

## VIII. OZONE DEPLETION POTENTIALS

*Relative Effects on Stratospheric Ozone of Halogenated Methanes and Ethanes of Social and Industrial Interest*

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## EXECUTIVE SUMMARY

Ozone Depletion Potentials (ODPs) have been defined and calculated in order to allow estimates of the relative effects of halocarbons on stratospheric ozone. Models using representations of homogeneous atmospheric chemical processes have estimated relative effects on global ozone. These estimates indicate that the ODPs of the hydrohalocarbons are generally one-tenth or less those of the CFC-11 and -12. The reduction in ODP that might be expected due to replacement of uses of a CFC by a hydrohalocarbon can be estimated by taking the ratio of the ODP of the hydrohalocarbon to the ODP of the CFC it might replace. For example, the reduction in ODP in replacing uses of CFC-12 by HCFC-22 is  $(0.049 \pm .015)/(.93) = .053 \pm .015$ . Of course, the relative quantities of the compound required in the use application must also be taken into account.

Although the values of ODPs reported here agree reasonably well among models, uncertainties in the values still exist due to the uncertainties in modeled chemistry and dynamics. Since reaction with OH dominates the chemistry of the HCFCs, uncertainties in the model calculated OH values remain a major source of uncertainty for both lifetimes and ODPs of these compounds. Uncertainties for some compounds may be reduced with new laboratory data on the ultraviolet absorption properties and the rate constants with hydroxyl for the HCFCs and HFCs.

Sensitivity analyses reveal that the global ODP values are affected to only a minor degree by the levels of  $N_2O$ ,  $CH_4$ ,  $CO_2$ ,  $CO$ , and Brx used in model calculations. Latitudinal relative effects on ozone depletion depend on the species - species with high altitude sinks show more latitudinal dependency than CFC-11. Those species destroyed in the lower stratosphere have latitudinal effects equivalent to CFC-11. Seasonal variation of relative ozone depletions are second order.

Another major uncertainty centers on the potential effects of heterogeneous chemistry in the lower stratosphere, particularly near the poles in winter-time. While these effects are believed to cause the Antarctic spring-time ozone decreases, they are not included in any of the model calculations of ODPs. Due to the cold stratospheric temperatures, polar stratospheric clouds become activation sites for chlorine compounds (by-products from the decomposition of the chlorocarbons) resulting in increased chlorine catalytic loss for ozone. Since ODP is defined relative to CFC-11, the effect of including heterogeneous chemistry will have little effect on the local ODP value compared to values determined assuming only homogeneous chemistry. However, polar contribution to global ozone loss would be greater such that global ODP values would be more heavily weighted by the polar values. Thus, species with large, positive latitudinal gradients in ODP would have global ODPs that are fractionally increased. On the other hand, inclusion of stronger polar dynamics would affect both the transport and the distribution of chlorine species and would directly impact both the local and global ODP values.

Upper bounds are placed on the local effects by a chlorine loading potential, i.e. the relative amount of chlorine added to the stratosphere by a given gas. A less conservative estimate derived from the relative values of  $Cly$  in the lower polar stratosphere in spring indicates that the potential effect can be substantially less than the Chlorine Loading Potential but would be above the homogeneous chemistry ODP value. The geographic extent of the heterogeneous effect on global ODP outside of the polar vortex is impossible to estimate at the present time.

Time-dependent Relative Ozone Depletions and Relative Chlorine Loading for HCFCs have values above the ODP and CLP values derived from steady-state calculations. For longer lived CFCs, the time-dependent values are always less than the ODP and CLP values.

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Range of Ozone Depletion Potentials (ODP) determined by one-dimensional and two-dimensional models, assuming scaling for HCFC ODPs by CH<sub>3</sub>CCl<sub>3</sub> observed lifetime (6.3 years).

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<u>Species</u>	<u>1-D Models*</u>	<u>2-D Models**</u>
CFC-11	1.0	1.0
CFC-12	0.9-1.0	0.9
CFC-113	0.8-0.9	0.8-0.9
CFC-114	0.6-0.8	0.6-0.8
CFC-115	0.4-0.5	0.3-0.4
HCFC-22	0.4-0.05	0.04-0.06
HCFC-123	0.013-0.016	0.013-0.022
HCFC-124	0.016-0.018	0.017-0.024
HFC-125	0	0
HFC-134a	0	0
HCFC-141b	0.07-0.08	0.09-0.11
HCFC-142b	0.05-0.06	0.05-0.06
HFC-134a	0	0
HFC-152a	0	0
CCl <sub>4</sub>	1.0-1.2	1.0-1.2
CH <sub>3</sub> CCl <sub>3</sub>	0.10-0.12	0.13-0.16

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\* 1-D models from AER, LLNL and DuPont.

\*\* 2-D models from AER, LLNL, University of Oslo, and DuPont.

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**RELATIVE EFFECTS ON STRATOSPHERIC OZONE OF HALOGENATED  
METHANES AND ETHANES OF SOCIAL AND INDUSTRIAL INTEREST**

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## ABSTRACT

Four atmospheric modeling groups have calculated relative effects of several halocarbons (CFCs -11, 12, 113, 114, and 115; HCFCs 22, 123, 124, 141b, and 142b; and HFCs 125, 134a, 143a, and 152a, carbon tetrachloride; and methyl chloroform) on stratospheric ozone. Effects on stratospheric ozone were calculated for each compound and normalized relative to the effect of CFC-11. These models include the representations for homogeneous physical and chemical processes in the middle atmosphere but do not account for either heterogeneous chemistry or polar dynamics which are important in the spring time loss of ozone over Antarctica.

Relative calculated effects using a range of models compare reasonably well. Within the limits of the uncertainties of these model results, compounds now under consideration as functional replacements for fully halogenated compounds have modeled stratospheric ozone reductions of 10% or less of that of CFC-11. Sensitivity analyses examined the sensitivity of relative calculated effects to levels of other trace gases, assumed transport in the models, and latitudinal and seasonal local dependencies. Relative effects on polar ozone are discussed in the context of evolving information on the special processes affecting ozone especially during polar winter-springtime. Lastly, the time dependency of relative effects have been calculated.

