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Potential impact of iodinated replacement compounds CF_3I and CH_3I on atmospheric ozone: a three-dimensional modeling study

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Abstract

The concept of Ozone Depletion Potentials (ODPs) is extensively used in policy considerations related to concerns about the effects of various halocarbons and other gases on stratospheric ozone. Many of the recent candidate replacement compounds have atmospheric lifetimes shorter than one year in order to limit their environmental effects, especially on stratospheric ozone. Using a three-dimensional global chemistry-transport model (CTM) of the troposphere and the stratosphere, the purpose of this study is to evaluate the potential effects of several very short-lived iodinated substances, namely iodotrifluoromethane (CF_3I) and methyl iodide (CH_3I), on atmospheric ozone. Like other chemicals with extremely short lifetimes, the stratospheric halogen loading and resulting ozone effects from these compounds are strongly dependent on the location of emissions. For CF_3I, a possible replacement candidate for bromotrifluoromethane (CF_3Br), ODPs derived by the three-dimensional model are 0.008 with chemical lifetime of 5.03 days and 0.016 with a lifetime of 1.13 days for emissions assumed to be evenly distributed over land surfaces at mid-latitudes and the tropics, respectively. While this is the first time the ODPs have been evaluated with a three-dimensional model, these values are in good agreement with those derived previously. The model calculations suggest that tropical convection could deliver a larger portion of the gas and their breakdown products to the upper troposphere and lower stratosphere if emission source is located in the tropics. The resulting ODP for CH_3I, emitted from mid-latitudes, is 0.017 with lifetime of 13.59 days. The validity of our model iodine chemistry to evaluate ODPs of the iodine species is guaranteed with good qualitative agreement between the model derived distribution of background CH_3I, based on global source emission fluxes from previous studies, and available observations especially in vertical profiles.

1 Introduction

A number of analyses indicate that human-related emissions of chlorine-containing and bromine-containing halocarbons, such as chlorofluorocarbons (CFCs), carbon tetrachloride (CCl_4), methyl chloroform (CH_3CCl_3) and bromochlorofluorocarbons (Halons), have been largely responsible for the observed decrease in stratospheric ozone concentrations over recent decades (WMO, 2007). Those ozone-depleting substances (ODSs) are primarily comprised of the halocarbons that have very long lifetimes in the atmosphere. Without strong policy actions, these human produced ODSs would have continued to have a significant impact on future levels of stratospheric ozone. Thus, it is not surprising that the development of our understanding of their effects on ozone led to international regulations of the ODSs under the landmark Montreal Protocol in 1987, and the amendments and adjustment to the Protocol that followed to further strengthen the Protocol (Velders et al., 2007). Because of the Protocol, a number of replacement compounds have arisen to replace the ODSs being controlled.

The concept of Ozone Depletion Potentials (ODPs) (Wuebbles, 1981, 1983) arose as a means of determining the relative ability of a chemical to destroy stratospheric ozone. ODPs are an integral part of national and international considerations on ozone-protection policy, including the Montreal Protocol and its Amendments and the US Clean Air Act. ODPs provide an important and relatively straightforward way of analyzing the potential for a new chemical to affect ozone relative to the CFCs, Halons, and other replacement compounds. ODPs are currently determined by two different means: calculations from chemistry-transport models (CTMs) of the global atmosphere (e.g., WMO, 1995, 1999, 2003, 2007), and calculations using a semi-empirical approach (Solomon et al., 1992; WMO, 1999). Traditionally, zonally averaged two-dimensional (2-D) CTMs have been the accepted tools for calculating the ozone response in the stratosphere. The past evaluations of ODP were conducted for chemicals with atmospheric lifetime sufficiently long (more than approximately one year). These long-lived gases are well mixed throughout the troposphere after surface release and large portion of surface emissions can reach the stratosphere.

However, many of the compounds being considered either for new applications or as replacements for substances controlled under the Montreal Protocol are now designed to be very or even extremely short-lived, on the order of days to a few months, so as to reduce the impacts on ozone and climate. Many of these very short-lived (VSL) compounds still contain halogens including chlorine, bromine and iodine. The VSL replacement gases still can be vertically transported into the lower stratosphere by intense convection in the tropical troposphere, which is relevant to possible effects on ozone from these compounds. Thus the ODP of a VSL species depends upon its distribution in the atmosphere and the location of its source (Wuebbles and Ko, 1999; Wuebbles et al., 2001; Ko and Poulet, 2003). Unfortunately, the determination of ODPs for these gases is not straightforward because their short atmospheric lifetimes leave them poorly mixed in the troposphere (Wuebbles and Ko, 1999; Wuebbles et al., 2001; Ko and Poulet, 2003; Butler et al., 2007). The traditional 2-D model analysis of ODPs also is not sufficiently accurate for calculating the integrated amount of the halogenated VSL source and reaction product gases in the troposphere that enter the stratosphere (Wuebbles et al., 2001).

Three-dimensional (3-D) CTMs fully representing the complete troposphere and stratosphere are necessary for evaluating the halogen loading and ozone depletion in the stratosphere for VSL species. Thus the definition of ODPs has been revised for VSL compounds (Wuebbles et al., 2001; WMO, 2003). The ODP definition for the VSL compounds thus now accounts for the variation that can occur in the ODP as a function of where and when the compound is used and emitted. The most important factor in evaluating the ODP of VLS compounds is shown to be geographical distribution, or latitude, of the surface emissions because gases emitted at higher latitudes take longer to reach the stratosphere than gases emitted in the tropics (Bridgeman et al., 2000; Olsen et al., 2000; Wuebbles et al., 2001). Seasonal variations in the emissions can also be important if that is a relevant criteria in the atmospheric emissions of the compound.

The only VSL compound currently evaluated and published using 3-D models of the chemistry and physics of the troposphere and stratosphere is n-propyl bromide (nPB, 1-C_3H_7Br); at this time, only limited studies and a range of estimated ODPs are available for it (Wuebbles et al., 2001; WMO, 2003, 2007). The past studies of the ODPs for nPB have been only partially based on 3-D model results (see Ko and Poulet (2003) for a more complete summary). 3-D CTMs, which include a much more comprehensive treatment of transport than the zonally-averaged 2-D models, are now much more preferable for calculations of ODPs both for both the longer-lived gases and for the very short-lived candidate replacement compounds. These models cannot only determine the amount of the substance reaching the stratosphere directly, without the simplifying assumptions of the 2-D models, but can also more directly follow the processes affecting the reaction products. Studies suggest that the vast majority of chlorine or bromine reaching the stratosphere from VSL substances is transported there in reaction products (Wuebbles et al., 2001; WMO, 2003, 2007).

