Modelling future changes to the stratospheric source gas injection of biogenic bromocarbons

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[1] Simulations with a chemistry-climate model (CCM) show a future increase in the stratospheric source gas injection (SGI) of biogenic very short-lived substances (VSLS). For 2000, the modelled SGI of bromine from VSLS is ∼1.7 parts per trillion (pptv) and largest over the tropical West Pacific. For 2100, this increases to ∼2.0 and ∼2.7 pptv when the model is forced with Intergovernmental Panel on Climate Change (IPCC) representative concentration pathways (RCPs) 4.5 and 8.5. The increase is largely due to stronger tropical deep convection transporting more $CHBr_3$ to the lower stratosphere. For CH_2Br_2, $CHBr_2Cl$, CH_2BrCl and $CHBrCl_2$, changes to primary oxidant OH determines their SGI contribution. Under RCP 4.5 (moderate warming), OH increases in a warmer, more humid troposphere. Under RCP 8.5 (extreme warming) OH decreases significantly due to a large methane increase, allowing greater SGI of bromine from these VSLS. Potentially enhanced VSLS emissions in the future would further increase these estimates. **Citation:** Hossaini, R., et al. (2012), Modelling future changes to the stratospheric source gas injection of biogenic bromocarbons, *Geophys. Res. Lett.*, *39*, L20813, doi:10.1029/2012GL053401.

1. Introduction

[2] The importance of active bromine radicals (Br_x = Br + BrO) in the catalytic destruction of stratospheric ozone (O_3) is well established [*Wofsy et al.*, 1975]. Due to a lack of stable reservoirs, BrO is the dominant inorganic bromine (Br_y) species in the stratosphere. Coupled cycles, involving analogous chlorine radicals, account for a significant total of seasonal O_3 loss observed over Antarctica [*Montzka et al.*, 2011]. At mid-latitudes, the BrO-ClO cycle is enhanced during periods of high aerosol loading due to heterogeneous halogen activation. The coupled BrO-HO₂ cycle is important for O_3 loss in the mid-latitude lower stratosphere [*Salawitch et al.*, 2005]. On a per-atom basis, bromine is a factor of ∼60 more efficient than chlorine as an O_3 sink in the lower stratosphere [*Sinnhuber et al.*, 2009]. Changes to stratospheric O_3 can impact surface temperature and climate.

[3] The dominant sources of stratospheric Br_y are the long-lived gases, methyl bromide (CH_3Br) and halons (e.g. Halon 1211, CF_2ClBr). Emissions of the former are largely of natural origin (∼65%), while halons, which were used as fire suppressants, are exclusively anthropogenic. As production is regulated under the Montreal Protocol, their abundance is expected to decline significantly in coming decades [*Montzka et al.*, 2003]. It is also known that very short-lived substances (VSLS), primarily emitted from macroalgae and plankton [e.g., *Quack and Wallace*, 2003], may also reach the stratosphere [e.g., *Sturges et al.*, 2000]. Their contribution to stratospheric Br_y (Br_y^{VSLS}) is estimated to be 1–8 pptv [*Montzka et al.*, 2011].

[4] The most abundant brominated VSLS are bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2). Average marine boundary layer (MBL) mixing ratios are ∼1.1 and 1.5 pptv [*Montzka et al.*, 2011]. The surface lifetime of a VSLS is less than 6 months. However, once transported to the upper troposphere, lifetimes may be considerably longer [*Hossaini et al.*, 2010]. Strong convective regions such as the tropical West Pacific are important for the troposphere-to-stratosphere transport of VSLS [*Aschmann et al.*, 2009].

