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

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Halogens released from long-lived anthropogenic substances, such as chlorofluorocarbons, are the principal cause of recent depletion of stratospheric ozone, a greenhouse gas^{1, 2, 3}. Recent observations show that very short-lived substances, with lifetimes generally under six months, are also an important source of stratospheric halogens^{4, 5}. 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 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^{6, 7, 8} or continued anthropogenic emissions⁹, 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 (ODS)³, 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^{4,5,10}. Their absolute contribution is
31 uncertain owing to poor constraints on the magnitude and distribution of VSLS emissions¹¹, a
32 limited understanding of their tropospheric processing¹², 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 chlorine³. 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 seaweed³ – a number of which are farmed⁹ – and by phytoplankton. Once transported to the
39 stratosphere they affect the natural balance of O_3 , particularly in the lower stratosphere¹³⁻¹⁵
40 (LS; altitudes ~ 12 to 25 km), where O_3 perturbations strongly impact surface temperature and
41 climate^{1,2}. 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^{6,7}.

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 model¹⁶, 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 ¹⁴.

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^{17,18} was used to diagnose the net change
51 (longwave + shortwave) in radiation at the tropopause due to VSLS-driven O₃ 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 O₃ 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 O₃ 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 O₃ loss in the springtime Antarctic ozone hole³ and
63 here contribute 81% of the total VSLS-driven O₃ loss in this region. Chlorine VSLS account
64 for a further 16% (i.e. a column O₃ 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⁻² due to the presence of
66 natural and anthropogenic VSLS and their influence on stratospheric O₃ 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 O₃ perturbations. We calculate VSLS currently reduce O₃ 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 (CHBr₃) and dibromomethane (CH₂Br₂), is responsible for the majority (~85%) of the LS O₃
73 decrease. The analogous chlorinated gases, chloroform (CHCl₃) and dichloromethane

74 (CH₂Cl₂), have anthropogenic sources^{19,20} 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 CHCl₃ and CH₂Cl₂ emissions, respectively³. As these
77 gases are not controlled by the Montreal Protocol and given potential for industrial growth,
78 quantifying their impact on O₃ is important. We find all chlorine VSLS reduce O₃ 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 O₃ change relative
81 to the control is <1%. An upper limit of O₃ reduction due to methyl iodide (CH₃I), 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^{3,21}.

84 Bromine (chlorine, iodine) accounts for ~87% (9%, 4%) of the global RE due to VSLS-
85 driven stratospheric O₃ loss (Supplementary Table S2). The relatively large RE of -0.07 (-
86 0.035 to -0.096) Wm⁻² due to O₃ loss from bromine VSLS can be compared to the RE from
87 stratospheric O₃ changes driven by long-lived anthropogenic ODS (Fig. 2b). For 2011, we
88 calculate the latter RE to be -0.17 Wm⁻² (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 O₃ 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 O₃ loss without a corresponding warming effect due to
97 their presence in the atmosphere. Accounting for VSLS will improve simulations of
98 stratospheric O₃, 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 O₃²²⁻²⁴. The true VSLS RE is therefore likely greater if
101 tropospheric O₃ impacts are also considered. We calculated a global mean RE due to
102 tropospheric O₃ loss from VSLS (Methods and Supplementary Table S3) of -0.12 Wm^{-2} ,
103 50% larger than the stratospheric RE, in good agreement with previous estimates²³. Bromine
104 and iodine combined contribute virtually all this tropospheric RE, most of which is from O₃
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) Wm^{-2} due to
110 VSLS-driven O₃ loss.

111 We found no trend in the influence of VSLS on global O₃ between 1979 and 2013. However,
112 in addition to bromine – whose impact on O₃ is enhanced following volcanic eruptions¹³⁻¹⁵ –
113 we find stratospheric O₃ 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 O₃ decrease following
116 the Pinatubo eruption (Supplementary Figure S2) but generally reproduces observed O₃
117 variations well. The sensitivity of VSLS-driven O₃ 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 particles²⁵.

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 Oscillation¹².
122 However, the pre-industrial influence of bromine VSLS on global O₃, 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 O₃ loss cycles. We
125 calculate this O₃ trend caused a contribution to the climate RF of -0.014 (-0.007 to -0.018)
126 Wm⁻² (out of the -0.17 Wm⁻² RF from long-lived anthropogenic ODS quoted above) which
127 will likely be reversed as stratospheric chlorine declines during the 21st 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 flux⁶ or a rise in seaweed cultivation⁷ – a rapidly growing
130 industry – would offset some of this reversal.

