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2. Supplementary Information:

A. Flat Files

Item	Present?	Filename This should be the name the file is saved as when it is uploaded to our system, and should include the file extension. The extension must be .pdf	A brief, numerical description of file contents. i.e.: *Supplementary Figures 1-4, Supplementary Discussion, and Supplementary Tables 1-4.*
Supplementary Information	Yes	17006_3_supp_168761_q1mrh5_convrt.	i.e.: Evaluation of halogens abundances and distributions in CAM-Chem, Supplementary

		pdf	Tables 1-9, and Supplementary Figures 1-11.
Reporting Summary	Yes	17006_3_supp_168760_q1mr24.pdf	

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B. Additional Supplementary Files

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Natural halogens buffer tropospheric ozone in a changing climate

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Abstract

Reactive atmospheric halogens destroy tropospheric ozone (O_3), an air pollutant and greenhouse gas. The primary source of natural halogens is emissions from marine phytoplankton and algae, as well as abiotic sources from ocean and tropospheric chemistry, but how their fluxes will change under climate warming –and the resulting impacts on O_3– are not well known. Here we use an Earth system model to estimate that natural halogens deplete approximately 13 % of tropospheric O_3 in the present-day climate. Despite increased levels of natural halogens through the twenty-first century, this fraction remains stable due to compensation from hemispheric, regional, and vertical heterogeneity in tropospheric O_3 loss. Notably, this halogen-driven O_3 buffering is projected to be greatest over polluted and populated regions, mainly due to iodine chemistry, with important implications for air quality.

Tropospheric O_3 is a trace gas that plays a key role in atmospheric chemistry, both as a greenhouse gas and as a component of photochemical smog, affecting air quality and public health.[1,2] Its abundance is controlled by a balance between in-situ

56   photochemistry, stratospheric influx and surface dry deposition.[3] Photochemical

57   destruction of O_3 occurs throughout the troposphere, primarily via its photolysis and

58   subsequent reaction with water vapor and direct loss by reaction with hydrogen

59   radicals.[4] Tropospheric O_3 is also destroyed by reactions with reactive halogens (Cl,

60   Br, I) through catalytic cycles, and its budget can only be understood when

61   tropospheric halogen chemistry is included.[5–8] Indeed, halogens are now increasingly

62   recognized by observational and modelling work as an important component of

63   tropospheric chemistry.[9,10] At present, they are estimated to reduce the global

64   tropospheric O_3 burden by about 10–20 %, having a large impact on surface O_3.[7,8,11,12]

65   Biogenic very short-lived (VSL) halocarbons –including $CHBr_3$, CH_2Br_2,

66   CH_3I and CH_2ICl– are naturally emitted from the ocean via the metabolism of marine

67   organisms such as phytoplankton, micro- and macroalgae. These halogen compounds

68   have lifetimes of fewer than ~6 months and are important sources of reactive chlorine,

69   bromine and iodine to the troposphere.[13] Furthermore, experimental research

70   demonstrates that the ocean is an abiotic source of inorganic iodine. This is a result of

71   O_3 deposition into the ocean and subsequent oxidation of seawater iodide to

72   hypoiodous acid (HOI) and molecular iodine (I_2), which are released to the

73   atmosphere.[14,15] In the troposphere, reactive bromine and chlorine effectively results

74   from the photo-oxidation of VSL halocarbons,[11,16,17] whereas oceanic emissions of

75   inorganic iodine can account for up to 75 % of its atmospheric budget.[18]

76   Changes in climate and socio-economic development have already altered

77   natural fluxes of VSL halocarbons (~7 % increase between 1979 and 2013)[19] and

78   inorganic iodine (tripled during 1950–2010)[20,21] and will likely continue doing so

79   during the 21st century. Previous studies have shown that climate change –primarily

80   warming sea surface temperatures (SSTs)– can accelerate air-sea exchange up to ~30

81   % for some halogenated VSL species[19,22] by the end of the century. However, how

82   changes in naturally-emitted halogens will affect O_3 and tropospheric chemistry and

83   climate remains unknown.

84   In this study, we use the Community Earth System Model (CESM)[23] to project

85   emissions of organic and inorganic halogens in a consistent framework coupled to

86   climate and atmospheric composition (see Methods), to quantify their influence on

87   tropospheric O_3 during 2000–2100. Low- and high-end Representative Concentration

88   Pathway (RCP) emission scenarios –including RCP2.6, RCP6.0 and RCP8.5– are

89   explored, providing a range and upper limit estimate of potential impacts. We find

90   that global tropospheric O_3 loss due to the inclusion of reactive halogens is nearly

91   constant regardless of the emission scenario, linked to the buffering capacity of the

92   natural system against external forcing. Our results reveal that over the century,

93   enhanced 'near'-surface O_3 loss by halogens offsets the negative effects of climate

94   and air quality from O_3 pollution over continental regions.

