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# Auxiliary Material: Impact of Very Short-lived Halogens on Stratospheric Ozone Abundance and UV radiation in a Geo-engineered Atmosphere

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## 1 Meteorology of the Polar Vortex

As described in the main text, we select meteorological conditions of the year 2040 from Tilmes et al. (2009) for simulations presented in this study. Chemical ozone loss in high latitudes is strongly linked to temperatures in the polar vortex, since the activation of chlorine is strongly temperature dependent (Drdla and Müller, 2012, and references therein). The activation of chlorine containing reservoirs is dominated by reactions on cold binary aerosol particles. A formulation to calculate the threshold temperature for the activation of chlorine ($\mathrm{T_{ACL}}$) was derived by Drdla and Müller (2012). $\mathrm{T_{ACL}}$ is dependent on potential temperature, water vapor and the surface area density (SAD). Vortex temperatures are therefore not directly correlated to chlorine activation. Tilmes et al. (2007) have introduced a measure for the potential for activated chlorine (PaCl). PaCl describes the fraction of the vortex where temperatures are below $\mathrm{T_{ACL}}$. This measure can be directly linked to chlorine activation and therefore ozone loss in the polar vortex (WMO, 2010).

In Figure S1, we compare the meteorology of the polar vortex used in this study based on WACCM results to MERRA reanalysis (Rienecker et al., 2011) for recent winters (as shown in Figure S1, left panel). For this, average temperatures of the Arctic and Antarctic polar vortex are compared. The polar vortex edge is calculated by using the criterion by Nash et al. (1996). In addition, we compare PACl derived using the WACCM meteorology and background SAD conditions to values derived using MERRA reanalysis (Figure S1, right panel).

Polar vortex temperatures over Antarctica in WACCM are lower compared to MERRA reanalysis, resulting in a colder and longer-lasting winter. After reaching $\mathrm{T_{ACL}}$, colder temperatures do not trigger more chlorine activation. PACl is therefore in good agreement with the values derived from MERRA between July and October. PACl in WACCM is larger in November compared to the reanalysis dataset, since temperatures are below $\mathrm{T_{ACL}}$ for a longer period. An overestimation of chemical ozone depletion in November compared to observations can be expected in this study.

Arctic average polar vortex temperatures tend to be warmer between January and March than recent cold Arctic winters. However, PACl is comparable to values derived from MERRA reanalysis for moderately cold Arctic winters. This is, because WACCM temperatures describe a temperature gradient in the polar vortex ranging from rather warm to very cold temperatures towards the vortex core. We therefore expect chlorine activation in the Arctic vortex to be comparable to a recently observed moderately cold Arctic winters. As for Antarctica, the Arctic vortex is more persistent and long-lasting compared to observed cold winters. In April, vortex temperatures are well below observed temperatures and PACl values are larger than what we expect from recent observations. However, the Arctic vortex is rather small compared to observations (not shown) and the expected overestimation in ozone loss only covers a small area north of 75°N.

## 2 Contributions of VSL organics ($\mathrm{Br_y^{VSL}}$) to the stratospheric total bromine ($\mathrm{Br_y}$)

In the main paper, three cases for stratospheric $\mathrm{Br_y^{VSL}}$ are considered. Here we justify the enhancement of $\mathrm{Br_y}$ of 6 ppt as an average estimate derived from earlier studies, and the enhancement of $\mathrm{Br_y}$ of 10 ppt plus an increase of $\mathrm{Cl_y}$ by 100 ppt, as an upper limit estimate considering stratospheric $\mathrm{Br_y^{VSL}}$.

The past three WMO/UNEP Scientific Assessment of Ozone Depletion reports have quantified the enhancement to stratospheric total inorganic bromine ($\mathrm{Br_y}$) due to VSL organics ($\mathrm{Br_y^{VSL}}$). Chapter 2 of WMO (2003) provides an overview of the chemical, biological, and physical processes that govern $\mathrm{Br_y^{VSL}}$. The largest contributions are from dibromomethane ($\mathrm{CH_2Br_2}$) and bromoform ($\mathrm{CHBr_3}$), which are produced by biological processes in the ocean. Sea-salt and halide-containing aerosols supply bromine to the lower troposphere, but likely do not play a strong role in affecting stratospheric $\mathrm{Br_y}$ (Yang et al., 2005).