131 Surface concentrations of CH₂Cl₂, an anthropogenic VSLS, have increased rapidly in recent
132 years (Fig. 3b). Between 2000 and 2012, surface CH₂Cl₂ 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, CH₂Cl₂ 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 CH₂Cl₂ on O₃ (Fig. 3) would increase significantly if the
138 observed trend continues. This is likely if increases in atmospheric CH₂Cl₂ are associated
139 with the increased industrialization of developing countries and, for example, use of CH₂Cl₂
140 as a feedstock for hydrofluorocarbon (HFC) production, such as HFC-32²⁶ – 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 future²⁷. Although
143 HFCs do not directly deplete O₃, a broader consideration of their production pathways
144 suggests a potential for direct influences on O₃ 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⁻² 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) Wm^{-2} and comparable in magnitude to, for example, the (positive) RF due to
149 aircraft contrails¹.

150 We have shown that, through interactions with O_3 , VSLS have a disproportionately large
151 climate impact compared to long-lived ODS, owing to their breakdown at climate-sensitive
152 altitudes. VSLS 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 VSLS 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 CH_2Cl_2 , here about
158 $\times 50$ larger than some recently detected CFCs and HCFCs²⁸, 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 VSLS on stratospheric ozone.** The 3-D chemistry transport model,
163 TOMCAT¹⁶, was used to simulate the breakdown of VSLS in the stratosphere. TOMCAT
164 contains a detailed gas-phase/heterogeneous chemistry scheme considering all major
165 stratospheric families; O_x , HO_x , NO_y , Cl_y , Br_y , and here we implemented an iodine scheme²¹.
166 The major VSLS considered were CHBr_3 , CH_2Br_2 , CHCl_3 , CH_2Cl_2 and CH_3I . 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 VSLS mixing ratios were time-independent quantities, scaled to give a range of stratospheric
170 loadings of bromine, chlorine and iodine from VSLS based on current best estimates and
171 lower/upper limits³ (Supplementary Table S1).

172 In all simulations the abundance of long-lived source gases (e.g. CFCs, halons, N₂O, CH₄)
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 O₃. A sensitivity experiment was
179 performed with a time-dependent stratospheric loading of CH₂Cl₂, 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 CH₃Br and ~500 ppt of CH₃Cl, based on ice-core records²⁹. From these
183 experiments, we calculated: [1.] the difference in the influence of bromine VSLS on O₃
184 between the pre-industrial period and 2011. This was also used to diagnose a RF from
185 bromine VSLS. [2.] The O₃ change attributable to anthropogenic long-lived ODS only
186 (Figure 2b). Simulations to quantify the impact of VSLS on tropospheric O₃ were also
187 performed. Details of these experiments are given in the Supplementary Information.

188 **Climate impact of VSLS.** The RE of VSLS-driven O₃ loss was calculated using the offline
189 Edwards and Slingo radiative transfer model¹⁷. 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 archive¹⁸.

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 O₃ 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 O₃ 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 O₃ loss arising from anthropogenic
202 long-lived ODS. This O₃ 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 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 O₃ loss from the pre-industrial period to 2011 caused by changes in anthropogenic chlorine
208 from long-lived ODSs. The relative O₃ 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 stratosphere³; the calculated RF is due to the pre-industrial to 2011 trend in
216 anthropogenic chlorine VSLS concentrations only.

217 **Long-term observations of CH₂Cl₂.** Observations from multiple sites in the ongoing
218 NOAA/ESRL Global Monitoring Program³⁰ are presented (Supplementary Table S4). Results
219 from paired flask samples collected at remote sites were used to derive surface CH₂Cl₂

220 mixing ratios over the 1995-2012 period averaged over each hemisphere with a weighting
221 based on sampling latitude³⁰. 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.

