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Atmospheric lifetimes and ozone depletion potentials of trans-1-chloro-3,3,3-trifluoropropylene and trans-1,2-dichloroethylene in a three-dimensional model

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Abstract

The chloroalkenes trans-1-chloro-3,3,3-trifluoropropylene (tCFP) and trans-1,2-dichloroethylene (tDCE) have been proposed as candidate replacements for other compounds in current use that cause concerns regarding potential environmental effects including destruction of stratospheric ozone. Because tCFP and tDCE contain chlorine atoms, the effects of these short-lived compounds on stratospheric ozone must be established. In this study, we derive the atmospheric lifetimes and Ozone Depletion Potentials (ODPs) for tCFP and for tDCE assuming emissions from land surfaces at latitudes 30° N to 60° N using the MOZART 3 three-dimensional model of atmospheric chemistry and physics. Both tCFP and tDCE are shown to primarily affect ozone in the troposphere, rather than in the stratosphere as generally expected from longer-lived chlorocarbons. The atmospheric lifetime of tCFP against chemical reaction is 40.4 days, and its ODP is quite small at 0.00034. The tDCE atmospheric lifetime is 12.7 days, and its ODP is 0.00024, which is the lowest ODP found for any chlorocarbon we have studied. Our study suggests that chlorine from tCFP and tDCE are unlikely to significantly affect ozone at quantities likely to be emitted to the atmosphere.

1 Introduction

After the destruction of stratospheric ozone by chlorine and bromine released by degradation of human-generated, long-lived halocarbon compounds was recognized (reviewed in WMO, 1992, 1995, 1999, 2003, 2007), industry has sought replacement compounds that perform the same functions without causing severe environmental effects. Most recent candidate replacement compounds are chosen so that they have short atmospheric lifetimes, and will typically be oxidized rapidly in the troposphere, in order to limit stratospheric ozone loss as well as possible climate effects from those substances.

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The Ozone Depletion Potential (ODP; Wuebbles, 1983) of a compound is defined as the reduction in total ozone (O_3) column per unit of mass for that compound divided by the reduction in total O_3 column per unit of mass for the reference compound trichlorofluoromethane ($CFCl_3$, often called CFC-11 or Freon-11). This value provides an index of the relative O_3 loss to be expected from a compound of interest that can then be used in policy considerations. In our work on candidate replacement compounds, ODPs are calculated using chemical-transport models (CTMs) of the global troposphere and stratosphere. The candidate compound is emitted at the surface in the CTM, and the CTM is run to a steady state. Through comparison to a reference run of the CTM without the candidate compound, we obtain the O_3 column reduction for the assumed annual emissions of the compound. A similar comparison for a $CFCl_3$ perturbation in the CTM compared to the reference CTM run yields the O_3 column reduction for the ODP reference compound.

The ODP concept was developed originally for ozone-depleting substances that are sufficiently long-lived to mix throughout the troposphere. ODP has recently been extended to shorter-lived replacement compound candidates. The atmospheric lifetime of the candidate and the fraction of the candidate plus its degradation products containing halogen that reaches the stratosphere are dependent on the latitude (possibly also longitude and season) of release, so that the ODP of a short-lived candidate is dependent on emission location. Because short-lived candidates are not well-mixed throughout the troposphere, a three-dimensional CTM should be used, whether directly on the candidate (Wuebbles et al., 2001, 2009, 2010; Wuebbles and Patten, 2009) or on a tracer (e.g., Bridgeman et al., 2000; Olsen et al., 2000), to adequately represent the distribution of the compound in the troposphere and the extent of injection of the compound plus halogenated degradation products from the compound into the stratosphere.

