~~Temporal Evolution of~~ Reformulating the Bromine Alpha Factor and ~~Equivalent Effective Stratospheric~~ EESC: Evolution of Ozone Destruction Rates of Bromine and Chlorine in Future Climate Scenarios

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Abstract. Future trajectories of the stratospheric trace gas background will alter the rates of bromine- and chlorine-mediated catalytic ozone destruction via changes in the partitioning of inorganic halogen reservoirs and the underlying temperature structure of the stratosphere. The current formulation of the bromine alpha factor, the ozone-destroying power of stratospheric bromine atoms relative to stratospheric chlorine atoms, is invariant with climate state. Here, we refactor the bromine alpha factor, introducing ~~climate~~ normalization to a benchmark chemistry/climate state, and ~~reformulate~~ formulate Equivalent Effective Stratospheric ~~Chlorine (EESC~~ Benchmark-normalized Chlorine (EESBnC) to reflect changes in the rates of both ~~chlorine- and bromine-mediated~~ bromine- and chlorine-mediated ozone loss catalysis with time. We show that the ozone-processing power of the extrapolar stratosphere is significantly perturbed by future climate assumptions. Furthermore, we show that our ~~EESC-based~~ EESBnC-based estimate of the extrapolar ozone-recovery date is in closer agreement with extrapolar ozone recovery dates predicted using more sophisticated 3-D ~~chemistry-climate models than prior formulations of EESCthat employ climate-invariant values of the bromine alpha factor~~ chemistry/climate models than predictions made using Equivalent Effective Stratospheric Chlorine (EESC).

1 Introduction

Anthropogenic emissions of ozone-destroying halocarbons have declined significantly since the implementation of the Montreal Protocol on Substances that Deplete the Ozone Layer (and its subsequent amendments); however, ~~the~~ stratospheric inorganic halogen ~~background still remains~~ inventories still remain elevated relative to levels prior to the first observations of the seasonal Antarctic ozone hole due to the exceptionally long lifetimes of the ~~inorganic halogen precursor compounds (World Meteorological Organization, 2018)~~ precursor compounds for inorganic halogen. Recovery of the halogen content of the stratosphere to the levels representative of the benchmark year 1980 is estimated to occur some time around the year 2060 in the extrapolar regions ~~(Newman et al., 2006; Engel et al., 2018a; World Meteorological Organization, 2018)~~ (Newman et al., 2006; Engel et al

; however, 3-D CCM simulations predict ozone recovery dates up to two decades sooner ~~(Dhomse et al., 2018)~~ (Dhomse et al., 2018; Braesi

as halogen inventory recovery is an imperfect proxy for ozone recovery.

The vast majority of inorganic chlorine in the <u>lower</u> stratosphere is present in the reservoir forms HCl and $ClONO_2$. ~~In the lower and middle stratosphere, it is typical that only a few percent of inorganic chlorine is present in active forms, such as ClO.~~

25 ~~Active halogen radical species participate in ozone-destroying chemical reaction cycles, such as the catalytic cycle presented in reactions ??–?? below, in which inorganic chlorine is rapidly interconverted between the chlorine radical and the chlorine monoxide radical.~~

~~$Cl + O_3 \rightarrow ClO + O_2 ClO + O \rightarrow Cl + O_2 Net: O_3 + O \rightarrow 2O_2$~~

The gas-phase ~~conversion of the dominant inorganic chlorine reservoirs to their active, ozone-destroying forms (reaction ??)~~

30 <u>reaction of these two reservoirs</u> is too slow to be of atmospheric importance; however, heterogeneous reactions on the surfaces of stratospheric aerosols (Solomon et al., 1986; Brasseur et al., 1990) ~~, as indicated in reactions ??–??, can be sufficiently fast to enable significant engagement of~~ <u>can be fast enough to enable chlorine activation and</u> ClO_x-mediated ozone-depletion cycling.

~~$HCl + ClONO_2 \xrightarrow{homogeneous} HNO_3 + Cl_2 HCl + ClONO_2 \xrightarrow{heterogeneous} HNO_3 + Cl_2 ClONO_2 + H_2O \xrightarrow{heterogeneous} HNO_3 + HOClHOCl + H$~~

<u>is typical that only a few percent of inorganic chlorine is present in the active forms in the lower stratosphere because conversion</u>

35 <u>of the Cl radical back to the inorganic reservoir can be quite fast, limiting the chain length (and it follows, extent of ozone loss) of mechanisms involving chlorine alone in this region of the stratosphere.</u>

Mechanisms of BrO_x-mediated ozone depletion are much less ~~dependent on~~ <u>sensitive to</u> the surrounding environment than mechanisms mediated by ClO_x. This is because inorganic reservoirs of bromine are significantly less stable, enhancing the quantity of reactive halogen available for ozone processing. Bromine is up to two orders of magnitude more likely to be found

40 in its active form than chlorine, depending on the physicochemical environment (Wofsy et al., 1975; Salawitch et al., 2005). Additionally, unlike the ~~chlorine cycle presented in reactions ??–?? which requires the presence of atomic oxygen and is accordingly slow in the lower stratosphere or in regions of low actinic flux~~<u>catalytic cycles of chlorine, in which the extent of ozone loss following the addition of chlorine atoms is limited by the relatively short chain length of the catalytic center</u>, catalytic processing of ozone facilitated by the addition of bromine is ~~effective in these regions. Reactions ??–??, the coupled~~

45 ~~odd bromine-chlorine cycle, and reactions ??–??, the coupled odd bromine-hydrogen cycle, are examples of this chemistry in which atomic oxygen is not involved.~~ <u>potentiated due to its greater (up to orders-of-magnitude in difference) chain effectiveness (Lary, 1997).</u> The bromine interfamily <u>ozone destruction</u> cycles are responsible for a similarly-sized fraction of global lower stratospheric ozone loss as the chlorine ~~cycle (reactions ?? – ??)~~ <u>cycles</u> (Salawitch et al., 2005; World Meteorological Organization, 2018; Koenig et al., 2020). This large fractional share of ozone destruction chemistry occurs despite the fact that bromine

50 is approximately two orders of magnitude less abundant than chlorine as a consequence of (a) the larger fraction of reactive bromine available at a given mixing ratio and (b) the catalytic reaction channels made accessible by the weaker bromine-oxygen molecular bond ~~(Yung et al., 1980; McElroy et al., 1986; Brune and Anderson, 1986; World Meteorological Organization, 2018)~~

~~. $ClO + BrO \rightarrow products \rightarrow Cl + Br + O_2 Cl + O_3 \rightarrow ClO + O_2 Br + O_3 \rightarrow BrO + O_2 Net: 2O_3 \rightarrow 3O_2 HO_2 + BrO \rightarrow HOBr + O_2 HOBr + H$~~

<u>.</u>

55 The bromine alpha factor, α_{Br}, is a metric that quantifies the ozone-depleting efficiency of a bromine atom relative to chlorine. This quantity is defined either as the ratio of ozone loss processing rates, as in Eq. (1) or as the ratio of the overall change in ozone abundance on a per-halogen-atom basis per Eq (2). In both formulations, α_{Br} is computed as a function of calendar date, t, and location in the atmosphere, ρ. Daniel et al. (1999) demonstrate that both equations provide identical results when changes in ozone are dominated by chemical rather than dynamical processes.

60
$$\alpha_{Br}(t,\rho) = \frac{\frac{\Delta O_3(t,\rho)}{\Delta t}\,(\text{Br rxns})\,/\,\Delta Br(t,\rho)}{\frac{\Delta O_3(t,\rho)}{\Delta t}\,(\text{Cl rxns})\,/\,\Delta Cl(t,\rho)} \tag{1}$$

$$\alpha_{Br}(t,\rho) = \frac{\Delta O_3(t,\rho)/\Delta Br(t,\rho)}{\Delta O_3(t,\rho)/\Delta Cl(t,\rho)} \tag{2}$$

Values of α_{Br} vary strongly as a function of pressure, latitude, and season. This variance is primarily a function of (a) chemical environment, (b) prevailing actinic flux, (c) aerosol surface area, and (d) temperature (Solomon et al., 1992; Danilin
65 et al., 1996; Ko et al., 1998; Daniel et al., 1999). Frequently, α_{Br} is reported as an effective value for the stratospheric column, computed in a similar manner as in Eq. (1) or Eq. (2), the key difference being that ρ represents the position of the stratospheric column. Likewise, it is common to provide a regional-annual average column α_{Br}, which is computed as the average of column α_{Br} values for all locations within a specified region across a calendar year. Global-annual average column values for α_{Br} are currently estimated between $60-65$, depending on the model employed and the ~~chemoclimatic boundary conditions~~
70 ~~(World Meteorological Organization, 2018; Sinnhuber et al., 2009)~~chemistry/climate boundary conditions (Engel et al., 2018b; Sinnhuber . Values of α_{Br} tend toward a minimum at the equator, maximizing in the boreal summer. Denitrification and heterogeneous activation produce a minimum in α_{Br} during the austral springtime. In vertical profiles, α_{Br} tends to maximize in the lower stratosphere where reactive chlorine is less prevalent than in the middle stratosphere.

The quantity α_{Br} is especially useful for the determination of parameterized estimates of the budget of reactive inorganic
75 halogens given a mixture of halogen-containing halocarbons of an arbitrary mean age, as in the metric of Equivalent Effective Stratospheric Chlorine (EESC). This quantity expresses the ozone-depleting power of a parcel of well-mixed stratospheric trace gases as a function of mean stratospheric age of the parcel, Γ, and the trace gas background of the stratosphere at time t (Daniel et al., 1995; Newman et al., 2007). Equation 3 provides the most recently suggested formulation of EESC, in which $\overline{f_i}(\Gamma)$ is the ~~time-independent~~ trend-independent fractional release factor for species i for a parcel of air with mean age Γ,
80 which contains $n_{i,Cl}$ chlorine atoms and $n_{i,Br}$ bromine atoms, scaled by $\alpha_{Br}(t,\Gamma)$, where it is assumed that Γ can serve as a proxy for ρ (Ostermöller et al., 2017; Engel et al., 2018a). Inside the integral, the mixing ratio of species i is computed for each element comprising the age spectrum and normalized to the contribution of that element to the age spectrum. The tropospheric mixing ratio of species i, $\chi_{0,i}$ is adjusted to account for transit time within the stratosphere, t', and multiplied by the normalized release-weighted transit time distribution, $G_{N,i}^{\#}(\Gamma^{\#},t')$, where $\Gamma_i^{\#}$ is the mean age of halogen-atom release.

