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Key Points:

- Using CH_3Br as surrogate for brominated very short-lived (VSL^{Br}) species reproduces upper stratosphere bromine, but the impact on lowermost stratospheric ozone is underestimated
- An explicit approach for $CHBr_3$ and CH_2Br_2 captures the expected bromine stratospheric injection but underestimates tropospheric impacts
- Only the full chemical treatment of VSL^{Br} sources results in a coherent bromine representation in the troposphere and lowermost stratosphere

Supporting Information:

- Supporting Information S1

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Intercomparison Between Surrogate, Explicit, and Full Treatments of VSL Bromine Chemistry Within the CAM-Chem Chemistry-Climate Model

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Abstract Many Chemistry-Climate Models (CCMs) include a simplified treatment of brominated very short-lived (VSL^{Br}) species by assuming CH_3Br as a surrogate for VSL^{Br}. However, neglecting a comprehensive treatment of VSL^{Br} in CCMs may yield an unrealistic representation of the associated impacts. Here, we use the Community Atmospheric Model with Chemistry (CAM-Chem) CCM to quantify the tropospheric and stratospheric changes between various VSL^{Br} chemical approaches with increasing degrees of complexity (i.e., surrogate, explicit, and full). Our CAM-Chem results highlight the improved accuracy achieved by considering a detailed treatment of VSL^{Br} photochemistry, including sea-salt aerosol dehalogenation and heterogeneous recycling on ice-crystals. Differences between the full and surrogate schemes maximize in the lowermost stratosphere and midlatitude free troposphere, resulting in a latitudinally dependent reduction of ~1–7 DU in total ozone column and a ~5%–15% decrease of the OH/HO_2 ratio. We encourage all CCMs to include a complete chemical treatment of VSL^{Br} in the troposphere and stratosphere.

Plain Language Summary The atmospheric bromine burden is dominated by anthropogenic long-lived bromocarbons, such as methyl bromide (CH_3Br) and halons (i.e., CBr_2F_2). Due to their small reactivity, these species do not influence tropospheric chemistry and are transported unaltered to the stratosphere, where they contribute to ozone layer depletion. The Montreal Protocol has banned the industrial production of halons and phased out the production of CH_3Br, and consequently their atmospheric abundances are declining. Accordingly, the relative contribution of natural very short-lived bromine (VSL^{Br}) species, such as bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2), has increased. Given that VSL^{Br} decompose more rapidly than long-lived species, their impact on upper tropospheric chemistry and lowermost stratospheric ozone cannot be neglected. In addition, heterogeneous recycling of inorganic bromine on sea-salt aerosol and ice-crystals enhances the tropospheric bromine burden. However, many Chemistry-Climate Models include a simplified approach by assuming CH_3Br as a surrogate for VSL^{Br}; while those that include an explicit VSL^{Br} approach only consider a simplified tropospheric chemical processing. Here, we compare a surrogate, an explicit and the full chemical treatment of VSL^{Br} source and product gases, and quantify the global impacts of these natural bromocarbons on tropospheric and stratospheric ozone, as well as on other oxidizing agents.

1. Introduction

During the last decades, scientific reports on stratospheric ozone depletion (WMO, 2011, 2014, 2018) have assessed that a total of ~5 ± 3 ppt of (organic + inorganic) bromine originating from very short-lived bromocarbons (VSL^{Br}) are injected to the stratosphere. This natural VSL^{Br} contribution is required to reconcile the best knowledge on anthropogenic long-lived bromine sources and chemistry with the available observations of inorganic bromine (Br_y) in the stratosphere. Due to the projected reduction of anthropogenic long-lived sources (WMO, 2018), as well as the possible enhancement on VSL^{Br} oceanic emissions during the 21st century (Iglesias-Suarez et al., 2020; Ziska et al., 2017), the current contribution of VSL^{Br} to total stratospheric bromine (~25% for year 2016) is expected to increase in the future. All of these factors highlight the importance of considering a consistent treatment of natural VSL^{Br} species within chemistry-climate model (CCM) projections.

The Chemistry-Climate Model Initiative (CCMI; Eyring et al., 2013; Hegglin et al., 2014) suggested two alternative methods for including VSL^{Br} species in CCMs: (i) the *explicit* approach, where a fixed surface mixing ratio of 1.2 ppt for each of the major VSL^{Br} species (bromoform, $CHBr_3$; and dibromomethane, CH_2Br_2) should be included as a model lower boundary condition (LBC); and (ii) the *surrogate* approach, where an additional enhancement of 5 ppt for methyl bromide (CH_3Br), representing the contribution from VSL^{Br}, should be added to the long-lived bromocarbons LBCs. Since, a fraction of the inorganic bromine released from the photochemical processing of short-lived bromocarbons is washed-out within the troposphere, the contribution of VSL^{Br} to the stratospheric organic source gas (SGI) and inorganic product gas (PGI) injection will depend on the specific approach (Aschmann & Sinnhuber, 2013; Fernandez et al., 2014; Liang et al., 2014; WMO, 2014, 2018). Recently, Wales et al. (2018) showed that CCMs that include an explicit representation of VSL^{Br} compare better with bromine observations in the lower stratosphere than those that utilize CH_3Br as a surrogate for VSL^{Br}.