## 1. INTRODUCTION

Concern over the global environmental consequences of fully halogenated chlorofluorocarbons (CFCs) has sparked development of replacement compounds. A systematic evaluation of potential environmental effects of replacement chemicals is clearly important. The two major environmental considerations for these chemicals are possible changes in stratospheric ozone and global climate. This paper will deal with estimation of potential effects on stratospheric ozone.

The candidates under intensive development are composed of either carbon, hydrogen and fluorine (hydrofluorocarbons or HFCs) or carbon, hydrogen, chlorine and fluorine (hydrochlorofluorocarbons or HCFCs). For simplicity, both classes of compounds are referred to as hydrohalocarbons. Because they contain hydrogen, the hydrohalocarbons are far more reactive with atmospheric hydroxyl radicals than CFCs. This destruction mechanism leads to significantly shorter atmospheric lifetimes for these compounds (e.g. Makide and Rowland, 1981) compared to those of the CFCs. The shorter atmospheric lifetime is a primary factor in the reduced potential of HCFCs and HFCs to affect both stratospheric ozone and global warming.

This paper examines the calculated effects of several one and two carbon halocarbons on stratospheric ozone. Estimation of each compound's effect on stratospheric ozone will be quantified as a relative Ozone Depletion Potential (or ODP). Estimates of relative potentials to enhance global warming (Halocarbons Global Warming Potential or HGWP) will be discussed in a subsequent publication (Fisher et al. 1989b).

Computer models have long been used to estimate the relative effects of trace gases on stratospheric ozone. Early reports were made in terms of an efficiency factor for different chemicals [Wofsy and McElroy (1974), Donahue et al. (1976), and Robbins and Stolarski, (1976)]. The concept of a relative Ozone Depletion Potential was introduced in 1981 (Wuebbles, 1981) and was adopted as a quick reference for estimating the relative potential of these trace gases to reduce stratospheric ozone. Several papers have

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reported model results as ODPs: Wuebbles (1983), Hammitt et al. (1987), Rognerud et al. (1988). Regulation of fully halogenated CFCs under the Montreal Protocol is based on the concept of ODP in order to establish relative weighting factors for each chemical.

ODP values for sixteen gases have been calculated by four atmospheric modeling groups; Atmospheric and Environmental Research, Inc. (AER), Du Pont Central Research (Du Pont), Lawrence Livermore National Laboratory (LLNL), and the University of Oslo. Each of these models is described in the literature [ko et al. (1984 & 1985), Kinnison et al. (1988), Miller et al. (1981), Miller et al. (1981a), Rognerud et al. (1988), Stordal et al. (1985), Sze and Ko (1981), Wuebbles (1983), and Wuebbles et al. (1988)]. The halocarbons considered in this study, their chemical formulate, and their IUPAC names are listed in Table 1.

This paper will describe a clearer definition of ODP, as well as examine the basis for selecting its definition, present calculated results from several models, and examine the differences and uncertainties in model results.

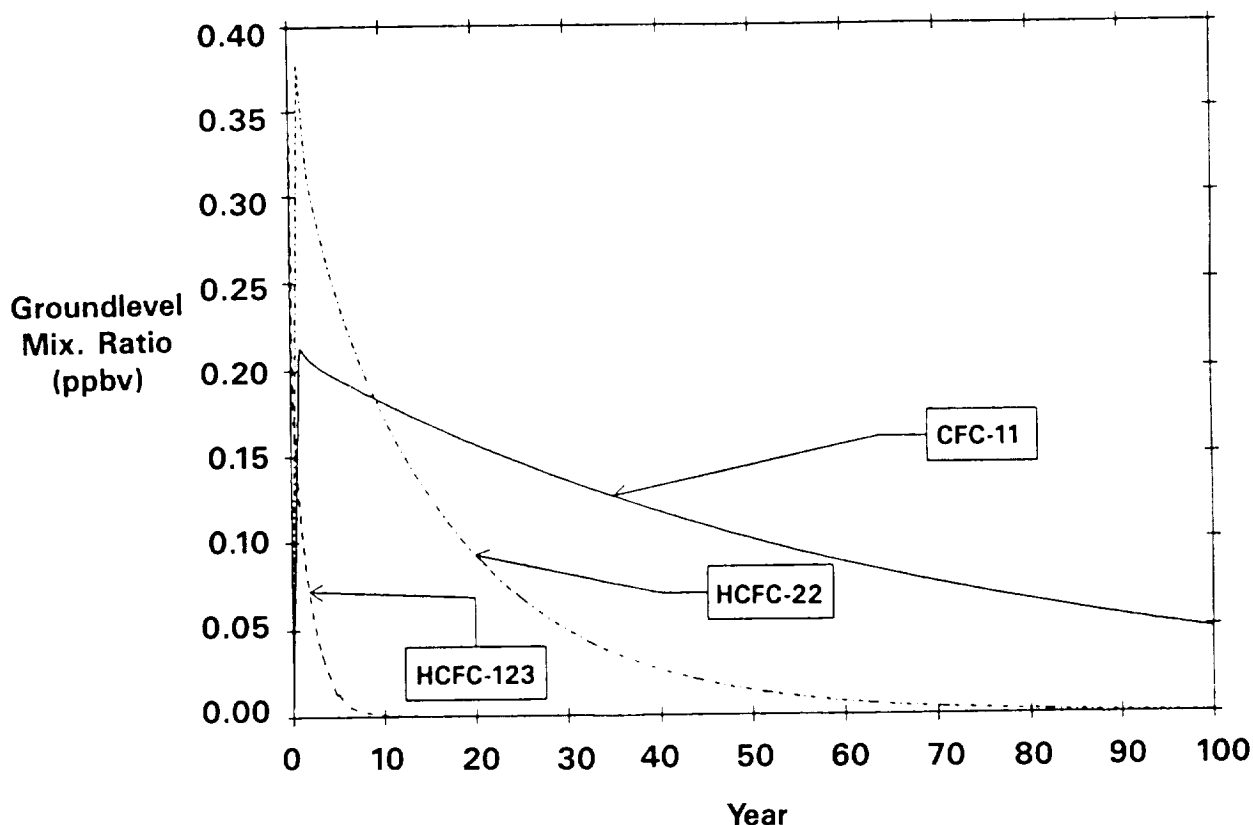
## 2. DEFINITION BASIS

Ozone Depletion Potential (ODP) has traditionally been defined as the ratio of model calculated ozone depletions under steady state conditions. More specifically, it is defined as the ratio of calculated ozone column change for each mass unit of a gas emitted into the atmosphere relative to the calculated depletion

