

Revising the Ozone Depletion Potentials Metric for Short-Lived Chemicals Such as CF₃I and CH₃IJun Zhang¹ , Donald J. Wuebbles¹ , Douglas E. Kinnison² , and Alfonso Saiz-Lopez³ ¹Department of Atmospheric Science, University of Illinois at Urbana-Champaign, Champaign, IL, USA, ²Atmospheric Chemistry Observations and Modeling Laboratory, National Center for Atmospheric Research, Boulder, CO, USA,³Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rocasolano, CSIC, Madrid, Spain

Key Points:

- Slightly higher Ozone Depletion Potentials for CF₃I and CH₃I are found relative to prior studies because of additional iodine chemistry
- Ozone destruction from CF₃I and CH₃I occurs mostly in the lower troposphere near emissions sources, with very little in the stratosphere
- New SODP metric would be useful along with traditional ODPs to clarify effects of VSLs on stratospheric ozone in policy considerations

Supporting Information:

- Supporting Information S1

Correspondence to:

D. J. Wuebbles,
wuebbles@illinois.edu

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Abstract Ozone depletion potentials (ODPs) are an important metric in national and international policy for evaluating the relative importance of different gases to affecting stratospheric ozone. In evaluating the ODPs of iodotrifluoromethane (CF₃I) and methyl iodide (CH₃I) using the recently updated understanding of atmospheric iodine chemistry, only minor ozone loss would be expected to occur in the stratosphere from the very short-lived (~6 days) CF₃I, with slightly larger destruction of stratospheric ozone from CH₃I (~12 days). In addition, most of the ozone destruction would likely occur in the lower troposphere over continental surfaces, reducing anthropogenic ozone pollution. The traditional ODP concept uses total column ozone change, but this is not an accurate representation of potential future use of very short-lived substances (VSLs) on the abundance of stratospheric ozone. A new metric, Stratospheric ODP (or SODP), is defined that only accounts for stratospheric ozone loss, providing a useful additional tool for policy considerations of VSLs on stratospheric ozone.

Plain Language Summary CF₃I and CH₃I are two very short-lived substances (VSLs) with potential commercial applications. This study updates their potential impact on atmospheric ozone based on recent advances in the understanding of atmospheric iodine chemistry. It also reconsiders the concept of ozone depletion potentials (ODPs) for such short-lived chemicals. Analyses of potential effects of ozone for some of these chemicals show very small effects on the total ozone column and almost all ozone loss occurring in the lower troposphere, where these VSLs would essentially reduce the overall human-produced ozone pollution. A new metric is introduced to help clarify the effects of these very short-lived chemicals on the global atmosphere in policy considerations.

1. Introduction

Iodotrifluoromethane (CF₃I) is considered to be a promising candidate for commercial applications, including as a fire-fighting agent and as an air conditioning and refrigeration agent. For the latter application, CF₃I would be a replacement for hydrofluorocarbons (HFCs) like 1,1,1,2 tetrafluoroethane (HFC-134a), difluoromethane (HFC-32), and pentafluoroethane (HFC-125), which are of concern environmentally because of their potential effects on climate—these compounds have long atmospheric lifetimes (14, 5.4, and 30 years, respectively) and correspondingly large Global Warming Potentials (GWP), with GWP values of 1,360, 705, and 3,450 for a 100-year time horizon, respectively (WMO, 2014, 2018). In contrast, CF₃I is a very short-lived substance (VSL). It photolyzes rapidly and the carbon-iodine bond in CF₃I is easily broken. As a result, CF₃I has a lifetime of only a few days, so it should have little radiative effect on climate. However, once released into the atmosphere, iodine atoms from CF₃I can react catalytically to destroy ozone, potentially adding to stratospheric ozone depletion if the iodine gets to the stratosphere (e.g., Solomon et al., 1994).

CH₃I could have potential human-related uses, including applications as a fire-extinguishing agent and as an insecticidal fumigant. Currently, ocean emissions of methyl iodide (CH₃I) are the primary natural source of global organic iodine in the atmosphere, with a global flux of 0.224 Tg yr⁻¹, accounting for 85% of the total CH₃I emissions. Other emission sources include rice paddies, biomass burning, wood fuel, and wetlands, with a flux of 0.016 Tg yr⁻¹ (Bell et al., 2002; Lee-Taylor & Redeker, 2005). CH₃I is also short-lived, with an atmospheric lifetime of 12–15 days. The removal of CH₃I is primarily through photolysis, with

secondary loss through reactions with the hydroxyl radical (OH). This dissociation quickly leads to reactive forms of atmospheric iodine which initiate catalytic ozone depletion reactions.

The concept of ozone depletion potential (ODP) is a metric developed originally as a single-value index to measure the potential impact of a chemical on stratospheric ozone. This concept is used extensively in policy, including the Montreal Protocol and the U.S. Clean Air Act. The ODP of a gas is defined as the integrated change in globally averaged total column ozone per unit mass emission of the gas, relative to the change in total column ozone per unit mass emission of CFC-11 (CFCl₃) (Solomon et al., 1992; WMO, 1995, 2018; Wuebbles, 1981; Wuebbles, 1983).

The ODP for CF₃I has been determined previously for different assumed emission locations (Solomon et al., 1994; Youn et al., 2010). Youn et al. (2010) (thereafter Y2010) took those analyses one step further, and evaluated the ODPs of both CF₃I and CH₃I with various emission locations using a three-dimensional model with tropospheric and stratospheric chemistry included. As noted by Y2010, the location of emissions matters for short-lived chemicals like CF₃I and CH₃I; the resulting ODP depends on the location of its emissions into the atmosphere. They showed that the derived ODP for CF₃I from a tropical perturbation is twice as large as the derived ODP from the perturbation in midlatitudes. Since those earlier studies, the understanding of atmospheric iodine chemistry has evolved greatly. Here, we reevaluate the ODPs of CF₃I and CH₃I using the up-to-date representation of iodine chemistry (Saiz-Lopez et al., 2014; Saiz-Lopez et al., 2015).