The impact of VSL^{Br} on stratospheric ozone peaks in the lowermost stratosphere (Barrera et al., 2020; Salawitch et al., 2005; Sinnhuber & Meul, 2015), an important atmospheric region because surface climate and ultraviolet radiation are quite sensitive to variations in ozone at these altitudes (Riese et al., 2012). Indeed, Hossaini et al. (2015) found that VSL^{Br} exerts a 3.6 times larger ozone radiative effect than that arising from long-lived substances. Within the troposphere, bromine affects the radiative balance and the oxidative capacity through changes in the OH/HO_2 ratio (Saiz-Lopez et al., 2012; Sherwen et al., 2017). Due to their shorter photochemical lifetimes compared to CH_3Br, the VSL^{Br} influence on tropospheric ozone and OH depends on the balance between the height and location of the bromine sources and sinks. The total tropospheric bromine burden is determined not only by the VSL^{Br} photodecomposition, but also by the washout and heterogeneous recycling efficiency of Br_y reservoirs (Aschmann et al., 2011; Fernandez et al., 2014; Liang et al., 2014) as well as the additional bromine release from sea-salt aerosol (SSA) due to uptake reactions (i.e., the so called SSA dehalogenation; see Badia et al., 2019; Fernandez et al., 2014; Koenig et al., 2017; Zhu et al., 2019).

In this work, we used the Community Atmospheric Model with Chemistry (CAM-Chem) model to evaluate the atmospheric impacts of different treatments of VSL^{Br} sources and chemistry. A triple set of sensitivities is considered, starting from an initial surrogate scheme based on CH_3Br; followed by an explicit treatment of $CHBr_3$ and CH_2Br_2 using the constant LBCs approach recommended by CCMI; and finally a full representation of geographically and seasonally resolved emissions of six VSL^{Br} species as well as the Br_y contribution from SSA dehalogenation and heterogeneous recycling. A comprehensive inter-comparison between the various approaches for year 2000 conditions is provided, with a special focus on the absolute and relative changes in bromocarbons, inorganic bromine and ozone within the upper troposphere and lower stratosphere.

2. Model Setup and Experiments

All simulations were performed with the CAM4-Chem model (Community Atmospheric Model with Chemistry, version 4), which includes a detailed treatment of tropospheric VSL^{Br} sources and chemistry (Fernandez et al., 2014, 2017). Briefly, our full halogenated VSL^{Br} setup includes geographically distributed and seasonally varying oceanic sources for six bromocarbons

($VSL^{Br} = 3 \times CHBr_3 + 2 \times CH_2Br_2 + CH_2BrCl + 2 \times CHBr_2Cl + CHBrCl_2 + CH_2IBr$) based on the Ordóñez et al. (2012) emissions inventory, as well as inorganic sources arising from the heterogeneous uptake of sea-salt bromide (SSA dehalogenation). A comprehensive representation of dry-deposition, wet-scavenging, and heterogeneous recycling of individual inorganic bromine reservoirs is considered. For the case of long-lived brominated species (i.e., CH_3Br and the halons H-1301, H-1211, H-1202, and H-2402), zonally averaged LBCs based on the A1 halogen scenario are used (Tilmes et al., 2016; WMO, 2011). Our standard setup has a 2° × 2.5° lat-lon resolution and 26 hybrid vertical levels from the Earth's surface to the middle stratosphere (~40 km; Lamarque et al., 2012; Saiz-Lopez et al., 2012). All long-lived surface LBCs considered are representative of year 2000, reaching 16.1 ppt total bromine (7.4 ppt for the halons and 8.7 ppt for CH_3Br). To guarantee an equivalent upper stratospheric bromine burden for all model runs and reduce inter-annual oscillations, the last 3-year-mean of a 13 years long cyclical simulation was used.

Three sensitivity setups were considered (see Table S1):

- *SURR*: baseline surrogate scheme including, in addition to the long-lived bromine LBCs, a fixed surface contribution of 5.0 ppt CH_3Br as a surrogate for VSL^{Br}
- $EXPL^{LBC}$: explicit + LBC setup where the surrogate CH_3Br is replaced by a constant surface LBC of the major VSL^{Br} species, following the CCMI recommendation (1.2 ppt for both $CHBr_3$ and CH_2Br_2, totaling 6 ppt bromine; Hegglin et al., 2014)
- $FULL^{TROP}$: explicit + emissions + tropospheric processing approach, where the constant surface LBCs are replaced by geographically and seasonally dependent VSL^{Br} sources (Ordóñez et al., 2012) that are cycled for year 2000. The inorganic bromine release from the SSA dehalogenation source as well as the heterogeneous recycling of bromine reservoirs on ice-crystals are also considered (Fernandez et al., 2014)

Figure S1 presents the spatial distributions of the long-lived and VSL^{Br} surface LBCs and oceanic sources considered in each scheme. Following the CCMI recommendation, the *SURR* and $EXPL^{LBC}$ approaches do not include any treatment of Br_y removal on upper tropospheric ice-crystals, while the $FULL^{TROP}$ setup considers washout and ice-uptake for individual bromine reservoir species (Fernandez et al., 2014). A complete validation of the $FULL^{TROP}$ setup can be found in the Supplement of Iglesias-Suarez et al. (2020).

