1 **How sensitive is the recovery of stratospheric ozone to changes in**
2 **concentrations of very short lived bromocarbons?**
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15
16 **Abstract**
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18 Naturally produced very short-lived substances (VSLS) account for almost a quarter of the
19 current stratospheric inorganic bromine, Br_y. Following VSLS oxidation, bromine radicals
20 (Br and BrO) can catalytically destroy ozone. The extent to which possible increases in
21 surface emissions or transport of these VSLS bromocarbons to the stratosphere could
22 counteract the effect of halogen reductions under the Montreal Protocol is an important
23 policy question. Here by using a chemistry-climate model, UM-UKCA, we investigate the
24 impact of a hypothetical doubling (an increase of 5 ppt Br_y) in VSLS bromocarbons on ozone
25 and how the resulting ozone changes depend on the background concentrations of chlorine
26 and bromine. Our model experiments indicate that for the 5 ppt increase in Br_y from VSLS,
27 the ozone decrease in the lowermost stratosphere of the southern hemisphere (SH) may reach
28 up to 10% in the annual mean; the ozone decrease in the northern hemisphere (NH) is smaller
29 (4-6%). The largest impact on the ozone column is found in the Antarctic spring. There is a
30 significantly larger ozone decrease following the doubling in VSLS burden under a high
31 stratospheric chlorine background than under a low chlorine background, indicating the
32 importance of the inter-halogen reactions. For example, the decline of the high latitude, lower
33 stratospheric ozone concentration as a function of Br_y is higher by about 30-40% when
34 stratospheric Cl_y is ~3 ppb (present day) compared with Cl_y of ~0.8 ppb (a pre-industrial or
35 projected future situation). Bromine will play an important role in the future ozone layer.
36 However, even if bromine levels from natural VSLS were to increase significantly later this
37 century, changes in the concentration of ozone will likely be dominated by the decrease of
38 anthropogenic chlorine. Our calculation suggests that for a 5 ppt increase in Br_y from VSLS,
39 the Antarctic ozone hole recover date could be delayed by approximately 6-8 years,
40 depending on Cl_y levels.
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42

1. Introduction

It is now very well established that stratospheric ozone loss since the 1970s has occurred as a consequence of emissions of halogenated species into the atmosphere. These gases, the CFCs and halons, are generally long lived in the troposphere but at sufficient altitudes in the stratosphere they can be oxidized to liberate chlorine (as suggested by Molina and Rowland, 1974) and bromine atoms (see Wofsy et al, 1975), which can subsequently play a role in catalytic ozone destruction. The 'ozone hole' in Antarctica was reported by Farman and his colleagues in 1985 (Farman et al., 1985) and intensive field, laboratory and modeling research was soon able to demonstrate that the observed decline in polar ozone was indeed a result of ozone destruction by halogen chemistry. First investigations (for details see the review by Solomon, 1999) focused on the role of chlorine but subsequent research (see, e.g., the observationally based study of Salawitch et al. (1998) and the modelling study of Chipperfield and Pyle, 1998) showed that coupled chlorine-bromine reactions made a substantial contribution to the polar loss, as first suggested by McElroy et al. (1986). Following on from the scientific understanding that anthropogenic halogens were responsible for ozone loss, the Montreal Protocol was enacted to regulate production and consumption of ozone-depleting substances. The Protocol has been a major success and atmospheric concentrations of the regulated chlorine- and bromine-gases are now in decline (WMO, 2011).

Chlorine in the stratosphere arises mainly from industrial compounds, principally the CFCs, with a contribution of about 0.6 ppb (~20% relative to current values) from long-lived, naturally occurring CH_3Cl (see, for example, Harper and Hamilton, 2003). In contrast the bromine budget of the stratosphere is less well constrained (Ko et al., 1998; Dorf et al, 2008). It is now thought that about 5 ppt (~20 to 25%) of stratospheric bromine may come from the oxidation of halocarbons with lifetimes of less than about 6 months (so-called Very Short Lived Substances, VSLS), while the majority comes from methyl bromide and the anthropogenic halons. Thorough reviews of these halogen gases are available in the recent UNEP/WMO ozone assessment (Montzka, Reimann et al., 2011), where the total stratospheric bromine concentration in 2008 is given as 22.5 ppt. In the preindustrial era, the VSLS contribution may have been as much as 50% of the total atmospheric bromine loading. VSLS bromocarbons are mainly produced by macro- and microalgae (Carpenter and Liss, 2000; Quack and Wallace 2003; Yokouchi et al., 2005). $CHBr_3$ and CH_2Br_2 are the dominant contributors to bromine VSLS species. Although their tropospheric lifetime is relatively short (a few weeks for $CHBr_3$ and several months for CH_2Br_2), they can be effectively lifted through deep convective systems and transported into the upper troposphere and/or lower stratosphere (UTLS) to make a significant contribution to the total ambient bromine (Sturges et al., 2000; Yang et al., 2005; Salawitch, 2006). Being short-lived, there are large uncertainties in using atmospheric concentration measurements to estimate their global fluxes and their net contribution to the stratospheric bromine (Warwick et al., 2006; Liang et al., 2010; Pyle et al., 2011; Ordóñez et al., 2012; Ziska et al., 2013; Hossaini et al., 2013). A large range of contributions to stratospheric inorganic bromine of 1-10 ppt can be found in the literature (Dorf et al., 2008; Salawich et al., 2010; Schofield et. al., 2011; Aschmann et al., 2011; Tegtmeier et al., 2012; Stachnik et al., 2012; Hossaini et al., 2012a). The UNEP/WMO Ozone Assessment of 2011 reports the value as 6(3-8) ppt (Montzka, Reimann et al., 2011).