85
$$\text{EESC}(t,\Gamma) = \sum_i \overline{f_i}(\Gamma)\left[n_{i,Cl} + \alpha_{Br}(t,\Gamma)\cdot n_{i,Br}\right] \int_0^\infty \chi_{0,i}(t-t')G_{N,i}^{\#}(t',\Gamma_i^{\#})dt' \tag{3}$$

EESC is frequently employed to ~~approximate~~ constrain the date of stratospheric ozone recovery, often by using graph theory to determine when stratospheric chlorine levels will return to the levels observed in 1980 as a benchmark ~~(Newman et al., 2006; World Meteor~~ (Newman et al., 2006; Engel et al., 2018b). The technique is fast and simple: EESC is calculated as a function of location in the stratosphere (for which Γ is a proxy) and future date, following which a horizontal line is propagated in time at the value of EESC in 1980, and the intercept of the two traces is interpreted as the date of halogen recovery (and, it follows, ~~the probable~~ an approximate date of ozone recovery). The extrapolation is built on the assumptions that, as the climate evolves: (1) the alpha factor remains constant and (2) the amount of ozone destroyed by chlorine, on a per-chlorine-atom basis, also remains constant. However, projections of the future physicochemical state of the stratosphere do not necessarily provide for these two assumptions to be true. Indeed, the envelope of future projections (e.g., RCP and SSP scenarios) of emissions of CH_4, N_2O, CO_2, among other relevant species, indicate that it is nearly certain that these two assumptions will not be true, especially in the extrapolar stratosphere.

Significant variations between different climate models and possible states of the future atmosphere limit the skill level of model simulations in predicting ozone recovery dates (Charlton-Perez et al., 2010). These large uncertainties notwithstanding, it is understood that there may be a super-recovery of global stratospheric ozone in the future as EESC declines, the Brewer-Dobson circulation accelerates, and the stratosphere cools (Austin and Wilson, 2006; Li et al., 2009; Eyring et al., 2013; Banerjee et al., 2016; Chiodo et al., 2018). The extent of super-recovery ~~is primarily dependent on the degree by which~~ can be attributed to both photochemical and dynamical factors. Future ozone abundance is expected to be controlled by photochemical factors in the middle-to-upper stratosphere. The degrees by which photochemical rates of bimolecular ozone-loss processes are slowed and the rate of the termolecular formation of ozone is increased ~~as~~ are a result of (a) local radiative cooling due to the enhancement of the stratospheric burden of anthropogenic greenhouse gases and (b) chemical suppression of ozone loss cycling due to reactive anthropogenic greenhouse gas emission (Rosenfield et al., 2002; Waugh et al., 2009; Oman et al., 2010; Eyring et al., 2013). ~~Future projections of ozone are also dependent on~~ In the lower stratosphere, where the photochemical lifetime of ozone is large, the expected super-recovery is dominated by dynamical factors, such as the model response of the Brewer-Dobson circulation to greenhouse gas perturbation, which alters both the stratospheric lifetime of long-lived inorganic halogen precursors and the transport of ozone from the tropics where it is produced (Butchart et al., 2006; Plummer et al., 2010; Zubov et al., 2013).

Dhomse et al. (2018) provide constraints on the dates stratospheric ozone might recover to year 1980 benchmark thickness using a comprehensive multi-model framework (20 models, 155 simulations) spanning multiple greenhouse gas emissions scenarios, finding that while the date of Antarctic springtime recovery is most sensitive to Cl_y inventories, extrapolar column recovery dates (and to a lesser extent, the Arctic springtime recovery date) are highly sensitive to the greenhouse gas forcing applied. In their analysis, Dhomse et al. (2018) indicate that mid-latitude ozone recovery will occur sooner in both hemispheres for scenarios with greater radiative forcing. When greenhouse gases are fixed, the dates projected for midlatitude recovery ($\sim$2060) are in close agreement with the EESC-based estimates provided in Engel et al. (2018a) of 2059; however, greenhouse gas perturbations hasten projected midlatitude recovery dates in 3-D models by $\sim$10 years in the northern hemisphere and $\sim$20 years in the southern hemisphere (Eyring et al., 2010, 2013; Dhomse et al., 2018).

Table 1. Experiment Schedule[a]

experiment prefix	decades[b]	climatology	CFCl$_3$A (pptv)	CFBr$_3$ (pptv)
bkg	[1980–2010]	historical[c]	0	0
bkg	[2020–2100]	RCP[2.6,4.5,6.0,8.5][d]	0	0
Cl	[1980–2010]	historical[c]	260	0
Cl	[2020–2100]	RCP[2.6,4.5,6.0,8.5][d]	260	0
Br	[1980–2010]	historical[c]	0	2.6
Br	[2020–2100]	RCP[2.6,4.5,6.0,8.5][d]	0	2.6

[a] All permutations of bracketed parameters were evaluated.

[b] Constant year for each decade (e.g., 1980, 1990, 2000)

[c] Informed by Fleming et al. (1999)

[d] Informed by Meinshausen et al. (2011) and Watanabe et al. (2011)

Regardless, it is known that the decay of EESC is the strongest driver of ozone recovery (Meul et al., 2014; Banerjee et al., 2016). While EESC is expected to decrease in the future, it is increasingly evident that the inorganic halogen background might be significantly perturbed by natural geological processes under certain circumstances (Klobas et al., 2017). Volcanic eruptions are now known to frequently inject small quantities of inorganic chlorine into the lower stratosphere (Carn et al., 2016), and there exists evidence for the periodic and profound volcanic injection of inorganic chlorine in the ice core record (Zdanowicz et al., 1999) following large, explosive eruptions. Additionally, it is now apparent that volcanic bromine and iodine may partition more effectively to the stratosphere than volcanic chlorine (Theys et al., 2009, 2014; Schönhardt et al., 2017; Gutmann et al., . The expected enhancement in ozone-loss processing rates due to additional volcanogenic inorganic halogens following a future, large, halogen-rich explosive eruption is not well constrained, partially because the temporal evolution of the ozone processing rates of bromine relative to chlorine is largely unknown.

In this work, we present the first assessment of column α_{Br} in future climate change scenarios. Additionally, we evaluate the sensitivity of column α_{Br} to prescribed perturbations of reactive greenhouse gases while anthropogenic halocarbons slowly decay as the century progresses. We then refactor α_{Br}, such that estimates of EESC such that parameterized estimates of ozone recovery can more accurately be related to the ozone-destroying power of the inorganic halogen background content of the stratosphere given a particular benchmark date. Finally, we show that this method provides much better agreement between EESC-based estimates and with 3-D CCM estimates of ozone recovery to the 1980 benchmark date than EESC-based estimates.

2   Model, Experiment, and Validation

The AER-2D chemical transport model was employed with 19 latitudes (90°S–90°N) and 51 levels (1000–0.2 hPa) for this work (Weisenstein et al., 1997, 2007). The model includes 104 chemical species, accounting for F$_y$, Cl$_y$, Br$_y$, I$_y$, NO$_y$, HO$_x$,

O_x, SO_x, and CHO_x chemistry. Chemical reactions (314 kinetic reactions and 108 photochemical reactions) were computed using rate constants and cross sections as recommended in the most recent (2015) JPL data evaluation (Burkholder et al., 2015). Additionally, the model features fully-prognostic aerosol microphysics and chemistry (e.g., nucleation, coagulation, condensation/evaporation, sedimentation, and heterogeneous chemical interactions in 40 sectional size bins). Future emissions of greenhouse gases were informed by the Representative Concentration Pathway framework (Van Vuuren et al., 2011; Meinshausen et al., 2011). Future climatological boundary conditions were obtained from the corresponding RCP experiments of MIROC-CHEM-ESM, an Earth System Model with stratospheric chemistry. Future halocarbon inventories were informed by Table 6-4 of the 2018 WMO Scientific Assessment of Ozone Depletion (World Meteorological Organization, 2018) with an additional 5 pptv stratospheric bromine from very-short lived bromocarbons (Wales et al., 2018). Experiments performed in the historical past were informed by historical climatologies obtained from Fleming et al. (1999). Specified dynamics corresponding to the 1978 – 2004 climatological average were employed for all historical and future experiments and were prepared using data obtained from Fleming et al. (1999).

Halogen perturbation scenarios were prepared in the manner of Daniel et al. (1999). ~~Namely,~~ Specifically, bromine alpha factors were determined per Eq. (2), in which ozone deficits were computed by column difference between control and halogen gas perturbation scenarios. CFC-11 proxy molecules ($CFCl_3A$ and $CFBr_3$) were constructed to provide identical transport and release of ~~halogen atoms between model~~ a known quantity of halogen atoms (Br or Cl, depending on the prescribed perturbation) between runs. For bookkeeping purposes, this was done for both chlorine and bromine delivery (e.g., the molecule labeled as $CFCl_3A$ has the same chemical kinetics and photolysis rates as CFC-11, providing 3 chlorine atoms upon decomposition, but can be perturbed in the model separately from ~~$CFCl_3$~~ CFC-11). Experiments were performed as outlined in Table 1, in which each permutation of the bracketed parameters were evaluated resulting in a total of 108 model realizations (2160 model years). Experiments of a certain scenario (e.g., ~~bkg2020RCP8~~ for the year 2100 RCP 8.5 experiment: bkg2100RCP8.5, ~~Cl2020RCP8~~ Cl2100RCP8.5, ~~Br2020RCP8~~ Br2100RCP8.5) were initialized from identical 20-year chemical-climatological spun-up boundary conditions. Evaluations were conducted at constant chemical and climatological conditions (i.e., time-slice boundary conditions) corresponding to the last year of each decade (e.g., 1980, 1990, ..., 2100). Perturbation and control experiments were evaluated over the course of 20 model years, a duration determined to be an appropriate period for the perturbation gas to reach chemical-dynamical steady-state. Data analysis was conducted on the final 12 months of each experiment and control run. Perturbation gas surface mixing ratios were selected to produce global and local ozone depletion of less than 1% in each climate state relative to the unperturbed condition to prevent instability in the chemical Jacobian.

