

Review of Brominated VSLS and their influence on ozone under a changing climate by Falk et al., ACPD, 2017

The paper presents an interesting modeling approach to evaluate how the future changes on temperature, dynamics and composition of the atmosphere will impact on the ocean-atmospheric source strength of very short-lived (VSL) source gases, as well as on the evolution of the tropopause height and stratospheric ozone. Based on a wide set of model experiments, an evaluation of different factors such as photolysis, OH reactivity, Age of Air (AOA) and temperature affecting the degradation of the most abundant VSL species (CHBr_3 and CH_2Br_2) are analyzed. The main results presented indicate that even when the VSLS ocean-atmospheric flux will increase $\sim 10\%$ between present time and 2100, the total amount of bromine from VSLS in the stratosphere will decrease during the 21st century.

I found the paper interesting and well diagramed, presenting results in a clear and complete format. But there are two major concerns that might be affecting the conclusions obtained from this work that must be clarified before final publication. One of them is regarding the relation of present EMAC modelling results with other published works in the literature with equivalent assumptions, and how the current model configuration could be affecting the interpretation of the VSLS flux evolution. The other main issue is regarding the tropospheric treatment of the inorganic product gas (PG) fraction and how additional factors/processes that are not considered in their analysis might be affecting the evolution of inorganic bromine injection. I believe the authors should be able to answer both of the main issues without the need of any further sensitivity simulation or changes in their model setup, so the paper can be accepted once those changes are included without any further review. At the end, several minor comments are given a) asking for relevant configuration details that are omitted, b) highlighting some sentences in the text that are not clear and should be modified and c) indicating where further discussions are required.

Major Comments:

1. There is a notorious omission to a strongly related paper from Ziska et al., (2017), which used exactly the same methodology to address the future evolution of the ocean-atmosphere flux of VSL through the 21st century. Even when the current study goes beyond the above-mentioned work by addressing the atmospheric factors controlling the VSL stratospheric injection and impact on ozone, a comparison and description of the similarities and differences regarding the Ziska et al. 2017 paper should be given.

(Ziska, F., Quack, B., Tegtmeier, S. et al. J Atmos Chem (2017). Future emissions of marine halogenated very-short lived substances under climate change. 74: 245. doi:10.1007/s10874-016-9355-3)

In particular:

- Ziska et al. considered the RCP 2.6 and RCP 8.5 scenarios, and determined a linear response only for the 1979-2005 period, but not when projecting into the future. Additionally, their RCP 2.6 increase of brominated emissions (9%) is of the same magnitude as the one found here for RCP 6.0 (10%).

- P3,L3: “In these simulations, OH concentrations have been set to zero in the lower troposphere (700–1000 hPa) to reduce the variability of ground level volume mixing ratio (VMR) of VSLs”. Thus, degradation of CHBr_3 and mostly CH_2Br_2 in the MBL and Lower troposphere is not well represented and might affect their tropospheric concentration (C_{air}). But eq. 1, which infers the future evolution of VSLs emissions, depends on the C_{air} concentration, which would be larger than if OH values would have not been forced to zero in the MBL. Could this assumed configuration be related to the similar % between RCP 2.6 from Ziska et al., 2017 and present work?
2. Consideration of heterogeneous recycling of Br_y^{VSL} in the UT and TTL might be of major importance in current study, and there is not a single mention of it neither in the model configuration nor in the results analysis. Many modelling studies, including some performed by the same group (Aschmann et al., 2009), other cited in the text (Liang et al., 2014) and many others not even mentioned in the manuscript (Parrella et al., 2012; Fernandez et al., 2014; Wang et al., 2015; Schmidt et al., 2016) highlight the importance of considering heterogeneous recycling occurring on ice-crystals and sea-salt aerosols as they can increase the lifetime against wet-removal or represent an additional source of bromine to the troposphere, respectively. Indeed, Fig. 5 and Fig 9. clearly shows that Br_y^{VSL} is the dominant fraction controlling the total stratospheric $\text{Br}_{\text{Tot}}^{\text{VSL}}$ change between present time and 2100, which highlight the importance of properly representing inorganic product gases chemistry in present study.
- Authors should decide whether performing additional simulations including and neglecting the heterogeneous recycling reactions is necessary or not. But if they instead want to focus on VSL source gases, at least the paper must mention how the uncertainties of heterogeneous recycling processes could be affecting their overall stratospheric results. A very rapid analysis could indicate that because of the increased tropospheric degradation, there is a larger Br_y fraction that is effectively washed out from the troposphere and never reaches the stratosphere. Thus, reducing the overall PG stratospheric injection. If that is the case, then it should be explicitly mentioned in the text, supported with more details about the deposition efficiencies of Br_y species.
 - Abstract, P1,L7: “A decrease in the tropospheric mixing ratios of VSLs and an increase in the lower stratosphere are attributed to changes in atmospheric chemistry and transport. Our model simulations reveal that, in line with the reduction in the troposphere, the total amount of bromine from VSLs in the stratosphere will decrease during the 21st century”. I found a contradiction between these two sentences included in the abstract, which is not clarified nor consistent with the final sentence in Section. 4.2
 - Section 4.2, P13,L15: “To summarize, the main reason to the apparent increase of bromine from VSLs above 100 hPa in RC2-base-05 of about 5–10% is the increase in vertical transport in the tropics. Although bromine loading from VSLs above 100 hPa is increased at the end of the 21st century, the stratospheric abundance of bromine from VSLs is not increasing but decreasing by about 1–2 ppt, if an upward shift of the tropopause is taken into consideration.” This summarizing result seems not to be consistent with the rest of the text nor what is shown in the figures. The