The compounds, trans-1-chloro-3,3,3-trifluoropropylene ($t\text{-CHCl=CHCF}_3$, which we abbreviate as tCFP below) and trans-1,2-dichloroethylene ($t\text{-CHCl=CHCl}$, which we abbreviate as tDCE), are in current use and have been proposed as replacements in

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uses such as electronics cleaning and foam blowing. These compounds include a double bond, which is more reactive toward atmospheric oxidants than are the halogenated alkanes that have typically been considered by industry and environmental policymakers. We obtain the atmospheric lifetime and the ODP for tCFP and for tDCE in this study in a current-generation, three-dimensional CTM of the global atmosphere. This is the first study of atmospheric lifetime and ODP for tCFP and tDCE, and indeed for any halogenated alkene, as far as we are aware.

2 Method

Chloroalkenes such as tCFP and tDCE are most readily removed from the atmosphere by oxidation initiated by addition of the hydroxyl (OH) radical, predominantly in the troposphere. This addition reaction can be treated as taking place at the high-pressure limit with a bimolecular rate constant having a weak negative temperature dependence. Possible reactions with other oxidants such as the ground and excited electronic states of oxygen atom ($O(^3P)$, $O(^1D)$, respectively), nitrogen trioxide (NO_3), and chlorine atom (Cl) and photolytic degradation are unlikely to be important in the troposphere and lower stratosphere where effectively all oxidation of species with atmospheric chemical lifetimes shorter than one year will occur. The reaction rate constant for tCFP with OH is taken as $4.4 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, based on the measurement of Sulbaek Andersen et al. (2008) at 295 K, assuming zero temperature dependence. The most recent measurement of the temperature dependence of tDCE reaction with OH we could find is from Zhang et al. (1991), which provided the reaction rate constant for temperature T in Kelvin as $1.01 \times 10^{-12} \exp((250 \text{ K})/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Release of chlorine atoms is likely to occur rapidly after the initial OH addition for both tCFP and tDCE. Any organochlorine oxidation products, such as formyl chloride $CHClO$, resulting from the oxidation of either tCFP or tDCE are expected to further oxidize quickly to release Cl under conditions suitable for the oxidation of the initial chloroalkene. Because organochlorine oxidation products of tCFP or tDCE could dissolve in water or

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adsorb on ice, the Cl contained could then be removed by wet deposition, so that our assumption of immediate Cl release sets an upper limit to ozone effects from tCFP and tDCE in the atmosphere.

The atmospheric mixing ratio profiles and lifetimes of tCFP and tDCE are calculated using the Model for Ozone and Related Tracers (MOZART) version 3 (Kinnison et al., 2007), a three-dimensional, global atmospheric chemical-transport model developed by the National Center for Atmospheric Research (NCAR) which includes a full representation of chemistry and physics affecting the atmosphere from the Earth's surface through the lower thermosphere. MOZART 3 represents the relevant chemical and physical processes affecting the troposphere and stratosphere, including all relevant chemistry in the hydrogen (HO_x), nitrogen (NO_y), chlorine (Cl_y), and bromine (Br_y) families of species important to affecting odd oxygen (ozone (O_3), $\text{O}(^3\text{P})$, and $\text{O}(^1\text{D})$). MOZART 3 also includes the oxidation chemistry of methane and of non-methane hydrocarbons (NMHCs) that are important to the tropospheric oxidation capacity through their effects on OH. MOZART 3 has been extensively evaluated by comparison to measurements of atmospheric trace gases from aircraft- and satellite-based observations (e.g., Kinnison et al., 2007; Pan et al., 2007).

Thermal and photolytic chemistry data for atmospheric reactions other than those of tCFP and tDCE follow the recommendations of Sander et al. (2003). Meteorology to drive MOZART 3 is from the Whole Atmosphere Community Climate Model (WACCM) version 1b (Sassi et al., 2004) representative of the climatological atmosphere derived for the late 1990s. MOZART 3 driven by this meteorology has a 2.8° resolution in latitude and in longitude, and the vertical grid is a hybrid sigma-pressure coordinate consisting of 66 layers from the surface to 5.1×10^{-6} hPa, or approximately 140 km altitude. In this coordinate, the pressure at each layer i is given by

$$P_i = a_i P_0 + b_i P_s, \quad (1)$$

where a_i and b_i are the coefficients of the hybrid coordinate for layer i , P_0 is the reference pressure of 1000 hPa, and P_s is the surface pressure, an input from the meteorology.

