



UNIVERSITY OF LEEDS

This is an author produced version of *Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone*.

White Rose Research Online URL for this paper:  
<http://eprints.whiterose.ac.uk/86501/>

---

**Article:**

Hossaini, R, Chipperfield, MP, Montzka, SA, Rap, A, Dhomse, S and Feng, W (2015) Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone. *Nature Geoscience*, 8. pp. 186-190. ISSN 1752-0894

<http://dx.doi.org/10.1038/ngeo2363>

---



*promoting access to  
White Rose research papers*

[eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk)  
<http://eprints.whiterose.ac.uk/>

# Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone

R. Hossaini<sup>1\*</sup>, M. P. Chipperfield<sup>1</sup>, S. A. Montzka<sup>2</sup>, A. Rap<sup>1</sup>, S. Dhomse<sup>1</sup>, and W. Feng<sup>1,3</sup>

1. School of Earth and Environment, University of Leeds, Leeds, UK

2. National Oceanic and Atmospheric Administration, Boulder, USA

3. National Centre for Atmospheric Science, University of Leeds, Leeds, UK

**Halogens released from long-lived anthropogenic substances, such as chlorofluorocarbons, are the principal cause of recent depletion of stratospheric ozone, a greenhouse gas<sup>1, 2, 3</sup>. Recent observations show that very short-lived substances, with lifetimes generally under six months, are also an important source of stratospheric halogens<sup>4, 5</sup>. Short-lived bromine substances are produced naturally by seaweed and phytoplankton, whereas short-lived chlorine substances are primarily anthropogenic. Here we used a chemical transport model to quantify the depletion of ozone in the lower stratosphere from short-lived halogen substances, and a radiative transfer model to quantify the radiative effects of that ozone depletion. According to our simulations, ozone loss from short-lived substances had a radiative effect nearly half that from long-lived halocarbons in 2011 and, since pre-industrial times, has contributed a total of about  $-0.02 \text{ W m}^{-2}$  to global radiative forcing. We find natural short-lived bromine substances exert a 3.6 times larger ozone radiative effect than long-lived halocarbons, normalized by halogen content, and show atmospheric levels of dichloromethane, a short-lived chlorine substance not controlled by the Montreal Protocol, are rapidly increasing. We conclude that potential further significant increases in the atmospheric abundance of short-lived halogen substances, through changing natural processes<sup>6, 7, 8</sup> or continued anthropogenic emissions<sup>9</sup>, could be important for future climate.**

25 Stratospheric ozone ( $O_3$ ) concentrations are maintained by a balance between photochemical  
26 production and loss. Increases in the loss rate, e.g. through emission of ozone-depleting  
27 substances (ODSs)<sup>3</sup>, leads to net  $O_3$  depletion, such as the formation of the Antarctic  $O_3$  hole.  
28 In addition to long-lived ODS, such as chlorofluorocarbons (CFCs) and halons, recent  
29 observations show that very short-lived substances (VSLS), with lifetimes  $< \sim 6$  months, are  
30 an important source of stratospheric bromine and chlorine<sup>4,5,10</sup>. Their absolute contribution is  
31 uncertain owing to poor constraints on the magnitude and distribution of VSLS emissions<sup>11</sup>, a  
32 limited understanding of their tropospheric processing<sup>12</sup>, and a paucity of VSLS observations  
33 (and their product gases) near the tropopause. At present, VSLS likely account for  $\sim 25\%$  of  
34 stratospheric bromine and a few percent of stratospheric chlorine<sup>3</sup>. These relative  
35 contributions will increase in the future, as long-lived anthropogenic ODS are phased out  
36 under the terms of the Montreal Protocol – the international treaty designed to safeguard the  
37 ozone layer. Bromine VSLS are mainly of oceanic origin, produced by various species of  
38 seaweed<sup>3</sup> – a number of which are farmed<sup>9</sup> – and by phytoplankton. Once transported to the  
39 stratosphere they affect the natural balance of  $O_3$ , particularly in the lower stratosphere<sup>13-15</sup>  
40 (LS; altitudes  $\sim 12$  to  $25$  km), where  $O_3$  perturbations strongly impact surface temperature and  
41 climate<sup>1,2</sup>. The radiative impacts of VSLS-driven  $O_3$  perturbations are unknown but important  
42 to understand as models predict that stratospheric VSLS loading may increase in the future<sup>6,7</sup>.

43 Two models were used to quantify the impact of VSLS on  $O_3$  and climate (Methods). First, a  
44 state-of-the-art three-dimensional atmospheric model<sup>16</sup>, TOMCAT, was used to simulate the  
45 transport and breakdown of bromine, chlorine, and iodine-containing VSLS (and their  
46 product gases) in the troposphere and stratosphere. The model contains a comprehensive  
47 treatment of atmospheric chemistry and has been widely used to study global  $O_3$ <sup>14</sup>.

48 Experiments were performed, including a control run with no VSLS, to determine the relative  
49 contribution of each halogen and the net impact of VSLS on  $O_3$  (Supplementary Table S1).

50 Second, an offline radiative transfer model<sup>17,18</sup> was used to diagnose the net change  
51 (longwave + shortwave) in radiation at the tropopause due to VSLS-driven O<sub>3</sub> perturbations  
52 in 2011 (i.e. the difference between simulations with/without VSLS). This “radiative effect”  
53 (RE) is used to estimate the significance of VSLS-driven O<sub>3</sub> loss on climate and is compared  
54 to the ozone RE due to long-lived ODS, calculated similarly for 2011. The related measure of  
55 “radiative forcing” (RF) here describes the change in RE between 2011 and pre-industrial  
56 times.

57 Figure 1 shows the simulated stratospheric column O<sub>3</sub> change due to all VSLS from natural  
58 and anthropogenic processes (relative to the control). Ozone concentrations are reduced  
59 globally, with a maximum column decrease of -6% (-3% to -8%) occurring over Antarctica  
60 (Fig. 1a) – corresponding to ~15 (8 to 21) Dobson Units. The range (Fig. 1b) quoted is due to  
61 uncertainty in the stratospheric loading of VSLS. Cycles including bromine account for  
62 approximately half of the total chemical O<sub>3</sub> loss in the springtime Antarctic ozone hole<sup>3</sup> and  
63 here contribute 81% of the total VSLS-driven O<sub>3</sub> loss in this region. Chlorine VSLS account  
64 for a further 16% (i.e. a column O<sub>3</sub> decrease from chlorine of ~1%) and iodine 3% of the  
65 total. Globally, we calculate a RE of -0.08 (-0.04 to -0.11) Wm<sup>-2</sup> due to the presence of  
66 natural and anthropogenic VSLS and their influence on stratospheric O<sub>3</sub> in 2011 (Fig. 1c,d).

67 Due to their short atmospheric lifetimes, if VSLS (or their degradation products) reach the LS  
68 they readily release halogens in a region where surface temperature and climate are most  
69 sensitive to O<sub>3</sub> perturbations. We calculate VSLS currently reduce O<sub>3</sub> by up to ~100 (50-140)  
70 parts per billion (ppb) in the LS (Fig. 2a), corresponding to percentage decreases in the range  
71 4-12%. Bromine, predominately from naturally-emitted oceanic VSLS such as bromoform  
72 (CHBr<sub>3</sub>) and dibromomethane (CH<sub>2</sub>Br<sub>2</sub>), is responsible for the majority (~85%) of the LS O<sub>3</sub>  
73 decrease. The analogous chlorinated gases, chloroform (CHCl<sub>3</sub>) and dichloromethane

74 (CH<sub>2</sub>Cl<sub>2</sub>), have anthropogenic sources<sup>19,20</sup> with applications as industrial solvents, foam  
75 blowing agents, fumigants and use in the paper and pulp industry. Anthropogenic sources  
76 account for ~25% and 80-100% of total CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> emissions, respectively<sup>3</sup>. As these  
77 gases are not controlled by the Montreal Protocol and given potential for industrial growth,  
78 quantifying their impact on O<sub>3</sub> is important. We find all chlorine VSLS reduce O<sub>3</sub> in the LS  
79 by ~11 (6-18) ppb (0.6-1.6%). A larger absolute impact is found in the upper stratosphere  
80 (~40 km) with decreases in the range 17-54 ppb, though at this altitude the O<sub>3</sub> change relative  
81 to the control is <1%. An upper limit of O<sub>3</sub> reduction due to methyl iodide (CH<sub>3</sub>I), the only  
82 iodine-containing VSLS with a sufficiently long lifetime to allow significant transport into  
83 the stratosphere, is ~3 ppb (<0.5%), suggesting a minor stratospheric role for iodine<sup>3,21</sup>.