The original ODP concept was developed for long-lived gases that would only affect stratospheric ozone, but it has also been used for short-lived gases, including VSLs with lifetimes shorter than 6 months, many of which have lifetimes of a few weeks or less (Bridgeman et al., 2000; Olsen et al., 2000). It was also recognized (Olsen et al., 2000; Wuebbles et al., 2001) that the ODP concept needed to be modified to account for where and when emissions occur for VSLs. Now, in revisiting the ODPs for CF₃I and CH₃I using the well-established Community Atmospheric Model with chemistry (CAM-Chem version 4), this paper demonstrates that an additional metric could be useful for short-lived chemicals to help the ODP concept satisfy its primary requirement of protecting stratospheric ozone, while allowing for the reasonable use of chemicals that have little impact on the stratosphere, or more generally, on the atmosphere.

2. Model and Experiments

This study uses the global three-dimensional CAM4-Chem chemistry-climate model within the Community Earth System Model framework (Community Earth System Model) (Lamarque et al., 2012; Tilmes et al., 2016). This model incorporates a state-of-the-art treatment of atmospheric chemistry, including halogen chemistry, for the troposphere through the upper stratosphere. Previous studies have evaluated the performance of CAM4-Chem on reproducing the atmospheric ozone (e.g., Tilmes et al., 2015, 2016; Young et al., 2013). As shown in Tilmes et al. (2016), the model can reproduce observed tropospheric ozone within 25% for most of the regions over the globe. In addition, the good model representation of ozone precursors such as carbon monoxide, hydrocarbons, and nitrogen dioxides from CAM4-Chem also indicates that the model is capable of simulating the formation of tropospheric ozone. The current setup includes an organic and inorganic halogen photochemistry mechanism for chlorine, bromine, and iodine halogenated species, that considers both natural and anthropogenic sources, heterogeneous recycling, higher order iodine oxides chemistry, and dry and wet deposition (Fernandez et al., 2014; Ordóñez et al., 2012; Saiz-Lopez et al., 2014, 2015). This iodine chemistry is a significant update from previous studies of the ODPs for CF₃I and CH₃I (Li et al., 2006; Youn et al., 2010); the new reactions especially add to the understanding of the formation, photochemistry, and thermal decomposition of higher iodine oxides (I_xO_y), and heterogeneous recycling processes of sea salt aerosols and ice crystals.

In this study, the model setup used for all simulations had a horizontal resolution of 0.94° (latitude) × 1.25° (longitude) with 56 hybrid vertical levels (22 levels above 100 hPa) (Text S1 in the supporting information). The model includes 216 species, associated with 660 chemical reactions. The model simulations include organic halogen sources from the photochemical breakdown of five very short-lived bromocarbons (CHBr₃, CH₂Br₂, CH₂BrCl, CHBrCl₂, CHBr₂Cl) and four iodocarbons (CH₃I, CH₂I₂, CH₂I₂, CH₂I₂), which are naturally emitted from the ocean to the atmosphere, following production by phytoplankton

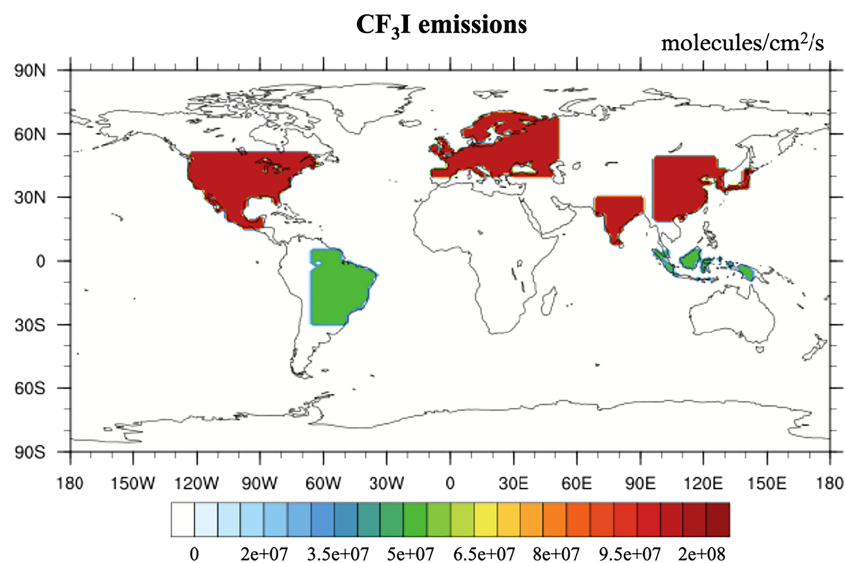


Figure 1. Land-based surface emission fluxes of CF_3I distributed over major emission countries in the unit of molecules $\text{cm}^{-2} \text{s}^{-1}$. These postulated emissions are inputs to model the CF_3I perturbation run (CH_3I surface emission has the same distribution, but with the flux scaled down based on its relative global lifetime compared to CF_3I).

and photochemical processes occurring at the ocean surface (Ordóñez et al., 2012). In addition, inorganic iodine oceanic sources of HOI and I_2 ($\sim 1.9 \text{ Tg(I) yr}^{-1}$) have been included in the lowest model layer based on the oxidation of aqueous iodide by atmospheric ozone deposited on the ocean surface (Carpenter et al., 2013; MacDonald et al., 2014; Prados-Roman et al., 2015). As an anthropogenic iodine source, CF_3I is likely to be used primarily at northern midlatitudes, with the emissions at the surface assumed to be concentrated evenly over major populated regions (United States, India, Europe, East China, Japan, Korean, Brazil, and Indonesia) (Biol, 2018). Among these regions, the United States, India, East Asia, and Europe are assumed to have greater emissions compared to Brazil and Indonesia, hence two emission levels are considered in this study.

