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Evaluating CFC Alternatives from the Atmospheric Viewpoint

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**Evaluating CFC Alternatives from the
Atmospheric Viewpoint**

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ABSTRACT

Current understanding of atmospheric processes in the troposphere and stratosphere, in particular stratospheric ozone-controlling photochemistry, allows evaluation of the effects on the stratosphere of chlorine-containing compounds envisioned as CFC (chlorofluorocarbon) replacements prior to their production and release. Such evaluations can help to direct decisions on selecting CFC alternatives and define acceptable levels of production or emission. We employ a two-dimensional (latitude and altitude) computational representation of the troposphere and stratosphere which incorporates physical processes, e.g. species transport and radiative transfer, and homogeneous photochemical processes. Laboratory measurements of OH and O(¹D) reactivity and spectral parameters of the alternative HCFC (hydrochlorofluorocarbon) compounds were used as input. The model-derived ozone depletion potential (ODP) is a defined quantity relating the effect on ozone of emission of a species to the model-calculated effect of a standard compound, here CFC-11 (CFCl₃).

Globally and annually averaged ozone depletion potentials vary from less than .02 to greater than 1.0 for various CFCs and HCFCs, primarily as a result of differences in calculated atmospheric lifetimes. Differences in stratospheric photochemistry among CFCs and HCFCs play a smaller but significant role. Zonally averaged ODPs for some compounds can range over a factor of three with latitude, however, as a result of differences in stratospheric lifetime and the altitude profile of Cl release in CFC or HCFC loss processes. While globally defined ODPs are useful in designing methods to reduce the overall stratospheric Cl burden and its impact on ozone, latitudinally and seasonally varying ODPs must be additionally considered as knowledge of specific areas of the impacts of decreasing ozone column abundance increases.

INTRODUCTION

Reductions in CFC production equal to or greater than the extent prescribed by the Montreal Protocol will be made possible, at least partially, through the development and use of compounds that functionally replace CFCs in their major applications. A necessary characteristic of an acceptable alternative compound is a reduced or eliminated potential for contributing to stratospheric chlorine and bromine abundance and subsequent declining ozone levels. One current focus is on hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). This paper discusses the use of computational models of global atmospheric photochemistry to evaluate the potential of alternative compounds (particularly HCFCs) to affect the stratosphere and compares model results for several alternatives of interest in relation to the calculated effects of CFCs currently produced in quantity and present in the stratosphere.

One way to quantify simply the calculated model results is with the concept of ozone depletion potential (ODP), relating computed ozone change of a compound of interest to results for a reference compound. CFC-11 is chosen for the reference because it is one of the most important contributors to the observed stratospheric chlorine abundance. These calculated ozone depletion potentials are also closely related to the calculated stratospheric inorganic chlorine abundance and depend on kinetic and spectroscopic properties of the CFCs and HCFCs.

There are benefits to evaluating CFC and HCFC effects relative to those of a reference compound, rather than by predicted absolute ozone changes. Calculated absolute ozone changes resulting from perturbations to the stratospheric chlorine abundance

are complicated functions of the interplay of many chemical and photochemical reactions, as well as assumptions about the future of developing trends in other trace atmospheric constituents such as N_2O and CH_4 . Now consider separating the problem into two parts; first, the atmospheric processes that control the distribution and atmospheric removal of the CFC or HCFC, and second, the subsequent interactions of the released chlorine with odd oxygen and other stratospheric chemical families. To the extent that the released inorganic chlorine has no memory of its source, the calculated effects of the CFCs and HCFCs, relative to a reference CFC, are independent of the complications of the second part of the problem. The ODP, unlike the absolute ozone change, should not depend on the details of trace gas scenario assumptions or even changing rate constant values for $Cl-O_3$ reactions from laboratory kinetic studies.

Additionally, the ODP does include direct and higher order effects and indirect feedbacks in transport and photochemistry that affect and respond to the distribution of released chlorine. Partly because of these distribution effects, however, the problem of chlorine's effect on ozone is not completely separable as presented above. The ODP will be somewhat sensitive to assumptions and changes in photochemical parameters, but less so than absolute ozone change. Finally, the heterogeneous processes currently thought to be of great importance in the Antarctic ozone hole phenomenon are not treated in the model. Since these effects appear to be related at least linearly to inorganic Cl abundance over the polar regions, the ODP concept may extend, perhaps roughly, to the effects of CFCs and HCFCs on polar spring ozone loss.

