

Environmental Aspects of Halon Replacements: Considerations for Advanced Agents and The Ozone Depletion Potential of CF₃I

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Introduction

The introduction of a new chemical species into the environment raises the question of the ultimate fate of that compound. In most cases, any compound which is introduced into the environment can undergo various transformations, physical and chemical. If it is solid or liquid, it can evaporate; from any form it can be dissolved into the aqueous; liquids or gases can be absorbed onto solids. Dissolved species can coagulate or precipitate. Of considerable importance is accumulation in the biosphere, which can take place when the chemical is lipid soluble. In this case, the concentration of the substance through the food chain becomes important. In concert with these physical transformations are chemical transformations such as oxidation, photolysis, hydrolysis, and complexation. Biodegradation also takes place, often enzymatically. It is important to understand both the rates and the mechanisms of these transformations in order to evaluate the environmental impact of a chemical species which may be introduced into the environment. Of course, for any particular species one pathway is likely to dominate its fate but, in general, all possibilities must be considered.

Due to the phase-out of the very popular fire suppressant CF₃Br, a major effort was initiated to develop alternative agents or strategies. Initial work involved the investigation primarily of other halogenated compounds, with particular emphasis on those containing iodine, especially CF₃I. Significant activity also involved hydrofluorocarbons. Over the past several years, we have focussed the efforts of our activities on the environmental fates of these replacement fire suppressants. This work has included studies of the reactivity of the hydroxyl radical towards some of these HFCs (Zhang et al., 1994), and thus their tropospheric lifetimes and an investigation of the subsequent behavior of the fluorinated peroxy radicals resulting from OH attack (Shoute et al., 1994). In recent work, we have estimated the ozone-depletion potential of CH₂ClBr, an alternate bromine-containing fire suppressant (Orkin et al., 1996). Some work has also addressed some of the more complex aspects of the tropospheric chemistry of iodine

(Williamson et al., 1996). These studies were carried out at both NIST and ARL and have involved the application of a number of experimental techniques. These have included flash photolysis-resonance fluorescence for the determination of OH rate constants, laser-flash photolysis-kinetic absorption spectroscopy for the study of atom-radical and radical-radical reactions, a discharge-flow system coupled to a beam-sampling triple-quadrupole mass spectrophotometer for the investigation of complex reaction mechanisms, and a far-uv spectrophotometer for measurement of absorption cross sections. In the work to be described subsequently, the modeling capabilities of LLNL and UI/UC were employed in order to convert the basic laboratory data into the practical information of interest: the ozone depletion potential. To **assess** the environmental impact of advanced fire-suppressant agents, all of these experimental and modelling approaches will be needed, along with many additional experimental techniques.

Because of the initial great interest in CF_3I , much of our work has focussed on the environmental fate of this compound. The effort required for CF_3I is instructive since, when suggested as a fire suppressant, it was considered environmentally benign due to its short tropospheric lifetime. Due to the likelihood of a very efficient ozone destruction cycle involving iodine, however, it became apparent that the ozone depletion potential needed to be established clearly before it was accepted for widespread use. To establish the importance of CF_3I in stratospheric ozone destruction, we first remeasured the absorption cross section of the molecule in the ultraviolet as a function of temperature to establish better its tropospheric photolysis rate (Fahr et al., 1994). Subsequently, we determined rate constants for the cross reactions, $\text{IO} + \text{ClO}$ and $\text{IO} + \text{BrO}$, and other reactions critical to the iodine-based ozone destruction cycle (Huie et al., 1995). In this paper we include a report on the conclusion of this effort: modeling the impact of tropospheric release of CF_3I on stratospheric ozone.

Although the investigation of the environmental behavior of CF_3I involved a particular progression of experimental and modelling studies, this particular set will not be true generally. Each compound or class will require its **own** screening process to determine which characteristics need to be investigated further in order to establish the environmental consequences of release. This is not surprising since these are all unique classes of chemicals. The initial search for new fire suppressants has expanded from the relatively well-studied area of the halocarbons towards what are termed advanced agents -- entirely new classes of chemicals which show promise as fire suppressants. Often, little is known about their environmental behavior. For some of the suggested compounds, information which can be obtained from the scientific literature may prove sufficient. It is more likely, however, that most will require at least data leading to a determination of the atmospheric lifetime and, possibly, information on possible accumulation in the biosphere. Two examples of classes of fire retardants which have been suggested recently are the fluorophosphazene and the perfluoroalkyl amines. These demonstrate the paucity of data and illustrate some of the various studies which need to be carried out.