3. Results and Discussions

3.1. Tropospheric and Stratospheric Bromine Burden

The VSL^{Br} and Br_y tropical vertical profiles shown in Figure 1 show that all scenarios present a realistic stratospheric bromine loading (i.e., ~21.7 ± 0.3 ppt of Br_y above ~30 km, see Table S2), in agreement with reported values for year 2000 (WMO, 2018). As CH_3Br is predominantly photo-decomposed after reaching the stratosphere, the tropospheric Br_y within the *SURR* scheme shows appreciable differences (i.e., >1 ppt Br_y) with respect to the full and explicit setups. Indeed, both the explicit and full approaches show an annual mean PGI at least ~2 ppt larger than for the *SURR* scheme, representing in both cases a significant difference that surpasses the model spatio-temporal standard deviation (stdv). Even though the $FULL^{TROP}$ and $EXPL^{LBC}$ experiments result in bromine vertical profiles with overlapping variability (see shaded areas in Figure 1), VSL^{Br} mixing ratios are larger for the $FULL^{TROP}$ scheme in the lower troposphere, while $EXPL^{LBC}$ shows the largest Br_y levels above ~5 km. These profiles result in slightly different SGI and PGI among the explicit and full simulations: the $FULL^{TROP}$ scheme shows ~0.3 ppt larger SGI (i.e., VSL^{Br}) and ~0.8 ppt smaller PGI (i.e., Br_y) than the $EXPL^{LBC}$ scheme (see Figures 1a and Table S2). This difference is explained by the omission of Br_y ice-scavenging within the $EXPL^{LBC}$ approach, which results in an infinite tropospheric lifetime of every bromine atom photochemically released in the upper troposphere. Most notably, Figure 1 shows that abundance of both VSL^{Br} and Br_y for the $FULL^{TROP}$ setup at the tropical tropopause (~16.8 km) lie in the middle of the most recently assessed ranges (SGI ≈ 2.2 (0.4–4.2) ppt; PGI ≈ 2.7 (1.7–4.2) ppt; see Table 1.5 in WMO, 2018). Overall, the total injection (SGI + PGI) for the *SURR*, $EXPL^{LBC}$, and $FULL^{TROP}$ simulations are 5.5, 5.6, and 5.2 ppt, respectively (see Table S2). Furthermore, even if the total amount of bromine reaching the stratosphere is equivalent for all three scenarios, the altitude where inorganic bromine is released depends on the photochemical lifetime and distribution of the various VSL^{Br} species (or CH_3Br) considered within each scheme (Wales et al., 2018).

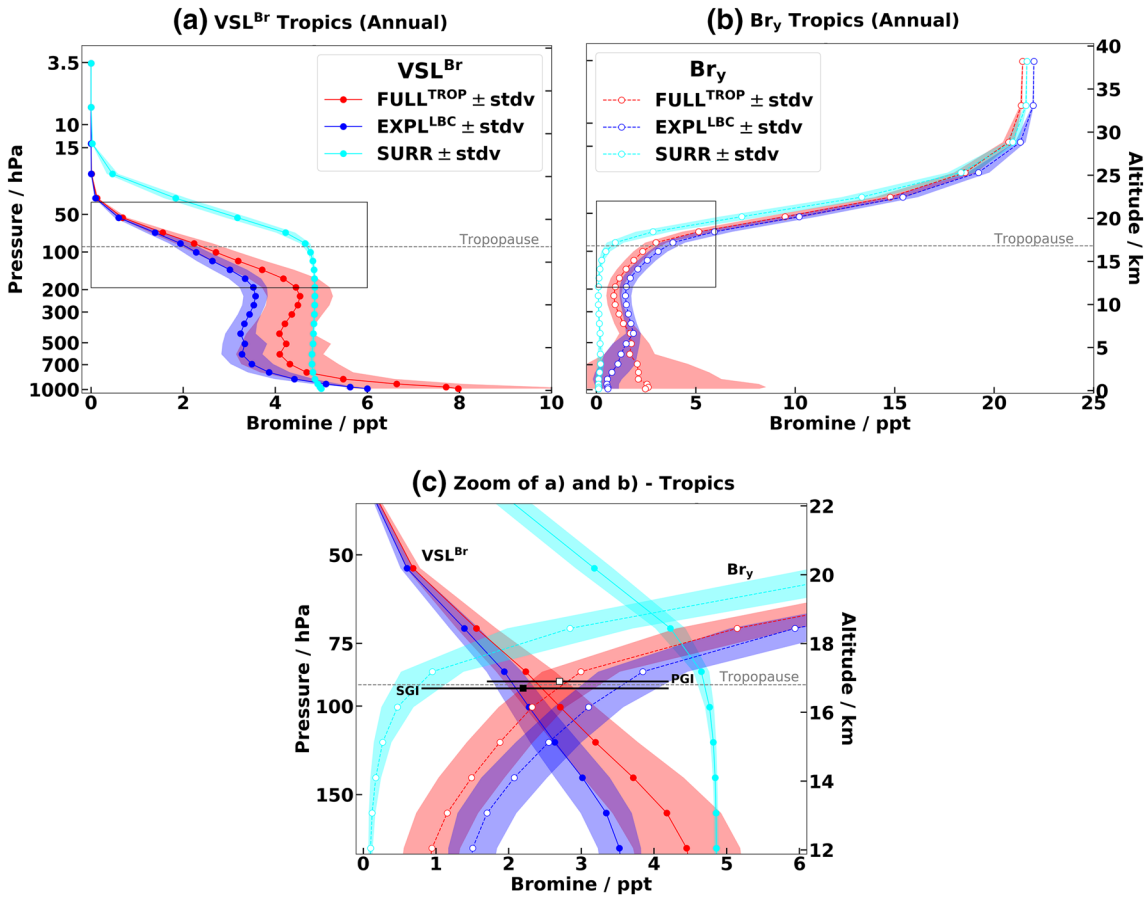

Figure 1. Tropical annual mean vertical distribution of (a) very-short lived bromocarbons (VSL^{Br}, filled circles) and (b) inorganic bromine (Br_y, empty circles) for the different CAM-Chem schemes. Shaded areas represent the model spatial and temporal variability within the Tropics (20°N–20°S). (c) Superimposed zoom of the gray boxes in panels (a) and (b). The SGI and PGI assessed values (mean ± range) from WMO (2018) are shown in black (altitude has been shifted ± 100 m with respect to the tropopause height [gray dotted line] for visual clarity).