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logical fields which depends on surface orography at each latitude and longitude and on time.

MOZART 3 is used to derive the atmospheric lifetimes and Ozone Depletion Potentials (ODPs) of tCFP and tDCE as follows. The background MOZART 3 steady-state atmosphere corresponding roughly to the year 2000 and the CFC-11 perturbation atmosphere needed as the denominator for ODP were previously determined in studies of the ODPs for HCFC-123 (Wuebbles and Patten, 2009) and for n-propyl bromide, trichloroethylene, and perchloroethylene (Wuebbles et al., 2010). The annually and globally-averaged surface mixing ratios of long-lived source gases set as inputs to MOZART 3 are based on those listed in WMO 2002 Scientific Assessment of Ozone Depletion Table 4B-2 (Chipperfield et al., 2003) except for CO_2 , CH_4 , and N_2O from historic values in Appendix II.2 of the IPCC Third Assessment Report on climate change (IPCC, 2001) linearly interpolated to the year 1999. Surface emissions rates of short-lived source gases except for tCFP and tDCE use the Precursors of Ozone and their Effects in the Troposphere (POET) data base (Granier et al., 2005; Olivier et al., 2003) for the year 2000 as were used in the MOZART 4 evaluation (Emmons et al., 2010).

To obtain atmospheric mixing ratios and chemical lifetimes, tCFP and tDCE are introduced as surface emissions into two separate MOZART 3 runs. These emissions are assumed to occur on all land masses from 30°N to 60°N , which represents the latitude range of the likely short-term usage for either replacement compound (small differences in the resulting effects would be expected if individual regions of North America, Europe or Asia were used instead). A tCFP flux of $1.64 \times 10^{10} \text{ molec cm}^{-2} \text{ s}^{-1}$ is added to MOZART 3, corresponding to a total tCFP emission of 50 Tg yr^{-1} . The tDCE flux of $2.21 \times 10^{10} \text{ molec cm}^{-2} \text{ s}^{-1}$ introduced to MOZART 3 corresponds to total tDCE emission of 50 Tg yr^{-1} . The fluxes of tCFP and tDCE introduced to the model are considerably larger than the expected production of these replacement compounds, by comparison to the 0.496 Tg total global demand for all HCFCs during 2002 listed in Campbell et al. (2005). However, such large fluxes of tCFP and tDCE are needed to produce a numerically significant percentage decrease in O_3 total column in MOZART

3. The model runs required six years to reach a near-steady-state suitable for atmospheric lifetime and ODP analysis.

These large fluxes of a short-lived ozone-depleting substance degraded in the troposphere could alter the OH field in a CTM, resulting in overestimation of the atmospheric lifetime. The reduction of ozone in the troposphere from the large amount of ozone-depleting substance decreases the amount of $O(^1D)$ to react with water vapor, decreasing the production term for OH. This possible lifetime distortion is tested for tDCE (the shorter-lived of the two compounds as determined below) by another MOZART 3 run using one-third the flux of the above run ($0.737 \times 10^{10} \text{ molec cm}^{-2} \text{ s}^{-1}$, or 16.7 Tg yr^{-1}). We expect that this effect will be smaller for tCFP because this longer-lived species should cause less O_3 destruction in the troposphere, so that we did not repeat this test.

3 Results

The first quantity to consider when evaluating ozone and climate effects of a potential replacement compound is the atmospheric lifetime, which can be obtained by evaluating the annual average total atmospheric burden divided by the annual, global total input of the compound. Burdens of tCFP and of tDCE for our MOZART 3 runs in this study are listed in Table 1 for each of the assumed surface emissions cases, along with the derived atmospheric lifetimes against atmospheric chemical reaction. The lifetimes in Table 1 are based on the OH reaction, and do not include the possible, but likely much smaller, additional sinks such as reactions with other oxidants such as O_3 , NO_3 , and Cl, surface deposition, and heterogeneous reactions on clouds or aerosols and thus are upper limits. Both chloroalkenes have short atmospheric lifetimes compared to most compounds they would replace. The lifetime for tCFP is 40.4 days, and that for tDCE with the lower surface emissions input is 12.7 days. The short lifetimes of tCFP and tDCE suggest that these compounds should have a small effect on stratospheric ozone and that they should reach the stratosphere only in very limited amounts.