only 1-2 ppt reduction occurs in Bry PG (Fig. 9a, center), which as I have mentioned above, might not be well represented in the modeling study and might be altering the interpretation of the results. Additionally, the 1-2 ppt difference appears for $\Delta P > 20$ hPa respect the tropopause, so changes in the tropopause height could be affecting the VLS bromine levels in the UTLS, but not in the stratospheric over-world.

- Forcing OH to be zero in the LT also reduces the total amount of inorganic bromine product gas species being available for heterogeneous recycling. This could reduce the additional source from sea-salt dehalogenation (if considered). How this forced OH assumption could be affecting the treatment of the PG being released from aerosols?
- P6,L16: “ ... and therefore increase the flux from the ocean to the atmosphere without increasing the actual amount which is transported to the stratosphere.” This is only the case for VLS source gases, but if PG are not washed out right away, they could also be transported to the stratosphere.
- P8,L10: “PG from VLS (Br_y^{VLS}), which have been traced within the simulation, are decreasing in the stratosphere in the future. For 2016, this decline is compatible with a decreasing amount of VLS in the troposphere. A slight excess of Br_y^{VLS} compared to 2016 and 2100 is found for 1980 in the stratosphere.” Please considering rephrasing this sentence, or at least relate it to the impact heterogeneous recycling might have on PG.
- P9,L11: It is important to note, that although there is an apparent increase of Br_{org}^{VLS} of 0.5 ppt in the stratosphere assuming constant ocean-atmosphere fluxes, the overall amount of bromine in the stratosphere due to VLS is decreasing in the future.” Why apparent? Should you end the sentence by adding “... when the time varying fluxes are considered”. Could you please explain and relate it to the Bry PG heterogeneous treatment?
- P9, Fig.4: The Figure panel indicates 1980 instead of 1990. The caption says “... an increase of roughly 10% in Br_y from VLS in the stratosphere is found, while the increase in Br_{org} amounts 8%”. First, could you show the tropopause height for each year in the Figure. Second, the 8% Br_{org} increase is at the tropopause?, Third, this sentence seems to contradict P1,L8 in the abstract that total amount of bromine from VLS in the stratosphere will decrease during the 21st century.
- There is a contradictory message between P10,L1 “, the overall amount of bromine in the stratosphere due to VLS is decreasing in the future” and P10,L9 “The increase of VLS in the stratosphere in the future can be attributed to”. Are VLS increasing or decreasing in the future stratosphere??
- Conclusions, P18,L21: “Due to the rise of the tropical tropopause by 0.81 hPa decade⁻¹, air which at present is considered stratospheric will be still tropospheric in the future. If taken into account by shifting VLS VMR profiles with respect to the mean model tropopause height, the total amount of bromine in the tropical UTLS is decreasing by roughly 2 ppt. Overall, the amount of bromine in the UTLS is decreasing in this future scenario.” The changes in VLS bromine are only affecting the UTLS or the overall stratosphere? Please make it clear and consistent with the abstract and main text in line of all abovementioned concerns.