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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**

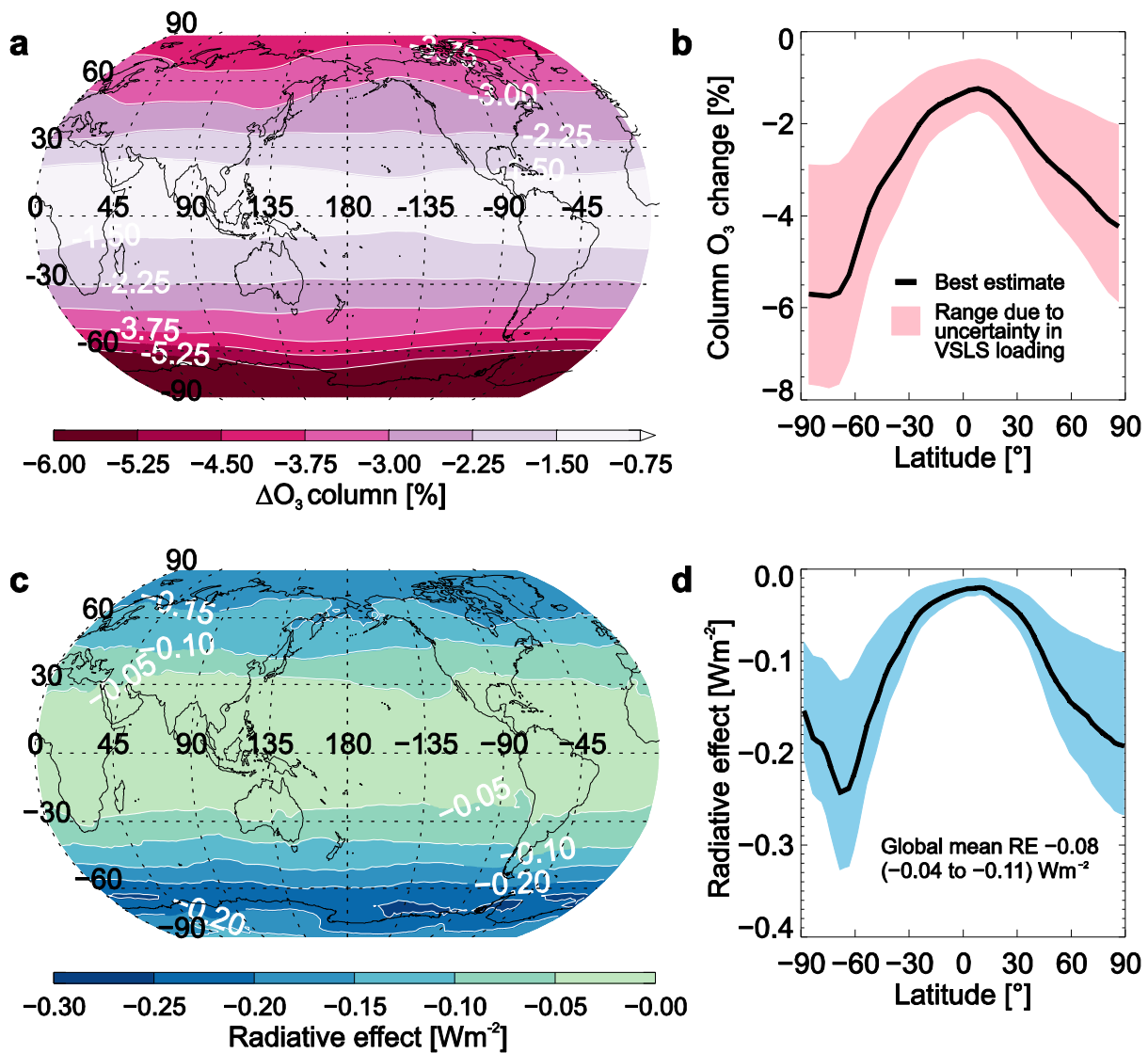
321 **Figure 1. Column ozone decrease due to VSLS and radiative effect.** (a) Annual mean
322 (2011) percentage (%) change in stratospheric column ozone due to best estimated
323 stratospheric loading of bromine, chlorine and iodine from VSLS. (b) Latitude-dependence of
324 column ozone change. Solid line denotes best estimate, shaded region represents the range
325 due to uncertainty in VSLS loading. (c) Net (longwave + shortwave) radiative effect (RE,
326 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 (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 O_3 loss due to
333 VSLS, expressed as percent (%) (top x axis). (b) as (a) but with the 2011 O_3 change due to
334 long-lived anthropogenic ODS also shown to highlight the difference in altitude of the O_3
335 changes.