Tris-(trifluoromethyl)-amine, $(\text{CF}_3)_3\text{N}$, has been suggested as a constituent in a number of applications, including fire suppression (Fukaya et al., 1993,1995). The broad range of applications points to the unreactivity of the species and its apparent lack of toxicity. Although this compound will have a negligible ozone depletion potential, possible

mechanisms for its removal from the environment need to be investigated. The presence of the three strongly-electron withdrawing substituents about the nitrogen argue against an oxidative mechanism but, coupled with the apparent relative weakness of the C-F bonds (Hayashi et al., 1988), suggests the possibility of reductive dehalogenation. We intend to investigate this possibility by use of pulse radiolysis and gamma radiolysis. Derivatives of $(CF_3)_3N$ have also been explored as fire suppressants (Takahashi et al., 1995). Many of these are likely to have much more rapid atmospheric loss reactions than $(CF_3)_3N$. One example that has shown good fire suppression efficiency is perfluoro(dimethylaminomethyl bromide), which was claimed to be reactive toward the hydroxyl radical (Taoda et al., 1993) .

Phosphazenes have also been suggested recently for flame suppression use, based partly on the use of this family in flame retardation (Skaggs et al., 1995). These compounds all contain the basic -P=N- structure, with various substituents usually bound to the phosphorus atom. Little is known about possible atmospheric reactions of these compounds, but hydroxyl addition certainly seems a possibility. We will establish the reactivity of the most basic fluorinated phosphazene, $N_3P_3F_6$, by use of flash photolysis-resonance fluorescence. The uv spectra of a number of the cyclic derivatives have been investigated. The absorption was in the far uv, with a weak band at about 260 nm and a stronger one at 210 nm, indicating a lack of aromaticity and no loss mechanism in the atmosphere due to photolysis (Lakatos et al., 1969).

Ozone Depletion Potential of CF_3I

We have calculated the Ozone Depletion Potential (ODP) of CF_3I using a combination of a three-dimensional transport model (IMPACT) including convection to determine the distributions of CF_3I and CH_3I , and a two-dimensional photochemical transport model (LOTUS) averaged over longitude to determine the photochemical response of ozone to the introduced iodine. We have used the new laboratory information on IO cross sections and the rate constants of the reactions of IO with O, ClO, and BrO to significantly reduce the uncertainties in the calculation. The atmospheric lifetimes of these iodine-containing source compounds are on the order of days as a result of their ability to decompose on absorption of visible sunlight. As discussed by Solomon and coworkers (Solomon et al., 1994), treating the transport and photochemistry of CF_3I and its iodine-containing decomposition products in a model without convection will not properly represent the delivery of iodine from the troposphere to the stratosphere. While 2-D zonal average models without convection are used to evaluate ODP's for longer-lived (order of years) chlorine- and bromine-containing substituted hydrocarbons, CF_3I 's ODP would be underpredicted by such a model.

Solomon and coworkers used observations of a short-lived surface-emitted radionuclide and a general circulation model calculation of the radionuclide's distribution, as well as their 2-D model, to estimate the ODP of CF_3I conservatively as 0.008 and more probably less than 0.0001. In this report, we have used a direct calculation of the distribution of CF_3I in a **3-D** model with a convective transport parametrization to drive a 2-D photochemical model of the ozone impact. Our calculated value most directly comparable to the Solomon et al. estimate is 0.0015, but depending on assumptions related to distributions of CF_3I surface emission and the wet deposition in the troposphere of iodine-containing products, our values of the

stratospheric ODP for surface emission of CF_3I range from 0.0008 to 0.006. A value as small as 0.0001 is unlikely in view of the recently measured rate constants for the important rate-limiting ozone destruction steps, $\text{IO}+\text{ClO}$ and $\text{IO}+\text{BrO}$.

Chameides and Davis (1980) and Chatfield and Crutzen (1990) have proposed photochemical mechanisms for the reactions of iodine compounds in the troposphere and have identified processes that can reduce tropospheric ozone, particularly through the reaction of IO with HO, to produce HOI. Although the 2-D model does not represent the zonal heterogeneity of the trace species in the troposphere, which can significantly affect free tropospheric ozone, it does produce an indication of the extent of ozone destruction which may occur in this region. Ten to fifteen per cent of the total ozone column resides in the troposphere and it is proportionately more important to controlling surface ultraviolet because of increased scattering. When the calculated change in tropospheric ozone is included, the ODP of the surface emission case is approximately doubled.

