



How sensitive is the recovery of stratospheric ozone

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This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

# How sensitive is the recovery of stratospheric ozone to changes in concentrations of very short lived bromocarbons?

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Received: 25 February 2014 – Accepted: 11 March 2014 – Published: 14 April 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

Naturally produced very short-lived substances (VSLS), like bromocarbons, account for almost a quarter of the current stratospheric inorganic bromine,  $\text{Br}_y$ . Following VSLS oxidation, bromine radicals ( $\text{Br}$  and  $\text{BrO}$ ) can catalytically destroy ozone. The extent to which possible increases in surface emissions or transport of these VSLS bromocarbons to the stratosphere could counteract the effect of halogen reductions under the Montreal Protocol is an important policy question. Here by using a chemistry–climate model, UM-UKCA, we investigate the impact of a hypothetical increase in VSLS on ozone and how that impact depends on the background concentrations of chlorine and bromine. Our model experiments indicate that for a  $\sim 5$  ppt increase in  $\text{Br}_y$  from VSLS, the local ozone loss in the lowermost stratosphere of the Southern Hemisphere (SH) may reach up to 10% in the annual mean; the ozone loss in the Northern Hemisphere (NH) is smaller (4–6%). There is more ozone loss following an increase in VSLS burden under a high stratospheric chlorine background than under a low chlorine background indicating the importance of the inter-halogen reactions. For example, the rate of decline of the stratospheric ozone concentration as a function of  $\text{Br}_y$  is higher by about 30–40% when stratospheric  $\text{Cl}_y$  is  $\sim 3$  ppb (present day) compared with  $\text{Cl}_y$  of  $\sim 0.8$  ppb (apre-industrial or projected future situation). Although bromine plays an important role in destroying ozone, inorganic chlorine is the dominant halogen compound. Even if bromine levels from natural VSLS were to increase significantly later this century, changes in the concentration of ozone will be dominated by the recovery of anthropogenic chlorine. Our calculation suggests that for a 5 ppt increase in  $\text{Br}_y$  from VSLS, the Antarctic ozone hole recover date could be delayed by approximately 7 years.

ACPD

14, 9729–9745, 2014

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## 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 showed that coupled chlorine-bromine reactions made a substantial contribution to the polar loss (e.g. Chipperfield and Pyle, 1998). 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<sub>3</sub>Cl. In contrast the bromine budget of the stratosphere is less well constrained (Dorf et al., 2008; Montzka and Reimann, 2011). 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) with the remainder from methyl bromide and the anthropogenic halons. 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; Yok-

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ouchi et al., 2005).  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  are the dominant contributors to bromine VSLs species. Although their tropospheric lifetime is relatively short (a few weeks for  $\text{CHBr}_3$  and several months for  $\text{CH}_2\text{Br}_2$ ), 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; Ordóñez et al., 2012; Ziska et al., 2013; Pyle et al., 2011; 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; Tegtemier 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 and Reimann, 2011).

While future anthropogenic halogen loading to the stratosphere should decrease in response to the Montreal Protocol, we do not know how natural halogens, like the VSLs, will respond. Their emissions could change with climate, perhaps depending on sea surface temperature, on ocean pH or on surface wind stress. We currently do not have a good enough understanding to allow confident predictions. Changes in transport to the stratosphere could also occur due to climate change. For example, Dessens et al. (2009) and Hossaini et al. (2012b) predict increases in convective and large-scale transport of bromine source gases to the stratosphere, amounting to ~2–3 ppt, under climate change.

Bromine is about 60 times more efficient than chlorine atoms as an ozone sink in the lower stratosphere (Sinnhuber et al., 2009). In addition, gas phase and heterogeneous inter-halogen reactions involving both bromine and chlorine contribute significantly to ozone loss. Thus, the ozone loss to bromine should be dependent on the chlorine concentration. Given that stratospheric inorganic chlorine has increased from pre-industrial levels of ~0.6 ppb to a peak of ~3 ppb in 1990s and will continue to decrease during

this century, it is relevant to investigate how ozone might respond to changes in VLSL loading under different chlorine backgrounds. To what extent could an increase in VLSL  $\text{Br}_y$  delay ozone recovery?

As with chlorine, the stratospheric inorganic bromine loading has been perturbed in recent decades due to the manufacture and release into the atmosphere of halocarbons and given that we do not have a good predictive understanding of future changes, a second aim of this study is to explore the ozone response to VLSL changes under different inorganic bromine backgrounds. In particular, we address how stratospheric ozone changes as a function of inorganic bromine concentrations under a fixed chlorine background.

