the Amazon which reduces the production of NO<sub>y</sub> in this region, hence reducing the global O<sub>3</sub> increase from isoprene.

In conclusion, this study represents a conservative estimate of the impact of both iodine and of isoprene on O<sub>3</sub> and OH compared to other model studies, most likely due to increased complexity in the model chemical schemes used here for halogens and VOCs. That iodine has a larger but opposite impact on O<sub>3</sub> to isoprene and a very small global impact on OH (if other halogens are not taken into account) is nevertheless robust across the more recent of these studies, as shown in Table 1.

## 5. Conclusions

Globally, iodine has a larger magnitude of impact on tropospheric O<sub>3</sub> than isoprene. The relative importance of each depends on location and season. Although iodine has the larger impact on O<sub>3</sub>, its impact on OH and methane lifetime are negligible compared to isoprene. The greater impact of iodine on globally-averaged surface O<sub>3</sub> concentrations has specific importance when considering background O<sub>3</sub> 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. Therefore, the emissions and subsequent chemistry of iodine should be considered with the same priority as isoprene.

The processes leading to inorganic iodine flux from the ocean surface are complex, much like isoprene emissions, however, the representation of these emissions is currently simplistic. Iodine emissions are dependent on the



downward flux of O<sub>3</sub> 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 data of the O<sub>3</sub> + I<sup>-</sup> 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. Additionally, recent advances in the role of iodine in aerosol formation and growth and understanding of efficient iodine recycling should be considered as development priorities for models.

## Data Availability Statement

GEOS-Chem source code is openly available on GitHub (<https://github.com/geoschem/geos-chem>). This work used model version 14.0.2 (GCC14.0.2, 2022).

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

## Acknowledgments

The authors would like to thank the editor and reviewers for their constructive comments during the review process. RJP and LJC acknowledge funding by the European Research Council (ERC) under the European Union's horizon 2020 programme—grant agreement No. 833290. MJE thanks the UK National Centre for Atmospheric Science for funding. We thank the GEOS-Chem community for developing the model over the past decades. The authors would like to thank Kelvin Bates for discussion of isoprene emissions in GEOS-Chem. We thank WMO GAW and the individual sites that make up this network, for the availability of the surface ozone data through EBAS, managed by Norwegian Institute for Air Research. This project was undertaken on the Viking Cluster, which is a high-performance compute facility provided by the University of York. We are grateful for computational support from the University of York High Performance Computing service, Viking and the Research Computing team.

