The Effect of Representing Bromine from VSLS on the Simulation and Evolution of Antarctic Ozone

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Key points:

1. Including 5 ppt of Br from VSLS reduces biases with observed ozone and BrO

2. Resolves a discrepancy with an observational derived parametric model

3. Causes a decade later recovery of Antarctic ozone to 1980 levels

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Abstract

We use the Goddard Earth Observing System Chemistry-Climate Model (GEOSCCM), a contributor to both the 2010 and 2014 WMO Ozone Assessment Reports, to show that inclusion of 5 parts per trillion (ppt) of stratospheric bromine (Br_y) from very short-lived substances (VSLS) is responsible for about a decade delay in ozone hole recovery. These results partially explain the significantly later recovery of Antarctic ozone noted in the 2014 report, as bromine from VSLS was not included in the 2010 Assessment. We show multiple lines of evidence that simulations that account for VSLS Br_y are in better agreement with both total column BrO and the seasonal evolution of Antarctic ozone reported by the Ozone Monitoring Instrument (OMI) on NASA's Aura satellite. In addition, the near zero ozone levels observed in the deep Antarctic lower stratospheric polar vortex are only reproduced in a simulation that includes this Br_y source from VSLS.

1. Introduction

Simulations of the future evolution of the ozone layer show that the time frame of ozone recovery depends on the halogen and greenhouse gas (GHG) emissions scenarios and forecast changes in the temperature and circulation of the stratosphere, each with varying importance dependent on latitude and season [*Eyring et al.,* 2013a; *Oman et al*., 2014; *World Meteorological Organization (WMO*), 2014]. Bromine plays an integral part in determining the atmospheric abundance of ozone and its effectiveness per molecule at destroying ozone is approximately 45-65 times greater than chlorine [*Daniel et al.*, 1999; *Sinnhuber et al*., 2009]. In addition, the bromine impact on ozone depletion is larger with higher chlorine [*McElroy et al*.,

67 1986] as well as with enhanced sulfate aerosol loading, like following large volcanic
68 eruptions [*Salawitch et al.*, 2005].

69 Bromine from very short-lived substances (VSLS), mainly bromoform
70 ($CHBr_3$) and dibromomethane (CH_2Br_2) has also been shown to be an important
71 part of the total atmospheric burden of bromine and ozone layer chemistry [*Ko et*
72 *al*., 1997; *Sturges et al*., 2000; *Salawitch et al.*, 2005]. *Theys et al*. [2007] estimated
73 that VSLS supply 6 to 8 parts per trillion (ppt) of stratospheric Br_y based on
74 retrieval of stratospheric and tropospheric column BrO at Reunion-Island (20.9°S).
75 *Salawitch et al*. [2010], focusing on the Arctic, found that 5 to 10 ppt of stratospheric
76 bromine from VSLS is needed to achieve consistency with aircraft and satellite
77 measurements of BrO. *Liang et al.* [2014] quantified the chemical and physical
78 transformations of VSLS after release into the marine boundary layer using the
79 Goddard Earth Observing System Chemistry-Climate Model (GEOSCCM) and
80 concluded VSLS supply about 8 ppt of bromine to the base of the tropical
81 tropopause layer. Measurements of upper stratospheric BrO from the Microwave
82 Limb Sounder (MLS), balloon-borne DOAS (Differential Optical Absorption
83 Spectroscopy), and the Scanning Imaging Absorption Spectrometer for Atmospheric
84 Chartography (SCIAMACHY) yield estimates for VSLS supply of stratospheric Br_y of
85 5 ± 4.5 ppt [*Millan et al*., 2012], 5.2 ± 2.5 ppt [*Dorf et al*., 2008], and 7 ± 6 ppt
86 [*Parrella et al*., 2013], respectively.

87 A few studies examined the impact of this additional bromine on
88 stratospheric ozone concentrations. *Frieler et al*. [2006] showed inclusion of
89 bromine from VSLS led to better agreement between observed and modeled loss of

Arctic ozone for a particular winter. *Feng et al.* [2007], focusing on midlatitude ozone, found a 10 DU decrease by including 5 ppt of bromine from VSLS. *Yang et al.* [2014] made a rough estimate of 6-8 years later recovery of the Antarctic ozone hole due to 5 ppt of bromine from VSLS based on time-slice experiments with various chlorine and bromine levels. *Sinnhuber and Meul* [2015] found closer agreement in a simulation with the chemistry climate model (CCM) EMAC to observed trends of global column ozone when including bromine from VSLS.