To address these questions, we use the UM-UKCA chemistry-climate model. We perform a number of idealized experiments under two different stratospheric chlorine concentrations. In each case we perturb the VLSL concentrations and consider a range of bromine concentrations. These experiments then allow us to explore how ozone loss due to short lived halocarbons could vary with background chlorine and bromine loading. The model and the experimental set-up are described in Sect. 2. The model results are presented in Sect. 3. Concluding discussion is found in Sect. 4.

## 2 Model and experiments

UM-UKCA is a chemistry-climate model; its dynamical core is the Met Office Unified Model (UM) version 7.3 running in the HadGEM3-A configuration (similar to Hewitt et al., 2011). The detailed chemistry scheme for the troposphere and stratosphere, CheST, combines the schemes described by Morgenstern et al. (2009) and O'Connor et al. (2014) and was further updated with tropospheric bromine chemistry based on our work in the  $p$ TOMCAT CTM (Yang et al., 2005, 2010). The stratospheric halogen scheme is improved by introducing a number of heterogeneous reactions on stratospheric particles (stratospheric polar clouds PSCs and sulphate aerosol) to account for inter-halogen (chlorine and bromine) reactivation as in our recent study (Braesicke

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et al., 2013). The model's horizontal resolution is  $3.75^\circ$  in longitude and  $2.5^\circ$  in latitude on an Arakawa-C grid. A hybrid sigma-geometric height coordinate is used to resolve the vertical range from the surface to  $\sim 84$  km with 60 levels. All experiments are performed for year 2000 boundary conditions with prescribed monthly sea surface temperatures (SSTs) and sea ice conditions. The radiative species concentrations for  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CH}_4$  are taken for year 2000; ozone is calculated interactively. Apart from the halocarbons (e.g. CFCs,  $\text{CH}_3\text{Br}$ ), chemical emissions are for the present day. The sulphate aerosol field is a monthly climatology. Polar stratospheric clouds and ice particles are calculated online based on water vapour fields and temperatures. To get significant results, each of the experiments was performed as a 40 year time-slice integration with the first 20 years as spin-up and the last 20 years for analysis.

Here we chose two stratospheric chlorine levels of  $\sim 0.8$  ppb and  $\sim 3$  ppb to represent a pre-industrial era and a present day situation respectively. These mixing ratios were achieved by applying fixed concentrations in the model's lowest layer for the major chlorine species, CFCs,  $\text{CH}_3\text{Cl}$  and  $\text{CCl}_4$ . Note that the low chlorine level of 0.8 ppb also represents a likely chlorine level in the future, on a Montreal Protocol trajectory towards "recovery", according to projected mitigation scenarios for 2100. For stratospheric inorganic bromine, we chose three levels of  $\sim 10$  ppt,  $\sim 15$  ppt and  $\sim 24$  ppt to represent a low (pre-industrial era), a medium and a high (present day) level respectively. These values all include  $\sim 5$  ppt from VLSL (as mentioned below) with the remaining  $\text{Br}_y$  coming from long-lived halons and  $\text{CH}_3\text{Br}$ . These values are somewhat arbitrary; our simple aim is to explore a range of  $\text{Br}_y$  values and, based on them, to investigate the ozone response to a perturbed (doubled) VLSL emission.

For the VLSL, we have introduced tracers for 5 additional species ( $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ ) with emissions based on the original work (scenario 5) of Warwick et al. (2006), except for emissions of  $\text{CH}_2\text{Br}_2$  which were updated to  $57 \text{ Ggyr}^{-1}$ , 50% of the original flux but now much more in accord with Liang et al. (2010), and Ordonez et al. (2012). Our updated fluxes gave  $\sim 5$  ppt of inorganic

bromine to the stratosphere (so that for a doubled VLSL emission, the  $\text{Br}_y$  from VLSL is about 10 ppt).