## References

- Amachi, S. (2008). Microbial contribution to global iodine cycling: Volatilization, accumulation, reduction, oxidation, and sorption of iodine. *Microbes and Environments*, 23(4), 269–276. <https://doi.org/10.1264/jsm2.ME08548>
- Andreae, M. O., & Crutzen, P. J. (1997). Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science*, 276(5315), 1052–1058. <https://doi.org/10.1126/science.276.5315.1052>
- Anttila, T., Langmann, B., Varghese, S., & O'Dowd, C. (2010). Contribution of isoprene oxidation products to marine aerosol over the North-East Atlantic. <https://doi.org/10.1155/2010/482603>
- Arnold, S. R., Spracklen, D. V., Williams, J., Yassaa, N., Sciare, J., Bonsang, B., et al. (2009). Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol. *Atmospheric Chemistry and Physics*, 9(4), 1253–1262. <https://doi.org/10.5194/acp-9-1253-2009>
- Atkinson, R., Aschmann, S. M., Tuazon, E. C., Arey, J., & Zielinska, B. (1989). Formation of 3-methylfuran from the gas-phase reaction of OH radicals with isoprene and the rate constant for its reaction with the OH radical. *International Journal of Chemical Kinetics*, 21(7), 593–604. <https://doi.org/10.1002/kin.550210709>
- Ayers, G., & Gillett, R. (2000). DMS and its oxidation products in the remote marine atmosphere: Implications for climate and atmospheric chemistry. *Journal of Sea Research*, 43(3), 275–286. [https://doi.org/10.1016/S1385-1101\(00\)00022-8](https://doi.org/10.1016/S1385-1101(00)00022-8)
- Badia, A., Iglesias-Suarez, F., Fernandez, R. P., Cuevas, C. A., Kinnison, D. E., Lamarque, J.-F., et al. (2021). The role of natural halogens in global tropospheric ozone chemistry and budget under different 21st century climate scenarios. *Journal of Geophysical Research: Atmospheres*, 126(20), e2021JD034859. <https://doi.org/10.1029/2021JD034859>
- Bates, K. H., & Jacob, D. J. (2019). A new model mechanism for atmospheric oxidation of isoprene: Global effects on oxidants, nitrogen oxides, organic products, and secondary organic aerosol. *Atmospheric Chemistry and Physics*, 19(14), 9613–9640. <https://doi.org/10.5194/acp-19-9613-2019>
- Bates, K. H., Jacob, D. J., Li, K., Ivatt, P. D., Evans, M. J., Yan, Y., & Lin, J. (2021). Development and evaluation of a new compact mechanism for aromatic oxidation in atmospheric models. *Atmospheric Chemistry and Physics*, 21(24), 18351–18374. <https://doi.org/10.5194/acp-21-18351-2021>
- Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., et al. (2001). Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation. *Journal of Geophysical Research*, 106(D19), 23073–23095. <https://doi.org/10.1029/2001JD000807>
- Biesenthal, T. A., & Shepson, P. B. (1997). Observations of anthropogenic inputs of the isoprene oxidation products methyl vinyl ketone and methacrolein to the atmosphere. *Geophysical Research Letters*, 24(11), 1375–1378. <https://doi.org/10.1029/97GL01337>
- Carpenter, L., Chance, R. J., Sherwen, T., Adams, T. J., Ball, S. M., Evans, M. J., et al. (2021). Marine iodine emissions in a changing world. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 477(2247), 20200824. <https://doi.org/10.1098/rspa.2020.0824>
- Carpenter, L., MacDonald, S., Shaw, M., Kumar, R., Saunders, R., Parthipan, R., et al. (2013). Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine. *Nature Geoscience*, 6(2), 108–111. <https://doi.org/10.1038/ngeo1687>
- Chance, R., Baker, A. R., Carpenter, L., & Jickells, T. D. (2014). The distribution of iodide at the sea surface. *Environmental Science: Processes and Impacts*, 16(8), 1841–1859. <https://doi.org/10.1039/C4EM00139G>
- Chance, R., Malin, G., Jickells, T., & Baker, A. R. (2007). Reduction of iodate to iodide by cold water diatom cultures. *Marine Chemistry*, 105(1), 169–180. <https://doi.org/10.1016/j.marchem.2006.06.008>
- Chen, Q., Schmidt, J. A., Shah, V., Jaeglé, L., Sherwen, T., & Alexander, B. (2017). Sulfate production by reactive bromine: Implications for the global sulfur and reactive bromine budgets. *Geophysical Research Letters*, 44(13), 7069–7078. <https://doi.org/10.1002/2017GL073812>
- Conte, L., Szopa, S., Aumont, O., Gros, V., & Bopp, L. (2020). Sources and sinks of isoprene in the global open ocean: Simulated patterns and emissions to the atmosphere. *Journal of Geophysical Research: Oceans*, 125(9), e2019JC015946. <https://doi.org/10.1029/2019JC015946>
- Cuevas, C. A., Fernandez, R. P., Kinnison, D. E., Li, Q., Lamarque, J.-F., Trabelsi, T., et al. (2022). The influence of iodine on the Antarctic stratospheric ozone hole. *Proceedings of the National Academy of Sciences*, 119(7), e2110864119. <https://doi.org/10.1073/pnas.2110864119>
- Cuevas, C. A., Maffezzoli, N., Corella, J. P., Spolaor, A., Vallelonga, P., Kjær, H. A., et al. (2018). Rapid increase in atmospheric iodine levels in the North Atlantic since the mid-20th century. *Nature Communications*, 9(1), 1452. <https://doi.org/10.1038/s41467-018-03756-1>
- Fairall, C. W., Helmig, D., Ganzeveld, L., & Hare, J. (2007). Water-side turbulence enhancement of ozone deposition to the ocean. *Atmospheric Chemistry and Physics*, 7(2), 443–451. <https://doi.org/10.5194/acp-7-443-2007>

