Comparing the importance of iodine and isoprene on tropospheric photochemistry

Ryan J Pound[1], Mathew J. Evans[1], and Lucy J. Carpenter[2]

[1]University of York
[2]University of York, UK

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Abstract

Naturally emitted reactive trace gases are thought to impact tropospheric composition, predominantly through the emission and chemistry of isoprene (C5H8). 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 O3 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 O3.

Comparing the importance of iodine and isoprene on tropospheric photochemistry

R. J. Pound[1], M. J. Evans[1,2], L. J. Carpenter[1]

[1]Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, YO10 5DD,

UK.

[2]National Centre for Atmospheric Science, University of York, YO10 5DD, UK.

Key Points:

- The global impact on O_3 of present-day inorganic iodine and biogenic isoprene emission are similar in magnitude but opposite in sign.
- At the surface, the impact of iodine on O_3 exceeds that for isoprene, and is notably larger in defining the background for Europe and North America.
- Iodine has a negligible impact on OH concentrations and CH_4 lifetimes compared to isoprene.

Corresponding author: Ryan J. Pound, `ryan.pound@york.ac.uk`

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-

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

Natural terrestrial biogenic emissions of volatile organic compounds (VOCs) have significant impacts on atmospheric oxidants (Trainer et al., 1987). Isoprene (C_5H_8) forms the largest of these emissions (500Tg yr^{-1} (Guenther et al., 2012, 2006)), 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; Schnitzler et al., 1997; Guenther et al., 2006). 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 (Wiedinmyer et al., 2001; Roberts et al., 1998; Starn et al., 1998; Biesenthal & Shepson, 1997) and in laboratory experiments (Atkinson et al., 1989; Paulson et al., 1992; Paulson & Seinfeld, 1992; Grosjean et al., 1993). Numerical models have been developed to incorporate known degradation chemistry (Trainer et al., 1987; Jenkin et al., 2015; Saunders et al., 2003; Bates & Jacob, 2019). Oxidation of isoprene is typically initiated by the hydroxyl radical (OH) and 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, with 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 net O_3 loss (Paulot et al., 2012; Horowitz et al., 2007). 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 (Pierce et al., 1998; Fiore et al., 2011; Squire et al., 2015; Bates & Jacob, 2019).

In contrast to isoprene, iodine emissions lead to the destruction of O_3. 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 2 Gg yr^{-1} of iodine to the global atmosphere. An additional 0.6 Gg 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 (Fairall et al., 2007; Carpenter et al., 2013; Luhar et al., 2017; Pound et al., 2020).

I^- 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).

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 oxidised 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 HOx (OH + HO_2) and NO_x (NO + NO_2) concentrations (Sommariva et al., 2012; Sherwen, Evans, et al., 2016). 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 also shows that iodine containing trace compounds can be exported from the troposphere into the stratosphere where they may play a role in modulating the concentration of stratospheric O_3 (Koenig et al., 2020; Cuevas et al., 2022).

Observations of reactive inorganic iodine compounds in the atmosphere are limited mainly 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., 2012, 2010). Although these emissions 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) however these are even more limited in their spatial distribution than those of IO.

Although the mass of isoprene (500 Tg yr-1 (Guenther et al., 2012)) and iodine (4 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 relatively 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 atmospheric composition.

2 Model description

This work uses the GEOS-Chem model (Bey et al., 2001) version 13.1.1 (GCC13.1.1, 2021) run globally at a spatial resolution of 2°x2.5° on the reduced vertical grid (47 vertical levels), running with full 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 photosynethically active radiation. 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 in 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 [Mol].

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

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

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].

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

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 O_3 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 O_3 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 O_3 extends up to around 6km 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 10% at 2km here translates to 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, O_3 concentrations decrease at the surface. This is for two reasons. Firstly the direct reaction between O_3 and isoprene increases the chemical loss of O_3 (10% of global isoprene emissions are oxidised by O_3 (Bates & Jacob, 2019)). Secondly the concentrations of NO_x in the region decrease as NO_x is shifted to reservoir species (NO_y, poly-aromatic nitrates (PAN) and organic nitrates) which reduces the chemical production of O_3 over the region (NO_x and NO_y are shown in the supplementary material (figures S2 and S3). 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. Away from these emission regions, transported NO_y increase NO_x concentrations over the remote oceans downwind of high isoprene emissions, 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 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 worlds O_3 production being NO_x limited (Ivatt et al., 2022).

Globally the impact of isoprene and iodine on O_3 are similar but opposite. Isoprene increases the tropospheric O_3 burden by 13.6 Tg (4.1%) whereas iodine decreases it by 16.5 Tg (5.4%). Close to the surface (0-1km), iodine's impact on O_3 (2.4 Tg, 8.9% decrease) is significantly larger than that of isoprene (1.2 Tg, 4.4% 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.
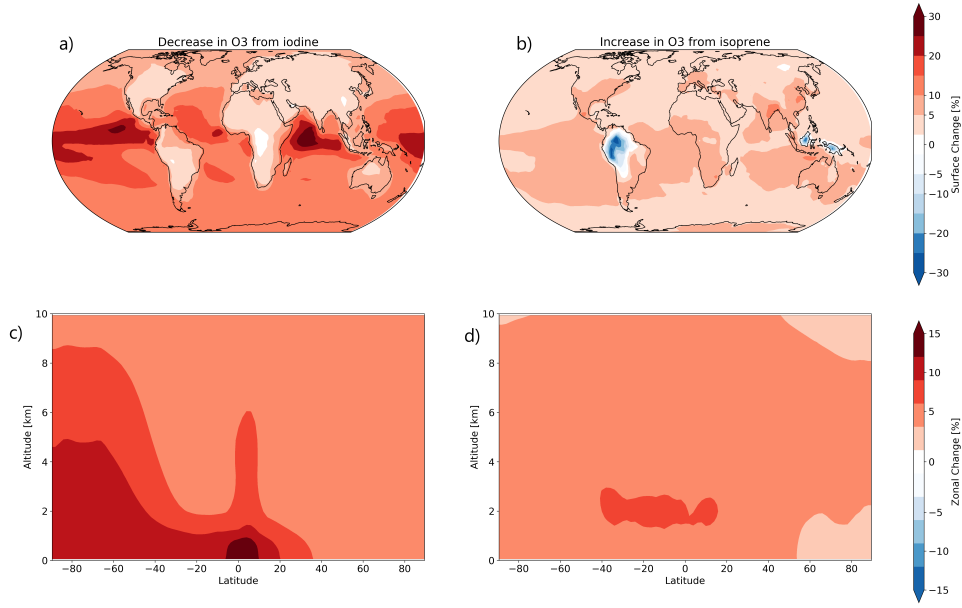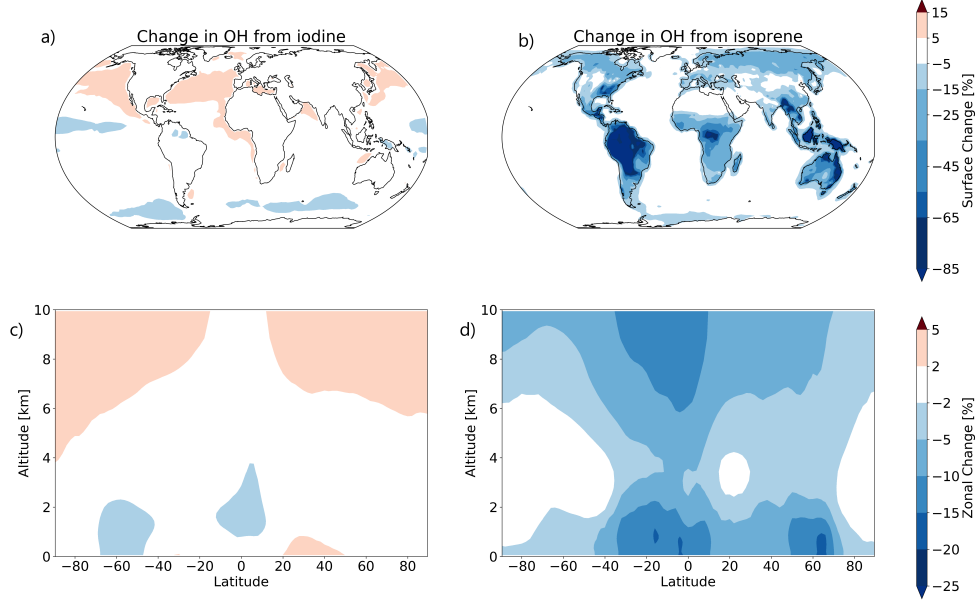
Figure 1. Annual average percentage decrease in surface [a) and b)] and zonal [c) and d)] O_3 from iodine emissions [a) and c)] and annual average percentage increase in surface and zonal O_3 from isoprene emissions [b) and d)].