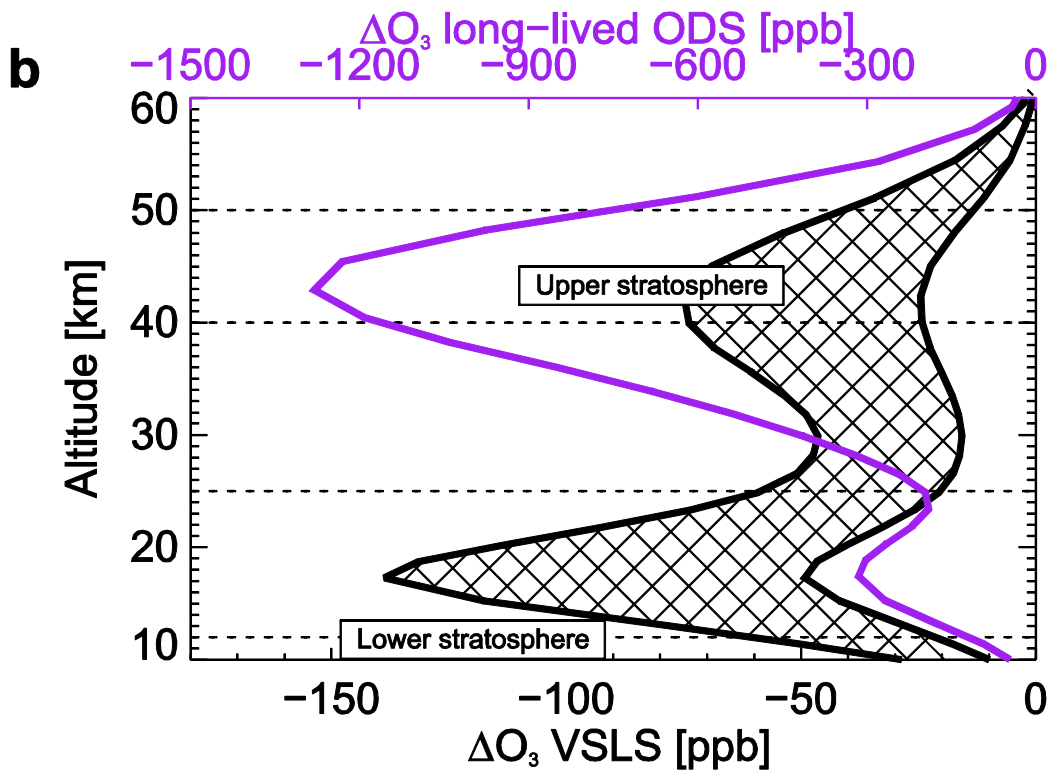
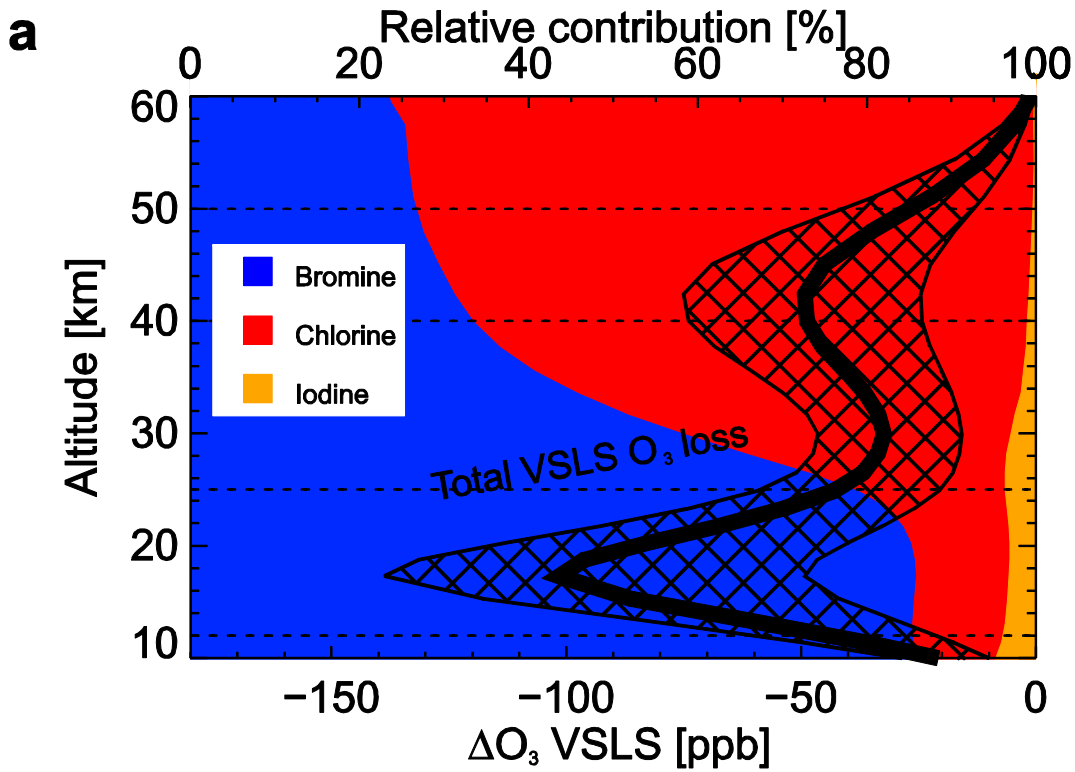
336 **Figure 3. Trend in VSLS-driven ozone loss and CH_2Cl_2 growth.** (a) Annual global mean