- Fiore, A. M., Levy, H., II, & Jaffe, D. A. (2011). North American isoprene influence on intercontinental ozone pollution. *Atmospheric Chemistry and Physics*, 11(4), 1697–1710. <https://doi.org/10.5194/acp-11-1697-2011>
- Fuentes, J. D., & Wang, D. (1999). On the seasonality of isoprene emissions from a mixed temperate forest. *Ecological Applications*, 9(4), 1118–1131. [https://doi.org/10.1890/1051-0761\(1999\)009\[1118:OTSOIE\]2.0.CO;2](https://doi.org/10.1890/1051-0761(1999)009[1118:OTSOIE]2.0.CO;2)
- GCC14.0.2. (2022). The international GEOS-Chem user community, geoschem/GCClassic: GEOS-Chem 13.1.1. *Zenodo* (Please see the LICENSE.txt and AUTHORS.txt files in the root folder for the GEOS-Chem license description (based on the MIT license) and a complete list of authors. For more information about GEOS-Chem in general, please see [www.geos-chem.org](http://www.geos-chem.org) and [wiki.geos-chem.org](http://wiki.geos-chem.org)). <https://doi.org/10.5281/zenodo.7383492>
- Gelaro, R., McCarty, W., Suárez, M. J., Todling, R., Molod, A., Takacs, L., et al. (2017). The modern-era retrospective analysis for research and applications, version 2 (MERRA-2). *Journal of Climate*, 30(14), 5419–5454. <https://doi.org/10.1175/JCLI-D-16-0758.1>
- Gómez Martín, J. C., Mahajan, A. S., Hay, T. D., Prados-Román, C., Ordóñez, C., MacDonald, S. M., et al. (2013). Iodine chemistry in the eastern Pacific marine boundary layer. *Journal of Geophysical Research: Atmospheres*, 118(2), 887–904. <https://doi.org/10.1002/jgrd.50132>
- Grosjean, D., Williams, E. L., & Grosjean, E. (1993). Atmospheric chemistry of isoprene and of its carbonyl products. *Environmental Science and Technology*, 27(5), 830–840. <https://doi.org/10.1021/es00042a004>
- Großmann, K., Frieb, U., Peters, E., Wittrock, F., Lampel, J., Yilmaz, S., et al. (2013). Iodine monoxide in the western Pacific marine boundary layer. *Atmospheric Chemistry and Physics*, 13(6), 3363–3378. <https://doi.org/10.5194/acp-13-3363-2013>
- Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., & Wang, X. (2012). The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions. *Geoscientific Model Development*, 5(6), 1471–1492. <https://doi.org/10.5194/gmd-5-1471-2012>
- Guenther, A. B., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., & Geron, C. (2006). Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmospheric Chemistry and Physics*, 6(11), 3181–3210. <https://doi.org/10.5194/acp-6-3181-2006>
- Harris, C. R., Millman, K. J., van der Walt, S. J., Gommers, R., Virtanen, P., Cournapeau, D., et al. (2020). Array programming with NumPy. *Nature*, 585(7825), 357–362. <https://doi.org/10.1038/s41586-020-2649-2>
- He, X.-C., Tham, Y. J., Dada, L., Wang, M., Finkenzeller, H., Stolzenburg, D., et al. (2021). Role of iodine oxoacids in atmospheric aerosol nucleation. *Science*, 371(6529), 589–595. <https://doi.org/10.1126/science.abe0298>
- Horowitz, L. W., Fiore, A. M., Milly, G. P., Cohen, R. C., Perring, A., Wooldridge, P. J., et al. (2007). Observational constraints on the chemistry of isoprene nitrates over the eastern United States. *Journal of Geophysical Research*, 112(D12), D12S08. <https://doi.org/10.1029/2006JD007747>
- Houweling, S., Dentener, F., & Lelieveld, J. (1998). The impact of nonmethane hydrocarbon compounds on tropospheric photochemistry. *Journal of Geophysical Research*, 103(D9), 10673–10696. <https://doi.org/10.1029/97JD03582>
- Hoyer, S., & Hamman, J. (2017). xarray: N-D labeled arrays and datasets in Python. *Journal of Open Research Software*, 5(1), 10. <https://doi.org/10.5334/jors.148>
- Huang, R.-J., Hoffmann, T., Ovadnevaite, J., Laaksonen, A., Kokkola, H., Xu, W., et al. (2022). Heterogeneous iodine-organic chemistry fast-tracks marine new particle formation. *Proceedings of the National Academy of Sciences*, 119(32), e2201729119. <https://doi.org/10.1073/pnas.2201729119>
- Hunter, J. D. (2007). Matplotlib: A 2D graphics environment. *Computing in Science & Engineering*, 9(3), 90–95. <https://doi.org/10.1109/MCSE.2007.55>