Emission at altitude in the 2-D model zones just below and above the tropopause results in enhanced ODP values of 0.4 to 6, respectively. For the ODP reference compound, CFCl_3 , as well as for longer-lived compounds like Halons 1301 and 1211, a significant percentage of the total atmospheric burden is decomposed by stratospheric photolysis and the altitude of emission does not materially affect how much halogen is released in the stratosphere. For CF_3I , only a small fraction of the total burden is decomposed in the stratosphere, so releasing CF_3I directly into the stratosphere will result in an effect on ozone that to first order is greater by that fraction. Release in the upper troposphere also enhances the opportunity for the compound to be entrained into the stratosphere by transport. This effect is indicated in the 2-D model results, although the processes of stratosphere-troposphere exchange are difficult to model well in two dimensions. These higher values may not really affect the viability of CF_3I as a replacement, however, since the proportion of emissions at altitude should be small.

Models and Methods

The 3-D transport model used in this report, IMPACT, has been developed at LLNL and used in several studies of radionuclide tracer and source gas transport and tropospheric NO, sources and distributions (Rotman et al., 1994 and Rotman, 1996). IMPACT transports species in three dimensions on a 2° latitude by 2.5° longitude horizontal grid with 25 vertical layers of varying thickness from the surface to about 1 mb. The winds used are supplied from the NASA/Goddard Data Assimilation System (DAS) model, which assimilates observations (from 1992 in this case) into a mass conserving flow field that is updated every 6 hours. The convective mass flow values are also taken from the DAS model and convective transport implemented in an implicit algorithm described by Walton et al. (1988). Convective mass flow can move air from near the surface to the region of the tropopause in minutes, much more rapidly than the advective winds, so that this process is crucial for determining the distribution of surface-emitted species that are otherwise destroyed near their sources. Atmospheric loss of CF_3I is dominated by photolysis, which is included in IMPACT as a first order loss operator. Both transport and photolysis operate on a three minute time step. Diurnally and zonally averaged photolysis rate constants were interpolated from monthly output of a 2-D simulation of CF_3I in the ambient atmosphere.

March monthly average CF_3I mixing ratios, calculated by IMPACT and zonally averaged, are shown for three altitudes in Figure 1, the surface (highest values) and about 8 (intermediate

values) and 14 km (lowest values). CF_3I at 14 km, near the tropopause in the equatorial region, is somewhat larger than 111000 times the surface value. Without the effects of convection, this value would be more than an order of magnitude smaller. Solomon and coworkers estimate this value would range between 1/20 and 1/100 at midlatitudes in spring and winter for ^{222}Rn , which has a 5.5 day lifetime compared to the shorter 1-3 day lifetime of CF_3I near the surface. The formation of the monthly and zonal averages reduces the peak upper tropospheric CF_3I values seen in the instantaneous IMPACT output, which can be an order of magnitude larger.

The 2-D zonal average photochemical model, LOTUS, was also developed at LLNL and represents photochemistry, transport, and long- and short-wave radiative transfer in the troposphere and stratosphere (Kinnison et al., 1994). The model's grid is 5° in latitude from pole to pole and about 1.5 km in altitude from the surface to 85 km. Transport of species in the model is self-consistently calculated using the predicted model ozone and seasonally varying climatological temperatures. In these simulations, CF_3I and CH_3I were **not** transported in LOTUS, but were constrained to IMPACT results. All other species, including the iodine-containing products of CF_3I photolysis, were subject to the mean meridional circulation and to eddy diffusive mixing. IMPACT monthly average CF_3I and CH_3I distributions were averaged over longitude and interpolated smoothly in time for the respective model runs. The photochemical mechanism represents the interactions of about 50 chemical species and 3 stratospheric aerosols with about 150 reactions. The mechanism contains the oxygen (O_x), hydrogen (HO_x), nitrogen (NO_x), chlorine (Cl_y), and bromine (Br_y) radical families and the source gases that produce them (N_2O , CFCs, Halons, etc.), with kinetic and spectral parameters taken usually from the NASA JPL recommendations (DeMore et al., 1994). The iodine chemistry added is shown in Table 1. The new laboratory measurements of the rate constants for $\text{IO} + \text{ClO}$ and $\text{IO} + \text{BrO}$ are 2-4 times slower than the values assumed by Solomon and coworkers to represent upper limits to the possible values.

LOTUS also contains a parametrization of wet deposition in the troposphere as altitude-dependent first order loss frequencies. Lifetimes for soluble species with respect to rain-out, which include the iodine-containing products of CF_3I photolysis, increase from 3-5 days between the surface to 8-9 km, to 10 days at 11-12 km, to 20-80 days near the tropopause.