The model performance and experiment design were validated using calculations of α_{Br} in a ~~chemistry-climate~~ chemistry/climate state representative of the year 2006. This climate condition has previously been evaluated for α_{Br} (Sinnhuber et al., 2009) using the JPL-2006 photochemical-kinetics recommendations (Sander et al., 2006). Validation runs for this work were informed by either JPL-2006 or JPL-2015 photochemical-kinetics packages. A comparison of the two model evaluations is presented in Figure 1 in which there is little qualitative difference in the annual variation in α_{Br} between JPL-2006 and JPL-2015 photochemical-kinetics packages. Implementation of JPL-2015 chemistry results in a general increase in column α_{Br} of ~ 10 relative to JPL-2006 contours in both polar and extrapolar regions. Our annually/globally averaged α_{Br} of 67 in the JPL-

2006 instance compares favorably to the results of Sinnhuber et al. (2009), who report an annually/globally averaged α_{Br} of 64 in their analysis of the same ~~chemistry-climate~~ chemistry/climate state using the same photochemistry and kinetics package. For the JPL-2015 evaluation, the annually/globally averaged α_{Br} is 74, which is larger than previously reported values. These differences are likely the result of a combination of changes in chemical rates between JPL-2006 and JPL-2015, such as: (a) 2% increase in rate of $Cl + CH_4$ at 200 K, (b) 8% increase in formation rate of NO by $N_2O + O(^1D)$ at 200 K, (c) 4% increase in the rate of $Br + O_3$ at 200 K, (d) 121% increase in the rate of $CHBr_3 + OH$ at 200 K, and (e) 5% increase in the rate of $Cl + ClOOCl$ at 200 K.

3 Results and Discussion

3.1 Refactoring α_{Br}: a new definition of EESC

Prior evaluations of α_{Br} were computed with static ~~chemistry-climate~~ chemistry/climate states. Because the relative ozone-processing rate of bromine to chlorine is likely to change ~~as timepropagates within chemistry-climate scenarios~~ with time, and also between ~~chemistry-climate~~ chemistry/climate scenarios at the same point in time, we add a dependence on the ~~chemical-climate~~ chemistry/climate state, ξ, to the defintion of α_{Br} (Eq. (4)).

$$\alpha_{\mathrm{Br}}(t,\rho,\xi) = \frac{\Delta O_3(t,\rho,\xi)/\Delta Br(t,\rho,\xi)}{\Delta O_3(t,\rho,\xi)/\Delta Cl(t,\rho,\xi)} \tag{4}$$

We can then replace the climate-invariant $\alpha_{\mathrm{Br}}(t,\Gamma)$ in Eq. (3) with $\alpha_{\mathrm{Br}}(t,\Gamma,\xi)$ to produce a climate-sensitive EESC that accounts for changes in the relative ozone-destroying efficiency of bromine to chlorine (Eq. (5)).

$$\mathrm{EESC}(t,\Gamma,\xi) = \sum_i \overline{f_i}(\Gamma)\left[n_{i,\mathrm{Cl}} + \alpha_{\mathrm{Br}}(t,\Gamma,\xi)\cdot n_{i,\mathrm{Br}}\right]\int_0^\infty \chi_{0,i}(t-t')\cdot G_{N,i}^{\#}(t',\Gamma_i^{\#})dt' \tag{5}$$

Furthermore, we recognize that the ozone-processing power of chlorine and bromine are independently sensitive to changes in the physicochemical background of the stratosphere. The two variables must be separated in order to understand the evolution of the change in the processing power of ~~bromine and chlorine~~ chlorine and bromine as a function of chemistry/climate state. To accomplish this, we define the eta factor, η_{Cl} and η_{Br}, in Eq. (6) and Eq. (7) as the ratio of the change in ozone following the addition of chlorine or bromine at time t, location ρ, and climate state ξ to the change in ozone following the same perturbation in a benchmark ~~chemical-climate~~ chemistry/climate state, Ξ. The eta factor thus expresses the ozone-depleting efficiency of a chlorine or bromine atom in an arbitrary chemistry/climate state relative to the ozone-depleting efficiency of a chlorine atom in the benchmark chemistry/climate state.

$$\eta_{\mathrm{Cl}}(t,\rho,\xi,\Xi) = \frac{\Delta O_3(t,\rho,\xi)/\Delta Cl(t,\rho,\xi)}{\Delta O_3(t,\rho,\Xi)/\Delta Cl(t,\rho,\Xi)} \tag{6}$$

$$\eta_{\mathrm{Br}}(t,\rho,\xi,\Xi) = \frac{\Delta O_3(t,\rho,\xi)/\Delta Br(t,\rho,\xi)}{\Delta O_3(t,\rho,\Xi)/\Delta Cl(t,\rho,\Xi)} \tag{7}$$
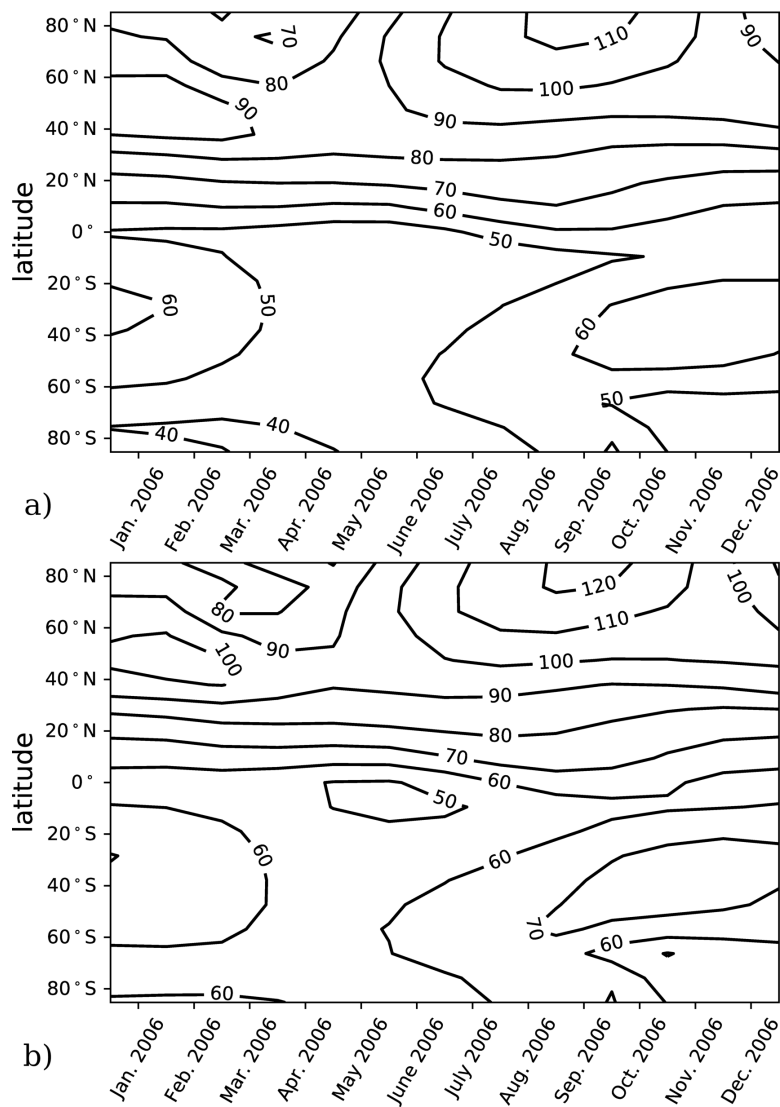
Figure 1. Column α_{Br} as a function of latitude and season for the year 2006. (a) Model results computed using JPL-2006 photochemistry and kinetics (Sander et al., 2006) for the year 2006. (b) Model results computed using JPL-2015 photochemistry and kinetics (Burkholder et al., 2015) for the year 2006.

It is apparent that the definition of α_{Br} given in Eq. (4) can be derived from η_{Br} and η_{Cl} provided that the benchmark ~~climate~~ ~~states are identical~~ chemistry/climate state is identical between the two expressions (Eq. (8)).

$$\alpha_{\text{Br}}(t,\rho,\xi) = \frac{\eta_{\text{Br}}(t,\rho,\xi,\Xi)}{\eta_{\text{Cl}}(t,\rho,\xi,\Xi)} \tag{8}$$

By substituting this refactored definition of α_{Br} into Eq. (5) for the computation of EESC, we can now quantify the Equivalent Effective Stratospheric Benchmark-normalized Chlorine (EESBnC) (Eq. (9)). The difference between EESC and EESBnC is significant; whereas EESC considers "the *relative* efficiency of chlorine and bromine for ozone depletion" (World Meteorological Organizat , EESBnC accounts for the *overall* efficiency of chlorine and bromine relative to a benchmark chemistry/climate state. Thus, EESBnC provides the ozone-depleting power of an air parcel in the stratosphere ~~, propagated in time without bias to~~ propagated independent of changes in the rates of ~~bromine and chlorine~~ chlorine or bromine ozone-loss catalysis~~(Eq. (9)) relative to the~~ ~~benchmark chemoclimatic state. Note again that ρ has been substituted with Γ per Engel et al. (2018a).~~

~~EESC~~EESBnC$(t,\Gamma,\xi,\Xi) = \eta_{\text{Cl}}(t,\Gamma,\xi,\Xi) \cdot \text{EESC}(t,\Gamma,\xi) =$

$$\sum_i \overline{f_i}(\Gamma) \left[\eta_{\text{Cl}}(t,\Gamma,\xi,\Xi) \cdot n_{\text{i,Cl}} + \eta_{\text{Br}}(t,\Gamma,\xi,\Xi) \cdot n_{\text{i,Br}} \right] \int\limits_0^\infty \chi_{0,i}(t-t') \cdot G_{N,i}^\#(t',\Gamma_i^\#) dt' \tag{9}$$

~~Equation 9 provides a more appropriate basis for a graph-theory approximation of future inorganic halogen ozone-loss processing than prior approaches because the ordinate now represents Equivalent Effective Stratospheric Chlorine normalized to a benchmark atmospheric state rather than an instantaneous equivalent EESC with a time-varying ozone-processing power per chlorine atom.~~

3.2 Calculation of Future RCP scenario α and η

Packaged within the definitions of α and η are both local (e.g., photochemical catalytic processing) and non-local influences on ozone abundance (e.g., dynamical effects, ozone layer self-healing effect, etc.), as illustrated in Eq. (10). These non-local factors do not cancel out in the evaluation of η_{Cl} per Eq. (6) or η_{Br} per Eq. (7) as they do in the calculation of α_{Br} per Eq. (1) or Eq. (2), because the non-local factors at time t in some evolved climate state are not likely to be the same as they were during the benchmark time period.

$$\frac{\Delta\text{O}_3(t,\rho,\xi)}{\Delta\text{O}_3(t,\rho,\Xi)} \simeq \frac{(\Delta\text{O}_3(t,\rho,\xi)_{\text{photochem.}} + \Delta\text{O}_3(t,\rho,\xi)_{\text{dyn.}})}{(\Delta\text{O}_3(t,\rho,\Xi)_{\text{photochem.}} + \Delta\text{O}_3(t,\rho,\Xi)_{\text{dyn.}})} \tag{10}$$