84 Bromine (chlorine, iodine) accounts for ~87% (9%, 4%) of the global RE due to VSLS-  
85 driven stratospheric O<sub>3</sub> loss (Supplementary Table S2). The relatively large RE of -0.07 (-  
86 0.035 to -0.096) Wm<sup>-2</sup> due to O<sub>3</sub> loss from bromine VSLS can be compared to the RE from  
87 stratospheric O<sub>3</sub> changes driven by long-lived anthropogenic ODS (Fig. 2b). For 2011, we  
88 calculate the latter RE to be -0.17 Wm<sup>-2</sup> (Methods) which also corresponds to a radiative  
89 forcing as anthropogenic ODS were not present in the pre-industrial atmosphere. Normalized  
90 by equivalent stratospheric chlorine (ESC), the RE due to bromine VSLS is ~3.6 times larger  
91 than that caused by long-lived anthropogenic ODS, owing to their influence on O<sub>3</sub> in the  
92 climate-sensitive LS. Compared to long-lived gases synonymous with ozone depletion, such  
93 as CFCs, VSLS possess significantly larger leverage to influence climate through ozone.

94 While CFCs, for example, are themselves potent greenhouse gases which have caused a large  
95 positive RF, this is not the case for VSLS due to their low abundances and short lifetimes;  
96 VSLS cause a cooling effect through O<sub>3</sub> loss without a corresponding warming effect due to  
97 their presence in the atmosphere. Accounting for VSLS will improve simulations of  
98 stratospheric O<sub>3</sub>, reducing uncertainty on related estimates of ozone-driven climate forcing.

99 In addition to the stratosphere, recent work has highlighted the significance of tropospheric  
100 halogen chemistry and its impact on O<sub>3</sub><sup>22-24</sup>. The true VSLS RE is therefore likely greater if  
101 tropospheric O<sub>3</sub> impacts are also considered. We calculated a global mean RE due to  
102 tropospheric O<sub>3</sub> loss from VSLS (Methods and Supplementary Table S3) of  $-0.12 \text{ Wm}^{-2}$ ,  
103 50% larger than the stratospheric RE, in good agreement with previous estimates<sup>23</sup>. Bromine  
104 and iodine combined contribute virtually all this tropospheric RE, most of which is from O<sub>3</sub>  
105 loss in the upper troposphere (Supplementary Figure S1). Chlorine from VSLS has a  
106 negligible impact due to the relatively long lifetime of the major VSLS themselves and  
107 because their degradation product gases (both organic intermediates and HCl) are subject to  
108 relatively efficient tropospheric wet removal in rainwater. Considering both the troposphere  
109 and stratosphere, we estimate a whole atmosphere RE of  $-0.20$  ( $-0.16$  to  $-0.23$ )  $\text{Wm}^{-2}$  due to  
110 VSLS-driven O<sub>3</sub> loss.

111 We found no trend in the influence of VSLS on global O<sub>3</sub> between 1979 and 2013. However,  
112 in addition to bromine – whose impact on O<sub>3</sub> is enhanced following volcanic eruptions<sup>13-15</sup> –  
113 we find stratospheric O<sub>3</sub> loss due to chlorine VSLS was also enhanced (up to  $\sim 2\times$ ) following  
114 the eruptions of El Chichón (1982) and Mt. Pinatubo (1991), relative to volcanically  
115 quiescent years (Fig. 3a). The model slightly overestimates the relative O<sub>3</sub> decrease following  
116 the Pinatubo eruption (Supplementary Figure S2) but generally reproduces observed O<sub>3</sub>  
117 variations well. The sensitivity of VSLS-driven O<sub>3</sub> perturbations (and RE) to the aerosol  
118 loading are, therefore, relevant for understanding the full impacts of geoengineering  
119 approaches to combat climate change by stratospheric injection of particles<sup>25</sup>.

120 There is currently no evidence of a historical trend in the stratospheric loading of natural  
121 bromine VSLS, beyond shorter term fluctuations due to the El Niño Southern Oscillation<sup>12</sup>.  
122 However, the pre-industrial influence of bromine VSLS on global O<sub>3</sub>, before anthropogenic

123 input of chlorine into the stratosphere, was ~30% smaller than present day (Supplementary  
124 Figure S3); anthropogenic activity has enhanced natural stratospheric O<sub>3</sub> loss cycles. We  
125 calculate this O<sub>3</sub> trend caused a contribution to the climate RF of -0.014 (-0.007 to -0.018)  
126 Wm<sup>-2</sup> (out of the -0.17 Wm<sup>-2</sup> RF from long-lived anthropogenic ODS quoted above) which  
127 will likely be reversed as stratospheric chlorine declines during the 21<sup>st</sup> century, in response  
128 to the Montreal Protocol. A future increase in VSLS emissions, potentially due to a climate-  
129 driven increase in their ocean-to-air flux<sup>6</sup> or a rise in seaweed cultivation<sup>7</sup> – a rapidly growing  
130 industry – would offset some of this reversal.

131 Surface concentrations of CH<sub>2</sub>Cl<sub>2</sub>, an anthropogenic VSLS, have increased rapidly in recent  
132 years (Fig. 3b). Between 2000 and 2012, surface CH<sub>2</sub>Cl<sub>2</sub> increased at a global mean growth  
133 rate of 7.7%/yr. Mean growth rates in the northern (NH) and southern hemispheres were  
134 ~8.3%/yr and 6.3%/yr, respectively, the larger NH growth reflecting the presence of  
135 industrial sources. Between 2012-2013, CH<sub>2</sub>Cl<sub>2</sub> growth accelerated with a NH growth rate of  
136 20%/yr; double the 2010-2013 average (Supplementary Table S4). Whilst modest at present,  
137 the impact of anthropogenic CH<sub>2</sub>Cl<sub>2</sub> on O<sub>3</sub> (Fig. 3) would increase significantly if the  
138 observed trend continues. This is likely if increases in atmospheric CH<sub>2</sub>Cl<sub>2</sub> are associated  
139 with the increased industrialization of developing countries and, for example, use of CH<sub>2</sub>Cl<sub>2</sub>  
140 as a feedstock for hydrofluorocarbon (HFC) production, such as HFC-32<sup>26</sup> – a refrigerant  
141 used in blends as a substitute for HCFC-22. Production of HFC-32 and other HFCs has  
142 increased rapidly in recent years and could increase substantially in the future<sup>27</sup>. Although  
143 HFCs do not directly deplete O<sub>3</sub>, a broader consideration of their production pathways  
144 suggests a potential for direct influences on O<sub>3</sub> layer chemistry and hence climate. We  
145 suggest despite the modest concentration changes to date, anthropogenic chlorine VSLS have  
146 already contributed -0.005 (-0.003 to -0.008) Wm<sup>-2</sup> to atmospheric RF (Methods). Combined  
147 with the larger RF due to bromine VSLS (discussed above), the total RF from VSLS is -0.02

148 (-0.01 to -0.03)  $\text{Wm}^{-2}$  and comparable in magnitude to, for example, the (positive) RF due to  
149 aircraft contrails<sup>1</sup>.

150 We have shown that, through interactions with  $\text{O}_3$ , VLSLs have a disproportionately large  
151 climate impact compared to long-lived ODS, owing to their breakdown at climate-sensitive  
152 altitudes. VLSLs have already contributed to climate forcing since the pre-industrial era,  
153 though this is so far unlikely to have caused a noticeable change to surface temperature, for  
154 example. However, crucially, given the large leverage VLSLs possess to influence climate,  
155 future increases in their emissions would drive a negative climate forcing and thereby offset a  
156 small fraction of the projected warming influence due to greenhouse gases. We note  
157 additionally that the observed atmospheric abundance of anthropogenic  $\text{CH}_2\text{Cl}_2$ , here about  
158  $\times 50$  larger than some recently detected CFCs and HCFCs<sup>28</sup>, is presently adding many times  
159 more chlorine to the atmosphere and, unlike those chemicals, is not controlled by the  
160 Montreal Protocol.