### 3 Result and discussions

Our experiments are designed to address the question of how changes in VLSL would impact stratospheric ozone, against a background of changes in stratospheric chlorine and bromine loading. Figure 1 shows the annual zonal mean ozone differences between pairs of runs in which the VLSL bromine contribution was increased by 5 ppt. (We plot the  $2 \times \text{VLSL} - 1 \times \text{VLSL}$  ozone differences.) The left column represents experiments with a low stratospheric  $\text{Cl}_y$  of 0.8 ppb, perhaps representative of a pre-industrial atmosphere or after a substantial reduction in halogen loading. The right column has  $\text{Cl}_y$  of  $\sim 3$  ppb, roughly representative of the present day. The panels from top to bottom have, respectively, a high inorganic bromine background of  $\sim 24$  ppt (Fig. 1a and b), of  $\sim 15$  ppt (Fig. 1c and d) and a low bromine background of  $\sim 10$  ppt (Fig. 1e and f).

For a doubled VLSL emission, with an extra  $\sim 5$  ppt  $\text{Br}_y$  in the stratosphere, the ozone changes in these runs are statistically significant ( $P < 0.05$ ) (marked with dots in Fig. 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 but changes there are small, and we focus here on the lowermost stratosphere where VLSL has a more important role. At these heights in the Southern Hemisphere (SH), the largest annual mean ozone loss is about 10 %, while in the Northern Hemisphere (NH) high latitudes, the ozone loss is  $\sim 4$ –6 %. Near the tropical tropopause, ozone losses of 2–4 % are modelled. In terms of the seasonal response, the significant ozone loss in the SH starts in local spring (October) and reaches its maximum of  $\sim 20$  % in earlier summer around November (not shown here).

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It is interesting to see that the ozone loss is significant in most of the troposphere, with a weak loss of < 2% in the tropics; 2–4% in high latitudes of the NH and 2–6% in the SH. The tropospheric ozone changes are likely a response to both the reduction in stratosphere to troposphere transport of ozone and in situ chemical loss, given the higher tropospheric bromine concentrations.

When  $Cl_y$  is  $\sim 3$  ppb, the maximum SH polar ozone loss of about 10% shown in Fig. 1 corresponds to  $\sim 100$  ppb, compared with  $\sim 70$  ppb for a  $Cl_y$  of 0.8 ppb. In the NH, the ozone loss is about half of the magnitude simulated in the SH and the tropical tropopause losses are only a few ppb.

Comparing the left and right panels in Fig. 1 for the same bromine loadings, we see greater ozone loss when the chlorine background is higher. Cycles involving both chlorine and bromine radicals will, of course, be more efficient at a given bromine concentration when chlorine levels are higher. To demonstrate this clearly, Fig. 2 plots the relationship between the ozone and inorganic  $Br_y$  concentrations at  $\sim 15$  km for (a)  $80^\circ$  S and (b)  $80^\circ$  N from our experiments with the different chlorine levels. In all cases, ozone decreases almost linearly with increasing  $Br_y$  concentrations; straight line fits are presented for each case. The rate of decline of the ozone concentration as a function of  $Br_y$  is higher by about 30–40% when  $Cl_y$  is  $\sim 3$  ppb compared with  $Cl_y$  of  $\sim 0.8$  ppb. As would be expected given the greater potential for heterogeneous chemistry, there is more ozone loss in the SH than in the NH under the same  $Cl_y$  level.

Comparing the red and black line in Fig. 2a, we can see that, for a given  $Br_y$  level, the ozone concentrations under a pre-industrial (or ozone-recovered)  $Cl_y$  of 0.8 ppb are  $\sim 500$  ppb higher than that at current  $Cl_y$  of  $\sim 3$  ppb in the SH. According to the fit lines in Fig. 2a, for a  $Br_y$  increase of 20 ppt (a roughly 4-fold increase of VSLs emissions), the ozone decreases are 190 ppb (red line) and 280 ppb (black line), respectively. So, even if bromine levels from natural VSLs were to increase very significantly later this century, changes in the concentration of ozone will be dominated by the recovery of anthropogenic chlorine.

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We have noted above that longer runs would be required to reveal statistically significant changes in the middle and upper stratosphere and consequently the changes in column ozone between the different experiments are somewhat noisy. Nevertheless, we can make a reasonable estimate of the impact on the column by averaging the different experiments for 0.8 ppb and 3.0 ppb  $\text{Cl}_y$ , respectively. These results, for the annual average, are shown in Fig. 3 and represent the average change in column ozone for an increase in  $\text{Br}_y$  of 5 ppt, for the two different chlorine loadings. The results are dominated by concentration changes below 20 km (where, if we similarly average the left and right columns of Fig. 1, where we see consistent, statistically significant reductions below about 20 km, and small, non-significant changes above). The largest reductions in the column occur in high latitudes, as expected, with a peak reduction of about 9 DU in southern high latitudes under the high chlorine scenario. The changes in Fig. 3 are smaller at low latitudes and appear to be relatively insensitive to the chlorine background.