Concepts similar to the ODP defined here have been presented in the literature. "Relative efficiencies" for ozone depletion by a number of CFCs based on 1-D model results have been reported by Wuebbles¹. Hammitt et al.² combined estimates of "relative depletion efficiency" for six CFCs with their economic analysis of CFC production and emission trends in calculating the associated probability distribution of change in the global average ozone abundance. The Montreal Protocol and other newly proposed CFC production and emission regulations include the ODP concept to account for differing impacts of different CFCs.

We present and discuss here our most recent results on ODPs for the five HCFCs, five CFCs, CH_3CCl_3 , and CCl_4 shown in Table I. We also discuss the photochemical and transport-related processes that affect both global and latitudinally varying ODPs.

Table I. CFCs and HCFCs of current or potential importance

CFC-11	CCl_3F
CFC-12	CCl_2F_2
CFC-113	CCl_2FCClF_2
CFC-114	$CClF_2CClF_2$
CFC-115	$CClF_2CF_3$
Methane, tetrachloro-	CCl_4
HCFC-22	$CHClF_2$
HCFC-123	CF_3CHCl_2
HCFC-124	CF_3CHClF
HCFC-141b	CCl_2FCH_3
HCFC-142b	$CClF_2CH_3$
Ethane, 1,1,1-trichloro-	CCl_3CH_3

METHOD

LLNL Models

The LLNL zonally-averaged two-dimensional chemical-radiative-transport model determines the distributions of 32 atmospheric trace constituents in the troposphere and stratosphere, including CCl_4 , CFCl_3 (CFC-11), CF_2Cl_2 (CFC-12), CH_3CCl_3 (methyl chloroform) and the additional CFC or HCFC being evaluated. The model domain extends from pole to pole, and from the ground to 0.56 mb (approximately 0 to 54 km). The horizontal resolution is about 10° in latitude. The vertical resolution is approximately 3 km. Reaction rate constants, solar flux data, absorption cross-sections, and quantum yields are based on the latest NASA panel recommendations³. More recent information is used for the HCFC compounds considered. Accurate diurnal calculations are used to derive time-varying factors for each chemical and photochemical reaction included in the diurnal-averaged version of the model.

The diabatic circulation for the ambient atmosphere is determined using net heating rates calculated in an internally consistent way with the derived species distributions. Temperatures for the ambient atmosphere vary continuously over the annual cycle, based on the reference model of Barnett and Corney⁴. Turbulent eddy transport is parameterized through diffusion coefficients K_{yy} and K_{zz} . A value of K_{yy} of $2 \times 10^9 \text{ cm}^2\text{s}^{-1}$ is assumed at all stratospheric altitudes and latitudes, with a value of $1 \times 10^{11} \text{ cm}^2\text{s}^{-1}$ in the troposphere. Values of K_{zz} are $1 \times 10^3 \text{ cm}^2\text{s}^{-1}$ in the lower stratosphere, increasing slowly with altitude.

The effects of changes in the abundances of individual CFCs on ozone are calculated with reference to a converged steady state mid-1980s model atmosphere. In the perturbed atmosphere, the diabatic circulation is assumed to be unchanged from the reference state. In most of the results presented here the temperature field is also held fixed. The effects of this assumption of fixed temperature on ODP are small.

A 1-dimensional model also used has been described previously². The results quoted here are again for a fixed temperature profile. For the 1-D calculations of the effects of individual CFCs on ozone, the surface CFC emission rate was specified to produce a total column ozone change of about 1%, and the model was integrated time-dependently until a steady state was approached (typically three or four atmospheric lifetimes of the relevant CFC). The reference atmosphere was taken to be free of CFCs and CH_3CCl_3 .

The Ozone Depletion Potential Definition

Ozone depletion potential, as defined in this study and adopted by other current studies, is the ratio of CFC-11 mass emission rate to the mass emission rate of the other (H)CFC, such that at steady state in each case the global ozone burden is reduced by 1% relative to the reference atmosphere. The choice of a 1% depletion in the global ozone burden is made to avoid any nonlinear effects that might occur if Cl photochemistry were to become the dominant ozone loss process throughout the stratosphere. We also consider, for the 2-D model, seasonal and latitudinal dependences of the ODP, defined as the ratio of the local seasonal and latitudinal change in total column ozone for a (H)CFC perturbation relative to the change calculated for CFC-11, at steady state and for a 1% global ozone change. Other definitions are possible, i.e. the ratio of ozone perturbation given a constant fixed mass emission rate, or the relative calculated ozone depletion on

a molar rather than a mass basis of CFC emission. The ODP should also be a function of the magnitude of the calculated ozone change allowed to occur. While the exact values would be different for these different definitions or assumptions, the conceptual meaning is the same.