3.2 Impact on OH

The similarity in the influence of 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 (-0.24%), 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 O_3 concentrations from iodine leads to lower primary OH production, 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

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)].

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 S4-7 of the supplementary material. 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 via increasing NO_y concentration, 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 iodine emissions in the northern hemisphere increase by 23% from minimum to maximum whereas isoprene increases by 270%.
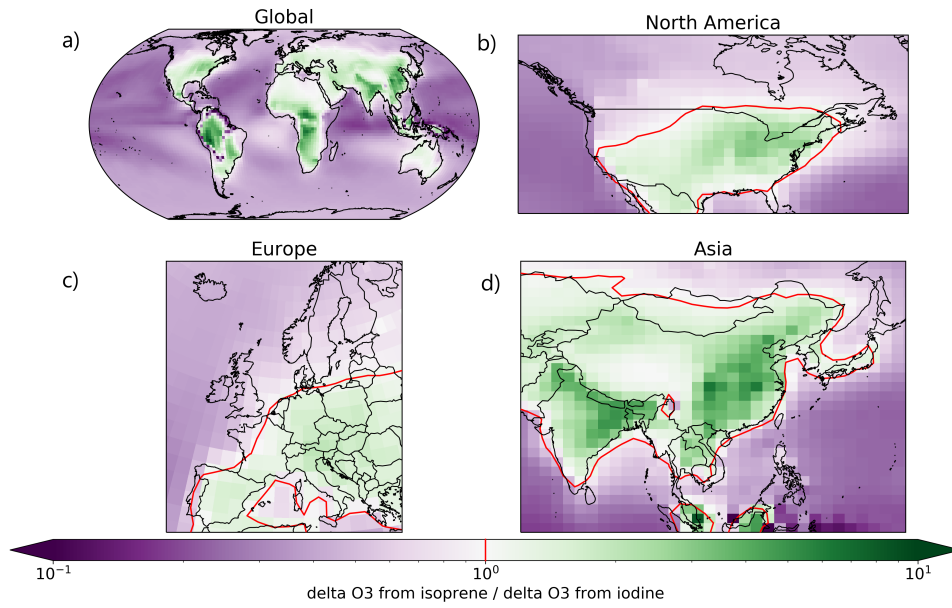
Figure 3. Average surface ratio of fractional change in O_3 from isoprene to fractional change in O_3 from iodine, globally [a)], North America [b)], Europe [c)] and Asia [d)]. Red contour lines on regional plots are drawn based on the value of the ratio being 1 (iodine and isoprene emissions have equal 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 constrains 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).

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. doi: 10.1264/jsme2.ME08548

Andreae, M. O., & Crutzen, P. J. (1997). Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science*, *276*(5315), 1052–1058. doi: 10.1126/science.276.5315.1052

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. Retrieved from https://onlinelibrary.wiley.com/doi/abs/10.1002/kin.550210709 doi: 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. doi: https://doi.org/10.1016/S1385-1101(00)00022-8

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. Retrieved from https://acp.copernicus.org/articles/19/9613/2019/ doi: 10.5194/acp-19-9613-2019

Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., . . . Schultz, M. G. (2001). Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation. *J GEOPHYS RES-ATMOS*, *106*(D19), 23073-23095. doi: 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. doi: https://doi.org/10.1029/97GL01337

Carpenter, L., Chance, R. J., Sherwen, T., Adams, T. J., Ball, S. M., Evans, M. J., . . . Wadley, M. R. (2021). Marine iodine emissions in a changing world. *Proceedings of the Royal Society A: Mathematical, Physi-*

306   *cal and Engineering Sciences*, *477*(2247), 20200824.   Retrieved from

307   https://royalsocietypublishing.org/doi/abs/10.1098/rspa.2020.0824

308   doi: 10.1098/rspa.2020.0824

309 Carpenter, L., MacDonald, S., Shaw, M., Kumar, R., Saunders, R., Parthipan,

310   R., ... Plane, J.   (2013).   Atmospheric iodine levels influenced by sea sur-

311   face emissions of inorganic iodine.   *Nature Geoscience*, *6*, 108–111.   doi:

312   https://doi.org/10.1038/ngeo1687

313 Chance, R., Baker, A. R., Carpenter, L., & Jickells, T. D.   (2014).   The distribution

314   of iodide at the sea surface.   *Environmental Science: Processes and Impacts*,

315   *16*, 1841-1859. doi: 10.1039/C4EM00139G

316 Chance, R., Malin, G., Jickells, T., & Baker, A. R.   (2007).   Reduction of iodate to

317   iodide by cold water diatom cultures.   *Marine Chemistry*, *105*(1), 169-180.