The ODP at steady state is calculated by referencing the effect on the global annual average of the total column of ozone of a constant release of the compound of interest to the effect of a release of a reference compound, usually CFCl_3 . The magnitude of the release affects the size of the ozone response. In these runs we imposed an emission quantity sufficient to reduce ozone by about 1 %

Three runs are needed to define a model-calculated ODP; a reference unperturbed ambient atmosphere, a reference perturbation, and the perturbation of CF_3I . LOTUS was first run to steady state with 1990 surface mole fractions specified for the Cl- and Br-containing source gases (which produces 1995-equivalent stratospheric abundances), and with the CH_3I distribution from IMPACT scaled to a surface mole fraction of 2 ppt. This corresponds to a global CH_3I source of about 0.7 Tg per year, which is in the range 0.3-3 indicated by observations (Solomon et al., 1994). Second, the surface abundance of CFCl_3 in the model was increased from 270.10 to 371.5 ppt and a 10 year run conducted to establish the reference sensitivity of ozone to a CFCl_3 perturbation. The results of this calculation for the change in

total column ozone are shown in Figure 2. This perturbation corresponds to a source emission of 0.042 Tg per year. The model circulation is normally calculated interactively during the run, but for this and subsequent runs was instead taken from the ambient atmosphere calculation to avoid complicating the results with the feedback of ozone change on circulation. Third, the IMPACT CF₃I distribution was imposed at a globally distributed surface value of 6.4 ppt, and another 10 year run conducted to establish the sensitivity of ozone to the iodine perturbation, This emission source of about 8.4 Tg per year resulted in a 1% ozone depletion. The total column ozone change for this run is shown in Figure 3. Although the total depletion is the same as in the reference run, the distribution with latitude and season is different, following the different photolysis distributions of CF₃I and CFCl.

Three additional runs were made to determine the effect of different assumptions on CF₃I emission distributions. First, an IMPACT run was made in which CF₃I surface emissions were restricted to latitudes between 20 and 60 degrees in the northern hemisphere, followed by the LOTUS run to calculate the ozone effect. In this case a surface value of 30 ppt between 20 and 60 N, corresponding to a source of about 10.5 Tg per year, was required to produce the desired 1% loss (Figure 4). Second, instead of a surface specification, CF₃I was injected directly into the stratosphere, into the 3 km region just above the tropopause (between 9-12 and 16-19 km altitude depending on latitude). A source rate of only 0.0084 Tg per year is necessary to produce the 1% ozone loss in this case, since all CF₃I emitted results in stratospheric iodine input (Figure 5). Third, the altitude of release was placed in the 1.5 km zone just below the model's tropopause. In this case a source rate of 0.115 Tg per year supported the 1% ozone decrease.

In the LOTUS model, the calculated global atmospheric lifetime of CFCl, is 57 years, the lifetime of CH₃I 9 days, and CF₃I between 3 and 5 days, depending on location of emission. CF₃I emitted directly in the stratosphere has the longer lifetime because the lower temperatures reduce the photolysis rate constant by reducing the CF₃I absorption cross section above 280 nm. These are diurnal average lifetimes including the zero loss night time, lifetimes in the sunlit atmosphere are shorter.

Results and Discussion

In our zonal average global CF₃I surface source calculation, only 0.027% of the total emission is photolyzed in the stratosphere. If we make the assumption, as do Solomon and coworkers, that because the inorganic iodine species are soluble, they will be rained out by the convective storm systems that serve to transport CF₃I to the stratosphere, we can use the stratospheric injection calculation to derive the ODP for surface emission subject to these assumptions. In this case, a surface CF₃I emission of about 31.3 Tg per year ($= 0.0084 \text{ Tg yr}^{-1} / 0.00027$) would produce a 1% ozone loss. Scaling the CFCl, source necessary to reduce ozone by 1% to a CFCl, lifetime of 80 years ($0.048 \text{ Tg yr}^{-1} = 0.042 * (57/50)$), as assumed by Solomon and coworkers, and taking the ratio of 0.048 and 31.3 gives an ODP for CF₃I of 0.0015. This is in reasonable agreement with their value of 0.008. We calculate a somewhat longer CF₃I lifetime, which tends to increase the ODP, but a lower fraction of surface emission reaching the stratosphere, which tends to reduce it. Our calculated catalytic ozone destruction efficiency for iodine is also somewhat lower, because the newly measured rate constants for the rate-limiting steps are lower than the Solomon et al. estimates and because the increased frequency of IO photolysis reduces the abundance of this important radical.