- Iglesias-Suarez, F., Badia, A., Fernandez, R. P., Cuevas, C. A., Kinnison, D. E., Tilmes, S., et al. (2020). Natural halogens buffer tropospheric ozone in a changing climate. *Nature Climate Change*, 10(2), 147–154. <https://doi.org/10.1038/s41558-019-0675-6>
- Ivatt, P. D., Evans, M. J., & Lewis, A. C. (2022). Suppression of surface ozone by an aerosol-inhibited photochemical ozone regime. *Nature Geoscience*, 15(7), 536–540. <https://doi.org/10.1038/s41561-022-00972-9>
- Jenkin, M. E., Young, J. C., & Rickard, A. R. (2015). The MCM v3.3.1 degradation scheme for isoprene. *Atmospheric Chemistry and Physics*, 15(20), 11433–11459. <https://doi.org/10.5194/acp-15-11433-2015>
- Jones, C. E., Hornsby, K. E., Sommariva, R., Dunk, R. M., von Glasow, R., McFiggans, G., & Carpenter, L. J. (2010). Quantifying the contribution of marine organic gases to atmospheric iodine. *Geophysical Research Letters*, 37(18). <https://doi.org/10.1029/2010GL043990>
- Koenig, T. K., Baidar, S., Campuzano-Jost, P., Cuevas, C. A., Dix, B., Fernandez, R. P., et al. (2020). Quantitative detection of iodine in the stratosphere. *Proceedings of the National Academy of Sciences*, 117(4), 1860–1866. <https://doi.org/10.1073/pnas.1916828117>
- Kwon, H. A., Park, R. J., Oak, Y. J., Nowlan, C., Janz, S., Kowalewski, M., et al. (2021). Top-down estimates of anthropogenic VOC emissions in South Korea using formaldehyde vertical column densities from aircraft during the KORUS-AQ campaign. *Elementa: Science of the Anthropocene*, 9(1), 00109. <https://doi.org/10.1525/elementa.2021.00109>
- Lawler, M. J., Mahajan, A. S., Saiz-Lopez, A., & Saltzman, E. S. (2014). Observations of I<sub>2</sub> at a remote marine site. *Atmospheric Chemistry and Physics*, 14(5), 2669–2678. <https://doi.org/10.5194/acp-14-2669-2014>
- Legrand, M., McConnell, J. R., Preunkert, S., Arienzo, M., Chellman, N., Gleason, K., et al. (2018). Alpine ice evidence of a three-fold increase in atmospheric iodine deposition since 1950 in Europe due to increasing oceanic emissions. *Proceedings of the National Academy of Sciences*, 115(48), 12136–12141. <https://doi.org/10.1073/pnas.1809867115>
- Lelieveld, J., Butler, T., Crowley, J., Fischer, H., Ganzeveld, L., Harder, H., et al. (2008). Atmospheric oxidation capacity sustained by a tropical forest. *Nature*, 452(7188), 737–740. <https://doi.org/10.1038/nature06870>
- Li, Q., Fernandez, R. P., Hossaini, R., Iglesias-Suarez, F., Cuevas, C. A., Apel, E. C., et al. (2022). Reactive halogens increase the global methane lifetime and radiative forcing in the 21st century. *Nature Communications*, 13(1), 2768. <https://doi.org/10.1038/s41467-022-30456-8>
- Luhar, A. K., Galbally, I. E., Woodhouse, M. T., & Thatcher, M. (2017). An improved parameterisation of ozone dry deposition to the ocean and its impact in a global climate-chemistry model. *Atmospheric Chemistry and Physics*, 17(5), 3749–3767. <https://doi.org/10.5194/acp-17-3749-2017>
- MacDonald, S. M., Gómez Martín, J. C., Chance, R., Warriner, S., Saiz-Lopez, A., Carpenter, L. J., & Plane, J. M. C. (2014). A laboratory characterisation of inorganic iodine emissions from the sea surface: Dependence on oceanic variables and parameterisation for global modelling. *Atmospheric Chemistry and Physics*, 14(11), 5841–5852. <https://doi.org/10.5194/acp-14-5841-2014>
- Mahajan, A. S., Gómez Martín, J. C., Hay, T. D., Royer, S.-J., Yvon-Lewis, S., Liu, Y., et al. (2012). Latitudinal distribution of reactive iodine in the eastern Pacific and its link to open ocean sources. *Atmospheric Chemistry and Physics*, 12(23), 11609–11617. <https://doi.org/10.5194/acp-12-11609-2012>
- Mahajan, A. S., Plane, J. M. C., Oetjen, H., Mendes, L., Saunders, R. W., Saiz-Lopez, A., et al. (2010). Measurement and modelling of tropospheric reactive halogen species over the tropical Atlantic ocean. *Atmospheric Chemistry and Physics*, 10(10), 4611–4624. <https://doi.org/10.5194/acp-10-4611-2010>