93   Stratospheric inorganic chlorine has increased from pre-industrial levels of ~0.6 ppb, to a
94   peak of greater than 3 ppb in the 1990s and, under the influence of the Montreal Protocol is
95   decreasing and is expected to continue to decrease during this century (WMO, 2011). The
96   sum of the concentrations of anthropogenic bromine compounds is now also declining. Under
97   the influence of the Montreal Protocol, the stratospheric ozone layer should recover later this
98   century.

100   While anthropogenic halogen loading to the stratosphere should decrease in response to the
101   Montreal Protocol, we do not know how the concentration of the VSLS bromocarbons will
102   change in the future. Since they are mainly produced by biochemical processes, mostly in the
103   ocean, their emissions could change with climate, perhaps depending on sea surface
104   temperature, on ocean pH or on surface wind stress (Gschwend et al., 1985; Keppler et al.,
105   2000). We currently do not have a good enough understanding to allow confident predictions.
106   Changes in transport to the stratosphere could also occur due to climate change. For example,
107   Hossaini et al. (2012b) predict 0.3-1.0 ppt increases in the direct transport of bromine source
108   gases to the stratosphere between 2000 and 2100 under RCPs 4.5 and 8.5 while the earlier
109   study of Dessens et al. (2009) projects a 1-2 ppt increase in total bromine in the lower
110   stratosphere.

112   Bromine is about 100 times more efficient than chlorine as an ozone sink in the high latitude
113   lower stratosphere, with an annual average global value of around 65 (Sinnhuber et al., 2009).
114   So, any future increases in stratospheric bromine, perhaps driven by increased emissions in
115   VSLS bromocarbon or their transport to the stratosphere, could affect stratospheric ozone
116   recovery. Our primary aim in this paper is to explore the sensitivity of ozone recovery to
117   changes in the concentrations of bromine in the stratosphere, arising from very short lived
118   bromocarbons.

120   Gas phase and heterogeneous inter-halogen reactions involving both bromine and chlorine
121   contribute significantly to ozone loss so that the ozone loss due to bromine should be
122   dependent on the chlorine concentration. A second aim of this paper is investigate how ozone
123   might respond to changes in VSLS loading when future stratospheric chlorine levels have
124   declined.

126   To address these aims, we use the UM-UKCA chemistry-climate model. We perform a
127   number of idealized experiments under two different stratospheric chlorine concentrations,
128   corresponding very roughly to the present day and to the end of the 21st century, and three
129   different bromine levels. The range of bromine concentrations chosen allows us to explore
130   the sensitivity of the coupled chlorine-bromine system. Each experiment is run twice, first
131   with a VSLS contribution of 5 ppt and then with an additional increase of 5 ppt. These
132   experiments allow us to explore how ozone loss due to short lived bromocarbons could vary
133   with background chlorine and bromine loading. We note that 5 ppt would represent a large
134   change in the contribution of shortlived bromine to the stratosphere; we reiterate that these
135   are idealized experiments designed to explore the sensitivity of ozone recovery to
136   hypothetical changes in bromine.

138   Other changes could also affect stratospheric ozone recovery (and the contribution of
139   bromine changes to ozone recovery). Several previous studies have looked at the impact of
140   VSLS bromocarbons on ozone trends in the recent past (e.g. Salawitch et al., 2005; Feng et
141   al., 2007; Sinnhuber et al, 2009). They show that the effect of VSLS on ozone is particularly
142   important under enhanced aerosol loading. Transient changes due to volcanic eruptions