95

96   **Natural halogen emissions during the 21st century**

97   Globally, present-day (defined as the 1990–2009 climatological mean; nominally year

98   2000) natural sources of organic VSL represented in the model –including nine

99   halocarbons containing chlorine, bromine and iodine–[13,24] are approximately 1.22

100   $Tg(Cl,Br,I)$ yr^{-1}. Bromocarbon emissions are slightly larger (0.63 $Tg(Br)$ yr^{-1}) than

101   iodocarbons (0.52 $Tg(I)$ yr^{-1}), whereas chlorocarbons represent only a small

102   contribution (0.07 $Tg(Cl)$ yr^{-1}). Geographically, these emissions are concentrated in

103   the tropics (~55 % between 20ºN–20ºS) and at midlatitudes (~40 % including both

104   hemispheres), with a marginal contribution from polar regions. In addition to its

105   organic sources, iodine is emitted from the ocean via an abiotic route, following O_3

106   deposition to the surface ocean.[14,15] Hence, inorganic iodine emissions largely depend

107   on the atmospheric O_3 burden and its deposition to the ocean, but also on SSTs and

108   wind speed.[14] Here, modelled present-day global emissions of inorganic iodine are

109   2.67 $Tg(I)$ yr^{-1}, mainly confined within subtropical regions (~85 % between 35ºN–

110   35ºS). Climate change can have a significant impact on organic and inorganic natural

111   halogen fluxes via changes in physical factors (e.g. SSTs),[25,26] biogeochemical cycles

112   (e.g. ocean organisms and nutrients availability),[27–29] and socio-economic

113   developments (e.g. O_3 precursors).[20]

114   Global and annual mean VSL halocarbon fluxes during 2000–2100 are shown

115   in Figure 1a. Physical climate-induced ("cliVSL" case; Supplementary Table 1)

116   changes in VSL halocarbon emissions increase by approximately 7.4 % and 13.5 %

117   for the RCP6.0 and RCP8.5 scenarios, respectively, by the end of the century (defined

118   as the climatological mean during 2080–2099; nominally year 2100) compared to

119   present-day. The rates of change of these fluxes are quasi-linear for both emission

120   scenarios and are primarily driven by changes occurring in midlatitudes (i.e., regions

121   with the largest SST changes relative to the year 2000 along with the tropics,

122   Supplementary Fig. 1). A sensitivity case for the RCP2.6 scenario (year 2100;

123   Supplementary Table 2) projects 3.5 % increases in VSL halocarbon emissions

124   (Supplementary Tables 3–7). Earth system models project a drop in global marine net

125   primary production associated with a warming climate over the 21st century,[27–29]

126   which will affect the production of halogen compounds in marine waters

127   (acknowledging a limited processed-based understanding).[30] Globally, our sensitivity

128   simulations, including physical and biogeochemical changes related to climate

129   ("cli+bioVSL"), show that declining marine primary production (~4 % by 2080)

130   results in approximately 2–3 % lower halocarbon emissions since mid-century,

131   compared to the "cliVSL" case. Changes in marine primary production are highly

132   heterogeneous due to a balance between direct (e.g., increase in phytoplankton

133   metabolic rates) and indirect (e.g., water stratification and nutrient limitations)

134   effects.[27] The relatively small global drop in halocarbon emissions associated with

135   changes in marine net primary production is the consequence of mid-to-high-latitude

136   increases offset by larger decreases in tropical and subtropical regions.

137   In the above scenarios, future halocarbon emissions change in response to

138   physical forcing and marine primary production. Due to uncertainties in the future

139   evolution of these emissions, we additionally extrapolate trends from the recent past

140   (1979–2013) out to 2100 ("obsVSL"; Supplementary Table 3), resulting in the largest

141   (18.1 %) increase in VSL halocarbon emissions compared to present. While this

142   monotonic increase in emissions (Fig. 1) likely represents an upper limit, we note that

143   under each scenario considered, VSL halocarbon emissions are larger at the end of the

144   21st century compared to present.

145   Future inorganic iodine emissions are largely driven by socio-economic

146   development and associated evolution of atmospheric O_3 and its deposition to the

147   ocean. Most O_3 precursor emissions decrease during the century in the RCP scenarios,

148   particularly since mid-century.[31] Methane emissions decrease and are relatively

149   unchanged for RCP2.6 and RCP6.0, respectively, while they double by 2100

150   compared to present for the RCP8.5 scenario.[32] While O_3 deposition to the ocean

151   increases 5.7 ± 1.8 % under RCP8.5 during 2000–2100 compared to present-day (260

152   ± 1 Tg(O_3) yr^{-1}; uncertainty range refers to one-sigma of the standard error unless

153   otherwise specified), it decreases −16.8 ± 3.3 % and −28.0 % for RCP6.0 and

154   RCP2.6, respectively. In turn, global oceanic emissions of inorganic iodine increase

155 by ~20 % following RCP8.5 over the same period, and they decrease around 10 %

156 and 20 % for RCP6.0 and RCP2.6, respectively (Fig. 1b).

157   Modelled changes in global and annual mean tropospheric concentrations of

158 reactive halogens over the century are shown in Figure 1c. Present-day globally

159 integrated tropospheric concentrations of reactive inorganic chlorine, bromine and

160 iodine are approximately 2.7 ppt, 1.8 ppt and 1.0 ppt from natural sources, and 9.6

161 ppt, 1.9 ppt and 1.0 ppt including both anthropogenic and natural sources,

162 respectively. By 2100, reactive halogen concentrations increase by approximately 4–

163 10 %, which depend on the precursor emission scenario and forcing, i.e. climate (~4

164 %) and marine production (1–2 %). While bromine drives these changes under

165 RCP6.0, iodine shows no significant change as a result of the interplay between

166 iodocarbons (increasing) and inorganic iodine (decreasing) fluxes. In contrast, both

167 bromine and iodine contribute equally to the change in reactive halogen loading for

