Preliminary report: Analyses of tCFP's potential impact on atmospheric ozone

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Abstract

Trans-1-chloro-3,3,3-trifluoropropylene (tCFP, $CHCl=CHCF_3$) is a chemical compound proposed to substitute for currently used blowing agents due to tCFP possessing advantages for fire safety, air quality, and climate properties. As a molecule containing a chlorine atom, tCFP might be of concern because of its potential to affect the amount of ozone in the global atmosphere. This study uses a state-of-the-art 3-D global atmosphere chemistry-climate model to evaluate such potential impacts. Our analyses indicate that that there is statistically zero (less than 0.01%) impact on global atmospheric (tropospheric and stratospheric) ozone abundance if tCFP were substituted for all compounds it might replace and assuming all of the tCFP used is released into the atmosphere. We also found that a tCFP source strength of 21.72Tg/yr would be necessary to result in a decrease of annually-averaged global atmospheric ozone of 0.1%, a small but statistically significant impact. We also derived that the ODP of tCFP is 0.00024 assuming emissions occurring in the major parts of the world that are heavy users of the blowing agents tCFP might replace.

Introduction

Trans-1-chloro-3,3,3-trifluoropropylene (tCFP, chemical formula $CHCl=CHCF_3$) has been proposed as a potential substitute compound for currently used blowing agents with potential climate issues (the hydrofluorocarbons (HFCs) HFC-254a, -365mfc, -134a, -227ea and the hydrochlorofluorocarbons (HCFCs) HCFC-141b, -142b, -22) or with flammability and air quality concerns (the hydrocarbons (HC) c-Pentane, n-Pentane). However, tCFP contains chlorine, and possible stratospheric ozone loss from its release of chlorine to the atmosphere is of concern. We carry out this study in order to assess tCFP's impact on ozone in the atmosphere with a state-of-the-art numerical model that simulates the chemistry and physics of the atmosphere. In particular, we are interested in how much the impact on atmospheric ozone would be if all blowing agents were substituted by tCFP and all tCFP used were released into the atmosphere. In addition, we are interested in how much tCFP would be necessary to result in 0.1% loss in global ozone. We develop two emission cases to address these two questions. This is a brief report of our preliminary findings.

Model description

For this study, we use the Whole Atmosphere Community Climate Model (WACCM) version 3.5.48, an atmosphere chemistry-climate model developed by the National Center for Atmospheric Research (NCAR). The model has been evaluated and used in a number of scientific studies, for example, in the Stratospheric Processes and their Role in Climate (SPARC) 2010 Report (Eyring et al., 2010). WACCM 3.5.48 numerically simulates the atmosphere from the surface up to 4.5 $\times 10^{-4}$ Pa (~145km). The horizontal resolution is 2.5° longitude ×1.9° latitude. The model is run in offline mode, which means that the meteorological fields are provided by a previous run of WACCM 3.5 representing the year 2000 atmosphere (Garcia, private communication, 2007). The model simulates 125 chemical species and uses the JPL06 recommendations (Sander et al., 2006) including extensions for non-methane hydrocarbon chemistry, which is key to good representation of tropospheric oxidative capacity. The model has good performance in simulating the stratosphere and the upper troposphere and lower stratosphere as shown in e.g., the Chemistry-Climate Model Validation Activity (CCMVal) (Eyring et al., 2010; Gettelman et al., 2010).

The tCFP decomposition in the atmosphere is primarily initiated by its reaction with hydroxyl radical (OH) in the troposphere. Here we adopt the most recent estimate of the reaction rate of 4.4×10^{-13} cm^3 $molec^{-1}$ s^{-1} (Anderson et al., 2008), assuming no temperature dependence.

The Modeling Studies

Two different types of analyses are done in this study towards understanding the potential effects of tCFP on ozone. The first case, *Perturbation 1*, is designed to determine the maximum impact tCFP emissions, assuming tCFP use as a blowing agent, could possibly have on atmospheric ozone. We assume in this scenario the currently used blowing agents, as listed for different regions in Table 1 (Rajiv Singh, private communication, 2011), are completely substituted by tCFP. The estimated release rate into the atmosphere is around 20%; however, here we assume that 100% of the tCFP used is released into the atmosphere, to study the maximum possible impact. Thus a global tCFP emission rate of 0.171 Tg/yr is derived. Based on the data in Table 1, we calculate tCFP emissions for European Union, Japan, China, India, Turkey, Middle East and North Africa, Latin America and North America, assuming that within each region tCFP is uniformly emitted both spatially and temporally. Figure 1 depicts tCFP emissions distribution in perturbation 1 scenario.