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).

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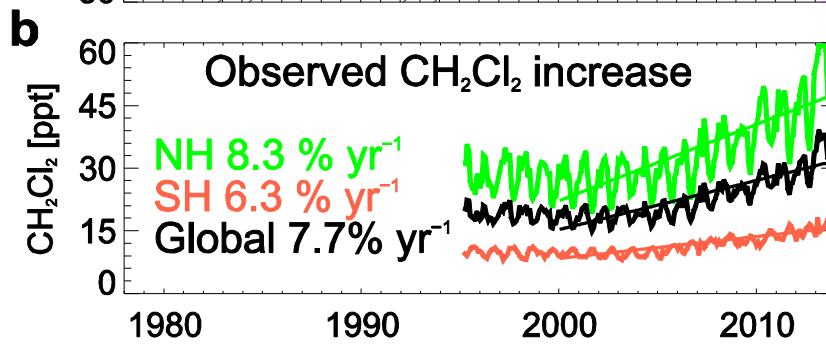
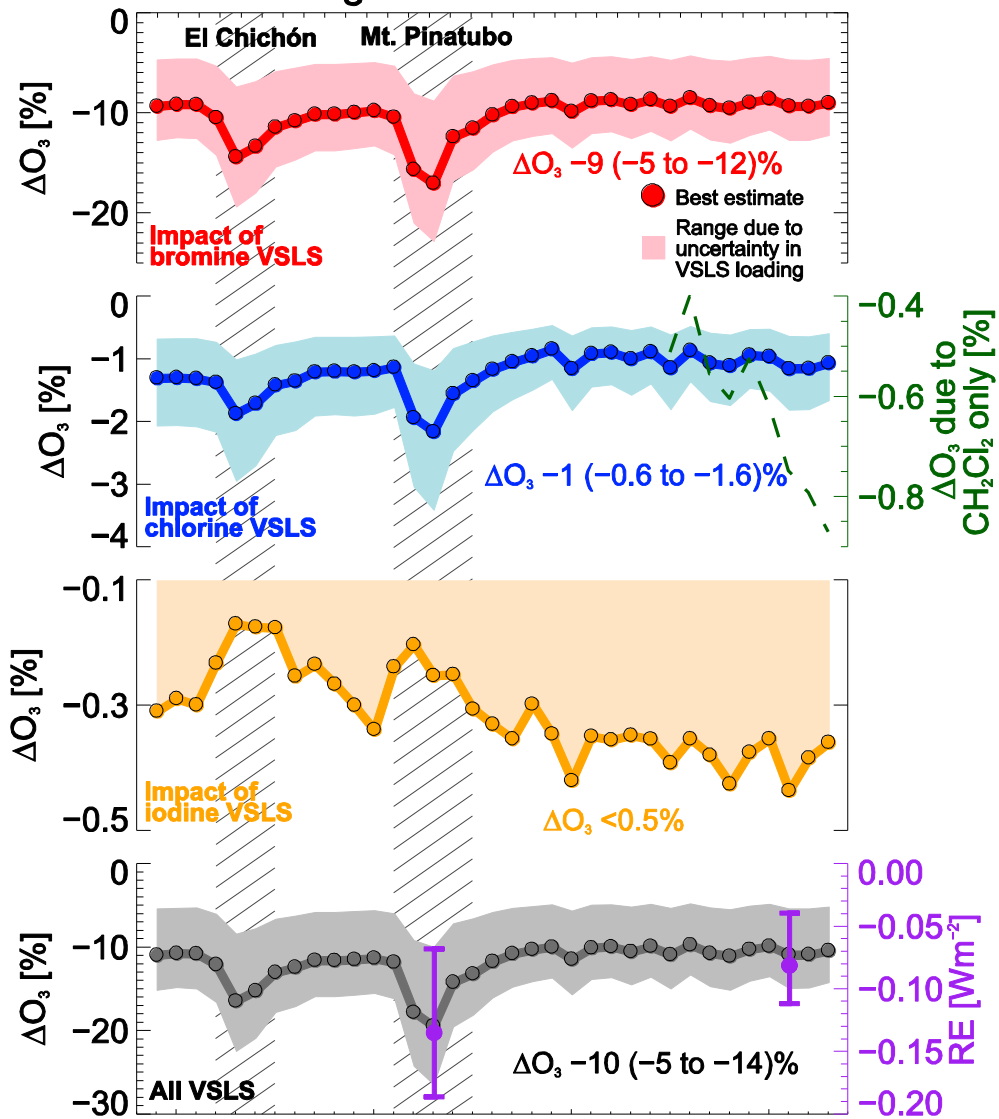
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a Ozone change due to VSLs 1979–2013