168 RCP8.5. Reactive halogen concentrations decrease for the RCP2.6 scenario (~5 %).

169

170 **Natural halogen impacts on 21st century tropospheric ozone**

171 The change in global tropospheric column-integrated O_3 during 2000–2100 is shown

172 in Figure 2 (the tropospheric O_3 budget is also given in Supplementary Table 8). The

173 upper and middle panels present absolute changes in tropospheric O_3 column and its

174 loss associated with reactive halogens, respectively. Compared to present-day,

175 halogen-driven tropospheric O_3 column loss increases towards mid-century,

176 coinciding with ever-rising VSL halocarbon emissions for RCP6.0 and RCP8.5. Two

177 different stories are drawn during the second half of the century. The impact of

178 reactive halogens on tropospheric O_3 remains relatively unchanged by 2100 under

179 RCP8.5, whereas smaller depletion is projected under RCP6.0. This response is

180 closely linked to the total amount of tropospheric O_3 and the key role of halogen

181 chemistry acting as a natural buffer (i.e., negative geochemical feedback; Fig. 1b).[8]

182 Hence, greater tropospheric O_3 results in an enhanced halogen-mediated loss and vice

183 versa. Notably, only a projection with constant natural halogen emissions ("fixVSL")

184 shows a disruption of the above natural buffering capacity linked to halogen

185 chemistry. One might think that increasing VSL halocarbon emissions in a changing

186 climate would result in greater tropospheric O_3 loss. Counterintuitively, however,

187 global halogen-driven tropospheric O_3 column loss is projected to remain nearly

188   constant throughout the century (~12.8 ± 0.8 %) regardless the emissions scenario

189   (lower panel in Fig. 2), including the RCP2.6 (not shown).

190   Zonal mean tropospheric O_3 loss associated with halogen chemistry for

191   present-day are illustrated in Figure 3a,b. On average, zonal mean loss of O_3 mass is

192   ~0.3 DU (3.9 DU globally integrated), to which bromine and iodine contribute

193   approximately 16 % and 80 %, respectively. Although halogen-mediated tropospheric

194   O_3 loss mixing ratios peak in the extratropical upper troposphere associated with

195   stratospheric O_3 depletion, the largest impacts of natural halogens on O_3 mass are

196   simulated in the free troposphere (65 % of the total loss occurs between 300–850

197   hPa). Halogen-mediated O_3 loss shows a clear hemispheric asymmetry –greater in the

198   SH at present– consistent with differences in ozone precursors and bromine-mediated

199   loss. VSL bromocarbons provide approximately 5 ± 2 ppt of bromine to the

200   stratosphere (i.e., on top of the brominated long-lived species),[11,16,17] resulting in

201   additional stratospheric O_3 depletion.[33] In the extratropical SH, the stratospheric

202   influx of O_3 is affected by a strong chemistry-climate feedback whereby a colder

203   lower stratosphere due to halogenated VSL-driven O_3 loss further enhances

204   stratospheric O_3 depletion via heterogeneous activation. This controls up to 70 % of

205   the tropospheric signal (Supplementary Fig. 5).[7] Smallest tropospheric O_3 decreases

206   are constrained to the tropical lower and upper troposphere (regions largely controlled

207   by reactions with water vapor and odd hydrogen radicals respectively). The

208   pronounced gradient in relative O_3 loss (Fig. 3b), increasing from upper to lower

209   troposphere and from north to south, responds to the O_3 burden distribution in the

210   troposphere.

211   Zonal mean tropospheric O_3 loss trends (% dec^{-1}) driven by natural halogens

212   during 2000–2100 for RCP6.0 and RCP8.5 are shown in Figures 3c,d. The resulting

213   pattern is heterogeneous, with marked hemispheric and vertical gradients, though

214   consistent for both emission scenarios (with differences in strength). Interestingly, the

215   relative O_3 loss driven by reactive halogens weakens in the mid- and upper

216   troposphere during the century (10–20 % at 250 hPa; Fig. 4a), which is explained by

217   an enhanced stratospheric influx due to greater stratospheric O_3 levels and rapid

218   general circulation.[34] This feature is amplified at high latitudes in the SH during the

219   first and second half of the century (Supplementary Fig. 8), linked to a strong

220   chemistry-climate feedback and the expected ozone hole recovery. Furthermore, in

221 the tropical free troposphere between 300 and 850 hPa, future O_3 loss by halogens
222 decreases towards the end of the century, suggesting that O_3 fate in this region will be
223 primarily controlled by other drivers, including photolysis and reactions with water
224 vapor and hydroxyl radicals (Fig. 3c-d and Fig. 4b). By contrast, in the lower
225 troposphere, halogen-driven O_3 loss is projected to be larger towards 2100,
226 accentuated during the second half of the century owing to decreases in O_3 precursor
227 emissions (Supplementary Fig. 8b). We find a pronounced hemispheric asymmetry
228 with a greater O_3 loss trend in the more "polluted" NH than in the "cleaner" SH.
229 Compared to present-day, future halogen-mediated O_3 loss is projected to increase by
230 up to 10–35 % depending on the region and the emission scenario (Fig. 4), being
231 largest within the boundary layer.

232   'Near'-surface (define here as the average over the first kilometer) O_3 loss
233 change between present-day and the end of the 21st century is shown in Figure 5.
234 Globally, natural halogen-induced near-surface O_3 loss change between 2000 and
235 2100 is greater for the RCP6.0 scenario (−15.0 ± 1.1 %) compared to RCP8.5 (−3.1 ±
236 0.7 %; Supplementary Table 9). A consistent feature for both emission scenarios is
237 that, while relatively small or even weaker losses are predicted in the tropics (e.g., the
238 Western Pacific region), enhanced O_3 loss is confined mainly to the extra-tropics,
239 peaking at midlatitudes (30º–60º) (Fig. 5b,d).