## 161 **Methods**

162 **Simulated impact of VLSLs on stratospheric ozone.** The 3-D chemistry transport model,  
163 TOMCAT<sup>16</sup>, was used to simulate the breakdown of VLSLs in the stratosphere. TOMCAT  
164 contains a detailed gas-phase/heterogeneous chemistry scheme considering all major  
165 stratospheric families;  $\text{O}_x$ ,  $\text{HO}_x$ ,  $\text{NO}_y$ ,  $\text{Cl}_y$ ,  $\text{Br}_y$ , and here we implemented an iodine scheme<sup>21</sup>.  
166 The major VLSLs considered were  $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{I}$ . Their  
167 degradation occurs by both photolysis and hydroxyl radical oxidation, with photochemical  
168 and kinetic data taken from the NASA Jet Propulsion Laboratory evaluation. The surface  
169 VLSL mixing ratios were time-independent quantities, scaled to give a range of stratospheric  
170 loadings of bromine, chlorine and iodine from VLSLs based on current best estimates and  
171 lower/upper limits<sup>3</sup> (Supplementary Table S1).

172 In all simulations the abundance of long-lived source gases (e.g. CFCs, halons, N<sub>2</sub>O, CH<sub>4</sub>)  
173 were constrained with time-dependent surface mixing ratio boundary conditions based on  
174 observations. Similarly, a time-dependent sulphate aerosol load was imposed based on  
175 Stratospheric Aerosol and Gas Experiment (SAGE) data. Ten model integrations covering the  
176 1979-2013 period were performed. A control experiment, in which VSLS were not  
177 considered, was followed by a series of experiments to determine the impact and relative  
178 contribution of bromine, chlorine and iodine VSLS on O<sub>3</sub>. A sensitivity experiment was  
179 performed with a time-dependent stratospheric loading of CH<sub>2</sub>Cl<sub>2</sub>, based on its observed  
180 surface trend and modelled tropospheric oxidation, between 2005-2013.

181 We also performed experiments with a pre-industrial stratospheric halogen loading  
182 containing ~6 ppt of CH<sub>3</sub>Br and ~500 ppt of CH<sub>3</sub>Cl, based on ice-core records<sup>29</sup>. From these  
183 experiments, we calculated: [1.] the difference in the influence of bromine VSLS on O<sub>3</sub>  
184 between the pre-industrial period and 2011. This was also used to diagnose a RF from  
185 bromine VSLS. [2.] The O<sub>3</sub> change attributable to anthropogenic long-lived ODS only  
186 (Figure 2b). Simulations to quantify the impact of VSLS on tropospheric O<sub>3</sub> were also  
187 performed. Details of these experiments are given in the Supplementary Information.

188 **Climate impact of VSLS.** The RE of VSLS-driven O<sub>3</sub> loss was calculated using the offline  
189 Edwards and Slingo radiative transfer model<sup>17</sup>. This model considers six bands in the  
190 shortwave, nine bands in the longwave and uses a delta-Eddington 2-stream scattering solver  
191 at all wavelengths. We used monthly mean climatologies of temperature, water vapour and  
192 trace gases based on ECMWF reanalysis data, together with surface albedo and cloud fields  
193 taken from the International Satellite Cloud Climatology Project archive<sup>18</sup>.

194 We normalized the RE due to bromine VSLS in the stratosphere (Supplementary Table S2)  
195 per unit of equivalent stratospheric chlorine (ESC = Cl + 60×Br). This was performed in

196 order to compare the RE of VSLS-driven O<sub>3</sub> changes with that of long-lived ODS,  
197 independent of the halogen loading that caused them, and in a way that considers the  
198 effectiveness of bromine relative to chlorine for O<sub>3</sub> loss. The stratospheric loading of bromine  
199 VSLS in our model (3, 6 or 8 ppt) corresponds to ESC loadings of 180, 360 and 480 ppt,  
200 respectively. The normalized RE from bromine VSLS is  $-1.9 \times 10^{-4} \text{ Wm}^{-2} (\text{ppt ESC})^{-1}$ .  
201 Similarly, we normalized the RE due to stratospheric O<sub>3</sub> loss arising from anthropogenic  
202 long-lived ODS. This O<sub>3</sub> change is shown in Figure 2b and was caused by an ESC difference  
203 of 3207 ppt from long-lived ODS (i.e. the 2011 minus pre-industrial ESC load). The  
204 calculated RE is  $-0.17 \text{ Wm}^{-2}$  and the normalized RE is  $-5.3 \times 10^{-5} (\text{ppt ESC})^{-1}$ ; a factor of ~3.6  
205 smaller than the normalized RE from bromine VSLS.

206 The RF contribution due to bromine VSLS arises because their presence affects the efficiency  
207 of O<sub>3</sub> loss from the pre-industrial period to 2011 caused by changes in anthropogenic chlorine  
208 from long-lived ODSs. The relative O<sub>3</sub> change due to bromine VSLS in each period  
209 (compared to simulations without bromine VSLS) was quantified (Supplementary Figure S3).  
210 The calculated difference in the corresponding RE between the two periods corresponds to a  
211 pre-industrial to 2011 RF.

212 The RF due to anthropogenic chlorine VSLS is due to a time-trend in their abundance since  
213 the pre-industrial period. This was estimated from the calculated RE limits given in  
214 Supplementary Table 2, reduced by 30% to account for the natural component of chlorine  
215 VSLS in the stratosphere<sup>3</sup>; the calculated RF is due to the pre-industrial to 2011 trend in  
216 anthropogenic chlorine VSLS concentrations only.

217 **Long-term observations of CH<sub>2</sub>Cl<sub>2</sub>.** Observations from multiple sites in the ongoing  
218 NOAA/ESRL Global Monitoring Program<sup>30</sup> are presented (Supplementary Table S4). Results  
219 from paired flask samples collected at remote sites were used to derive surface CH<sub>2</sub>Cl<sub>2</sub>

220 mixing ratios over the 1995-2012 period averaged over each hemisphere with a weighting  
221 based on sampling latitude<sup>30</sup>. These data are publically available:  
222 <http://www.esrl.noaa.gov/gmd/dv/ftpdata.html>.

223 **Code Availability.** The TOMCAT model is supported by NERC and NCAS and is available  
224 to UK academic institutions working with these organizations. The output from model  
225 simulations used here and post processing code is available on request.

## 226 **References**

- 227 1 Myhre, G. et al. in *Climate Change 2013: The Physical Science Basis. Contribution*  
228 *of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on*  
229 *Climate Change* (eds Stocker T. F. et al.) Ch. 8, 659–740 (IPCC, Cambridge Univ.  
230 Press, 2013).
- 231 2 Riese, M. et al. Impact of uncertainties in atmospheric mixing on simulated UTLS  
232 composition and related radiative effects. *J. Geophys. Res. [Atmos.]* **117**, D16305  
233 (2012).
- 234 3 Montzka, S. A. & Reimann, S. in *Scientific Assessment of Ozone Depletion: 2010,*  
235 *Global Ozone Research and Monitoring Project, Report No.52* Ch. 1 (World  
236 Meteorological Organization, 2011).
- 237 4 Sturges, W. T., Oram, D. E., Carpenter, L. J., Penkett, S. A. & Engel, A. Bromoform  
238 as a source of stratospheric bromine. *Geophys. Res. Lett.* **27**, 2081-2084 (2000).
- 239 5 Laube, J. C. et al. Contribution of very short-lived organic substances to stratospheric  
240 chlorine and bromine in the tropics – a case study. *Atmos. Chem. Phys.* **8**, 7325-7334  
241 (2008).
- 242 6 Dessens, O., Zeng, G., Warwick, N. & Pyle, J. Short-lived bromine compounds in the

243 lower stratosphere; impact of climate change on ozone. *Atmos. Sci. Lett.* **10**, 201-206  
244 (2009).

245 7 Hossaini, R. et al. Modelling future changes to the stratospheric source gas injection  
246 of biogenic bromocarbons. *Geophys. Res. Lett.* **39**, L20813 (2012).

247 8 Hepach, H. et al. Drivers of diel and regional variations of halocarbon emissions from  
248 the tropical North East Atlantic. *Atmos. Chem. Phys.* **14**, 1255-1275 (2014).

249 9 Leedham, E. C. et al. Emission of atmospherically significant halocarbons by  
250 naturally occurring and farmed tropical macroalgae. *Biogeosciences* **10**, 3615-3633  
251 (2013).

252 10 Dorf, M. et al. Bromine in the tropical troposphere and stratosphere as derived from  
253 balloon-borne BrO observations. *Atmos. Chem. Phys.* **8**, 7265-7271 (2008).

254 11 Hossaini, R. et al. Evaluating global emission inventories of biogenic bromocarbons.  
255 *Atmos. Chem. Phys.* **13**, 11819-11838 (2013).