143 would certainly affect the trajectory of recovery while a sustained increase in stratospheric
144 aerosol would also lead to a general decrease in ozone and an increased role of bromine, and
145 chlorine, heterogeneous processing. However, in the calculations here aerosol loading is held
146 constant. Climate change will also affect the recovery of stratospheric ozone, as is well
147 known. Salawitch et al. (2005) show that, while the effect of bromine on ozone is dominated
148 by the ClO+BrO reaction in the lowermost stratosphere, the reaction of $BrO+HO_2$ becomes
149 increasingly important with increasing VSLS. Thus any change in HO_2 in the future could
150 potentially affect the estimation of the ozone impact from these changes in halogens. We do
151 not deal with this in detail here although we do mention in Section 3 possible changes in the
152 flux through the $BrO+HO_2$ reaction under climate change.
153
154 The model and the experimental set-up are described in more detail in Section 2. The model
155 results are presented in Section 3. Concluding discussion is found in Section 4.
156
157 **2. Model and Experiments**
158
159 UM-UKCA is a chemistry-climate model; its dynamical core is the Met Office Unified
160 Model (UM) version 7.3 running in the HadGEM3-A configuration (similar to Hewitt et al.,
161 2011). The detailed chemistry scheme for the troposphere and stratosphere, CheST, combines
162 the schemes described by Morgenstern et al. (2009) and O'Connor et al. (2014) and was
163 further updated with tropospheric bromine chemistry based on our work in the *p*TOMCAT
164 chemistry transport model (Yang et al., 2005; 2010). The stratospheric halogen scheme is
165 improved by introducing a number of heterogeneous reactions on stratospheric particles
166 (polar stratospheric clouds (PSCs) and sulphate aerosol) to account for inter-halogen
167 (chlorine and bromine) reactivation as in our recent study (Braesicke et al., 2013). The
168 model's horizontal resolution is 3.75 degree in longitude and 2.5 degree in latitude on an
169 Arakawa-C grid. A hybrid sigma-geometric height coordinate is used to resolve the vertical
170 range from the surface to ~84 km with 60 levels. All experiments are performed for year
171 2000 boundary conditions with prescribed monthly sea surface temperatures (SSTs) and sea
172 ice conditions. The radiative species concentrations for CO_2, N_2O and CH_4 are taken for year
173 2000; ozone is calculated interactively. Apart from the halocarbons (eg CFCs, CH_3Br),
174 chemical emissions are for the present day. The sulphate aerosol field is a monthly
175 climatology. PSCs and ice particles are calculated online based on water vapour fields and
176 temperatures. To get significant results, each of the experiments was performed as a 40-year
177 time-slice integration with the first 20 years as spin-up and the last 20 years for analysis.
178
179 For the VSLS bromocarbons in the model, we have introduced tracers for 5 additional species
180 ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$ and $CHBrCl_2$) with emissions based on the original
181 work (scenario 5) of Warwick et al. (2006), except for emissions of CH_2Br_2 which were
182 updated to 57 Gg yr^{-1}, 50% of the original flux but now much more in accord with Liang et al
183 (2010) and Ordóñez et al (2012). Our updated fluxes provide ~5 ppt of inorganic bromine to
184 the stratosphere.
185
186 We have 6 base experiments, using 2 different stratospheric chlorine loadings and 3 different
187 stratospheric bromine loadings designed to cover a range of past, present and possible future
188 halogen loadings. We chose stratospheric chlorine levels of ~0.8 ppb and ~3 ppb achieved by
189 applying fixed concentrations in the model's lowest layer for the major chlorine species,
190 CFCs, CH_3Cl and CCl_4 (from the A1 Scenario of WMO 2011). 3 ppb is roughly a present day
191 stratospheric chlorine loading. The low chlorine level of 0.8 ppb represents both a
192 preindustrial chlorine value (when CH_3Cl at 0.6 ppb was the major chlorine-carrier as well as

a likely chlorine level towards the end of the century, on a Montreal Protocol trajectory towards 'recovery', according to projected mitigation scenarios for 2100. For stratospheric inorganic bromine, we chose three levels of ~10 ppt, ~15 ppt and ~23 ppt to represent approximately a low (~pre-industrial era, when ice core data suggests a methyl bromide concentration of about 5 ppt (Saltzman et al., 2008)), a medium and a high (~present day) level respectively. These values all include ~5 ppt from VSLS (as described above) with the remaining Br_y coming from long-lived halons and CH_3Br. These values are somewhat arbitrary; our simple aim is to explore a range of Br_y values and, based on them, to investigate the ozone response to perturbed VSLS bromocarbon emissions.

Our study is designed to address how changes in VSLS bromocarbons would impact stratospheric ozone, against a background of changes in stratospheric chlorine and bromine loading. So, each base experiment is then repeated with the VSLS bromocarbon contribution doubled, to about 10 ppt. In the next section for each base experiment we look at the difference in the ozone results between the 2xVSLS and 1xVSLS (a ~5 ppt increase in stratospheric Br_y) integrations.

3. Result and Discussions

Figure 1 shows the annual zonal mean ozone differences between pairs of runs in which the VSLS bromine contribution was increased by 5 ppt. The plots show the 2xVSLS - 1xVSLS ozone differences in percentage. The left column shows ozone changes for a low stratospheric Cl_y of 0.8 ppb, representative either of a pre-industrial atmosphere or after a substantial reduction in halogen loading. The right column has Cl_y of ~3 ppb, roughly representative of the present day. The panels from top to bottom have, respectively, a high inorganic bromine background of ~23 ppt (Figure 1a, 1b), of ~15 ppt (figure 1c, 1d) and a low bromine background of ~10 ppt (figure 1e, 1f).

For a doubled VSLS emission, with an extra ~5 ppt Br_y in the stratosphere, the ozone differences in these runs are statistically significant (P<0.05) (marked with dots in figure 1) in most of the atmosphere below 20 km. The less significant signals above 20 km are likely due to the strong dynamical feedback rather than chemical response, as addressed in a related paper by Braesicke et al. (2013). Longer runs would be required to ensure statistical significance in the middle and upper stratosphere where the relative changes in ozone are small, and we focus here on the lowermost stratosphere where VSLS has a more important role.