240   Naturally-emitted halocarbons are relatively long-lived within the
241 troposphere.[16,17] Thus, they can be transported from the oceans over the continents,
242 resulting in significant concentrations of reactive inorganic species. We find that the
243 largest O_3 loss is projected to occur towards the end of the century over polluted
244 continental regions rather than in remote marine environments, with a marked
245 hemispheric asymmetry. Particularly, large halogen-driven O_3 losses are anticipated
246 over the eastern United States, Europe, and eastern Asia of −71.5 ± 12.9 %, −30.9 ±
247 4.2 %, and −6.9 ± 10.1 % for RCP6.0, and −48.2 ± 12.6 %, −18.3 ± 3.2 % and −23.2
248 ± 10.9 % for RCP8.5 (Fig. 6). Future changes in near-surface O_3 loss due to reactive
249 halogens are robust in this set of simulations for the emission scenarios considered
250 here (Supplementary Table 9). No significant differences are generally found between
251 RCP2.6 and RCP6.0, though larger differences are found compared to RCP8.5,
252 associated with a warmer and moister climate coupled to greater methane
253 concentrations.

254   The impact of natural halogens on surface O_3 is largely driven by iodine

255   catalytic cycles, especially over polluted areas that experience the largest change in

256   future O_3 precursor emissions (Supplementary Fig. 11). The relative shift in surface

257   O_3 loss chemistry over polluted regions, towards a more iodine-mediated chemical

258   processing, is compensated by a relative decrease in other key families (i.e.,

259   photolysis and reaction with water vapor and direct loss via hydrogen radicals).

260

261   **Discussion and concluding remarks**

262   Very short-lived halocarbons are naturally emitted from the ocean and strongly linked

263   to climate (primarily SSTs);[13] whereas inorganic iodine emissions depend on O_3

264   deposition to the ocean.[14,15] Therefore, future changes in fluxes and distributions of

265   natural halogens will be determined by a combination of climate sensitivity, future

266   anthropogenic emissions, and atmospheric chemistry.

267   Marine biota will be influenced by a number of factors as climate changes

268   (e.g., acidification, nutrients availability, water temperatures and stratification), which

269   will affect seawater concentrations of halocarbons and, therefore, their sea-to-air

270   fluxes. Here, changes in physical factors coupled with ocean biogeochemical cycles

271   result in a relatively small drop in global VSL halocarbon fluxes (~2–3 %; see Fig. 1),

272   although it shows a marked geographical re-distribution. Natural halocarbon

273   emissions remained largely unchanged in the tropics (±1 %) compared to present-day,

274   compensated by larger increases at higher latitudes. Although global VSL halocarbon

275   emissions are smaller when changes in marine net primary production are included

276   ("cli+bioVSL") compared to when they are neglected ("cliVSL"), their impacts on

277   tropospheric O_3 loss generally are not significantly different at the 95 % confidence

278   interval in this analysis.

279   Surface O_3 is highly sensitive to meteorological conditions and climate

280   change.[35] Strong observational and modelling evidence suggests that climate-related

281   impacts over the next century will have negative effects for O_3 pollution ('climate

282   penalty'),[36] though this is strongly dependent on future socio-economic development.

283   By the end of the 21st century, projections of near-surface O_3 without halogens show

284   relatively large decreases of ~10–35 % for the lower and middle end of the emission

285   scenarios considered here (RCP2.6 and RCP6.0), and a range of −8 to +2 % for

286   RCP8.5 over populated regions –eastern United States, Europe and eastern Asia–

11

287 compared to the present (~40–55 ppb), consistent with multi-model projections.[36,37] A

288 robust feature in our simulations is that near-surface O_3 loss due to natural halogens

289 (mainly iodine) will be enhanced up to ~70 % over the eastern United States by 2100

290 compared to present-day (Figs. 5–6). For example, over the eastern United States,

291 halogen-driven near-surface O_3 loss is predicted to deplete approximately an extra ppb

292 for the emission scenarios considered here (Supplementary Table 9), despite having

293 lower O_3 levels by 2100 (8–25 %). Notably, the RCPs adopt stringent air quality

294 policies that reduce anthropogenic emissions of nitrogen oxides, carbon monoxide and

295 volatile organic compounds –though not methane– under RCP8.5.[31,32] Should future

296 policies on anthropogenic emissions be more relaxed, such as the former Special

297 Report on Emission Scenarios[38] (SRES) or the newly-adopted Shared Socioeconomic

298 Pathways[39] (SSP), the implications of halogen chemistry for surface O_3 in a changing

299 climate (opposing the climate penalty effect) would be even more relevant for air

300 quality and human health.

301   In summary, we find that globally-integrated, halogen-driven tropospheric O_3

302 column loss is constant (~13 %) throughout the 21st century despite varying natural

303 halogen emissions. This is the result of a tradeoff between different regions.

304 Tropospheric O_3 loss by halogens shows a marked hemispheric asymmetry for both

305 present-day and end-of-century. This work also reveals that the largest halogen-

306 mediated O_3 losses (up to 70 %) are projected near the surface over polluted regions

307 of the NH (eastern United States, Europe and eastern Asia), with beneficial

308 implications for air quality and mitigating O_3 pollution. We conclude that halogen

309 chemistry is a key component of the troposphere, controlling a large fraction of O_3 at

310 present and determining its abundance and distribution under twenty-first-century

311 climate change.

