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Key Points:

- Natural emissions of bromocarbons strongly impact stratospheric ozone trends
- This process has so far been neglected in most chemistry climate model studies
- Including bromocarbon emissions, our model better reproduces past ozone trends

Supporting Information:

- Text S1 and S2 and Figures S1 and S2

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Simulating the impact of emissions of brominated very short lived substances on past stratospheric ozone trends

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Abstract Bromine from very short lived substances (VSLS), primarily from natural oceanic sources, contributes substantially to the stratospheric bromine loading. This source of stratospheric bromine has so far been ignored in most chemistry climate model calculations of stratospheric ozone trends. Here we present a transient simulation with the chemistry climate model EMAC for the period 1960–2005 including emissions of the five brominated VSLS $CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBrCl_2$, and $CHBr_2Cl$. The emissions lead to a realistic stratospheric bromine loading of about 20 pptv for present-day conditions. Comparison with a standard model simulation without VSLS shows large differences in modeled ozone in the extratropical lowermost stratosphere and in the troposphere. Differences in ozone maximize in the Antarctic Ozone Hole, resulting in more than 20% less ozone when VSLS are included. Even though the emissions of VSLS are assumed to be constant in time, the model simulation with VSLS included shows a much larger ozone decrease in the lowermost stratosphere during the 1979–1995 period and a faster ozone increase during 1996–2005, in better agreement with observed ozone trends than the standard simulation without VSLS emissions.

1. Introduction

Bromine plays an important role in stratospheric chemistry. The main sources of stratospheric bromine in the present-day atmosphere are methyl bromide (CH_3Br), which has both natural and anthropogenic sources, and the halons, which are anthropogenic. In addition, very short lived substances (VSLS), primarily of natural biogenic origin, contribute about 20–30% to the present-day stratospheric bromine loading [e.g., *Sinnhuber et al.*, 2005; *Dorf et al.*, 2006; *World Meteorological Organization (WMO)*, 2011]. The most abundant VSLS are bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2), whereas the mixed chlorine-bromine VSLS CH_2BrCl, $CHBr_2Cl$, and $CHBrCl_2$ have a smaller contribution to the total VSLS amount. The stratospheric bromine loading has reached a maximum around the year 2001 and shows since then a decline of about −1%/yr due to the reduction of bromine emissions by the Montreal Protocol and its amendments [*Hendrick et al.*, 2008].

It has long been suggested that VSLS could have contributed significantly to past ozone trends in the extratropical lower stratosphere by providing additional bromine that can act as a reaction partner for chlorine and bromine from anthropogenic sources [*Dvortsov et al.*, 1999]. Two-dimensional model calculations have shown that VSLS can indeed significantly increase stratospheric ozone trends, in particular in the lowermost stratosphere and for periods with enhanced (volcanic) stratospheric aerosol loading [*Salawitch et al.*, 2005; *Sinnhuber et al.*, 2009]. There has been considerable progress in recent years to consider the contribution of VSLS to stratospheric bromine in chemical transport models and chemistry climate models [e.g., *Warwick et al.*, 2006; *Sinnhuber and Folkins*, 2006; *Kerkweg et al.*, 2008; *Aschmann et al.*, 2009; *Gettelman et al.*, 2009; *Liang et al.*, 2010; *Hossaini et al.*, 2010; *Aschmann et al.*, 2011; *Ordóñez et al.*, 2012; *Tilmes et al.*, 2012; *Hossaini et al.*, 2013]. However, previous chemistry climate model calculations that are used for attribution of past stratospheric ozone changes and for projections of future stratospheric changes have so far generally ignored the contribution of brominated VSLS. Here we present a chemistry climate model simulation of the period 1960 to 2005 with emissions of VSLS taken into account. This simulation is compared to a standard model simulation without VSLS emissions to investigate the impact of VSLS on past stratospheric ozone trends.