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354 **Supporting Information to:**

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

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364 **Supplementary Information**

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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 CH₂Cl₂ 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 CH₂Cl₂ 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 O₃
378 changes due to bromine VSLs in 2011 and also in an atmosphere with a pre-industrial
379 stratospheric halogen load.

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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 ⁺	0	0	0	No VSLS, control run
STRAT2 ⁺	6	0	0	Br - best
STRAT3 ⁺	3	0	0	Br - lower
STRAT4 ⁺	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 [^]	3	40	0	All - lower
STRAT10 [^]	8	130	0.15	All - upper

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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 CH₂Cl₂
 407 trend.

408 + In addition, also performed with a fixed pre-industrial stratospheric halogen load
 409 comprising background CH₃Br and CH₃Cl only.

410 ^ Extreme ranges used to determine the uncertainty on O₃ changes and RE due to VSLS.

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414 **Table S2. Radiative effect (RE) due to VSLS-driven O₃ perturbations.** Net RE (longwave
415 + shortwave) reported as global mean area-weighted averages for 2011 (Wm⁻²). Range shown
416 in brackets is due to uncertainty in VSLS loading.

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

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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.

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

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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^{S4-5} of
428 the following VSLS: CHBr₃, CH₂Br₂, CHBr₂Cl, CH₂BrCl, CHBrCl₂, CH₃I, CH₂I₂, CH₂ICl,
429 CH₂IBr, C₂H₅I and C₃H₇I. A latitude-dependent mixing ratio boundary condition, derived
430 from available global surface observations, was used to constrain the abundance of CHCl₃,
431 CH₂Cl₂, CH₂ClCH₂Cl, C₂HCl₃ and C₂Cl₄ in the model. TOMCAT has been used extensively
432 for previous studies of tropospheric halogen chemistry^{S1} and studies examining the

433 emission^{S2}, transport and chemistry of VLSL^{S3}. The above model configuration has been
 434 shown previously to perform well in reproducing atmospheric observations of a range of
 435 VLSL in the troposphere^{S2-3}.

436 **Table S4. Observed surface mixing ratio (ppt) and growth rate of CH₂Cl₂.** 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.

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Monitoring Site	Annual Mean Mixing Ratio [ppt]				Growth Rate	
	2010	2011	2012	2013	ppt yr ⁻¹	% yr ⁻¹
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
All site average	35.5	35.6	37.6	45.6	3.3	8.3

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442 Notes:

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

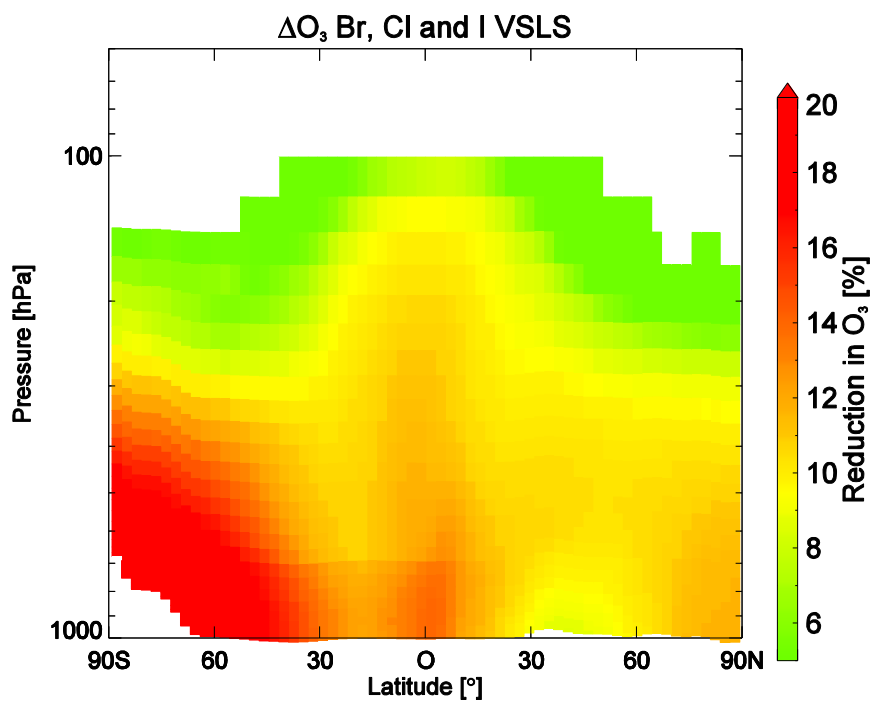
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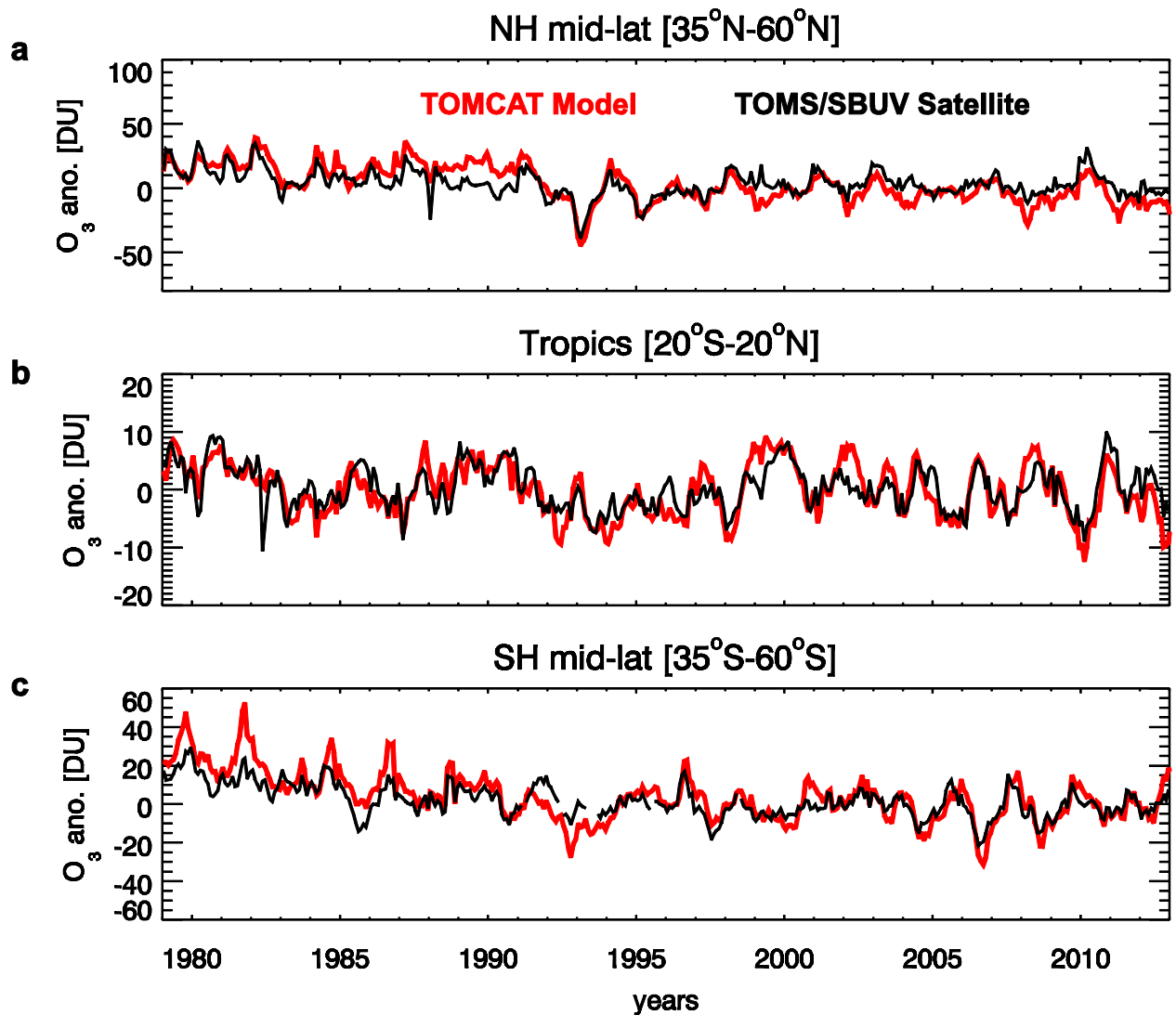
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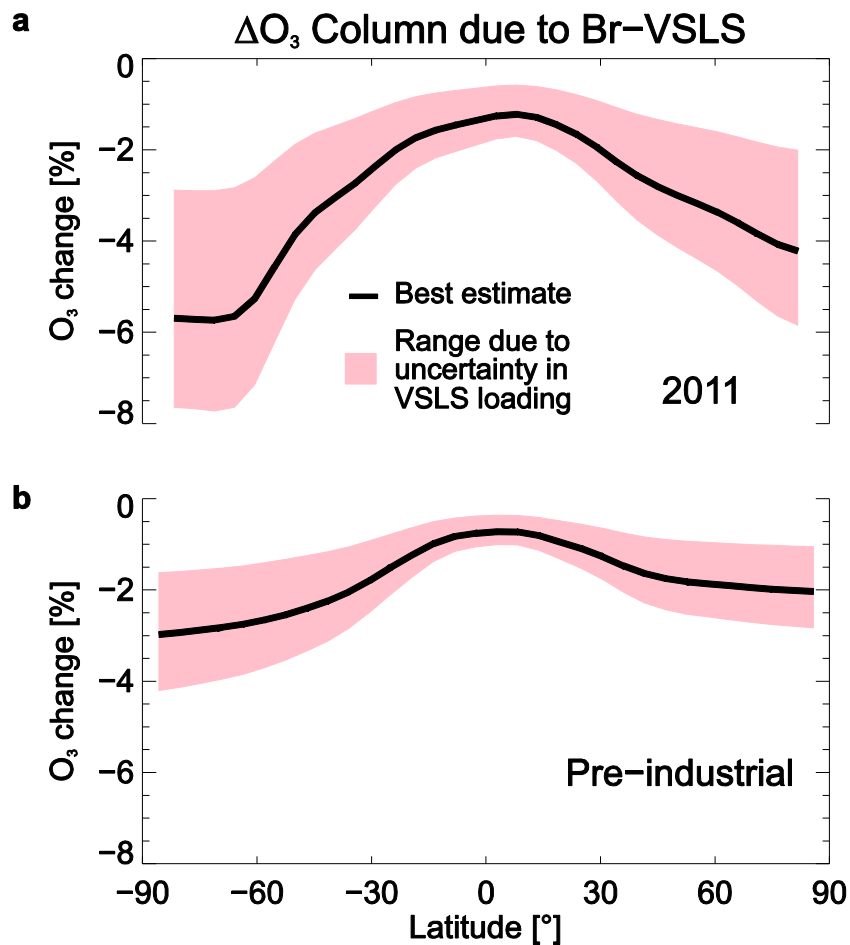
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Figure S1. Impact of VLS on tropospheric ozone. Simulated O₃ reduction (%) due to combined influence of bromine, chlorine and iodine from VLS in 2011 (relative to a control run with no VLS). The impact of chlorine VLS on tropospheric ozone is here negligible (<0.5%).



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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.



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471 **Figure S3. Present day and pre-industrial impact of bromine VSLs on column ozone.**
 472 Simulated column ozone change (%) due to a best estimate of 6 parts per trillion (ppt) of
 473 bromine VSLs in the stratosphere relative to a run with no VSLs in (a) 2011 and (b) the pre-
 474 industrial stratosphere (background CH₃Br and CH₃Cl only). Globally averaged, the
 475 influence of bromine VSLs on column ozone is ~30% smaller in the pre-industrial
 476 stratosphere. The shaded regions denote the range due to uncertainty in the stratospheric
 477 loading of bromine VSLs; simulations were also performed with 3 ppt and 8 ppt.

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