Figures 2a and 2b present the zonal mean change in the inorganic bromine burden (ΔBr_y) between $FULL^{TROP}$ and $EXPL^{LBC}$ with respect to the *SURR* setup, respectively, while Figures 2c and 2d show the mean tropical (20°N–20°S) and midlatitudinal (25°N–50°N & 25°S–50°S) bromine difference, distinguishing between the bromocarbon (ΔVSL^{Br}) and ΔBr_y fractions. The observed maximum enhancement of stratospheric Br_y with respect to the surrogate scheme within the tropics is ~2.3 ppt for the $FULL^{TROP}$ setup and ~3.1 ppt for the $EXPL^{LBC}$ experiment. The maximum ΔBr_y differences occur above the tropical tropopause at ~18.5 km due to the shorter photochemical lifetime of VSL^{Br} (mostly dibromomethane, $\tau_{CH2Br2} \approx 130$ days) compared to methyl bromide ($\tau_{CH3Br} \approx 6$ months). The respective ΔBr_y enhancement within the midlatitudes is only slightly smaller (~2.0 ppt and ~2.9 ppt for $FULL^{TROP}$ and $EXPL^{LBC}$, respectively) and peaks at lower altitudes due to isentropic transport within the lowermost stratosphere (~16 km or ~100 hPa; see Figure 2). Here, quasi-horizontal transport along lines of constant potential temperature, in addition to the lower branch of the Brewer-Dobson circulation, contribute to rapid mixing of lowermost stratospheric air at midlatitudes (Randel et al., 1993). Above the tropopause, the rapid increase of Br_y with height arises from the photochemical degradation of VSL^{Br}, the long-lived halons, and CH_3Br (see Tables S2 and S3). However, the equivalent enhancement of ΔBr_y within the tropics and midlatitudes suggests that: (i) a fraction of the air parcels within the tropical tropopause layer (TTL) are directly transported to the midlatitude stratosphere (Levine et al., 2007); and (ii) lowermost stratospheric Br_y could also be influenced by the direct extra-tropical exchange of both VSL^{Br} and Br_y across the midlatitude tropopause (Keber et al., 2020).

Within the tropical free troposphere, the geographically and seasonally varying VSL^{Br} emissions within the $FULL^{TROP}$ scheme (which exhibit clear maxima within the tropics, see Figure S1c) result in ΔVSL^{Br}