2. Model and Data

The model experiments have been performed with the chemistry climate model (CCM) EMAC (ECHAM/MESSy Atmospheric Chemistry) version 1.7 [*Roeckner et al.*, 2006; *Jöckel et al.*, 2006]. EMAC is a three-dimensional atmospheric circulation model with the fully coupled interactive chemistry module MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere) [*Sander et al.*, 2005]. The model is used with a standard set of submodels describing tropospheric and middle atmosphere processes (e.g., radiation and convection). The processes of wet deposition and liquid phase chemistry for gas phase and aerosol species are calculated in the scavenging module (SCAV) [*Tost et al.*, 2006]. The standard radiation scheme is extended by the highly resolved shortwave radiation parameterization FUBRad [*Nissen et al.*, 2007]. The model was applied in a spectral T42 resolution (2.8° × 2.8°) and 39 hybrid layers in the vertical with a model top at 0.01 hPa (≈80km). At the Freie Universität Berlin a transient simulation has been integrated from 1960 to 2005 according to the recommendations of the SPARC CCMVal initiative [*SPARC CCMVal*, 2010] for the REF-B1 scenario (REF-B1). Additionally, an equivalent simulation has been performed but with taking the emissions of brominated VSLS into consideration (REF-B1-VSLS). This is realized by prescribing the emissions of $CHBr_3$, CH_2Br_2, $CHClBr_2$, $CHCl_2Br$ and CH_2ClBr following the emission scenario 5 of *Warwick et al.* [2006] as used by *Kerkweg et al.* [2008], and by adding the corresponding photolysis reactions as well as the reactions with OH to the set of the selected chemical reactions. Rate coefficients have been used according to JPL2006 [*Sander et al.*, 2006]. Recent laboratory studies of the bromoform absorption cross section [*Papanastasiou et al.*, 2014] and the reaction of bromoform with OH radicals [*Orkin et al.*, 2013] suggest a slower photolysis and a faster loss due to OH reaction for bromoform compared to the JPL2006 recommendations that together will lead to an increase of total bromoform loss rate within about 10% in the tropical troposphere [*Papanastasiou et al.*, 2014]. Tropospheric concentrations of OH in the model runs compare generally well with the climatology of *Spivakovsky et al.* [2000], with the tropospheric global mean OH concentration in the REF-B1-VSLS simulation about 17% smaller and the tropical mean tropospheric OH concentration about 10% smaller than the climatology of *Spivakovsky et al.* [2000]. No iodine chemistry is included in these simulations. Natural forcings such as solar variability, El Niño–Southern Oscillation, quasi-biennial oscillation (QBO), and volcanic eruptions are included in both simulations. Inadvertently, the prescribed stratospheric sulfate aerosol is shifted by 2 years relative to observations in both of our simulations so that the effect of large volcanic eruptions occur 2 years early in our simulation as compared to the real atmosphere.

The performance of EMAC in reproducing past ozone trends is discussed in *Austin et al.* [2010] and *WMO* [2011] for the transient SCN-B2d simulation defined within *Eyring et al.* [2008]. Between 1960 and 2000 the ozone change in EMAC is in the range of the other CCMs, while the Antarctic ozone loss is underestimated compared to other CCMs and observations.

The bromoform emissions of 595 Gg/yr in this run following scenario 5 of *Warwick et al.* [2006] are well within the range of other emission scenarios [e.g., *Ordóñez et al.*, 2012, and references therein] but are significantly larger than the recent bottom-up scenario of *Ziska et al.* [2013], who estimated a net bromoform flux of between 120 and 210 Gg/yr. Emissions of CH_2Br_2 from *Warwick et al.* [2006] as used in our simulation amount to 113 Gg/yr, which is larger by almost a factor of 2 compared to more recent emission scenarios [*Hossaini et al.*, 2013]. The ocean to atmosphere flux of VSLS in our emission scenarios is constant in time. Very little is currently known on seasonal, interannual, and possible long-term changes in VSLS emissions. However, *Ziska et al.* [2013] present evidence for a long-term increase in VSLS emissions over the past decades.