When CF₃I surface emissions are restricted to northern mid latitudes, a given emission is about half as effective in reducing stratospheric ozone as for the global emission case, suggesting a value of about 0.0008 for this case.

Actually, in the global surface CF₃I emission calculation only about 60% of the stratospheric inorganic iodine perturbation is introduced directly by photolysis of CF₃I in the stratosphere. The remaining 40% results from transport of iodine-containing photolysis products upward across the tropopause. If the assumption is made that the LOTUS wet deposition parametrization is appropriate, iodine species in the upper troposphere survive long enough that a non-negligible portion can be transported to the stratosphere. When this additional source of stratospheric iodine is allowed to perturb stratospheric ozone, we derive an ODP of 0.0025 (= 0.0015 / 0.6).

An additional characteristic of the surface CF₃I source calculations is a direct effect on the portion of the ozone column in the troposphere. Reactions of I with O₃ and HO, and the reaction of IO with HO, provide a catalytic ozone loss cycle that operates in the troposphere, driven by tropospheric photolysis of CF₃I. This process actually contributes about 55% of the total ozone column depletion in the global emission case. Figure 6 shows the vertical profiles of overhead ozone column loss as a function of altitude for CF₃I and CFCI, at 47 N in March, where the column loss is about 1% at the surface in both cases. Including this effect produces an ODP of 0.006. Tropospheric ozone loss may contribute disproportionately to surface uv increase, relative to the same column loss in the stratosphere, because greater scattering in the troposphere produces longer effective path lengths for radiation. Table 2 below summarizes the calculated ODP values for the various sets of assumptions.

While there remain uncertainties in the kinetics of iodine in the stratosphere, clearly the major uncertainties in the CF₃I ODP are related to the processes controlling the distributions of CF₃I and the inorganic iodine photolysis products in the upper troposphere and lower stratosphere. Important questions include whether photolysis products released in the troposphere survive long enough to be transported to the stratosphere or are effectively completely removed by wet deposition, the magnitude of the contribution of tropospheric ozone decreases to the total column effect, and the response of ozone when the full three-dimensional character of the CF₃I distribution, including the episodic nature of convection, is taken into account. A full 3-D photochemical model treatment may be necessary to reduce these remaining uncertainties in the atmospheric impacts of CF₃I emissions.

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TABLE 1

Thermal Reactions	A	E/R	
$I + O_2 = IO + O$,	2.00e-11	890.	DeMore et al., 1994
$I + HO_2 = HI + O_2$,	1.50e-11	1090.	DeMore et al., 1994
$I + BrO = IO + Br$	1.20e-11	0.	Huie et al., 1995.
$IO + O = I + O_2$,	1.20e-10	0.	Huie et al., 1995
$IO + HO_2 = HOI + O_2$,	8.40e-11	0.	DeMore et al., 1994
$IO + NO = I + NO_2$,	7.30e-12	-330.	DeMore et al., 1994
$IO + ClO = I + Cl + O_2$,	6.20e-12	-280.	Gilles et al., 1995; Huie et al., 1995
$IO + BrO = I + Br + O_2$,	6.90e-11	0.	Huie et al., 1995
$HI + OH = H_2O + I$	3.00e-11	0.	DeMore et al., 1994
$CH_3I + OH = I$	3.10e-12	1120.	DeMore et al., 1994
$CF_3I + OH = HOI$	3.10e-14	0.	DeMore et al., 1994
(Three-body Troe expression)	k_0	n	k_{inf} m ($F_c=0.6$)
$IO + NO_2 = IONO_2$,	5.90e-31	3.5	9.00e-12 1.5 DeMore et al., 1994
Photolysis Reactions			
$IO + hv = I + O$			Huie et al., 1995
$HI + hv = H + I$			Ogilvie, 1971
$HOI + hv = I + OH$			Atkinson et al., 1992
$IONO_2 + hv = I + NO_2$,			BrONO ₂ redshifted by 50 nm
$CH_3I + hv = I$			Ito et al., 1961
$CF_3I + hv = I$			Solomon et al., 1994; Fahr et al., 1994

TABLE 2

Run Description	Calculated ODP
Global/CF ₃ I/surface emission/stratospheric column	0.0015
NH/CF ₃ I/surface emission/stratospheric column	0.0008
Global/CF ₃ I+I _y /surface emission/stratospheric column	0.0025
NH/CF ₃ I+I _y /surface emission/stratospheric column	0.0016
Global/CF ₃ I+I _y /surface emission/total column	0.0057
NH/CF ₃ I+I _y /surface emission/total column	0.0046
Global/CF ₃ I+I _y /upper tropospheric emission/stratospheric column	0.39
Global/CF ₃ I+I _y /lower stratospheric emission/stratospheric column	5.9