Table 1-9 of WMO (2010) gives a range for $\mathrm{Br_y^{VSL}}$ of 1 to 8 ppt based on tropospheric focused studies. Table 1-14 of WMO (2010) gives an ensemble mean estimate of 6 ppt for $\mathrm{Br_y^{VSL}}$ based on stratospheric focused studies. The tropospheric focused estimate is based on observed abundances of VSL bromocarbons near the cold point tropopause combined with model estimates of efficiency of transport, to the stratosphere, of product gases formed when VSL bromocarbons decompose in the troposphere. The stratospheric studies are all based on observations of BrO; $\mathrm{Br_y^{VSL}}$ is inferred from the difference between $\mathrm{Br_y}$ calculated from observed BrO (typically in the middle and upper stratosphere) and the amount of $\mathrm{Br_y}$ that is supplied by long-lived methyl bromine ($\mathrm{CH_3Br}$) and

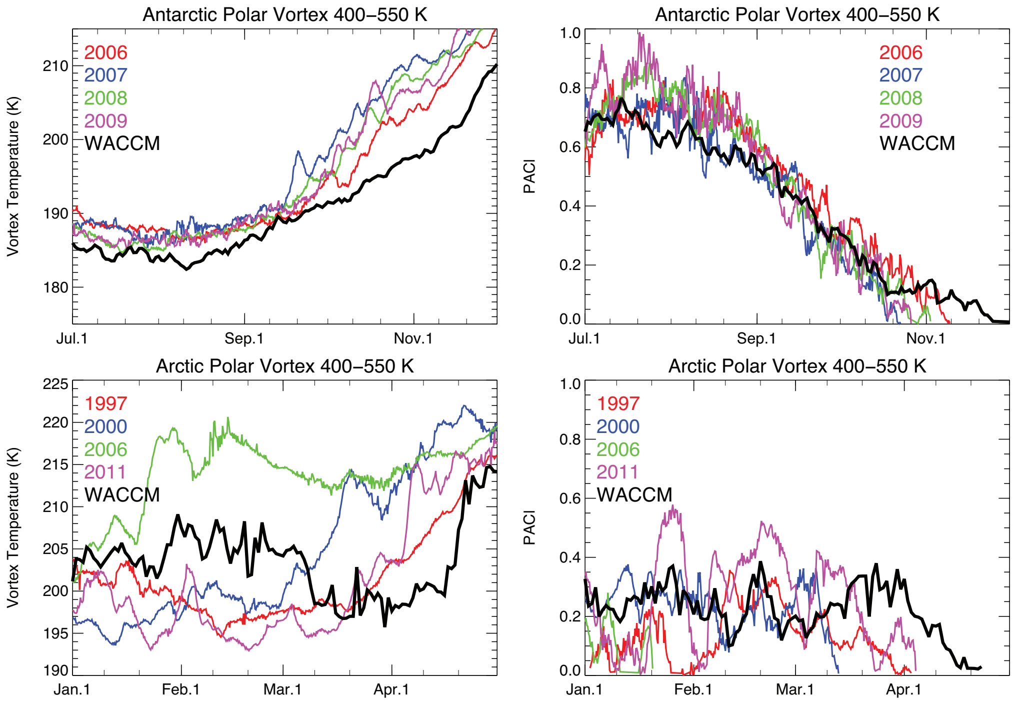

Fig. 1: Left panels: WACCM averaged polar vortex temperature between 400-550 K for the Antarctic (top) and Arctic (bottom) compared to MERRA reanalysis for different years (different colors). For the Arctic, three cold winters (1997, 2000, and 2011) and one very warm winter (1997) are selected. Right panels: potential for activated chlorine (PACl) (Tilmes et al., 2009) derived using WACCM results and MERRA reanalysis for background SAD conditions. See text for more details.

halons.

In the main text we consider three cases for $\mathrm{Br_y^{VSL}}$: 0, 6, and 10 ppt. The 6 ppt value is based on the ensemble mean from Table 1-14 of WMO (2010). The upper limit of 10 ppt is chosen because 7 of the 12 studies represented in Table 1-14 have upper limits of 10 ppt or higher. The plausibility of the 10 ppt upper limit is further supported by an analysis of consistency between satellite observations of total column BrO versus the sum of tropospheric partial column BrO (based on in situ aircraft data) and stratospheric partial column BrO (based on a model), published after WMO (2010), that reported best agreement for $\mathrm{Br_y^{VSL}}$ of 9 ppt (Choi et al., 2012).