[5] There have been suggestions that Br_y^{VSLS} may increase in a future climate [e.g., *Pyle et al.*, 2007]. *Dessens et al.* [2009] found dynamical changes due to global warming will likely enhance troposphere-to-stratosphere transport of VSLS. However, they did not explicitly model future changes to primary oxidant OH and thus the impact of a perturbed oxidizing capacity on the stratospheric flux of VSLS remains unclear. Understanding these processes is required to assess the role of (biogenic) bromine on the future evolution/recovery of stratospheric O_3. In this paper we quantify changes to the entrainment of brominated VSL source gases into the lower stratosphere under projected 2100 climates. The relative influence of changes to the tropospheric oxidizing capacity and tropospheric transport are examined. The impact of VSLS on stratospheric O_3 is not examined here.

2. Model and Experiments

[6] The United Kingdom Chemistry and Aerosols (UKCA) CCM is based on the dynamical core of the Met Office Unified Model (UM) version 7.3. The model recently took part in the Stratospheric Processes and their Role in Climate (SPARC) Chemistry-Climate Model Validation Activity [*Erying et al.*, 2010]. UKCA contains detailed stratospheric chemistry and photolysis rates are computed online using the FAST-JX scheme [*Morgenstern et al.*,

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Table 1. Prescribed Surface Volume Mixing Ratio of Key Greenhouse Gases and Long-Lived Bromocarbons

Experiment	CO_2 (ppm)	CH_4 (ppb)	N_2O (ppb)	H-1211 (ppt)	H-1202 (ppt)	H-1301 (ppt)	H-2402 (ppt)	CH_3Br (ppt)
$S-2000$	370	1765	316	4.04	0.05	2.73	0.41	8.66
$S-RCP4.5$	538	1577	372	0.05	<0.01	0.98	<0.01	6.40
$S-RCP8.5$	935	3750	435	0.04	<0.01	0.78	<0.01	5.70

2009]. The following gases are interactive with radiation [*Edwards and Slingo*, 1996]: O_3, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons.

[7] UKCA was run with a horizontal resolution of 3.75° longitude × 2.5° latitude and with 60 hybrid-height levels (surface to ~80 km). Three 20-year time slice experiments were performed in *atmosphere-only* mode, corresponding to 2000 and 2100 conditions; S-2000, S-RCP4.5 and S-RCP8.5. For 2000, UKCA was forced with prescribed monthly mean fields of sea surface temperature (SST) and sea ice [*Rayner et al.*, 2003]. For 2100, output of the Had-GEM2-CCS climate model [*Martin et al.*, 2011] was used for these fields. For 2000, greenhouse gas (GHG) loading and long-lived halocarbons (e.g. halons, CFCs), were pre-scribed according to the WMO A1 scenario [*Montzka et al.*, 2011]. For 2100 experiments (S-RCP4.5 and S-RCP8.5) these gases were constrained by IPCC RCP 4.5 and 8.5 [*van Vuuren et al.*, 2011] (see Table 1). These scenarios span moderate to extreme climate change resulting in a projected surface warming in the region of ~2.0 K and ~4.0 K by 2100, respectively.

[8] In this study, five biogenic VSLS tracers were added to UKCA. For major VSLS $CHBr_3$ and CH_2Br_2, the monthly-varying emission estimates of *Ordóñez et al.* [2012] were used for both 2000 and 2100 experiments. Their global source strengths are 533 Gg yr^{-1} and 67.3 Gg yr^{-1}. For minor (and relatively long-lived) VSLS $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl, a prescribed mixing ratio (0.3, 0.3 and 0.5 pptv), based on observations in the MBL [*Montzka et al.*, 2011], was used to constrain their surface abundance. This model set up has been evaluated extensively with ground-based and aircraft observations.

3. Results and Discussion

[9] Aircraft observations suggest 0.09(0.0–0.31) pptv of $CHBr_3$ at the tropical (±20° latitude) tropopause (TT, ~17 km) [*Montzka et al.*, 2011]. In this region, UKCA is able to reproduce observed mixing ratios of major VSLS (see auxiliary material).[1] The modelled 2000 zonally aver-aged TT abundance of $CHBr_3$ is ~0.1 pptv. For 2100, this estimate increases to 0.2 pptv under RCP 4.5, and signifi-cantly to 0.36 pptv, under RCP 8.5. The local increase is largest over the West Pacific during northern hemisphere winter (DJF, Figure 1), when transport through the TTL is most rapid [*Fueglistaler et al.*, 2005]. Here the modelled $CHBr_3$ increase peaks at ~0.7 pptv (i.e. 2.1 pptv more of bromine).