3. Also, comparison with the results of a recent study (Fernandez et al., 2017) that estimated the effect of biogenic VSLBr species in the evolution of the Antarctic ozone hole during the 21st century should be made.
(Fernandez et al., *Impact of biogenic very short-lived bromine on the Antarctic ozone hole during the 21st century*, *Atmos. Chem. Phys.*, 17, 1673-1688, 2017)

Minor Comments:

P2,L20: "... how transport and *tropospheric* chemistry influence the stratospheric bromine abundance" ... "and how *stratospheric* ozone will be affected ...". I suggest adding the italic words to make the text clear.

P2,L27: Simplified and full bromine chemistry: What are the main differences between both chemical mechanism, and how the simplified treatment could be affecting the Br₂ production, recycling and removal. Additionally: Br₂ is considered in the chemical mechanism? Because it explicitly appears in P2,L12 but it doesn't in P3,L9.

P3,L7: What do you mean by "... commuted into Br₂"

P3,L19: RT1a and RT1b both include online computation of aerosol formation: What types of aerosols: tropospheric or stratospheric. What type of interaction is included in the model regarding VSL species and the aerosol module?

P4,L1: Could you briefly mention the main differences between the Wanninkhof (1992) and Nightingale et al. (2000) parameterizations of K_w. How these differences can be affecting the VSL ocean-atmosphere flux?

P4,L11: "cloud coupling had not been activated". Is this of relevance only for the radiative transfer scheme? Can it affect the model wet-removal computation?

P4,L19: How many vertical levels does the model include, and how many of them belong to the troposphere and how many to the stratosphere?

P5,L20: what do you mean by "Relative to the absolute zonal fluxes"? Is it the global mean?

P5,L30: "Distinct maxima in the seasonal cycles ... and minima occurring in late winter". Please rephrase.

P5,L31: "In case of CH₂Br₂, even negative emissions are found during winter at high-latitudes on the northern hemisphere.". First, you could explicitly indicate that negative emissions represent a net sink of atmospheric VSL. Second, how the forcing of LT OH to zero could be affecting this negative flux?

P6, Table 2 caption: "Average absolute flux for year 2000 ..."

P6,L11: I suggest indicating also the absolute increase in VSL surface VMR.

P5,L15 and P6,L14: The dependence of the emission flux on wind speed is not explicitly mentioned in Eq. 1.

P6,L17: "Much stronger fluxes (1.3–1.5 times) have been found in the former simulation in comparison to the latter." First, could you rephrase to make it clear which is the former and which the latter. Second, could the flux difference be due to the different OH zeroing treatment between experiments within the MBL and LT?

P8, Fig 3: How did you set the C_w from the Ziska et al., 2013 paper for regions in the Arctic that were covered by sea-ice at present time but are not longer covered in the future?

P12,L18 and elsewhere in the text: is it *ansatz* an accepted English word?

P13, Fig.6: Have you thought about including the CH_2Br_2 and CHBr_3 photolysis rate vertical profile in a second panel?

P13,L11: "At about 20 hPa" ... Do you mean a 20hPa difference from the mean tropopause? Regarding Fig. 9, and considering P8,L1 "There is an upward shift of the tropopause height of about 8 hPa between present day and future". Why do you show such a large shift in pressure respect to the mean tropopause (± 100 hPa) if the difference in the tropopause pressure is smaller than 10 hPa? I would expect the changes in the tropopause height to affect only the UTLS, and the partitioning between SG and PG, but not the overall total bromine abundances in the middle and upper stratosphere.

P15,L14: If the authors are willing to address the impact of VSLs in the future evolution of Antarctic ozone, they should at least compare their results respect to Oman et al., 2016 and Fernandez et al., 2017.

P18,L29: "... and aerosol formation have been taken into consideration". While a full aerosol treatment has been considered for some of the simulations, the sentence gives the impression that an aerosol formation module for VSLs has been considered in this work. I suggest rephrasing to avoid misleading interpretations.