The second case, *Perturbation 2*, examines how much tCFP would cause a 0.1% loss in global column ozone. A previous study by Patten and Wuebbles (2010) found that a 50.0 Tg/yr tCFP emission resulted in 0.321% decrease in global column ozone. Thus in the second scenario we assume globally 15.57 Tg tCFP is emitted into the atmosphere per year. The geographic pattern of this emission is the same as that in Figure 1, except that the emission rate is 91 times larger than that in Figure 1. It is expected to cause nearly 0.1% loss in total atmospheric ozone in this

scenario. In this study the model result can be different from being exactly 0.1% loss. In this case, we can scale the emission so as to achieve 0.1% ozone loss. This is justified because previous studies have shown that within this still small magnitude of perturbation ozone changes linearly with emissions.

In addition to the two tCFP perturbation scenarios, we run a *reference* scenario which is identical to the perturbation scenarios except that no tCFP is emitted. The emissions and lower boundary concentrations of the major source gases correspond to year 2004 background atmosphere. NO_x source from lightning is 5.0 TgN, according to Schumann and Huntrieser (2007). The model set-up is described in Patten et al. (2011).

Results

To ensure that the model is run to chemical steady state, we carry out seven years of simulation for each of the above stated scenarios. The year-to-year variation is less than 0.02% for ozone and less than 0.03% for tCFP. Only the seventh year's result is shown here.

The steady state global atmospheric burdens of tCFP derived for the two scenarios are 0.014 and 1.313 Tg (Table 2) for Perturbations 1 and 2, respectively. These correspond to the assumed tCFP emissions of 0.171 and 15.57 Tg/yr, respectively. Based on these simulations, the first-order estimate of tCFP's lifetime is ~29.9 and ~30.8 days based on the first and second perturbation scenarios, respectively. These are lower than the ~ 40 day lifetime estimate of Patten and Wuebbles (2010). The difference may arise both from differences in the assumed emission distribution and from this study using an updated version of the atmospheric model.

Simulated tCFP mixing ratios are highest near the surface in the Northern Hemisphere and decrease quickly with altitude, with extremely little tCFP reaching the Southern Hemisphere (Figures 2 and 3). Peak zonal mean mixing ratios are ~ 3.4 ppt for the Perturbation 1 scenario, the maximum possible real world emissions. In Perturbation 2, peak mixing ratios are as high as 400 pptv. These features, mixing ratio decreases with altitude and decreases southward, are to be expected given tCFP's short lifetime and its predominant emissions in the Northern Hemisphere.

In the first perturbation scenario the Cl_y (= Cl + 2×Cl + ClO + OClO + 2×Cl_2O_2 + HCl + HOCl + $ClONO_2$ + BrCl) mixing ratio increased by no more than 10% in the troposphere, with more increase in the lower troposphere at northern mid- and high-latitudes (Figure 4). In the second perturbation scenario, the Cl_y mixing ratio increases to more than 6 times of that in the reference atmosphere in the lower northern troposphere (Figure 5).

Figures 6 and 7 show the relative change (%) of annual, zonal mean ozone mixing ratios in the perturbation cases compared with those in the reference scenario. As shown in Figure 6, there is no systematic shift of ozone mixing ratios in the perturbation 1 scenario. These emissions result in a 0.0073% change in global ozone burden (Table 3). Changes of this magnitude are not

statistically significant from the model variability, and thus are not statistically different from zero.

In Perturbation scenario 2, with the 15.57 Tg tCFP emission (designed specifically to achieve a statistically significant change), there is 0.072% total atmospheric ozone loss much of which occurs in the troposphere. As shown in Figure 6, there is 0.2%~0.8% ozone loss in troposphere in the northern hemisphere, with largest relative loss at high-latitudes. Overall tropospheric ozone decreases by 0.29%. Scaling this result we estimate that a 21.72 Tg per year tCFP emission would lead to a 0.1% loss in global ozone. Thus, in order for tCFP to have caused an ozone loss of 0.1% it would need to be emitted at a rate nearly two orders of magnitude greater than the worst case real world estimates used in Perturbation scenario 1. Also from this simulation we calculate the ODP of tCFP using an approach akin to that used in Patten and Wuebbles (2010). The derived ODP for this assumed distribution of emissions was found to be 0.00024. Although this is slightly lower than the ODP of 0.00034 determined in Patten and Wuebbles (2010), it is similar in magnitude. As with the difference in lifetime this difference may arise both from differences in the assumed emission distribution and from this study using an updated version of the atmospheric model.

Conclusions

Our modeling study suggests that the potential impact of tCFP on ozone in the atmosphere is likely to be extremely small, essentially immeasurable. If currently used blowing agents were to be entirely replaced by tCFP and all of the tCFP used were released to the atmosphere, the impact on atmospheric ozone will be statistically zero (less than 0.01% change in total column ozone). To cause a statistically significant level of 0.1% loss in total column atmospheric ozone, tCFP emission must reach 21.72 Tg/yr, which is nearly 130 times above the current emissions of all blowing agents usage in 2010. The ODP for tCFP using the regionally assumed emissions in this study is 0.00024, an extremely small value.

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Table 1. HFCs, HCFCs and hydrocarbons (HC) usage (in Mlbs) as blowing agents in 2010 in major regions of the world that have heavy users of blowing agents (Rajiv Singh, private communication, 2011).