We compare the simulated VSLS profiles with observations taken during a set of aircraft campaigns: TRACE-A in 1992; STRAT in 1996; PEM-Tropics in 1996 and 1999; ACCENT in 1999; TRACE-P in 2001; Pre-AVE, AVE, and CR-AVE in 2004 and 2006; TC4 in 2007; HIPPO-1 to HIPPO-5 between 2009 and 2011; SHIVA in 2011; and TACTS/ESMVal in 2012, as well as data from the CARIBIC project [*Wisher et al.*, 2014] (see supporting information).

3. Results

3.1. Bromine Loading

Our model simulation with VSLS emissions results in a realistic atmospheric bromine loading that agrees generally well with atmospheric observations (Figure 1). The total stratospheric bromine loading increases

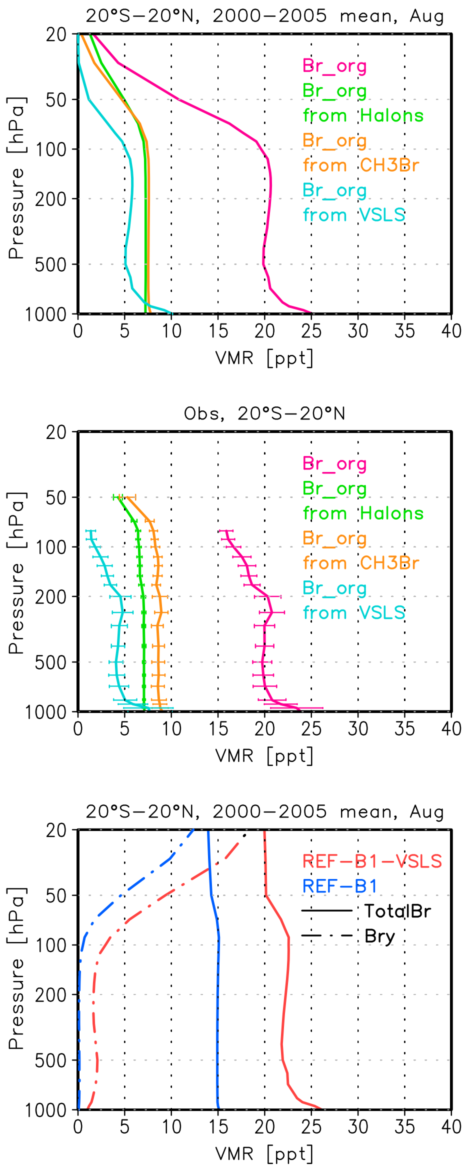

Figure 1. Vertical profile of organic bromine volume mixing ratios (in parts per trillion, ppt) and its contribution from halons (green), CH_3Br (orange), and VSLS (blue) in the tropics (20°S–20°N) for (top) August in the REF-B1-VSLS simulation and (middle) observations compiled during various aircraft campaigns. (bottom) Total bromine (solid) and inorganic bromine (dash-dotted) mixing ratio for the REF-B1 (blue) and REF-B1-VSLS (red) simulations.

for present-day situations (2000–2005) from about 14 ppt in REF-B1 to about 20 ppt in REF-B1-VSLS, i.e., an increase of more than 40%. The stratospheric bromine loading of 20 ppt agrees well with observations, and the corresponding contribution from VSLS of about 6 ppt is well within the range of available observations [*WMO*, 2011].

VSLS and organic bromine from the REF-B1-VSLS simulation averaged over the tropics agree generally well with averaged profiles from the set of aircraft campaigns (Figure 1). Both observations and the model simulation show up to 10 ppt of VSLS in the marine boundary layer, decreasing to a free tropospheric value of around 5 ppt (slightly less in the observations, slightly larger in the simulation) and an upper tropospheric maximum of about 6 ppt. Correspondingly, total organic bromine is about 25 ppt in the boundary layer, decreases to about 20 ppt in the free troposphere, and shows an upper tropospheric maximum of 21–22 ppt. A comparison of the individual bromocarbons between our EMAC simulation and the set of aircraft observations (see supporting information) reveals that the model simulations using the emission scenario of *Warwick et al.* [2006] slightly overestimate $CHBr_3$ and more significantly overestimate CH_2Br_2 by about 0.5 ppt below 200 hPa, while the mixed chloro-bromocarbons $CHCl_2Br$, $CHClBr_2$, and CH_2ClBr that together account for about 0.8 ppt of bromine in the tropical troposphere are underestimated in our simulation. Moreover our EMAC simulation has too much VSLS transported into the tropopause region: while the observations show a VSLS maximum at about 200 hPa, the EMAC simulation has the maximum at about 150 hPa. This results in a larger contribution of direct source gas injection (SGI) and a smaller contribution of product gas injection (PGI) into the stratosphere in EMAC compared to other estimates; see also the discussion on SGI/PGI by *Aschmann and Sinnhuber* [2013] and *Fernandez et al.* [2014]. While the standard simulation without VSLS emissions has very low inorganic bromine in the troposphere, the VSLS emissions lead to a tropospheric inorganic bromine loading of about 1.5–2 pptv (Figure 1, bottom).