256 12 Aschmann, J., Sinnhuber, B. M., Chipperfield, M. P. & Hossaini, R. Impact of deep  
257 convection and dehydration on bromine loading in the upper troposphere and lower  
258 stratosphere. *Atmos. Chem. Phys.* **11**, 2671-2687 (2011).

259 13 Salawitch, R. J. et al. Sensitivity of ozone to bromine in the lower stratosphere.  
260 *Geophys. Res. Lett.* **32**, L05811 (2005).

261 14 Feng, W., Chipperfield, M. P., Dorf, M., Pfeilsticker, K. & Ricaud, P. Mid-latitude  
262 ozone changes: studies with a 3-D CTM forced by ERA-40 analyses. *Atmos. Chem.*  
263 *Phys.* **7**, 2357-2369 (2007).

264 15 Sinnhuber, B. M., Sheode, N., Sinnhuber, M., Chipperfield, M. P. & Feng, W. The  
265 contribution of anthropogenic bromine emissions to past stratospheric ozone trends: a  
266 modelling study. *Atmos. Chem. Phys.* **9**, 2863-2871 (2009).

267 16 Chipperfield, M. P. New version of the TOMCAT/SLIMCAT off-line chemical

268 transport model: Intercomparison of stratospheric tracer experiments. *Q. J. Roy.*  
269 *Meteorol. Soc.* **132**, 1179-1203 (2006).

270 17 Edwards, J. M. & Slingo, A. Studies with a flexible new radiation code .1. Choosing a  
271 configuration for a large-scale model. *Q. J. Roy. Meteorol. Soc.* **122**, 689-719 (1996).

272 18 Rap, A. et al. Natural aerosol direct and indirect radiative effects. *Geophys. Res. Lett.*  
273 **40**, 3297-3301 (2013).

274 19 Simmonds, P. G. et al. Global trends, seasonal cycles, and European emissions of  
275 dichloromethane, trichloroethene, and tetrachloroethene from the AGAGE  
276 observations at Mace Head, Ireland, and Cape Grim, Tasmania. *J. Geophys. Res.*  
277 *[Atmos.]* **111**, D18304 (2006).

278 20 Worton, D. R. et al. 20th century trends and budget implications of chloroform and  
279 related tri-and dihalomethanes inferred from firn air. *Atmos. Chem. Phys.* **6**, 2847-  
280 2863 (2006).

281 21 Bosch, H. et al. Upper limits of stratospheric IO and OIO inferred from center-to-  
282 limb-darkening-corrected balloon-borne solar occultation visible spectra: Implications  
283 for total gaseous iodine and stratospheric ozone. *J. Geophys. Res. [Atmos.]* **108**, 4455  
284 (2003).

285 22 Carpenter, L. J. et al. Atmospheric iodine levels influenced by sea surface emissions  
286 of inorganic iodine. *Nat. Geosci.* **6**, 108-111 (2013).

287 23 Saiz-Lopez, A. et al. Estimating the climate significance of halogen-driven ozone loss  
288 in the tropical marine troposphere. *Atmos. Chem. Phys.* **12**, 3939-3949 (2012).

289 24 Dix, B. et al. Detection of iodine monoxide in the tropical free troposphere. *Proc. Nat.*  
290 *Acad. Sci. U.S.A.* **110**, 2035-2040 (2013).

291 25 Rasch, P. J. et al. An overview of geoengineering of climate using stratospheric  
292 sulphate aerosols. *Phil. Trans. R. Soc. Ser. A* **366**, 4007-4037 (2008).

- 293 26 Campbell, N. et al. in Safeguarding the Ozone Layer and the Global Climate System:  
294 Issues Related to Hydrofluorocarbons and Perfluorocarbons (eds Metz, B. et al.) Ch.  
295 11, 403-436 (IPCC/TEAP, Cambridge Univ. Press, 2005).
- 296 27 Velders, G. J. M., Fahey, D. W., Daniel, J. S., McFarland, M. & Andersen, S. O. The  
297 large contribution of projected HFC emissions to future climate forcing. Proc. Nat.  
298 Acad. Sci. U.S.A. **106**, 10949-10954 (2009).
- 299 28 Laube, J. C. et al. Newly detected ozone-depleting substances in the atmosphere. Nat.  
300 Geosci. **7**, 266-269 (2014).
- 301 29 Saltzman, E. S., Aydin, M., Williams, M. B., Verhulst, K. R. & Gun, B. Methyl  
302 chloride in a deep ice core from Siple Dome, Antarctica. Geophys. Res. Lett. **36**,  
303 L03822 (2009).
- 304 30 Montzka, S. A. et al. Small interannual variability of global atmospheric hydroxyl.  
305 Science **331**, 67-69 (2011).

### 306 **Corresponding Author**

307 Correspondence and requests for materials to Ryan Hossaini (r.hossaini@leeds.ac.uk).

### 308 **Acknowledgments**

309 We thank NERC for funding (TropHal project, NE/J02449X/1). Ground-based observations  
310 of CH<sub>2</sub>Cl<sub>2</sub> are supported in part by NOAA's Climate Program Office through its  
311 Atmospheric, Chemistry, Carbon Cycle and Climate Program. C. Siso, B. Hall, J. Elkins and  
312 B. Miller provided assistance in making and standardizing these measurements.

### 313 **Author Contributions**

314 R.H., M.P.C., W.F. and S.D. designed and performed all experiments using the TOMCAT  
315 model. A.R. performed experiments with the radiative transfer model. S.A.M. provided

316 ground-based observations. All authors discussed the results and commented on the  
317 manuscript.

### 318 **Competing Financial Interests statement**

319 The authors declare no competing financial interests.

### 320 **Figure Captions**

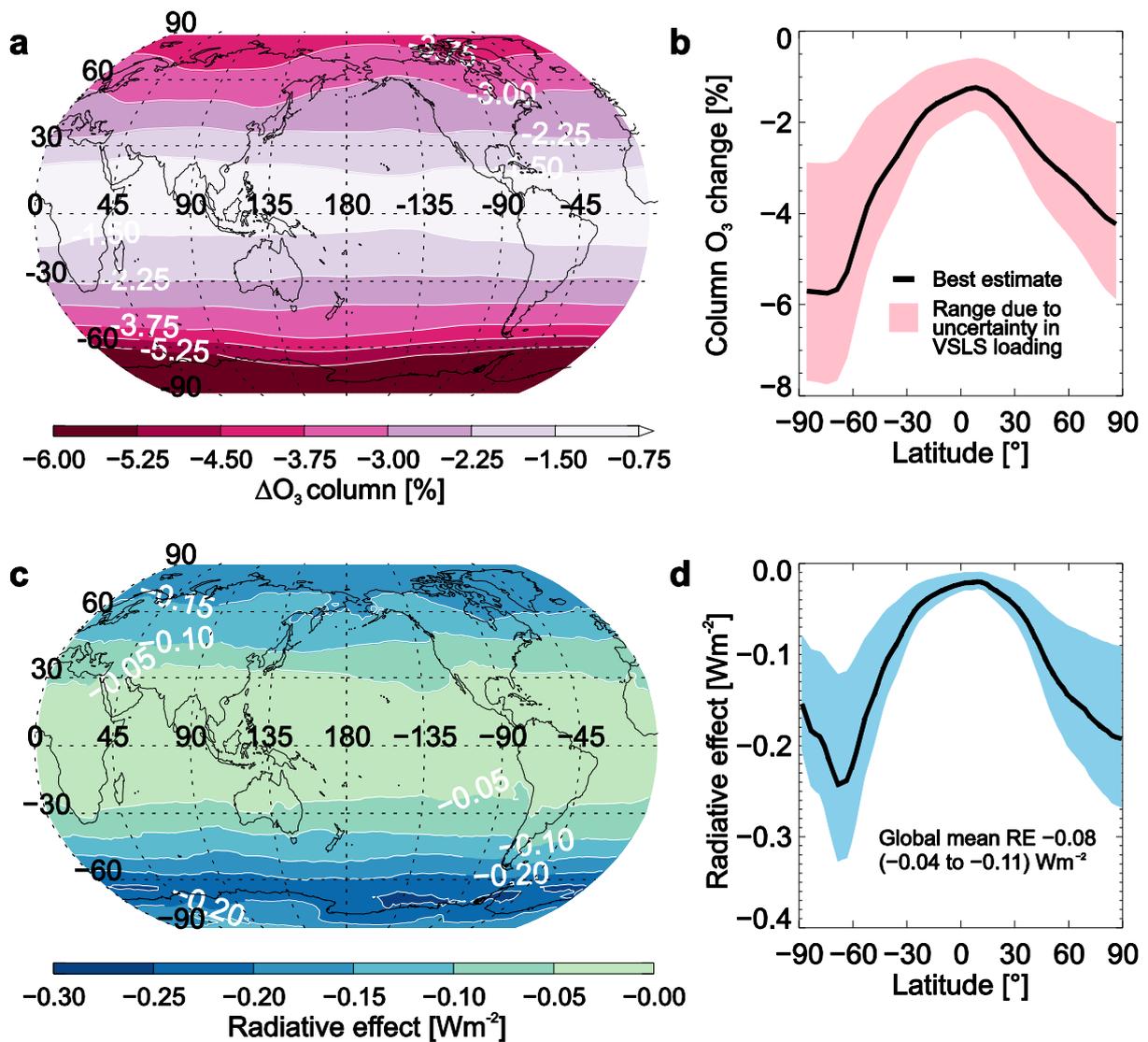
321 **Figure 1. Column ozone decrease due to VSLS and radiative effect.** (a) Annual mean  
322 (2011) percentage (%) change in stratospheric column ozone due to best estimated  
323 stratospheric loading of bromine, chlorine and iodine from VSLS. (b) Latitude-dependence of  
324 column ozone change. Solid line denotes best estimate, shaded region represents the range  
325 due to uncertainty in VSLS loading. (c) Net (longwave + shortwave) radiative effect (RE,  
326  $\text{Wm}^{-2}$ ) due to VSLS-driven ozone loss calculated at the tropopause. (d) Latitude-dependence  
327 of RE. Solid line denotes best estimate, shaded region represents the range due to uncertainty  
328 in VSLS loading.