An outstanding issue has been the difference in Antarctic ozone recovery projections obtained using CCMs and projections derived from observations. *Newman et al.* [2006] used an observationally derived parametric model of ozone hole area to predict recovery of Antarctic ozone to 1980 levels around 2068 under the Ab halogen scenario [*WMO*, 2003]. CCMs used in the WMO 2010 Assessment [*WMO*, 2011] returned Antarctic column ozone to 1980 levels by 2051 on average, much earlier than forecast by the parametric model. The scientific summary suggested that failure of the parametric model to account for an upper stratospheric ozone increase, which would be caused by GHG-induced changes in circulation and temperature, could explain this difference [*WMO*, 2011],. However, *Eyring et al.* [2010] found only a small difference in October Antarctic ozone values for simulations using various GHG scenarios.

Significantly later recovery of October Antarctic ozone was noted in Chapter 3 of the 2014 WMO Ozone Assessment [*WMO*, 2014] by each of the four models (CMAM, GEOSCCM, UMSLIMCAT, WACCM) that contributed simulations for this most recent Assessment, compared to results from a larger number of models that

113 contributed to the 2010 Assessment [*WMO*, 2011]. However, they were unable to
114 explain the cause of the later recovery, given the model simulations available at the
115 time. The multi-model mean of these latest simulations indicated that return of
116 Antarctic O_3 to 1980 levels would not occur until after 2080. Small differences in the
117 base ozone depleting substance (ODS) scenario relative to that used in the prior
118 Assessment [*Velders and Daniel*, 2014] caused a small 3-4% increase in vortex Cl_y in
119 the later half of the 21st century for the updated simulations [*Oman and Douglass*,
120 2014] and do not explain the later recovery. However, all of the new simulations
121 represented the impact of VSLS on stratospheric Br_y in the form of a constant, extra
122 5 ppt of bromine (note: VSLS bromine is independent of ODS specifications, since
123 the VSLS are biogenic and not anthropogenic). The impact of VSLS-based Br_y on
124 ozone recovery was not simulated in the 2010 Assessment.
125 Here we use the GEOSCCM, which contributed to both the 2010 and 2014
126 WMO Assessments, to quantify the effect of an additional 5 ppt of stratospheric
127 bromine from VSLS on both the recovery of the ozone layer over the 21st century
128 and the current seasonal evolution of the Antarctic ozone hole. We use 5 ppt for
129 VSLS bromine because this is the best estimate given by *WMO* [2014]. We show that
130 inclusion of bromine from VSLS partly explains why the 2014 Assessment reported
131 a significant delay in the recovery of the Antarctic ozone layer. Section 2 describes
132 the model and forcing scenarios as well as the measurements used to evaluate the
133 effect of this additional bromine. Results of these simulations and conclusions
134 follow.
135

2. Model, Forcing Scenarios, and Observations

The GEOSCCM coupled to the stratospheric chemistry module, StratChem [*Pawson et al*., 2008; *Oman and Douglass*, 2014], was used to quantify the impact of including VSLS bromine on the ozone layer, focusing on the effects over Antarctica. The model was run at 2° × 2.5° (lat. × long.) horizontal resolution with 72 vertical layers from the surface up to 80 km, with photochemical input data from JPL 2010 [*Sander et al.,* 2011]. Evaluation of GEOSCCM using process-oriented diagnostics was conducted in both CCMVal-1 [*Erying et al.,* 2006] and CCMVal-2 [*SPARC CCMVal* 2010]. GEOSCCM performed well in both chemical and transport related processes [*SPARC CCMVal* 2010; *Strahan et al*., 2011; *Douglass et al*., 2012] and some additional improvements were reported in *Oman and Douglass* [2014].

Both GEOSCCM simulations described here used GHG concentrations from the Representative Concentration Pathway (RCP) 6.0, which produces 6.0 W/m^2 anthropogenic radiative forcing of climate by 2100 [*Meinshausen et al*., 2011; *Moss et al*., 2010]. Both used the A1 2014 scenario for ODS [*Velders and Daniel*, 2014], the same as used in the 2014 WMO Assessment [*WMO*, 2014]. The first of these, the control simulation (A12014_0Br), does not include any Br_y from VSLS, as assumed for the 2010 WMO [*WMO*, 2011] and earlier Assessments. The second simulation (A12014_5Br) includes an extra 5 ppt of CH_3Br to represent VSLS, as recommended by the Chemistry Climate Modeling Initiative (CCMI) [*Eyring et al.,* 2013b].