318   Retrieved from https://www.sciencedirect.com/science/article/pii/

319   S0304420306001150   doi: https://doi.org/10.1016/j.marchem.2006.06.008

320 Cuevas, C. A., Fernandez, R. P., Kinnison, D. E., Li, Q., Lamarque, J.-F., Trabelsi,

321   T., ... Saiz-Lopez, A.   (2022).   The influence of iodine on the antarctic strato-

322   spheric ozone hole.   *Proceedings of the National Academy of Sciences*, *119*(7),

323   e2110864119. doi: 10.1073/pnas.2110864119

324 Cuevas, C. A., Maffezzoli, N., Corella, J. P., Spolaor, A., Vallelonga, P., Kjær, H. A.,

325   ... Saiz-Lopez, A.   (2018).   Rapid increase in atmospheric iodine levels in the

326   north atlantic since the mid-20th century.   *Nature Communications*, *9*, 1452.

327   doi: 10.1038/s41467-018-03756-1

328 Fairall, C. W., Helmig, D., Ganzeveld, L., & Hare, J.   (2007).   Water-side turbulence

329   enhancement of ozone deposition to the ocean.   *ATMOS CHEM PHYS*, *7*(2),

330   443–451.   Retrieved from https://www.atmos-chem-phys.net/7/443/2007/

331   doi: 10.5194/acp-7-443-2007

332 Fiore, A. M., Levy II, H., & Jaffe, D. A.   (2011).   North american isoprene influ-

333   ence on intercontinental ozone pollution.   *Atmospheric Chemistry and Physics*,

334   *11*(4), 1697–1710.   Retrieved from https://acp.copernicus.org/articles/

335   11/1697/2011/   doi: 10.5194/acp-11-1697-2011

336 Fuentes, J. D., & Wang, D.   (1999).   On the seasonality of isoprene emissions from a

337   mixed temperate forest. *Ecological Applications*, *9*(4), 1118-1131. doi: https://

338   doi.org/10.1890/1051-0761(1999)009[1118:OTSOIE]2.0.CO;2

GCC13.1.1. (2021, June). *The international geos-chem user community, geoschem/gcclassic: Geos-chem 13.1.1.* Zenodo. Retrieved from `https://doi.org/10.5281/zenodo.5014891` (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 and wiki.geos-chem.org.) doi: 10.5281/zenodo.5014891

Gelaro, R., McCarty, W., Suárez, M. J., Todling, R., Molod, A., Takacs, L., . . . Zhao, B. (2017). The modern-era retrospective analysis for research and applications, version 2 (merra-2). *Journal of Climate*, *30*(14), 5419-5454. doi: 10.1175/JCLI-D-16-0758.1

Grosjean, D., Williams, E. L., & Grosjean, E. (1993). Atmospheric chemistry of isoprene and of its carbonyl products. *Environmental Science and Technology*, *27*, 830–840. doi: 10.1021/es00042a004

Großmann, K., Frieß, U., Peters, E., Wittrock, F., Lampel, J., Yilmaz, S., . . . Platt, U. (2013). Iodine monoxide in the western pacific marine boundary layer. *Atmospheric Chemistry and Physics*, *13*(6), 3363–3378. Retrieved from `https://acp.copernicus.org/articles/13/3363/2013/` doi: 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. Retrieved from `https://gmd.copernicus.org/articles/5/1471/2012/` doi: 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. Retrieved from `https://acp.copernicus.org/articles/6/3181/2006/` doi: 10.5194/acp-6-3181-2006

Gómez Martín, J. C., Mahajan, A. S., Hay, T. D., Prados-Román, C., Ordóñez, C., MacDonald, S. M., . . . Saiz-Lopez, A. (2013). Iodine chemistry in the eastern pacific marine boundary layer. *Journal of Geophysical Research: Atmospheres*,

118(2), 887-904. doi: https://doi.org/10.1002/jgrd.50132

Harris, C. R., Millman, K. J., van der Walt, S. J., Gommers, R., Virtanen, P., Cournapeau, D., . . . Oliphant, T. E. (2020, September). Array programming with NumPy. *Nature*, *585*(7825), 357–362. Retrieved from `https://doi.org/10.1038/s41586-020-2649-2` doi: 10.1038/s41586-020-2649-2

Horowitz, L. W., Fiore, A. M., Milly, G. P., Cohen, R. C., Perring, A., Wooldridge, P. J., . . . Lamarque, J.-F. (2007). Observational constraints on the chemistry of isoprene nitrates over the eastern united states. *Journal of Geophysical Research: Atmospheres*, *112*(D12). doi: https://doi.org/10.1029/2006JD007747

Hoyer, S., & Hamman, J. (2017). xarray: N-d labeled arrays and datasets in python. *Journal of Open Research Software*, *5(1)*. doi: DOI:http://doi.org/10.5334/jors.148

Hunter, J. D. (2007). Matplotlib: A 2d graphics environment. *Computing in Science & Engineering*, *9*(3), 90–95. doi: 10.1109/MCSE.2007.55

Ivatt, P. D., Evans, M. J., & Lewis, A. C. (2022). Suppression of surface ozone by an aerosol-inhibited photochemical ozone regime. *Nature Geoscience*, *15*, 536-540. doi: 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. Retrieved from `https://acp.copernicus.org/articles/15/11433/2015/` doi: 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). doi: https://doi.org/10.1029/2010GL043990

Koenig, T. K., Baidar, S., Campuzano-Jost, P., Cuevas, C. A., Dix, B., Fernandez, R. P., . . . Volkamer, R. (2020). Quantitative detection of iodine in the stratosphere. *Proceedings of the National Academy of Sciences*, *117*(4), 1860-1866. Retrieved from `https://www.pnas.org/doi/abs/10.1073/pnas.1916828117` doi: 10.1073/pnas.1916828117

Lawler, M. J., Mahajan, A. S., Saiz-Lopez, A., & Saltzman, E. S. (2014). Observations of i$_2$ at a remote marine site. *Atmospheric Chemistry and Physics*, *14*(5), 2669–2678. Retrieved from `https://acp.copernicus.org/articles/`

14/2669/2014/ doi: 10.5194/acp-14-2669-2014

Legrand, M., McConnell, J. R., Preunkert, S., Arienzo, M., Chellman, N., Gleason, K., . . . Carpenter, L. J. (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. doi: 10.1073/pnas.1809867115