[10] SGI refers to the transport of organic VSLS to the stratosphere where, on degradation, they release in-situ Br_y^{VSLS}. Efficient SGI requires troposphere-to-stratosphere transport to be on timescales comparable to, or shorter than,

tropospheric loss rates. $CHBr_3$, which may account for ~35% of the total SGI from VSLS [*Hossaini et al.*, 2012], has a surface lifetime of ~24 days and its primary tropo-spheric sink is photolysis. As the shortest lived gas consid-ered here, its abundance in the lower stratosphere is most sensitive to changes to the tropospheric circulation, particu-larly in the tropics where emissions are large.

[11] The modelled 2100 convective updraft mass flux mostly decreases in the tropical lower and mid-troposphere (see auxiliary material). In the upper troposphere (UT, ~12–17 km), the change is positive with large increases over the Western Pacific (Figure 2a), where strong convection is sustained to higher altitudes. The prevalence of deep con-vection, important for the transport of VSLS to the UT, may increase in response to global warming [e.g., *Chou and Chen*, 2010]. The results here are consistent with *Stevenson et al.* [2005] and *Dessens et al.* [2009] who also show an increase in the updraft strength in the UT. Age-of-air, here defined as the mean time since a parcel was in contact with the surface, is reduced (Figure 2b). This reduction reflects change to both large-scale and convective-scale motions and correlates with enhanced $CHBr_3$ at 17 km (Figure 2c).

[12] For CH_2BrCl, CH_2Br_2 (Figure 2d), $CHBrCl_2$ and $CHBr_2Cl$, whose surface lifetimes (137, 123, 78 and 59 days) are considerably longer [*Montzka et al.*, 2011], perturbations to tropospheric transport time-scales have a significant,
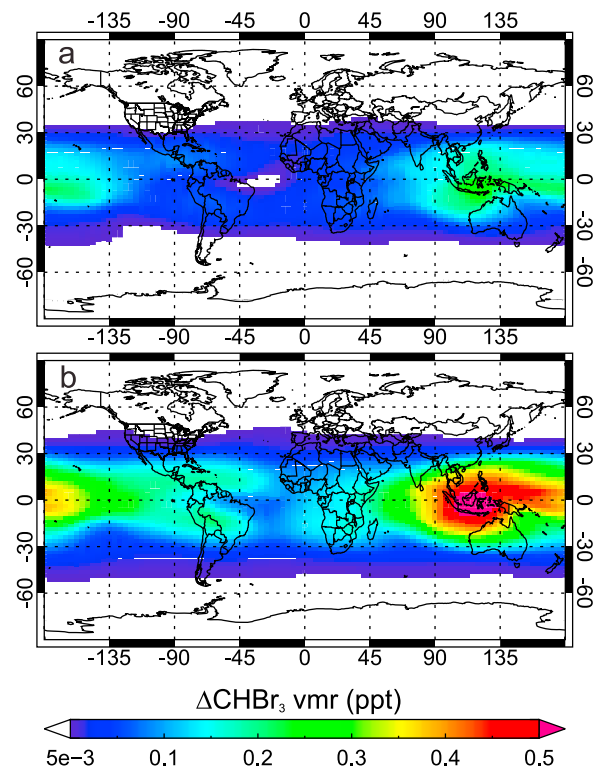

Figure 1. DJF mean increase in $CHBr_3$ volume mixing ratio (pptv) at ~17 km for (a) RCP 4.5 and (b) RCP 8.5.