Iodotrifluoromethane (CF_3I) is a gaseous fire suppression flooding agent for in-flight aircraft and electronic equipment fires and a candidate replacement for bromotrifluoromethane (Halon-1301, CF_3Br). Methyl iodide (CH_3I), a potential replacement fumigant for methyl bromide (CH_3Br), has been of interest as a natural source of atmospheric iodine that is primarily emitted from the oceans and as a potentially useful tracer of marine convection and the subsequent role of iodine in atmospheric photochemistry (Bell et al., 2002; Cohan et al., 2003; Vogt et al., 1999). Since the C-I bond is easily cleaved, CF_3I can be rapidly photo-dissociated even at low UV intensity and visible light under daylight conditions in the planetary boundary layer or the troposphere. CH_3I also readily photolyzes under day light conditions as well as reacting with the hydroxyl radical (OH). For both species, the initial reaction results rapidly in the availability of atmospheric iodine for chemical reactions with ozone and other gases. Although current atmospheric concentrations of iodine-containing gases are very small, CF_3I and CH_3I are both a potentially significant source of atmospheric iodine despite being very short-lived and are of interest in the upper troposphere and lower stratosphere as a source of iodine radicals for ozone destruction (WMO, 2007). Ozone destruction in the lower stratosphere due to catalytic cycles involving iodine was not well understood, but recent laboratory studies have improved the understanding of atmospheric chemical processes of iodine species including their photochemistry (WMO, 2007; Li et al., 2006; Bösch et al., 2003).

As the next stage for further analysis of the compounds on ozone beyond the previous studies using 2-D models (Li et al., 2006; Solomon et al., 1994), ODPs of the two iodinated VSL replacement compounds CF_3I and CH_3I are evaluated using the National Center for Atmospheric Research (NCAR) Model for OZone And Related Tracers version 3 (MOZART-3) 3-D chemistry-transport model (we also update the ODP using the latest version of the University of Illinois at Urbana-Champaign (UIUC) 2-D chemical-radiative-transport (CRT) model). A through understanding of the potential effects of the iodine compounds on stratospheric ozone builds upon the previous two-dimensional studies (Li et al., 2006). Using the available analyses of global source emissions for CH_3I (Lee-Taylor and Redeker, 2005; Bell et al., 2002), background CH_3I concentrations in the atmosphere are also evaluated and compared with observational data towards determining the capabilities of 3-D models towards accounting for CH_3I chemistry.

This paper is organized as follows. In Sect. 2, the methodologies to obtain ODPs for very short-lived substances (VSLS) are described and discussed. A brief description of models used for model-derived ODPs is given in Sect. 3 and simulated CH_3I concentrations are discussed and compared with observational datasets in Sect. 4. Results of ODPs are presented in Sect. 5. Discussion and conclusions of the findings are in Sect. 6.

2 Methodology

The concept of ODPs provides a relative cumulative measure of the expected effects, on stratospheric ozone, of the emissions of a gas relative to one of the gases of most concern to ozone change, namely CFC-11 ($CFCl_3$) (Wuebbles et al., 1981, 1983; WMO, 1995, 1999, 2003, 2007). The ODP of a gas is defined as the integrated change in total ozone per unit mass emission of the gas, relative to the change in total ozone per unit mass emission of CFC-11. As a relative measure, ODPs are subject to fewer uncertainties than estimates of the absolute percentage of ozone depletion caused by different gases. ODPs provide an important and relatively straightforward way of analyzing the potential for a new chemical to affect ozone relative to CFCs, Halons, and other replacement compounds. However, a chemical compound with extremely short lifetime, on the order of several to tens of days, is not expected to be well mixed in the atmosphere and thus has ODPs that should be dependent on location of the emissions (Wuebbles and Ko, 1999; Wuebbles et al., 2001; Ko and Poulet, 2003).

The ODP of an ozone-destroying species χ is defined by:

$$\mathrm{ODP}_{\chi} = \frac{\Delta \mathrm{O}_3(\chi)}{\phi(\chi)} \Bigg/ \frac{\Delta \mathrm{O}_3(\text{CFC-11})}{\phi(\text{CFC-11})} \tag{1}$$

where the percent change in O_3 burden ($\Delta O_3(\chi)$) for a surface emission of the compound χ is divided by the same factors for CFC-11. The flux of the compound χ introduced into the atmospheric boundary layer is represented by $\phi(\chi)$, and the CFC-11 flux in the perturbation run minus that in the reference run is represented by ϕ(CFC-11).

Therefore, the derivation of the ODP for a given compound for assumed emissions at given locations and/or seasons requires two steady-state perturbation model runs with the CTM, for an assumed flux of the gases χ and CFC-11 relative to a steady-state reference atmosphere. A CFC-11 perturbed atmosphere is obtained from the CFC-11 perturbation run by increasing the surface mixing ratio of CFC-11 from its value in the reference atmosphere run. When the reference and CFC-11 perturbed steady-state atmospheres are produced, the atmospheric burdens of O_3 and CFC-11 as well as the total chemical removal rate of CFC-11 from the atmosphere are calculated to provide a denominator for the ODP as given in Eq. (1). In a separate χ perturbation run, χ is introduced as a surface flux emission for specific latitude ranges to provide the ODP numerator. The model-derived ODPs are steady-state ODPs.

VSL compounds (assumed to be those with atmospheric lifetimes less than 0.5 year) generally do not mix evenly in the troposphere, and most of the surface fluxes are oxidized within the troposphere rather than reaching the stratosphere. It is important to note that through the degradation process, halogen-containing product gases can be transported to the stratosphere. Thus in analyzing such short-lived gases, chemical degradation in the troposphere, removal of degradation products by incorporation into clouds and rainout, and transport of the gases and their degradation products to the stratosphere must be treated accurately. Because tropospheric transport processes cannot be accurately treated in a zonally-averaged two-dimensional model, a three-dimensional model is required to investigate the impact of halogenated replacement compounds on ozone depletion as a function of location (Wuebbles et al., 2001). However, at this time, ODP studies have not been done with a fully coupled CTM of the troposphere and stratosphere.