To estimate the sensitivity of the modeled VSLS distribution to the emission scenario, we performed a set of sensitivity simulations with EMAC using the emission scenarios of *Liang et al.* [2010], *Ordóñez et al.* [2012] and *Ziska et al.* [2013] in comparison to our standard simulation using emission scenario 5 of *Warwick et al.* [2006] (see supporting information). The scenarios of *Liang et al.* [2010] or *Ordóñez et al.* [2012] lead to significantly lower CH_2Br_2 and $CHBr_3$ profiles than the emission scenario 5 of *Warwick et al.* [2006]. For CH_2Br_2 and for $CHBr_3$ the observational data are between the simulations using *Warwick et al.* [2006] and the simulations using *Liang et al.* [2010] or *Ordóñez et al.* [2012]. While our standard simulation using emissions of *Warwick et al.* [2006] results in an increase of stratospheric bromine of about 6 ppt, using the emission scenarios of *Liang et al.* [2010], *Ordóñez et al.* [2012], and *Ziska et al.* [2013] results in an increase of stratospheric bromine of only about 3–4 ppt. This is qualitatively similar to the results of *Hossaini et al.* [2013], although the absolute increase in stratospheric bromine due to VSLS is smaller in our simulation.

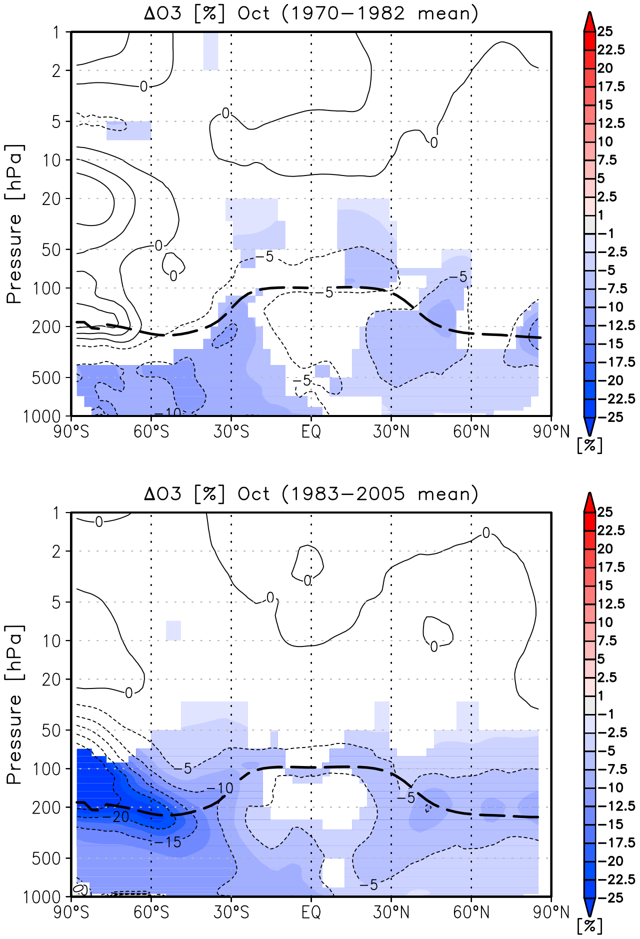

Figure 2. Modeled changes in ozone due to the inclusion of VSLS for October. (top) Pre-ozone hole period (1970–1982) and (bottom) 1983–2005. Color shading indicates statistically significant differences on the 95% confidence level. The position of tropopause is shown by the black dashed line.