 Below 20 km in the Southern Hemisphere the largest annual mean decrease is about 10%, while in the northern hemisphere high latitudes, the ozone decreases by 4-6%. Near the tropical tropopause, an ozone decline of 2-4% is modelled. Since the ozone concentration near the tropopause is low, these losses are small in absolute terms (<10 ppbv). In terms of the seasonal response, a maximum local ozone reduction of ~20% is simulated in the SH high latitude during spring to early summer. The seasonal variation of column ozone loss in the SH high latitude is discussion below.

It is interesting to see that ozone decrease is significant in most of the troposphere, with a small deficit of <2% in the tropics; 2-4% in high latitudes of the NH and 2-6% in the SH. In absolute terms, the ozone decline, in most of the free troposphere is smaller than 2 ppb. Further experiments in which we switched off the inter-halogen heterogeneous reactions suggest that the tropical response is due to *in situ* tropospheric chemistry. The changes in

243 tropospheric ozone in high latitudes, in contrast, are largely due to transport of ozone-
244 depleted air from the lower stratosphere.
245
246 When Cl_y is ~3 ppb, the maximum SH polar ozone decrease of about 10% shown in figure 1
247 corresponds to ~100 ppb, compared with ~70 ppb for a Cl_y mixing ratio of 0.8 ppb. In the
248 NH, the ozone decrease is about half of the magnitude simulated in the SH.
249
250 Comparing the left and right panels in Figure 1 for the same bromine loadings, we see greater
251 ozone decrease when the chlorine background is higher. Cycles involving both chlorine and
252 bromine radicals will be more efficient at a given bromine concentration when chlorine levels
253 are higher. To demonstrate this clearly, Fig 2 plots the relationship between the ozone and
254 total inorganic Br_y concentrations at ~15 km for (a) 80ºS and (b) 80ºN from our experiments
255 with the different chlorine levels. We note that in all cases ozone decreases almost linearly
256 with increasing Br_y concentrations; straight line fits are given for each Cl_y value. The gradient
257 of the ozone decrease as a function of increasing Br_y is larger by about 30-40% when Cl_y is
258 ~3 ppb compared with Cl_y of ~0.8 ppb. As would be expected given the greater potential for
259 heterogeneous chemistry, there is more ozone loss in the SH than in the NH under the same
260 Cl_y level.
261
262 Comparing the red and blue lines in Figure 2a, we can see that, for a given Br_y level, the
263 ozone concentrations under a pre-industrial (or ozone-recovered) Cl_y of 0.8 ppb are ~500 ppb
264 higher than that at current Cl_y of ~3 ppb in the SH. According to the fit lines in Figure 2a, for
265 a Br_y increase of 20 ppt (a roughly 4-fold increase of VSLS emissions), the ozone decreases
266 are 190 ppb (red line) and 280 ppb (blue line), respectively, considerably less than the
267 chlorine-driven changes. So, even if bromine levels from natural VSLS were to increase very
268 significantly later this century, changes in the concentration of ozone will likely be dominated
269 by the recovery of anthropogenic chlorine.
270
271 We have noted above that longer runs would be required to reveal statistically significant
272 changes in the pairwise ozone differences in the middle and upper stratosphere shown in
273 Figure 1. Consequently, changes in column ozone between the different experiments can be
274 somewhat noisy. However, spatial and temporal averaging, as well as the grouping of
275 experiments together, can improve the statistical significance of the column ozone changes.
276 Focusing on the importance of a 5 ppt Br_y increase under the two different chlorine loadings
277 we can achieve a reasonable estimate of the difference in column ozone by averaging the
278 results from the three different Bry backgrounds for each of the 0.8 ppb and 3.0 ppb Cl_y
279 cases, respectively.
280
281 Figure 3 shows the seasonal evolution of column ozone in high southern latitudes, plotting
282 the average difference when VSLS bromine is increased by 5 pppt for each of the two
283 background chlorine loadings. Again, the relative change in ozone is higher under the higher
284 chlorine loading. Under higher chlorine (red line) we model much lower column ozone
285 globally and a larger ozone hole compared with the Cl_y=0.8 ppb case (black line). For 3 ppb
286 of chlorine a more pronounced seasonal cycle emerges with the ozone differences peaking in
287 Antarctic spring. In spring (October), the modelled total column ozone decrease is about 9
288 DU for the 0.8 ppb chlorine case and about 11 DU for the 3 ppb case. Column differences in
289 the Arctic are only marginal significant, at best, (see figure 4) so we do not discuss the
290 northern hemisphere seasonal evolution.
291
292 Figure 4 shows annually averaged column ozone differences as a function of latitude. The

largest reductions in the column occur in high latitudes, as expected, with a peak reduction of above 8 DU in southern high latitudes under the high chlorine scenario (Figure 4a), which is about 3.5% of the total column ozone (Figure 4b). The changes in figure 4 are smaller at low latitudes (~2 DU or ~1%) and appear to be relatively insensitive to the chlorine background. Note the reduced area of statistical significance in the northern hemisphere (as indicated by the horizontal lines in Figure 4b, see caption for details), especially under low chlorine loading, consistent with much greater dynamical variability there.