Sea surface temperature and sea ice concentrations were prescribed from a simulation using the Community Earth System Model version 1 (CESM1) conducted from 1960-2099 [*Gent et al*., 2011], forced with the same RCP 6.0 GHG scenario.

159 Observations from the Ozone Monitoring Instrument (OMI) and Microwave Limb
160 Sounder (MLS) on the NASA Aura satellite are used to evaluate the simulation of
161 ozone and bromine monoxide (BrO) from Jan. 2005 to Dec. 2015. OMI level-3
162 gridded daily total column ozone values are determined using the OMTO3 version
163 8.5 retrieval algorithm (*Bhartia*, 2007). In addition, vertical daily ozone
164 measurements from MLS level-2 version 4.2 [*Livesey et al.,* 2015] were used in the
165 evaluation. Description and access to these satellite data records is at
166 http://disc.sci.gsfc.nasa.gov/Aura .
167 For the comparison of modeled and measured BrO, model output is sampled
168 at the locations for which OMI measurements are available. Due to the diel cycle of
169 BrO, model output was sampling at 2 p.m. local solar time, close to the time of OMI
170 overpass. Version 3 retrievals of total column BrO from OMI were used for
171 comparison with the GEOSCCM output; data and description are at
172 http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/ombro_v003.shtml .
173 Destriped, level-2 total column observations (OMBRO.003) and 1σ uncertainties
174 (based on spectral fitting) were filtered using flags "xtrackqualityflag" to account for
175 the OMI row anomaly and "maindataqualityflag" to remove invalid data. The
176 filtered data were then gridded to match the latitudes and longitudes of the
177 GEOSCCM simulations. Daily, gridded satellite observations of total column BrO and
178 the associated uncertainty were cosine weighted and averaged between 60 to 90°S.
179 Similarly, GEOSCCM output at 2 p.m. was weighted and averaged, but only for those
180 model grid points where corresponding observations were available. Finally, time
181 series of seasonal averages (JJA) were generated for modeled total column BrO, as

182 well as for satellite observation and uncertainty of total column BrO.

183

184 **3. Results/ Discussion**

185 Here, we show that inclusion of 5 ppt of CH_3Br to represent the bromine from
186 VSLS impacts both the present seasonal evolution of the Antarctic ozone layer and
187 its recovery over the 21st century. The simulated present day seasonal cycle of
188 ozone over Antarctica compares better with OMI total column ozone measurements
189 when the VSLS contribution is included. Figure 1 shows the daily average total
190 column ozone (DU) amounts from 60-90°S for the A12014_5Br (blue curve) and
191 A12014_0Br (red curve) simulations and from OMI observations (black curve), with
192 both observations and simulations averaged over 2005-2015. The additional
193 bromine decreases ozone between 6-20 DU, with the largest decline occurring in
194 September. The faster onset of the ozone hole formation and the minimum ozone
195 amounts, around 1 October are in better agreement with observation than found
196 using the simulation without VSLS bromine. GEOSCCM does have a somewhat
197 delayed breakup of the polar vortex, which is seen in the slower ozone increase
198 during November and December.

199 It is well known that ozone deep in the Antarctic polar vortex between 14-18
200 km drops to near zero levels, typically in the last week of September and the first
201 week of October [*Hofmann et al*., 1997]. Figure 2 shows the daily ozone partial
202 pressure (millipascals) at 80°S for the simulations A12014_5Br and A12014_0Br,
203 and MLS ozone from 1 September to 30 October, all averaged over 2005-2009. The
204 simulation including VSLS bromine is much closer to the very low abundance of

ozone observed from MLS and the South Pole ozonesonde record in the lower stratosphere, with the near zero values routinely reached during the mid-late 1990s and early 2000s. These near zero values are not seen the A12014_0Br simulation. The ozone profile difference (%) between these two simulations and MLS observations over 60 to 82°S, for a few select days surrounding the ozone minimum, is shown in Figure S1. This comparison also shows improved agreement between pressures of 200 to 10 hPa when the VSLS source of 5 ppt of bromine is included.