The global flux of CF_3I used in the model for the ODP studies is $\sim 0.7 \text{ Tg yr}^{-1}$. This emission rate is used in our study toward getting statistically meaningful perturbation, roughly a 1% total column ozone change. This emission magnitude is much higher than what is realistically likely and also much greater than the current global anthropogenic production of iodine, $\sim 0.031 \text{ Tg}$ (U.S. Geological Survey, 2018). The assumed human emission is comparable to the current natural organic iodine emissions of about 0.65 Tg yr^{-1} (Bell et al., 2002; Ordóñez et al., 2012). The perturbed flux for determining the ODP of anthropogenic CH_3I is assumed to have the same distribution as used for CF_3I , but with a smaller total emission flux of 0.2 Tg yr^{-1} . We have done two sets of studies both for CF_3I and CH_3I based on different emission scenarios. The first scenario (Scenario 1) is focused on the most likely case where emissions occur in select populated regions, as shown in Figure 1. For Scenario 2, emissions are evenly distributed on land between 30°N and 60°N (see Figure S1), the scenario used in Y2010. This scenario was evaluated for comparison with that earlier study. The emission inventory for other species (e.g., CH_4 , CO , SO_2 , NO_x , NMVOC, NH_3 , PM10, PM2.5, BC, and OC) are from the combination of second phase of the Task Force on Hemispheric Transport of Air Pollutants (HTAP2), Fire INventory from NCAR (FINN) version 1.5 and Chemistry-Climate Model Initiative data. Deep and shallow convection schemes in the model follow Zhang and McFarlane (1995) and Hack et al. (1993), respectively, with the recent modifications and adjustments.

A set of simulations was conducted to study the ODPs for anthropogenic CF_3I and CH_3I : one reference run with all the natural halogen sources and then steady-state perturbation model runs for CF_3I , CH_3I , and CFC-11 relative to a steady-state reference atmosphere. A CF_3I (CH_3I) simulation is performed by adding surface CF_3I (CH_3I) emission based on the reference run with the total emissions chosen to give a small ($<1\%$) change in total column ozone. A CFC-11 perturbed atmosphere is obtained from the CFC-11 perturbation run by increasing 80 pptv of the surface mixing ratio of CFC-11 from its value in the reference

Table 1
Lifetimes and ODPs Calculated From This Study Compared to Y2010

Species and model scenario	Global emission rate (Tg (SG) /yr ^a)	Derived global lifetime (days)	Global ozone change per unit mass emission (% yr Tg)	Derived ODP	Stratospheric ozone change per unit mass emission (% yr Tg)	Ozone depletion (%)	Derived stratospheric ODP (SODP)
CF ₃ I SC1	0.71	6.16	−0.358	0.019	0 ^{**}	0 ^b strat	0 ^b
CF ₃ I SC2	1.00	6.35	−0.369	0.019	0 ^b	0 ^b strat	0 ^b
CF ₃ I SC2 (Y2010)	0.74	5.03	−0.126	0.008	-	-	-
CH ₃ I SC1	0.2	11.77	−0.701	0.036	−0.021	3.0 strat 97 trop	0.001
CH ₃ I SC2	0.54	15.48	−0.653	0.034	−0.085	13.1 strat 86.9 trop	0.004
CH ₃ I SC2 (Y2010)	0.54	13.59	−0.255	0.017	-	-	-

Note. Scenario 1 (SC1) is focused on emission in select populated regions where the gases are mostly likely to be used, while for Scenario 2 (SC2), the emissions are evenly distributed on land between 30°N to 60°N following the approach used in Y2010.

^aThe unit of emission rate used in the study is in Tg of source gas per year (Tg (SG) /yr). ^bThe ozone change in the stratosphere from model is not 0 for CF₃I SC1 and SC2—The simulation results in an extremely small positive change due to model noise.

atmosphere run (the corresponding emissions flux of 0.04 Tg yr^{−1} for CFC-11 is then derived). All of the model runs have been performed in a specified dynamics mode with year 2014 meteorological fields obtained from the Modern-Era Retrospective Analysis for Research and Applications, Version 2 (MERRA-2) reanalysis produced by the GEOS of the NASA Global Modeling and Assimilation Office (Gelaro et al., 2017). All the simulations were run to steady state and the last year outputs were used in the analysis.

3. Results and Discussion

3.1. ODP for CF₃I and CH₃I

The lifetimes and ODPs derived for the CF₃I and CH₃I perturbation scenarios are given in Table 1, along with the earlier Y2010 results. The ODP analyses use the traditional approach of evaluating the ozone change for total column ozone. In addition, the stratospheric ozone loss and the fraction of ozone loss in the stratosphere versus the troposphere are shown in Table 1. As will be discussed more later, we have also derived ODPs only accounting for the stratospheric ozone loss, as listed in the rightmost column in Table 1. Using the traditional approach, the ODP of CF₃I (CH₃I) is 0.019 (0.034) for Scenario 2, which is still quite small, but higher than the ODP of 0.008 (0.017) derived earlier by Y2010. This larger ODP is primarily due to including the additional reactions in the updated representation of tropospheric iodine chemistry scheme in the CAM4-Chem runs. The iodine chemistry has now included more complete pathways of higher-order iodine oxides I_xO_y (e.g., I₂O₂, I₂O₃, and I₂O₄), accounting for their formation, photochemical and thermal decomposition (Saiz-Lopez et al., 2014), plus other iodine reactions not considered in Y2010. For instance, the photochemistry of I_xO_y species were not considered in earlier studies. A set of reactions included in this study are listed in Table S1.

Note that the heterogeneous processing, thermal decomposition, and photochemistry of the higher iodine oxides is not well-established and may be an important uncertainty in the atmospheric iodine cycling that impacts the transport of reactive iodine to the stratosphere. For the photolysis of OIO, two possible pathways are presented from previous NASA/JPL evaluation (Burkholder et al., 2015)—O₂ + I and O + OI. The I atom produced from the first pathway can be further involved in ozone depletion catalytic cycle and destroy more ozone. If O and OI are produced, many of the key reaction sequences lead to a null cycle for stratospheric ozone. In this study, we treated the products as I and O₂ in order to provide an estimation of the upper limit of ozone depletion in the stratosphere. As better knowledge of the photolysis pathway becomes available, it would be worthwhile to reinvestigate the impacts on the resulting ODPs.

I_xO_y are formed from a recombination of IO and OIO (IO + IO, IO + OIO, OIO + OIO) in the atmosphere, then part of I_xO_y is removed from the gaseous phase via washout or scavenging in water and ice clouds and dry deposition, while the other part of I_xO_y experiences recycling processes back to I, IO, and OIO (Saiz-Lopez et al., 2014). With the inclusion of heterogeneous recycling reactions occurring on the surface

of ice particles (Saiz-Lopez et al., 2014, 2015), the main iodine reservoir species hypoiodous acid (HOI) and iodine nitrate (IONO₂) can go through the reactive ice uptake recycling process on the surface of a halogen-enriched (chloride and bromide) aerosol, regenerating more reactive iodine species. Both advances elongate the period that the reactive iodine from CF₃I and CH₃I stays in the atmosphere and can further be involved in efficient ozone depletion catalytic cycles, resulting in a higher ODP. Based on this analysis, it is clear that evaluation of ODPs for VSLs need to fully consider the representation of tropospheric chemistry. In investigating the spatial distribution of the ozone loss further, we found that, although the calculated ODP is higher in this new study, almost all ozone depletion caused by CF₃I and CH₃I emissions occurs in the troposphere and concentrated to continental regions where emissions occur.