312

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439   **Author Contributions**
440   A.S.-L. devised the research. F.I.-S. and A.S.-L. initiated the study in collaboration with A.B., R.P.F.,
441   C.A.C., D.E.K., S.T., J-F.L., M.C.L. and R.H.; F.I.-S., with the help of A.B. and R.P.F., developed and
442   performed the CAM-Chem simulations. All authors discussed the findings and commented on the
443   manuscript. F.I.-S., and A.S.-L. wrote the manuscript with contributions from all authors.
444

445   **Competing interests.** The authors declare no competing interests.
446

447   **Additional information**
448   Supplementary information accompanies this manuscript at…
449

Methods

451   **CESM (CAM-Chem) model, experiment design and evaluation**
452   The community Earth System Model (CESM; version 1.1.1), with the Community Atmospheric Model
453   including interactive chemistry (CAM-Chem; version 4),[40,41] was used to explore halogen-driven
454   tropospheric O_3 loss in the 21st century. The model extends from the surface to approximately 40 km
455   (3.5 hPa in the upper stratosphere) with 26 levels (18 levels below 100 hPa) and includes a horizontal
456   resolution of 1.9º x 2.5º (latitude by longitude). The 'standard' chemical scheme represented in CAM-
457   Chem represents 169 species with comprehensive photochemistry (gas-phase and heterogeneous
458   reactions) coupled to the radiation scheme.[23] In addition, the chemical mechanism here includes a state-
459   of-the-art photochemistry scheme, heterogeneous recycling, wet and dry deposition for natural
460   halogens (containing chlorine, bromine and iodine) in the troposphere and the stratosphere.[6,7,11,42]
461   Natural halogen sources include both, biogenic and abiotic routes. Biogenic sources comprise 9
462   halocarbons ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$, $CHBrCl_2$, CH_3I, CH_2I_2, CH_2IBr, and CH_2ICl),

463   which are the result of phytoplankton and (micro-) macroalgae metabolism and photochemistry at the

464   ocean's surface.[13] Abiotic iodine source gas (HOI and I_2) emissions are directly emitted from the ocean

465   as a consequence of O_3 deposition and reactions with seawater iodide.[14,15] Present-day global inorganic

466   iodine emissions in this set of simulations (~2.67 Tg(I) yr^{-1}) are ~40 % higher than previously

467   reported,[8,20] reflecting differences in boundary conditions (e.g. O_3 precursors and SSTs). Nevertheless,

468   tropospheric O_3 deposition to the ocean modelled here (260 Tg(O_3) yr^{-1}) is within observational

469   estimates (200–350 Tg(O_3) yr^{-1}).[43] Concentrations of reactive halogens are defined for chlorine (Cl_y =

470    $Cl + ClO + 2 \times Cl_2 + 2 \times Cl_2O_2 + OClO + HOCl + ClONO_2 + HCl + BrCl + ClNO_2 + ICl$), bromine ($Br_y$ =

471    $Br + BrO + HOBr + BrONO_2 + HBr + BrCl + 2 \times Br_2 + BrNO_2 + IBr$), and iodine ($I_y$ = $I + 2 \times I_2 + IO +$

472    $OIO + HI + HOI + INO + INO_2 + IONO_2 + IBr + ICl + 2 \times I_2O_2 + 2 \times I_2O_3 + 2 \times I_2O_4$).

473   The model set-up was based on the Chemistry–Climate Model Initiative (CCMI) REFC2

474   experiment (transient simulation between 1960 and 2100).[44] Future (2006–2100) projections followed

475   the Representative Concentration Pathway emission scenarios RCP6.0 and RCP8.5. Monthly and

476   seasonally varying boundary conditions were specified for CO_2, N_2O, CH_4, as well as long-lived

477   halogen-containing species (CH_3Cl, CH_3CCl_3, CCl_4, CFC-11, CFC-12, CFC-113, HCFC-22, CFC-114,

478   CFC-115, HCFC-141b, HCFC-142b, CH_3Br, H-1301, H-1211, H-1202, and H-2402) following the A1

479   halogen scenario.[45] Note that imposing long-lived gas concentrations as lower boundary conditions

480   neglects the halogen-induced CH_4 oxidation feedback. Detailed description of tropospheric bromine

481   and iodine chemical processing included in the chemical scheme, for both day- and nighttime, has been

482   documented in previous work,[7,11,46,47] as well as an extensive evaluation of tropospheric mixing ratios

483   of organic and inorganic halogenated species.[13,18] Furthermore, modelled present-day O_3 –represented

484   in CAM-Chem with an equivalent experimental set-up and the standard chemical scheme– has been

485   recently evaluated against a number of observational data sets.[23] Simulated tropospheric O_3 column lies

486   within ±10 DU compared to satellite measurements, showing best agreement in the tropics and

487   midlatitudes during spring and summer, though largest deviations at midlatitudes during winter and

488   fall. Regionally, simulated tropospheric O_3 shows, both good agreement with available measurements

489   (±25 %), and skills reproducing observed features (e.g. O_3 midlatitudes-to-tropics gradient and

490   summertime maximum over the Mediterranean basin). The inclusion of natural halogen chemistry and

491   emissions generally improves CAM-Chem's performance compared to observations (Supplementary

