

We thank all the three referees for their thoughtful comments and their efforts towards improving the manuscript. We have considered their comments and respond below.

Anonymous Referee #1

General Comments

The work by Yang et al. presents a simple modeling experiment using a complex 3-D climatic model to give an estimation of the changes in the ozone depletion due to a hypothetical increase of VSL bromine stratospheric injection. **the experiments and results are not presented clearly.**

We thank the referee for helping us to clarify our paper. Our detailed response is given below.

Mayor Comments

The description of the experiments and the results obtained is not presented in an easy ..format.

D) **referencing previous publications for the proposed scenarios:** ... They clearly define the range of stratospheric bromine values publishedbut.... **there are no other references supporting the inorganic chlorine levels they used for the simulations.** See for example the following sentences related to inorganic chlorine. page 9731, line 20 (present day burden) page 9732, line 30 (evolution from past to present) page 9734, line 12 (model setup) Even when the work is mostly based on bromine-mediated ozone losses, I suggest the authors to introduce proper references related to inorganic chlorine burden and evolution.

We have substantially revised Section 1 and 2 and have added references to support our "pre-industrial" values (e.g., Harper and Hamilton, 2003 for chlorine and Saltzman et al, 2008, for bromine). We hope that we have now clarified in the paper why we made the concentration choices that we have. We reiterate that the precise details do not affect the experimental design. Our purpose is the study a RANGE of chlorine and bromine concentrations and we have now explained that motivation more clearly in the text. We further explain that the boundary conditions come from published scenarios, e.g., as used in the WMO/UNEP assessments.

What would usually be a minor comment is that the authors cite (Eyring et al., 2010) and the correspondent bibliography is missing in the reference section. The omission in this case is not minor as they point out to a specific table on that publication, which is used to compute an ozone recovery rate of 1.4 DU yr^{-1} . Please introduce the

missing reference and make clear how you reached that value using the data from Table 4 of Eyring et al., ACP, 2010.

Apologies. This reference is now included and we say the 1.4DU yr⁻¹ come from the linear trend using the values given from 2025 and 2075. See our response to Referee 2, below.

II) Describing the details of the experimental setup for each run.

We have completely restructured section 2, describing the experimental design, and have also added new clarifying text. We trust that the set up is now understandable.

III) Presenting clearly the results when comparing a pair of runs.

Figure 1: Even when the work is focused on stratospheric ozone changes, the authors state that “It is interesting to see that the ozone loss is significant in most of the troposphere” and they present percentage differences. But do not describe whether those differences depend on the Cly and Bry background, or on the doubling of VSLs. Also they recognize that “Near the tropical tropopause, ozone losses of 2–4 [*we think there was something missing here from the referee’s report?*]

*We have added a small piece of text to explain the origin of the tropospheric changes. But please note that our objective here is to look at the impact of VSLs on stratospheric ozone recovery. Tropospheric ozone change is not the focus of this paper. Paragraph now reads: “It is interesting to see that the 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 tropospheric ozone in high latitudes, in contrast, are largely due to transport of ozone-depleted air from the lower stratosphere.”*

Figure 2: What is the purpose of the linear fitting for each Cly experiment? The authors do not discuss at all why this relationship is linear. The authors also mention a “black” line (i.e. line 21 (page 9736), and somewhere else), but the figure only includes “blue” and “red” lines.

The colours were wrongly labelled. This has been corrected.

There is no agenda (no extra purpose) in showing the linear fits. It is a FACT that when we plot ozone vs Bry we find the linear relationship as given; that is all that we are saying.

Figure 3: I am not sure if the procedure used for averaging simulations in Figure 3 is useful, or instead, it makes difficult the interpretation and may be misleading. Why have the authors averaged simulations with different background stratospheric Bry and identical Cly? Even when they mention that it reduces noise in the middle and upper stratosphere, most of the O3 column changes between 1xVSL and 2xVSL occur in the lower stratosphere, where the O3 loss is different for each of the Bry background scenarios (Fig. 1). I suggest describing the averaging method in a more clear way, as well as introducing in the Figure a caption/label indicating if the lines correspond to a specific pair of simulations (background Bry), or to the average of them. Also, the sentence following “. . .if we similarly average the left and right columns of Fig. 1. . .” is confusing or not well explained, confusing the reader on the procedure applied to generate Figure 3.

We now include a bit more discussion on statistical significance as well as including more detail in the figure captions. We think that the new figure 4 quite nicely demonstrates the significance issue – the northern hemisphere changes are only significant in some locations, even when averaged annually.