Lelieveld, J., Butler, T., Crowley, J., Fischer, H., Ganzeveld, L., Harder, H., . . . Williams, J. (2008). Atmospheric oxidation capacity sustained by a tropical forest. *Nature*, *452*, 737-740. doi: https://doi.org/10.1038/nature06870

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. *ATMOS CHEM PHYS*, *17*, 3749–3767. doi: 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. *ATMOS CHEM PHYS*, *14*(11), 5841–5852. Retrieved from `https://www.atmos-chem-phys.net/14/5841/2014/` doi: 10.5194/acp-14-5841-2014

Mahajan, A. S., Gómez Martín, J. C., Hay, T. D., Royer, S.-J., Yvon-Lewis, S., Liu, Y., . . . Saiz-Lopez, A. (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. Retrieved from `https://acp.copernicus.org/articles/12/11609/2012/` doi: 10.5194/acp-12-11609-2012

Mahajan, A. S., Plane, J. M. C., Oetjen, H., Mendes, L., Saunders, R. W., Saiz-Lopez, A., . . . McFiggans, G. B. (2010). Measurement and modelling of tropospheric reactive halogen species over the tropical atlantic ocean. *Atmospheric Chemistry and Physics*, *10*(10), 4611–4624. Retrieved from `https://acp.copernicus.org/articles/10/4611/2010/` doi: 10.5194/acp-10-4611-2010

Met Office. (2010 - 2015). Cartopy: a cartographic python library with a matplotlib interface [Computer software manual]. Exeter, Devon. Retrieved from `http://scitools.org.uk/cartopy`

Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., ... Saiz-Lopez, A. (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. Retrieved from https://acp.copernicus.org/articles/12/1423/2012/ doi: 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. Retrieved from https://acp.copernicus.org/articles/12/1307/2012/ doi: 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. Retrieved from https://onlinelibrary.wiley.com/doi/abs/10.1002/kin.550240109 doi: 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: Atmospheres*, *97*(D18), 20703-20715. Retrieved from https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/92JD01914 doi: 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: Atmospheres*, *103*(D19), 25611-25629. doi: https://doi.org/10.1029/98JD01804

Pound, R. J. (2022, August). *Analysis code for "comparing the importance of iodine and isoprene on tropospheric photochemistry"*. Zenodo. Retrieved from https://doi.org/10.5281/zenodo.7016985 doi: 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. Retrieved from https://acp.copernicus.org/articles/20/4227/2020/ doi: 10.5194/acp-20-4227-2020

Prados-Roman, C., Cuevas, C. A., Hay, T., Fernandez, R. P., Mahajan, A. S.,

Royer, S.-J., . . . Saiz-Lopez, A. (2015). Iodine oxide in the global marine boundary layer. *Atmospheric Chemistry and Physics*, *15*(2), 583–593. Retrieved from `https://acp.copernicus.org/articles/15/583/2015/` doi: 10.5194/acp-15-583-2015

Roberts, J. M., Williams, J., Baumann, K., Buhr, M. P., Goldan, P. D., Holloway, J., . . . Young, V. L. (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: Atmospheres*, *103*(D17), 22473-22490. doi: https://doi.org/10.1029/98JD01637

Sarwar, G., Gantt, B., Foley, K., Fahey, K., Spero, T. L., Kang, D., . . . Saiz-Lopez, A. (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. Retrieved from `https://www.sciencedirect.com/science/article/pii/S135223101930411X` doi: 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. Retrieved from `https://acp.copernicus.org/articles/3/161/2003/` doi: 10.5194/acp-3-161-2003

Schnitzler, J.-P., Lehning, 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. doi: https://doi.org/10.1111/j.1438-8677.1997.tb00635.x

Shaw, G. (1983). Bio-controlled thermostasis involving the sulfur cycle. *Climatic Change 5*, 297–303. doi: https://doi.org/10.1007/BF02423524

Sherwen, T., Evans, M. J., Carpenter, L. J., Andrews, S. J., Lidster, R. T., Dix, B., . . . Ordóñez, C. (2016). Iodine's impact on tropospheric oxidants: a global model study in geos-chem. *Atmospheric Chemistry and Physics*, *16*(2), 1161–1186. Retrieved from `https://acp.copernicus.org/articles/16/1161/2016/` doi: 10.5194/acp-16-1161-2016

Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., East-

ham, S. D., ... Ordóñez, C. (2016). Global impacts of tropospheric halogens (cl, br, i) on oxidants and composition in geos-chem. *ATMOS CHEM PHYS*, *16*(18), 12239–12271. Retrieved from `https://www.atmos-chem-phys.net/16/12239/2016/` doi: 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 meso-cosm experiment. *Atmospheric Chemistry and Physics*, *7*(3), 739–755. Retrieved from `https://acp.copernicus.org/articles/7/739/2007/` doi: 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. Retrieved from `https://www.sciencedirect.com/science/article/pii/S1352231012003627` doi: 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 mod-elled changes in tropospheric ozone due to climate and land use over the 21st century. *Atmospheric Chemistry and Physics*, *15*(9), 5123–5143. Retrieved from `https://acp.copernicus.org/articles/15/5123/2015/` doi: 10.5194/acp-15-5123-2015

Starn, T. K., Shepson, P. B., Bertman, S. B., Riemer, D. D., Zika, R. G., & Ol-szyna, K. (1998). Nighttime isoprene chemistry at an urban-impacted forest site. *Journal of Geophysical Research: Atmospheres*, *103*(D17), 22437-22447. doi: https://doi.org/10.1029/98JD01201

Trainer, M., Williams, E., Parrish, D., Buhr, M., Allwine, E., Westberg, H., ... Liu, S. (1987). Models and observations of the impact of natural hydrocarbons on rural ozone. *Nature*, *329*, 705–707. doi: https://doi.org/10.1038/329705a0

Volkamer, R., Baidar, S., Campos, T. L., Coburn, S., DiGangi, J. P., Dix, B., ... Romashkin, P. A. (2015). Aircraft measurements of bro, io, glyoxal, no$_2$, h$_2$o, o$_2$–o$_2$ and aerosol extinction profiles in the tropics: comparison with aircraft-/ship-based in situ and lidar measurements. *Atmospheric Measurement Techniques*, *8*(5), 2121–2148. Retrieved from `https://amt.copernicus.org/articles/8/2121/2015/` doi: 10.5194/amt-8-2121-2015

Wang, S., Schmidt, J. A., Baidar, S., Coburn, S., Dix, B., Koenig, T. K., . . . Volkamer, R. (2015). Active and widespread halogen chemistry in the tropical and subtropical free troposphere. *Proceedings of the National Academy of Sciences*, *112*(30), 9281-9286. doi: 10.1073/pnas.1505142112