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The effect of tropospheric O_3 reduction on tDCE lifetime is demonstrated through the difference in lifetimes calculated for 50.0 Tg yr^{-1} versus 16.7 Tg yr^{-1} of tDCE surface flux shown in Table 1. The 50.0 Tg yr^{-1} run obtained an apparent tDCE lifetime of 13.5 days, six percent higher than that from the 16.7 Tg yr^{-1} run. This lifetime increase is smaller than the 10% or greater uncertainty of most reaction rate constants including that for tDCE+OH (Zhang et al., 1991). This shows that the OH decrease in the CTM due to tropospheric O_3 loss is a minimal but nonzero effect for the 50 Tg yr^{-1} run. However, the 50 Tg yr^{-1} run was needed for an adequate O_3 perturbation: the 16.7 Tg yr^{-1} run produced less than 0.1% decrease in total O_3 column compared to that of the reference run, which we have found insufficient for numerical stability in ODP calculations.

Figure 1 shows annually and zonally-averaged mixing ratios in ppt of tCFP (Fig. 1a) and tDCE (Fig. 1b) obtained in MOZART 3 for emissions corresponding to 50 Tg yr^{-1} . In this figure and in other figures of approximate pressure versus latitude that follow, the vertical coordinate is the sum of the hybrid sigma-pressure coordinate coefficients times 1000 hPa, that is $(1000 \text{ hPa}) \times (a_i + b_j)$. Annual and zonal mean tropopause pressure, defined by the WMO thermal tropopause criterion of temperature decrease less than 2 K km^{-1} constrained to altitudes of 6 to 18 km, is indicated by white dotted lines on each of these figures. For both tCFP and tDCE in Fig. 1, high mixing ratios are confined to the Northern troposphere with peak values over 2000 ppt near the surface that decrease strongly toward the tropics or at higher altitudes (lower pressures). The tCFP mixing ratio in the MOZART tropical upper troposphere, shown in Fig. 1a, is around 25 ppt or some 1% of the peak mixing ratio. Figure 1b shows that tDCE is even more strongly constrained to the Northern troposphere, with mixing ratios below 1.0 ppt throughout the tropical upper troposphere and much of the tDCE shown in the Northern lower stratosphere seemingly transported through the midlatitude tropopause. The burdens of tCFP and tDCE separated into troposphere and stratosphere (and above) components, listed in Table 2, indicate the extent to which these candidate replacement compounds are constrained to the troposphere. Stratospheric tCFP accounts for only

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0.84% of the total burden, and stratospheric tDCE is only 0.12% of the total burden. By this measure, neither tCFP nor tDCE reach the stratosphere to a significant extent even at a surface flux as large as 50 Tg yr^{-1} , as expected from their short lifetimes.

Since tCFP and tDCE do not reach the stratosphere in quantity, transport of Cl_y produced by oxidation of these replacement compounds from the troposphere to the stratosphere should be considered as a mechanism for secondary injection. Figure 2 shows the chlorine species perturbations from tCFP and from tDCE obtained in MOZART 3 for 50 Tg yr^{-1} surface flux of each. Total inorganic chlorine Cl_y due to tCFP (Fig. 2a) peaks near the southern limit of the emission latitudes and falls off rapidly in the tropics and the Southern troposphere. The entire MOZART 3 stratosphere has a Cl_y increase of 25 ppt or more, and a secondary maximum (more than 50 ppt) of Cl_y perturbation from tCFP ranges from the North Polar lower stratosphere to the tropics. Comparison to the tCFP perturbation in Fig. 1a suggests that about half of the Cl_y perturbation from tCFP is due to Cl_y transport from the troposphere.