To avoid this complication, we employ specified dynamics corresponding to the 1978 – 2004 climatological average in order to calculate only the photochemical component of the ozone tendency. These dynamics tend to produce less seasonal variation in α_{Br} in the extrapolar southern hemisphere than in the extrapolar northern hemisphere, as depicted in Figure 1. Because of the carefully controlled magnitude of the imposed ozone deficit ($\sim$1%), changes in ozone between experiment and control scenarios from all other effects can be assumed to be insignificant relative to the ozone changes produced by the chemical perturbation.
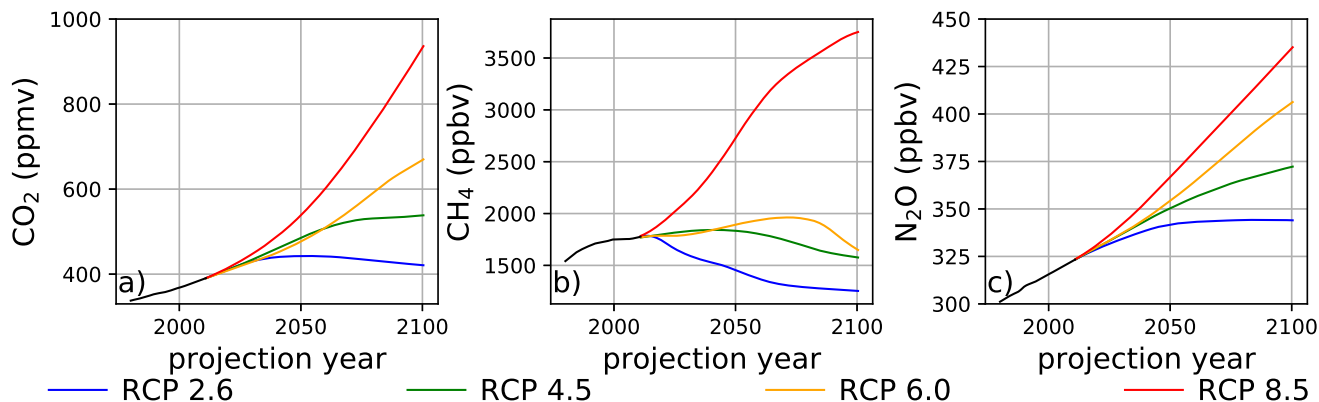
Figure 2. Surface mixing ratios of (a) CO_2, (b) CH_4, and (c) N_2O as a function of time and RCP scenario. Data obtained from Meinshausen et al. (2011).

~~Diagnostic trajectories~~ The temporal dependencies of the well-mixed greenhouse gases employed in the climatological perturbations are illustrated in Figure 2, constructed from data provided by Meinshausen et al. (2011). Prescribed mixing ratios of CO_2, which is chemically inert in this model and only perturbs ozone chemistry via thermal effects, are provided in panel (a). The trajectories of CH_4 in panel (b) and N_2O in panel (c) are particularly noteworthy because these species are closely coupled with the ozone steady-state via changes in inorganic halogen reservoir inventories. In the instance of RCP 8.5, CH_4 increases nearly 2.5 times by the year 2100 from the 1980 mixing ratio, and N_2O increases by a factor of 1.4 during the same time period. The reactive greenhouse gas situation in RCP 2.6 is significantly different: CH_4 mixing ratios decline by 19% and N_2O mixing ratios increase by 14% ~~.~~ during the period spanning the year 1980 and the year 2100. The intermediate scenarios, RCP 4.5 and RCP 6.0, both feature small end-of-century increases in CH_4 mixing ratios of less than 10% relative to the year 1980 value, but with modest increases during the middle-half of the 21st century. ~~Prescribed~~ For RCP 4.5 and RCP 6.0, prescribed N_2O emissions increase ~~monotonically~~ by 24% and 35% respectively over the same time interval.

Values of annually-averaged extrapolar η_{Cl} and η_{Br} (60°S – 60°N) were computed on a decadal basis for every decade between 1990 – 2010 using historical data, and for each decade between 2020 – 2100, for each RCP scenario. For all results reported in this work, the chemistry-climatology corresponding to the year 1980 was selected as the benchmark state ($\Xi = 1980$). These values are presented, along with the corresponding alpha factors, in Table 2 for the historical period and for future scenarios. These results are also visualized in Figure 3 for (a) extrapolar α_{Br}, (b) extrapolar η_{Cl}, and (c) extrapolar η_{Br}. It is immediately apparent that, while α_{Br} deviates by less than 10% from its 1980 value for all evaluated future atmospheres as presented in panel (d), that the corresponding η_{Cl} and η_{Br} values are generally observed to decline by a much more significant extent in panels (e) and (f), respectively.

We highlight the clear qualitative trends of decreasing η_{Cl} and η_{Br} with climatological forcing scenario severity. Particular notice should be directed to results corresponding to RCP 8.5, in which α_{Br} does not demonstrate a significant coefficient of variation throughout the 21st century ($CV(\alpha_{Br}) = 2.1\%$), but η factors decline precipitously as the century progresses ($CV(\eta_{Cl})$

Table 2. Values of extrapolar $(60°S - 60°N)$ $\alpha_{\mathrm{Br}}{}^{a}$, $\eta_{\mathrm{Cl}}{}^{b}$, and $\eta_{\mathrm{Br}}{}^{b}$ for historical and future scenarios

Year	Historical			Year	RCP 2.6			RCP 4.5			RCP 6.0			RCP 8.5		
	α_{Br}	η_{Cl}	η_{Br}		α_{Br}	η_{Cl}	η_{Br}	α_{Br}	η_{Cl}	η_{Br}	α_{Br}	η_{Cl}	η_{Br}	α_{Br}	η_{Cl}	η_{Br}
1980	70	1.0	70	2020	75	0.96	72	75	0.94	71	74	0.93	69	73	0.91	67
1990	74	0.99	74	2030	75	0.94	70	75	0.92	69	72	0.95	69	72	0.93	67
2000	76	0.97	73	2040	73	0.94	69	73	0.90	66	71	0.96	68	71	0.91	65
2010	75	0.94	71	2050	72	0.95	68	72	0.89	64	70	0.93	65	72	0.84	60
				2060	70	0.96	67	71	0.88	63	70	0.90	63	72	0.78	56
				2070	69	0.96	67	70	0.87	61	69	0.89	61	72	0.74	54
				2080	67	0.98	66	69	0.88	61	69	0.85	58	73	0.70	51
				2090	66	0.98	65	68	0.88	60	67	0.85	57	73	0.67	49
				2100	65	0.99	64	66	0.87	57	67	0.84	57	73	0.65	47

[a] α_{Br} calculated per Eq. (4).

[b] η_{Cl} calculated per Eq. (6) and η_{Br} calculated per Eq. (7), $\Xi = 1980$.

Historical temperature fields obtained from Fleming et al. (1999).

Historical and future greenhouse gas emissions specified per Meinshausen et al. (2011).

Future temperature fields derived from Watanabe et al. (2011).

$= 14.3\%$ and $CV(\eta_{\mathrm{Br}}) = 14.5\%$). This behavior follows the sensitivity expected when there is a large increase in N_2O and CH_4. A downward trend in α_{Br} is observed as time propagates in RCP scenarios 2.6, 4.5, and 6.0. This effect is dominated by the declining availability of ClO_x as a result of the slow decay of long-lived ozone-depleting substances. In the case of RCP 2.6, a slight increase in η_{Cl} occurs after the year 2040, driven by the continuous decline in the CH_4 mixing ratio and the stabilization of the N_2O mixing ratio in the scenario prescription.

A sensitivity analysis was conducted on α_{Br}, η_{Cl}, and η_{Br} in order to clarify the differences presented in Figure 3. In this analysis, α_{Br}, η_{Cl}, and η_{Br} were calculated in the manner previously described, but with the ~~chemistry-climate~~ chemistry/climate perturbation, ξ, identical to the ~~chemoclimatic~~ chemistry/climate benchmark, Ξ, except for a single perturbed parameter. Four variables were perturbed separately: (a) N_2O, (b) CH_4, (c) Br_y/Cl_y ratio, and (d) temperature profile. For each perturbation experiment, all factors except for the perturbed factor were constrained to their year 1980 value(s). Perturbation values were intentionally selected to induce large variations in model response. For N_2O and CH_4, mixing ratios were scaled between pre-industrial values and twice the RCP 8.5 year 2100 value. Br_y/Cl_y ratios were selected to range between low values representative of the year 1990, moderate values representative of the year 2000, and high values representative of the year 2100 WMO Table 6-4 projections. Stratospheric temperature profile perturbations spanned a minimum as parameterized by the RCP 8.5 year 2100 projection to a maximum value representative of the climatological average of the years 1978-2004.

Panel (a) of Figure 4 demonstrates that α_{Br} is only slightly sensitive to changes in the mixing ratio of N_2O between pre-industrial and 2x RCP 8.5 year 2100 levels. Unlike α_{Br}, both η_{Cl} and η_{Br}, as shown in panels (e) and (i), decline monotonically
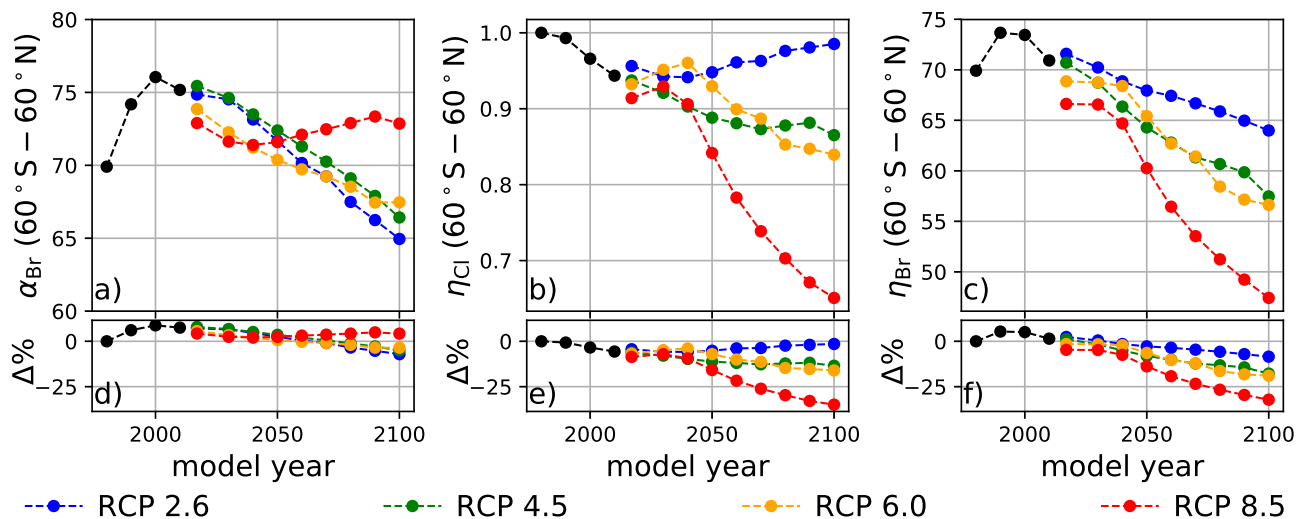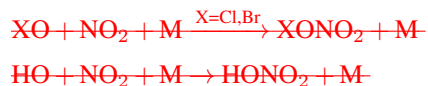
Figure 3. Extrapolar α and η computed on a decadal basis as a function of RCP scenario. Black traces were calculated using historical boundary conditions. (a) α_{Br}, (b) η_{Cl}, and (c) η_{Br}. Percent differences of values in (a), (b), and (c) relative to the year 1980 are presented in panels (d), (e), and (f) respectively.