329 **Figure 2. Altitude-resolved ozone decrease due to VSLS and long-lived ODS.** (a) Annual  
330 global mean (2011) change in stratospheric ozone ( $\text{O}_3$ ) volume mixing ratio (ppb) due to  
331 VSLS (bottom x axis). The grated area shows the range due to uncertainty in VSLS loading.  
332 The shaded regions represent the contribution of each halogen to the total  $\text{O}_3$  loss due to  
333 VSLS, expressed as percent (%) (top x axis). (b) as (a) but with the 2011  $\text{O}_3$  change due to  
334 long-lived anthropogenic ODS also shown to highlight the difference in altitude of the  $\text{O}_3$   
335 changes.

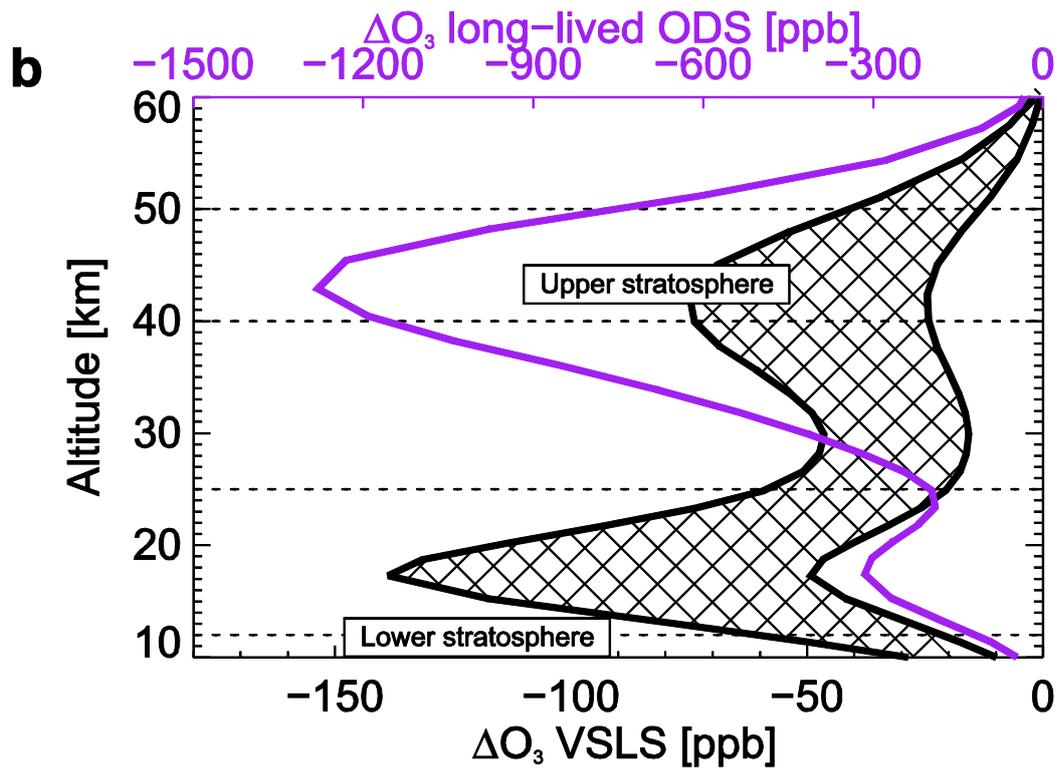
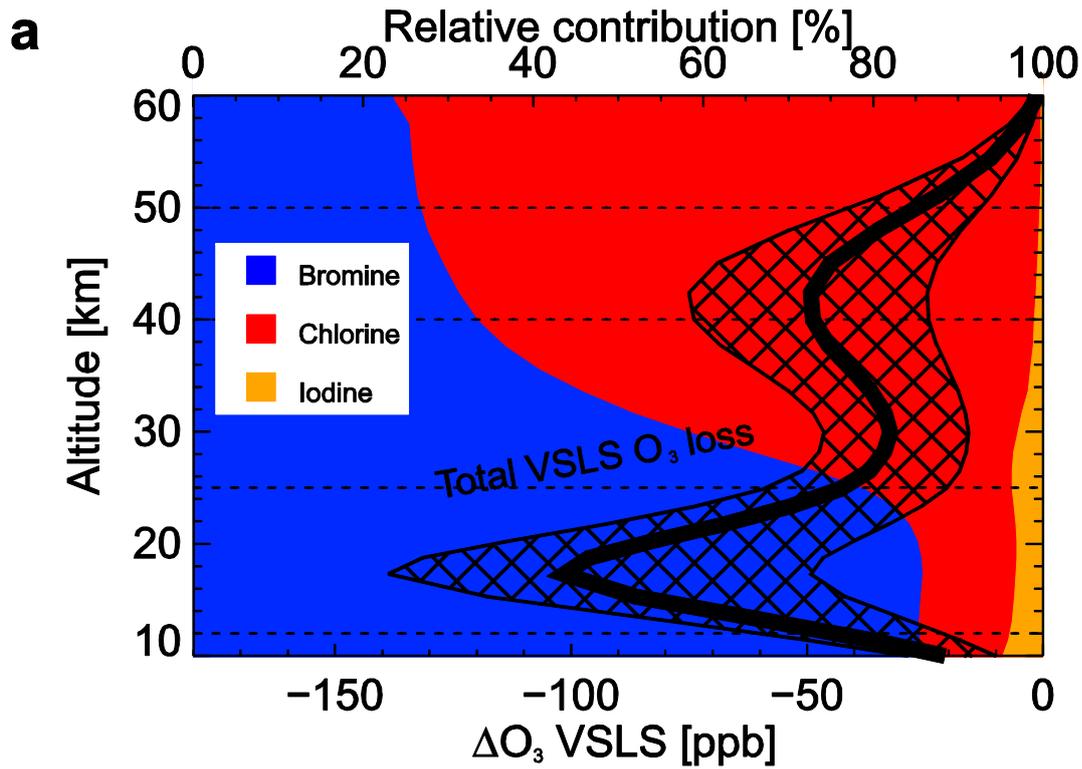
336 **Figure 3. Trend in VSLS-driven ozone loss and  $\text{CH}_2\text{Cl}_2$  growth.** (a) Annual global mean

337 ozone change (%) due to bromine, chlorine and iodine VSLs in the lower stratosphere (1979-  
 338 2013). Solid lines denote best estimate, shading indicates range due to uncertainty in VSLs  
 339 loading. 2003-2013 mean  $O_3$  change is annotated. Radiative effect (RE,  $Wm^{-2}$ ) of VSLs-  
 340 driven ozone loss and range due to uncertainty in VSLs loading is shown with error bars  
 341 (purple). Dashed line (green) denotes ozone change due to  $CH_2Cl_2$  alone. **(b)** Observed  
 342 monthly mean surface  $CH_2Cl_2$  mixing ratio (ppt) and trend. Annotated are 2000-2012  
 343 hemispheric growth rates (%/yr).