Chapter1 and 2 of (WMO, 2007) and Chapter 1 of (WMO, 2010) quantified the enhancement to stratospheric total inorganic chlorine ($\mathrm{Cl_y}$) due to VSL chlorocarbons ($\mathrm{Cl_y^{VSL}}$). Two lines of evidence were pursued. Time series of HCl measured in the upper stratosphere by three instruments, ATMOS, MLS, and ACE, are most consistent with expectations if 100 ppt is added to the burden of stratospheric $\mathrm{Cl_y}$ supplied by long lived sources. In contrast, upper stratospheric HCl from HALOE suggests $\mathrm{Cl_y^{VSL}}$ is close to zero (Froidevaux, et al., 2006, Fig. 1-2 of WMO). Interpretation of tropospheric data is complicated because: a) various VSL organics decompose to form phosgene $(COCl_2)$ that is likely transported into the stratosphere, but phosgene is also a byproduct of the decomposition of long-lived chlorocarbons (which undergo slight loss in the troposphere) (WMO, 2007, Section 2.5.1.2); b) HCl has been observed in the sub-tropical upper troposphere but the source could be either local decomposition of VSL chlorocarbons or irreversible stratosphere to troposphere mixing of air (Marcy et al., 2004). In this study, we consider two cases for $Cl_y^{VSL}$: 0 and 100 ppt. The 100 ppt value is consistent with upper stratospheric HCl from ATMOS, MLS, and ACE as well as the range for $Cl_y^{VSL}$ of 25 to 170 ppt given in Table 1-9 of WMO (2010).

### 2.1 Changes in ozone loss rates: Baseline – Geo-engineering

The impact of volcanic aerosols on ozone destroying cycles was discussed in various studies (e.g., Brasseur et al., 1990; Solomon, 1999), as well as the sensitivity to ozone loss cycles on increases in bromine (e.g., Salawitch et al., 1994; Solomon et al., 1996; Solomon, 1999). Here, we investigate the impact of geo-engineering on ozone loss rates for projected 2040 chemical conditions and further quantify the impact of additional stratospheric bromine from VSL.

The increase of aerosol particles and therefore heterogeneous reactions was shown to lead to a reduced $NO_x/NO_y$ ratio between 15-25 km (e.g., Fahey et al., 1993). This results in decreasing ozone loss rates in mid- and low latitudes around 20 km. The reduction of $NO_x$ further induces changes in the gas phase chemistry (Solomon et al., 1996). For mid-latitudes, $NO_x$ ozone loss rates are strongly reduced for the geo-engineering simulation compared to the baseline simulation, whereas $HO_x$, $ClO_x$, and $BrO_x$ loss rates are increased at the same altitudes (Figure S2, 5th and 6th row), second column. Changes in $Br_y^{VSL}$ and $Cl_y^{VSL}$ do not influence $NO_x$ ozone loss rates, as expected, see Figure S2, 3th and 4th column.

In high polar latitudes in winter and spring, increased heterogeneous reactions due to geo-engineering lead to a doubling of $ClO_x + BrO_x$ loss rates in the lower stratosphere. At this time of the year, the $HO_x$ cycle is less important and geo-engineering induces only a small increase in $HO_x$ ozone loss rates. For the NH, enhanced bromine (VSL = 6) results in an increase of $ClO_x + BrO_x$ ozone loss rates by another 50%. For $Br_y^{VSL}$ = 10 ppt, $Cl_y^{VSL}$ = 100 ppt, $ClO_x + BrO_x$ loss rates double compared to the VSL = 0 case and reach 3 times the amount derived from the baseline simulation.

In the Austral spring and summer in the SH, Figure S2, third row, the increase of $ClO_x + BrO_x$ rates due to geo-engineering is of similar magnitude as for the NH, but is relatively less important. Additional $Br_y$ and $Cl_y$ in the stratosphere results in a decrease of the $ClO_x + BrO_x$ rates in a geo-engineered environment for some altitudes (Figure S2, thrid row). In contrast to the VSL = 0 case, ozone reaches very small values at the end of spring and the reduction of loss rates for the geo-engineering simulation is limited.

During polar summer (MJJ for the NH and NDJ for the SH), temperatures are warming up and heterogeneous reaction are less important. Only a small increase of the $ClO_x + BrO_x$ cycle is simulated around 12 km due to geo-engineering. On the other hand, the $\mathrm{HO_x}$ cycle is much more important at this time of the year, especially for the NH. The additional bromine appoximately doubles the $\mathrm{HO_x}$ cycle and strongly increases the $\mathrm{ClO_x + BrO_x}$ ozone loss rates in the lowermost stratosphere (around 12 km).

For summer mid-latitudes in the NH, increased heterogeneous reactions in spring and summer result in reduced $\mathrm{NO_x}$ ozone loss rates and increased $\mathrm{ClO_x + BrO_x}$ and $\mathrm{HO_x}$ rates around 25 km. The consideration of additional $\mathrm{Br_y}$ from VSL halogen compounds results in a large increase in the $\mathrm{ClO_x + BrO_x}$ rates, which doubles the impact of geoengineering on column ozone (from about 2% to 4% for MJJ, as discussed in the main text).