and with nearly identical gradients, as both the bromine and chlorine cycles are suppressed through reactions with NO_x. This suppression arises primarily via the direct formation of the halogen nitrate~~, as in reaction ??, but also due to a reduction in the~~

275 ~~availability of HO_x reaction partners as a result of reaction ??~~.

$$\text{XO} + \text{NO}_2 + \text{M} \xrightarrow{\text{X=Cl,Br}} \text{XONO}_2 + \text{M}$$

$$\text{HO} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M}$$

Variation in the model output as a function of the mixing ratio of CH_4 is presented in Figure 4 panels (b),(f), and (j). Unlike the case of N_2O, α_{Br}, panel (b), is a strong function of CH_4, increasing as the mixing ratio is increased from the pre-industrial

280 value to 2x RCP 8.5 year 2100 quantities. The reason for this behavior is made evident upon evaluation of η_{Cl} and η_{Br} in panels (f) and (j). The reaction of Cl with CH_4 is fast, forming the inorganic reservoir HCl, but the analogous reaction of Br with CH_4 does not effectively occur. Despite these factors, some suppression of the bromine cycle does occur as a result of competition with enhanced HO_x (from the oxidation of CH_4) for a reduced quantity of ClO_x reaction partners.

The effect of changing Br_y/Cl_y ratios was investigated over the range of ~~0.0054~~ 0.0057 – ~~0.0088~~0.0093. This range en-

285 capsulates the minimum and maximum ratios expected between the years 1980 – 2100 according to WMO 2018 Table 6-4. These values were computed according to Eq. (11) using ~~halocarbon mixing ratios prescribed by WMO 2018 Table 6-4, the~~ the trend-independent fractional release factors of ~~Newman et al. (2006), and an age spectrum of the form of Hall and Plumb (1994)~~
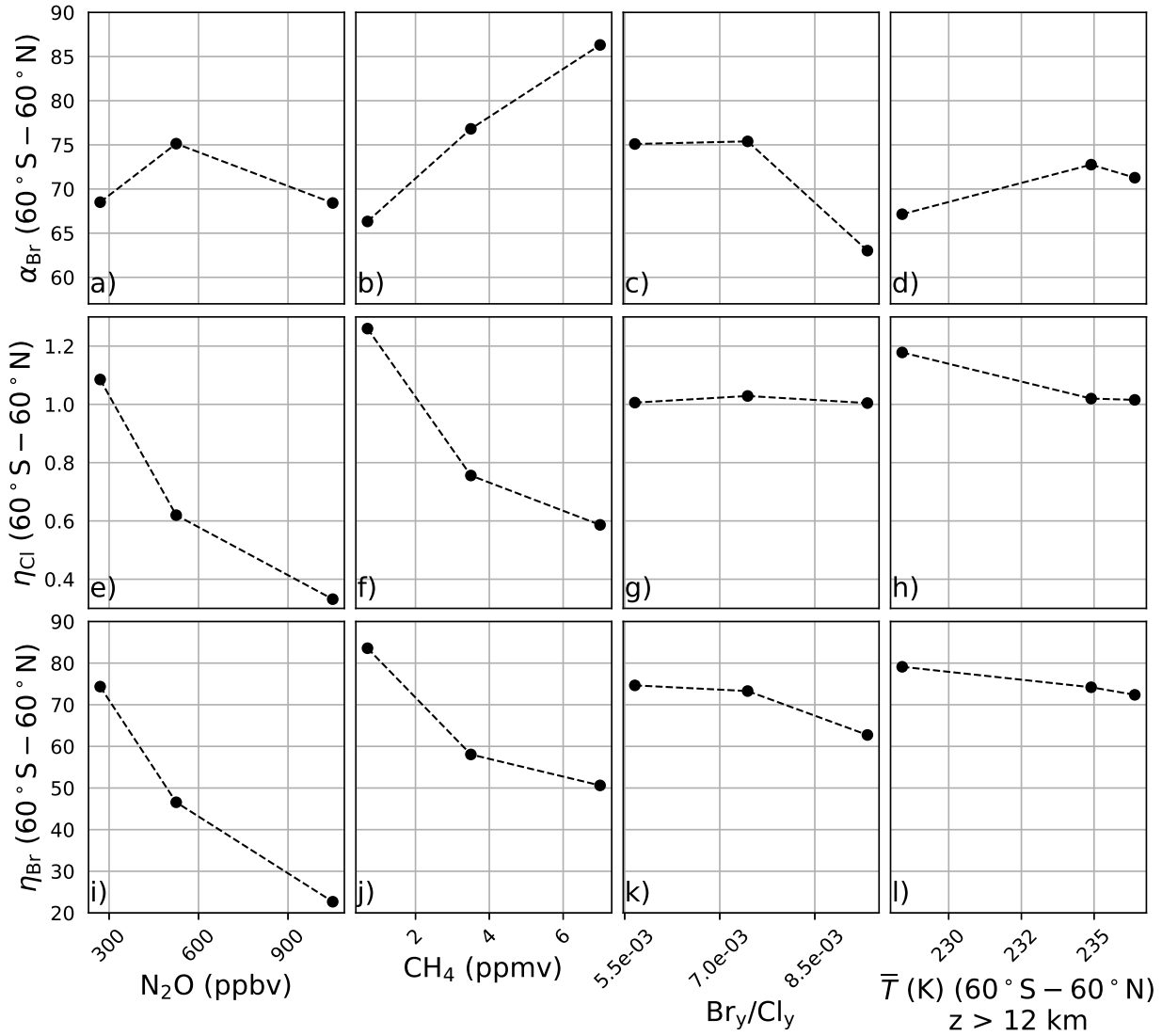
Figure 4. Extrapolar α and η sensitivity to perturbation parameters. N_2O: (a) α_{Br}, (e) η_{Cl}, (i) η_{Br}. CH_4: (b) α_{Br}, (f) η_{Cl}, (j) η_{Br}. Br_y/Cl_y: (c) α_{Br}, (g) η_{Cl}, (k) η_{Br}. Temperature: (d) α_{Br}, (h) η_{Cl}, (l) η_{Br}.

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Engel et al. (2018a). The values of α_{Br}, η_{Cl}, and η_{Br} are presented in Figure 4 panels (c), (g), and (k), respectively. Values of α_{Br} ~~generally~~ are generally expected to decrease as the ratio of Br_y/Cl_y increases.

$$\frac{Br_y}{Cl_y}(t,\Gamma) = \frac{\sum_i f_i(\Gamma)\, n_{i,Br} \int_0^\infty \chi_{0,i}(t-t')\, G(t',\Gamma)\, dt'}{\sum_i f_i(\Gamma)\, n_{i,Cl} \int_0^\infty \chi_{0,i}(t-t')\, G(t',\Gamma)\, dt'} \frac{\sum_i \overline{f_i}(\Gamma)\, n_{i,Br} \cdot \chi_{0,i}(t)}{\sum_i \overline{f_i}(\Gamma)\, n_{i,Cl} \cdot \chi_{0,i}(t)} \tag{11}$$

Both Chipperfield and Pyle (1998) and Danilin et al. (1996) demonstrated that α_{Br} in the polar vortex is highly dependent on the relative mixing ratios of available bromine and chlorine, maximizing at low Br_y/Cl_y because of the enhanced abundance of ClO reaction partners for each BrO radical in those conditions. Within the polar vortex the fraction of ozone loss due to the ~~slower~~ chlorine peroxide cycle declines as Br_y/Cl_y increases; however, the extent of ozone depletion following the addition of bromine does not increase proportionately because the system is controlled by the chlorine abundance. While the same relationship between α_{Br} and Br_y/Cl_y exists in the extrapolar stratosphere, the chemistry responsible for this effect is different. The higher temperatures of the extrapolar stratosphere render the chlorine peroxide cycle ineffective for the loss of ozone. We find that the extent of ozone loss following the addition of bromine increases significantly due to BrO_x-ClO_x and BrO_x-HO_x cycles ~~rather than staying essentially constant as in the polar vortex conditions of Danilin et al. (1996)~~, and we derive extrapolar α_{Br} values as function of Br_y/Cl_y qualitatively consistent with the extrapolar results of Chipperfield and Pyle (1998).

Evaluations of the model in which stratospheric temperature profiles were varied between RCP 8.5 year 2100 (low), RCP 2.6 year 2030 (medium), and 1978 – 2004 climatological averages (high) demonstrate a dampened sensitivity of α_{Br}, as presented in Figure 4 panel (d), in which α_{Br} increases by only 6% from the coldest scenario to the warmest scenario. Heterogeneous activation of chlorine in the coldest scenario boosts η_{Cl} by about 17%, as shown in panel (h). The heterogeneous conversion of bromine reservoirs to active bromine is much less temperature-sensitive than the analogous reactions for chlorine, and this insensitivity is indicated in panel (l); however, η_{Br} does respond to the temperature perturbation primarily as a function of changes in the partitioning of Cl_y, as in the sensitivity studies of CH_4 and Br_y/Cl_y.

3.3   Future EESC

Propagation of EESC using climate-invariant α_{Br} per Eq. (3) or climate-varying α_{Br} per Eq. (5) produces significantly different dates of extrapolar halogen recovery than propagation of ~~EESC~~ EESBnC using η-factor normalization as in Eq. (9). EESC and EESBnC values are presented in Table 3 for historical and future ~~chemistry-climate~~ chemistry/climate scenarios. In all cases, ~~EESC compuations~~ the computations were informed by the ~~time-independent~~ trend-independent fractional release factors provided in Table 1 of Engel et al. (2018a) ~~. These EESC~~ ; though fractional release factors are likely to vary as the climate evolves (Leedham-Elvidge et al., 2018), these factors correlate with the specified dynamics employed in this analysis. The EESC and EESBnC calculations are visualized in Figure 5.