344



345



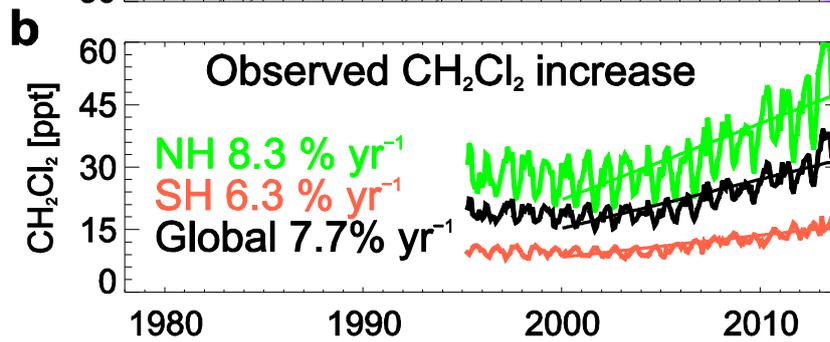
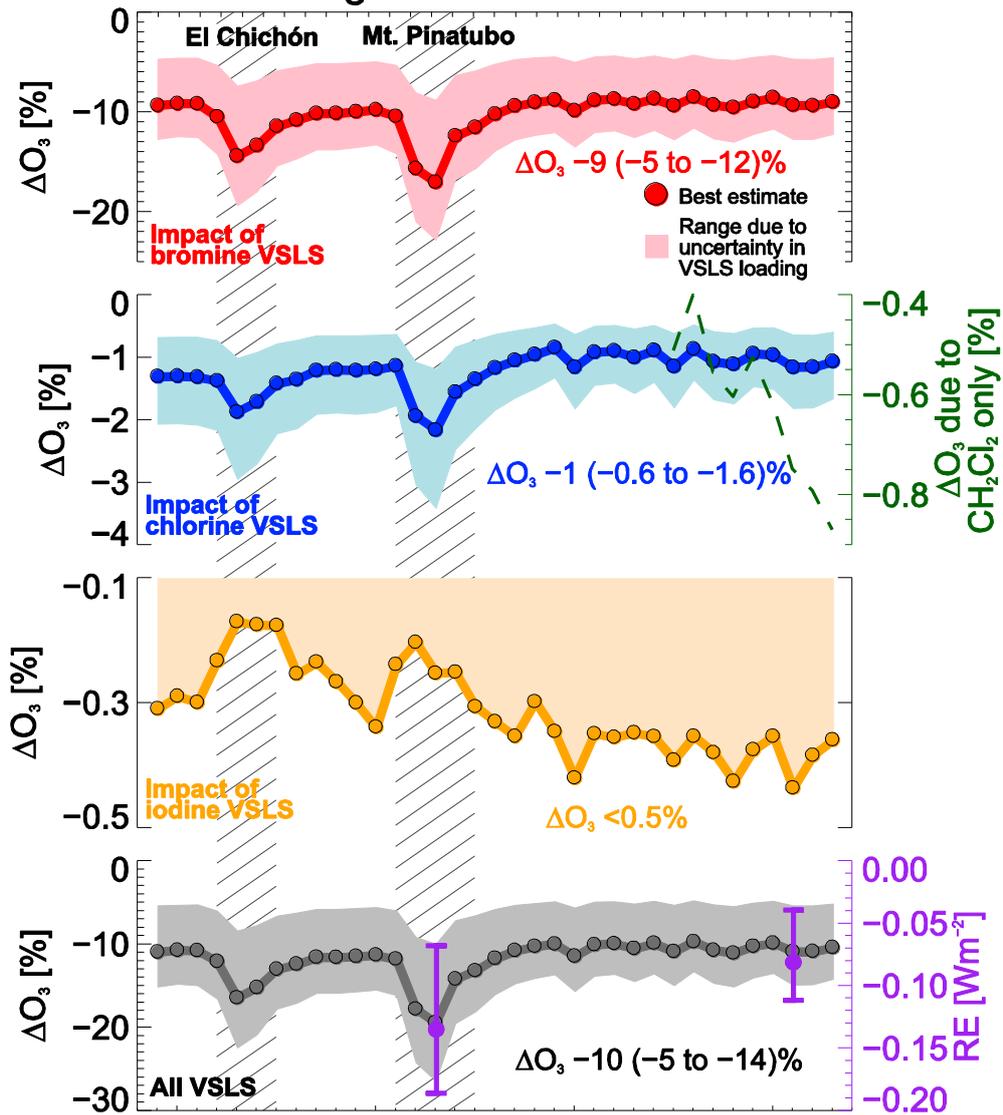
346

347

348

349

**a** Ozone change due to VSLs 1979–2013



350

351

352

353

354 **Supporting Information to:**

355 **Efficiency of short-lived halogens at influencing climate**  
356 **through depletion of stratospheric ozone**

357 R. Hossaini<sup>1\*</sup>, M. P. Chipperfield<sup>1</sup>, S. A. Montzka<sup>2</sup>, A. Rap<sup>1</sup>, S. Dhomse<sup>1</sup>, and W. Feng<sup>1,3</sup>

- 358 1. School of Earth and Environment, University of Leeds, Leeds, UK  
359 2. National Oceanic and Atmospheric Administration, Boulder, USA  
360 3. National Centre for Atmospheric Science, University of Leeds, Leeds, UK

361 \* Corresponding author ([r.hossaini@leeds.ac.uk](mailto:r.hossaini@leeds.ac.uk))

362  
363  
364 **Supplementary Information**

365  
366 This supplement contains 4 tables and 3 figures. Table S1 gives a summary of model  
367 experiments and their design to examine the impact of halogens from VSLs in the  
368 stratosphere. Table S2 gives the calculated global mean radiative effect caused by VSLs-  
369 driven ozone perturbations. Table S3 gives a summary of additional model experiments that  
370 were performed to examine the impact of VSLs on ozone in the troposphere. Table S4  
371 presents observed CH<sub>2</sub>Cl<sub>2</sub> mixing ratios at 13 surface locations from the ongoing monitoring  
372 program of the National Oceanic and Atmospheric Administration (NOAA) Earth System  
373 Research Laboratory (ESRL). Table S4 also contains the site-wise CH<sub>2</sub>Cl<sub>2</sub> growth rate over  
374 the 2010-2013 period along with hemispheric and global averages. Figure S1 shows the 2011  
375 mean simulated ozone change due to VSLs in the troposphere. Figure S2 shows a  
376 comparison between long-term ozone anomalies from the TOMCAT model and  
377 TOMS/SBUV satellite data between 1985 and 2013. Finally, Figure S3 shows column O<sub>3</sub>  
378 changes due to bromine VSLs in 2011 and also in an atmosphere with a pre-industrial  
379 stratospheric halogen load.

393  
 394  
 395  
 396  
 397  
 398

**Table S1. Summary of stratospheric model experiments and halogen load from VSLS.**  
 Experiments were designed to examine the individual and combined impact of halogens from VSLS on ozone.

Experiment*	VSLS Loading [ppt] **			Comment
	Bromine (Br)	Chlorine (Cl)	Iodine (I)	
STRAT1 <sup>+</sup>	0	0	0	No VSLS, control run
STRAT2 <sup>+</sup>	6	0	0	Br - best
STRAT3 <sup>+</sup>	3	0	0	Br - lower
STRAT4 <sup>+</sup>	8	0	0	Br - upper
STRAT5	6	40	0	Br - best Cl - lower
STRAT6	6	80	0	Br - best Cl - best
STRAT7	6	130	0	Br - best Cl - upper
STRAT8	6	80	0.15	Br - best Cl - best I - upper
STRAT9 <sup>^</sup>	3	40	0	All - lower
STRAT10 <sup>^</sup>	8	130	0.15	All - upper

399

400 Notes:

401 \* The model was run for the 1979-2013 period at a resolution of ~5.6° longitude by ~5.6°  
 402 latitude and with 32 levels from the surface to ~60 km. Meteorological forcing data was taken  
 403 from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim (6-  
 404 hourly) reanalysis.

405 \*\* Range and best estimates based on the World Meteorological Organization Scientific  
 406 Assessment of Ozone Depletion 2010. Upper limit of Cl encompasses the recent CH<sub>2</sub>Cl<sub>2</sub>  
 407 trend.