Since VSL compounds are likely to be used primarily at northern mid-latitudes, the emissions at the surface are assumed to occur for latitudes from 30° N to 60° N (see Fig. 1). The surface emissions in the MOZART-3 perturbation run are considered only over land grid cells while those in the 2-D model are assumed equally distributed over the latitude range. The emissions are assumed to be the same over model land grids and assigned with fractional land surface emissions at boundary grids between land and ocean/lake surfaces considering the actual land fraction. Total annual masses emitted into the atmosphere in the 3-D model were adjusted to match those in the 2-D model for comparison purpose. Model ODPs of the iodinated compounds have been derived assuming the mid-latitude emissions. Model analysis of a tropical emissions case has also been carried out for CF_3I. Global atmospheric lifetimes are calculated based on model atmospheric loading and chemical loss rate of the compounds.

3 Modeling tools

The 3-D model better represents some of the physical processes affecting ozone as well as transport processes, especially in the troposphere and the polar stratosphere, than the 2-D model does. Therefore, 3-D CTMs are now the tool of choice and much more preferable for evaluating ODPs both for longer-lived gases and for the very short-lived candidate replacement compounds. These models can not only determine the amount of the substance reaching the stratosphere directly but can also follow the processes affecting the reaction products. The drawback in using 3-D models is that they are very computationally expensive and require much additional human resources for analysis.

In this study, the National Center for Atmospheric Research (NCAR) Model for OZone And Related Tracers version 3 (MOZART-3) (Kinnison et al., 2007) has been used to explicitly calculate the impact of VSL iodinated compounds on ozone. The MOZART-3 CTM of the global atmosphere is one of the leading tools for the study and prediction of current and future atmospheric composition and of possible effects from anthropogenic emissions into the atmosphere. The model was updated to incorporate the complete set of iodine chemistry used in the previous 2-D modeling study by Li et al. (2006). Major chemistry reactions and rates that could impact effects of CF_3I and CH_3I on atmospheric ozone concentrations relative to earlier studies (e.g., Solomon et al., 1994) include: CF_3I, CH_3I, IO, HOI, INO, INO_2, $IONO_2$, OIO, ICl, IBr, and I_2 absorption cross-sections for photochemical reactions (Sander et al., 2003, 2007), thermal reaction-rate coefficients of $CH_3I + OH \rightarrow I + H_2O + CH_2O$, and catalytic cycles involving reactions of IO with ClO or BrO and I with O_3, HO_2 or O (see Li et al., 2006).

The MOZART-3 model includes a complete representation of stratospheric processes and extends to altitudes greater than 80 km as described and evaluated in Kinnison et al. (2007). It incorporates a full stratosphere, including the chemistry of chlorine species (Cl_y) and bromine species (Br_y) important to stratospheric ozone as well as updated hydrogen, nitrogen, and hydrocarbon oxidation chemistry relevant to stratospheric and tropospheric chemistry included in its predecessor model MOZART version 2 (Horowitz et al., 2003; Lin et al., 2008). State-of-the-art representations of relevant heterogeneous and physical processes for winter/spring polar vortex related to ozone destruction are also fully included in the model. This model has been evaluated extensively via comparisons with measurements of atmospheric trace gases from satellite data and a large number of aircraft field campaigns (e.g., Kinnison et al., 2007; Pan et al., 2007; Horowitz et al., 2003; Wei et al., 2003).

Chemical reaction-rate constants and photochemical data follow the recommendations of Sander et al. (2003). The MOZART-3 CTM used in this study is driven by a meteorology field derived from the Whole Atmosphere Community Climate Model (WACCM) version 1b. The MOZART-3 thus has a 2.8° resolution in latitude and longitude and a hybrid sigma-pressure vertical coordinate including 66 layers from the surface to 5.1×10^{-6} mbar (approximately 140 km).

The UIUC 2-D CRT model (see Youn et al., 2006, 2009; Guillas et al., 2006) updated from the version used in Li et al. (2006) is also used. The UIUC 2-D CRT model has been an adequate and efficient tool for the evaluation of ODPs although 2-D models have limitations in adequately representing the zonally asymmetric features such as tropospheric transport processes and the edge and evolution of the ozone hole. The 2-D model applied to traditional ODP studies, especially for long-lived compounds, has been performed in a daily-average mode with a time step of one day outside the operators. However, the 2-D model runs in this study of evaluating the impact of VSL compounds on atmospheric ozone were conducted in more detailed integration with a time step of 20 min. due to extremely short lifetimes of the source and product gases although the above-mentioned limitations exist. The 2-D model still has the advantage of being much more computationally efficient compared to 3-D models, and thus can provide a quick reference to the slower 3-D simulations (Youn et al., 2009).

4 Simulation of CH_3I background concentration

CH_3I, an effective carrier of iodine from the biosphere into the atmosphere, is emitted into the atmosphere mainly as a result of biological methylation of iodine (Moore and Groszko, 1999; Amachi et al., 2001) along with photochemical production in open sea (Happell and Wallace, 1996; Li et al., 2001; Yokouchi et al., 2001). Photolysis of CH_3I is a main pathway of its removal from the troposphere, so as to produce iodine atoms even under visible light conditions (Chameides and Davis, 1980; Davis et al., 1996). As described in detail by Bell et al. (2002), the known or extrapolated global budget of oceanic CH_3I emissions ranges from 130 to 1300 Gg yr^{-1}. However, land-based sources may be important regionally. CH_3I fluxes from growing rice are significant compared to other land-based sources such as inland and coastal wetlands, peatlands, and biomass burning (Lee-Taylor and Redeker, 2005, and references therein). Flux rates from inland and coastal wetlands, peatlands, and biomass burning all yield global source terms below 10 Gg yr^{-1} (Lee-Taylor and Redeker, 2005).

Table 1 shows the annual emission flux of CH_3I to the atmosphere used in this modeling study. The CH_3I emission sources include ocean, rice paddies, biomass burning, wood fuel, and wetlands. Except for emissions from rice paddies, all of the emissions in Table 1 are computed following Bell et al. (2002), using the GEOS-Chem global 3-D model of tropospheric chemistry (Park et al., 2006; Bey et al., 2001) driven by assimilated meteorological data from the Goddard Earth Observing System (GEOS-4) of the NASA Data Assimilation Office for year 2001. The emission fluxes from oceans are from an oceanic mixed layer model coupled to the GEOS-Chem model. The estimated global oceanic CH_3I source of 0.224 Tg yr^{-1} in Table 1 is very similar to that of 0.214 Tg yr^{-1} by Bell et al. (2002), but about three times smaller than the global estimate by Butler et al. (2007). The CH_3I flux from rice is the most important among the land sources. However, earlier estimates of the rice-origin CH_3I flux of 71 Gg yr^{-1} (Redeker et al., 2000) seem to overestimate the boundary layer concentrations of CH_3I off the China coast in a 3-D model study as noted by Bell et al. (2002). We use the recent global CH_3I flux data from rice paddies provided by Lee-Taylor and Redeker (2005), with the reduced global estimate of 16 Gg yr^{-1} found to yield better agreement between model and measurement. Figure 2 shows the geographical distribution of the annual average surface emission fluxes of CH_3I used to simulate background CH_3I concentrations. The source emissions include fluxes from ocean, rice paddies, biomass burning, wetlands, and wood burning to the atmosphere.