	EU[a]	Japan	China	India	Turkey	MENA[b]	L.A.[c]	N.A.[d]	total
total	83.4	15.0	116.2	22.0	11.5	22.9	39.9	65.8	376.7

[a] EU: European Union
[b] MENA: Middle East and North Africa
[c] L.A.: Latin America
[d] N.A.: North America

Table 2. Global tCFP emissions (Tg/yr) used in the model, and the derived atmospheric burdens (Tg) and lifetimes (days) in the two perturbation cases.

	global emission (Tg/yr)	atmospheric burden (Tg)	lifetime (days)
Perturbation 1	0.171	0.014	29.9
Perturbation 2	15.57	1.313	30.8

Table 3. Global atmospheric, tropospheric and stratospheric ozone burdens (Tg) derived in the model for the scenarios studied, and the determined percentage changes in ozone relative to the reference scenario.

	global O_3	% change from ref.	trop. O_3	% change from ref.	strat. O_3	% change from ref.
Reference	3139.86		369.18		2770.68	
Perturbation 1	3140.09	+0.0073	369.20	+0.0054	2770.88	+0.0072
Perturbation 2	3137.60	-0.0717	368.12	-0.2881	2769.49	-0.0429

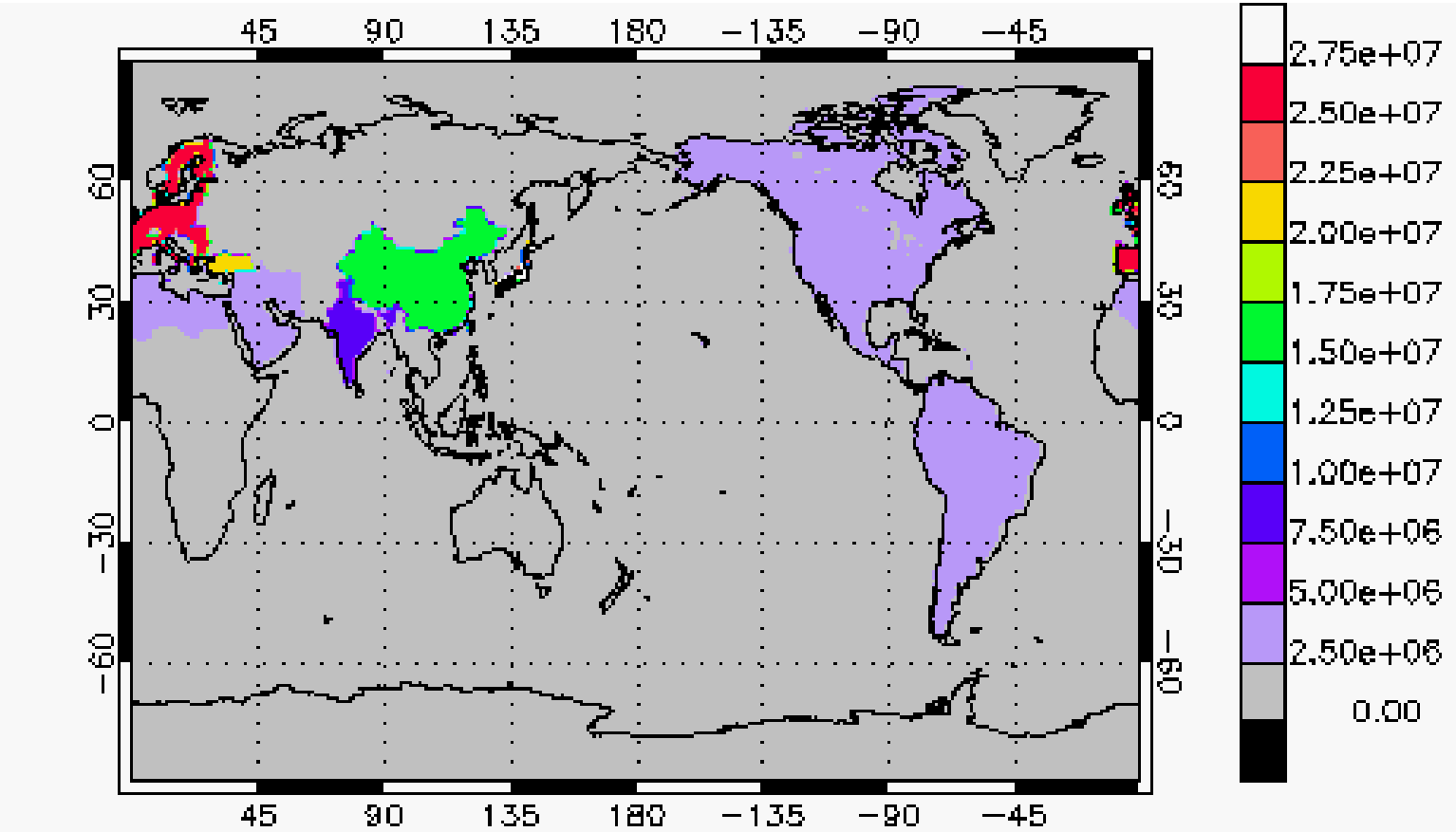

Figure 1. The assumed tCFP emissions (molecules/cm^2 s) in the Perturbation 1 scenario.