Wang, X., Jacob, D. J., Downs, W., Zhai, S., Zhu, L., Shah, V., . . . Thornton, J. A. (2021). Global tropospheric halogen (cl, br, i) chemistry and its impact on oxidants. *Atmospheric Chemistry and Physics*, *21*(18), 13973–13996. Retrieved from `https://acp.copernicus.org/articles/21/13973/2021/` doi: 10.5194/acp-21-13973-2021

Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., . . . Seinfeld, J. H. (2018). Gas-phase reactions of isoprene and its major oxidation products. *Chemical Reviews*, *118*, 3337-3390. doi: 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. Retrieved from `https://www.sciencedirect.com/science/article/pii/S1352231000004064` doi: https://doi.org/10.1016/S1352-2310(00)00406-4

Yang, M., Huebert, B. J., Blomquist, B. W., Howell, S. G., Shank, L. M., McNaughton, C. S., . . . Collett, J. L. (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. doi: 10.5194/acp-11-5079-2011

Supporting Information for "Comparing the importance of iodine and isoprene in tropospheric photochemistry"

R. J. Pound[1], M. J. Evans[1,2]L. J. Carpenter[1]

[1]Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, UK.

[2]National Centre for Atmospheric Science, University of York, UK.

Contents of this file

1. Text S1 and S2

2. Figures S1 to S7

Introduction This supplemental material covers additional figures and description of results for the paper Comparing the importance of iodine and isoprene in tropospheric photochemistry.

Text S1. - Additional plots for tropospheric changes

Iodine has a negligible impact on tropospheric CO concentration (figure S1). Iodine's impacts CO via CO lifetime, as iodine has a negligible impact on tropospheric OH, a negligible change in CO is also the result. Isoprene significantly increases global CO concentrations, and as with OH and O_3, the increase is more pronounced in the southern

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hemisphere. The increase in CO concentration from isoprene emissions is due to the oxidation and subsequent reactions of isoprene.

Isoprene increases NO_x in remote regions and decreases NO_x over tropical regions (figure S2). This is through conversion of NO_x into NO_y (figure S3) in the tropical locations which is then transported and subsequently reacts in remote regions, increasing NO_x there. Increase in NO_x and NO_y from iodine emissions are likely a result of nitrogenated iodine compounds. For figure S3 NO_y was defined as the sum of species (with GEOS-Chem species name where needed) NO, NO_2, NO_3, HNO_2 HNO_3, HNO_4, $BrNO_2$, $BrNO_3$, $ClNO_2$, $ClNO_3$, ethanal nitrate (ETHLN), ethyl nitrate (ETNO3), monoterpene organic nitrate (HONIT), isoprene nitrates and dinitrates (ICN, IDN, IHN1, IHN2, IHN3, IHN4, INPB, INPD, ITCN, ITHN), hydroxynitrate from methacrolein (MCRHN, MCRHNB), methyl nitrate (MENO3), organic nitrate from monoterpene (MONITA, MONITS, MONITU), peroxymethacroyl nitrate (MPAN), methyl peroxy nitrate (MPN), hydroxynitrate from methyl vinyl ketone (MVKN), N_2O_5, n-propyl nitrte (NPRNO3), peroxyacetylnitrate (PAN), peroxypropionylnitrate (PPN), propanone nitrate (PROPNN) and alkylnitrates greater than or equal to C4 (R4N2).

Text S2. - Seasonal plots for ratio of iodine and isoprene changes to surface ozone

Figures S4 - S7 show the seasonal variation in each region and globally from figure **??**. These are northern hemisphere seasons, with winter defined as December, January and