**Table 1** Compounds Examined in this Study

HALOCARBON	FORMULA	IUPAC NAME
CFC-11	$\text{CCl}_3\text{F}$	METHANE, TRICHLOROFLUORO-
CFC-12	$\text{CCl}_2\text{F}_2$	METHANE, DICHLORODIFLUORO-
CFC-113	$\text{CCl}_2\text{FCClF}_2$	ETHANE, 1,1,2-TRICHLORO-1,2,2-TRIFLUORO-
CFC-114	$\text{CCCIF}_2\text{ClF}_2$	ETHANE, 1,2-DICHLORO-1,1,2,2-TETRAFLUORO-
CFC-115	$\text{CClF}_2\text{CF}_3$	ETHANE, CHLOROPENTAFLUORO-
HCFC-22	$\text{CHClF}_2$	METHANE, CHLORODIFLUORO-
HCFC-123	$\text{CF}_3\text{CHCl}_2$	ETHANE, 2,2-DICHLORO-1,1,1-TRIFLUORO-
HCFC-124	$\text{CF}_3\text{CHClF}$	ETHANE, 2-CHLORO-1,1,1,2-TETRAFLUORO-
HFC-125	$\text{CF}_3\text{CHF}_2$	ETHANE, PENTAFLUORO-
HFC-134a	$\text{CF}_3\text{CH}_2\text{F}$	ETHANE, 1,1,1,2-TETRAFLUORO-
HCFC-141b	$\text{CCl}_2\text{FCH}_3$	ETHANE, 1,1-DICHLORO-1-FLUORO-
HCFC-142b	$\text{CClF}_2\text{CH}_3$	ETHANE, 1-CHLORO-1,1-DIFLUORO-
HFC-143a	$\text{CF}_3\text{CH}_3$	ETHANE, 1,1,1-TRIFLUORO-
HFC-152a	$\text{CHF}_2\text{CH}_3$	ETHANE, 1,1-DIFLUORO-
CARBON- TETRACHLORIDE	$\text{CCl}_4$	METHANE, TETRACHLORO-
METHYL CHLOROFORM	$\text{CCl}_3\text{CH}_3$	ETHANE, 1,1,1-TRICHLORO-





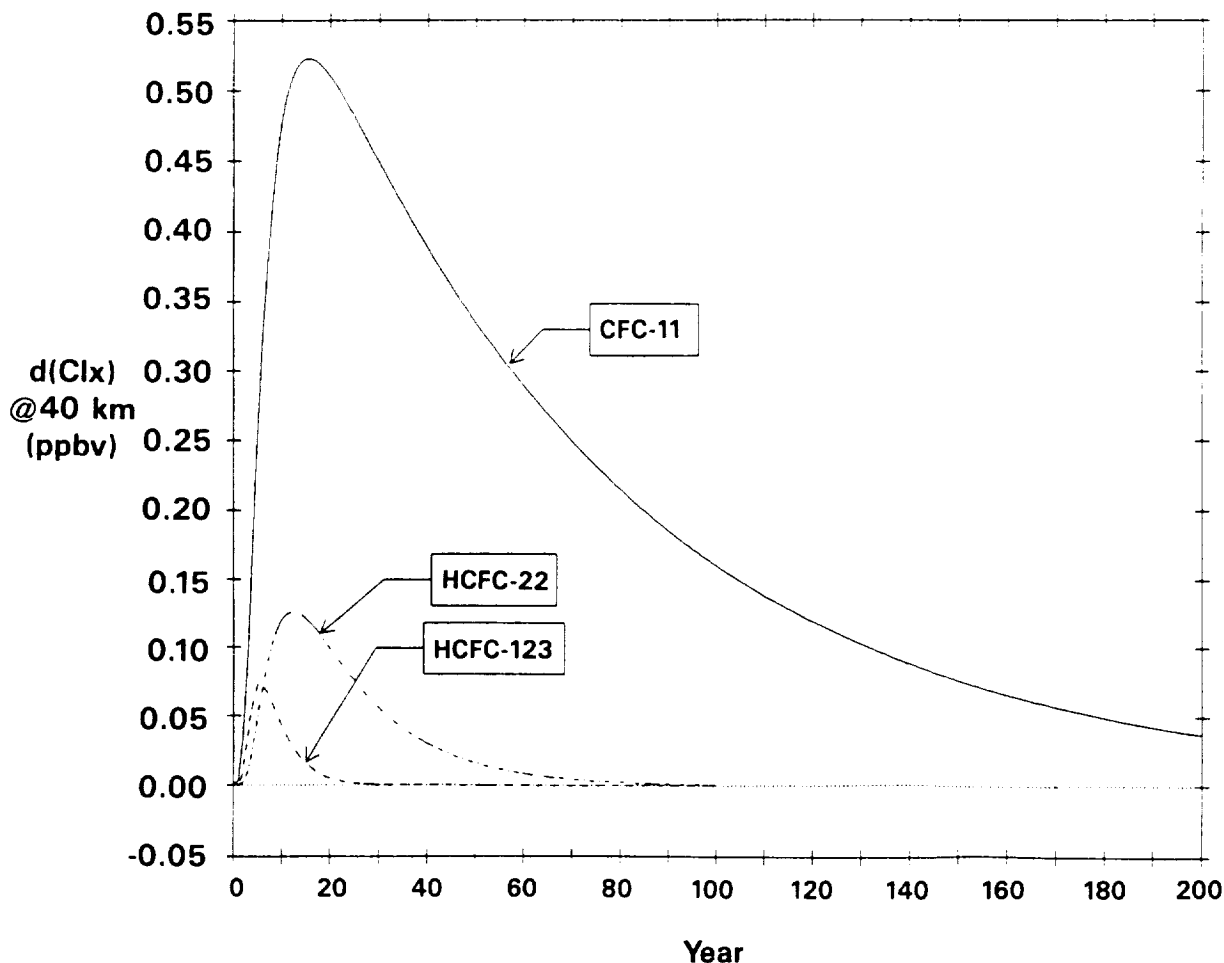
**Figure 1.** Calculated Tropospheric Mixing Ratio of Specified Gas Following a Pulsed Input of  $5.0 \times 10^9$  kg. (DuPont 1-D Model)

for the reference gas CFC-11. Column ozone is the total amount of ozone between the Earth's surface and space, or mathematically, it is the vertical integral of ozone concentration (molecules/cubic cm.) through the entire atmosphere. Defined in this manner, ODP is a useful measure of the potential for each compound to affect stratospheric ozone since:

- (1) It provides a measure of the cumulative chronic effect on ozone for each unit released into the atmosphere (more discussion below).
- (2) The ODP yields a single value for each compound rather than a time varying multitude of values.
- (3) It provides an estimate of the calculated effect of a compound compared to the maximum calculated effect of CFC-11 on an equal mass basis.
- (4) Calculations are easy and inexpensive, especially using models designed to calculate steady state ozone changes directly rather than through a time step approach.

The first reason for choosing this definition, and perhaps the most critical, is that it estimates the cumulative chronic effect on atmospheric ozone of each unit released. This effect is illustrated by the follow-

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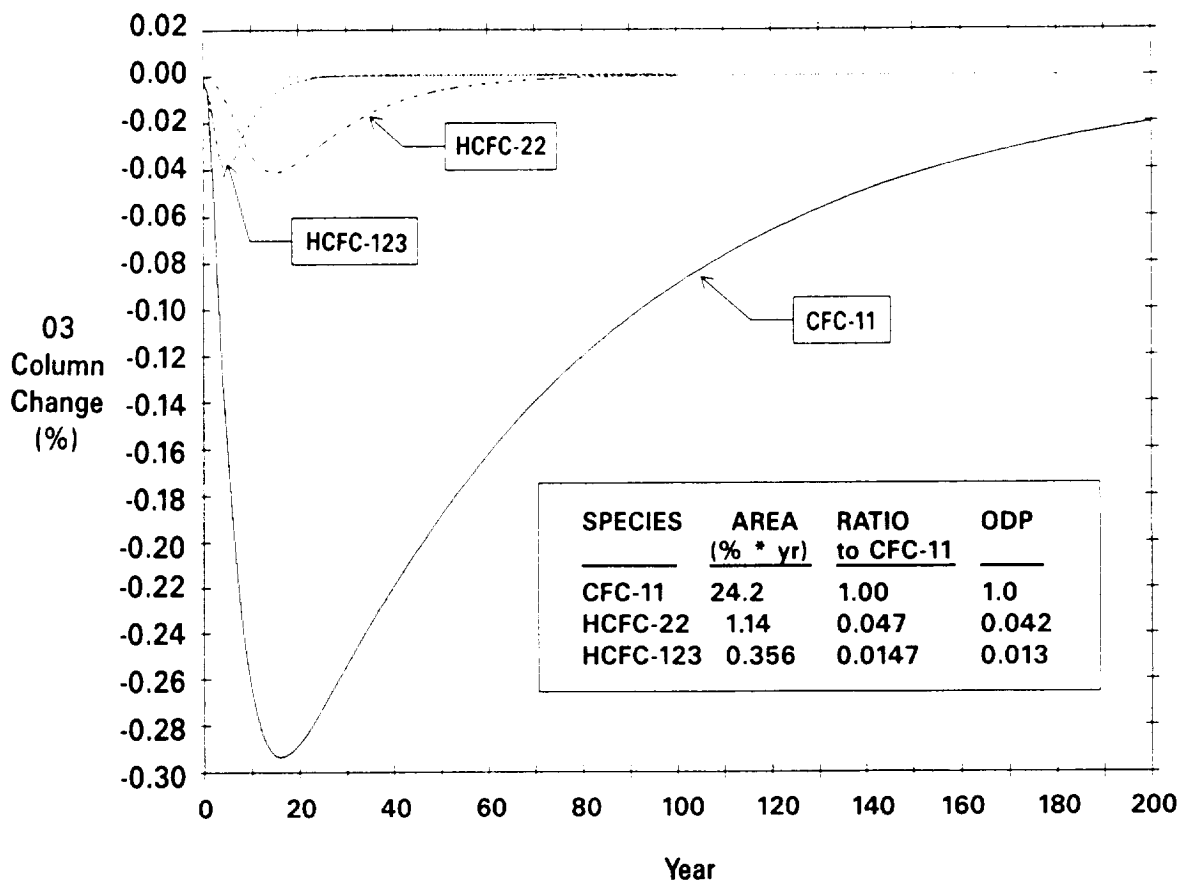


**Figure 2.** Calculated Change in Inorganic Chlorine at 40 km Following a Pulsed Input of  $5.0 \times 10^9$  kg of Specified Gas. (DuPont 1-D Model)

ing test performed using the Du Pont one dimensional model to determine relative effects of a given release of HCFC-123, HCFC-22, and CFC-11. This test assumed that a quantity ( $5 \times 10^9$  kg) of each halocarbon was emitted into the atmosphere during the first model year. Subsequent model years had zero modeled emissions and the transient atmospheric responses were calculated.

Transient results from the model are shown in Figures 1 to 3. Figure 1 shows the calculated tropospheric concentration of each gas, peaking at the year of the release, and then diminishing over time as a result of chemical reaction in the atmosphere. The decay time constant (on an exponential scale) corresponds to the calculated lifetime of the gas.