The ODP concept we discuss is based on steady state or equilibrium perturbation calculations and is essentially asymptotic. In a time-dependent integration, HCFCs such as CH_3CCl_3 , with a lifetime shorter than the lifetime of the reference compound CFC-11, will appear initially to have a larger effective ODP, while the reverse would be true of a long-lived species such as CFC-115. Defined at steady state, the ODP is thus not a completely comprehensive indicator of the near term effects of individual (H)CFC emission rates on ozone.

RESULTS

Globally-Averaged and One-Dimensional Results and Discussion

The most important variables on which ODP values depend are the formula of the compound (the number of Cl atoms) and the total atmospheric lifetime, followed by the molecular weight (for ODP as defined here on a mass rather than molar basis). The lifetimes of the HCFC compounds studied here depend almost entirely on their reaction with tropospheric OH. Both temperature and hydroxyl radical concentration drop rapidly with altitude near the surface. The better vertical resolution of the 1-D model probably results in a better estimate than the 2-D model of HCFC lifetimes, especially when the HCFC-OH reaction rate constant has a large activation energy. The 2-D model, with its thicker surface layer, will tend to underestimate HCFC lifetimes. For the CFCs however, loss occurs predominantly by photolysis in the stratosphere. The better physical basis of the representation of horizontal and vertical mixing in the 2-D model, as well as incorporation of the latitudinal and seasonal variation in solar flux, should result in better lifetime estimates for the fully halogenated compounds in the 2-D model. Calculated total atmospheric equilibrium lifetimes from both models are given in Table II.

Table II. Calculated global atmospheric lifetimes.

<u>Compound</u>	<u>2-D model</u>	<u>1-D model</u>
CFC-11	52	years
CFC-12	101	
CFC-113	79	154
CFC-114	197	96
CFC-115	393	208
CCl_4	47	680
		73
HCFC-22	15	20
HCFC-123	1.8	2.3
HCFC-124	6	8
HCFC-141b	9	11
HCFC-142b	21	27
CH_3CCl_3	5.8	7.4

ODP values from the 1-D model and globally and annually averaged ODP values from the 2-D model are given in Table III. The 1-D result is intended to be representative of the global average. The agreement between models is generally good. Differences in ODP values for HCFCs-22, -124 and -142b are discussed below. Interestingly, the 2-D model is about 25% less sensitive to stratospheric Cl loading than the 1-D model, as derived from the emission flux of CFC-11 required to produce a 1% ozone decrease in both cases. This demonstrates the insensitivity of ODP to calculated absolute ozone change, since the ODPs are similar. The third and fourth columns in Table III show what the 2- and 1-D ODP values would be if they depended only on the product of lifetime and Cl weight percent (~ #Cl/Mol.Wt.). The reasons for the close correspondence with ODP in some cases and divergence in others are also discussed below.

Table III. Calculated ozone depletion potentials.

<u>Compound</u>	ODP*		#Cl(Lifetime/Mol.Wt.)*	
	<u>2-D model</u>	<u>1-D model</u>	<u>2-D model</u>	<u>1-D model</u>
CFC-11	1.0	1.0	1.0	1.0
CFC-12	0.9	1.0	1.5	1.5
CFC-113	0.8	0.8	1.1	0.9
CFC-114	0.6	0.8	2.0	1.4
CFC-115	0.3	0.4	2.2	2.5
CCl ₄	1.1	1.1	1.1	1.1
HCFC-22	0.042	0.051	0.16	0.13
HCFC-123	0.018	0.018	0.021	0.017
HCFC-124	0.015	0.018	0.04	0.03
HCFC-141b	0.08	0.10	0.13	0.11
HCFC-142b	0.04	0.07	0.18	0.15
CH ₃ CCl ₃	0.12	0.11	0.11	0.09

a. Referenced to respective CFC-11 value.

The shorter lifetimes of the HCFCs compared to the CFCs are shown in Table II, and the effect of the shorter lifetimes on ODP is shown in the values in Table III. Because of the coarser tropospheric resolution of the 2-D model leads to underestimates of HCFC lifetimes, as noted above, some of the HCFC ODPs are smaller in the 2-D model than the 1-D. However the better 2-D treatment of vertical mixing and solar flux also results in a reduced lifetime for the reference compound, CFC-11, relative to the 1-D model. This effect partially or completely offsets the effect of shorter HCFC lifetimes in the 2-D model. Some of the ODPs reported here for the HCFCs from both models may then somewhat underestimate the true values, for differing reasons.