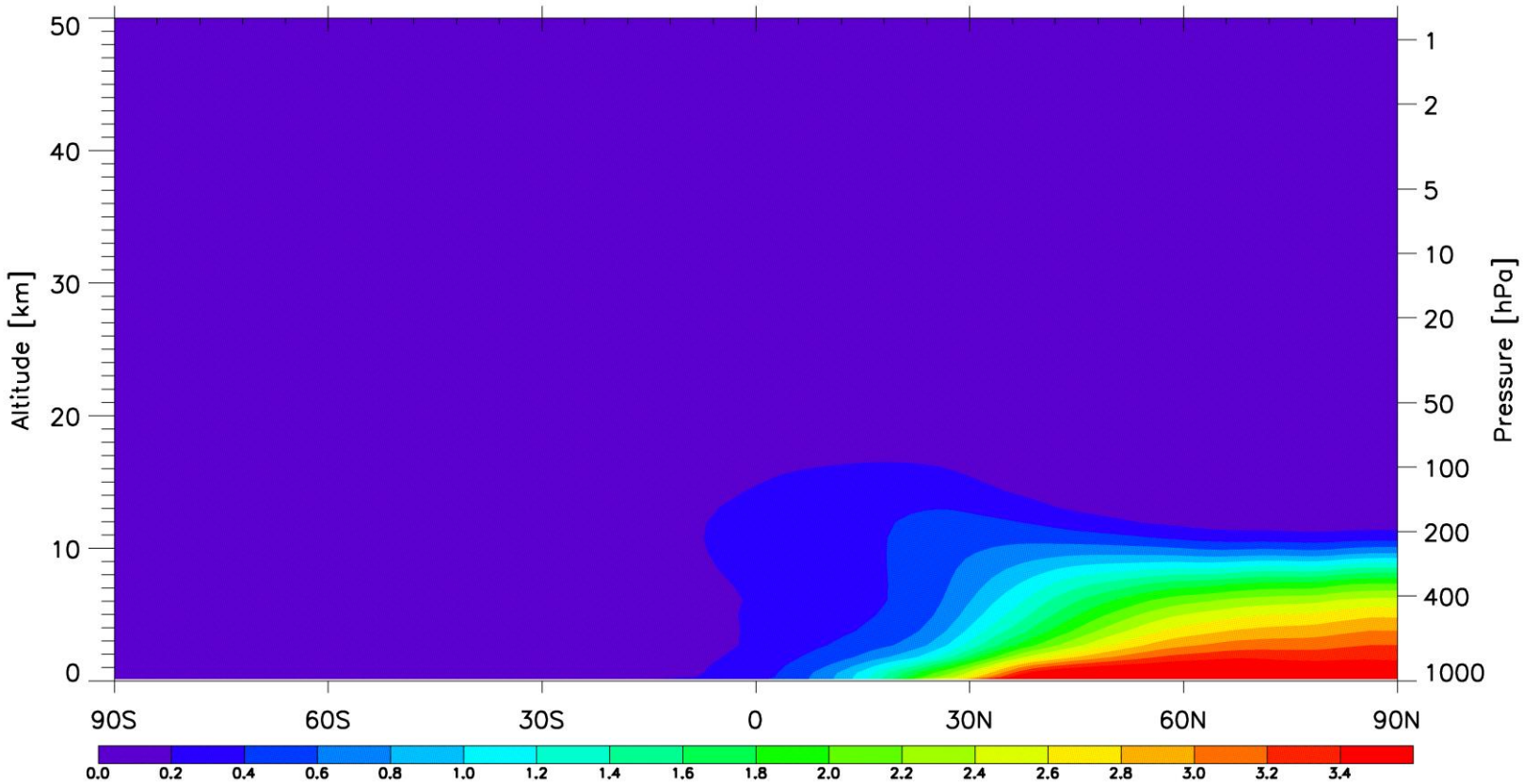

Figure 2. Annual, zonal mean tCFP mixing ratio (pptv) derived for Perturbation 1, the scenario in which currently used blowing agents have been substituted by tCFP and the used tCFP is completely released to the atmosphere.