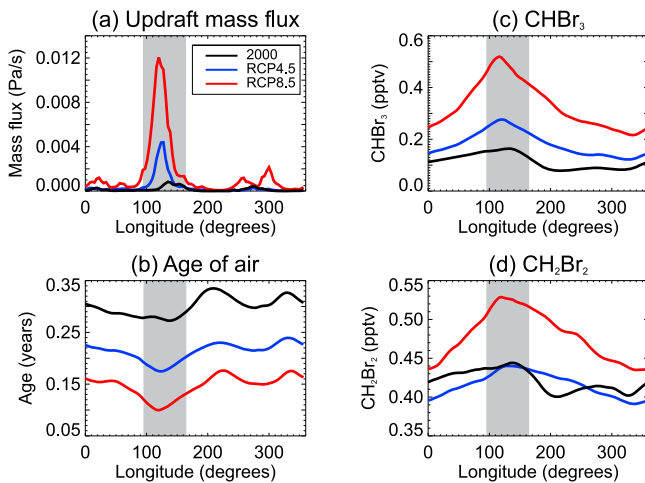[1]Auxiliary materials are available in the HTML. doi:10.1029/2012GL053401.

Figure 2. Longitudinal dependence of (a) convective updraft mass flux (Pa/s), (b) age-of-air (years), (c) $CHBr_3$ (pptv) and (d) CH_2Br_2 (pptv) averaged over the tropics ($\pm20°$) at ~17 km for 2000 and 2100 experiments. The West Pacific region (95–165° longitude) is shaded.

yet smaller impact on their abundance in the lower stratosphere. Rather, these less photolabile gases are more sensitive to changes to primary oxidant OH.

[13] Figure 3a shows the modelled 2100 change in [OH] with respect to (w.r.t.) 2000. Warmer lower atmospheric temperature leads to enhanced water vapour and thus enhanced OH production through the $H_2O + O(^1D)$ channel. Under RCP 4.5, [OH] increases throughout the troposphere, with a peak mean increase of $\sim0.2 \times 10^6$ molecules cm^{-3} (15% increase w.r.t. 2000) occurring at ~15 km. *Zeng et al.* [2008] show a similar response for a 2100 CCM experiment in which $[CO_2]$ was doubled. Due to difference in experimental set up, a direct comparison of results is not appropriate. However, qualitatively, increased tropospheric [OH] is consistent between models and is of a similar magnitude.

[14] However for RCP 8.5, despite enhanced water vapour, below ~10 km the [OH] response is negative. Between RCPs there is large variation in $[CH_4]$ (Table 1). Under RCP 4.5, a scenario where GHG emissions are mitigated, 2100 CH_4 is $\sim10\%$ lower w.r.t. 2000. Conversely, under RCP 8.5, a non-mitigation scenario, it increases by $\sim112\%$. Enhanced CH_4 tends to decrease [OH] [e.g., *Wuebbles et al.*, 1989] and has a positive feedback on its own lifetime. The rate of the $CH_4 + OH$ reaction has a strong

temperature-dependence and increases with the large increase in tropospheric temperature under RCP 8.5 (>4.5 K at the surface).

[15] Changes to the tropospheric oxidizing capacity have a small impact on $CHBr_3$. Although, enhanced [OH] under RCP 4.5 reduces the $CHBr_3$ lifetime, particularly near the surface, where oxidation by OH can compete with the faster photolysis sink [*Hossaini et al.*, 2010]. However, overall the $CHBr_3$ change w.r.t. 2000 (Figure 3b) is small. Under RCP 8.5, the dominant process is the significant increase in the strength of deep tropical convection which enables more $CHBr_3$ to reach the upper troposphere-lower stratosphere (UTLS) (See Figure 2 also).