408 + In addition, also performed with a fixed pre-industrial stratospheric halogen load  
 409 comprising background CH<sub>3</sub>Br and CH<sub>3</sub>Cl only.

410 ^ Extreme ranges used to determine the uncertainty on O<sub>3</sub> changes and RE due to VSLS.

411

412

413

414 **Table S2. Radiative effect (RE) due to VSLS-driven O<sub>3</sub> perturbations.** Net RE (longwave  
415 + shortwave) reported as global mean area-weighted averages for 2011 (Wm<sup>-2</sup>). Range shown  
416 in brackets is due to uncertainty in VSLS loading.

417

	VLSL halogen	Global Mean RE [Wm <sup>-2</sup> ]
<b>Stratosphere</b>	Bromine	-0.07 (-0.035 to -0.096)
	Chlorine	-0.007 (-0.004 to -0.011)
	Iodine	< -0.003
	<b>Combined stratosphere</b>	<b>-0.08 (-0.04 to -0.11)</b>
<b>Troposphere</b>	Chlorine	Negligible
	Bromine & Iodine	-0.12
	Bromine & Iodine [ref 23]	~ -0.1
	<b>Combined troposphere</b>	<b>-0.12</b>
	<b>Whole atmosphere</b>	<b>-0.20 (-0.16 to -0.23)</b>

418

419 **Table S3. Summary of tropospheric model experiments.** Experiments were designed to  
420 examine the individual and combined impact of halogens from VSLS on ozone.

421

<b>Experiment*</b>	<b>Inclusion of VSLS**</b>			<b>Comment</b>
	<b>Bromine (Br)</b>	<b>Chlorine (Cl)</b>	<b>Iodine (I)</b>	
<b>TROP1</b>	No	No	No	No VSLS
<b>TROP2</b>	Yes	No	No	Br only
<b>TROP3</b>	Yes	Yes	No	Br and Cl
<b>TROP4</b>	Yes	Yes	Yes	Br, Cl and I

422

423 Notes:

424 \* The model was run for the 2009 to 2013 period at a resolution of ~2.8° longitude by ~2.8°  
425 latitude and with 31 levels from the surface to ~30 km. Meteorological forcing data was taken  
426 from the ECMWF ERA-Interim (6-hourly) reanalysis.

427 \*\* The tropospheric configuration of the TOMCAT model considers explicit emissions<sup>S4-5</sup> of  
428 the following VSLS: CHBr<sub>3</sub>, CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>2</sub>Cl, CH<sub>2</sub>BrCl, CHBrCl<sub>2</sub>, CH<sub>3</sub>I, CH<sub>2</sub>I<sub>2</sub>, CH<sub>2</sub>ICl,  
429 CH<sub>2</sub>IBr, C<sub>2</sub>H<sub>5</sub>I and C<sub>3</sub>H<sub>7</sub>I. A latitude-dependent mixing ratio boundary condition, derived  
430 from available global surface observations, was used to constrain the abundance of CHCl<sub>3</sub>,  
431 CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>ClCH<sub>2</sub>Cl, C<sub>2</sub>HCl<sub>3</sub> and C<sub>2</sub>Cl<sub>4</sub> in the model. TOMCAT has been used extensively  
432 for previous studies of tropospheric halogen chemistry<sup>S1</sup> and studies examining the

433 emission<sup>S2</sup>, transport and chemistry of VLSLS<sup>S3</sup>. The above model configuration has been  
 434 shown previously to perform well in reproducing atmospheric observations of a range of  
 435 VLSLS in the troposphere<sup>S2-3</sup>.

436 **Table S4. Observed surface mixing ratio (ppt) and growth rate of CH<sub>2</sub>Cl<sub>2</sub>.** Observations  
 437 made as part of the ongoing National Oceanic and Atmospheric Administration Earth System  
 438 Research Laboratory (NOAA/ESRL) monitoring program. Average growth rates at all sites  
 439 calculated between 2010-2013.

440

Monitoring Site	Annual Mean Mixing Ratio [ppt]				Growth Rate	
	2010	2011	2012	2013	ppt yr <sup>-1</sup>	% yr <sup>-1</sup>
Alert, NW Territories, Canada*	46.0	47.0	48.1	59.6	4.5	8.6
Summit, Greenland	46.8	45.7	47.5	60.2	4.5	8.4
Pt. Barrow, Alaska, USA*	46.5	46.3	48.2	59.8	4.4	8.4
Mace Head, Ireland	46.7	45.7	48.1	58.9	4.1	7.8
Wisconsin, USA	48.8	48.4	52.0	62.0	4.4	8.0
Trinidad Head, USA	48.6	48.6	49.7	61.5	4.3	7.9
Niwot Ridge, Colorado, USA*	44.0	45.7	50.7	60.3	5.4	10.5
Cape Kumukahi, Hawaii, USA*	42.9	42.3	45.0	53.9	3.7	7.6
Mauna Loa, Hawaii, USA*	39.2	37.4	41.9	52.0	4.3	9.4
Cape Matatula, American Samoa*	14.9	15.6	16.4	19.3	1.4	8.5
Cape Grim, Tasmania, Australia*	13.1	13.7	14.3	15.6	0.9	6.0
Palmer Station, Antarctica	12.7	13.4	13.4	15.3	0.9	6.3
South Pole*	12.1	13.3	13.3	14.2	0.7	5.4
Northern Hemisphere	43.7	43.7	46.8	57.1	4.5	8.9
Southern Hemisphere	13.4	14.2	14.7	16.4	1.0	6.8
<b>All site average</b>	<b>35.5</b>	<b>35.6</b>	<b>37.6</b>	<b>45.6</b>	<b>3.3</b>	<b>8.3</b>

441

442 Notes:

443 \* Sites used in estimating hemispheric mean mixing ratios in Table S3 and in Figure 3.