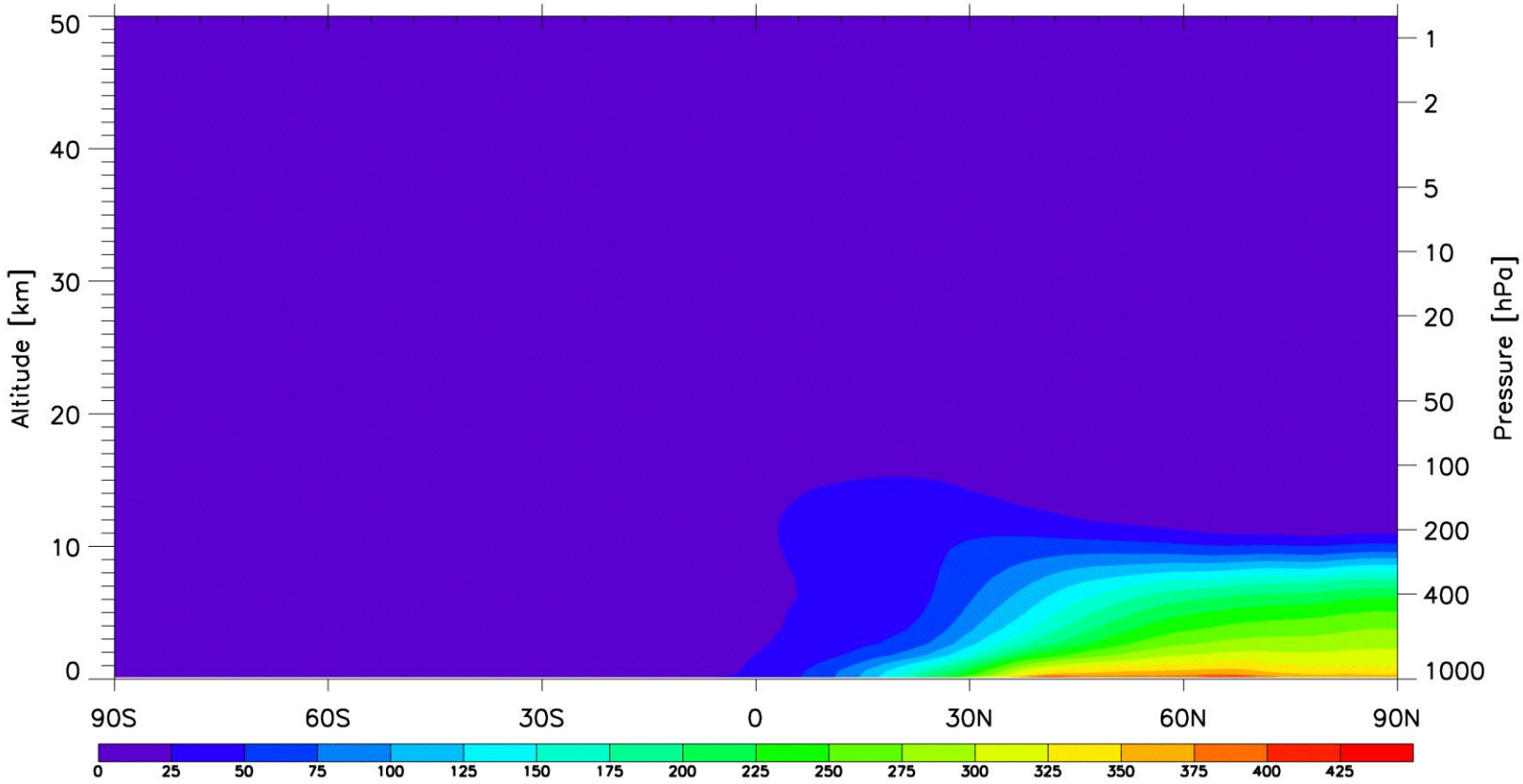

Figure 3. Annual, zonal mean tCFP mixing ratio (pptv) derived for the 15.57 Tg tCFP per year emission scenario.