Based on CH_3I source emission fluxes from the previous studies, we simulate background concentrations of CH_3I using the MOZART-3 3-D CTM and compare the results with aircraft measurement data that are vertically resolved. Aircraft measurements used in this study are from the Pacific Exploratory Mission(s) (PEM): PEM Tropics A for August–October 1996 and PEM-Tropics B for March–April 1999 (Colman et al., 2001; Blake et al., 2001). Simulated atmospheric burden of CH_3I amounting to 8.0 Gg and photolysis loss rate of 264.0 Gg yr^{-1} in the model yield lifetimes of 11.1 days. The lifetime of 11.1 days is about twice as large as that in Bell et al. (2002). It should be noted that if total iodine is defined as $I_y = I + IO + HOI + INO + INO_2 + IONO_2 + OIO + ICl + IBr + I_2 + CH_3I$, simulated total iodine in the stratosphere using the CH_3I emissions in Table 1 constitutes about 2.6% of total atmospheric I_y.

Besides uncertainty ranges of source emissions, a horizontal resolution of approximately 250 km in the MOZART 3-D CTM is coarse for comparison with aircraft measurements. Satellite observations of CH_3I, if any, could be used for the better comparison. However, since our current ultimate target is evaluating ODPs of two iodinated compounds, the following comparisons of 3-D model results with aircraft measurements are used to check if the model chemistry of atmospheric iodine described by Li et al. (2006) is reasonable enough to evaluate ODPs of iodine species. Figure 3 shows atmospheric concentrations of simulated and measured CH_3I in the marine boundary layer (MBL, averaged between 0 and 1 km). The distribution of atmospheric CH_3I in the MOZART-3 model shows distinct differences with overlay circles denoting collocated aircraft CH_3I MBL concentrations. The model overestimates observed mixing ratios over the Southern Ocean, the Tasmanian Sea and the Northern Pacific at mid-latitudes. However, recently reported cruise data by Butler et al. (2007) and Yokouchi et al. (2001) show high values over 1.5 pptv (see their Fig. 4) over the regions in the same months. The correlation between simulated and measured concentrations in MBL is weak ($r = 0.29$). The discrepancies suggest an overestimated source or a missing sink for CH_3I in the ocean and the model's difficulty of reproducing the patterns in the CH_3I MBL concentration field is discussed by Bell et al. (2002).

Observed vertical profiles of CH_3I are gridded into the MOZART-3 model grid boxes at the same locations and months. The observed CH_3I profiles for selected locations with enough vertical information are compared with those of model results in Fig. 4. Selected locations include grids near Fiji (18° S, 178° E), Hawaii (19° N, 155° W), Tahiti (17° S, 149° W), New Zealand (38° S, 180° W), Easter Island (27° S, 109◦ W), and tropical central Pacific. Both simulated and observed CH_3I concentrations decrease with height up to 4–6 km. Many of the profiles in Fig. 4 show enhanced concentration in the middle and upper troposphere (UT) associated with deep convection, as also found in Bell et al. (2002). The simulated and observed profiles are in good agreement; the model reproduces the vertical gradient (decrease) with altitude in the lower atmosphere. However, over tropical central Pacific regions, the simulated concentrations are over 4 times lower than observed. The simulation of MBL CH_3I concentrations has errors possibly due to the lack in understanding of emission fluxes over oceans. The MOZART-3 CTM in the present study is driven by the WACCM meteorology. Since the climate model meteorology compared to assimilated data will not provide a good simulation of deep marine convective mass fluxes over the Pacific, it is not surprising that the MOZART-3 results show a less defined "C-Shaped" profile than the GEOS-Chem does in Bell et al. (2002).

Discrepancy in spatial patterns of the simulated and observed CH_3I concentrations in the MBL is associated with uncertain source emissions that need to be better understood. However, the current model results qualitatively agree with aircraft measurement data in vertical profiles. It supports that our current model chemistry of atmospheric iodine used in the MOZART-3 model is reasonable to evaluate ODPs of iodine species based on postulated emissions in Fig. 1.

5 Ozone depletion potentials for CF_3I and CH_3I

Several earlier studies have evaluated potential effects of CF_3I on ozone in terms of ODPs. Assuming CF_3I emissions from the Earth surface only, early studies obtained extremely small ODPs of CF_3I, which were <0.008 by Solomon et al. (1994) and 0.006 by Connell et al. (1996). Since the earlier studies, the laboratory results on iodine reactions keep being updated. Using the 2004 version UIUC 2-D model, Li et al. (2006) re-evaluated the ODPs for surface emissions of CF_3I and determined ODPs of 0.013 for emissions evenly distributed over the Northern Hemisphere, 0.011 for emissions distributed over 30° N to 60° N, and 0.018 for emissions distributed over 5° S to 30° N. The model used an updated representation of iodine chemistry (see Tables 1 and 2 and Fig. 1 in Li et al., 2006) relative to the earlier studies of the ODP of CF_3I (Solomon et al., 1994).

In this study, the ODPs for CF_3I and CH_3I have been evaluated using the state-of-the-art MOZART-3 3-D CTM incorporated with the chemical processes relative to the iodine-containing compounds as in Li et al. (2006). We also use the current UIUC 2-D CRT model for direct comparison to the 3-D model results. Three-dimensional model case studies for mid-latitude emissions of CF_3I and CH_3I and for tropical emissions of CF_3I have been conducted to evaluate the potential effects of these postulated anthropogenic surface flux emissions of halogenated VSL compounds on atmospheric ozone based on the geographic distributions of emissions in Fig. 1. Land-based emissions of CF_3I and CH_3I over the latitude range of 30° N to 60° N used in the model correspond to a total emission rate of 0.74 and 0.536 $\mathrm{Tg\,yr^{-1}}$, respectively. An additional simulation for CF_3I land emission (total 0.73 $\mathrm{Tg\,yr^{-1}}$) for 20° S to 20° N was also carried out to show the dependency of ODP on the source location.