October average Antarctic total column ozone is the commonly used measure of ozone depletion and recovery in WMO Ozone Assessments and the SPARC CCMVal-2 Report (*SPARC CCMVal*, 2010). Figure 3 shows the October average total column ozone (DU) over 60-90°S from 1960-2099 for our two simulations. The A12014_5Br simulation shows almost a decade later recovery of Antarctic polar ozone to 1980 levels. As expected, the largest ozone differences between these two simulations occur when chlorine loading levels are within 50% of the maximum. GEOSCCM October total column ozone returns to 1980 levels by approximately 2062 in the A12014_0Br simulation and around 2071 in the A12014_5Br simulation. These simulations represent a pair of runs, the difference between these two simulations could be amplified of damped by natural internal variability. However, the recovery date is also delayed by over a decade for the four models that included VSLS bromine for the 2014 assessment but not for 2010. Therefore, we expect that the significant difference between our pair of simulations would persist over multiple ensemble members. This later recovery date is now similar to the estimate from a parametric model [*Newman et al*., 2006] using available data at the time and

228 resolves a discrepancy between it and recovery estimates from previous WMO
229 Assessments [2011].

230 Comparisons of total column BrO retrieved from the OMI instrument with
231 simulated BrO columns supports inclusion of a contribution of VSLS, similar to
232 results obtained by *Salawitch et al.* [2010] and *Liang et al.* [2014]. Figure S2 shows
233 total column BrO from OMI averaged over the months of June to August, for 60 to
234 90°S, for the years 2005 to 2015 compared to GEOSCCM simulations for the same
235 months, latitude range, and year. Inclusion of the extra 5 ppt of bromine reduces,
236 but does not completely eliminate, a systematic low bias between simulated and
237 observed column BrO. Enhanced tropospheric BrO from surface release is not
238 included in our GEOSCCM simulations, which could account for the low bias in
239 modeled BrO. *Roscoe et al.* [2014] show surface release of bromine typically
240 contributes between 1 and 3×10^{13} mol cm^{-2} of tropospheric BrO, distributed
241 throughout the free troposphere, at Halley Bay (75.6°S). Another possibility for the
242 underestimate of column BrO could be model misrepresentation of the BrO/Br_y in
243 the troposphere. On the other hand, the actual contribution from VSLS to
244 stratospheric Br_y could be larger than 5 ppt. The results presented in Figure S2 are
245 consistent with estimates of at least 5 ppt of bromine being supplied by VSLS
246 [*Salawitch et al.,* 2005; *Dorf et al*., 2008; *Theys et al*., 2007; *Salawitch et al.,* 2010;
247 *Parrella et al.*, 2013, *Liang et al.,* 2014].

248 Time series of BrO, BrCl, and OClO at 50 hPa from the two GEOSCCM
249 simulations, averaged over 60-90°S during Aug.-Oct are shown in Figure S3. Neither
250 BrO, BrCl, nor OClO return to their respective 1980 levels by the end of the

simulations. The time series of OClO behaves in a similar manner to BrO and BrCl because the abundance of OClO in the polar vortex is much more sensitive to BrO than ClO [*Salawitch et al*., 1988]. The difference between the two simulations grows larger with time, reflecting a much larger role for ozone loss due to the BrO+ClO cycle in A12014_5Br than the A12014_0Br simulation during the latter part of this century. Together, Figures 3, S2, and S3 show that including all the sources of stratospheric bromine causes about a decade delay in the recovery of the Antarctic ozone hole.

Including supply of stratospheric bromine from VSLS reduces ozone columns nearly everywhere in the model, with the smallest changes in the tropics and the largest decreases over the high latitudes during spring (Figure 4). The effect of this extra bromine is largest during the time period of peak chlorine (1990 – 2019). For this three-decade period, inclusion of Br_y from VSLS decreases total column ozone by 16-22 DU over Antarctica during September. In the Northern Hemisphere high latitudes, ozone is reduced by 10-20 DU during March. The tropical total column ozone decrease is typically less than 2 DU. This three-decade time period also includes the eruption of Mt. Pinatubo in June 1991, shortly after which ozone loss due to bromine was larger in the A1204_5Br simulation. However, the enhanced ozone loss following the eruption of Mt Pinatubo follows the aerosol lifetime in the stratosphere of 1-3 years and does not significantly impact the 30-year average response.