3.2. Impact on Ozone

The additional bromine due to VSLS in the model leads to reduced ozone concentrations throughout most of the atmosphere, with largest changes in the lower stratosphere and troposphere. The differences in ozone between the simulation with VSLS and the standard simulation without VSLS reaches 5 to 10% in the lowermost stratosphere and the troposphere (Figure 2), with largest changes around the tropopause. Calculated ozone changes due to VSLS from our simulations are qualitatively in agreement with the impact of VSLS in the model experiments shown by *Braesicke et al.* [2013] and *Yang et al.* [2014]. As our simulation does not include a detailed tropospheric bromine chemistry, the impact on tropospheric ozone from our simulations should be treated with caution. Nevertheless, the calculated reduction of tropospheric ozone due to VSLS emissions of 6% for 1970–1982 and 7% for 1983–2005 agrees well with similar results of *Yang et al.* [2014] and also the 6.5% reduction of tropospheric ozone due to bromine chemistry as given by *Parrella et al.* [2012] (which, however, includes also the effect of bromine from sea-salt aerosols) or the 10% reduction of tropical tropospheric ozone due to bromine and iodine given by *Saiz-Lopez et al.* [2012]. Although the VSLS emissions are constant in time, the impact on stratospheric ozone is larger in the more recent decades with enhanced chlorine loading, due to combined bromine-chlorine catalytic ozone loss cycles. The maximum impact is seen for the Antarctic ozone hole, where the inclusion of VSLS leads to more than 20% lower ozone concentrations in the October monthly mean zonal mean. Part of the modeled tropospheric changes at high latitudes are clearly attributable to intrusions from the stratosphere.

3.3. Impact of VSLS on Ozone Trends

Even though the VSLS emissions in our model simulation are constant in time, the additional bromine due to VSLS has an impact on ozone trends by providing an additional chemical reaction partner for the anthropogenic halogen loading. Total ozone relative to 1979/1980 for various latitude bands is shown in Figure 3 for both EMAC simulations, compared to ground-based observations. In all latitude bands, the model with VSLS emissions shows stronger ozone trends than the standard model, resulting in an evolution of total ozone in better agreement with the ground-based observations. The enhanced ozone reductions are particularly pronounced for the 1990s. For the Southern Hemisphere high latitudes (south of 60°S) during October, the simulation with VSLS reaches total ozone changes of more than 30% in the mid-1990s relative to 1980, in excellent agreement with ground-based observations, while the standard simulation shows ozone changes of less than 10% over this period. Generally, the impact of VSLS on ozone changes is largest during the 1990s and becomes insignificant in the latest years after 2000. The enhanced ozone reduction due to VSLS in the 1990s and the much smaller impact after 2000 is qualitatively consistent with the earlier