The HCFC lifetimes and ODPs are predominately controlled by tropospheric OH. Although precise and accurate direct observations of the OH distribution are not yet available, an estimate of the lifetime of CH₃CCl₃ (7.0 years⁵) is reported based on global sampling. If we scale the model-derived HCFC lifetimes and ODPs by the ratio of the predicted CH₃CCl₃ lifetime to the observed 7.0 year value, some of the model-induced variability in ODP may be removed. This represents an implicit adjustment of the average OH abundance in the model troposphere. As a result of the differences in activation energies among the HCFC+OH reaction rate constants (1000-1800 K vs. 1800 K for

CH_3CCl_3), though, this adjustment is not completely correct in all cases. The adjusted HCFC ODPs are presented in Table IV. The agreement between models is somewhat improved.

Table IV. HCFC ODPs adjusted by CH_3CCl_3 lifetime.

<u>Compound</u>	<u>2-D model</u>	<u>1-D model</u>
HCFC-22	0.051	0.049
HCFC-123	0.022	0.017
HCFC-124	0.019	0.017
HCFC-141b	0.10	0.10
HCFC-142b	0.052	0.057
CH_3CCl_3	0.15	0.11

Referring back to Table III and as noted above, most of the spread in ODP among the CFCs and HCFCs is the result of differences in atmospheric lifetime, number of Cl atoms and molecular weight. Were all sources of stratospheric Cl equivalent in the photochemical sense once they reached the stratosphere, the ODPs would be completely explained by these factors and columns 1 and 2 in Table III would compare identically to columns 3 and 4, respectively. However, ODPs for several compounds are substantially smaller than would be expected on this basis, while none are significantly larger.

There are three major reasons for the apparently low ODP values. First, most of the HCFCs have a sufficiently short lifetime that they are not well-mixed in the model troposphere at steady state. The resulting gradient in tropospheric HCFC mole fraction with altitude causes air entering the stratosphere to be slightly depleted in HCFC compared to the atmospheric average, causing the stratospheric Cl and ozone perturbations to be smaller than predicted from lifetime alone.

Second, mono- and some bi-chlorinated (H)CFCs tend to have higher energy $n \leftrightarrow \sigma^*$ transitions on absorption of uv radiation than poly-chlorinated CFCs, corresponding to smaller uv cross sections around 200 nm and longer stratospheric lifetimes with respect to photodissociation. At steady state, in the region of the stratosphere where Cl photochemistry is important for determining ozone abundance, these CFCs are incompletely dissociated. This effect also decreases the Cl abundance and subsequent ozone perturbation below the simple prediction based only on total atmospheric lifetime. Because stratospheric lifetime is not always directly proportional to total atmospheric lifetime, some short-lived HCFCs show this effect. For example, HCFC-22 is about 70% dissociated by 35 km, while CFC-11 is essentially 100% dissociated at that altitude.

Finally, differences among (H)CFCs in absorption cross sections and reactivity with OH and O(¹D) produce differences in the profile of the stratospheric inorganic chlorine release with varying effects on ozone-related photochemistry. A combination of effects contributes to differences in ozone change profiles with altitude. For example, Figure 1 compares 2-D results for HCFC-22 and CFC-11, for which the globally and annually averaged ozone change is 1%. The CFC-11 perturbation (solid line) results in reduced ozone throughout the stratosphere, except for a small positive lobe around 22 km. The HCFC-22 perturbation (dashed line) producing an equivalent 1% global ozone loss is roughly 25 times the CFC-11 emission mass flux and exhibits a larger ozone reduction between 35 and 40 km, but also a larger positive lobe in the lower stratosphere.