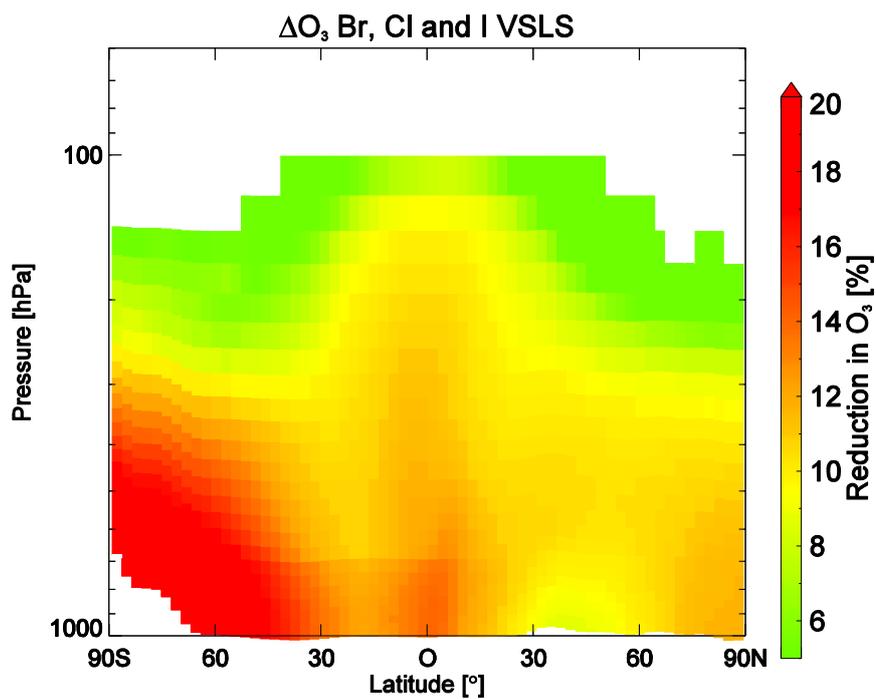
444

445

446

447

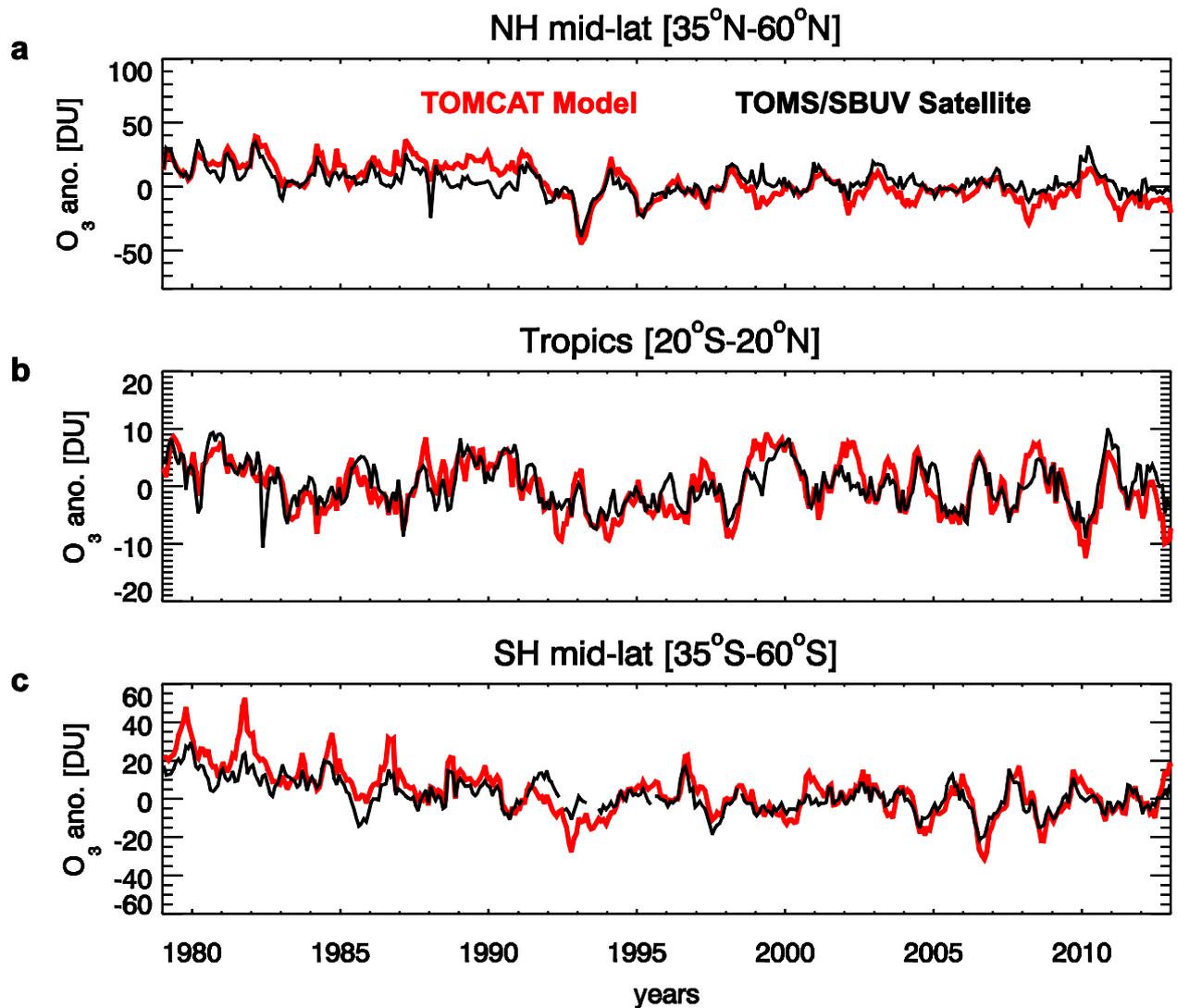
448



449  
450

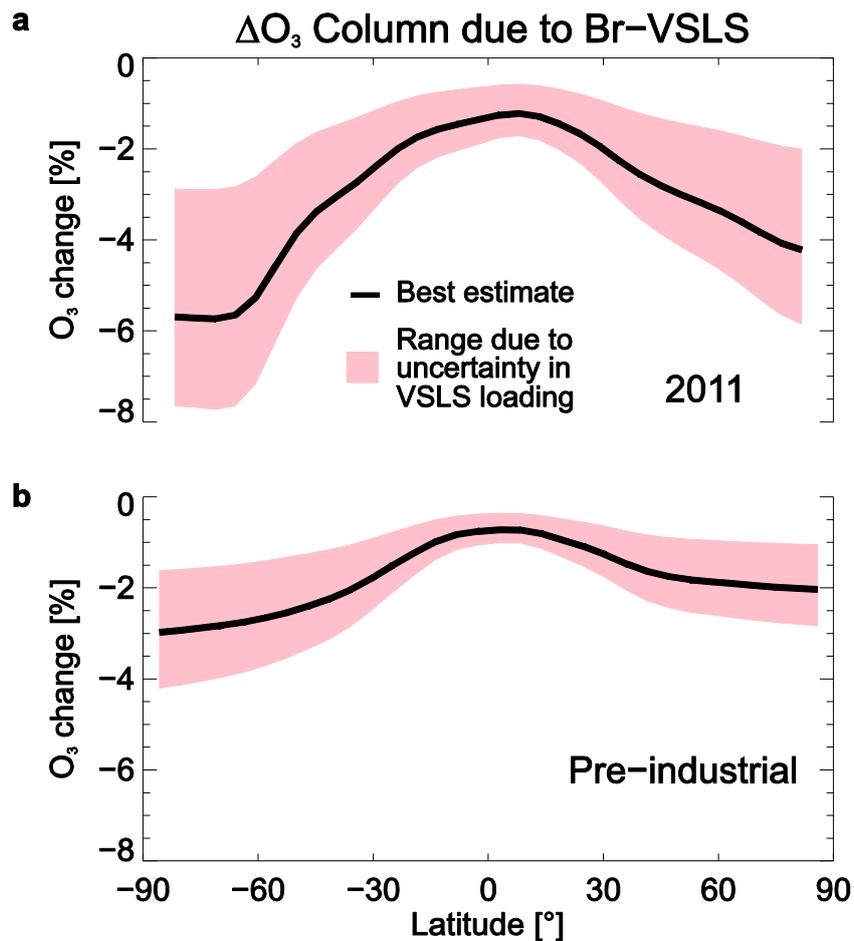
451 **Figure S1. Impact of VLS on tropospheric ozone.** Simulated O<sub>3</sub> reduction (%) due to  
452 combined influence of bromine, chlorine and iodine from VLS in 2011 (relative to a control  
453 run with no VLS). The impact of chlorine VLS on tropospheric ozone is here negligible  
454 (<0.5%).

455



456  
 457  
 458  
 459  
 460  
 461  
 462  
 463  
 464  
 465  
 466  
 467  
 468

**Figure S2. Long-term ozone anomalies from observations and model.** Comparison of total ozone anomalies (Dobson Units) for (a) northern hemisphere mid-latitudes (35°N-60°N), (b) tropics (20°S-20°N) and (c) southern hemisphere mid-latitudes (35°S-60°S). Anomalies are calculated by subtracting climatological monthly mean column ozone values (1990-2005) from monthly mean values.



469  
 470  
 471  
 472  
 473  
 474  
 475  
 476  
 477  
 478  
 479  
 480  
 481  
 482  
 483  
 484  
 485  
 486  
 487  
 488  
 489  
 490

**Figure S3. Present day and pre-industrial impact of bromine VSLs on column ozone.** Simulated column ozone change (%) due to a best estimate of 6 parts per trillion (ppt) of bromine VSLs in the stratosphere relative to a run with no VSLs in (a) 2011 and (b) the pre-industrial stratosphere (background CH<sub>3</sub>Br and CH<sub>3</sub>Cl only). Globally averaged, the influence of bromine VSLs on column ozone is ~30% smaller in the pre-industrial stratosphere. The shaded regions denote the range due to uncertainty in the stratospheric loading of bromine VSLs; simulations were also performed with 3 ppt and 8 ppt.

491 **Supplementary References**

492 S1 Breider, T. J. et al. Impact of BrO on dimethylsulfide in the remote marine boundary  
493 layer. *Geophys. Res. Lett.*, 37, L02807 (2010).

494

495 S2 Hossaini, R. et al. Evaluating global emission inventories of biogenic bromocarbons.  
496 *Atmos. Chem. Phys.* **13**, 11819-11838 (2013).

497

498 S3 Hossaini, R. et al. The contribution of natural and anthropogenic very short-lived species  
499 to stratospheric bromine. *Atmos. Chem. Phys.* **12**, 371-380 (2012).

500

501 S4 Ordóñez, C. et al. Bromine and iodine chemistry in a global chemistry-climate model:  
502 description and evaluation of very short-lived oceanic sources. *Atmos. Chem. Phys.* **12**, 1423-  
503 1447 (2012).

504

505 S5 Ziska, F. et al. Global sea-to-air flux climatology for bromoform, dibromomethane and  
506 methyl iodide. *Atmos. Chem. Phys.* **13**, 8915-8934 (2013).

507

508