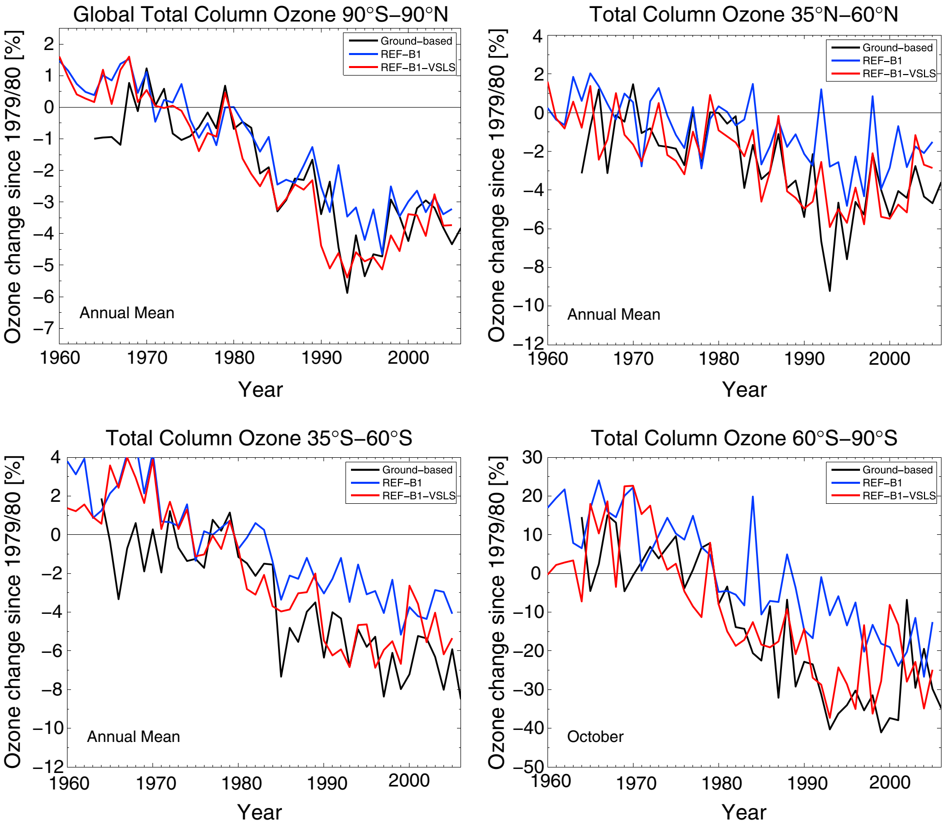

Figure 3. Modeled evolution of total ozone for (top, left) the global mean, (top, right) Northern Hemisphere midlatitudes (35°N–60°N), (bottom, left) Southern Hemisphere midlatitudes (35°S–60°S), and (bottom, right) Southern Hemisphere high latitudes (60°S-90°S, October). Standard simulation without VSLS in blue, with VSLS emissions in red, compared to ground-based observations (black).

two-dimensional model simulations of *Salawitch et al.* [2005] and *Sinnhuber et al.* [2009] and the chemical transport model simulation of *Feng et al.* [2007].

The impact of VSLS on ozone trends is largest in the lowermost stratosphere. Figure 4 shows Northern Hemisphere midlatitude ozone profile trends over the periods 1979–1995 and 1996–2005. This figure may be compared to Figures 2–25 of *WMO* [2011], which show the corresponding trends of a set of CCM calculations without VSLS. Our standard simulation exhibits very small ozone trends in the lower and lowermost stratosphere, in agreement with other CCM simulations that rate high in an evaluation of transport and chemistry [*WMO*, 2011, Figures 2–25]. Inclusion of VSLS emission leads to much larger ozone decreases in the lowermost stratosphere during 1979–1995 and a larger ozone increase during 1996–2005. Trends are calculated using a multivariate regression taking into account the solar cycle, two orthogonal terms of the equatorial wind quasi-biennial oscillation (QBO), and the stratospheric aerosol loading. Note that we used the model's own aerosol loading, so that the wrong timing in volcanic eruptions is to a first order accounted for. We consider two different methods to account for ozone trends: a piecewise linear trend (PW) or a regression to equivalent effective stratospheric chlorine (EESC). While both methods result in different trend estimates, the effect of VSLS on the trends is comparable for both methods.

The model simulation with VSLS shows enhanced negative ozone trends during the period 1979–1995 and a larger ozone increase during 1996–2005, in better agreement with observations than the standard model. Although the model with VSLS shows a larger ozone trend in better agreement with observations, it also underestimates observed ozone trends taken from *WMO* [2011] in the lowermost stratosphere over the 1979–1995 period. However, there is also a significant discrepancy between ozone trends calculated from different observational data sets in the lower stratosphere. The PW trend shows a larger ozone increase in the lowermost stratosphere during 1996–2005 than the EESC trend, indicating that the modeled ozone increase over this period is only partly a result of decreasing EESC. *Feng et al.* [2007] calculate a smaller