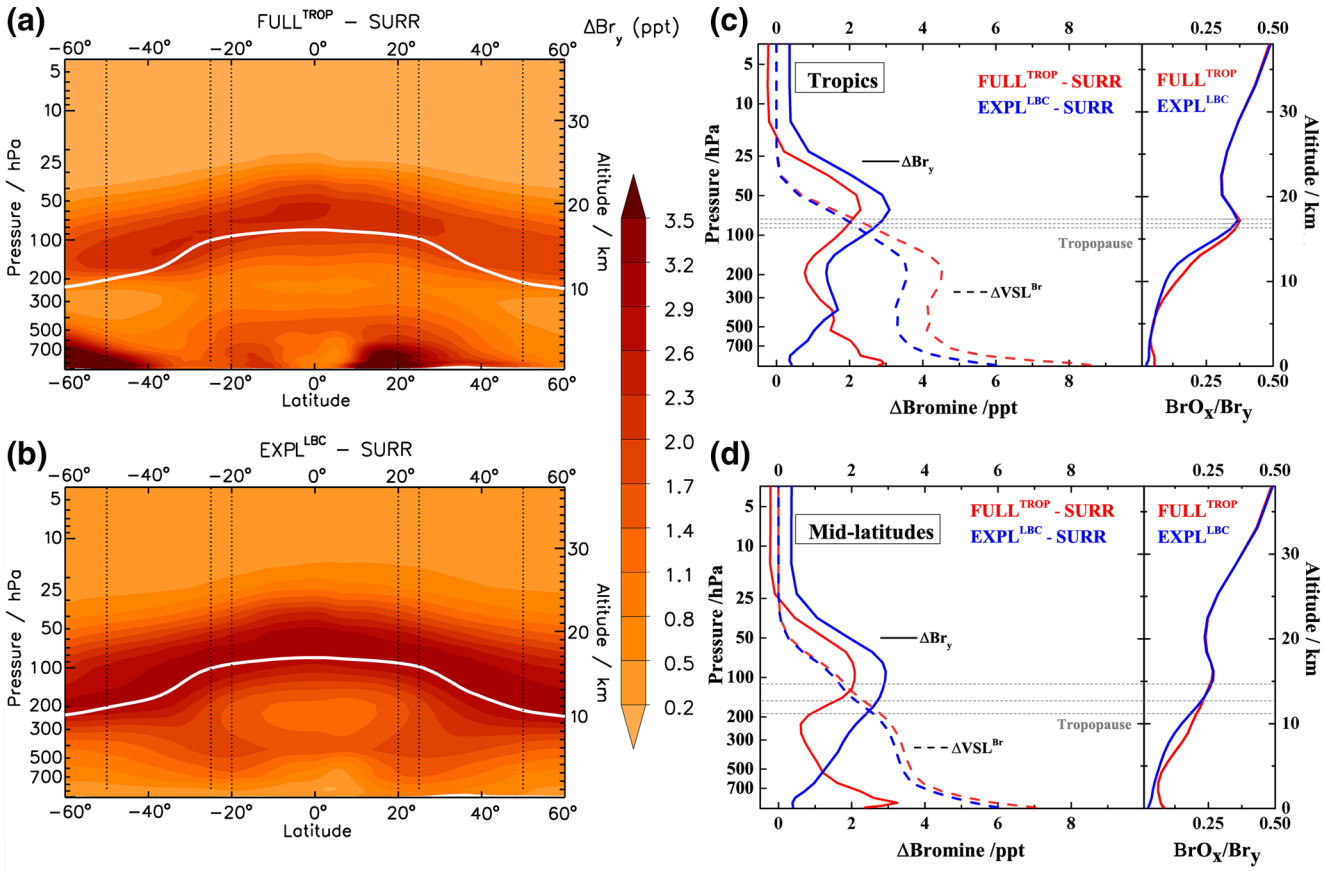

Figure 2. Change in bromine distribution between the *FULL*^{TROP} and *EXPL*^{LBC} schemes with respect to *SURR*: (a), (b) annual zonal mean change in inorganic bromine (ΔBr_y). The white lines show the mean chemical tropopause (O_3 = 150 ppb), while the dotted vertical lines indicate the Tropics (20°N–20°S) and Midlatitude (25°–50°N/S) bands. (c), (d) Mean vertical profile changes in bromocarbons (ΔVSL^{Br}) and ΔBr_y within the Tropics and Midlatitudes. The rightmost panels show the BrO_x/Br_y ratio for the *FULL*^{TROP} and *EXPL*^{LBC} schemes. The dotted horizontal gray lines indicate the mean location of the chemical tropopause ± stdv within each region.

enhancements that are ~1 ppt larger than those for the *EXPL*^{LBC} setup (Figure 2c). This difference reaches 2.5 ppt at the surface. In contrast, due to the less efficient vertical transport and smaller source strength, equivalent vertical profiles for ΔVSL^{Br} occur for *FULL*^{TROP} and *EXPL*^{LBC} in the midlatitude troposphere (Figure 2d). Another important difference appears below ~500 hPa at all latitudes, where due to the inclusion of the SSA-dehalogenation source the *FULL*^{TROP} setup results in a ΔBr_y enhancement with respect to the surrogate scheme that is at least 2 times larger than for *EXPL*^{LBC}. Note that this SSA-derived Br_y source occurs only in the lower marine atmosphere and is mostly washed-out before reaching the free troposphere. However, as described in Section 3.3, SSA recycling can be of major importance within regions of strong convection where Br_y-rich air masses from the ocean surface are rapidly transported to the TTL (Koenig et al., 2017).

3.2. Impact on Ozone and OH/HO_2 Ratio

Figure 3 shows the mean annual change in the Partial Ozone Column (ΔpO_3), as well as the relative changes in the OH/HO_2 ratio, for the same set of simulations shown in Figure 2. As expected, the largest ozone changes are co-located with the greatest changes in Br_y. The maximum absolute differences in O_3 with respect to the *SURR* setup within the tropics occurs at ~22.5 km, reaching 0.18 DU (15 ppb) for *EXPL*^{LBC} and 0.15 DU (12 ppb) for *FULL*^{TROP}. The corresponding changes in O_3 at the tropical tropopause are similar for both scenarios, reaching ~2% (4 ppb). The slightly larger ozone impact in the lowermost stratosphere for *EXPL*^{LBC} arises due to the ~0.5 ppt larger value of Br_y, which in turn results from the omission of bromine