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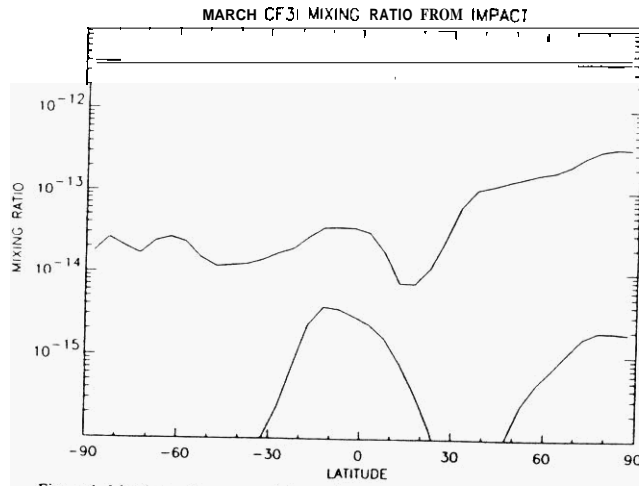


Figure 1. March zonal average mixing ratios at three altitudes for CF_3I calculated by the IMPACT model with convection. The values decrease with increasing altitude (0, 8, and 14 km are shown).

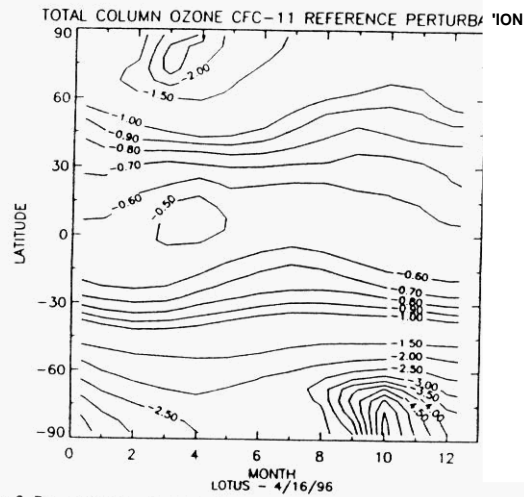


Figure 2. Per cent change in total column ozone produced by the $CFCl_3$ perturbation as a function of season and latitude. This distribution averages to a 1% global decrease. The largest effects are seen in the polar springs where PSC processes increase the efficiency of Cl-driven catalytic ozone loss.

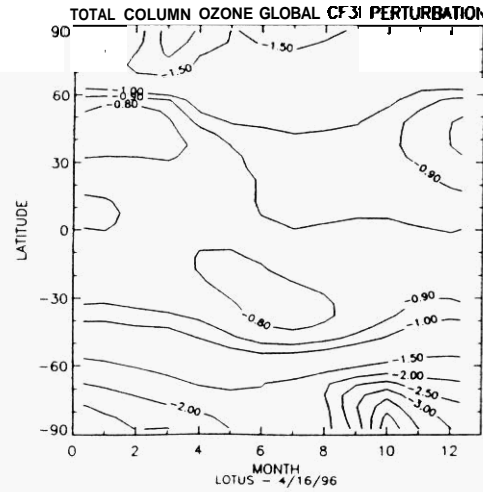


Figure 3. Per cent change in total column ozone produced by the globally- distributed CF_3I emission.

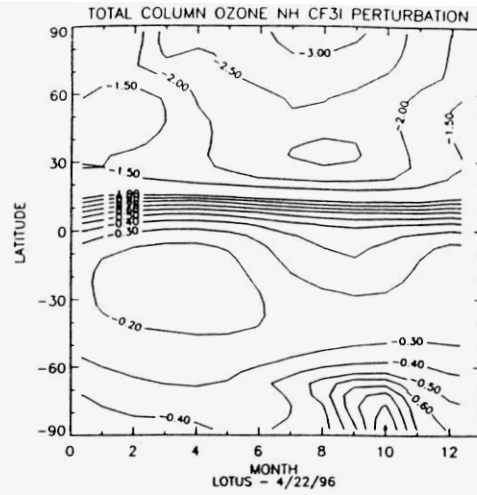


Figure 4. Per cent change in total column ozone produced by the northern hemisphere CF_3I emission.