4. Conclusions

Inclusion of 5 ppt of stratospheric bromine to represent VSLS in GEOSCCM results in better agreement with OMI measurement of total column BrO and causes several important changes in the simulation of the seasonal evolution and recovery over the 21st century of Antarctic ozone. A high bias in simulated SH polar total column ozone with respect to OMI observations collected over 2005 to 2015 is significantly reduced. Including VSLS bromine causes the minimum seasonal ozone column to occur about a week earlier, in closer agreement with OMI observations. The very low to near zero ozone concentrations observed in the deep Antarctic lower stratospheric polar vortex during late September into early October during the mid-late 1990s and into the early 2000s are only simulated when the VSLS bromine source is included.

According to our GEOSCCM simulations, recovery of Antarctic ozone is delayed by about a decade upon including the VSLS contribution to stratospheric bromine. October Antarctic ozone columns are projected to return to 1980 levels around 2071, in close agreement with a recovery year of 2068 based on an empirical, parametric model [*Newman et al*., 2006]. The 2010 WMO Assessment [*WMO*, 2011] attributed an earlier recovery year of ~2051, provided by simulations from 17 CCMs, to meteorological and dynamical effects of GHGs on Antarctic ozone that were not considered in the parametric model. However, most of the CCM simulations used in *WMO* [2011] neglected VSLS bromine and *WMO* [2014] showed the meteorological and dynamical effects of GHGs on Antarctic ozone recovery was small. These results show that a constant addition of 5 ppt of bromine cause almost a decade later recovery of Antarctic ozone and suggest that any future growth or

297 new emissions of bromine containing compounds, as low as a couple ppt, could
298 significantly impact the projected ozone recovery date. Our study also suggests
299 models estimates of polar ozone recovery for the next Assessment should include a
300 realistic treatment of the VSLS contribution to stratospheric bromine. If bromine
301 from VSLS are neglected, recovery dates will be biased early by perhaps as much as
302 a decade.
303
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Figures