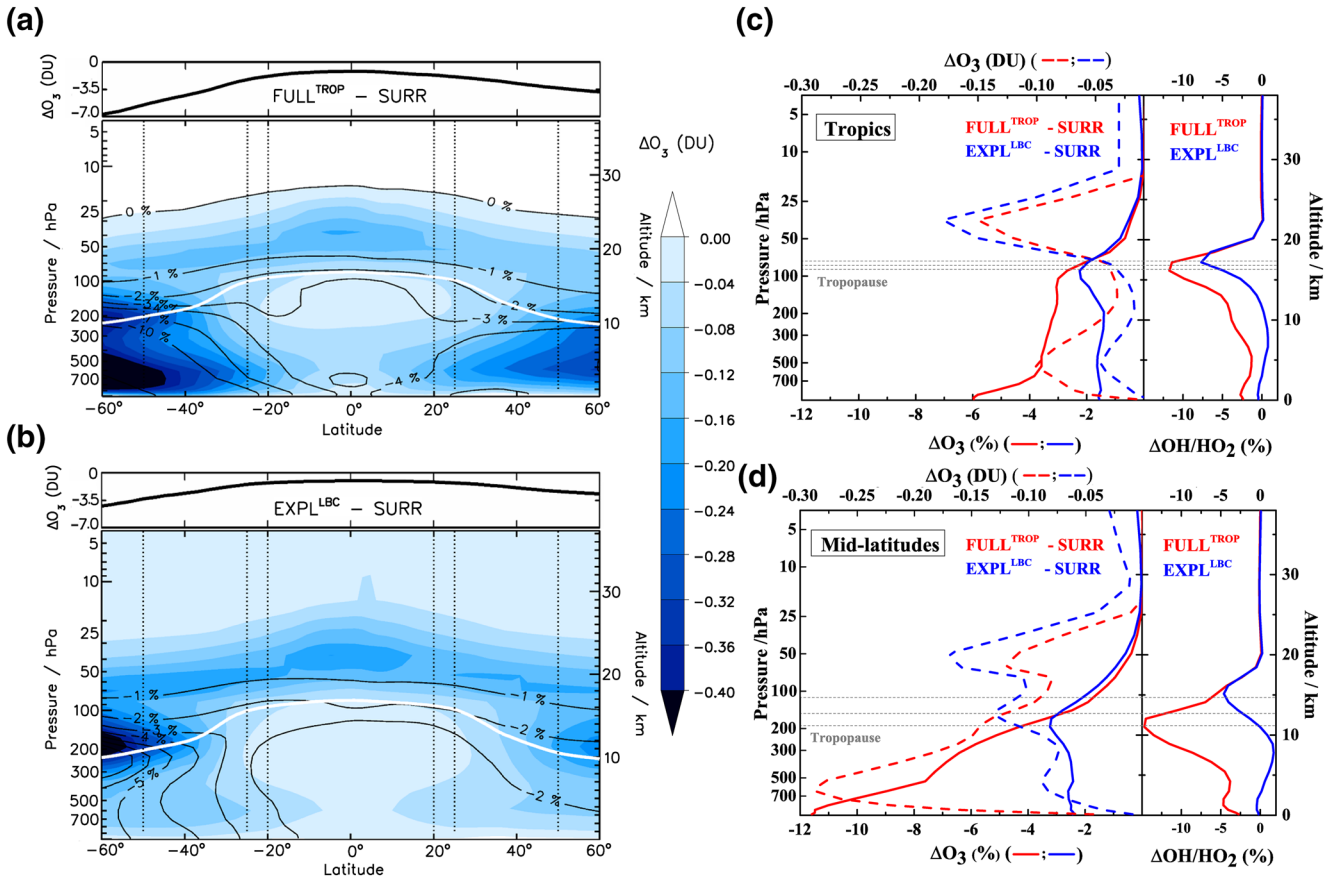

Figure 3. Change in ozone partial column (ΔpO_3) between the *FULL*^{TROP} and *EXPL*^{LBC} schemes with respect to *SURR*: (a), (b) absolute (color contour) and relative (contour lines) annual zonal mean. The change in total ozone column ($\Delta TO_3 = \Sigma\Delta pO_3$) is shown on the top panel. (c), (d) Mean absolute (top *x*-axis) and relative (bottom *x*-axis) ozone change within the Tropics and Midlatitudes. The rightmost panels show the relative change in the OH/HO_2 ratio.

ice-scavenging. Conversely, the larger relative ozone impact within the upper troposphere for *FULL*^{TROP} (>3%) arises because of the inclusion of heterogeneous re-activation reactions on ice-crystals (Fernandez et al., 2014), which increases the relative fraction of reactive bromine (BrO_x) with respect to total Br_y (Figures 2c and 2d). The total column ozone change ($\Delta TO_3 = \sum\Delta pO_3$) with respect to *SURR* is between 1 and 4 DU for *EXPL*^{LBC} and 1 and 7 DU for *FULL*^{TROP}, with these differences being larger in midlatitudes than the tropics (top panel in Figures 3a and 3b). Most of this ΔpO_3 difference is located in the lower stratosphere (dashed lines in Figures 3c and 3d, see also Figure S2), within a region where a unit mass ozone perturbation produces a radiative imbalance up to 2 times larger than an equivalent perturbation in the middle stratosphere (Riese et al., 2012). In the upper troposphere, the mean additional annual ozone reduction for the *FULL*^{TROP} and *EXPL*^{LBC} schemes reaches ~3%–8 % and ~1.5%–2.5 %, respectively, with larger percentage values within midlatitudes. The overall reduction in the tropospheric radiative budget for *FULL*^{TROP} compared to *SURR* agrees with previous estimates (Hossaini et al., 2015; Saiz-Lopez et al., 2012; Sherwen et al., 2017).

It is well known that halogen chemistry can affect the oxidation capacity of the troposphere by altering the OH/HO_2 ratio (Saiz-Lopez & von Glasow, 2012). Maximum reductions of ~12% (~15%) for the OH/HO_2 ratio are reached at the cold point tropopause within the tropics (midlatitudes) for the *FULL*^{TROP} scheme (see right panels on Figures 3c and 3d). The relative changes in the OH/HO_2 ratio appear at lower altitudes compared to ΔpO_3, highlighting the non-linear response to temperature of the dominant oxidative bromine mediated channels as described in Saiz-Lopez and Fernandez (2016). For the *FULL*^{TROP} scheme, the reduction of OH/HO_2 is driven by: i) a decrease in the mean abundance of OH of up to 5% (9%) and an increase in HO_2 of up to 8% (11%) within the tropics (midlatitudes), with each offset peaking at different altitudes and expanding well into the lowermost stratosphere (see Figure S3 for further details); and ii) larger denoxification