February. Spring is defined as March, April and May. Summer is June, July and August.
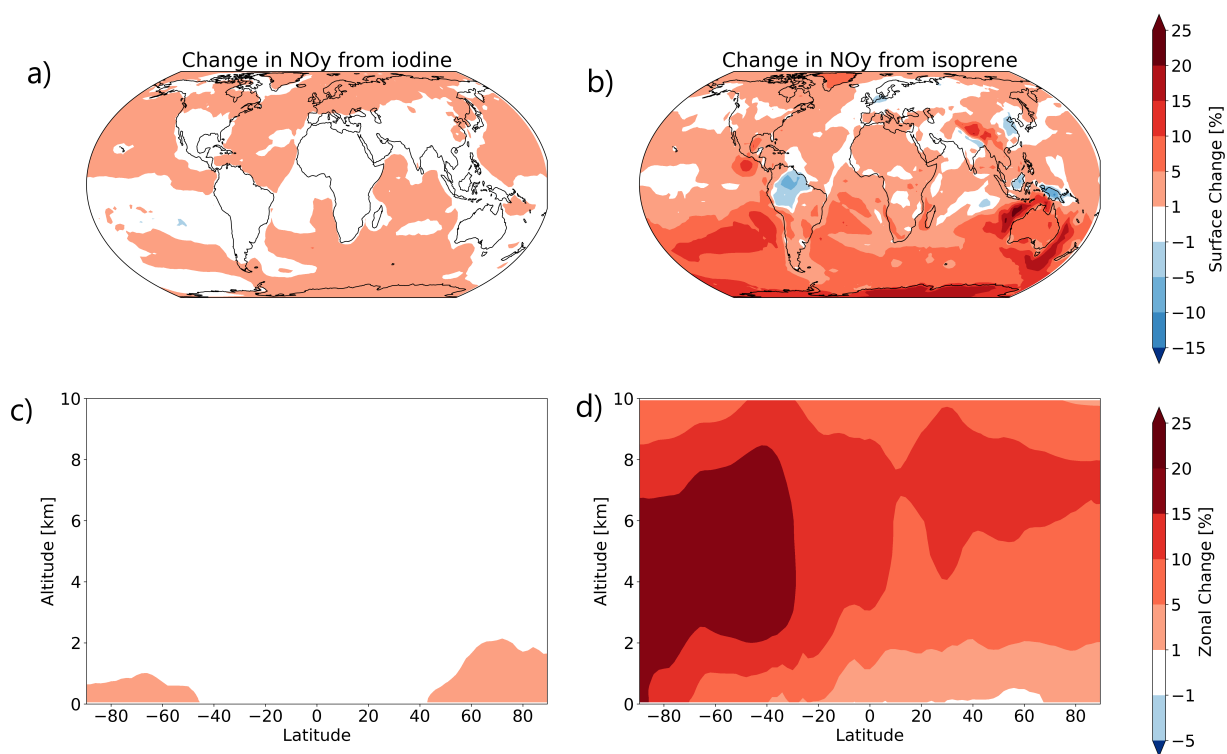
Autumn is September, October, November.
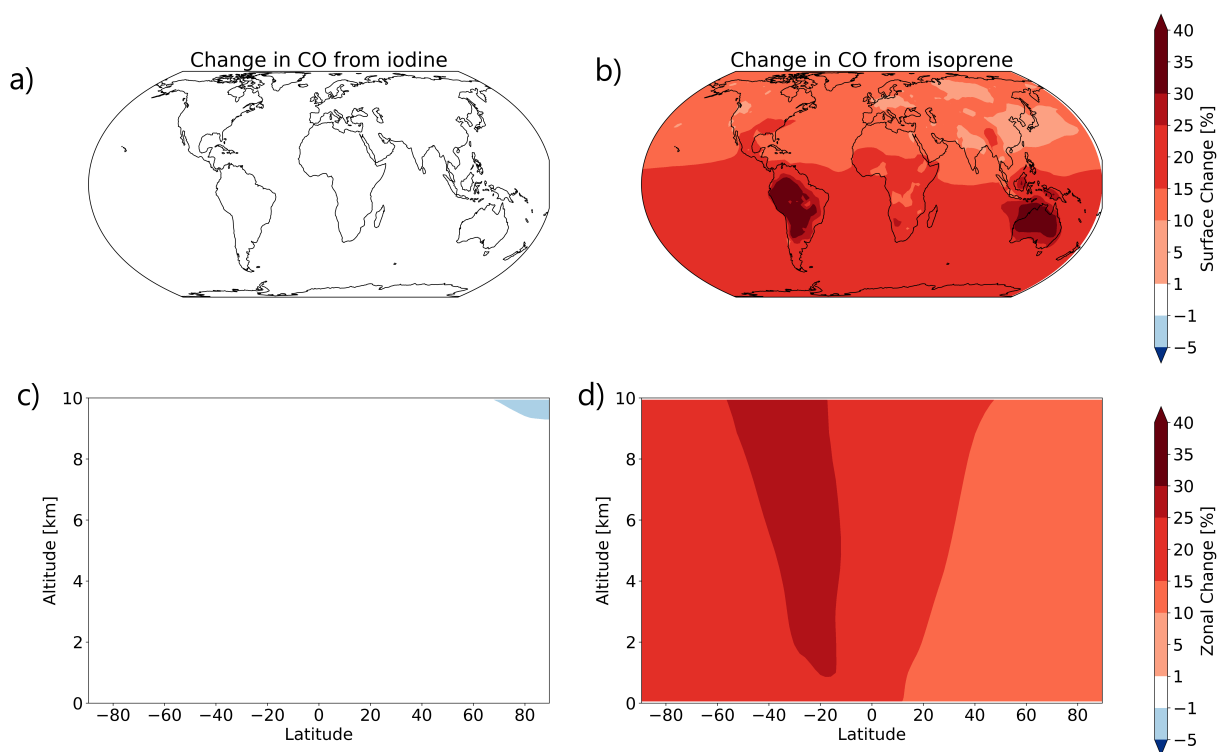
Figure S1. Annual average percentage change in surface [a) and b)] and zonal [c) and d)] CO from iodine emissions [a) and c)] and isoprene emissions [b) and d)].
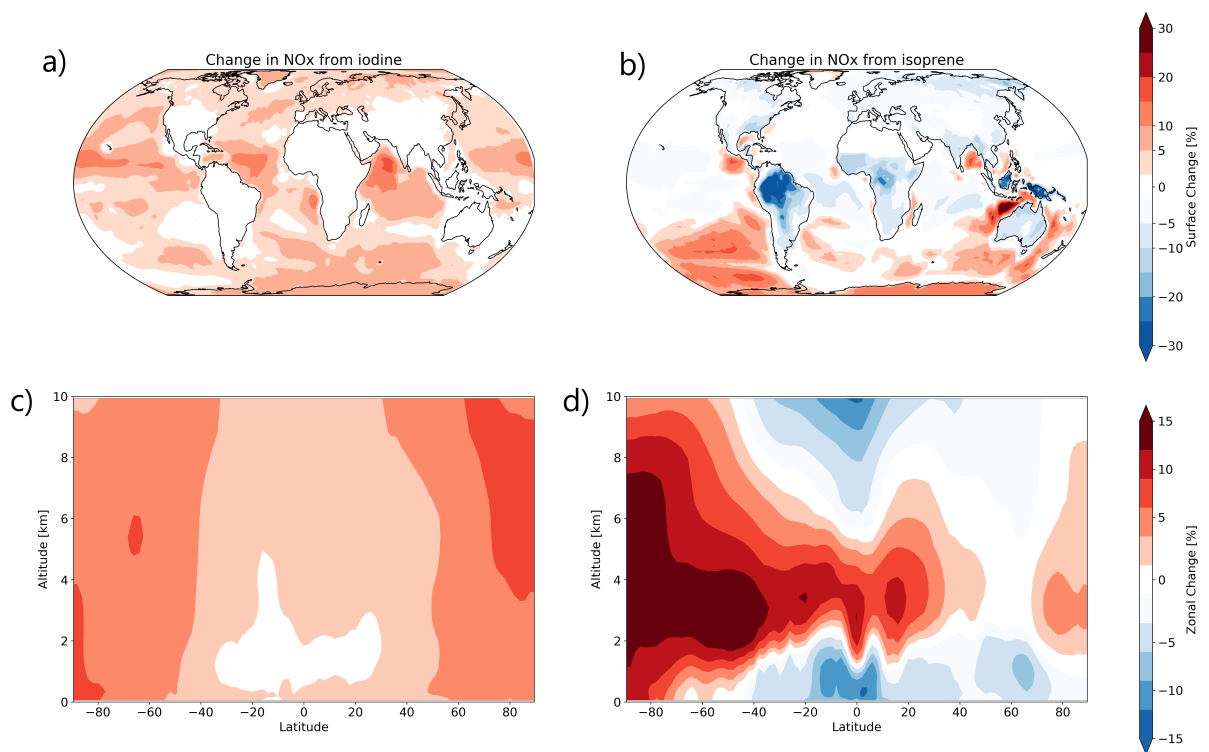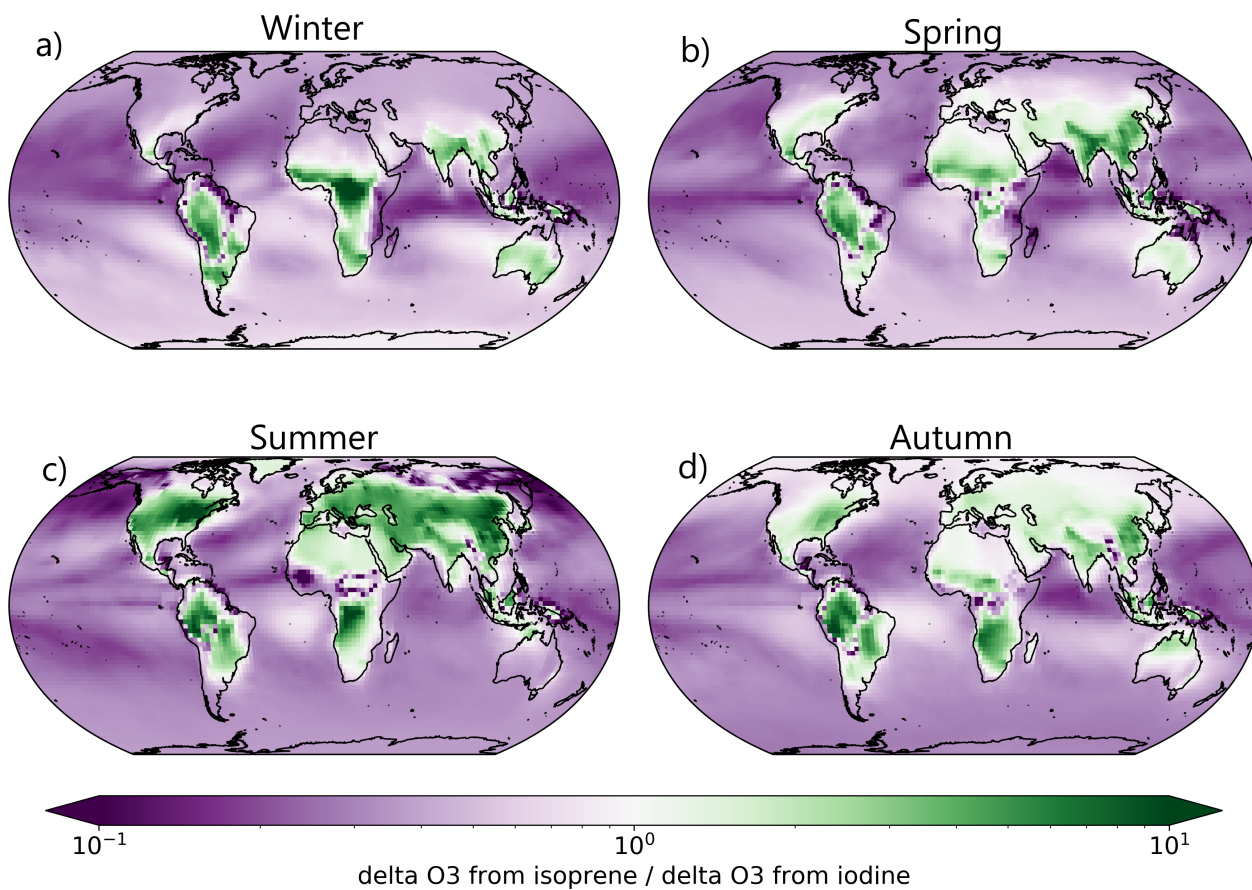
Figure S2. Annual average percentage change in surface [a) and b)] and zonal [c) and d)] NO_x ($NO + NO_2$) from iodine emissions [a) and c)] and isoprene emissions [b) and d)].