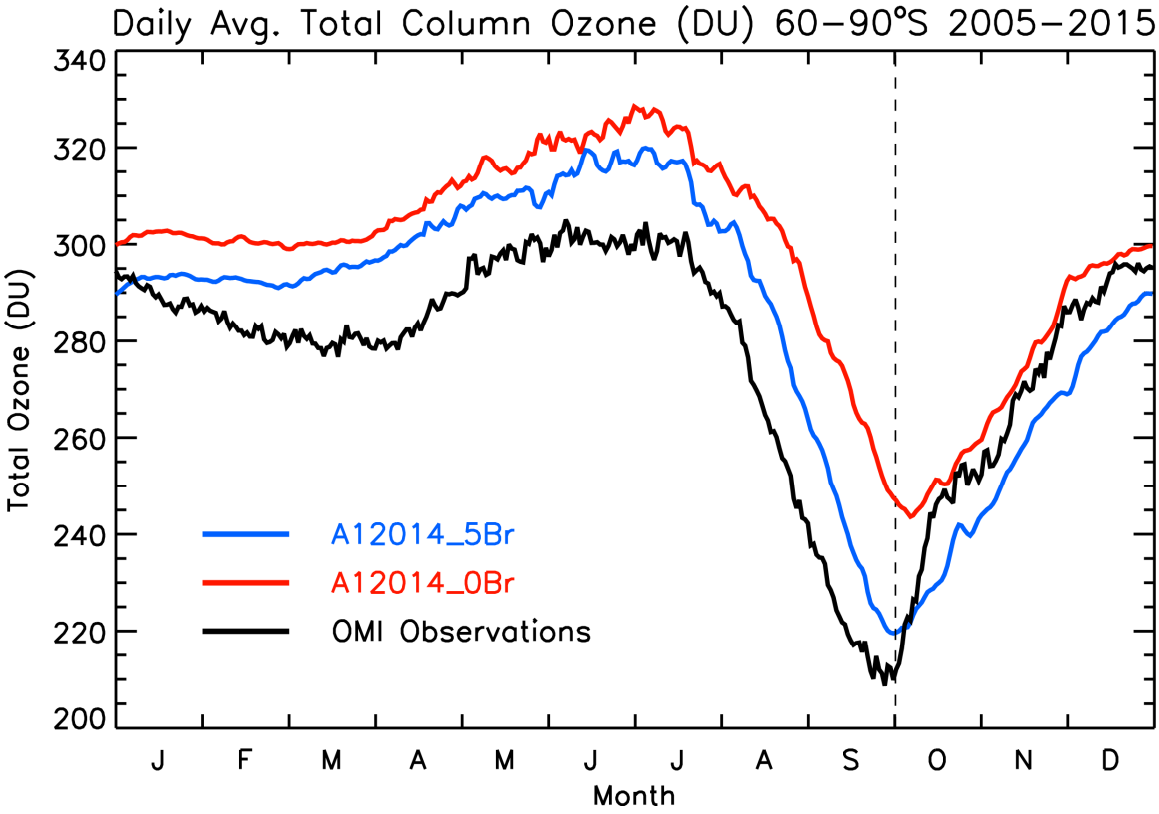

Figure 1. The daily average total column ozone (DU) between 60-90°S for 2005-2015. The blue curve shows the A12014_5Br simulation, the red curve is the A12014_0Br simulation, and the black curve is the OMI observation. A dashed black line shows 1 October.