3.2. Ozone Depletion From CF₃I and CH₃I

CF₃I, a very short-lived substance, photolyzes rapidly to form reactive iodine atoms under a sunlit atmosphere and its lifetime is on the order of several hours to days, depending largely on location of the emissions. Due to the efficient ozone-depleting catalytic cycles, if the reactive iodine atom reaches the stratosphere, it can substantially destroy stratospheric ozone. However, the extremely short lifetime of CF₃I greatly limits its transport to the stratosphere when released at the surface, especially within the mid-latitudes. Therefore, the specific locations of the CF₃I emissions have a large impact on the resulting effects on ozone.

The source and product gas injection to the stratosphere from CF₃I and CH₃I emission Scenario 1 are shown in Figure 2, with units of parts per trillion by volume (pptv). The maximum CF₃I (CH₃I) mixing ratio is 6 pptv (2.2 pptv) in the emission region and the intact CF₃I and CH₃I transport to the stratosphere are both extremely small, positive but statistically close to zero (Figures 2a and 2b). Total inorganic iodine is defined as IO_y = I + 2I₂ + IO + OIO + HI + HOI + INO + INO₂ + IONO₂ + IBr + ICl + 2I₂O₂ + 2I₂O₃ + 2I₂O₄. The vertical distribution of IO_y concentration derived for the background atmosphere from natural iodinated compound emissions (Figure S2a) is comparable to that derived by Saiz-Lopez et al. (2015) as shown in their Figure 2b. The amount of IO_y injection into the stratosphere relative to the ground level is 13% of the initial emissions in this study compared with 15% in Saiz-Lopez et al. (2015).

For the perturbation runs, the changes in potential product gas IO_y injection to the stratosphere, relative to the reference background atmosphere run, are around 0.095 and 0.06 pptv, respectively, for CF₃I and CH₃I emissions Scenario 1 (Figure S2b). The IO_y perturbations (pptv) to the stratosphere are concentrated in the emission regions, with mixing of IO_y from both CF₃I and CH₃I emissions occurring from the upper troposphere in the northern extratropics (Figures 2c and 2d). Transport into the stratosphere is limited by the large amount of iodine removed by rainout. Only small amounts of IO_y change are found throughout most of the stratosphere, or in the Southern Hemisphere troposphere, for the levels of emissions assumed in both the CF₃I and CH₃I cases.

The resulting change in the distribution of tropospheric and stratospheric ozone for CF₃I and CH₃I emissions indicates that almost all of the ozone depletion occurs in the troposphere (Figure 3). The iodine effects on Odd Oxygen (O_x = O + O₃) can be categorized into four types of catalytic cycles: IO_x-ClO_x/BrO_x, IO_x-O_x, IO_x-HO_x and IO_x-NO_x (Figure 4). The iodine catalytic cycle with HO_x is found to be the dominant O_x loss cycle (greater than 80% contribution) (Figure 4d). Almost all of the O_x loss happens in the lower troposphere, and is concentrated at midlatitudes over the Northern Hemisphere. The maximum ozone destruction rate occurs at around near the ground level, approximately at 857.5 hPa (Figure 4a).

Figure 5 shows the annual average global geophysical distribution of IO_x loss and ozone loss for Scenario 1 at the maximum depletion level 857.5 hPa. Most of the ozone depletion is found over continental regions, close to where the human-related CF₃I and CH₃I emissions are assumed to occur. This finding is in contrast to the effects of natural iodine emissions where both the emissions and resulting effects on ozone occur primarily in the marine atmosphere. Because of the longer tropospheric lifetime of ozone, the actual ozone loss is spread out more than the IO_x loss rates, indicating a stronger overall hemispheric effect. Ozone loss at the surface indicates a similar pattern as the ozone loss at the 857.5 hPa model layer, and with a smaller magnitude (Figure S3).