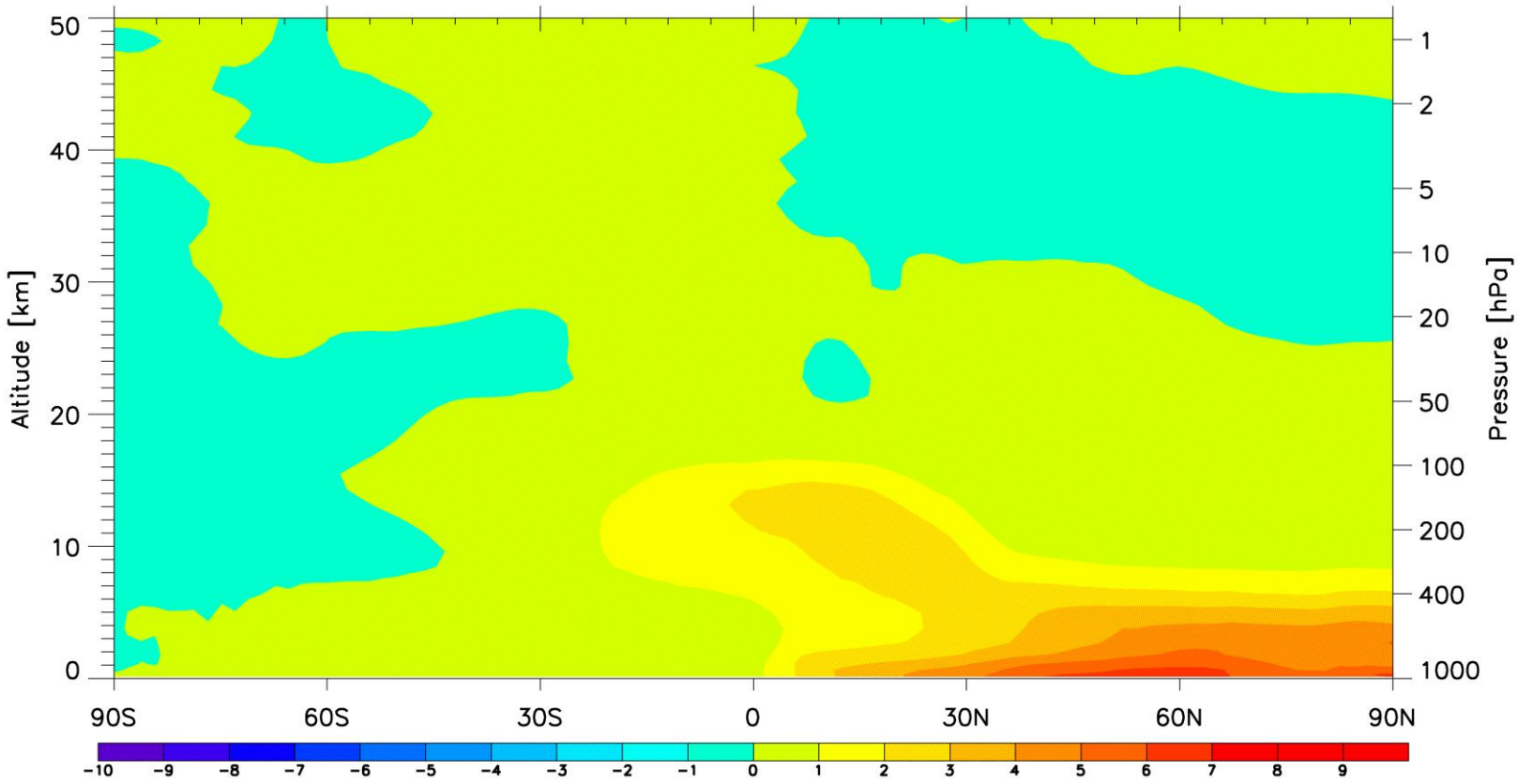

Figure 4. Change (%) in annual, zonal mean Cl_y mixing ratio derived for Perturbation 1, the scenario in which currently used blowing agents have been substituted by tCFP and the used tCFP is completely released to the atmosphere, relative to the reference scenario.