Figure 2 shows the calculated change of inorganic chlorine level at 40 km for each of the cases. Inorganic chlorine concentration (total of Cl, ClO, OCLO, Cl<sub>2</sub>O<sub>2</sub>, HCl, HOCl, and ClONO<sub>2</sub>), is an important parameter in the stratospheric chemistry since rate of chlorine catalysis of ozone destruction, among other factors, is directly related to its magnitude. Differences in inorganic chlorine concentrations for the these



**Figure 3.** Calculated Column Ozone Change Following a Pulsed Input of  $5.0 \times 10^9$  kg of Specified Gas. (DuPont 1-D Model)

compounds are due to three factors: (1) The weight percent of chlorine in each species is somewhat different ranging from 71% in CFC-11 to 41% of HCFC-22. (2) Location of decomposition of the species is important. HCFCs -123 and -22 are mainly destroyed in the troposphere such that only a fraction of the chlorine reaches the stratosphere as inorganic products. CFC-11, on the other hand, passes through the troposphere unreacted, such that all the chlorine is transported to the stratosphere where it eventually is broken down (primarily through photolysis) to inorganic chlorine. (3) Once in the stratosphere, compounds break down at different altitudes resulting in different levels of inorganic chlorine.

Figure 3 shows the change in column ozone for all cases. As seen in the insert table, the cumulative effects (time integrated) from emissions of  $5 \times 10^9$  kg of each halocarbon are closely, proportional to the ODP values for each chemical. Appendix A discusses the mathematical relationships that exist between the ODP calculated based on steady state perturbations and this transient problem. In summary, this test validates ODP as a measure of the cumulative effect on stratospheric ozone for each mass unit emitted to the atmosphere.

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Just as valuable as knowing the applicability of ODP, we also should recognize the limitations of the ODP definition in order to not extend interpretation beyond its valid scope. For instance, since ODP is defined at steady state, it is not representative of relative transient effects, especially during the early years of emissions. This fact is illustrated in Figure 4 showing the tropospheric concentration of two compounds following the onset of a constant emission level of each. One of the compounds has a 100 year lifetime (comparable to lifetimes of CFCs) and the other compound has a 5 year lifetime (comparable to lifetimes of hydrohalocarbons). We see that the ratio of the relative atmosphere concentration ratio does not approach steady state until about 400 years. Since the ODPs are based on steady state relative effects which are (nearly) proportional to CFC concentrations, the calculated relative effects for short-lived compounds during the approach to steady state are larger than indicated by the ODP value. This is simply because the effect from the short-lived species has reached its full strength whereas the effect from the long-lived species is still short of its steady state value. Further discussion on these transient effects will be covered in a later section of this paper.

### 3. DEFINITIONS

In order to make the ODP definition consistent among models the following criteria were selected:

1) Depletion level-the calculations are based on emission rates of each compound required to give a modeled ozone depletion of approximately 1%. This value of depletion was selected in order to yield results large enough to avoid the noise level inherent with numerical models, yet small enough to remain in the linear perturbation region.

2) Trace gas levels-changing concentrations of other trace gases affect calculated tropospheric OH levels [Sze (1977) and Chameides et al. (1977)] and future depletions. However, we chose to base the calculations on current levels of CO<sub>2</sub>, CH<sub>4</sub>, CO and N<sub>2</sub>O due to the uncertainties in future concentrations. The constant concentration assumption was chosen for clarity and simplicity.

3) Chlorine levels-since the long lived CFCs are present in today's atmosphere and will affect chlorine chemistry over the time scales that hydrohalocarbons might be used, background halocarbon concentrations were assumed constant at current levels (3.0 ppbv in the stratosphere with the exception of Oslo which used a background amount of 5.2 ppbv. Prior calculations with the Oslo model indicate little effect on the derived ODPs from the assumed chlorine background).

4) Bromine chemistry-current levels of bromine compounds were included in the model chemistry where appropriate.

Using the above provisions, the ODPs were then calculated as:

$$\text{ODP} = \frac{\begin{array}{l} \text{Calculated Steady State O3 depletion due to Compound X} \\ \text{-----} \\ \text{Emission rate of compound X to give depletion of 1\%} \end{array}}{\begin{array}{l} \text{Calculated Steady State O3 depletion due to CFC-11} \\ \text{-----} \\ \text{Emission rate of CFC-11 to give depletion of 1\%} \end{array}}$$

CFC-11 is used as the reference gas consistent with previous work (Wuebbles 1981).

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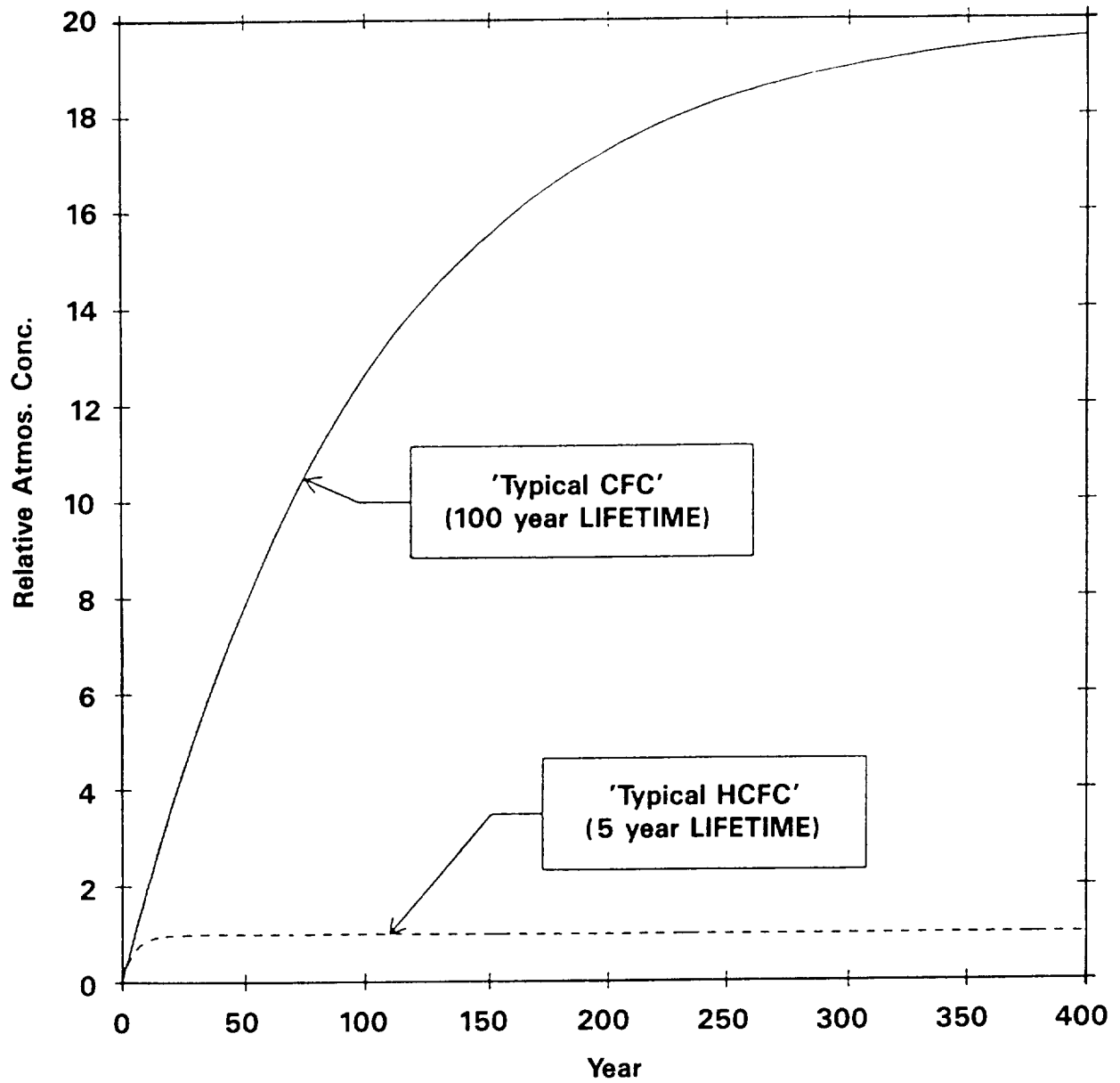