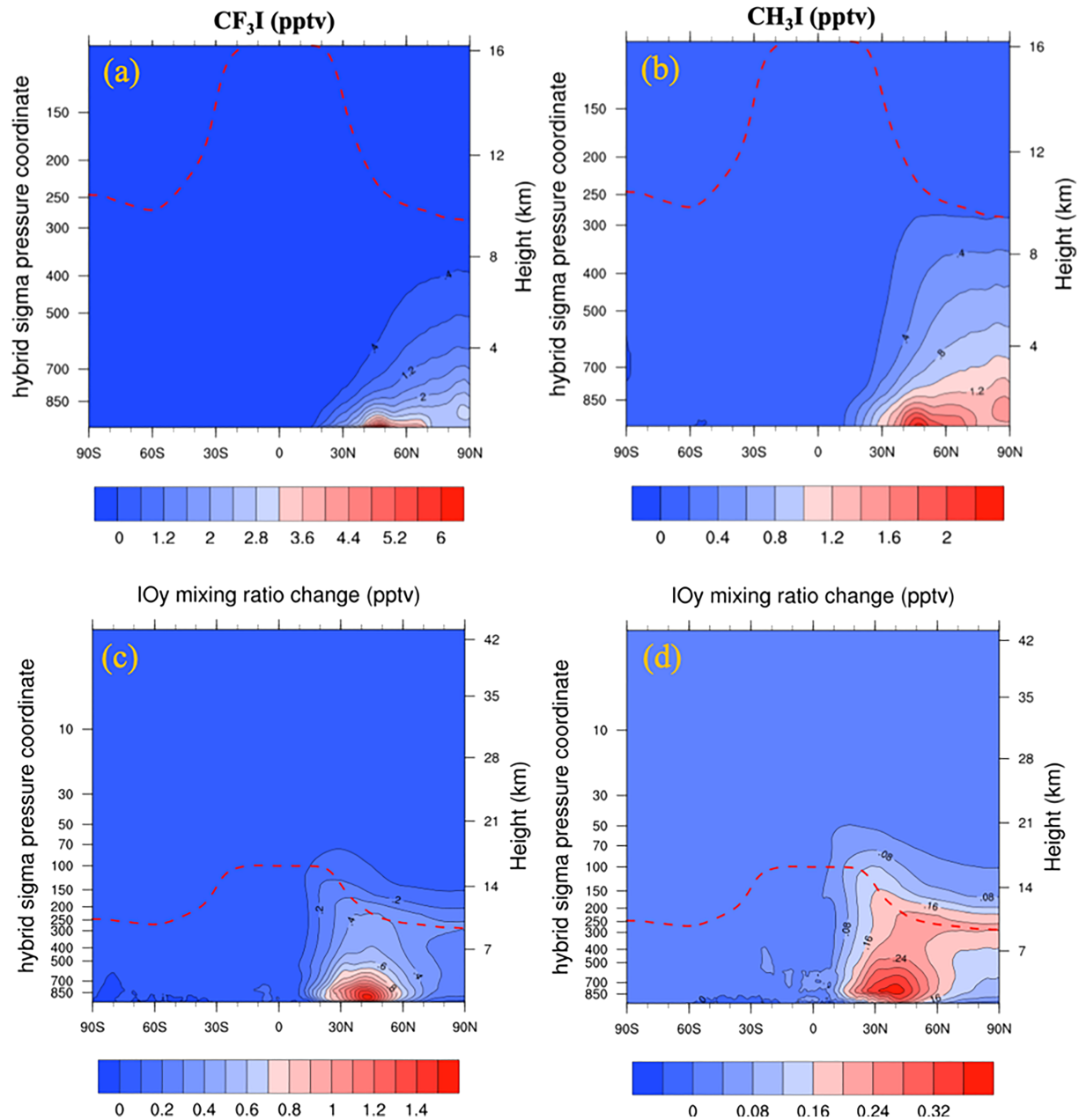


Figure 2. Annual and zonal-average mixing ratio delta changes relative to the reference run in pptv calculated from CF₃I (left) and CH₃I (right) emission scenario 1 for (a) CF₃I; (b) CH₃I; (c) IO_y from CF₃I emission; (d) IO_y from CH₃I emission. Red dashed lines are the tropopause height derived from the World Meteorological Organization (WMO) lapse rate definition.

For the emissions assumed in Scenario 1, the maximum tropospheric column ozone depletion by CF₃I and CH₃I can reach 7% and 5%, respectively, on a regional basis (Figure S4). The ozone losses resulting from CF₃I and CH₃I emission Scenario 1 are mostly constrained to the lower troposphere in the Northern Hemisphere. The ozone loss in the stratosphere is positive, but extremely small, essentially zero statistically, for the assumed CF₃I emissions scenario. For CH₃I, with a somewhat longer lifetime (Table 1), the emissions in Scenario 1 results in 97% of the ozone destruction occurring in the troposphere and 3% in the stratosphere. In general, the ozone loss is largely confined to altitudes near the surface in the lower troposphere. As a result, both the CF₃I and CH₃I emissions can act as an anthropogenic ozone pollution buffer in the lower troposphere over continental regions.

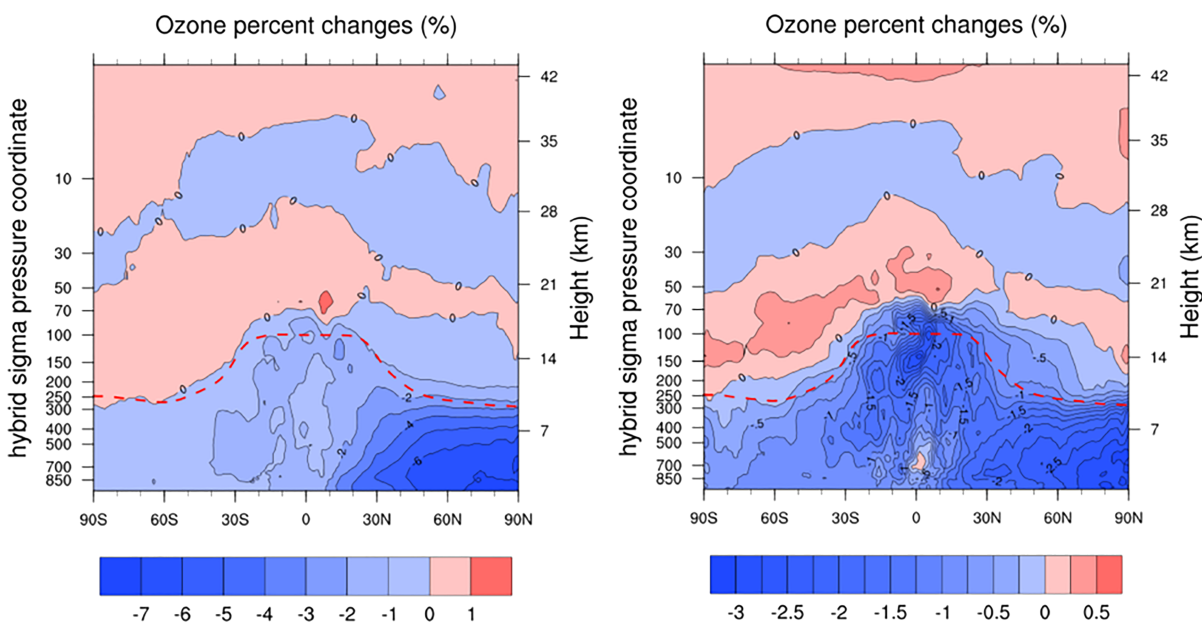


Figure 3. Delta zonal annual average distribution of tropospheric and stratospheric ozone percentage change for (a) CF_3I and (b) CH_3I in emission scenario 1.

4. Implications for the ODP Definition

The ODP concept was initially developed to measure the potential impact of long-lived gases, those with multiyear atmosphere lifetimes, on stratospheric ozone (Wuebbles, 1981, 1983). The motivation for a focus on stratospheric ozone largely occurred because roughly 90% of atmospheric ozone is in the stratosphere, with the rest largely in the troposphere. However, the ODP concept uses the decline in total column ozone because it is the total column decrease that is of concern to protecting humans and the biosphere from increases in ultraviolet radiation. At the same time, it is important to recognize that tropospheric ozone has increased substantially over the last century, largely as the result of emissions from human activities (Cooper et al., 2014; Hough & Derwent, 1990; Shindell et al., 2006).