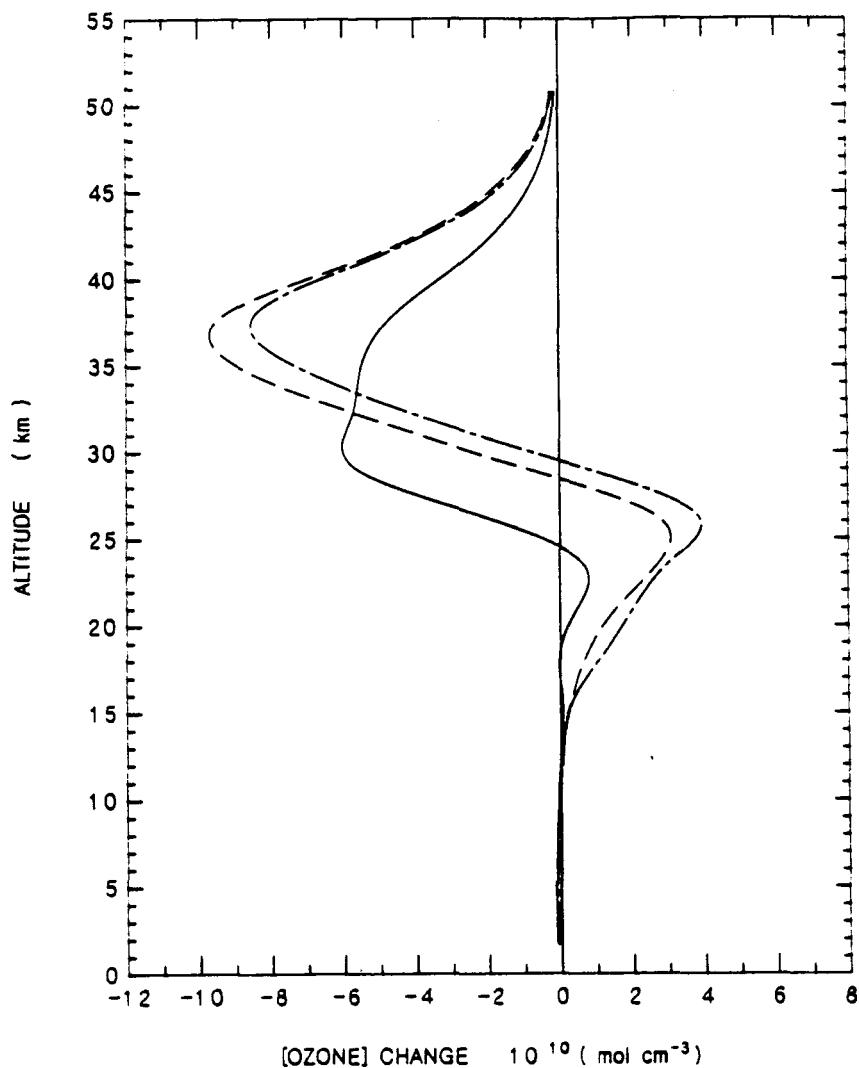


Figure 1. Altitude profile of calculated global ozone change in 2-D model for emission of (a) 136×10^6 kg/yr of CFC-11, solid line, (b) 3383×10^6 kg/yr of HCFC-22, dashed line, and (c) 136×10^6 kg/yr of HCFC-22 scaled by $1/(\text{HCFC-22 ODP})$, dashed and dotted line.

If HCFC-22 were emitted instead at the same mass flux as for the CFC-11 perturbation (dash-dot line, scaled by the HCFC-22 ODP) the lower stratospheric ozone increase becomes even larger relative to the overhead ozone loss. In the region of the ozone maximum around 25 km, the dominant ozone loss process depends on NO and NO_2 as catalysts. Increased levels of ClO have the effect of decreasing the ozone loss catalyzed by NO_2 , by reacting with NO_2 to form ClONO_2 . However, lower stratospheric inorganic chlorine also directly catalyzes odd oxygen loss. HCFC-22 is destroyed higher in the stratosphere than CFC-11, so that the inorganic Cl input into the lower stratosphere is smaller.

Another effect related to the shape of the vertical profile of ozone loss is the depth of penetration into the stratosphere of solar uv in the 200-240 nm wavelength region. Loss of ozone in the lower stratosphere has little effect on the atmosphere below, because most of the radiation is already screened out in the upper stratosphere by the ozone above. An upper stratospheric ozone decrease, however, is accompanied by

greater photolysis of oxygen in the lower stratosphere, causing a negative feedback on the calculated total column change. The larger upper stratospheric ozone decrease in the case of HCFC-22 brings about an increase in photolysis of molecular oxygen in the lower stratosphere, compared to CFC-11.