## 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; Hos-saini 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  $\sim 5$  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. 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. Changes in the ozone column are highest in high latitudes, are greater for higher chlorine levels and are dominated by the ozone reductions in the low stratosphere. The Southern Hemisphere sees the largest reductions, with an annual average around 8 DU; changes in middle and low latitudes are small.

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 with  $\text{Cl}_y = 0.8$  ppb, the increase of  $\text{Br}_y$  by 5 ppt leads to a reduction in modelled springtime Antarctic ozone of about 10 DU. A range of chemistry-climate models reported in WMO (2011) and Eyring et al. (2010) give an average Antarctic spring time (October) ozone recovery rate of  $1.4 \text{ DU yr}^{-1}$  since year 2000 (see Fig. 3.11 and Table 4 of those papers, respectively). So, our modelled decrease of 10DU corresponds to a delayed recovery of about 7 years due to the additional 5 ppt of bromine. We note, in passing, that although Antarctic ozone recovery is predicted consistently for the second half of this century, there are large model-model differences.

*Acknowledgements.* JAP and XY thank the EU for support through SHIVA (SHIVA-226224-EP7-ENV-2008-1) and the ERC for support through the ACCI project (Project number 267760). We thank NCAS-CMS for modelling support. Model integrations have been performed using the UK National Supercomputing Service HECToR.

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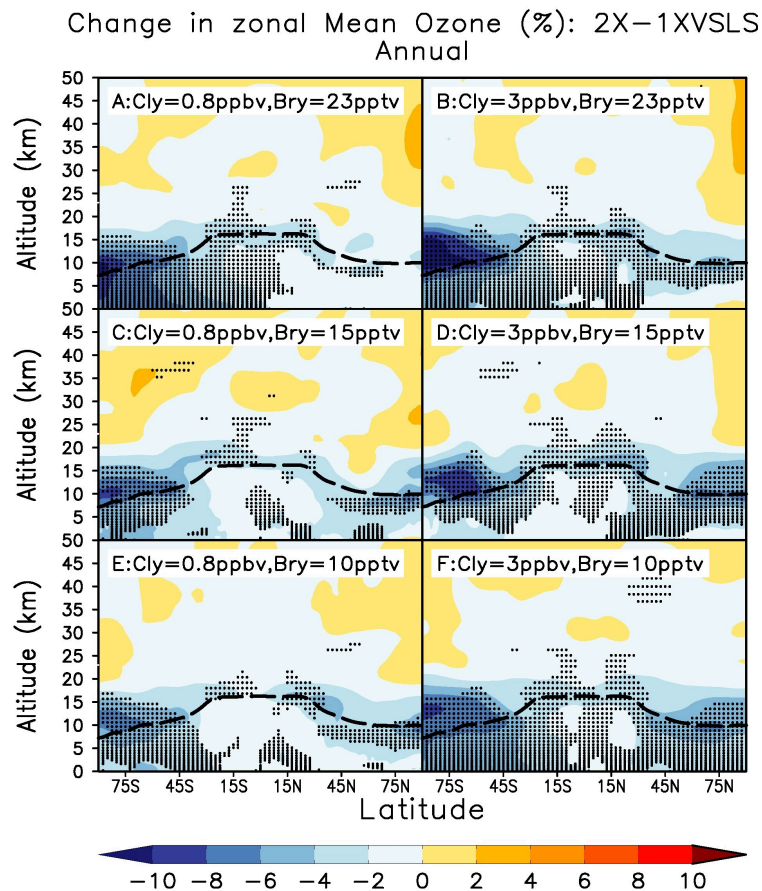
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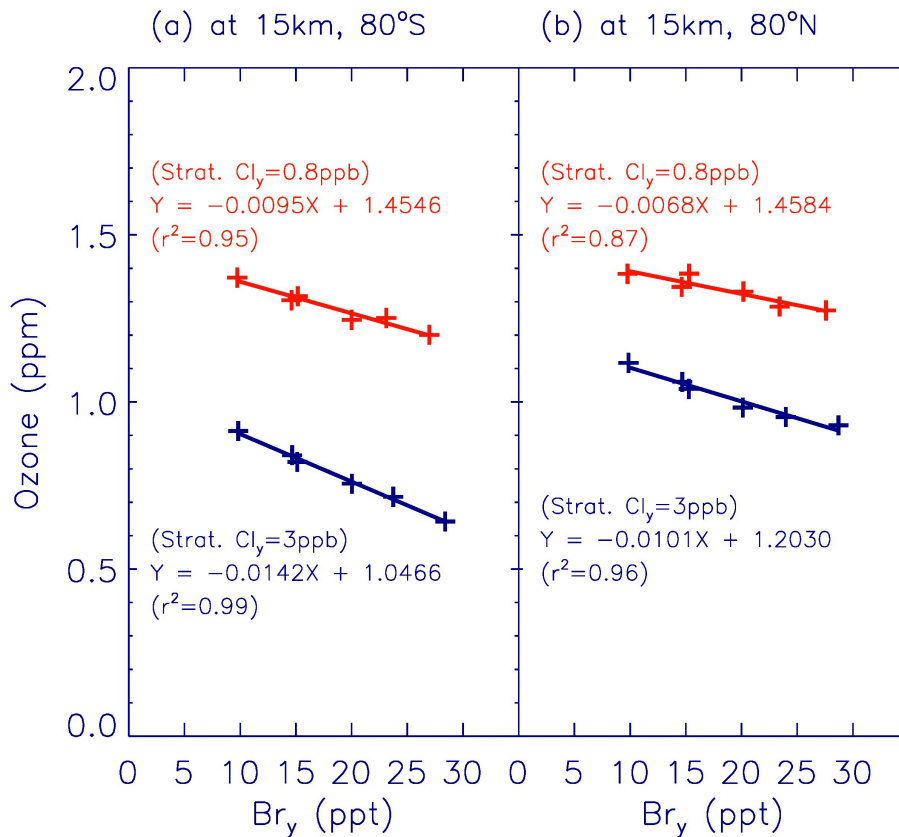