Only the fraction of Cl_y that reacts with odd oxygen species $\text{O}_x = \text{O}_3 + \text{O}(^3\text{P}) + \text{O}(^1\text{D})$ is destructive to ozone. Figure 2b shows the annual and zonally-averaged change in $\text{ClO}_x = \text{Cl} + \text{ClO}$, those Cl_y species most reactive to the O_x species, as calculated in MOZART 3. Despite increases in Cl_y of at least 10 ppt throughout much of the region shown, the most prominent increase in ClO_x is that in the upper troposphere to lower stratosphere for latitudes north of 40°N , although increases over 1 ppt exist throughout most of the stratosphere except for a decrease in the region subject to polar stratospheric cloud (PSC) chemistry.

The shorter lifetime of tDCE more effectively constrains Cl_y perturbations to the Northern troposphere and lower stratosphere below the tropical tropopause, as shown in Fig. 2c. The maximum Cl_y perturbation, over 500 ppt, appears within emission latitudes near the surface. The Cl_y perturbation extends upward and crosses into the stratosphere predominantly at mid-latitudes: Cl_y perturbation is no higher than 10 ppt at the tropopause for latitudes south of 20°N , and even in the Northern latitudes, the 10 ppt contour never reaches an altitude greater than the 150 hPa layer within the lower

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stratosphere. The ClO_x increase resulting from the introduction of tDCE, shown in Fig. 2d, is effectively contained in the Northern troposphere and lower stratosphere; a ClO_x decrease appears in the PSC region as with tCFP in Fig. 2b.

Minimal ClO_x increases in the stratosphere indicate that much of the O_3 loss from tCFP and tDCE can be expected to be contained within the Northern troposphere and lower stratosphere. Figure 3 shows the annual and zonal mean O_3 mixing ratio perturbation from tCFP (Fig. 3a) and from tDCE (Fig. 3b) compared to the reference atmosphere in percent. Most of the stratosphere in Fig. 3a has O_3 within 0.1% of that for the reference run, and mixing ratio decreases of 1% or more exist only in the Northern troposphere and lowermost stratosphere and in the South Polar upper troposphere/lower stratosphere region. For the tDCE perturbation in Fig. 3b, O_3 decreases by 1% or more only in the Northern troposphere and lowermost stratosphere, and indeed O_3 in parts of the Southern and lower tropical stratosphere increases by more than 0.1%.

As part of the ODP calculation, the change in annually averaged total O_3 column due to emission of tCFP and of tDCE incorporated into MOZART 3 is evaluated. ODPs obtained from these calculations with respect to the O_3 column perturbation obtained in the previous CFC-11 run (Wuebbles and Patten, 2009) are listed in Table 3. The ODP of tCFP is 0.00034, and that of tDCE is 0.00024. These are the lowest ODPs obtained for chlorocarbon species in our chemical-transport modeling of ozone-depleting substances. These low ODPs suggest that the O_3 effects of industrial emissions up to 50 Tg yr^{-1} over the latitude range 30°N to 60°N should be minimal.

A calculation similar to that of O_3 column change for ODP can be used to separate O_3 column changes into tropospheric and stratospheric (and above) components, and multiplication of these column components by the area of Earth gives the changes in O_3 tropospheric and stratospheric burden due to the compound. Table 4 lists the changes in O_3 tropospheric and stratospheric burden from tCFP and tDCE in MOZART 3. For the 50 Tg year^{-1} surface emissions of each compound, the total reduction of O_3 burden is approximately 10 Tg, but the fraction of O_3 burden decrease in the stratosphere is nearly half for tCFP, but only 3.5% for tDCE. Though the total O_3 change in the

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16.7 Tgyr⁻¹ tDCE test may be too low to provide a reliable ODP, we proceeded with the O₃ burden calculations for Table 4, and the stratospheric O₃ burden decrease at this lower tDCE flux decreases to 1.9%. High tDCE fluxes in MOZART 3 potentially saturate the oxidizing capacity of the Northern troposphere sufficiently that a slightly larger fraction of the Cl_y perturbation from tDCE reaches the stratosphere to cause O₃ depletion. Notably, Table 4 and Fig. 3 show that much of the O₃ depletion arising from tCFP and most of that from tDCE would occur in the troposphere, rather than the stratospheric ozone layer where most of the long-lived ozone-depleting substances cause O₃ loss.