New paragraph in section 3: “We have noted above that longer runs would be required to reveal statistically significant changes in the pairwise ozone differences in the middle and upper stratosphere shown in Figure 1. Consequently, changes in column ozone between the different experiments can be somewhat noisy. However, spatial and temporal averaging, as well as the grouping of experiments together, can improve the statistical significance of the column ozone changes. Focusing on the importance of a 5ppt Br_y increase under the two different chlorine loadings we can achieve a reasonable estimate of the difference in column ozone by averaging the results from the three different Bry backgrounds for each of the 0.8ppb and 3.0ppb Cl_y cases, respectively. ”

The authors also state that “The Southern Hemisphere sees the largest reductions, with an annual average around 8 DU”. It is not clear how they reach that value looking at Figure 3? Which latitudinal range within the SH are the authors pointing at? For which Cly and Bry backgrounds? Also, as the averaging procedure is not well justified, the final conclusion (“crude estimate”) reached at the end of the paper on the delay of antarctic ozone recovery is quite uncertain, and should be further justified.

We now explain more clearly where the figure of 8DU comes from and that this applies to high southern latitudes only, and not to all the SH.

New text: Lines 292-294: 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...

Lines 334-336: The southern hemisphere high latitudes see the largest reductions, with an annual average south of 70°S of around 8DU (Figure 4a); changes in middle and low latitudes are small.

Minor comments:

Even when the 10, 15 and 24 ppt values can be chosen “somewhat arbitrary”, the authors should indicate the *reasons/references* that lead them to restrict the sensitivity study to that specific range.

****We believe the revised sections 1 and 2 make this clear now.****

As main results and conclusions are expected to be included in the abstract, the use of “for example” in this context is not appropriate. Additionally, what do you mean by *compound* in the following sentence of the abstract (line18): “Although bromine plays an important role in destroying ozone, inorganic chlorine is the dominant halogen compound.”

‘For example’ is now removed.

Avoid using the word “perhaps” or “of course”. In any case, cite a corresponding reference, or explain why this would be the case (i.e., page 9732, line 17; page 9736 line 12).

We cannot see any reason why these words should not be used. However, it is not a big issue and we are content to comply.

P9732. (Our line 104) We have added references to Gschwand et al and Keppler et al. indicating that oceanic production of the bromomcarbons is a biochemical process; it follows that the emissions will likely depend on the processes mentioned.

P9736, removed

The sentence starting at page 9733 line 4 is very long and should be re-written.

Done. Section 1 has been substantially reordered and should now be much clearer.

What do you mean by “against” in the first sentence of Section 3, Results and Discussions?

That sentence has now gone.

Page 9735, line 8. The complete sentence cannot be included into a parenthesis.

Please consider re-writing: “(We plot the $2 \times \text{VSLs} - 1 \times \text{VSLs}$ ozone differences.)”

Parentheses now removed.

Typo errors:

There is a “space” missing in the abstract: line 18. a (space) pre-industrial There is no sense on defining acronyms for NH and SH if they are not used later in the abstract.

Agreed, changed.

Anonymous Referee #2

This study investigates the sensitivity of stratospheric ozone to bromine from very short lived source gases (VSLS) under different levels of the stratospheric chlorine and bromine loading. It is based on a set of idealized time slice calculations with a chemistry climate model to represent possible future bromine and chlorine levels. This study addresses an important topic and should be published in ACP after consideration of the following, mostly minor, points. The manuscript is generally well written and I have only a few suggestions for improving the language.

Thanks for these positive comments.

General comments

1. There are *previous studies* that have investigated the impact of additional bromine from VSLS on stratospheric ozone that need to be cited here.

Salawitch et al., GRL, 2005 and Feng et al., ACP, 2007 are now cited

2. Salawitch et al. (2005) and Sinnhuber et al. (2009) have noted that the impact of VSLS on stratospheric ozone is particularly strong in the presence of enhanced aerosol loading. This study uses year 2000 conditions, that may represent a grand minimum in the I would recommend to include at least a discussion or caveat, how the aerosol loading may effect the results of this study.

These paper are now mentioned and the caveat included.

3. As the authors rightly say, we have very little understanding at present if or how the emission of VSLS may change in the coming decades. In this respect the finding of a 7 year delay in the recovery of the ozone hole for a 5ppt increase in bromine from VSLS has to be treated just as a sensitivity calculation. However, the chemistry climate models reported in WMO (2011) when following the REF-B2 specifications did not consider bromine from VSLS. So you could probably make the much stronger statement here, that considering VSLS with a likely present day contribution of about 5ppt will lead to a delay of the projected ozone hole recovery by about 7 years relative to previous estimates.