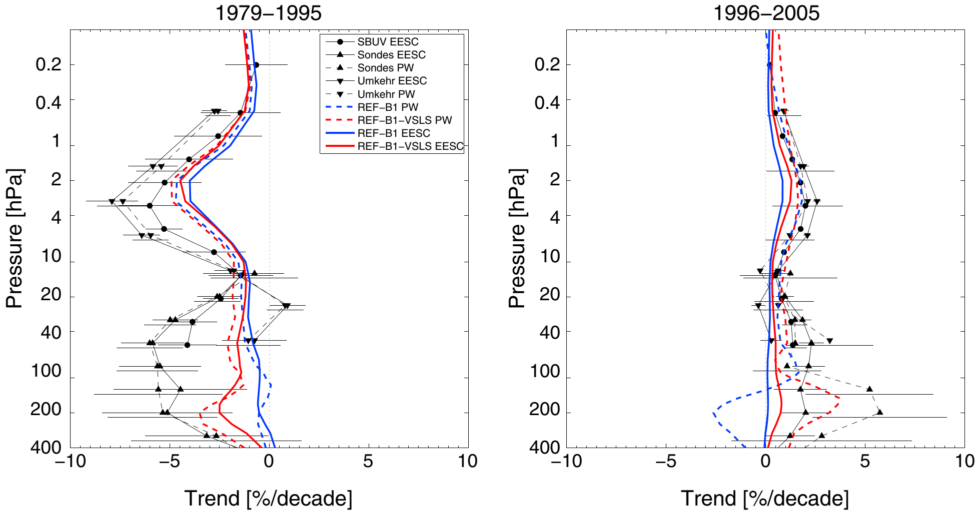

Figure 4. Ozone trends in the Northern Hemisphere midlatitudes (35°N–60°N) from the model simulations with (red) and without (blue) VSLS emissions, together with ozone trends derived from various observations, identical to Figures 2–7 of *WMO* [2011]. Both piecewise linear (PW) trends and trends based on a regression to effective equivalent stratospheric chlorine (EESC) are shown; (left) 1979–1995 and (right) 1996–2005. A corresponding plot for global mean trends is shown in the accompanying supporting information.

impact of VSLS on midlatitude ozone profile trends for the period 1980–2004, which is not necessarily inconsistent with our results, as we not only find a larger loss for the period 1979–1995 but also a faster recovery over the period 1996–2005. However, note that the chemical transport model of *Feng et al.* [2007] reproduces much larger ozone trends in the lowermost stratosphere, in better agreement with observed trends than the free-running CCM simulations.

4. Discussion and Conclusions

We have presented a set of CCM simulations over the period 1960–2005, following the protocol of CCMVal-2 REF-B1 simulations but taking into account the effect of brominated VSLS that have up to now been ignored in CCM studies of past ozone changes. We find that VSLS emissions that result in a realistic stratospheric bromine loading have a significant impact on modeled ozone and ozone trends. Global mean total ozone is reduced by about 5–10 Dobson units in the simulation with an additional bromine loading by about 6 ppt due to VSLS, with the largest impact on the lower stratosphere and the troposphere. The impact of VSLS is larger for enhanced halogen loading and for enhanced stratospheric aerosol loading following large volcanic eruptions, in agreement with earlier two-dimensional model studies [*Salawitch et al.*, 2005; *Sinnhuber et al.*, 2009] and chemistry transport model studies [*Feng et al.*, 2007]. We find that the inclusion of VSLS emissions in the CCM leads to significantly larger ozone trends, with larger losses over the period 1979–1995 and a faster recovery over the period 1996–2005, in better agreement with observations than the standard model without VSLS emissions. Possible long-term changes in VSLS emissions [*Ziska et al.*, 2013] would have an additional impact on stratospheric ozone trends that is not considered in our study, but the effect can be estimated from our simulations with and without VSLS. We thus suggest that future CCM simulations of stratospheric ozone depletion and recovery should include realistic VSLS emissions. The recent study of *Hossaini et al.* [2013] and results from the TransCom-VSLS model intercomparison exercise (R. Hossaini, personal communication, 2014) may provide some guidance on which VSLS emission scenarios to use in future studies. One obvious next step will be to perform similar model simulations as we did here for the future, to study the effect of VSLS emissions on the recovery of stratospheric ozone during the 21st century.

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