4 Summary

Atmospheric lifetimes and Ozone Depletion Potentials (ODPs) have been derived for the two chloroalkenes 1-chloro-3,3,3-trifluoropropylene (tCFP) and trans-1,2-dichloroethylene (tDCE) using the MOZART 3 chemical-transport model of the global atmosphere. When emitted from land surfaces in the latitude range 30° N to 60° N in MOZART, the atmospheric lifetime of tCFP is 40.4 days, and its ODP is 0.00034. Emission of tDCE from the same locations in MOZART gives an atmospheric lifetime of 12.7 days and an ODP of 0.00024 for that compound. Based on these results, industrial uses of these compounds are unlikely to lead to significant ozone depletion effects. Much of the minimal ozone loss that does result from these compounds, especially tDCE, occurs in the troposphere.

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Table 1. Annual averaged, global total burdens and atmospheric lifetimes against atmospheric chemical reaction derived for the chloroalkenes trans-1-chloro-3,3,3-trifluoropropylene (tCFP) and trans-1,2-dichloroethylene (tDCE) in MOZART 3.

Compound	Flux (Tg yr^{-1})	Burden (Tg)	Lifetime (days)
tCFP	50.0	5.54	40.4
tDCE	50.0	1.85	13.5
tDCE	16.7	0.582	12.7

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Table 2. Burdens of tCFP and tDCE calculated in MOZART 3 troposphere and stratosphere for 50.0 Tg yr^{-1} surface flux of each compound.

Compound	Troposphere		Stratosphere	
	Burden (Tg)	% of total	Burden (Tg)	% of total
tCFP	5.494	99.16	0.046	0.84
tDCE	1.8499	99.88	0.0023	0.12

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Table 3. Ozone depletion potentials (ODPs) derived for tCFP and for tDCE.

Candidate Compound	ODP
tCFP	0.00034
tDCE	0.00024

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Table 4. Annually averaged, global tropospheric and stratospheric ozone burden changes (Tg) calculated in MOZART 3 for surface fluxes of tCFP and of tDCE.

Compound	Surface flux, Tg yr ⁻¹	Troposphere		Stratosphere	
		ΔO_3 burden (Tg)	% of change	ΔO_3 burden (Tg)	% of change
tCFP	50.0	5.756	53.1	5.093	46.9
tDCE	50.0	9.870	96.5	0.361	3.5
tDCE	16.7	3.192	98.1	0.061	1.9

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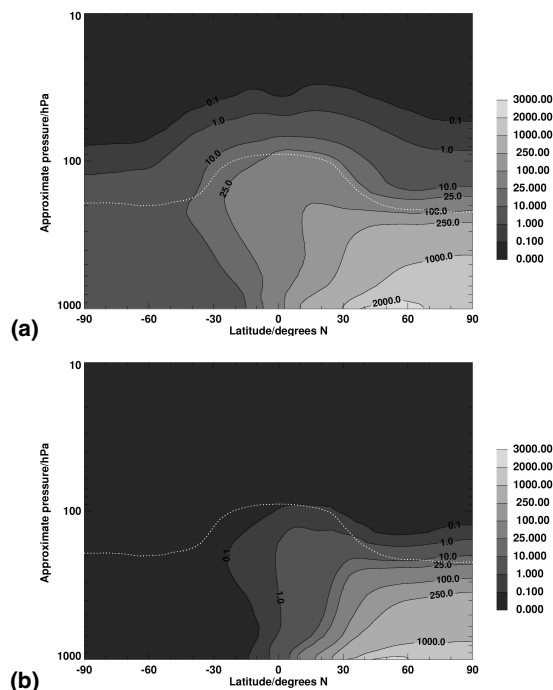


Fig. 1. Annually and zonally-averaged mixing ratio in ppt of the chloroalkenes obtained in MOZART 3 for emissions from the land masses between 30° N and 60° N. In this and the following figures, the white dotted line shows the average tropopause pressure. **(a)** trans-1-chloro-3,3,3-trifluoropropylene (tCFP) at 1.64×10^{10} molec cm⁻² s⁻¹. **(b)** trans-1,2-dichloroethylene (tDCE) at 2.21×10^{10} molec cm⁻² s⁻¹.