Referee 1, in contrast, wanted us to be more cautious about this statement. We have left the message essentially unchanged from the first draft but we have expanded the argument slightly, qualifying the 7 years. Readers, of course, may draw this interesting conclusion.

Modified text now reads: 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.

4. The results show the largest impact in the SH high latitude lowermost stratosphere, likely related to the Antarctic ozone hole. But why are Figs. 1 to 3 restricted to annual means only? If possible it may be worth showing also October for SH and March for NH in Figs. 1 and 2, or showing the total ozone changes in Fig. 3 as a function of latitude and season.

We have added a further figure, a new figure 3, showing the seasonal changes in high southern latitudes (where the column changes are largest). We don't show seasonal changes in the north where dynamical variability dominates and the chemical changes are not always statistically significant. We have added more text about statistical significance and hope that this is clear now.

Specific comments

p.9730, l.2: "like bromocarbons": the bromine containing VSLs are all bromocarbons, so the phrase should be changed accordingly

Removed

p.9730, l.20: "inorganic chlorine is the dominant halogen compound". What do you mean here? Ozone loss is dominated by chlorine? What about mixed bromine/chlorine cycles, how to attribute these? Bromine increases the importance of chlorine, but without chlorine, bromine is less effective...

That sentence which also confused referee 1 has been removed. The message we were trying to convey is now incorporated into a new sentence (lines 36-38) "However, even if bromine levels from natural VSLs were to increase significantly later this century, changes in the concentration of ozone will likely be dominated by the decrease of anthropogenic chlorine. "

p.9730, l.21: "recovery of anthropogenic chlorine". I suggest to better say "decrease of anthropogenic chlorine"

Done

p.9731, l.25: I find it slightly odd to call the remaining 80% the "remainder". p.9731,

Removed

l.27: Reference for pre-industrial VSLs contribution?

See our earlier responses to Referee 1 concerning the Cly and Bry values considered. Turning specifically to VSLs, we are not aware of any published estimates of PI values – we very much doubt there are any. Keeping the 5ppt constant seems the most sensible approach. Note that we do now mention the Saltzman et al ice core paper, which allows an estimate of PI methyl bromide.

p.9732, l.17: natural halogens will not respond to the Montreal Protocol. Better say "... may change in the future".

Changed as requested.

p.9732, l.22: I could not find a statement on a possible increase of 2-3ppt of bromine in Hossaini et al. (2012).

Thanks. That sentence now reads: "For example, Hossaini et al. (2012b) predict 0.3-1.0 ppt increases in the direct transport of bromine source gases to the stratosphere between 2000 and 2100 under RCPs 4.5 and 8.5 while the earlier study of Dessens et al. (2009) projects a 1-2 ppt increase in total bromine in the lower stratosphere."

p.9732, l.25: Strictly speaking, the value of 60 is valid for global mean total ozone. In the lower stratosphere the efficiency of bromine relative to chlorine is even larger than the factor 60 (see Sinnhuber et al., 2009).

We now say: “Bromine is about 100 times more efficient than chlorine as an ozone sink in the high latitude lower stratosphere, with an annual average global value of around 65 (Sinnhuber et al., 2009).”

p.9733, 1.4: sentence hard to read. please rephrase.

Section 1 has been changed substantially and this sentence no longer appears.

p.9735, 1.23: Near the tropical tropopause the ozone response to VLSL seems to be largely independent of the chlorine loading, which makes sense as inorganic chlorine is very low there. This impact on tropical ozone may be worth discussing in a bit more detail. Can you put these 2-4% changes due to VLSL into context of other projected changes? I.e., do VLSL play an important role for tropical ozone, or is this of minor importance?

The modelled change is very small (<10ppb) and this is now mentioned for context on line 231-233. “Near the tropical tropopause, an ozone decline of 2-4% is modelled. Since the ozone concentration near the tropopause is low, these losses are very small in absolute terms (<10 ppbv).”

p.9738, 1.15: Again, the changes in the tropics are smaller than in the extra tropics, but that does not mean they are not important. In particular as they are largely independent of the chlorine loading.

We prefer to keep to the statement that low latitude changes are small.

Fig.1: The label "Bry=23ppt" etc. is unclear. As I understand this represents the difference between Bry=28ppt and Bry=23ppt, right?

Yes, you are right. The text in section 2 and the figure caption have both been changed to clarify what we are doing and what we have plotted.

Fig.2: (a) Is this annual mean? (b) Why is Bry different for different chlorine levels? Was local Bry used in these plots?