In panel (a) of Figure 5, EESC is computed per Eq. (3) for static $\alpha_{Br} = 60$ (grey dashed line) and $\alpha_{Br} = 70$ (magenta dashed line) and per Eq. (5) using climate-varying α_{Br} for the four RCP scenarios (colored solid lines). Values of α_{Br} were interpolated between values indicated in Table 2. For reference, the black dots indicate 1980 EESC mixing ratios with $\alpha_{Br}=70$. Notably, there exists very little variation between the RCP scenarios computed using Eq. (5), with maximum deviation of 1.5 years

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Table 3. EESC (pptv) and EESBnC (pptv) for historical and future ~~chemistry-climate~~ chemistry/climate states[a]

Year	previous method[b]		Historical[c,d]		Year	previous method[b]		RCP 2.6[c,d]		RCP 4.5[c,d]		RCP 6.0[c,d]		RCP 8.5[c,d]	
	$\alpha_{Br}=60$	$\alpha_{Br}=70$	α_{Br}	η		$\alpha_{Br}=60$	$\alpha_{Br}=70$	α_{Br}	η	α_{Br}	η	α_{Br}	η	α_{Br}	η
1980	1067	1115	1115	1115	2020	1614	1694	1733	1653	1737	1623	1723	1611	1716	1572
1990	1575	1642	1664	1663	2030	1478	1550	1582	1493	1583	1460	1567	1488	1562	1450
2000	1911	2003	2056	1992	2040	1335	1399	1420	1337	1423	1287	1408	1351	1408	1279
2010	1757	1848	1896	1793	2050	1198	1257	1268	1201	1272	1132	1260	1175	1267	1074
					2060	1084	1139	1140	1094	1146	1011	1137	1026	1150	907
					2070	990	1042	1039	1000	1049	917	1039	922	1055	784
					2080	914	964	952	928	960	843	957	819	978	691
					2090	851	899	881	864	889	784	887	752	915	617
					2100	798	845	822	810	829	719	833	700	859	561

[a] Stratospheric mean age-of-air = 3 years.

[b] EESC using static α_{Br} calculated per Eq. (3).

[c] Climate-variant EESC (column indicated by α_{Br}) calculated per Eq. (5).

[d] EESBnC (column indicated by η) calculated per Eq. (9) and benchmarked to Ξ=1980.

Table 4. Date of EESC ~~and~~ EESBnC recovery to 1980 Benchmark Value[a]

previous method[b]		RCP 2.6[c,d]		RCP 4.5[c,d]		RCP 6.0[c,d]		RCP 8.5[c,d]	
$\alpha_{Br} = 60$	$\alpha_{Br} = 70$	α_{Br}	η	α_{Br}	η	α_{Br}	η	α_{Br}	η
2061.6	2062.2	2062.3	2057.9	2063.0	2051.1	2062.0	2053.7	2063.5	2047.9

[a] Stratospheric mean age-of-air = 3 years. Fractional years provided to better demonstrate sensitivity of perturbation parameters.

[b] EESC using static α_{Br} calculated per Eq. (3)

[c] Climate-variant EESC (column indicated by α_{Br}) calculated per Eq. (5).

[d] EESBnC (column indicated by η) calculated per Eq. (9) and benchmarked to Ξ=1980.

(spanning January 2062 – June 2063) for recovery to 1980 EESC values, as shown in Table 4. Scenarios of climate-invariant α_{Br}=60 or α_{Br}=70 provide EESC recovery dates (June 2061 and March 2062, respectively) in close agreement with the RCP scenarios. Note that for clarity, the 1980 EESC reference line for α_{Br}=60 is not plotted in Figure 5 panel (a).

Taking ~~chemistry-climate~~ chemistry/climate changes into account (when Eq. (9) is used for ~~EESC~~ EESBnC computation) results in significant variations in future ~~EESC~~ EESBnC between the RCP scenarios, as shown in panel (b) of Figure 5. For comparison purposes, as in panel (a), the black dots provide the 1980 chemistry/climate benchmark EESC mixing ratio with α_{Br}=70, and the dashed magenta line shows EESC propagated with climate-invariant $\alpha_{Br} = 70$ (equivalently calculated here with η_{Cl} =1 and η_{Br} =70). The range of values for the return of ~~EESC~~ EESBnC to 1980 levels between the RCP scenarios in panel (b) spans a decade, 2048 to 2058, as shown in Table 4. For all RCP scenarios, the expected recovery date of the inorganic halogen content of the stratosphere to the ozone-depleting equivalent of the year 1980 is significantly sooner than the date expected using ~~α_{Br}~~EESC. Importantly, the earlier ozone recovery dates predicted ~~with our eta factor method~~ by EESBnC using Eq. (9) are in closer agreement with the 3-D CCM results of Dhomse et al. (2018) than ~~EESC~~ recovery dates calculated using ~~bromine alpha factors~~EESC. We note that this analysis does not include the impact of an accelerated Brewer-Dobson circulation, which would further hasten our projected date of recovery.

The divergences of expected ~~EESC~~ values between the calculation techniques are even more pronounced as the century unfolds. Panel (c) of Figure 5 provides the differences between EESC calculated ~~using climate-dependent α_{Br}~~ with Eq. (5) and ~~climate-normalized EESC~~ EESBnC calculated using Eq. (9). As the century ends, ~~our eta factor~~ the EESBnC method shows that there is a ~~deficit~~ difference exceeding 300 pptv ~~EESC~~ equivalent stratospheric Cl in the RCP 8.5 scenario relative to a calculation of EESC~~using the alpha factor method. These differences~~. These discrepancies are negligible in the RCP 2.6 scenario because the greenhouse gas inventory of the RCP 2.6 year 2100 scenario is very similar to the greenhouse gas inventory of the contemporary stratosphere. Intermediate GHG scenarios lie in between these two extremes.

4 Conclusions

The future stratosphere will be very different than the stratosphere of today in terms of trace gas loading, temperature structure, and radiative-dynamical transport. In this work, we used a 2-D chemical-transport/aerosol model to evaluate how differences
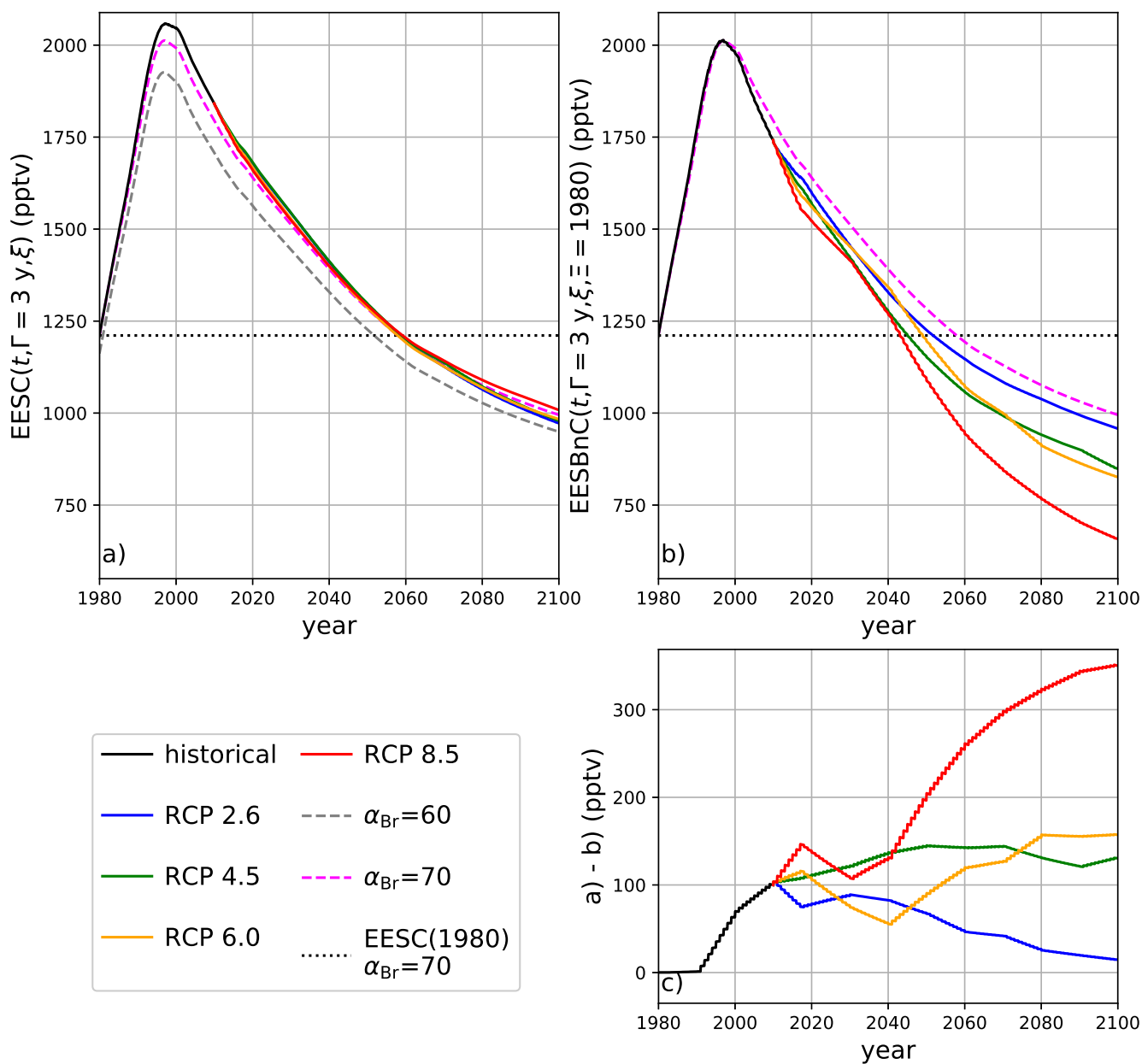
Figure 5. Calculations of EESC and EESBnC from 1980 – 2100 using 3-year stratospheric mean age. (a) EESC calculated per Eq. (3) and Eq. (5). Dashed traces: constant α_{Br} as indicated in the legend. Solid traces: α_{Br} interpolated as a function of time from values indicated in Table 2. Dotted black line: EESC corresponding to the year 1980 with α_{Br}=70. (b) Calculation of ~~climate-normalized EESC~~ EESBnC per Eq. (9) with benchmark ~~date~~ chemistry/climate state Ξ = 1980. Solid lines: η_{Cl} and η_{Br} interpolated as a function of time from values indicated in Table 2. Magenta dashed line: ~~EESC~~ EESBnC propagated with static η_{Cl}=1 and η_{Br}=70 (equivalent to EESC calculated per Eq. (3) with α_{Br}=70, as in panel (a)). Dotted black line: EESC corresponding to the year 1980 with α_{Br}=70. (c) RCP scenario differences between panel (a) and panel (b).