[16] For CH_2Br_2, under RCP 4.5 the change w.r.t. 2000 (Figure 3c) closely follows Δ[OH]. Its tropospheric lifetime is reduced due to enhanced [OH] and the positive temperature-dependence of the oxidation. For RCP 8.5, the situation is more complex. The CH_2Br_2 lifetime is extended near the surface (due to decreased [OH]). However, the significantly warmer surface temperature compensates by speeding up the OH sink reaction and overall resulting in little change below 10 km. In the upper troposphere, where this sink is significantly slower, the enhanced convective mass flux dominates by transporting more tracer to the UTLS region.

[17] Overall, the total SGI from brominated-VSLS increases from a zonally averaged 1.7 pptv (2000) to 2.0 pptv (2100, RCP 4.5) and 2.7 pptv (2100, RCP 8.5). Our experiments have assumed 2100 VSLS emissions are the same as present day. It is currently unknown if and how emissions may change in response to climate or other forcings. However, an increase in the tropical MBL abundance of VSLS due to changes to primary production, sea-air fluxes, land-use practice or indeed any other factors, would likely increase the SGI estimates reported here. The use of climatological SSTs in this study means variability associated with the El Niño-Southern Oscillation (ENSO) is not captured. The so-called product gas injection pathway (PGI), which is significantly more uncertain at present, has not been considered here but will be the subject of future work.

4. Concluding Remarks

[18] The stratospheric source gas injection of VSLS will likely increase in response to climate change. The magnitude of this increase will be determined by competing chemical and dynamical factors. For relatively short-lived gases such as bromoform, whose primary tropospheric sink is photolysis, and therefore subject to relatively minor
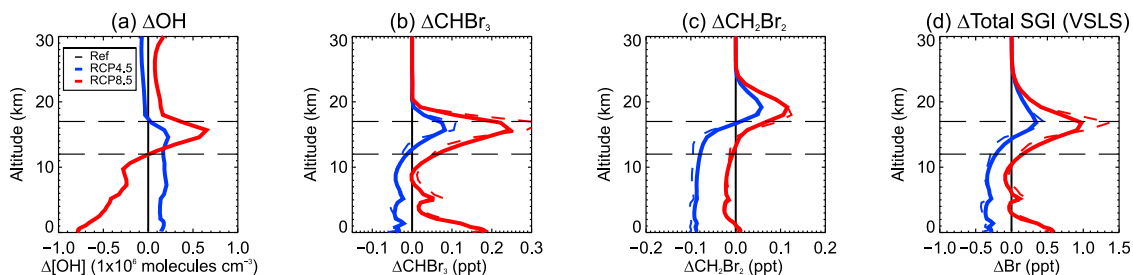

Figure 3. 2100 annual zonal mean change w.r.t. 2000 of (a) OH, (b) $CHBr_3$, (c) CH_2Br_2 and (d) total SGI from all VSLS in the tropics ($\pm20°$). Upper and lower dashed lines denotes the cold point tropopause and the approximate base of the tropical tropopause layer, respectively. Dashed profiles represent mean over the tropical Western Pacific region (90–165° longitude).

change, enhanced convection in 2100 leads to an increase in their lower stratospheric abundance. For dibromomethane, and other VSLS whose primary tropospheric sink is through oxidation, their abundance is highly sensitive to changes to the hydroxyl radical. For IPCC RCP 4.5 and RCP 8.5, the tropospheric oxidizing capacity may differ significantly and more work is required to best constrain such changes.

[19] As for 2000, based on our CCM results, the tropical West Pacific will continue to be an efficient source region for the future transport of VSLS to the stratosphere. Changes to regional land use and practice, such as seaweed farming, which is currently a growing sector, could potentially significantly increase the surface loading of VSLS. This would likely increase the loading of VSLS into the stratosphere, particularly under a significantly warmer climate such as that of the IPCC RCP 8.5 projection.

[20] To assess the significance of VSLS on future global stratospheric ozone, further work is required to 1). determine potential changes to VSLS emission rates and 2). determine the efficiency of Br_x O_3 loss cycles under evolving stratospheric composition (e.g. decreasing chlorine, and potentially increasing hydrogen oxides).

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