All our integrations have used year 2000 boundary conditions so the impact of climate change on the chemistry here has not been considered. Separate integrations looking at ozone recovery under a range of different greenhouse gas scenarios, but with constant boundary conditions for chlorine and bromine source gases, (see Banerjee et al., 2014) do throw some light on possible changes in some key bromine reaction fluxes. For example, focussing just on changes in the stratosphere, the change in the flux through the reaction HO_2+BrO between 2000 and 2100 under RCP8.5 is less than 10% in the lower stratosphere of high southern latitudes, where the calculated changes reported here are highest. Slightly larger changes are found in the tropical very low stratosphere, where ozone concentrations are low, and just above the tropopause in high northern latitudes where dynamically-driven variability in ozone is high. We believe that while climate change will certainly affect the impact of VSLS on ozone recovery it will not change the general results presented here.

4. Conclusions and Discussions

Naturally produced VSLS bromocarbons account for almost a quarter of the current stratospheric inorganic bromine and about half of that in the pre-industrial era. Fundamental emission processes for the VSLS are not well understood so that we are unsure how emissions might have changed in the past or how they will respond to future climate change. Model calculations do suggest (e.g. Dessens et al, 2009; Hossaini et al, 2013) that transport to the stratosphere, where these compounds play an important role in regulating lower stratospheric ozone, will increase in the future. To what extent possible increases in VSLS surface emissions or transport to the stratosphere could counteract the effect of halogen reductions under the Montreal Protocol is an important research question, which we have addressed here using a simple experimental design. In particular, we have asked to what extent the impact of a hypothetical increase in VSLS (we use 5 ppt here) could affect ozone in the lower stratosphere and how that impact depends on the background concentrations of chlorine and bromine.

Our model experiments indicate that for a ~5 ppt increase in inorganic bromine from VSLS, the depletion of stratospheric ozone can reach up to 10% in the annual mean in the lowermost stratosphere of the SH polar region and 4-6% in the NH. Decreases in the ozone column are largest in high latitudes, are greater for higher chlorine levels and are dominated by the ozone reductions in the low stratosphere. The southern hemisphere high latitudes see the largest reductions, with an annual average south of 70°S of around 8 DU (Figure 4a); changes in middle and low latitudes are small.

Ozone losses following an increase in VSLS burden are highest under a high stratospheric chlorine background, indicating the importance of the inter-halogen reactions. Although bromine plays an important role in destroying atmospheric ozone, chlorine concentrations largely dominate the changes in stratospheric ozone concentrations. Even if bromine levels from natural VSLS were to increase significantly later this century, the concentration of

ozone will be dominated by the recovery of anthropogenic chlorine.

It is possible to make a crude estimate of the possible impact on ozone recovery of a hypothetical increase of VSLS bromine. In our calculations, the increase of Br_y by 5 ppt leads to a reduction in modelled springtime (October) Antarctic ozone of about 9 DU for the 0.8 ppb chlorine case and ~11 DU for the 3 ppb chlorine case. A range of chemistry-climate models reported in WMO (2011) and Eyring et al. (2010) give a linearly averaged Antarctic spring time (October) ozone recovery rate of about 1.4 DU/yr between the years 2025 and 2075 (see Figure 3.11 and Table 4 of those papers, respectively). So, our modelled decrease of 9 and 11 DUs, due to the additional 5 ppt of bromine under two different chlorine levels, correspond to a delayed recovery of about 6 and 8 years, respectively. We note, in passing, that although Antarctic ozone recovery is predicted consistently by models for the second half of this century, there are large model-model differences.

In these model studies we have only considered the effect of variations in chlorine and bromine concentrations. We recognize that other changes, including changes in climate and aerosol loading, could also modulate the impact on ozone of changed VSLS emissions. Further studies are required.