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in the trace gas loading and the temperature structure of the future atmosphere might influence the relative rates at which
345 inorganic halogen species destroy ozone. These differences can be quite large and are very sensitive to the ~~chemistry-climate~~ chemistry/climate boundary conditions imposed.

~~The most significant perturbations of the stratospheric halogen background in the future are likely to arise from geological impulses. In this work, we~~ We provide the framework for adjusting EESC to accommodate changes in the ozone processing rates of both chlorine and bromine driven by climate and chemistry~~, such that EESC may be employed to predict ozone loss~~
350 ~~following such an event~~. Current formulations of the bromine alpha factor obfuscate the fact that rates of ozone destruction by ~~bromine~~ chlorine are changing alongside rates of ozone destruction by ~~chlorine~~bromine. In some cases, as in RCP 8.5, these rates change in concert, producing a largely time-invariant α_{Br} over the course of the twenty-first century; however, the actual rates of ozone destruction facilitated by chlorine and bromine would have changed significantly, ~~producing an expected return to~~ declining to about 65% of their 1980 values~~14 years earlier than predicted using prior formulations of EESC~~. For this
355 reason, we have refactored the bromine alpha factor in terms of a climate normalization using new eta factors, which provide an indication of the ozone-processing power of the atmosphere relative to a benchmark ~~date~~chemistry/climate state.

~~Inserting~~ When we insert η_{Cl} and η_{Br} into the formulation for the time-propagation of EESC ~~, as in~~ (Eq. (9)~~,~~), we obtain EESBnC. This metric teases out differences in the capability of the inorganic halogen background of the stratosphere to destroy ozone as a function of future chemistry/climate scenario. Using this treatment, we find that the emission of large quan-
360 tities of CH_4 and N_2O, as in the RCP 8.5 emission scenario, decreases the ozone-processing power of the end-of-century future atmosphere by 36% relative to what would be expected by calculating EESC ~~using α_{Br} only~~ (as in Eq. (5)). ~~Our chemistry-climate correction to the current method of calculating EESC brings EESC-parameterized~~ Using EESBnC, the recovery of the stratospheric ozone layer to the thickness observed in 1980 is predicted to be 14 years earlier than the date obtained using EESC in the RCP 8.5 scenario, bringing parameterized estimates of the extrapolar ozone recovery date into
365 closer agreement with more costly 3-D CCM simulations.

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Interactive comment on "Temporal Evolution of the Bromine Alpha Factor and Equivalent Effective Stratospheric Chlorine in Future Climate Scenarios" *by* J. Eric Klobas et al.

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We thank the referee for his thorough and thoughtful remarks. We have revised our manuscript accordingly. The referee's comments are presented below in **bold text** and our responses to the referee appear in plain text.

The title has its emphasis on Bromine, but actually the changing efficiency of Chlorine is also studies, so the authors might consider adjusting the title to take this into account.

Good suggestion. We have changed the title to:

Reformulating the Bromine Alpha Factor and EESC: Evolution of Ozone Destruction Rates of Bromine and Chlorine in Future Climate Scenarios

(i) As explained above, I believe that the authors should give some more consideration to what the new proxy really is and if it should still be named EESC, in particular as not only the α value for bromine becomes a variably, but also the effectiveness of chlorine to destroy ozone (η) becomes a variable. This was not considered in EESC so far as EESC so far was not really an ozone recovery proxy (see e.g. the discussion in box 1-4 of WMO 2018), even though it has often been used as such.

I would consider naming this differently, maybe something like "Equivalent Ozone-effective stratospheric chlorine (EOESC)" or something along this line.

We agree with the referee that Equation (9) provides a quantity that can be differentiated from prior definitions of EESC. Equation (9) is a scalar multiplication of EESC with the chlorine eta factor (effectively a benchmark-state normalization of chlorine). We now call this metric Equivalent Effective Stratospheric Benchmark-normalized Chlorine (EESBnC).

Further, the nice thing about EESC as it is used now is that it can be easily calculated and applied to a new scenario, without the need for a model. This advantage is lost with the new concept, unless a method to parametrise the η factors needed in eq. (9) is given.

We note that our method adds no further complication to the calculation of EESC (or our new proxy) than is already present. The alpha factor is itself a parameterized quantity derived from 2-D modeling studies.

(ii) The study is performed with a 2D model.

Nearly all prior model determinations of alpha factor that we are aware of were also computed with 2-D models, e.g., Danilin et al., 1996, Ko et al., 1998, Daniel et al.,

1999, Sinnhuber et al., 2009, and unpublished results discussed in Chapter 8 of the 2006 WMO Ozone Assessment. We decided to employ the AER-2D model for this work because it (a) provides a direct linkage with prior determinations of the bromine alpha factor for validation purposes, (b) provides adequate spatial and temporal resolution for the determination of regional-annual parameterizations of the alpha- and eta-factors, and (c) provides these results with reasonable computational cost scaling. We note that the results presented in this work constitute over 2160 model years of evaluation, requiring more than a year-and-a-half of single-threaded computing time on the Harvard Cannon supercomputer. Because we report regional-annual average phenomena which are reproduced quite well by the model (Weisenstein et al., 1997, Weisenstein et al., 2007), the quality of our results are not materially degraded relative to the results we would have obtained if we had employed a 3-D model at significantly higher computational cost.

How is the climate state taken into account, i.e. the change in temperature and the changes in dynamics due to the expected accelerated BDC? While the changes in temperature and chemical environment can be simulated in a 2D model, the change in the Brewer-Dobson circulation which is projected by the 3D climate models is most probably not included.

Correct, we do not include changes in the Brewer-Dobson circulation. Our methodology, as outlined on lines 229 - 234 of the original manuscript, employs specified dynamics based upon a climatology from 1978 to 2004. The inclusion of varying circulation patterns is interesting; such a study is complicated because non-local factors influencing ozone mixing ratios might no longer be negligible when comparing the climate perturbation and climate benchmark scenario, and the magnitude of these non-local effects will likely differ between various models. A quantification of the effect of an accelerating Brewer-Dobson circulation on alpha- and eta-factors would be valuable and interesting on its own and in relation to this work.

Under such changing climatic conditions, the new fractional release factor for-

mulation by Ostermöller et al., (2017) is independent of the trend of the species but it does depend on the state of the atmosphere, in particular it is expected to change with time for a given mean age value due to dynamical changes (accelerating BDC).

We acknowledge the dependence of the fractional release factor on the synoptic circulation and have added text to discuss this on lines 270 - 273 of the revised manuscript:

In all cases, the computations were informed by the trend-independent fractional release factors provided in Table 1 of Engel et al. (2018a); though fractional release factors are likely to vary as the climate evolves (Leedham-Elvidge et al., 2018), these factors correlate with the specified dynamics employed in this analysis.

We note that our work uses specified dynamics corresponding to the circulation patterns of the contemporary era. In the context of our analysis, which provides ozone-loss processing rates as a function of changing temperature and trace-gas inventories, but not changing circulation, the fractional release factors would vary in only a slight manner, due to small changes in certain chemical terms such at the rate of halocarbon activation expected following stratospheric cooling [for example: CFC-12 + O1D -> ClO + products: k(240 K) =1.55E-10, k(230 K) = 1.56E-10 using JPL-2015 kinetics]. Consequently, the fractional release factors provided by Ostermöller et al. (2017) are appropriate fractional release factors to employ in our analysis.

(iii) Unfortunately, the explanation of the model experiments is rather unclear and difficult to follow. The paper lacks a clear explanation of which model runs have been performed, and exactly how they have been forced.

We have added further text to the experiment description beginning on line 164 of the original manuscript in an effort to more clearly describe the experiments that were performed. We note that our discussion on the treatment of data to derive the reported quantities of the bromine alpha factor and the chlorine and bromine eta factors is described elsewhere in the text. This is because our definition of alpha factor and eta

factor are novel and must be introduced first.

In particular, the dynamical forcing is not described and it is unclear if changes in the Brewer-Dobson circulation are included in the simulations from the description in section 2. Only on p.15, l.329 it is clearly stated that changes in the BDC are not included. A clearer description is required here to ensure that the results can be understood and reproduced.

We have revised the text to explicitly indicate that specified dynamics were employed in the model description. The perturbation experiments are now described more explicitly.

(iv) In section 3.1. it would be important to describe more clearly the physical meaning of the new EESC formulation (9). The definition of the η values for chlorine and bromine is always relative to the Ozone sensitivity with respect to Cl in the reference state. Therefore, EESC defined in (9) is also referenced to dO3/dCl in that reference state. It would be good to explain this concept more clearly and give a more intuitive explanation of this quantity. In my understanding the new formulation in eq. 9 describes the 1980- equivalent stratospheric chlorine impact on ozone, adjusted for changing stratospheric temperature and changing chemical environment, but not for changing dynamics.

We have added a more intuitive discussion of the meaning of Eq. (9) to section 3.1 on lines 176 - 180 of the revised manuscript:

The difference between EESC and EESBnC is significant; whereas EESC considers "the *relative* efficiency of chlorine and bromine for ozone depletion" (World Meteorological Organization, 2018), EESBnC accounts for the *overall* efficiency of chlorine and bromine relative to a benchmark chemistry/climate state. Thus, EESBnC provides the ozone-depleting power of an air parcel in the stratosphere propagated independent of changes in the rates of chlorine or bromine ozone-loss catalysis

Minor comments: General: the term background is used in many places (e.g.

l. 148: inorganic halogen background). A background is a state against which something is referenced. I suppose level or content might be more appropriate.

We have reviewed every instance of the word 'background' and have clarified our meaning when appropriate.

l. 15.: what is meant by inorganic halogen precursor compounds? I suppose this is the source gases? Then I would term this the precursor compounds for inorganic halogen.

We have no preference for either phrasing and have adopted the phrasing suggested by the referee.

l. 45: the use of "unlike" is unclear to me: in the absence of chlorine, also Br would require the oxygen atom and there are also other Cl-recycling reactions.

Yes, it is useful to consider the chain effectiveness (e.g., Lary (1997)) when comparing catalytic cycles involving chain centers with large differences in mixing ratio. We have revised our discussion to express this concept and relevant citations.

l. 49: please specify what you mean by lower stratosphere here.

We would refer the reader to the individual cited documents for the boundaries of the lower stratosphere as they vary between publications.

l. 54 (and other places): please be more specific with respect to the WMO 2018 citations: Usually the respective chapter should be cited in order to allow the reader to find the Information.

We have reviewed every instance in which the WMO Scientific Assessment of Ozone Depletion is cited, and now cite individual chapters when the information being cited is found primarily in one chapter. We retain citation to the document as a whole for information which can be found throughout the entire document.