492   Fig. 2).

493   The CAM-Chem including interactive chemistry was also used in specified dynamics (SD)

494   mode,[40] with equivalent emissions and boundary conditions to the reference simulations (transient runs)

495   for both, present-day (year 2000) and the end of the 21st century (year 2100). Three years of

496   meteorological fields (every 3-hours) were derived from perpetual year 2000 and year 2100 (following

497   three RCPs scenarios) simulations. The chemistry sensitivity simulations in SD mode were driven by

498   identical meteorology (temperature, winds, and surface pressure), emissions and boundary conditions

499   representative of both periods, present-day and year 2100, only natural halogens emissions and

500   chemistry change ("SD–noVSL" and "SD–cliVSL" cases). All SD simulations were run for three years

501   each, using initial conditions from the equivalent reference simulation (as a spun up), and the last year

502   was used for the analysis.

503

Climate-induced changes in halocarbon fluxes

Sea-air gas flux (F),[48] as implemented in CAM-Chem (following Johnson),[49] is governed by its exchange velocity (k) and concentration gradient (Δc) as follows:

$$F = k \cdot \Delta c = k \cdot (c_w - \frac{c_a}{H}) \tag{1}$$

where k (= $[\,1/k_w + 1/(H\,k_a)\,]^{-1}$) is parameterized distinguishing between water- (k_w) and air-phase (k_a) exchange velocities (i.e. primarily determined by SSTs and surface wind speed), c_w and c_a are the gas seawater and air concentrations respectively, and H is the dimensionless Henry coefficient (i.e. temperature dependent gas-over-liquid expression of the Henry's law constant). Since k and H are dependent on climate-related physical factors, halocarbons fluxes will vary as climate changes.

Climate-induced changes in physical factors (i.e., SSTs and salinity) were used to drive changes in natural sources of organic halogens for the "cliVSL" case, while holding c_w and c_a constant. Changes in VSL halocarbons were forced to depart from Ordoñez et al.[13] emission inventory using the ratio of the flux at a given time-step compared to that at present-day (i.e. monthly and seasonally varying present-day climatology). Present-day (1990–2009) c_w and c_a of CHBr$_3$, CH$_2$Br$_2$ and CH$_3$I were derived from a previous simulation (not used in this analysis) following Ordoñez et al.[13] emission inventory scaled to the inventory of Ziska et al.[25] (scaling factor of 0.26, 1.19 and 1.06 respectively), as follows:

$$\Delta c_0 = \frac{F_0}{k_0} \cdot \text{scaling factor} \tag{2}$$

where Δc_0, F_0 and k_0 are the concentration gradient, the sea-air gas exchange and the transfer velocity at present, respectively. Present-day sea-water halogen concentration (c_{w0}) was derived by:

$$c_{w0} = (\Delta c_0 + \frac{c_{a0}}{H_0}) \tag{3}$$

where c_{a0} and H_0 are the air halogen concentration and Henry coefficient (dimensionless) at present from the model output. Therefore, Δc_0 and c_{w0} are consistent with both, observationally derived concentrations of Ziska et al.[25] and VSL halogens distributions of Ordoñez et al.[13] Due to the lack of a global climatology for c_w and c_a of other halocarbons considered here, changes in their fluxes followed that of CHBr$_3$ (CHBr$_2$Cl and CHBrCl$_2$), CH$_2$Br$_2$ (CH$_2$BrCl) and CH$_3$I (CH$_2$I$_2$, CH$_2$ICl and CH$_2$IBr). For example, present-day fluxes for a given grid cell (or region) of CH$_2$Br$_2$ and CH$_2$BrCl experienced equivalent changes by 2100. Note the VSL emission inventory used here does not include fluxes at the sea-ice interface, and therefore its changes as SSTs warm during the century did not involve additional emissions (sea-ice bromocarbon fluxes could contribute up to 10 % to the tropospheric reactive bromine abundances).[50]

Surface wind speed was held "constant" to drive future changes in VSL fluxes in this work (i.e. using a present-day seasonally varying climatology). Instantaneous wind speed may cause errors on gas-exchange fluxes, e.g. high-frequency wind variabilities can enhance fluxes more than a factor of 2.[51] Since we are projecting changes in halocarbon fluxes based on a monthly-mean emission inventory for present-day,[13] implementing instantaneous wind speed would have led to unreasonable fluxes (not shown). Nevertheless, zonal mean changes in surface wind speed over the century are small compared

17

538   to present-day (approximately ± 0.1 ms^{-1} or ± 2 %) and not believed to play an important role driving

539   natural halocarbon fluxes (consistent with previous work).[22] Our simulated changes in VSL emissions

540   due to physical changes (i.e. SSTs and salinity in "cliVSL") are broadly consistent with previous

541   "offline"[19] and "semi-offline"[22] calculations –largest absolute and relative changes occur in the tropics

542   and poleward, respectively–, and differences are mainly associated with the underlying climate model

543   (i.e., changes in SSTs).