- Met Office. (2010–2015). *Cartopy: A cartographic python library with a matplotlib interface* [Computer software manual]. Exeter. Retrieved from <http://scitools.org.uk/cartopy>
- Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., et al. (2012). Bromine and iodine chemistry in a global chemistry-climate model: Description and evaluation of very short-lived oceanic sources. *Atmospheric Chemistry and Physics*, *12*(3), 1423–1447. <https://doi.org/10.5194/acp-12-1423-2012>
- Paulot, F., Henze, D. K., & Wennberg, P. O. (2012). Impact of the isoprene photochemical cascade on tropical ozone. *Atmospheric Chemistry and Physics*, *12*(3), 1307–1325. <https://doi.org/10.5194/acp-12-1307-2012>
- Paulson, S. E., Flagan, R. C., & Seinfeld, J. H. (1992). Atmospheric photooxidation of isoprene Part I: The hydroxyl radical and ground state atomic oxygen reactions. *International Journal of Chemical Kinetics*, *24*(1), 79–101. <https://doi.org/10.1002/kin.550240109>
- Paulson, S. E., & Seinfeld, J. H. (1992). Development and evaluation of a photooxidation mechanism for isoprene. *Journal of Geophysical Research*, *97*(D18), 20703–20715. <https://doi.org/10.1029/92JD01914>
- Pierce, T., Geron, C., Bender, L., Dennis, R., Tonnesen, G., & Guenther, A. (1998). Influence of increased isoprene emissions on regional ozone modeling. *Journal of Geophysical Research*, *103*(D19), 25611–25629. <https://doi.org/10.1029/98JD01804>
- Pike, R. C., & Young, P. J. (2009). How plants can influence tropospheric chemistry: The role of isoprene emissions from the biosphere. *Weather*, *64*(12), 332–336. <https://doi.org/10.1002/wea.416>
- Pound, R. J. (2022). Analysis code for “comparing the importance of iodine and isoprene on tropospheric photochemistry”. *Zenodo*. <https://doi.org/10.5281/zenodo.7016985>
- Pound, R. J., Sherwen, T., Helmig, D., Carpenter, L. J., & Evans, M. J. (2020). Influences of oceanic ozone deposition on tropospheric photochemistry. *Atmospheric Chemistry and Physics*, *20*(7), 4227–4239. <https://doi.org/10.5194/acp-20-4227-2020>
- Prados-Roman, C., Cuevas, C. A., Hay, T., Fernandez, R. P., Mahajan, A. S., Royer, S.-J., et al. (2015). Iodine oxide in the global marine boundary layer. *Atmospheric Chemistry and Physics*, *15*(2), 583–593. <https://doi.org/10.5194/acp-15-583-2015>
- Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard, D. E., et al. (2008). Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean. *Nature*, *453*(7199), 1232–1235. <https://doi.org/10.1038/nature07035>
- Roberts, J. M., Williams, J., Baumann, K., Buhr, M. P., Goldan, P. D., Holloway, J., et al. (1998). Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville intensives of the Southern Oxidant Study: Implications for regional ozone production from biogenic hydrocarbons. *Journal of Geophysical Research*, *103*(D17), 22473–22490. <https://doi.org/10.1029/98JD01637>