Additionally, we have removed several citations to the WMO Scientific Assessment

of Ozone Depletion because the information cited is trivial: line 15 of the original manuscript, line 54 of the original manuscript.

l. 86: what do you mean by chemoclimatic?

Chemoclimatic: of or relating to the confluence of chemical and climatic properties. We have replaced all instances of this word with chemistry/climate.

l. 107: see for example discussion in box 1-4 of WMO 2018: EESC should really not be used as an ozone recovery proxy. It is a halogen recovery proxy. See also major comment above.

We agree with the referee that EESC should not be considered an ozone recovery proxy and note that we state that EESC is a halogen recovery proxy ourselves on the same line. That said, EESC is commonly employed to predict the date of, or set limits on the date of, ozone recovery. One key result of this work is to provide a new quantity which is better suited for this purpose.

We thank the referee for suggesting that we differentiate the name of this proxy from EESC.

l. 114-125: the projected super recovery of stratospheric ozone is mainly due to changes in dynamics, not changes in chemistry. This section reads like the chemical influences are dominating.

We have modified our discussion to better express that the expected super-recovery is dependent on both photochemical and dynamical controls in different parts of the stratosphere.

Section 2: In this section a clearer discussion of the model set-up is required, in particular how the dynamics (and possibly changing dynamics) have been incorporated.

We have revised our model description to provide a clearer understanding of how the

C7

experiment was conducted and how dynamics were incorporated.

l. 171ff: The concept of the perturbation experiments should be clearer explained.

We have rewritten portions of this section to more clearly explain the perturbation procedure.

l. 202-204: A clearer description should be given specifying that both sensitivities are given relative to the sensitivity of ozone to chlorine in the benchmark chemical-climate state.

We have now clarified the meaning of this this new variable on lines 166-168 of the revised manuscript:

The eta factor thus expresses the ozone-depleting efficiency of a chlorine or bromine atom in an arbitrary chemistry/climate state relative to the ozone-depleting efficiency of a chlorine atom in the benchmark chemistry/climate state.

Section 3.2.: have perturbations in T and in chemistry been performed independently? i.e. can it be distinguished between an effect due to increased CH_4 and increased HO_x with respect to an effect due to increased T?

Yes, we direct the referee to the sensitivity studies described in the text beginning on line 261 of the original manuscript and summarized in figure 4, where the sensitivity parameters of CH_4, N_2O, T, and Br_y:Cl_y were perturbed independently.

l. 235: I suggest using the term temporal evolution or temporal development instead of trajectory, as trajectory has a different meaning in atmospheric sciences.

We do not have a preference for the terminology and have adopted the phrase 'temporal dependencies' per the referee's suggestion.

l. 243: please give the percentage increases relative to what? Also monotonic

C8

and percentual do not go very well together. I suppose what is meant is a linear trend resulting in an increase of xx

We clarified that the percentage increases are relative to year 1980 and also removed the word monotonically.

eq. (11): which time series is used here? If I understand correctly, the model is run for 20 years to the (constant) mixing ratio and the whole integral would become the (constant) mixing ratio.

We thank the referee for bringing this question to our attention. The $Br_y : Cl_y$ ratios should be computed using a constant tropospheric mixing ratio for each halocarbon species. The quantities have been recalculated and Figure 4 has been regenerated. Eq. (11) has been modified to reflect this. We note that the results of this sensitivity study are not qualitatively changed.

l. 312: The values in Table 1 in Engel et al. (2018) are trend-independent. Fractional release factors are expected to change for different climate states.

We have reworded the sentence to express that the FRF are trend-independent and subject to change with future climate evolution.

l. 314 and Figure 5: the grey used here looked very "blue-gray" on my printout. I suggest to use a clearer grey colour for better distinction

Figure 5 has been regenerated to change the label on the y-axis of panel (b). We have changed the color of the grey to be less blue in the process.

l. 317.: why does the EESC formulation according to Engel et al. show differences for different RCP scenarios at all? Should EESC not be independent of RCP in this formulation?

The EESC formulation according to Engel et al. (eq. (3)) does not take climate as an input parameter. The EESC formulations according to our eq. (5) do take climate as

input parameters and vary according to the RCP scenario. We have modified the sentence to more clearly specify that the plots with climate dependence were calculated according to eq. (5).

l. 329.: This information should come much earlier and be discussed in section 2.

Though we state that we employ specified dynamics in several locations in the original text, we now more explicitly discuss this in section 2.

l. 344: Can the dominance by geological perturbations (I supposes volcanoes) be substantiated by a reference?

Please refer to Klobas, et al., (2017) and references cited therein for more information regarding the potential of future halogen-rich eruptions to perturb ozone.

These statements have been removed per the anonymous referee's suggestion.

l.345: processing rates of what? I suppose ozone?

Yes, we now specify that these rates are ozone-processing rates.

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We thank the anonymous referee for his or her thoughtful criticism which has resulted in changes that have improved the quality of our manuscript. We provide point-by-point responses to the referee's comments (**bold text**) in plain text below.

My feeling is that one should not change the EESC definition. However, that being said, I do think there is merit in attempting to include a diagnostic that does address climate impacts on EESC, that is simple, and does not require running a large ensemble of CCMs. Therefore, I wouldn't change the EESC definition above, but would create a new definition. This work is a first step towards this

C1

goal. I would recommend that this work be published assuming my comments are addressed below.

Per the recommendation of both referees regarding changing the variable name, we have opted to call this proxy Equivalent Effective Stratospheric Benchmark-normalized Chlorine (EESBnC) and will refer to it as such in our responses here.

Specific Comments: Line 35: I don't believe (just a suggestion) you need to discuss homogeneous reactions (i.e., like R4) in discussion of lower stratospheric ozone loss. This is a topic that has been explained in hundreds of publications. Just reference the Solomon et al., 1999 review article. You also don't need to summarize the heterogeneous reactions either (i.e., R5-R7).

We have revised the introduction to eliminate them.

Lines 135-144: RE: Discussion of Volcanic emission of Cl and Br. I find this discussion topic distracts from the point of this paper. Why go into possible random inputs of these species into a future atmosphere. You might as well discuss the possibility of an ocean surface asteroid impact injecting Cl and Br into the stratosphere. This topic seems like a separate study/discussion to me. I would just focus on the modified "EESC" technique you are proposing.

We have removed this paragraph and the associated statement in the conclusion.

Lines 152-163: The model description section is very confusing (at first read). One has to have a basic understanding of Daniel et al., 1999 to make sense on where you are going with the scenarios. Evidently you are running time slice experiments (every 10-years, with a duration of 20 years) using constant mole fraction lower boundary conditions for the 20-year period? E.g., Table 1: for "d" superscript you state "informed by Meinshausen et al. (2011) and Watanabe et al. (2011)". This means you are getting the initial conditions for say year 2020 from Watenabe et al. and the lower boundary mole fraction from Meinshausen et

C2

al.?

We have revised the model and experiment description sections to better communicate the procedure we followed. The referee's interpretation is correct. We employ 20-year time slice experiments for each decade spanning 1980 - 2100. Temperature fields are obtained from RCP scenario realizations of the MIROC-CHEM-ESM from the CMIP5 archive (Watanabe et al., 2011), while chemical boundary conditions for our model evaluation are obtained from RCP scenario specifications (Meinshausen et al., 2011).

For "c" you are not using the same model, but a 2D model from Fleming et al., (1999)? Why not use the same model for hindcast and future conditions (i.e., MIROC-CHEM-ESM)?

For 'c', historical past simulations were evaluated using climatological and temperature fields prepared previously. We employ these climatological conditions because (1) these climatological fields were used in previous studies and facilitated validation of model performance, and (2) the climatological fields prepared from MIROC-CHEM-ESM for the present do not significantly differ with the climatological fields we employ.

Line 164: You state that you are using the Daniel et al. (1999) approach. Essentially you are using the approach for equation (2) in Daniel et al., correct? [Your equation (2)] This is also why you have three scenarios to derive alpha-Br from a given atmospheric state, correct? I would restate (in your words) the procedure on page 23,874 Daniel et al. (1999). This will greatly help the first-time reader of this work.

The reviewer is correct on all counts. We have reworded the procedure such that it is more clearly communicated to a reader who does not have prior knowledge of Daniel et al. (1999).

Line 218: You probably should define the basic technique of graph-theory.

We note that the technique is described immediately following this line.

C3

Line 229: Specified dynamics details are needed here. What are you specifying for the dynamical fields and where did they come from?

We now provide the information the referee requests in Section 2, model description.

Lines 325-330. This is a very interesting result [i.e., better comparison of EESC to 1980 values compared to Dhomse et al. (2018)]. The Dhomse et al. study was an average of many models. Have you looked at one model, say the MIROC-CHEM-ESM, of which was used for the initial condition, for this work?

In response to the referee's question, we performed a quick investigation and found that MIROC-CHEM-ESM RCP / HISTORICAL experiments from CMIP5 show a similar qualitative trend to our results (extrapolar RCP8.5 recovering to 1980 ozone layer thickness sooner and extrapolar RCP 2.6 recovering to 1980 ozone layer thickness later). The dates of recovery from these experiments are not exactly the same as the dates we derive from our EESBnC treatment in Table 4, which is not unexpected given that our prognostication is based upon halocarbon inventories and our eta parameters are derived using a model with different chemical/aerosol/transport schema.

We note that Eyring et al., 2013 explored ozone layer recovery to 1980 thickness and the authors included MIROC-CHEM-ESM in their model ensemble.

Lines 329-330. You state that this analysis does not include the "impact of an accelerated BDC, which would hasten the projected recovery". Since you are using a CCM for your initial state, is part of this process "baked into" the calculation? Certainly, the temperature affect is; but isn't it possible that the dynamical state is also influencing the equation 10 result?

It's true that certain parameters such as scale height will be dependent on the imposed temperature structure, such that the dynamics deviate slightly between model realizations. If we review vertical profiles of ozone for the control runs in our temperature sensitivity studies, we find very little variation between midlatitude ozone profiles in the

C4

lower stratosphere where ozone is subject to dynamical control, especially with regard to circulation-induced ozone super-recovery. However, regions where photochemistry dominates the ozone steady-state do exhibit variation in ozone as a function of temperature boundary conditions.

From these comparisons, we infer that any variation in ozone due to dynamics baked-in to our boundary conditions are insignificant to photochemical changes in ozone as a result of the temperature perturbation.

NOTE: I would find it very interesting to add an additional figure (like Figure 1) showing the column alpha-Br (latitude vs time) for year 2100. Here I would show four panels, depicting the result for RCP2.6, 4.5, 6.0, and 8.5.

We agree that such a plot is quite interesting, but we are reserving this type of analysis for a future manuscript involving a method which is more sensitive to PSC response to climate changes in the polar regions.

C5