Latitudinal (2-D) Effects - Results and Discussion

Figure 2 shows the two-dimensional field of total column ozone change for a CFC-11 perturbation averaging globally to 1%. The larger losses calculated at higher latitudes and in the respective hemispheric spring seasons are consistent with other 2-D studies of CFC perturbations⁶. Because the overall advective transport is upward from the troposphere into the stratosphere near the equator and then poleward in the stratosphere, one might expect that (H)CFCs rapidly destroyed in the stratosphere would show a flatter inorganic Cl and ozone perturbation with latitude than those decomposed more slowly. Because CFC-11 is relatively rapidly photolyzed, ODPs for less reactive compounds such as CFC-12 and HCFC-22 should increase from equator to pole.

This is in fact what the 2-D model predicts. For example, the seasonal and latitudinal dependence of the ozone depletion potential of CH_3CCl_3 relative to CFC-11 is small, because the photolytic cross sections are similar. There is actually a small decrease with increasing latitude in both hemispheres, because CH_3CCl_3 also reacts with stratospheric OH, releasing Cl. The result for CFC-12 relative to CFC-11 is quite different (Figure 3). A strong latitudinal gradient is calculated. Lower Cl abundances in the lower stratosphere reduce the importance of changes in the rates of NO_x^- and ClO_x^- .

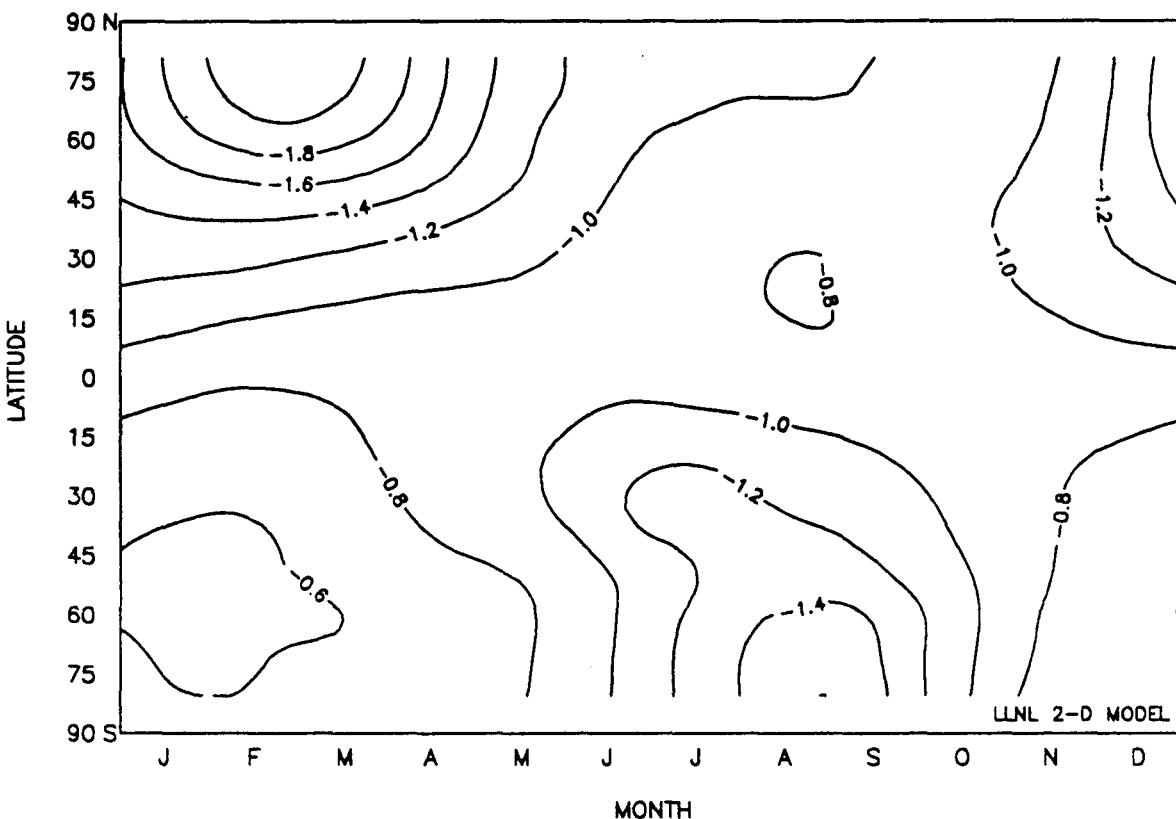


Figure 2. Total column ozone decrease as a function of latitude and season for an emission of $136 \times 10^6 \text{ kg/yr}$ of CFC-11 in the 2-D model.