Figure 4. Atmospheric Concentrations of Halocarbons with 5- and 100- Year Lifetimes.

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### 4. MODEL CALCULATIONS

Atmospheric chemistry models use mathematical expressions to describe the chemical reaction rates, transport, and photolysis processes that determine the chemical fate of the halocarbons. Figure 5 illustrates a generalized image of the chemical life cycle of halocarbons in the atmosphere. Each compound enters the atmosphere at ground level and, in general, is removed by a combination of chemical processes: reaction with hydroxyl (OH) in the troposphere and the stratosphere, reaction with excited state oxygen in the stratosphere, and photolytic breakdown by ultraviolet light in the stratosphere. Laboratory measurements indicate that CFCs (e.g. CFC-11, -12, -113, -114 and -115) are primarily destroyed by ultraviolet light in the stratosphere and to a lesser degree, reaction with excited atomic oxygen; reaction with hydroxyl radical is inconsequential. Hydrohalocarbons are removed by all three processes, but the predominant mechanism is reaction with OH in the troposphere. The reaction of the hydrohalocarbons with hydroxyl radicals leads to appreciably shorter atmospheric lifetimes and reduced ODPs compared to the CFCs. Additionally, the HFCs have no calculated effect on ozone because they contain no chlorine and current theory indicates that fluorine released in their destruction will rapidly be converted to hydrogen fluoride, which has no effect on ozone.

Reaction rate constants and photolysis cross sections required as model input were obtained from a number of sources. When available, rate data recently reevaluated by Hampson et al. (1989), Hampson (1989), and Molina (1989) have been used. The secondary data source was the most recent evaluation of rate data by the NASA Panel (DeMore et al. 1987). In the absence of these recommendations, some reaction rate parameters were obtained from the open literature [Davidson et al (1978), Hubrich and Stuhl (1980)]. Some data were only available from unpublished sources (Magid 1988). Finally, no photolysis measurements could be found for HFC-125 and HFC-143 so photolytic destruction was assumed zero. Since photolysis is generally of little consequence for the hydrogenated halocarbons, this is a reasonable assumption. Table 2 lists reference sources, and when possible, the values for each kinetic parameters. All models utilize their "best" representations for transport and radiation processes, generally derived from first principles as well as fitting to key observed values for trace species.

Both one- and two-dimensional models have been used for these evaluations. One dimensional models calculate the altitudinal variation of the relevant atmospheric chemical processes at an average point on the surface of the earth with an average temperature profile. These models all share the advantage that they are easy to operate and evaluate. Two-dimensional (2-D) models on the other hand allow examination of calculated effects over the full range of latitudes and seasons. As such, their added complexity, is offset by better representation of nonlinear characteristics of global stratospheric transport and radiative processes. Ozone changes calculated by 2-D models are averaged with respect to both latitude and seasons before calculation of the ODP values.

The calculated atmospheric lifetime of each gas species provides a key comparison for modeled results. Table 3 shows a comparison of lifetime values calculated by the models.

ODP values are reported in Table 4. Note that the HFCs (molecules without chlorine) have zero calculated effect on ozone and therefore  $ODP = 0$ . Each of the ODP is reported to 2 figures, in reality, the results are credible to less than two significant figures due to uncertainties in model input parameters.