Yes, it is annual mean and the Bry values used in figure 2 are local numbers (ie. it is Bry at ~ 15 km, as stated in the caption). The Bry gradients in the stratosphere are very small so that it makes a very small difference whether local or upper stratospheric Bry is used (for example, the difference in the coefficients of the straight line fit are at most a few percents).

Again, we hope that the new text (and figure captions) explains more clearly what we are doing.

Fig.3: I understand this figure has been constructed by averaging the simulations with different bromine loading. Can you give a measure for the coherence between the simulations, e.g. by including error bars of the standard deviation or similar? Where are changes between high chlorine and low chlorine (red and black lines) significant?

This figure has now become figure 4 (where we plot both absolute and relative changes). Statistical significance is explained and indicated in the figure.

Technical corrections

p.9730, 1.18: "apre" -> "a pre"

p.9732, 1.12: "Tegtemier" -> "Tegtmeier"

p.9733, 1.26: "stratospheric polar clouds" -> "polar stratospheric clouds" p.9736, 1.21: "black" -> "blue"

p.9737, 1.9: "where" -> "we"

All these changes have been made.

Anonymous Referee #3

Major Comments:

1. There is so much more that could be done to study the effect of VSLS on ozone.
2. Most of the modeled the impact of VSLS halocarbons on atmospheric ozone is found below the tropopause. Yet, iodine is apparently not in the model....

Referee 3 criticises us mainly because we did not write a more extensive paper covering a large number of possible issues related to ozone recovery.

In contrast, our aim is stated very clearly – to address the issue of the impact of possible increases in VSLS bromocarbons on stratospheric ozone in the future. This is a simple, highly focussed objective and we have tried to write a correspondingly short and direct paper to this effect.

The paper deals with stratospheric ozone; we neither focus on nor discuss in detail the tropospheric changes seen in our global model (but their contribution to column changes is small). So, dealing with iodine, its tropospheric chemistry and extremely uncertain emission regions and emission strengths would completely change the focus of the paper. Similarly VSLS chlorocarbons are indeed starting to be discussed but, at this stage, any modelling studies would be highly speculative. There would be nothing wrong with that; it simply is not our aim here.

We restrict our integrations to a present day climate (but have considered future climate in our papers by Dessens et al and Hossaini et al). The referee specifically raises the role under climate change of HO₂+BrO.....

We have added caveats in the paper saying that we have not, for example, considered changes in aerosol loading (and we refer to further papers). We have also added a few sentences about HO₂+BrO where calculations by our colleague Tara Banerjee suggest that changes with climate change are generally small.

New text: lines 138-152, at end of section 1: “Other changes could also affect stratospheric ozone recovery (and the contribution of bromine changes to ozone recovery). Several previous studies have looked at the impact of VSLS bromocarbons on ozone trends in the recent past (e.g. Salawitch et al., 2005; Feng et al., 2007; Sinnhuber et al, 2009). They show that the effect of VSLS on ozone is particularly important under enhanced aerosol loading. Transient changes due to volcanic eruptions would certainly affect the trajectory of recovery while a sustained increase in stratospheric aerosol would also lead to a general decrease in ozone and an increased role of bromine, and chlorine, heterogeneous processing. However, in the calculations here aerosol loading is held constant. Climate change will also affect the recovery of stratospheric ozone, as is well known. Salawitch et al. (2005) show that, while the effect of bromine on ozone is dominated by the ClO+BrO reaction in the lowermost stratosphere, the reaction of BrO+HO₂ becomes increasingly important with increasing VSLS. Thus any change in HO₂ in the future could potentially affect the estimation of the ozone impact from these changes in halogens. We do not deal with this in detail here although we do mention in Section 3 possible changes in the flux through the BrO+HO₂ reaction under climate change.”

Lines 301-312 at end of section 3: “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 $\text{HO}_2 + \text{BrO}$ 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.”

A further issues mentioned by the referee includes geoengineering. The issues mentioned are all potential areas for future investigation but they are simply not what this paper is about. We state our aims and objectives very clearly. We strongly reject the notion that we have ‘swept under the rug’ these other issues. I am sure the referee did not intend to suggest that we are hiding material but we did find that phrasing very unfortunate.

Referee 3 Minor comments:

- 1. 2. We have changed the introduction and added the references as requested. The referee will see that we hadn’t intended to write any kind of history of stratospheric bromine studies. Instead, we had focussed more on bromocarbon emissions. Nevertheless we are very happy to adopt the referee’s suggestions.***
- 3. Colours have been revised, as suggested.***