- Sarwar, G., Gantt, B., Foley, K., Fahey, K., Spero, T. L., Kang, D., et al. (2019). Influence of bromine and iodine chemistry on annual, seasonal, diurnal, and background ozone: CMAQ simulations over the Northern Hemisphere. *Atmospheric Environment*, *213*, 395–404. <https://doi.org/10.1016/j.atmosenv.2019.06.020>
- Saunders, S. M., Jenkin, M. E., Derwent, R. G., & Pilling, M. J. (2003). Protocol for the development of the master chemical mechanism, MCM v3 (Part A): Tropospheric degradation of non-aromatic volatile organic compounds. *Atmospheric Chemistry and Physics*, *3*(1), 161–180. <https://doi.org/10.5194/acp-3-161-2003>
- Schnitzler, J.-P., Lehnig, A., & Steinbrecher, R. (1997). Seasonal pattern of isoprene synthase activity in *Quercus robur* leaves and its significance for modeling isoprene emission rates. *Botanica Acta*, *110*(3), 240–243. <https://doi.org/10.1111/j.1438-8677.1997.tb00635.x>
- Shaw, G. (1983). Bio-controlled thermostatism involving the sulfur cycle. *Climatic Change*, *5*(3), 297–303. <https://doi.org/10.1007/BF02423524>
- Sherwen, T., Evans, M. J., Carpenter, L. J., Andrews, S. J., Lidster, R. T., Dix, B., et al. (2016). Iodine’s impact on tropospheric oxidants: A global model study in geos-chem. *Atmospheric Chemistry and Physics*, *16*(2), 1161–1186. <https://doi.org/10.5194/acp-16-1161-2016>
- Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Eastham, S. D., et al. (2016). Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem. *Atmospheric Chemistry and Physics*, *16*(18), 12239–12271. <https://doi.org/10.5194/acp-16-12239-2016>
- Sinha, V., Williams, J., Meyerhöfer, M., Riebesell, U., Paulino, A. I., & Larsen, A. (2007). Air-sea fluxes of methanol, acetone, acetaldehyde, isoprene and DMS from a Norwegian fjord following a phytoplankton bloom in a mesocosm experiment. *Atmospheric Chemistry and Physics*, *7*(3), 739–755. <https://doi.org/10.5194/acp-7-739-2007>
- Sommariva, R., Bloss, W., & von Glasow, R. (2012). Uncertainties in gas-phase atmospheric iodine chemistry. *Atmospheric Environment*, *57*, 219–232. <https://doi.org/10.1016/j.atmosenv.2012.04.032>
- Squire, O. J., Archibald, A. T., Griffiths, P. T., Jenkin, M. E., Smith, D., & Pyle, J. A. (2015). Influence of isoprene chemical mechanism on modelled changes in tropospheric ozone due to climate and land use over the 21st century. *Atmospheric Chemistry and Physics*, *15*(9), 5123–5143. <https://doi.org/10.5194/acp-15-5123-2015>
- Starn, T. K., Shepson, P. B., Bertman, S. B., Riemer, D. D., Zika, R. G., & Olszyna, K. (1998). Nighttime isoprene chemistry at an urban-impacted forest site. *Journal of Geophysical Research*, *103*(D17), 22437–22447. <https://doi.org/10.1029/98JD01201>
- Tham, Y. J., He, X.-C., Li, Q., Cuevas, C. A., Shen, J., Kalliokoski, J., et al. (2021). Direct field evidence of autocatalytic iodine release from atmospheric aerosol. *Proceedings of the National Academy of Sciences*, *118*(4), e2009951118. <https://doi.org/10.1073/pnas.2009951118>
- Trainer, M., Williams, E., Parrish, D., Buhr, M., Allwine, E., Westberg, H., et al. (1987). Models and observations of the impact of natural hydrocarbons on rural ozone. *Nature*, *329*(6141), 705–707. <https://doi.org/10.1038/329705a0>