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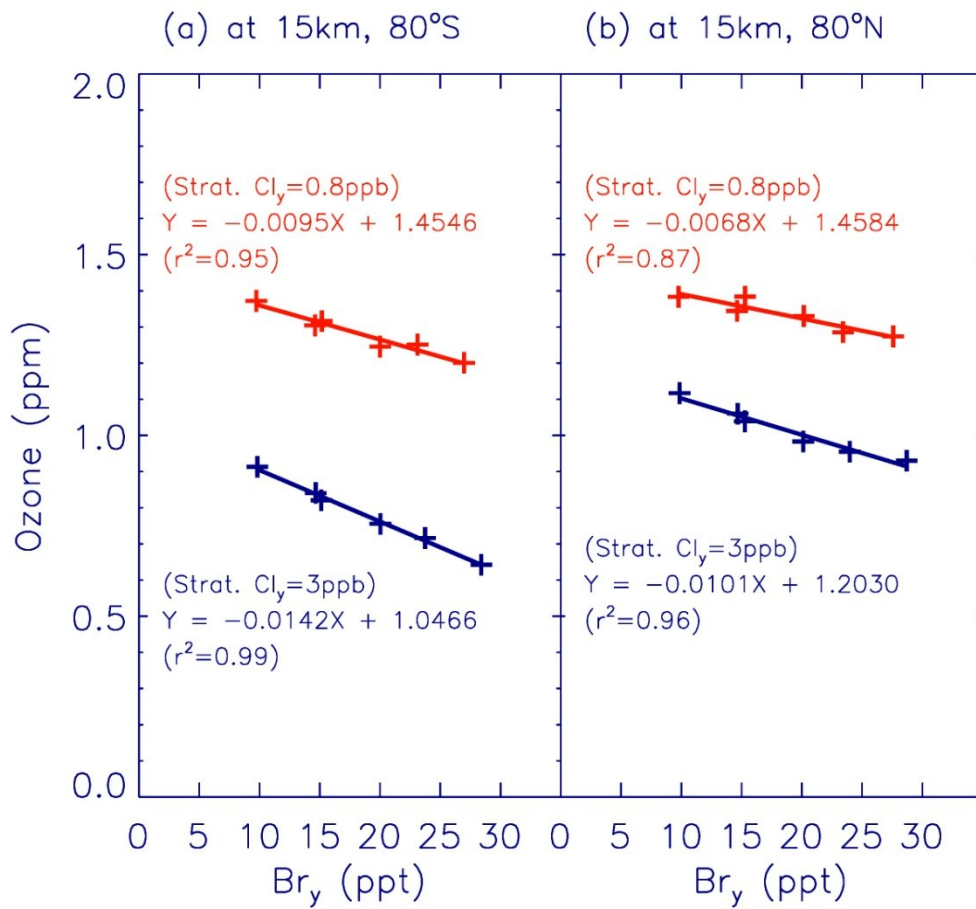503   Geophys. Res.-Atmos., 110, D23309, doi:10.1029/2005JD006303, 2005.
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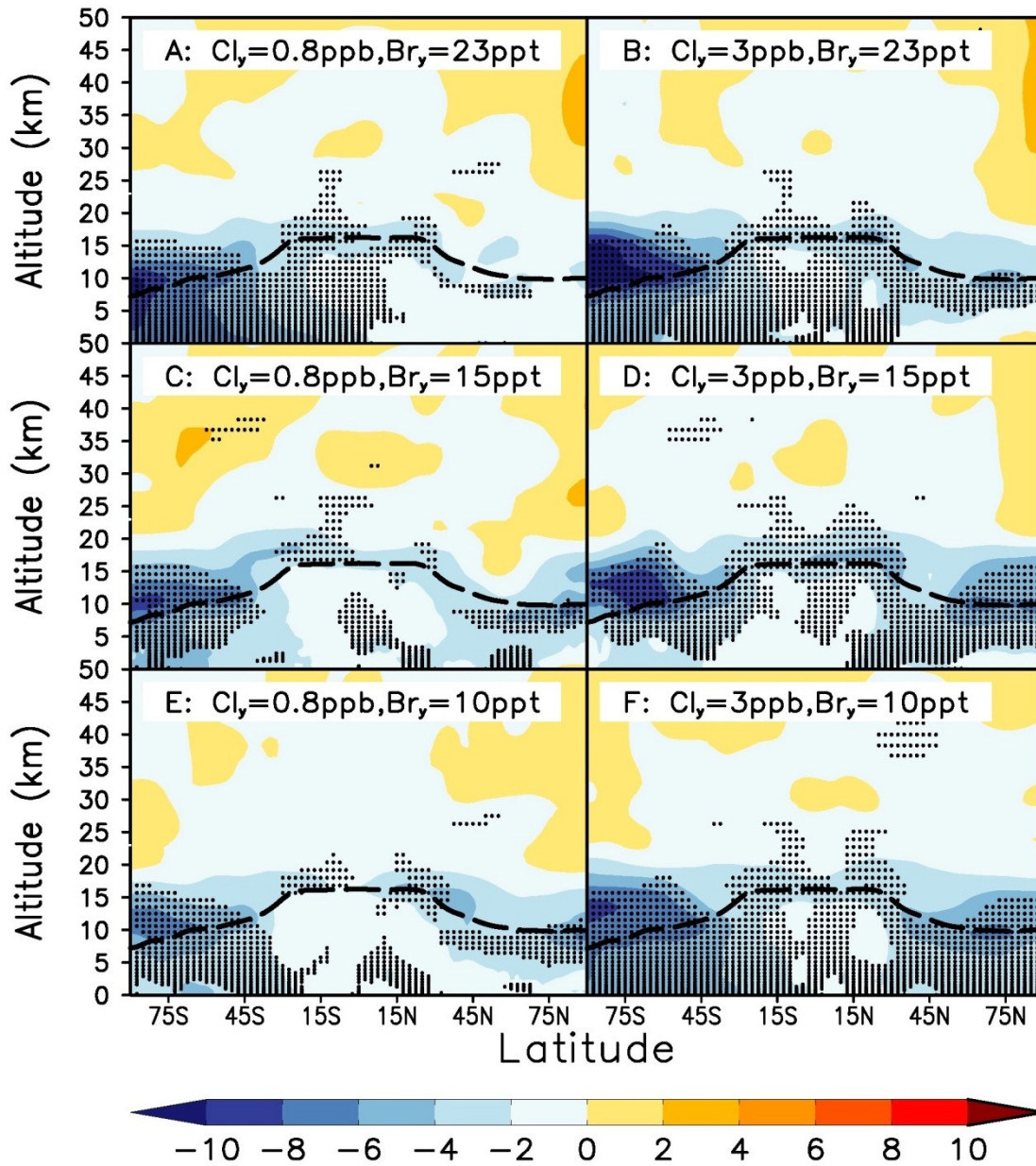
Figure 1 Relative ozone changes (in %) arising from doubling VSLS emissions under 0.8 ppb Cl_y (left column) and 3 ppb Cl_y (right column). The base case Br_y concentrations (with 1xVSLS, representing 5ppt of the total Br_y) increase from the bottom to the top row as indicated in the panels. The dotted regions represent statistically significant signals on a confidence level above 95% as calculated by Student's t-test.