ODPs for halogenated compounds have continued to be updated in all of the international ozone assessments (World Meteorological Organization, 1995, 1999, 2003, 2007, 2011, 2014) as input to policymakers, including the Montreal Protocol. Those longer-lived gases that have been subject to policy control measures have almost all of their impact on stratospheric ozone. However, the ODPs were evaluated for total column ozone change so that any small amount of ozone loss in the troposphere could also be included. For example, the ozone depletion in the troposphere is accounted for in the total column ozone change when evaluating the effects on ozone from emissions of hydrogenated chlorofluorocarbons, HCFCs, that still have atmospheric lifetimes of a few years or more, much shorter than the lifetimes of the chlorofluorocarbons (CFCs) of original concern.

However, the chemical compounds now being considered for potential use tend to have very short atmospheric lifetimes, lifetimes less than a few months, which greatly reduces their potential impacts on climate and on ozone. These VSLs are not expected to spread globally and their concentrations are not expected to be well-mixed globally like the long-lived gases; as a result, these gases would generally be expected to have less effect on climate and stratospheric ozone. In fact, most of their effects occur in a troposphere that has already been perturbed by other human-related emissions.

For the cases of CF_3I and CH_3I examined here, these VSLs have almost all of their ozone loss in the lower troposphere, not in the stratosphere. In fact, the stratospheric column ozone loss of CF_3I in the study done here was essentially zero (within statistical error), while producing significant changes in tropospheric ozone. A very small nonzero value is found for the relatively longer-lived CH_3I (Table 1). As shown in this study, despite a larger ODP for the total column ozone change than found in earlier studies, the actual effect on stratospheric ozone column for CF_3I and CH_3I is quite small, for reasonable levels of emissions. As a

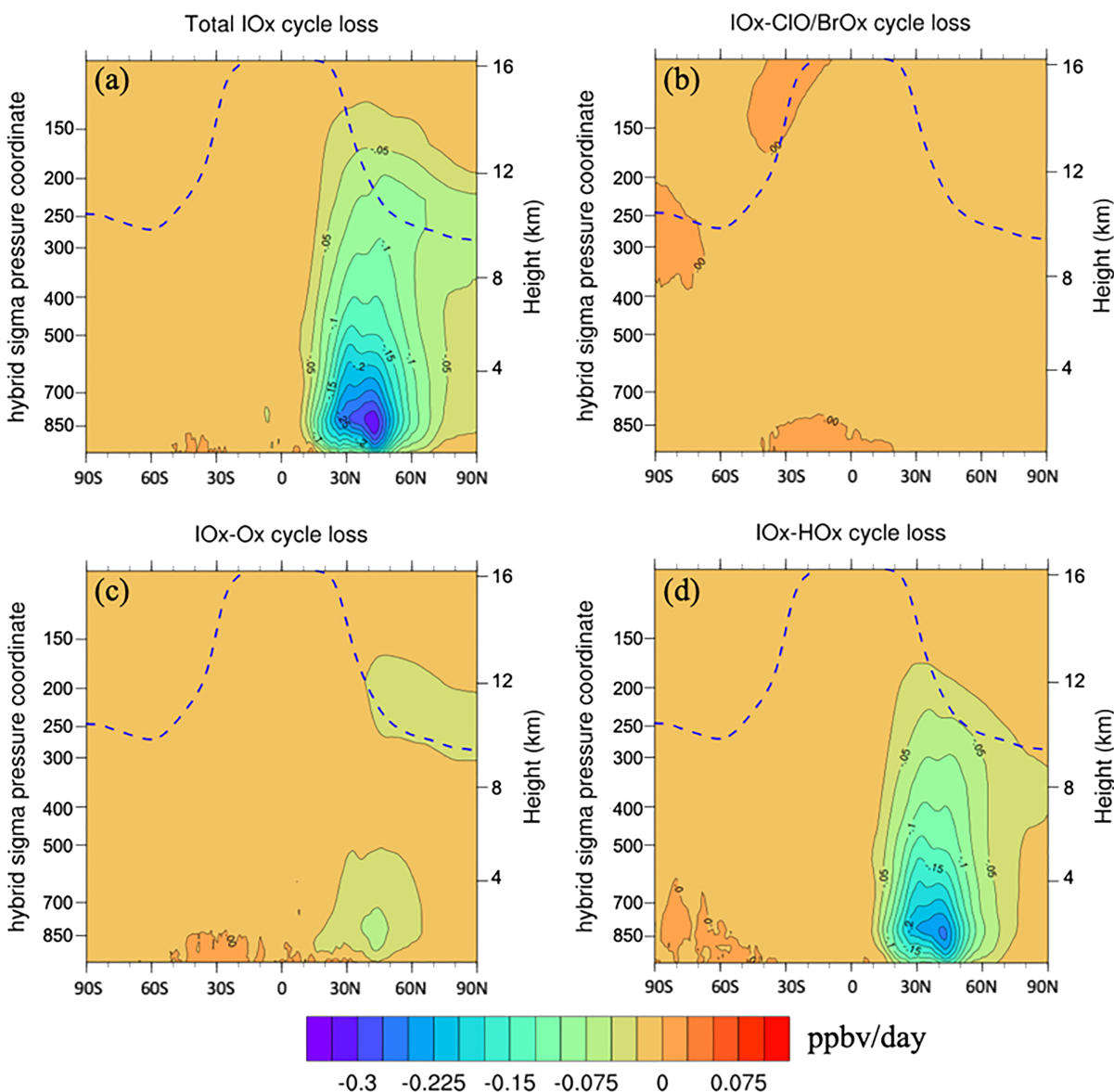


Figure 4. Delta zonal annual average distribution of tropospheric odd oxygen changes from CF_3I emission Scenario 1 for (a) total iodine-driven ox loss (IOx-ox loss + IOx-HOx loss + IOx-NOx loss + IOx-ClOx/BrOx loss); (b) coupled IOx-ClOx/BrOx odd oxygen loss; (c) coupled IOx-ox odd oxygen loss; (d) coupled IOx-HOx odd oxygen loss. Blue dashed lines are the tropopause height. The delta ox change induced by CF_3I (CH_3I) emission is calculated from the difference between the reference run and the experiment CF_3I (CH_3I) run. I and IO are termed collectively as reactive iodine IOx (IOx = I + IO).

result, we suggest that policy considerations for VSLs not only consider the traditional total column values for ODP, but should also account for the ODP due to stratospheric ozone loss only, termed here as Stratospheric ODP (SODP).