544   The Community Earth System Model large ensemble (CESM-LE; 34 ensemble members)

545   following the RCP8.5 emissions scenario, is used to explore varying spatial distributions and

546   magnitude of halocarbons emissions, resulting from anthropogenic-driven changes in marine primary

547   production ("cli+bioVSL"). This case represents a sensitivity study to the physical climate-induced

548   changes in VSL halocarbon emissions, providing a first order magnitude of O_3 loss associated with

549   potential changes in biogeochemical cycles. We adopt a non-mechanistic approach by relating seawater

550   halocarbon concentrations to long-term changes in vertically integrated marine primary production (1:1

551   correlation in relative terms). Although the approach adopted here advances the field with the specific

552   benefits of (a) being robust and (b) being relatively simple to implement in Earth system models, a

553   number of limitations and uncertainties should be noted. Future changes in marine primary production

554   simulated by CESM lies in the lower end of Earth system models.[52] Changes in net primary production

555   used here –using the Community Atmospheric Model (CAM-Chem)– for the RCP8.5 emission

556   scenario are consistent (i.e., projected changes in SSTs between CESM-LE and CAM-Chem are

557   equivalent). However, these may have been overestimated for the RCP6.0 scenario (globally, the

558   difference in marine primary production between the RCP4.5 and RCP8.5 scenarios is approximately 2

559   % by the end of the century).[27] Furthermore, current understanding in oceanic production of

560   halocarbons at the process-based level is limited. For example, bromoform in the open ocean can be in-

561   situ produced by phytoplankton (i.e., the amount produced varies among species) and can be, in part,

562   transported from coastal regions (i.e., mainly produced by macroalgae).[30] Future research in the field

563   and its advances will benefit our understanding of natural halocarbon emissions in a changing climate.

564

565   **Oceanic inorganic iodine emissions**

566   Iodine is also emitted from the ocean via an abiotic route, due to the oxidation of aqueous iodide (I^-_{aq})

567   following O_3 deposition to seawater. The abiotic route of iodine emissions (HOI and I_2) from the ocean

568   was first implemented in CAM-Chem by Prados-Roman et al.[8] and dependent on surface O_3

569   concentration, wind speed, and SSTs as follows:

$$F_{HOI} = [\text{surf. } O_3] \times \left\{ 4.15 \times 10^5 \times \left(\frac{\sqrt{[I^-_{aq}]}}{ws} \right) - \left(\frac{20.6}{ws} \right) - 23{,}600 \times \sqrt{[I^-_{aq}]} \right\} \quad (4)$$

$$F_{I_2} = [\text{surf. } O_3] \times [I^-_{aq}]^{1.3} \{ 1.74 \times 10^9 - (6.54 \times 10^8 \times \ln ws) \} \quad (5)$$

570   where [surf.O_3], ws and [I^-_{aq}] represent surface O_3 concentration (ppb), wind speed (ms^{-1}) and aqueous

571   iodine concentration (mol dm^{-3}), respectively.[14] [I^-_{aq}] is parameterized using SSTs as a proxy:[53]

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

18

572 Although observational studies found that SSTs are currently the best proxy for $[I^-_{aq}]$,[53,54] further

573 research is needed to understand the processes involved in its distribution. Due to the parameterization

574 used here results in lower $[I^-_{aq}]$ compared to Chance et al.[54] and electronic affinity between O_3 and

575 iodide is neglected, inorganic iodine emissions in this work may be considered as a lower limit.

576

577 **Relative changes and trends in tropospheric ozone loss**

578 Relative changes and trends in O_3 loss associated with natural halogens (normalized to O_3 levels) are

579 computed as follows:

$$\Delta O_3 loss_{i,j,k,t} = \frac{\left\{ \left(\frac{O_{3[VSL]} - O_{3[noVSL]}}{O_{3[noVSL]}} \right)_{i,j,k,t} - \left(\frac{O_{3[VSL]} - O_{3[noVSL]}}{O_{3[noVSL]}} \right)_{i,j,k,t_0} \right\}}{abs\left(\frac{O_{3[VSL]} - O_{3[noVSL]}}{O_{3[noVSL]}} \right)_{i,j,k,t_0}} \quad (7)$$

580 where t and t_0 refers to time (year) and present-day (1990–2009), respectively. Longitude, latitude and

581 pressure level are represented by i, j and k respectively, and [VSL] and [noVSL] are for the cases with

582 and without natural halogens. Linear trends (Fig. 3) and time-series (Fig. 6) are calculated from

583 $\Delta O_3 loss_{i,j,k,t}$ and expressed in % dec^{-1} and %, respectively. Changes between present-day and the end of

584 the 21st century are also calculated from $\Delta O_3 loss_{i,j,k,t}$, but t refers to the 2080–2099 period (Fig. 4 and

585 5). Future relative changes in halogen-driven tropospheric O_3 loss normalized to O_3 abundances, allow

586 to explore halogen chemical processing impacts.

587

588 **Data availability**

589 The data used in this study are available from the corresponding author on reasonable request.

590

591 **Code availability**

592 The software code for the CESM model is available from http://www.cesm.ucar.edu/models/.

593

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638

Figure 1 | Global and annual mean changes in natural halogens. a) Natural sources of VSL halocarbon fluxes, **b)** inorganic iodine emissions, and **c)** tropospheric natural reactive halogens concentrations (VSL cases minus "noVSL") from 2000 to 2100, following the RCP6.0 (blue) and RCP8.5 (red) emission scenarios. Changes are shown for the "cliVSL" (solid), "obsVSL" (dashed), and "cli+bioVSL" (dotted) simulations. VSL halocarbon fluxes for the "obsVSL" case are shown in black, elsewhere RCP6.0 and RCP8.5 are differentiated. The shaded area represents the range between the "cliVSL" (physical climate-induced only) and "cli+bioVSL" (physical climate-induced and marine primary production) simulations. Natural halogen fluxes both, organic and inorganic, are summarized in Supplementary Tables 3–7. Note (c) is with respect to present-day levels (only focusing on reactive inorganic bromine and iodine, which represent ~97 % of the total halogen chemistry in the troposphere). The tropopause is based on a chemical definition ("noVSL" 150 ppb ozone level) at present-day. The horizontal dashed black lines help compare changes with present-day. Time-series, normalized through the origin, are smoothed applying lowess filtering (0.2 fraction).