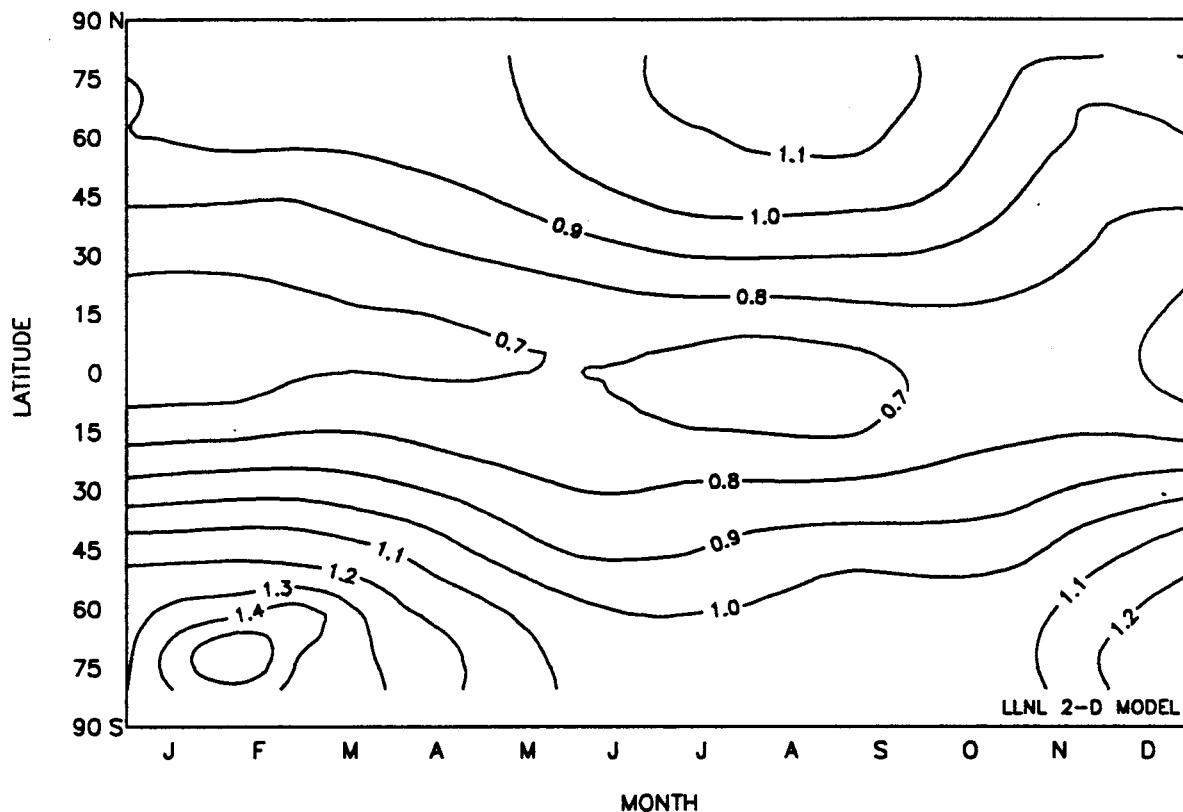


Figure 3. Latitudinal and seasonal dependence of the CFC-12 ODP.

catalyzed odd oxygen loss, allowing the increase in oxygen photolysis following upper stratospheric ozone loss to dominate and result in greater negative feedback to the overall column ozone change. This regime persists into the midlatitudes. At higher latitudes, though, transport from lower latitudes begins to dominate the lower stratosphere and reduced penetration of solar uv slows lower stratospheric photochemistry. The higher Cl abundance in the upper stratosphere for the CFC-12 perturbation results in larger column ozone depletion relative to CFC-11.

The 2-D representation of the HCFC-22 ODP (Figure 4) shows similar characteristics to CFC-12 (Figure 3). HCFCs 124 and 142b also behave similarly, as do CFCs 114 and 115.

CONCLUSION

We intend the ODP concept to be a simple representation of the potential relative importance of individual CFCs and HCFCs in perturbing stratospheric photochemistry, which nonetheless incorporates the nonlinear effects and feedback processes present in comprehensive models of atmospheric photochemistry. Calculated ODP values should be relatively insensitive to errors in the model's representation of the photochemistry of families of species other than ClO_x , as well as to the actual ClO_x catalytic cycles. The values will be sensitive to the calculation of tropospheric OH and solar flux as a function of altitude and wavelength and to laboratory measurements of HCFC+OH rate constants and uv absorption cross sections.