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**Fig. 1.** Ozone percentage changes arising from doubling VLSL emissions. The region with dots represents a statistically significant signal on confidence level of 95%.

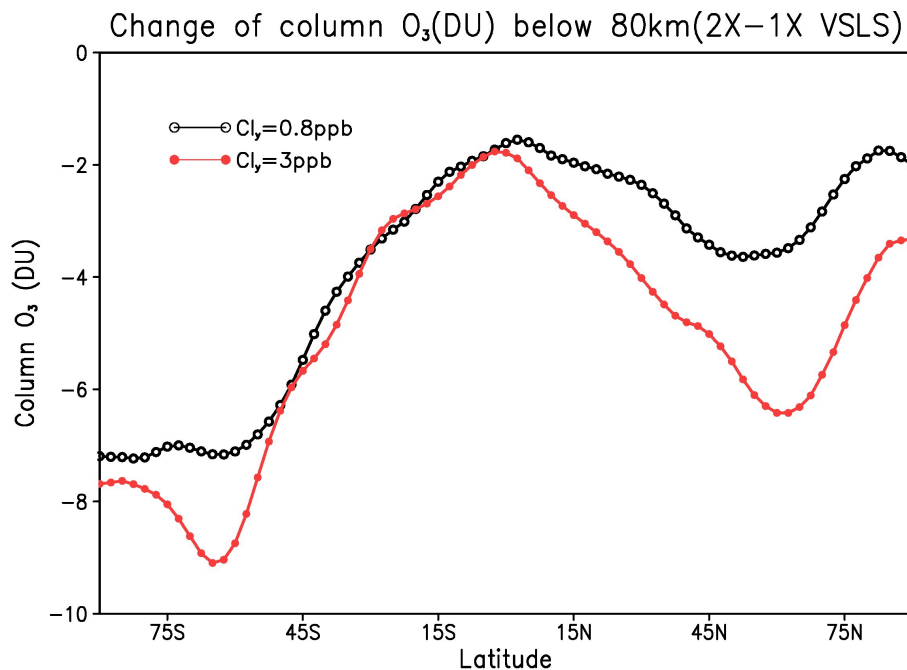


**Fig. 2.** Relationship between stratospheric ozone concentrations and  $\text{Br}_y$  at height of  $\sim 15$  km over  $80^\circ$  S (a) and  $80^\circ$  N (b). Note that a straight line is fitted applied for each case.



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**Fig. 3.** Annual average change in total column ozone (Dobson units) between runs with and without an additional 5 ppt VLSL  $Br_y$ , for  $Cl_y = 0.8$  ppb (open black circles) and  $Cl_y = 3$  ppb (filled red circles).

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