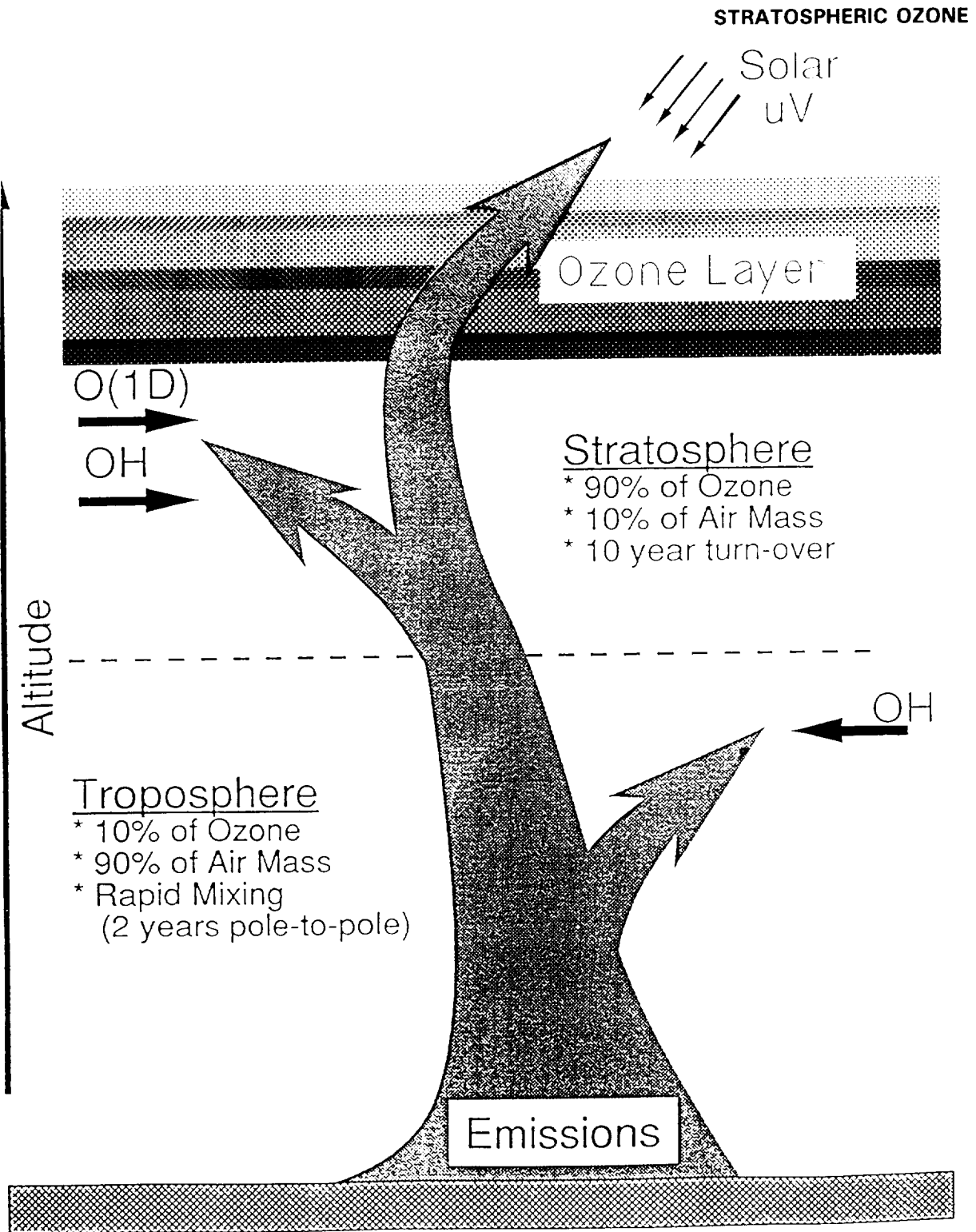


Figure 5. Generalized Chemical Lifecycle of a Halocarbon in the Atmosphere.

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**Table 2** Chemical Rate Data Used in ODP Calculations

Species	Photolysis	Reaction A	Rate(*) E/R	OH Reactions		O( <sup>1</sup> D) Reactions	
	UV X-Section			Refer.	Reaction Rate (**)	Branching Ratio (#)	Refer. (##)
CFC 11	JPL p130	—	—	—	2.3(-10)	.75	JPL
CFC 12	JPL p131	—	—	—	1.4(-10)	.86	JPL
CFC113	H&S (1980)	—	—	-	2.0(-10)	.80	Dav.
CFC 114	H&S (1980)	—	—	—	1.6(-10)	.80	Dav.
CFC 115	H&S (1980)	—	—	—	.89(-10)	.80	Dav.
HCFC 22	JPL p133	1.2(-12)	1650	Hamp	1.0(-10)	1.	Hamp
HCFC 123	Molina	6.4(-13)	850	Hamp	2.3(-10)	1.	Hamp
HCFC 124	Molina	6.6(-13)	1250	Hamp	1.0(-10)	1.	Hamp__a
HFC 125	—	3.8(-13)	1500	Hamp	0.5(-10)	1.	Hamp
HFC 134a	Allied	1.7(-12)	1750	Hamp	0.5(-10)	1.	Hamp__a
HCFC 141b	Molina	2.7(-13)	1050	Hamp	1.5(-10)	1.	Hamp__a
HCFC 142b	Molina	9.6(-13)	1650	Hamp	1.4(-10)	1.	Hamp
HFC 143a	—	2.6(-13)	1500	Hamp	0.6(-10)	1.	Hamp
HFC 152a	Allied	1.5(-12)	1100	Hamp	1.0(-10)	1.	Hamp__a
Carbon Tet. Methyl	JPL p129	—	—	—	3.3(-10)	.86	JPL
Chloro.	JPL p167	5.0(-12)	1800	JPL	3.18(-10)	80	Dav.

\* Reaction Rate Constant of form:  $k = A \exp[-E/(RT)]$ , where A and k have the units of  $\text{cm}^3/(\text{molecule sec})$ .

\*\* Reaction rate constant with units  $\text{cm}^3/(\text{molecule sec})$ .

# Fraction of O(<sup>1</sup>D) disappearances proceeding through reaction channel, remainder pass through quenching channel to O(3p) and no reaction with the halocarbon.

## Measurements reported in Davidson et al. were used. Data for remaining gases generated using the estimation formula developed in that reference. Branching ratios of 0.8 were assumed values.