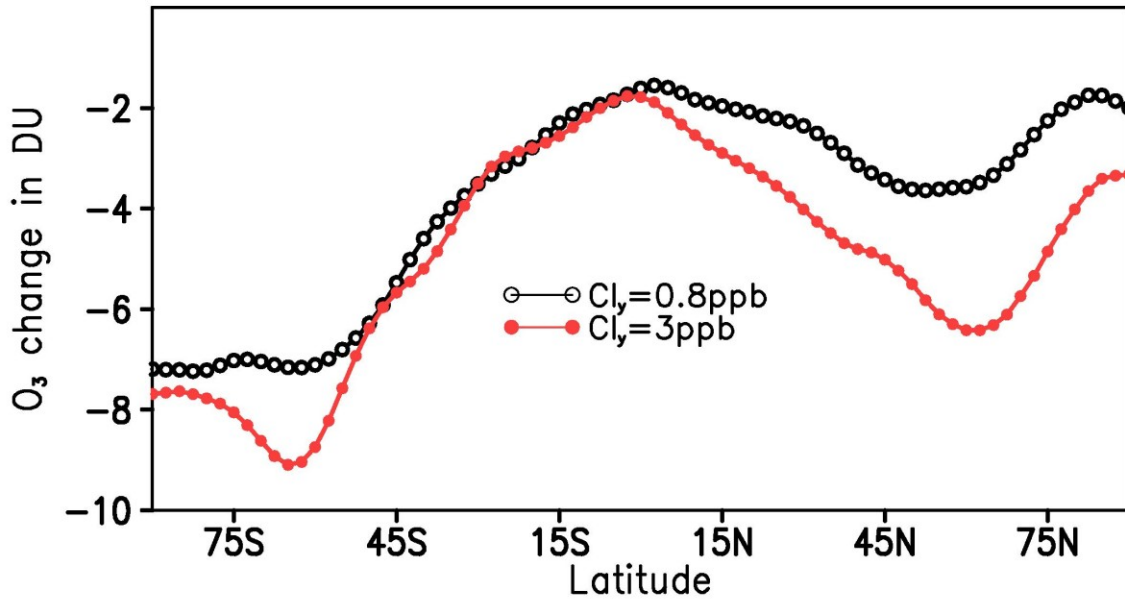(a) at 15km, 80°S

(Strat. Cl_y=0.8ppb)
Y = −0.0095X + 1.4546
(r^2=0.95)

(Strat. Cl_y=3ppb)
Y = −0.0142X + 1.0466
(r^2=0.99)

(b) at 15km, 80°N

(Strat. Cl_y=0.8ppb)
Y = −0.0068X + 1.4584
(r^2=0.87)

(Strat. Cl_y=3ppb)
Y = −0.0101X + 1.2030
(r^2=0.96)