SODPs would be determined by evaluating the stratospheric ozone loss for compound “X” due to a given level of emissions (E) relative to the same emissions of CFC-11 (equation 1). In this case, the SODP for CFC-11 would be 1.0 while the SODP for CF_3I would be nearly zero in both emissions scenarios, and the SODP for CH_3I would be 0.001 and 0.004 for Scenario 1 and Scenario 2, respectively.

$$\text{SODP} = \frac{\text{Stratospheric } \Delta O_3(X, E)}{\text{Stratospheric } \Delta O_3(\text{CFC} - 11, E)} \quad (1)$$

The SODP concept can be applied to other gases as well, but will be most important for evaluating the potential effects on atmospheric ozone from VSLs, where they should be considered with and contrasted with

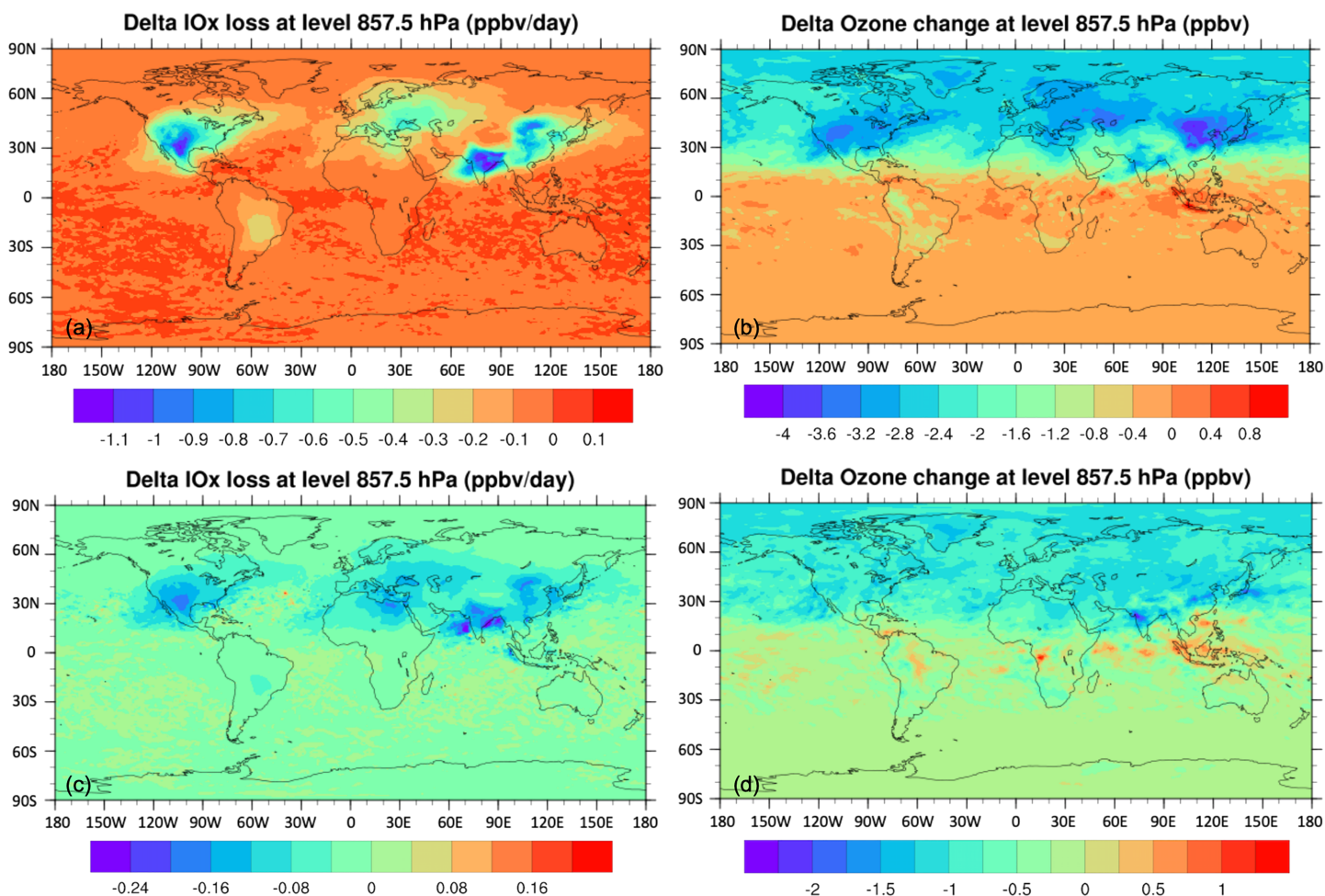


Figure 5. Annual average distribution of (a) IOx odd oxygen loss and (b) delta ozone change at level 857.5 hPa from CF₃I emission scenario 1; (c) and (d) are the same as (a) and (b) but for CH₃I emission Scenario 1.

traditional ODP values. For long-lived species, ODP and SODP values should be nearly the same because almost all of the ozone depletion occurs in the stratosphere. However, for many VSLs, especially those with very short atmospheric lifetimes, ODP and SODP values can be quite different. For a given VSL, the SODP value can be much smaller than the traditional ODP value, even though traditional ODPs for VSLs are often relatively small compared to long-lived compounds they might replace. Our new formulation can be especially relevant in policy considerations (e.g., when policymakers have arbitrarily chosen a certain ODP level as “unacceptable”).