The atmospheric burden changes of CF_3I (CH_3I), I_y, and O_3 per Tg yr^{-1} of CF_3I (CH_3I) surface flux introduced to the UIUC 2D CTM and MOZART are evaluated for the troposphere and the stratosphere. The burden is obviously higher in the troposphere where the species is being emitted or and its by-products are produced via degradation. Stratospheric burdens are smaller because removal processes including photo-dissociation of CF_3I and wet scavenging of its reaction products prohibit those iodine species from being transported into stratosphere.

Latitude-height distributions of zonal mean CF_3I determined by the UIUC 2-D and the MOZART-3 3-D model for mid-latitude and tropical emissions are shown in Fig. 5. The contour lines are isolines of the base-10 logarithms of CF_3I volume mixing ratios where the mixing ratios are scaled as per teragram of one year CF_3I loading. 3-D model-determined distributions of annually averaged CF_3I including topography and the tropopause variations along longitudes show more detailed features than those from the two-dimensional model. In general, CF_3I distributions from the different model simulations compare relatively well, including the annual variation from January to December (not shown).

The annual average change in total inorganic iodine (I_y) mixing ratios per Tg yr^{-1} of CF_3I surface flux in Fig. 6 shows agreement in pattern with that in CF_3I in Fig. 5. As expected for CF_3I mid-latitude emissions, the Northern Hemisphere has a larger increase in mixing ratio of I_y because of the direct influence of CF_3I emission. The UIUC 2-D and MOZART 3-D models show a general agreement in the transport and distribution of the I_y. However, 3-D simulated I_y for mid-latitude emissions shows smaller mixing ratio in the Southern Hemispheric stratosphere than 2-D simulated one does. Larger amounts of 3-D I_y for tropics emissions are elevated up to the tropopause level.

Annually averaged ozone percent changes for mid-latitude and tropical emission scenarios relative to background atmospheric conditions are shown in Fig. 7 in the unit of % Tg^{-1} yr. Slight increases in ozone can be seen in the SH stratosphere but the increases are very small (Fig. 7a). 3-D model simulations show larger ozone depletion than the 2-D model simulations as a result of the larger atmospheric CF_3I loading and subsequent more inorganic iodine products as seen in Figs. 5 and 6. There is general agreement between the 2-D and 3-D model-simulated patterns and amounts of ozone depletion per teragram of one year CF_3I loading. Only a small amount of I_y reaches the levels above the tropopause.

Figure 8 shows changes in annually-averaged CH_3I, I_y, and O_3 that are made by CH_3I surface emissions over mid-latitude range of 30° N to 60° N. Spatial patterns of changes in I_y and O_3 due to the CF_3I and CH_3I mid-latitude scenarios in Figs. 6a and 7a and Fig. 8 are very similar. However, the loading of CH_3I into the atmosphere yields larger depletion of atmospheric ozone than that of CF_3I does because CH_3I has longer lifetime (see Table 2).

ODPs are a vital part of the current US Clean Air Act, in which 0.2 is the upper bound of ODP values of any chemical that is not controlled. However much smaller ODPs are considered to still be of concern in recent policy considerations. Global atmospheric chemical lifetimes and ODPs of iodine compounds derived by the two different models for the surface emission scenarios in Fig. 1 are summarized in Table 2. The 3-D model-based ODPs for mid-latitude emission cases of CF_3I and CH_3I are 0.008 and 0.017, respectively, and that for tropical emission case of CF_3I is 0.016. For comparison, the 2-D model-based ODPs obtained are 0.006 and 0.016, respectively, for CF_3I and CH_3I emissions evenly distributed over the mid-latitudes of 30° N to 60° N, while the ODP for CF_3I emissions distributed over 20° to 20° N is 0.013.

The 2-D and 3-D model-derived lifetimes of CF_3I and CH_3I are comparable to the values reported in Chapter 2 of WMO (2003, 2007). Consistently with ozone depletion distributions in Fig. 7, three-dimensional ODP values for CF_3I and CH_3I are higher but are in good agreement with 2-D ODPs. Both models show the dependence of the ODP values of CF_3I on the location of emissions. The CF_3I ODP for tropical emissions is twice that found for mid-latitude emissions. The consistent results obtained with different models for the two iodine compounds is in part attributable to the consistent set of chemistry incorporated into the models. The computationally efficient zonally-averaged 2-D model still appears to perform relatively well in the ODP studies of those VSL species. This is in part because the residual circulation used in the 2-D advection well represents mass transport in meridional and vertical directions.

The global lifetimes of CF_3I are smaller than those for CH_3I. This accounts for the smaller ODP values of CF_3I than that of CH_3I. The shorter lifetimes of the iodinated VSL compounds, when compared with most brominated VSL compounds, suggest less efficient transport of total inorganic iodine to the stratosphere and thus smaller ODPs.

6 Key findings and conclusions

The MOZART-3 3-D CTM, fully representing the troposphere and stratosphere, as well as the current version of the UIUC 2-D model, has been used to evaluate the potential effects of CF_3I and CH_3I on atmospheric ozone. Through the model analyses, we have calculated ODPs for the two iodinated VSL compounds to evaluate the relative effects on global atmospheric ozone from surface emissions of such questionable gases.

The fraction of VSL compounds involved in ozone depletion depends strongly on the location of the surface sources. The atmospheric distribution of the source gases is determined by competitive atmospheric processes including vertical transport and chemical destruction or removal via washout. 3-D model-derived ODPs of CF_3I and CH_3I for mid-latitude emissions case are 0.008 and 0.017, respectively. The 2-D model gives similar ODP values, 0.006 for CF_3I and 0.016 for CH_3I, despite of the limited 2-D representations of atmospheric processes. The 3-D and 2-D model-derived CF_3I ODP for tropical emissions, 0.016 and 0.013, respectively, also agree well. The chemical lifetime of CF_3I from tropical emissions is shorter than that for mid-latitude emissions due to fast photolysis but the model-derived ODP values for CF_3I tropical emissions are larger (see Table 2). The larger CF_3I ODPs for tropical emissions can be explained by the rapid vertical transport due to convective activities in equatorial regions that is more effective in the vertical transport of total halogens since the transport timescale in convection events (hours) is shorter than chemical loss or washout removal timescale.