520
521   Figure 2 Relationship between stratospheric ozone concentrations and Br_y at ~15 km and (a)
522   80ºS and (b) 80ºN. Straight lines have been fitted for each Cl_y concentration (red:
523   Cl_y=0.8ppb; blue: Cl_y=3 ppb) and the quality of the fit is indicated by the correlation
524   coefficient (r^2).
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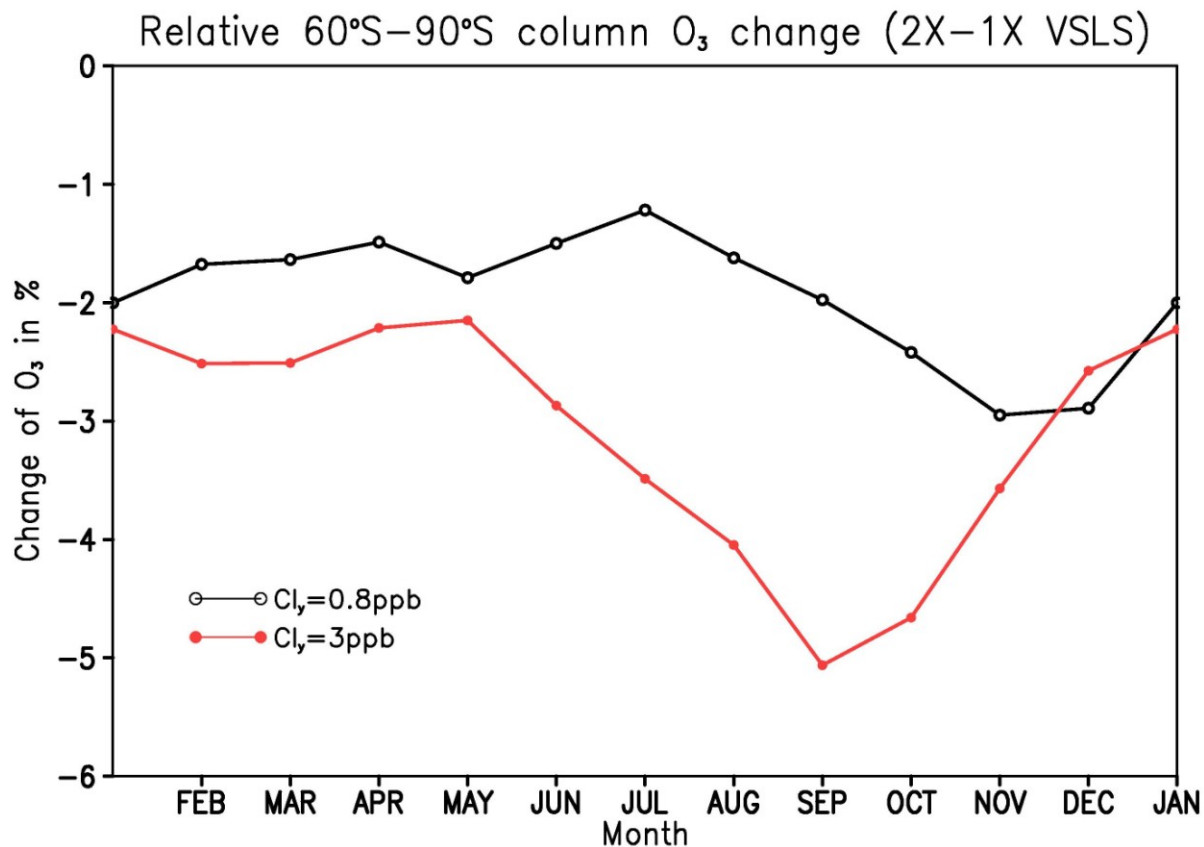
531
532   Figure 3 Relative change of column ozone (in %) due to a doubling of VSLS Br_y averaged
533   over 60°S-90°S. Each line represents one particular Cl_y level (black-open circles: Cl_y=0.8
534   ppb; red-closed circles: Cl_y= 3 ppb). Note that we average the ozone difference over the three
535   different Br_y concentrations for each Cl_y case. The individual results for different background
536   Br_y are shown in Figures 1 and 2.
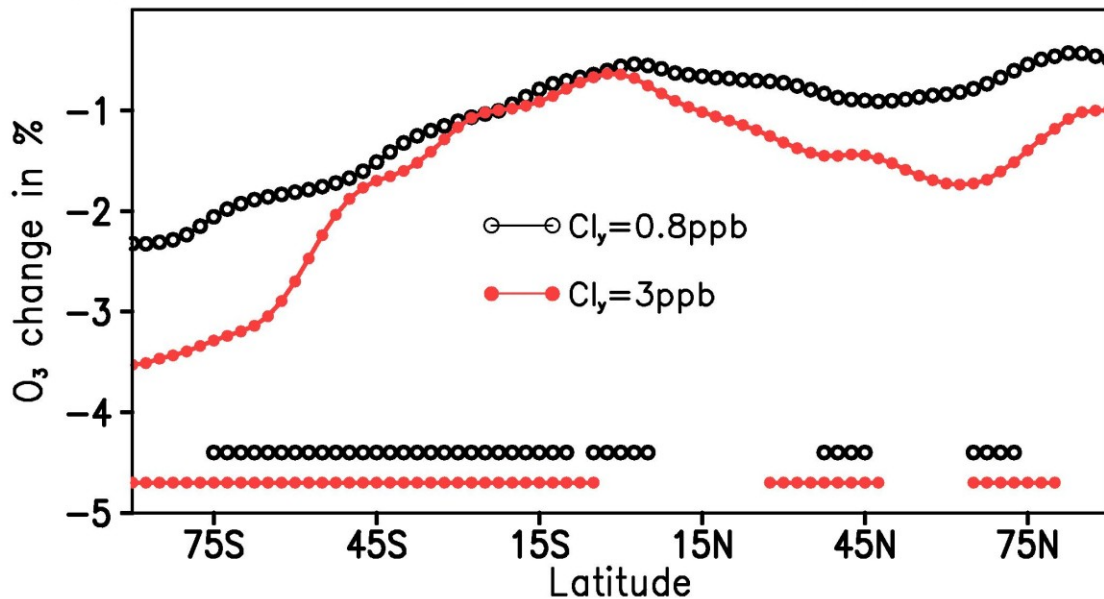
Figure 4 Latitude distributions of annual mean total ozone changes due to a doubling of VSLS. The top panel (a) shows the absolute changes in Dobson Units and the bottom panel (b) shows the relative changes in %. Each line represents one particular Cl_y level (black-open circles: Cl_y=0.8 ppb; red-closed circles: Cl_y= 3 ppb). Note that we average the ozone difference over the three different Br_y concentrations for each Cly case. Corresponding horizontal lines indicate where the differences are significant in each of the three pairs of integrations above a confidence level of 99% as calculated by Student's t-test.