655 **Figure 2 | Global and annual mean tropospheric O$_3$ column time-series from**
656 **2000 to 2100. (upper panel)**, Absolute changes (DU); **(middle panel)** Absolute and
657 **(lower panel)** relative (%) halogen-driven tropospheric O$_3$ column loss (VSL cases
658 minus "noVSL"). Time-series are shown for the "cliVSL" (solid), "obsVSL"
659 (dashed), "cli+bioVSL" (dotted), and "fixVSL" (solid light) simulations. The shaded
660 area represents the range between the "cliVSL" (climate-induced only) and
661 "cli+bioVSL" (climate-induced and marine primary production) simulations. The
662 tropopause is based on a chemical definition ("noVSL" 150 ppb ozone level) at
663 present-day. Time-series, normalized through the origin, are smoothed applying
664 lowess filtering (0.2 fraction).
665

Figure 3 | Zonal mean tropospheric O$_3$ loss due to reactive halogens. Present-day halogen-mediated tropospheric O$_3$ loss ("cliVSL" minus "noVSL") is shown in **a)** absolute (DU) and **b)** relative (%) values. Future trends in halogen-driven tropospheric O$_3$ loss (% dec^{-1}) from 2000 to 2100, relative to present-day and normalized to O$_3$ levels, are shown for the **c)** RCP6.0 and **d)** RCP8.5 emission scenarios. Hatching indicates trends are not significant at the 95 % confidence interval (two-sigma of the standard error trend). The tropopause is based on a chemical definition ("noVSL" 150 ppb ozone level) at present-day. The full set of simulations is included in the Supplementary Information, including the specified dynamics simulations for the RCP2.6 scenario.

677 **Figure 4 | Vertically-resolved changes in partial column O$_3$ loss due to reactive**
678 **halogens between present-day (1990–2009) and the end of the century (2080–**
679 **2099).** Profiles are shown for: **a)** global; **b)** tropics; **c)** NH; and **d)** SH. Relative
680 changes are normalized to O$_3$ levels. As Fig. 1, the results are shown for the RCP6.0
681 (blue) and RCP8.5 (red) emission scenarios, as well as the "cliVSL" (solid),
682 "obsVSL" (dashed), "cli+bioVSL" (dotted), and "fixVSL" (solid light) simulations.
683 The tropopause is based on a chemical definition ("noVSL" 150 ppb ozone level) at
684 present-day.
685
686

687　**Figure 5 | Maps of halogen-driven 'near'-surface O$_3$ loss change between**
688　**present-day (1990–2009) and the end of the century (2080–2099).** Maps are shown
689　for: **a)** the RCP6.0, and **c)** RCP8.5 emission scenarios ("cliVSL"). Changes are
690　normalized to O$_3$ levels. Near-surface O$_3$ refers to the average of the four lowermost
691　model layers (i.e. first kilometer). Hatchings are for not statistically significant
692　changes at the 5 % level using a two-tailed Student's *t* test. **Right** panels show zonal
693　mean O$_3$ loss changes, as Fig. 1, for the **b)** RCP6.0 and **d)** RCP8.5 emission scenarios,
694　as well as the "cliVSL" (solid), "obsVSL" (dashed), "cli+bioVSL" (dotted), and
695　"fixVSL" (solid light) simulations. Zonal mean O$_3$ loss changes are latitudinally
696　weighted (i.e. using latitudinal cosines). The specified dynamics simulations are
697　included in the Supplementary Information.
698
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Figure 6 | Halogen-driven 'near'-surface O$_3$ loss time-series from 2000 to 2100.
Time-series are shown for: **a)** global, **b)** eastern United States (95ºW–75ºW and 30ºN–45ºN), **c)** Europe and the Mediterranean Sea (10ºW–36ºE and 30ºN–55ºN), and **d)** eastern Asia (100ºE–120ºE and 10ºN–40ºN), following the RCP6.0 (blue) and RCP8.5 (red) emission scenarios. Relative changes with respect to present-day (normalized to O$_3$ levels) are shown for the "cliVSL" (solid), "obsVSL" (dashed), "cli+bioVSL" (dotted), and "fixVSL" (light) simulations. Near-surface O$_3$ refers to the average of the four lowermost model layers (i.e. first kilometer). Time-series, normalized through the origin, are smoothed applying lowess filtering (0.2 fraction).

a) VSL halocarbons

b) Inorganic iodine

RCP8.5   "obsVSL"
RCP6.0   "cliVSL"
               "cli+bioVSL"

c) Reactive halogens

Years

Figure with four panels:

a) Global — y-axis: ΔO_3 (%), values from 20 to −80

Legend:
- RCP6.0 (blue)
- RCP8.5 (red)
- "cliVSL" (solid)
- "obsVSL" (dashed)
- "cli+bioVSL" (dotted)
- "fixVSL" (light solid)

b) Eastern United States

c) Europe and Mediterranean Sea — y-axis: ΔO_3 (%), x-axis: Years (2000–2100)

d) Eastern Asia — x-axis: Years (2000–2100)