- Volkamer, R., Baidar, S., Campos, T. L., Coburn, S., DiGangi, J. P., Dix, B., et al. (2015). Aircraft measurements of BrO, IO, glyoxal, NO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>-O<sub>2</sub> and aerosol extinction profiles in the tropics: Comparison with aircraft-/ship-based in situ and lidar measurements. *Atmospheric Measurement Techniques*, *8*(5), 2121–2148. <https://doi.org/10.5194/amt-8-2121-2015>
- von Kuhlmann, R., Lawrence, M. G., Pöschl, U., & Crutzen, P. J. (2004). Sensitivities in global scale modeling of isoprene. *Atmospheric Chemistry and Physics*, *4*(1), 1–17. <https://doi.org/10.5194/acp-4-1-2004>
- Wang, S., Schmidt, J. A., Baidar, S., Coburn, S., Dix, B., Koenig, T. K., et al. (2015). Active and widespread halogen chemistry in the tropical and subtropical free troposphere. *Proceedings of the National Academy of Sciences*, *112*(30), 9281–9286. <https://doi.org/10.1073/pnas.1505142112>
- Wang, X., Jacob, D. J., Downs, W., Zhai, S., Zhu, L., Shah, V., et al. (2021). Global tropospheric halogen (Cl, Br, I) chemistry and its impact on oxidants. *Atmospheric Chemistry and Physics*, *21*(18), 13973–13996. <https://doi.org/10.5194/acp-21-13973-2021>
- Wang, X., Jacob, D. J., Eastham, S. D., Sulprizio, M. P., Zhu, L., Chen, Q., et al. (2019). The role of chlorine in global tropospheric chemistry. *Atmospheric Chemistry and Physics*, *19*(6), 3981–4003. <https://doi.org/10.5194/acp-19-3981-2019>
- Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., et al. (2018). Gas-phase reactions of isoprene and its major oxidation products. *Chemical Reviews*, *118*(7), 3337–3390. <https://doi.org/10.1021/acs.chemrev.7b00439>
- Wiedinmyer, C., Friedfeld, S., Baugh, W., Greenberg, J., Guenther, A., Fraser, M., & Allen, D. (2001). Measurement and analysis of atmospheric concentrations of isoprene and its reaction products in central Texas. *Atmospheric Environment*, *35*(6), 1001–1013. [https://doi.org/10.1016/S1352-2310\(00\)00406-4](https://doi.org/10.1016/S1352-2310(00)00406-4)
- Wu, D., Du, J., Deng, H., Wang, W., Xiao, H., & Li, P. (2014). Estimation of atmospheric iodine emission from coal combustion. *International Journal of Environmental Science and Technology*, *11*(2), 357–366. <https://doi.org/10.1007/s13762-013-0193-4>

- Yang, M., Huebert, B. J., Blomquist, B. W., Howell, S. G., Shank, L. M., McNaughton, C. S., et al. (2011). Atmospheric sulfur cycling in the southeastern Pacific—Longitudinal distribution, vertical profile, and diel variability observed during VOCALS-REX. *Atmospheric Chemistry and Physics*, *11*(10), 5079–5097. <https://doi.org/10.5194/acp-11-5079-2011>
- Zhao, X., Hou, X., & Zhou, W. (2019). Atmospheric iodine (127I and 129I) record in spruce tree rings in the northeast Qinghai-Tibet Plateau. *Environmental Science and Technology*, *53*(15), 8706–8714. <https://doi.org/10.1021/acs.est.9b01160>