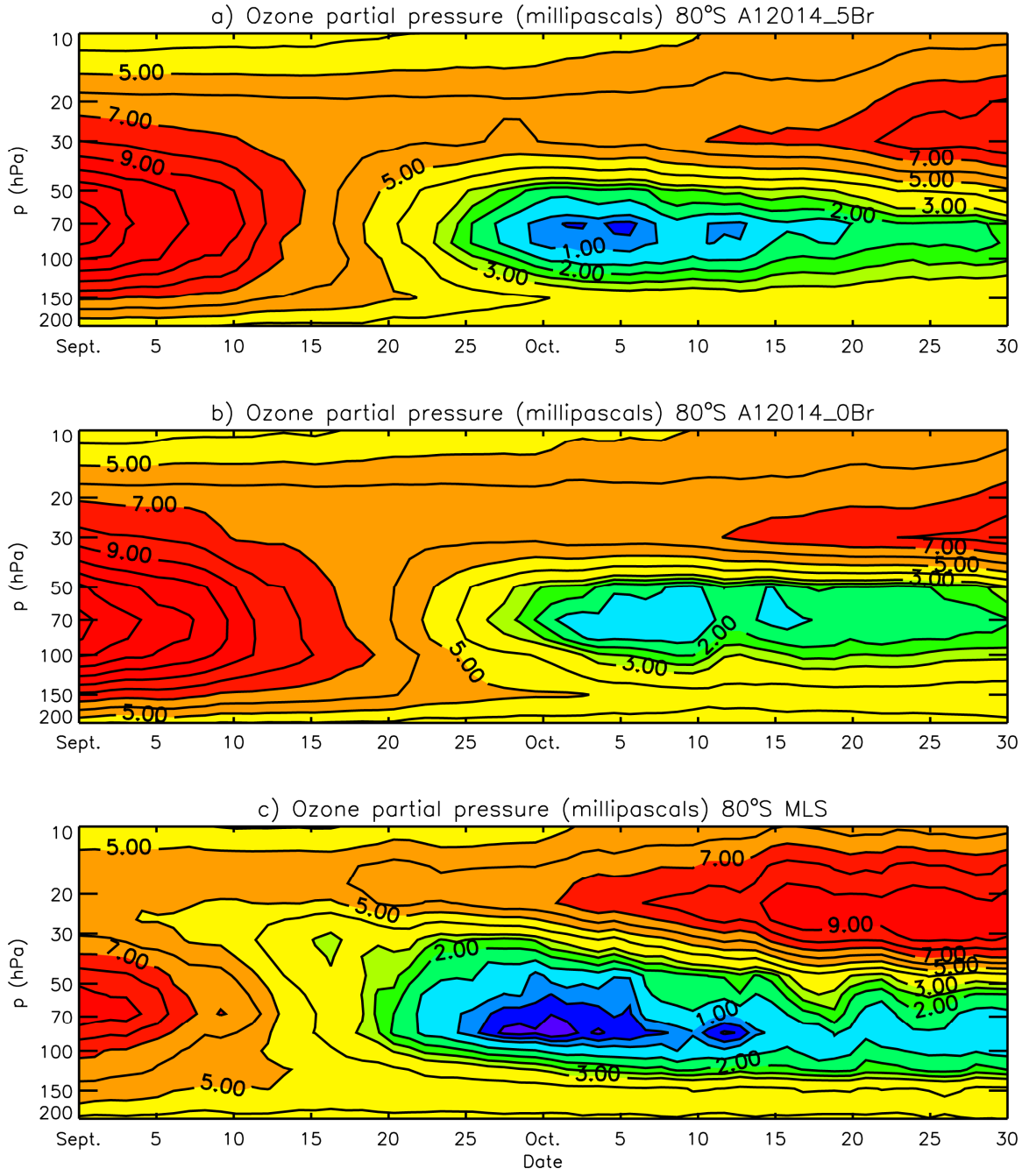

Figure 2. Daily ozone partial pressure (millipascals) at 80°S for a) A12014_5Br, b) A12014_0Br, and c) MLS measurements from 1 September to 30 October averaged over 2005-2009. The contour interval is 0.25 between 0 and 1 and 0.5 between 1 and 3 and 1 above 3.

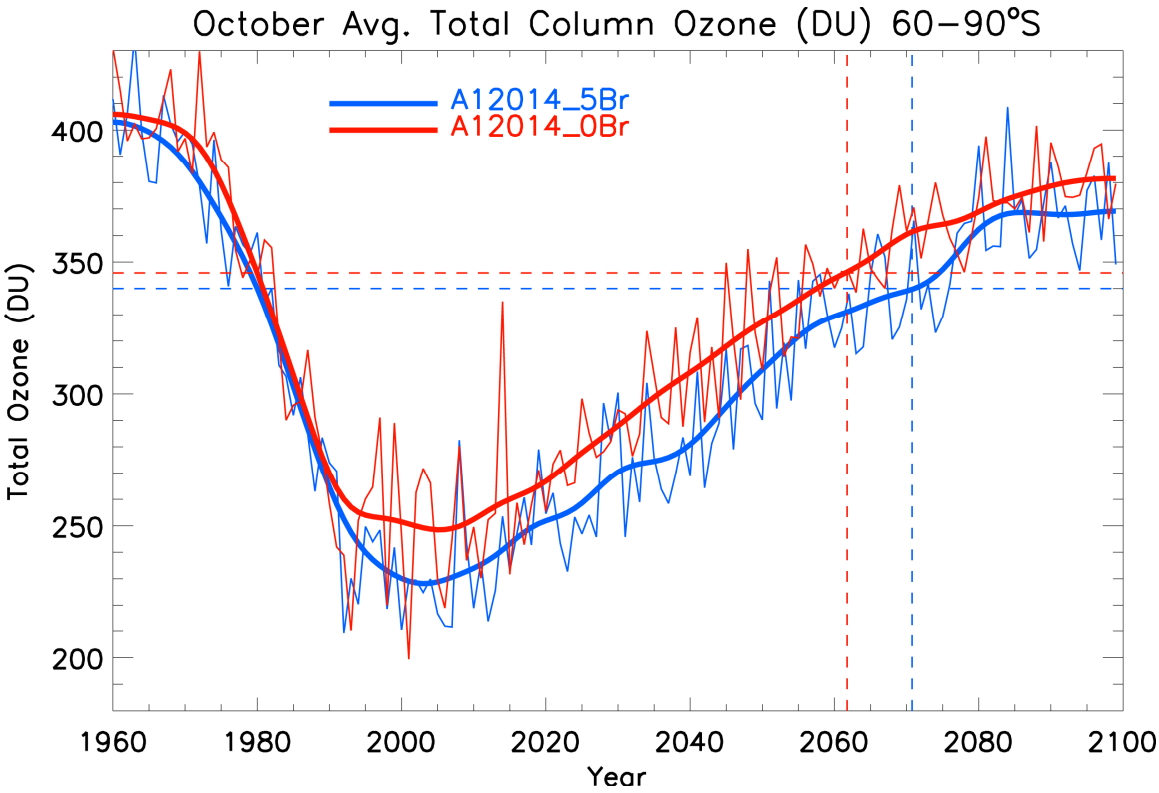

Figure 3. The October average total column ozone (DU) between 60-90°S from 1960 to 2099. The blue curves show the individual year values (thin) and low pass filtered values (thick) for the simulation with an extra 5 ppt of bromine. The red curves show the individual year values (thin) and low pass filtered values (thick) for the simulation without a representation of bromine from VSLS. The vertical dashed red and black lines represent the return to 1980 levels using the smoothed curves without the extra Br and the simulation with the extra Br.