As a further examination of the SODP concept, we examined the most recent published literature for ODPs determined for other VSLs (Table 2) and we also provide our estimate of the resulting fraction of ozone loss in the stratosphere versus the troposphere for some of these studies, for example, those VSLs containing chlorine or bromine that can also affect ozone. However, we are unable to provide estimated SODPs for these studies listed in Table 2 due to the following reasons. Some of the ODPs determined in these studies for VSLs, instead of using a model, were calculated from a simplified semiempirical approach, that may not be applicable to such short-lived gases. Some other studies derived ODPs from modeling studies that only consider stratospheric chemistry (an estimate of the transfer of the gas to the stratosphere), and that did not include the complete treatment of tropospheric processes. As a result, those studies did not actually determine the ozone loss in the troposphere (Brioude et al., 2010; Claxton et al., 2019). The approach used in each study is listed in Table 2. Only a few studies have evaluated ODPs of VSLs using

Table 2
ODPs of VSLs Derived in Past Literature

VSLs	Emission location ^a	Global lifetime (days) ^b	ODP ^c	Ozone depletion ^d (%)	Approach ^e	Reference
trans-1-chloro-3,3,3-trifluoropropylene (t-CHCl = CHCF ₃)	30–60°N	40.4	0.00034	53.1 trop 46.9 strat	Trop + Strat full chemistry	Patten and Wuebbles (2010)
trans-1,2-dichloroethylene (t-CHCl = CHCl)	30–60°N	13.5	0.00024	96.5 trop 3.5 strat	Trop + Strat full chemistry	Patten and Wuebbles (2010)
Trichloroethylene (ClCH=CCl ₂)	30–60°N	13.8	0.00037	>90 troposphere ^f	Trop + Strat full chemistry	Wuebbles et al. (2011)
Perchloroethylene (C ₂ Cl ₄)	30–60°N	111	0.0050	>90 stratosphere ^f	Trop + Strat full chemistry	Wuebbles et al. (2011)
n-propyl bromide (CH ₃ CH ₂ CH ₂ Br)	30–60°N, 60°S–70°N	19.6–24.7	0.0049–0.011	42.5 trop 57.5 strat	Trop + Strat full chemistry	Wuebbles et al. (2011)
2-bromo-3,3,3-trifluoropropene (CH ₂ = CBrCF ₃)	30–60°N	7.0	0.0028	73.3 trop 26.7 strat	Trop + Strat full chemistry	Patten et al. (2011)
CHCl ₃	Eur, TemAs, TemLA, TemNA, TroAs ^g	97–119	0.0143–0.0264	—	Tropospheric trajectory + Stratospheric chemistry	Claxton et al. (2019)
CH ₂ Cl ₂	Eur, TemAs, TemLA, TemNA, TroAs ^g	97–119	0.0097–0.0208	—	Tropospheric trajectory + Stratospheric chemistry	Claxton et al. (2019)
C ₂ H ₄ Cl ₂	Eur, TemAs, TemLA, TemNA, TroAs ^g	41–50	0.0029–0.0119	—	Tropospheric trajectory + Stratospheric chemistry	Claxton et al. (2019)
CH ₃ CH ₂ Br	EU, MLNA, EA, IS ^h	40–66	0.11–0.46	—	Semiempirical approach	Brioude et al. (2010)
CH ₂ = CBrCF ₃	EU, MLNA, EA, IS ^h	3.1–7.1	0.0013–0.044	—	Semiempirical approach	Brioude et al. (2010)
n-C ₃ H ₇ Br	EU, MLNA, EA, IS ^h	11–27	0.015–0.17	—	Semiempirical approach	Brioude et al. (2010)
C ₂ HCl ₃	EU, MLNA, EA, IS ^h	4.5–12	0.0001–0.0041	—	Semiempirical approach	Brioude et al. (2010)
CCl ₃ CHO	EU, MLNA, EA, IS ^h	8.5–24	0.0004–0.0062	—	Semiempirical approach	Brioude et al. (2010)
CHBr ₃	EU, MLNA, EA, IS ^h	33–66	0.33–1.8	—	Semiempirical approach	Brioude et al. (2010)

^aThe emission location used in each study. Multiple emission locations are tested in some studies. ^bGlobal lifetime derived from each study, unit in days. ^cOzone depletion potential derived from each study. Ranges are due to different emission locations. ^dOur estimate of ozone depletion ratio in troposphere versus stratosphere, unit in %. ^eApproaches used in each study to derive ODP. ^fNo value given in the original paper, values listed here are estimated approximately from the figures shown in the original literature. ^gEmissions assumed to occur over temperate North America (TemNA), Europe (Eur), temperate Latin America (TemLA), temperate Asia (TemAs), and tropical Asia (TroAs). ^hEmissions assumed to occur over Europe (EU), midlatitude North America (MLNA), East Asia (EA), and India subcontinent (IS).

three-dimensional models with full tropospheric and stratospheric chemistry (Patten et al., 2011; Patten & Wuebbles, 2010; Wuebbles et al., 2011).

Due to insufficient information to determine the SODP in some studies we examined, we can only estimate the effects on stratospheric ozone versus tropospheric ozone from a few papers. Different emission rates and geographical distributions used in previous studies are listed for those VSLs—in all cases the aim is to assume a small enough emission as to have a statistically significant effect on total column ozone but not so large as to give a nonlinear result. Those VSLs with very short atmospheric lifetimes of less than a month generally show most of the ozone depletion occurring in the troposphere. For example, t-CHCl=CHCl, ClCH=CCl₂, CH₂=CBrCF₃, and t-CHCl=CHCF₃ have around 50% or more ozone loss in the troposphere (Table 2). As a result, their derived ODP would be more than double the SODP value. This difference between ODP and SODP value is particularly distinct for VSLs with lifetimes of less than about 2 weeks, where more than 90% ozone loss occurs for many of these gases in the troposphere such as the case for CF₃I and CH₃I in this study.

The ODP concept was designed primarily to protect stratospheric ozone, but it is not serving that purpose if the derived ozone loss is primarily occurring in the troposphere. One could certainly argue that reducing the ozone in the lower troposphere, often termed bad ozone because of its health impacts on the human

respiratory system, could be considered a positive benefit (Bell et al., 2006). Current levels of tropospheric ozone have been significantly increased by other human activities.

The consideration of the new SODP concept adds additional information to the evaluation of a compound by providing quantitative details to the policymaker about where the ozone loss would occur. If the ODP value and the SODP value are vastly different, then the ozone effect is primarily in the troposphere, a factor worth taking into account in policy considerations.

Finally, there are many uncertainties in evaluating model-derived ODPs for short-lived halogen compounds (e.g., the role of heterogeneous chemistry, convection and transport processes, and magnitude of regional emission inventories). These and other processes would be best evaluated in the context of a multimodel study using the same short-lived halogen emission inventories in future work.

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