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Figure S3. Annual average percentage change in surface [a) and b)] and zonal [c) and d)] NO$_y$ from iodine emissions [a) and c)] and isoprene emissions [b) and d)].
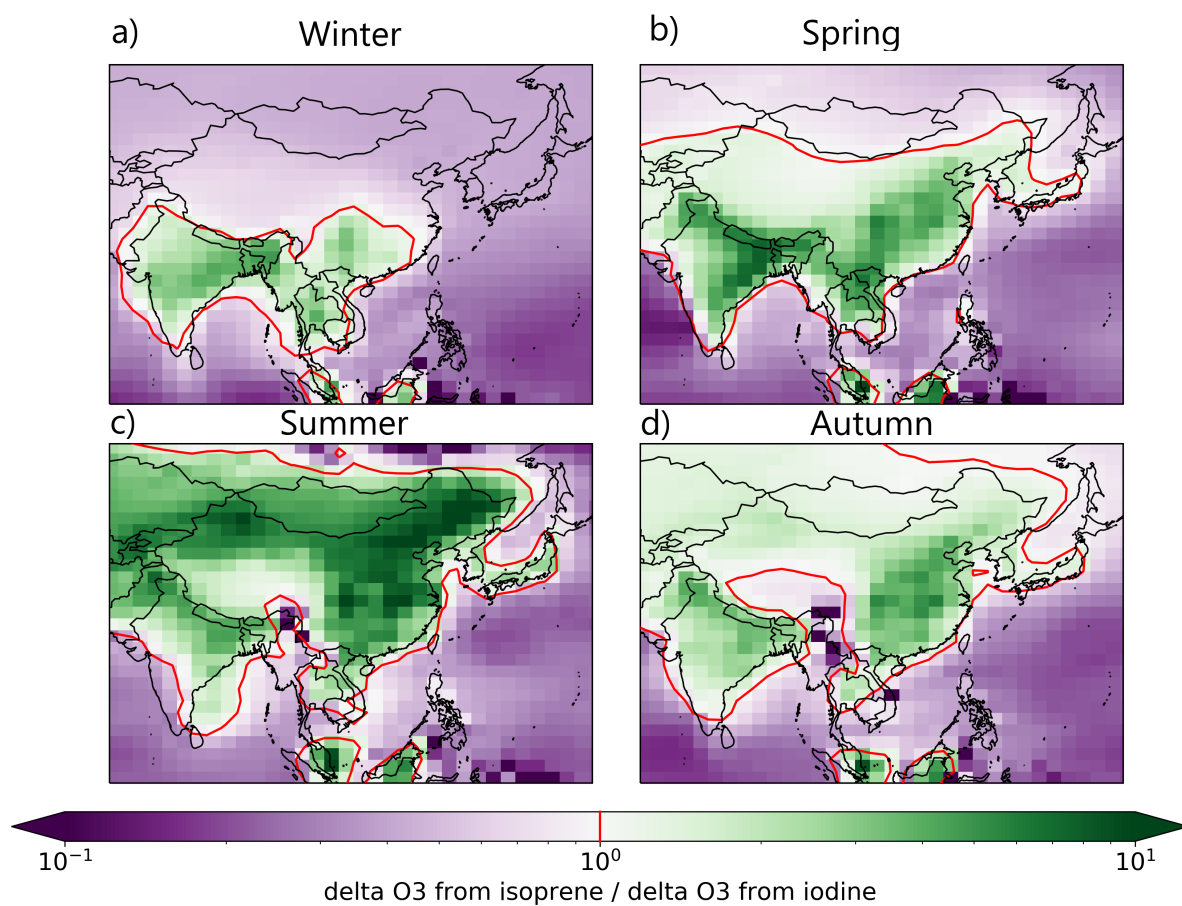
Figure S4. Global seasonal surface ratio of magnitude of change in O_3 from isoprene to magnitude of change in O_3 from iodine. Red contour lines represent value of the ratio as 1 (iodine and isoprene have the same magnitude impact on surface O_3)