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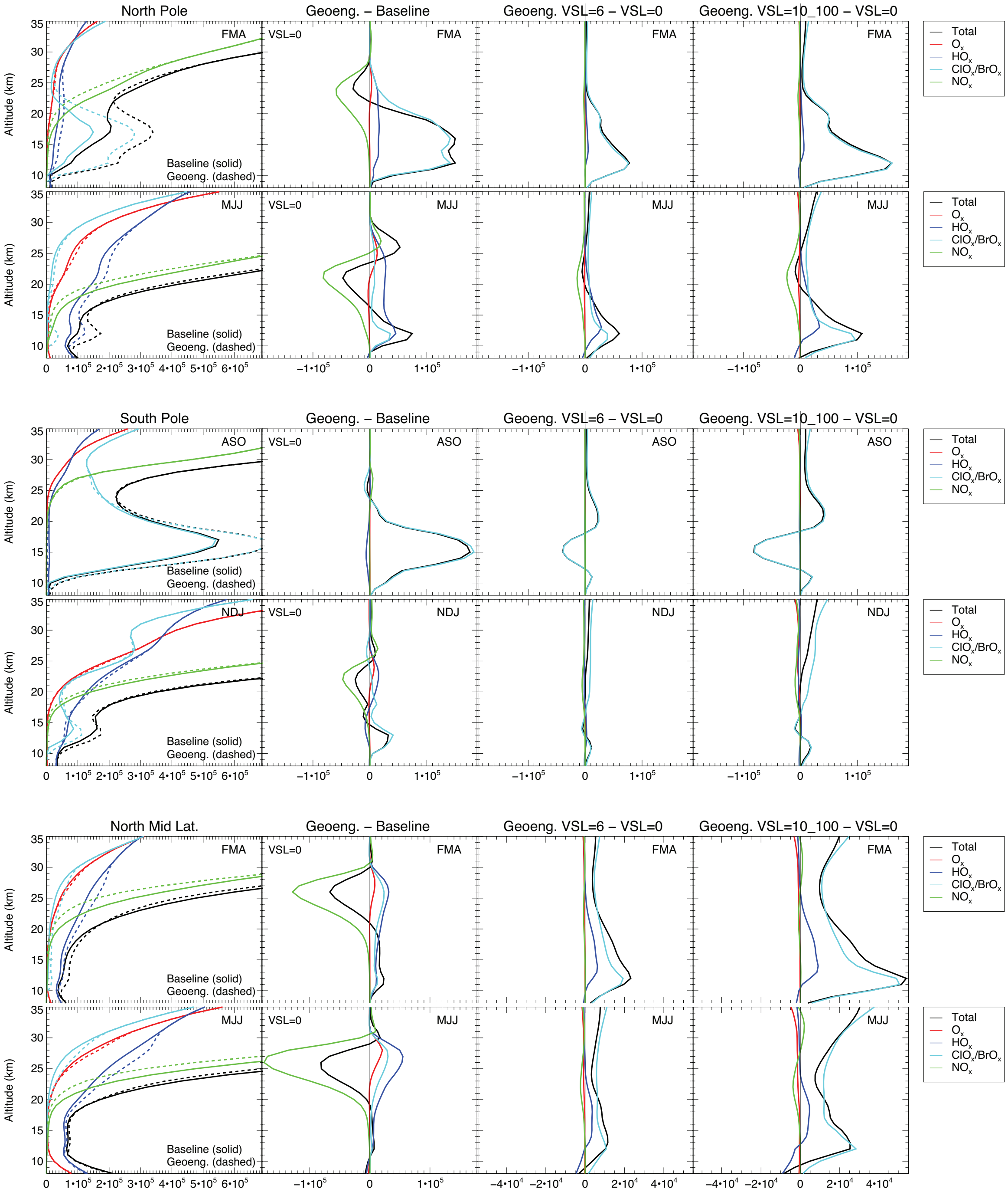

Fig. 2: First column: ozone loss rates for different ozone destroying cycles (different colors) and total ozone loss rates (black); baseline simulations (solid) and geo-engineering simulation (dashed) in 2040 for VSL = 0 (see main text for definition) considering different seasons and regions. Second column: differences between geo-engineering and baseline simulations as shown on the left. Third column: differences between VSL = 6 and VSL = 0 case for the geo-engineering simulations only. Fourth column: differences between VSL = 10 + 100 and VSL = 0 case for the geo-engineering simulation only.