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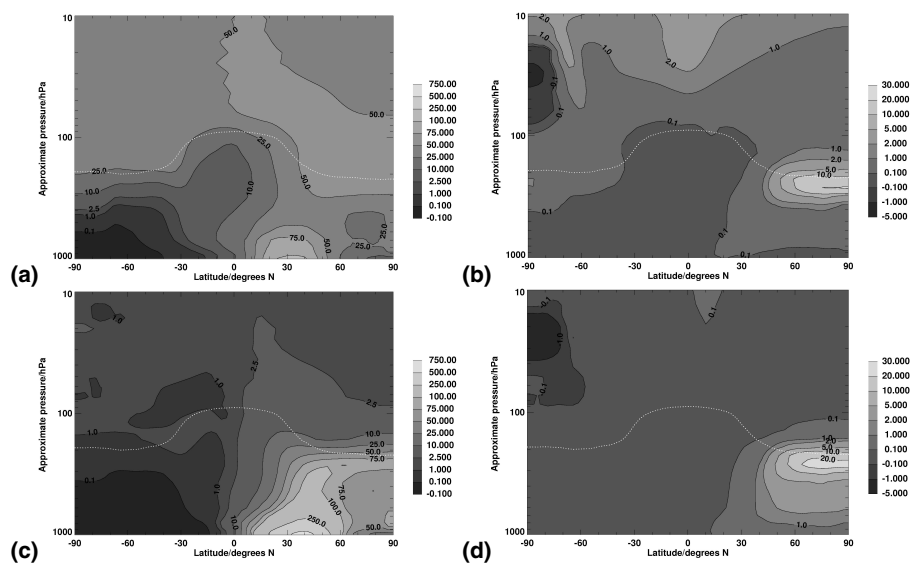


Fig. 2. Annual and zonally-average chlorine perturbations (mixing ratio, ppt) in MOZART 3 resulting from the chloroalkene source gases. **(a)** All inorganic chlorine (Cl_y) from tCFP. **(b)** Reactive chlorine (ClO_x) from tCFP. **(c)** Cl_y from tDCE. **(d)** ClO_x from tDCE.

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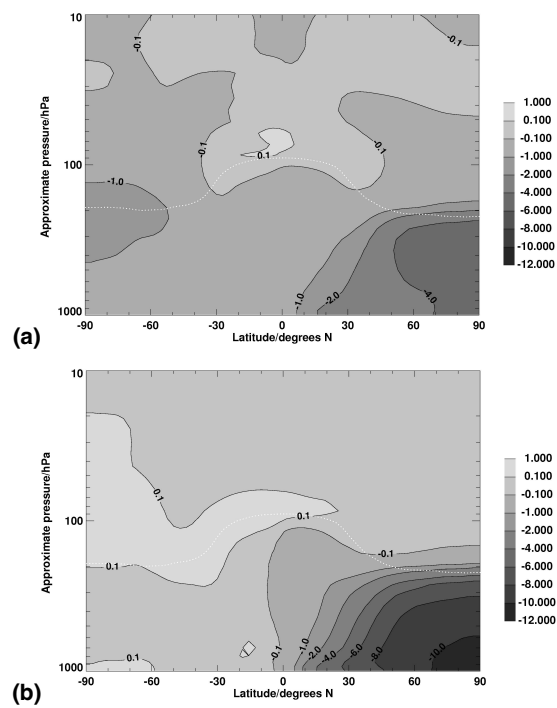


Fig. 3. Annual and zonally-averaged percent change in ozone arising from the chloroalkenes in MOZART 3. **(a)** tCFP, **(b)** tDCE.