We simulate background concentrations of CH_3I using the MOZART-3 3-D CTM to evaluate the model results with aircraft measurement data. Using CH_3I source emission fluxes reported by the previous studies and calculated from the oceanic mixed layer model coupled to the GEOS-Chem 3-D CTM, there were discrepancies in spatial patterns of simulated and observed CH_3I concentrations in MBL. However, the current model results qualitatively agree with aircraft measurement data in vertical profiles of CH_3I in the atmosphere. Therefore, the MOZART-3 model can be used to evaluate ODPs of iodine species as long as postulated emissions are used.

The extremely small ODP values indicate that little of the CF_3I or CH_3I, and their reaction products containing iodine atoms, would reach the stratosphere. Most of the iodine would be removed rapidly from the atmosphere by rainout processes. These studies also emphasize the importance of using state-of-the-art three-dimensional numerical models of the chemistry and physics of the troposphere and stratosphere in evaluating the ODPs of replacement compounds for short-lived compounds.

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Table 1. Global source emission fluxes of CH_3I used in MOZART-3 3-D model to simulate background concentrations in the model.

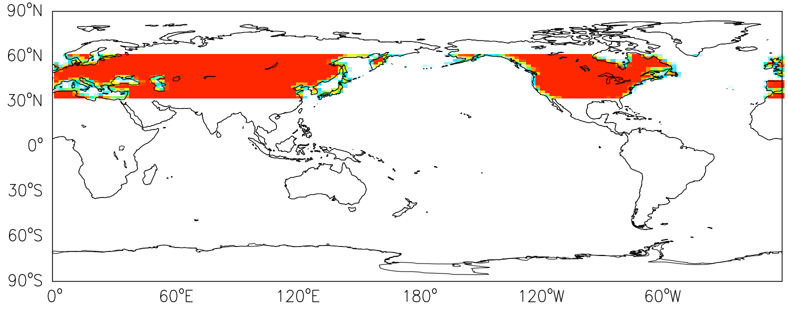
Source	Value [$\mathrm{Tg\,yr^{-1}}$]	Reference
Oceans	0.224	Bell et al. (2002)
Rice paddies	0.016	Lee-Taylor and Redeker (2005)
Biomass burning	0.009	Bell et al. (2002)
Wood fuel	0.008	Bell et al. (2002)
Wet land	0.008	Bell et al. (2002)
Total source	0.264	

Table 2. Derived ODP values of CF_3I for mid-latitudes and tropics emission scenarios and CH_3I for mid-latitudes emission scenarios using the UIUC 2-D and the MOZART-3 3-D models.

Species and Model Scenario	Derived Global Lifetime*		Global Ozone Change per Mass Emission [% yr Tg]		Derived ODP	
	2-D	3-D	2-D	3-D	2-D	3-D
CFC-11 perturbation	57.3 yr	53.7 yr	−12.949	−14.911	1.000	1.000
CF_3I midlatitudes perturbation scenario	3.83 days	5.03 days	−0.075	−0.126	0.006	0.008
CF_3I tropical perturbation	0.99 day	1.13 day	−0.173	−0.245	0.013	0.016
CH_3I midlatitudes perturbation	13.49 days	13.59 days	−0.207	−0.255	0.016	0.017

[*] Derived lifetimes are global chemical lifetimes calculated using atmospheric total burden (loading) and chemical loss-rates in the models.

(a) CF3I Land Emissions at the surface over mid-latitudes of 30N-60N



(b) CF3I Land Emissions at the surface over tropics of 20S-20N

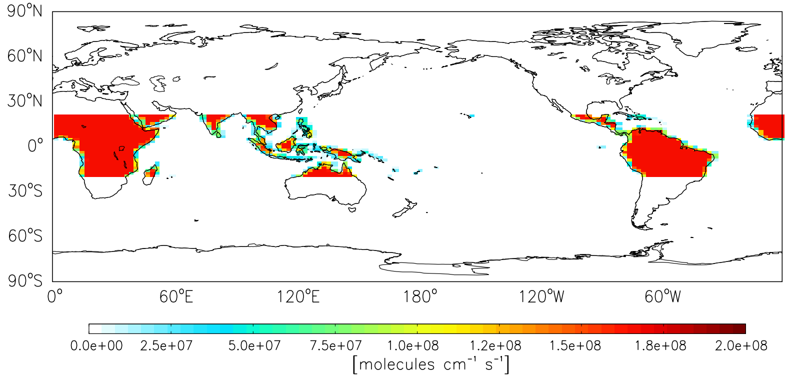


Fig. 1. Land-based surface emission fluxes of CF_3I over **(a)** 30° N to 60° N and **(b)** 20° S to 20° N in the unit of molecules cm^{-1} s^{-1}. These postulated emissions are inputs to model perturbation runs. The surface flux is adjusted at boundary grids considering actual land fractions.

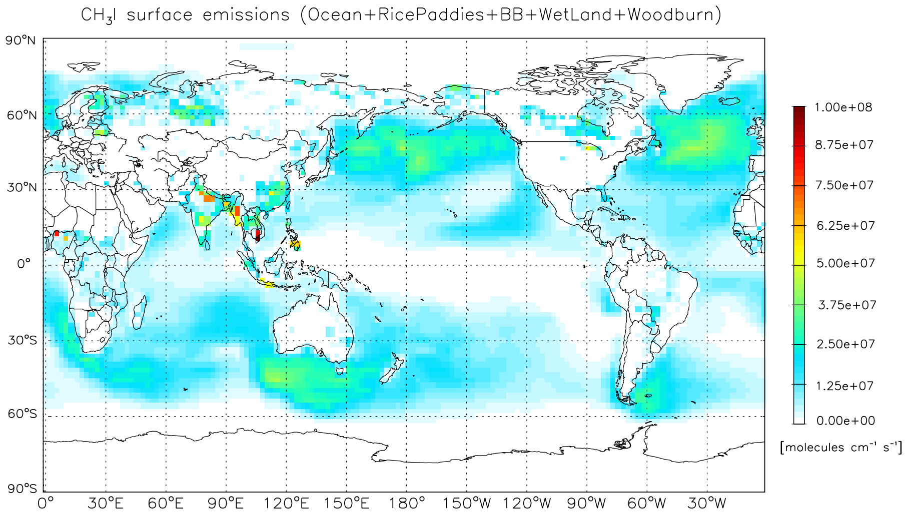


Fig. 2. Annual average surface emission fluxes of CH$_3$I in the unit of molecules cm^{-1} s^{-1}. The emissions include fluxes from ocean, rice paddies, biomass burning, wetlands, and wood burning to the atmosphere.