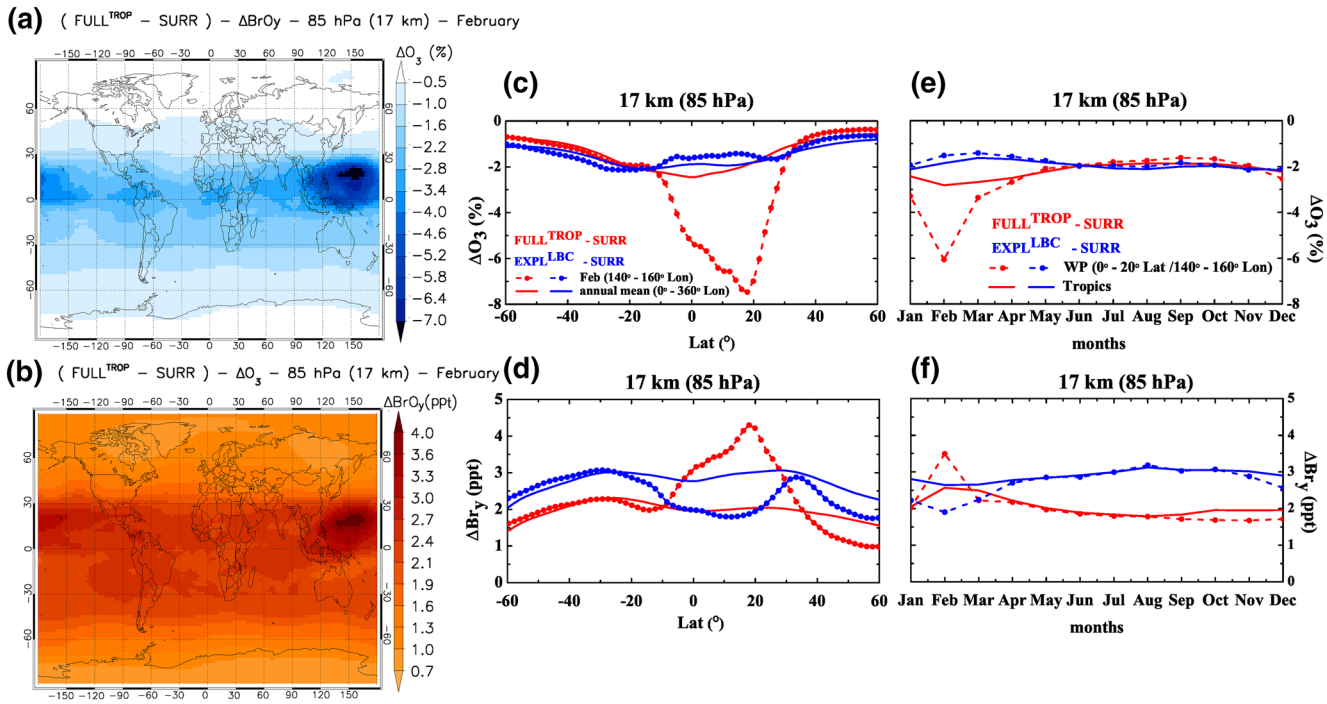

Figure 4. Spatio-temporal variability of ΔpO_3 (top) and ΔBr_y (bottom) at ~17 km (~85 hPa): (a), (b) February mean geographical distribution for the *FULL*^{TROP}-*SURR* schemes. (c), (d) Latitudinal variation for the annual zonal mean (0°W–360°W) and the February monthly mean within the 140°E–160°E band. (e), (f) Seasonal variability of the tropical (20°N–20°S) meridional mean and the Western Pacific (WP) warm pool region (0°N–20°N & 140°E–160°E). Solid lines indicate the tropical/annual mean, while symbol-lines show the February/WP monthly mean.

of the mid to upper troposphere due to the explicit consideration of wet removal of brominated reservoir species such as $BrONO_2$ and $BrNO_2$ (Fernandez et al., 2014). These bromine-driven changes in OH and HO_2 are expected to slow-down the oxidative processing of greenhouse gases (i.e., increasing the CH_4 lifetime) before injection to the stratosphere (Saiz-Lopez & von Glasow, 2012).

Below ~500 hPa, the impact on ozone of the *FULL*^{TROP} scheme within the tropics is at least twice that of *EXPL*^{LBC} due to the SSA dehalogenation source (Figure 3c), increasing to more than triple for midlatitudes (Figure 3d). In addition to the SSA dehalogenation source, the larger impacts for *FULL*^{TROP} arise because: (i) the inclusion of minor VSL^{Br} species (such as $CHBr_2Cl$ and CH_2IBr), which possess shorter lifetimes than the major VSL^{Br} species and are consequently converted to Br_y closer to the surface; and (ii) the Ordóñez et al. (2012) emissions inventory includes proportionally larger emissions within the tropics and coastal areas compared to the constant surface LBCs of the explicit setup (Figure S1). Finally, the pronounced tropospheric ozone differences observed for *FULL*^{TROP} in the southern high-latitudes arise mostly because the SSA dehalogenation source has a strong seasonality that maximizes over the southern ocean (Fernandez et al., 2019).