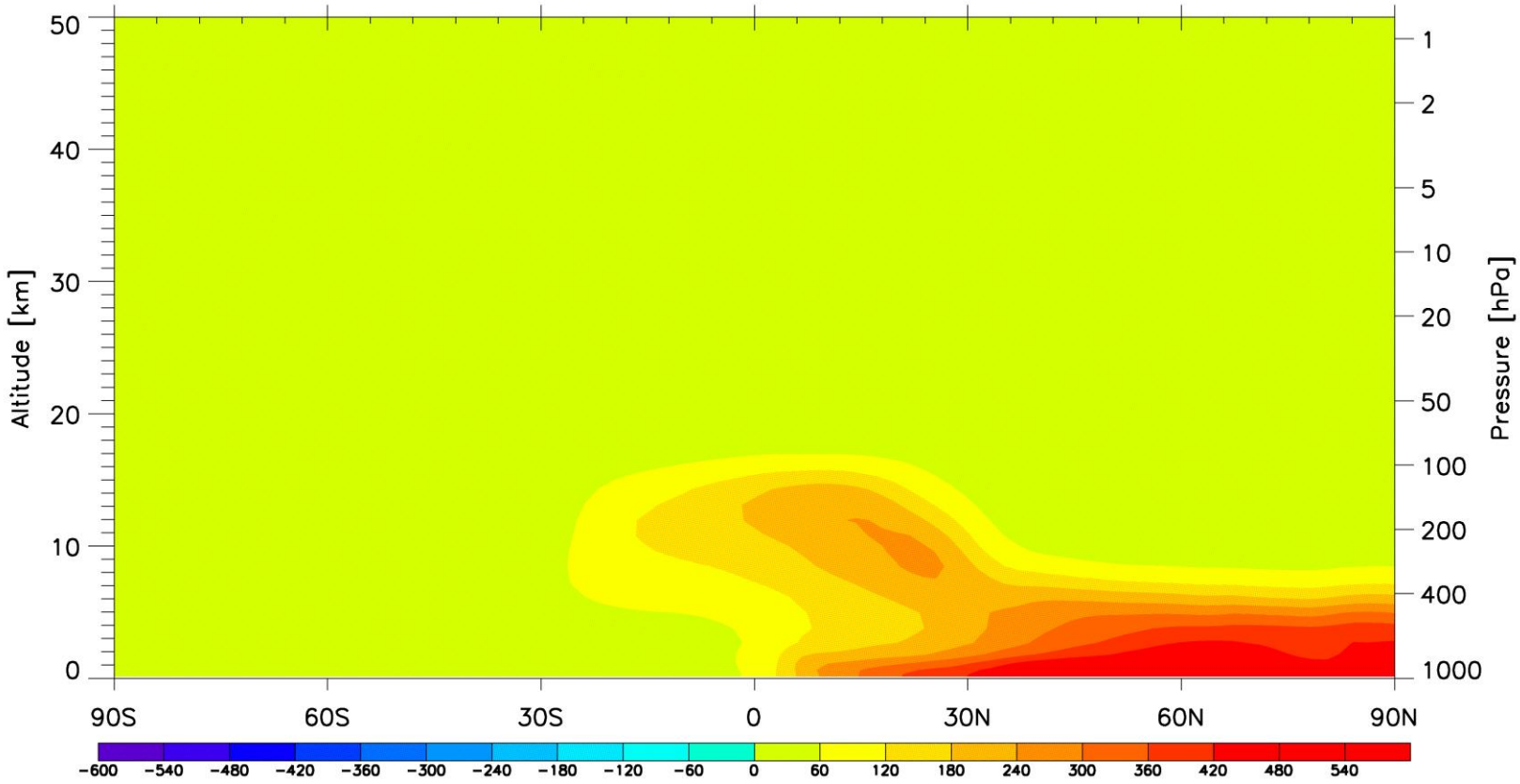

Figure 5. Change (%) in annual and zonal mean Cl_y mixing ratio derived for the 15.57 Tg tCFP per year emission scenario (Perturbation 2) relative to the reference scenario.