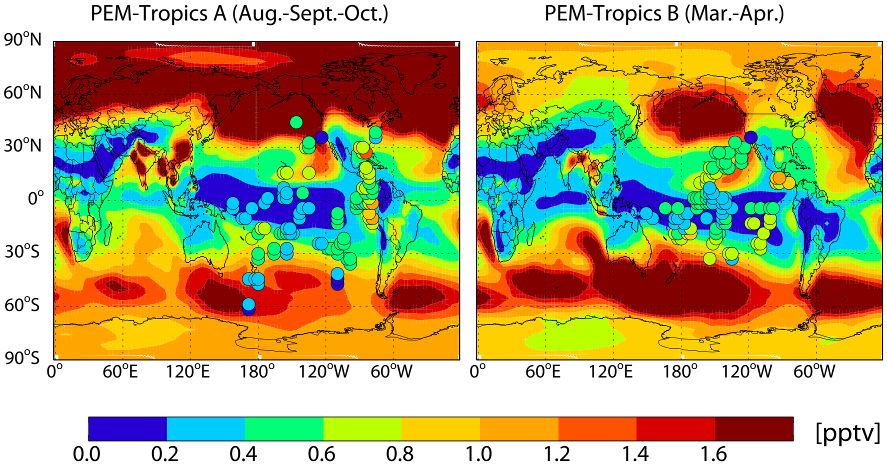


Fig. 3. Atmospheric concentrations of CH_3I in the marine boundary layer. Circles are aircraft measurement data from PEM-Tropics A in August–October (left) and PEM-Tropics B in March–April (right). The aircraft and model data are averaged between 0 and 1 km for boundary layer concentrations.

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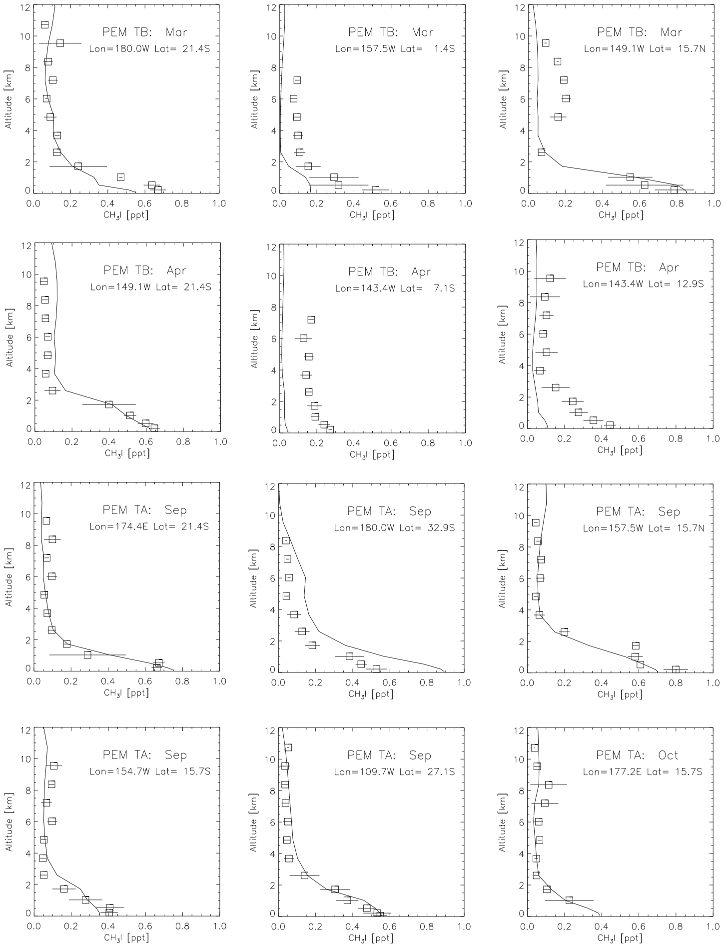
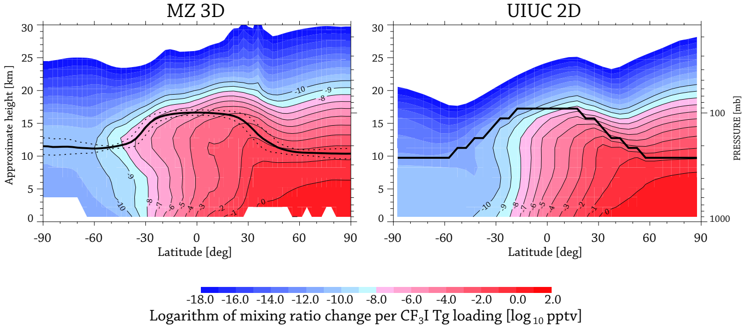


Fig. 4. Vertical profiles of CH$_3$I concentrations measured from aircraft and simulated by model. Horizontal bars are standard deviations computed from the individual measurements. Solid black lines denote the corresponding model profiles.

(a) CF_3I for surface emissions over 30N-60N



(b) CF_3I for surface emissions over 20S-20N

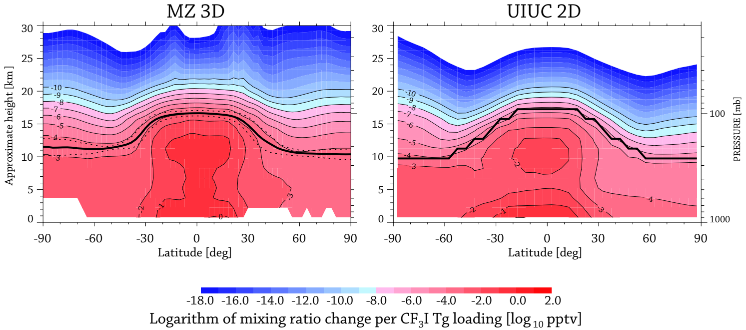
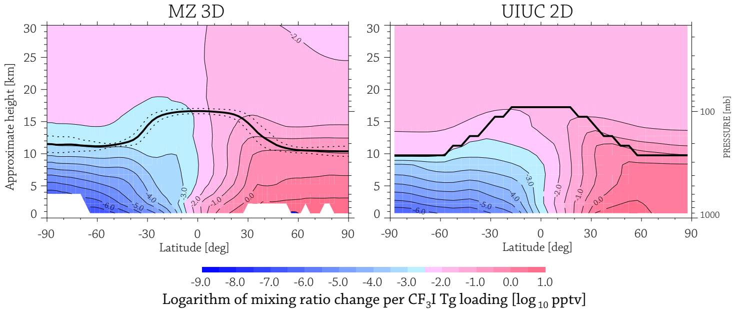


Fig. 5. Annually averaged CF_3I mixing ratios introduced into the atmosphere by one teragram of total CF_3I surface emissions in ranges of **(a)** mid-latitudes and **(b)** tropics. The base 10 logarithm was taken of the CF_3I mixing ratios determined by the two scenarios using two different models after being scaled as per teragram CF_3I loading. The MOZART-3 3-D (UIUC 2-D) model results are on the left-hand-side (right-hand-side). The tropopause levels are denoted by thick line and the 3-D model results only includes detailed topography and tropopause variations.