3.3. Geographical and Seasonal Variations

Figure 4 shows that within the Western Pacific (WP) warm pool region (140°E–160°E; 0°N–20°N), the *FULL*^{TROP} setup results in larger enhancements of Br_y and stronger reductions of O_3 compared to the *EXPL*^{LBC} scheme. These differences are due to strong convective uplift in the WP that can directly transport enhanced SSA-derived Br_y from the marine boundary layer to the upper troposphere. The additional ozone depletion during February reaches ~8% at the tropical tropopause, extending between ~200 and ~50 hPa and beyond the 20°N parallel, well into the lower stratosphere (Figures 4c and 4d). In contrast, the reduced photochemical decomposition of VSL^{Br} due to the more rapid vertical lifting during February results in a smaller release of Br_y and lower impact on ozone for the *EXPL*^{LBC} scheme, compared to the annual mean. These results are in agreement with previous studies that highlighted the large spatial

and temporal variability in the vertical uplift of oceanic VSL^{Br} species within strong convective regions (Butler et al., 2018; Tegtmeier et al., 2020). However, those studies did not consider the additional contribution arising from the SSA dehalogenation source (Fernandez et al., 2014) and consequently underestimated the additional tropospheric Br_y enhancement that can impact the local and seasonal bromine burden. Here, only the $FULL^{TROP}$ setup results in upper tropospheric mixing ratios compatible with the observed BrO and inferred Br_y profiles in the WP during February (BrO^{12km} (daytime) = 0.4 ± 0.2 ppt; Br_y^{12km} = 1.9 ± 0.7 ppt; see Figure 6 in Koenig et al., 2017). The different ΔpO_3 profiles between the $FULL^{TROP}$ and $EXPL^{LBC}$ schemes (Figure 4c) indicate that most of the impact on ozone within strong convective regions occurs when SSA dehalogenation is considered. The larger VSL^{Br} impacts within the tropical WP are also related to the cold temperatures in this region that enhance the bromine-driven ozone destruction (Saiz-Lopez & Fernandez, 2016), as well as to the occurrence of localized high-ozone low-water vapor structures that can alter the efficiency of all oxidizing families within the upper troposphere (Anderson et al., 2016; Randel et al., 2016).

The seasonal variation of ΔpO_3 (%) and ΔBr_y between $FULL^{TROP}$ and $EXPL^{LBC}$ for the tropical mean and within the WP region is shown in Figures 4e and 4f (see also Figures S4 and S5). Modeled ΔBr_y for the tropical mean exhibits a clear seasonal maximum during late boreal winter and early spring for the $FULL^{TROP}$ setup, while for the $EXPL^{LBC}$ scheme the Br_y enhancement occurs during boreal summer and fall. This effect is related to the seasonal variation of the tropical tropopause height within specific regions, which facilitates the vertical mixing of aged (i.e., Br_y and O_3 rich) stratospheric air with young (i.e., VSL^{Br} rich) upper tropospheric air-parcels. Given the different washout treatments between $FULL^{TROP}$ and $EXPL^{LBC}$, the latter shows a stratospheric-like seasonality, while the former exhibits a behavior that follows Br_y in the free troposphere. Further experimental and modeling research is required to determine the complex chemical processes occurring within SSA- and cloud-rich regions (such as heterogeneous recycling, in-cloud washout and ice-scavenging) and quantify the impact of these localized chemical enhancements on ozone trends in the lowermost stratosphere (Ball et al., 2018, 2019; Chipperfield et al., 2018).

4. Concluding Remarks

Even though the contribution from VSL^{Br} to the total stratospheric Br_y burden has been recognized since the beginning of the century, most CCMs still consider a simplified treatment that does not account for the large spatial, vertical, and temporal variabilities related to tropospheric bromine photochemistry. This work presents a complete inter-comparison of the most common treatments considered by CCMs to represent VSL^{Br} sources and chemistry; namely the surrogate (*SURR*), explicit ($EXPL^{LBC}$), and full tropospheric ($FULL^{TROP}$) approaches. Our results indicate that even if a realistic Br_y burden is achieved with all schemes for the upper stratosphere, an explicit treatment of VSL^{Br} species (based on either LBCs or oceanic emissions) introduces additional photochemical destruction of ozone that maximizes in the tropical and midlatitude lowermost stratosphere. Most notably, the relative partitioning between SGI and PGI differs between the $EXPL^{LBC}$ and $FULL^{TROP}$ approaches, mainly due to the different treatment in the tropospheric representation of SSA Br_y sources, heterogeneous recycling and washout. The $FULL^{TROP}$ approach results in larger impacts on ozone within strong convective regions, because only this photochemistry treatment allows tropospheric air masses with enhanced Br_y to be directly transported across the tropopause.

The $FULL^{TROP}$ treatment also influences the oxidative capacity of the global troposphere, reducing the OH/HO_2 ratio and increasing the partitioning between reactive and reservoir brominated species. These strongly coupled, spatially variable and temperature-dependent interactions, which here are described for close to present day conditions, are expected to also depend on the past and future trends of the dominant natural and anthropogenic sources of tropospheric oxidants. Given the negligible additional computational cost and chemical complexity, we encourage all CCMs oriented to projecting the coupled evolution of stratospheric ozone within a changing climate (i.e., considering tropospheric-to-stratospheric exchange) to include a complete tropospheric representation of VSL^{Br} sources and chemistry.

Data Availability Statement

Data supporting this work can be obtained from Mendeley Datasets ("2020_Surrogate_Explicit_Full", http://dx.doi.org/10.17632/xnx7p847p4.1).

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