Differences in the profiles of the abundances of active Cl species, resulting from

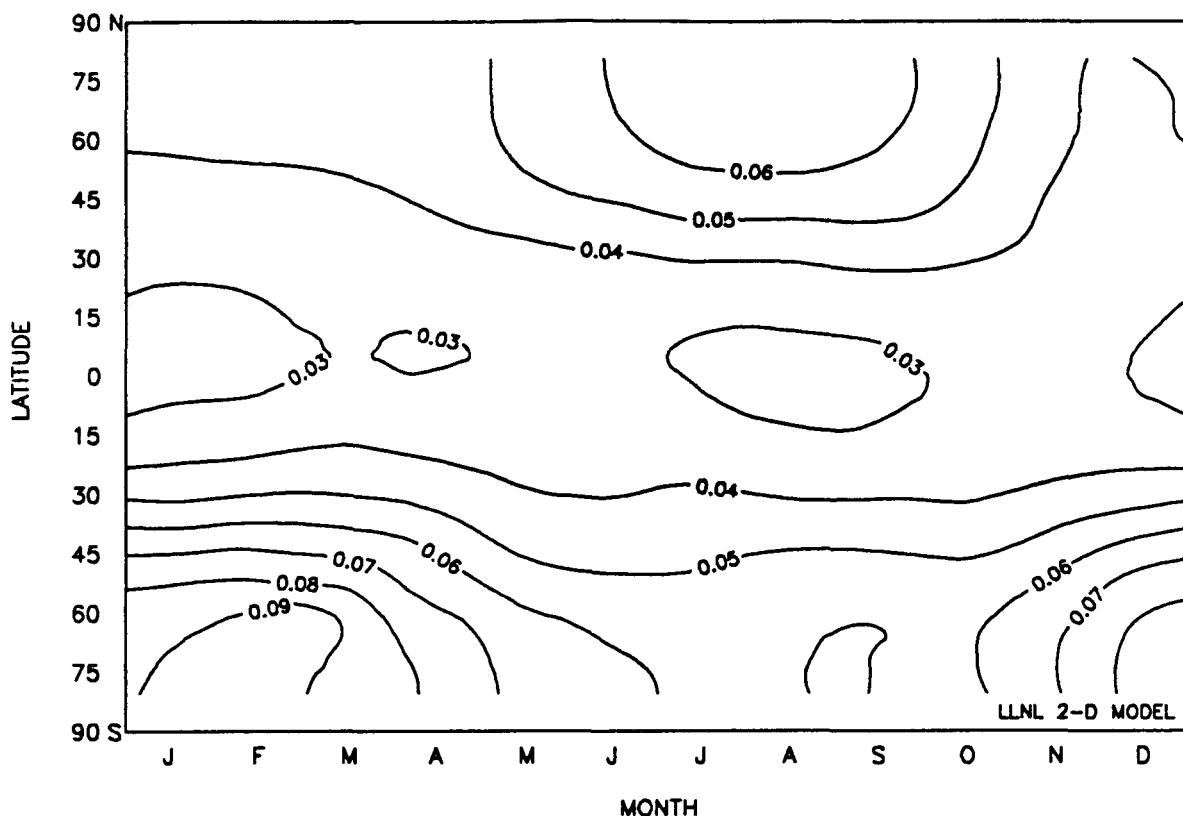


Figure 4. Latitudinal and seasonal dependence of the HCFC-22 ODP.

the nature of the diabatic transport in the 2-D model and differences in CFC uv absorption coefficients, can introduce substantial latitudinal dependence into the ozone depletion potential relative to CFC-11 for some CFCs and HCFCs. If a consequence of a depleted ozone column is, for example, more significant at higher latitudes than near the equator, a globally averaged ODP may substantially underestimate the potential for effect of a particular compound relative to emissions of CFC-11. A related consideration in interpreting 2-D model predictions of the effect of assumed future CFC scenarios is that the latitudinal distribution of the result will depend on the prescribed mix of individual CFC emissions as well as on the total stratospheric Cl perturbation produced.

Finally, the ODPs of the HCFC and HFC replacements for CFCs currently under consideration all have ODPs less than about 0.10. However, the information expressed in a compound's ODP is only a part of what should be considered in evaluating atmospheric impacts. For example, the ODP of CFC-115 is only 0.3-0.4, but its very long atmospheric lifetime and potential contribution to greenhouse trapping of infrared radiation would make it a poor choice as an alternative compound.

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