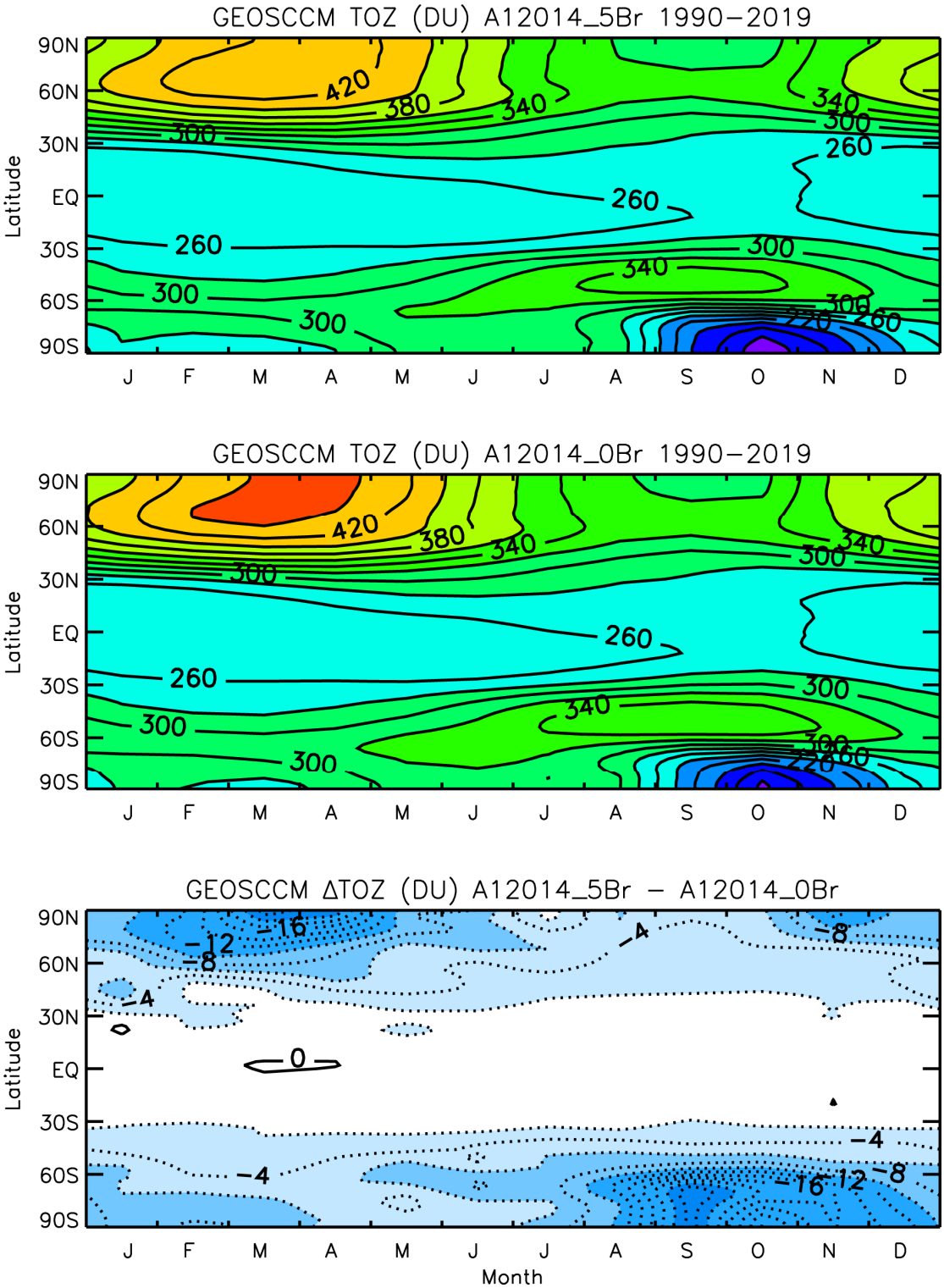

Figure 4. The latitude by month total column ozone (DU) for the A12014_5Br (top panel) and A12014_0Br (middle panel) simulations average over 1990-2019. The bottom panel shows the difference in total column ozone (DU) between the two simulations.