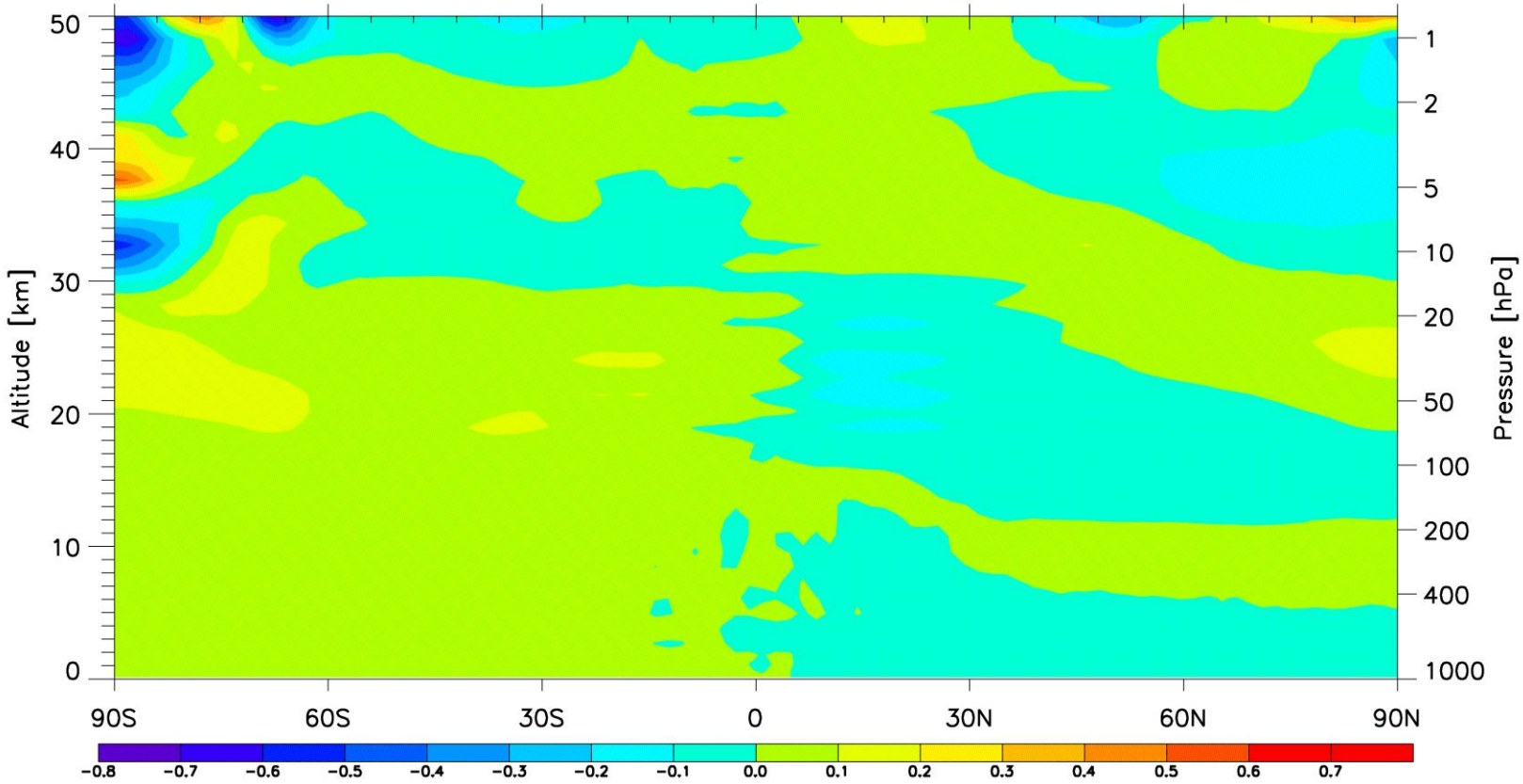

Figure 6. Change (%) in annual, zonal mean ozone mixing ratio derived for Perturbation 1, the scenario in which currently used blowing agents have been substituted by tCFP and the used tCFP is completely released to the atmosphere.

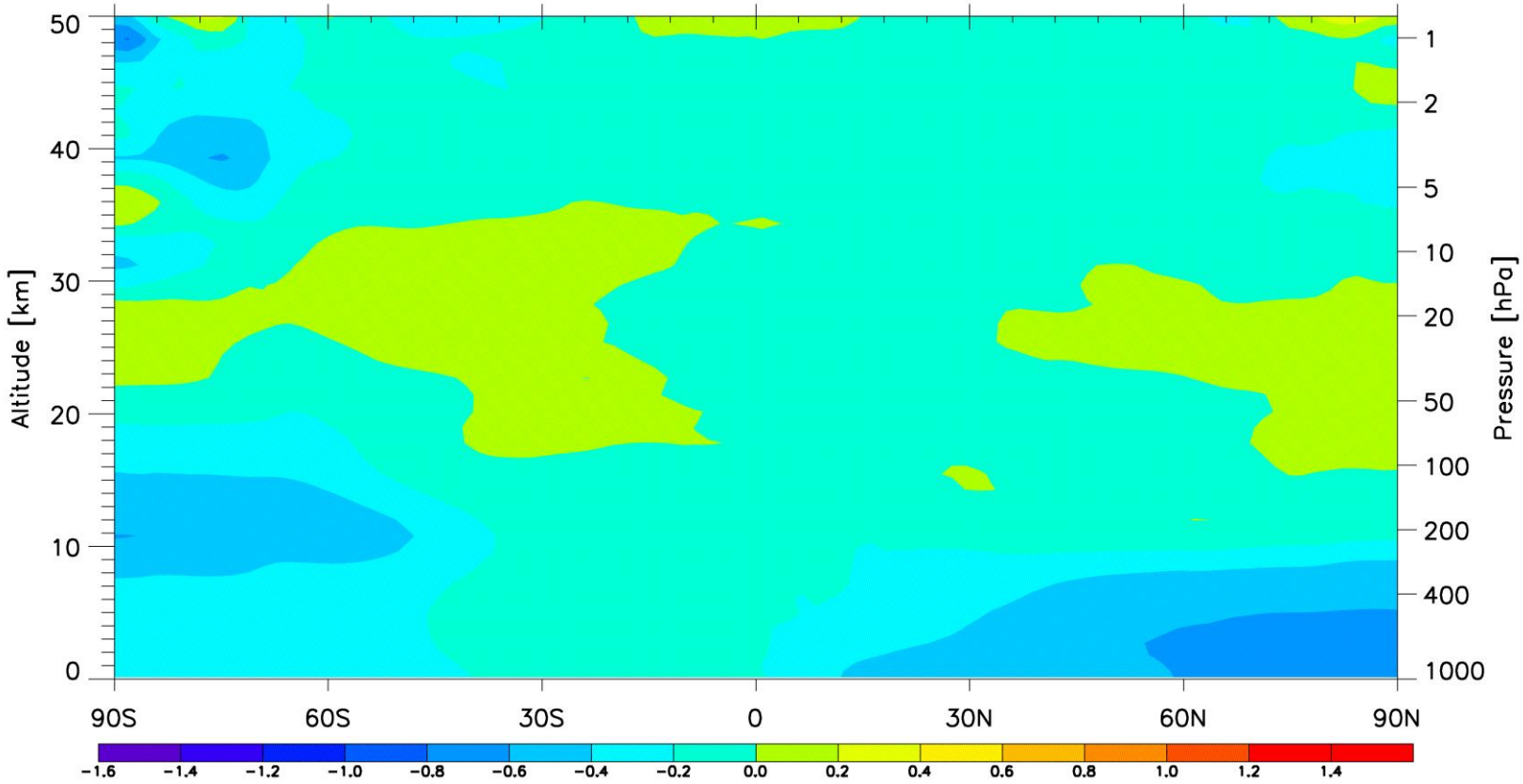

Figure 7. Change (%) in annual, zonal mean ozone mixing ratio derived for the 15.57 Tg tCFP per year emission scenario (Perturbation 2) relative to the reference scenario.