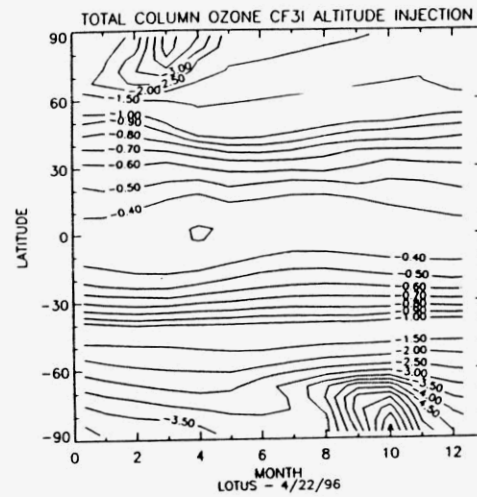


Figure 5. Per cent change in total column ozone produced by direct stratospheric injection of CF_3I .

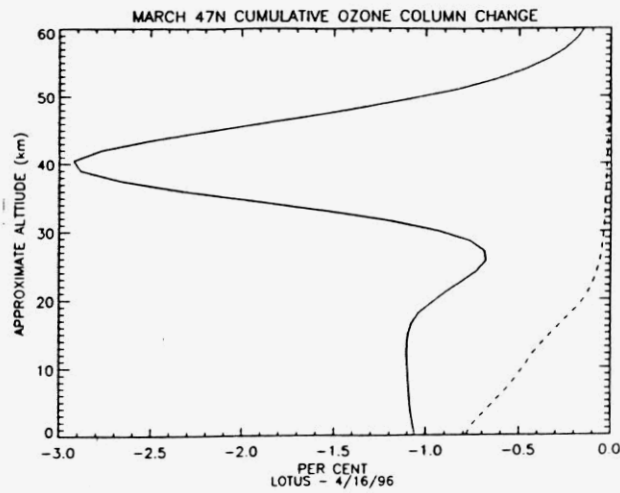


Figure 6. The per cent change in overhead ozone column as a function of altitude for CFCl_3 (solid line) and CF_3I (dashed line) in March at 47 N.

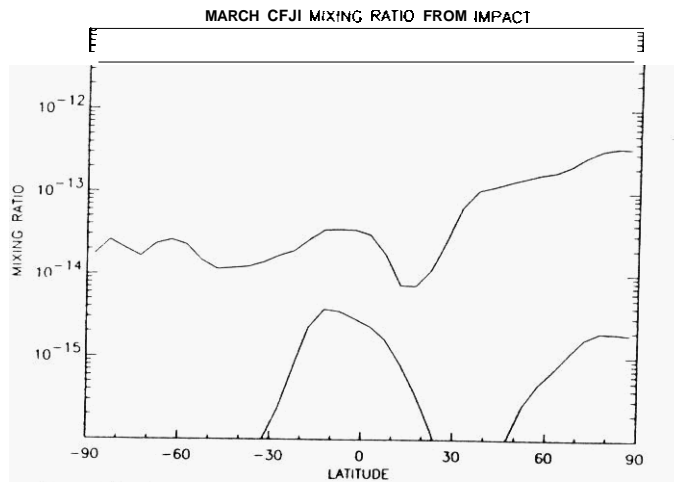


Figure 1. March zonal average mixing ratios at three altitudes for CF₃I calculated by the IMPACT model with convection. The values decrease with increasing altitude (0, 8, and 14 km are shown).

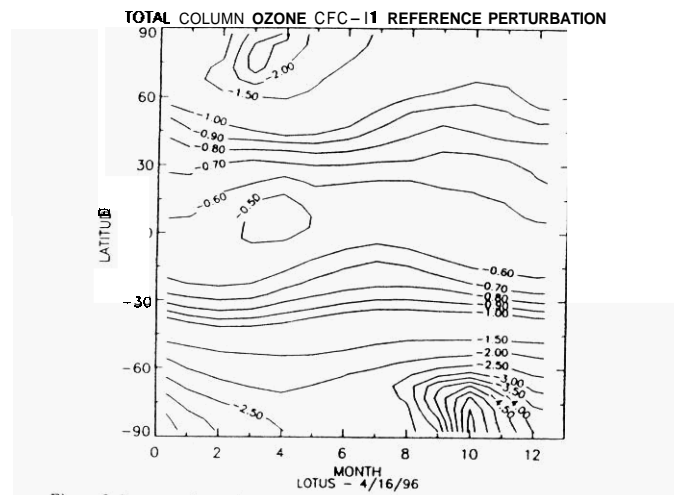


Figure 2. Per cent change in total column ozone produced by the CFC₁₁ perturbation as a function of season and latitude. This distribution averages to a 1% global decrease. The largest effects are seen in the polar springs where PSC processes increase the efficiency of Cl-driven catalytic ozone loss.