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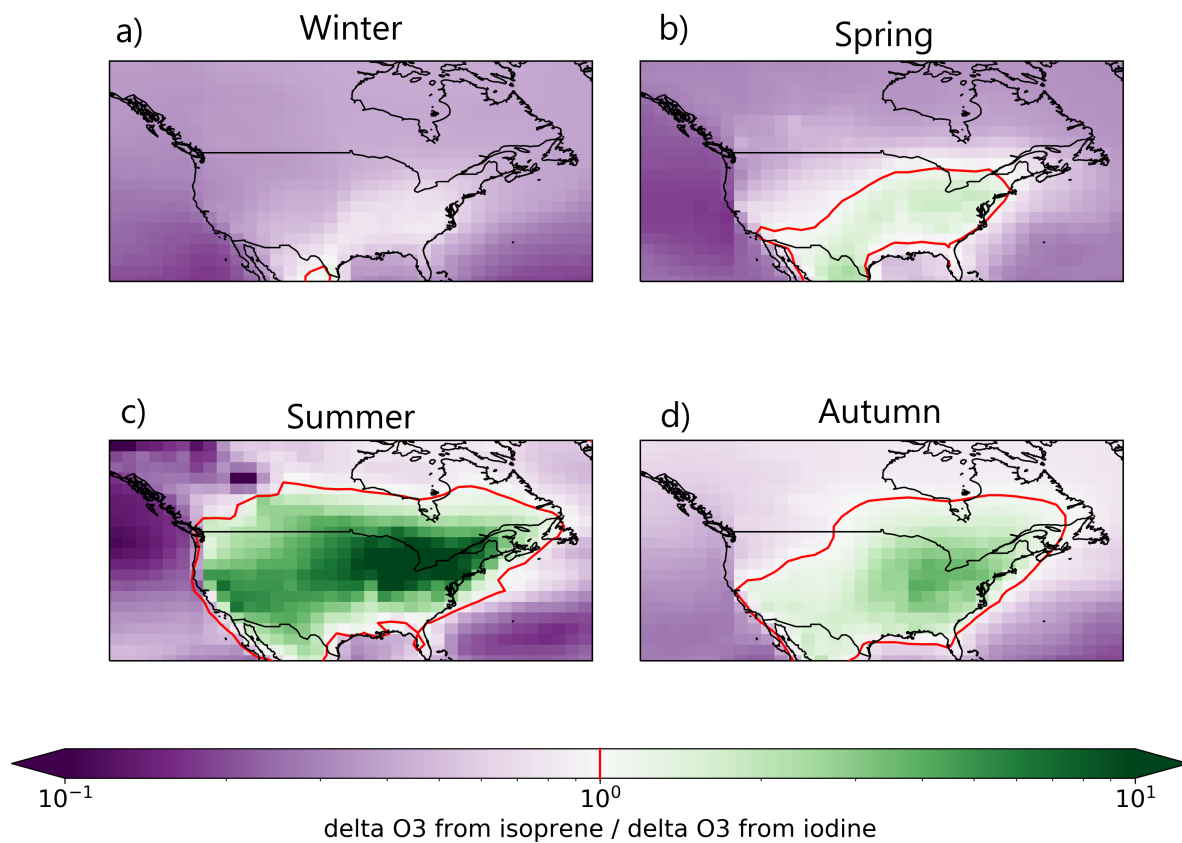
Figure S5. Seasonal surface ratio of magnitude of change in O_3 from isoprene to magnitude of change in O_3 from iodine over North America. The red contour line represents value of 1 (iodine and isoprene have the same magnitude impact on surface O_3)

a) Winter b) Spring

c) Summer d) Autumn

10^{-1} 10^{0} 10^{1}
delta O3 from isoprene / delta O3 from iodine
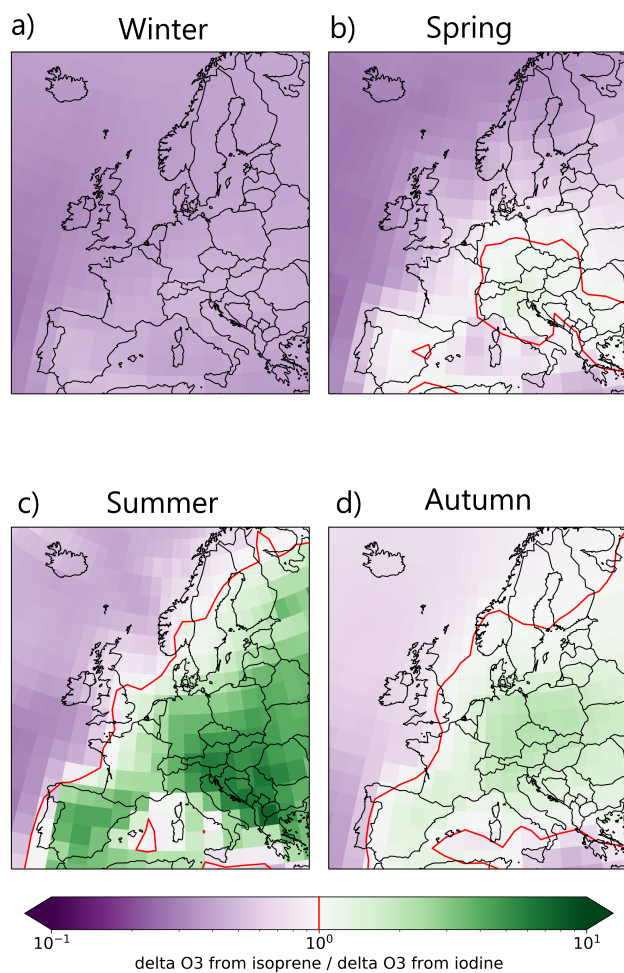
Figure S6. Seasonal surface ratio of magnitude of change in O_3 from isoprene to magnitude of change in O_3 from iodine over Europe. The red contour line represents value of 1 (iodine and isoprene have the same magnitude impact on surface O_3)

Figure S7. Seasonal surface ratio of magnitude of change in O_3 from isoprene to magnitude of change in O_3 from iodine over Asia. The red contour line represents value of 1 (iodine and isoprene have the same magnitude impact on surface O_3)