(a) I_y for surface emissions over 30N-60N



(b) I_y for surface emissions over 20S-20N

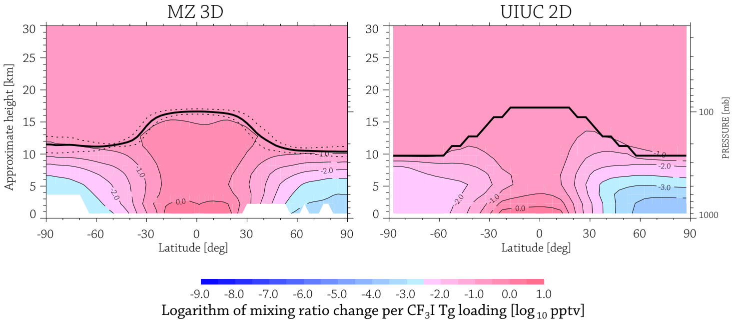
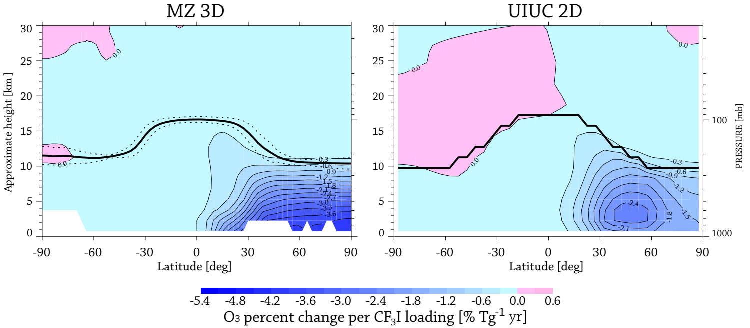


Fig. 6. Logarithm of annually averaged I_y mixing ratio changes per CF_3I Tg loading for **(a)** mid-latitude and **(b)** tropical emission scenarios.

(a) O_3 Change for CF_3I Emission over 30N-60N



(b) O_3 Change for CF_3I Emission over 20S-20N

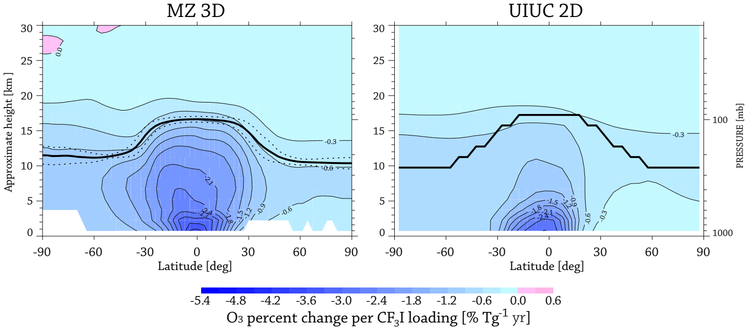


Fig. 7. Annually averaged ozone percent changes for **(a)** mid-latitude and **(b)** tropical emission scenarios relative to background atmospheric conditions without CF_3I emissions in the unit of % Tg^{-1} yr.

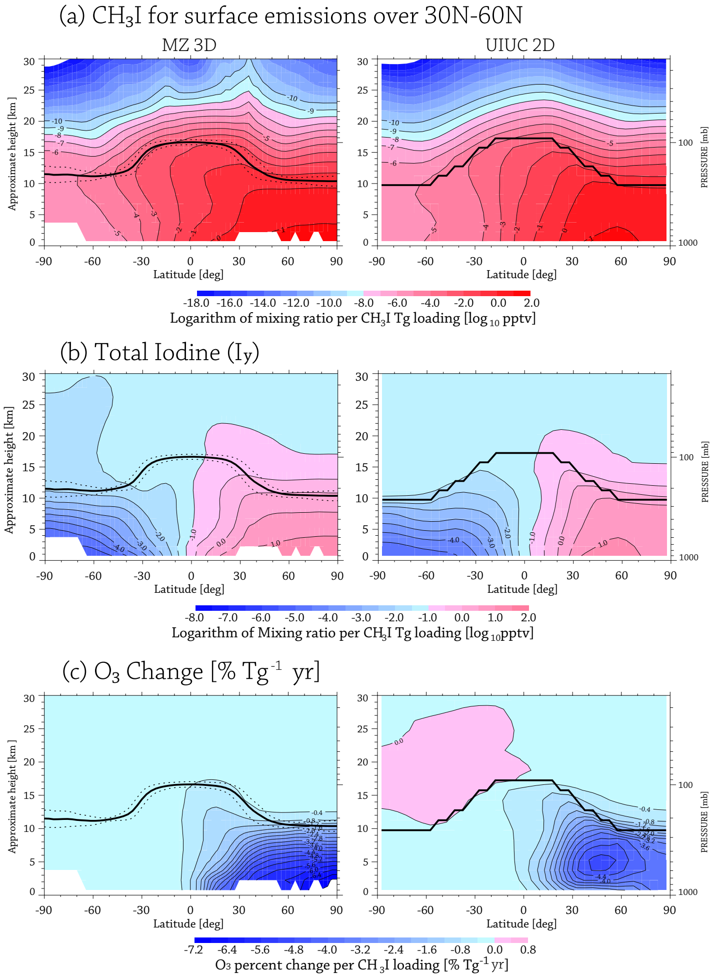


Fig. 8. Annually averaged changes in **(a)** CH$_3$I, **(b)** I$_y$, and **(c)** ozone for CH$_3$I mid-latitude emission scenario relative to background atmospheric conditions without CH$_3$I emissions.