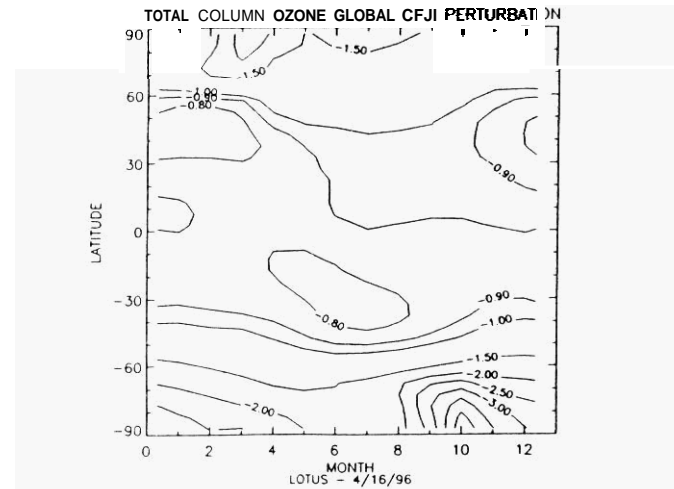


Figure 3. Per cent change in total column ozone produced by the globally-distributed CF₃I emission.

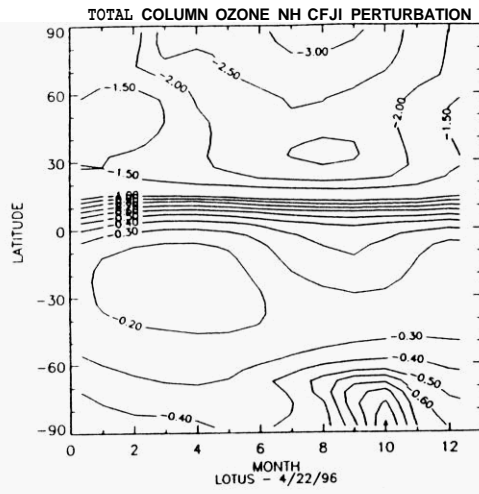


Figure 4. Per cent change in total column ozone produced by the northern hemisphere CF_3I emission.

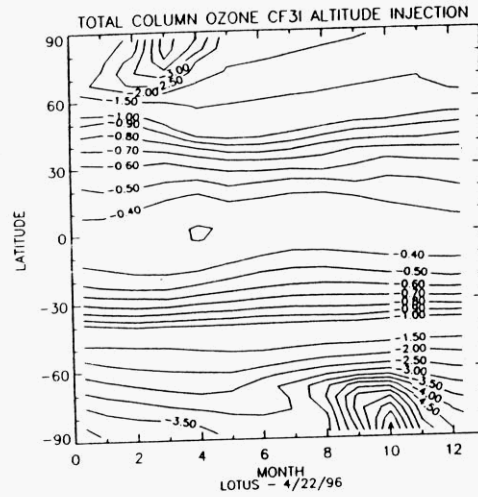


Figure 5. Per cent change in total column ozone produced by direct stratospheric injection of CF_3I .

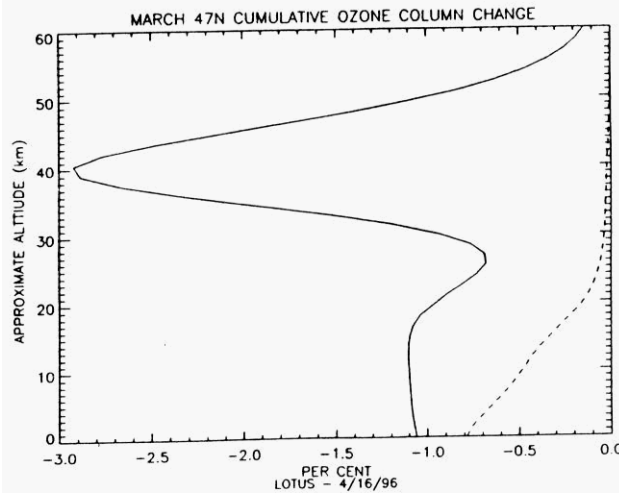


Figure 6. The per cent change in overhead ozone column as a function of altitude for $CFCl_3$ (solid line) and CF_3I (dashed line) in March at 41 N.