Reference Key:

- Allied —Magid (1988)
- Dav. —Davidson et al.(1978)
- Hamp —Hampson, Kurylo, and Sander (1989)
- Hamp\_\_a —Hampson (1989)
- H&S —Hubrich and Stuhl (1980)
- Molina —Molina (1989)
- JPL —DeMore et al. (1987)



Table 3 Lifetimes (Years)

Species	1-D Model Results			Oslo	2-D Model Results		
	LLNL	AER	Du Pont		LLNL	AER	Du Pont
CFCII	80.	60.	71.	60.	52.	47.	46.
CFC12	154.	125.	154.	105.	101.	95.	118.
CFC113	96.	96.	117.	101.	79.		
CFC114	209.	260.	319.	236.	197.		
CFC115	680.	690.	548.	522.	393.	399.	
HCFC22	20.	20.0	16.	17.	15.	24.	12.7
HCFC123	1.9	2.1	1.6	1.7	1.5	2.4	1.2
HCFC124	8.4	8.8	6.9	7.4	6.5	10.	5.3
HFC125	37.	37.	25.	27.	43.	19.	
HFC134a	21.	21.	16.	15.	24.	12.5	
HCFC141b	8.9	9.4	7.8	8.0	6.9	11.	5.8
HCFC142b	25.	25.	19.	21.0	19.	28.	15.1
HFC143a	54.	52.	42.	40.			
HFC152a	2.1	2.3	1.7	1.5	2.7	1.3	
CCl <sub>4</sub>	73.	53.	61.	52.2	47.	40.	40.
CH <sub>3</sub> CCl <sub>3</sub>	7.4	7.4	6.0	6.3	5.8	7.9	4.7

Differences in calculated tropospheric hydroxyl concentrations account for many of the lifetime differences. Several factors could contribute to the differences in the calculated concentrations of tropospheric OH. First, there is inadequate information on the distributions of a number of gases (e.g., CO, O<sub>3</sub> and NO<sub>x</sub>) that play critical roles in the determination of tropospheric OH levels. Different modeling groups are likely using different boundary conditions for these gases. Second, there are uncertainties in many tropospheric processes, especially in rates for key reactions.

However, hydrohalocarbon lifetimes are generally consistent among the models. The sensitivity of calculated lifetimes to chemical rate information is most pronounced in the case of HFC-143a. Because its UV absorption spectrum was unreported, reaction with hydroxyl radical was the only modelled loss process. Its recommended OH reaction rate constant is the slowest of the hydrohalocarbons, so its calculated lifetime is long. Inclusion of photolysis will impact the chemical lifetime of this species.

Analysis of data for atmospheric CH<sub>3</sub>CCl<sub>3</sub> may provide a reasonable though indirect check on the calculated lifetime of CH<sub>3</sub>CCl<sub>3</sub> and therefore the global average concentration of OH. Based on the observed trends of CH<sub>3</sub>CCl<sub>3</sub> and the estimated emission data, analysis indicates a globally averaged CH<sub>3</sub>CCl<sub>3</sub> atmospheric lifetime of  $6.3 \pm 1.1$  years [Prinn et al. (1987, NASA (1988))], compared with model calculated values which range from 4.7 to 7.8 years (see table 3 for the various models). The deduced average OH from CH<sub>3</sub>CCl<sub>3</sub> data, while useful for placing important constraints on theoretical models, must be

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**Table 4** Ozone Depletion Potentials

Species	1-D Model Results			Oslo	2-D Model Results		
	LLNL	AER	Du Pont		LLNL	AER	Du Pont
CFC11	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CFC12	1.0	0.92	1.0	0.92	0.87	0.88	0.89
CFC113	0.82	0.83	0.89	0.86	0.76		
CFC114	0.76	0.63	0.79	0.82	0.56		
CFC115	0.43	0.36	0.45	0.40	0.27	0.37	
HCFC22	0.053	0.057	0.042	0.046	0.043	0.071	0.032
HCFC123	0.016	0.019	0.013	0.013	0.016	0.027	0.013
HCFC124	0.019	0.021	0.016	0.018	0.017	0.030	0.013
HFC125	-0-	-0-	-0-	-0-	-0-	-0-	-0-
HFC134a	-0-	-0-	-0-	-0-	-0-	-0-	-0-
HCFC141b	0.081	0.092	0.066	0.089	0.081	0.14	0.065
HCFC142b	0.059	0.056	0.053	0.056	0.045	0.077	0.035
HFC143a	-0-	-0-	-0-	-0-	-0-	-0-	-0-
HFC152a	-0-	-0-	-0-	-0-	-0-	-0-	-0-
CCl <sub>4</sub>	1.1	1.16	1.1	1.2	1.1	0.95	1.2
CH <sub>3</sub> CCl <sub>3</sub>	0.11	0.14	0.092	0.14	0.12	0.20	.11

interpreted as an appropriate density and temperature-weighted average characteristic to CH<sub>3</sub>CCl<sub>3</sub>. Since the concentration of OH is expected to fluctuate appreciably in both time and space, using globally averaged OH deduced from CH<sub>3</sub>CCl<sub>3</sub> to calculate lifetimes for other HCFCs may not necessarily be accurate, particularly for those HCFCs with lifetimes substantially different from that of CH<sub>3</sub>CCl<sub>3</sub>. The approach used here is to calculate tropospheric OH based on chemical models rather than adopt a single OH value derived from CH<sub>3</sub>CCl<sub>3</sub> data.

**Table 5** Scaled by Methyl Chloroform Lifetime of 6.3 years

Species	1-D Model Results			Oslo	2-D Model Results		
	LLNL	AER	Du Pont		LLNL	AER	Du Pont
HCFC22	0.045	0.049	0.044	0.046	0.047	0.057	0.043
HCFC123	0.013	0.016	0.013	0.013	0.017	0.022	0.017
HCFC124	0.016	0.018	0.017	0.018	0.019	0.024	0.017
HCFC141b	0.069	0.078	0.069	0.089	0.089	0.11	0.088
HCFC 142b	0.051	0.048	0.055	0.056	0.050	0.062	0.047
CH <sub>3</sub> CCl <sub>3</sub>	0.094	0.12	0.096	0.14	0.13	0.16	0.149

However, as a way to examine differences in ODPs due to differences in model calculated OH, the calculated ODPs can be scaled using the ratio of measured lifetime for methylchloroform of 6.3 years (NASA 1988) to the calculated lifetimes from each of the models. This normalization leads to a more consistent set of ODP values as shown in Table 5. This set of calculations indicate that the HCFCs have ozone depletion potentials one-tenth or less of CFC-11 and that the values calculated by different modeling groups agree fairly well.

## 5. SENSITIVITY STUDIES

The above globally averaged ODP values are derived from model calculations assuming present day atmospheric gas concentrations conditions using "best" representations of transport processes. To check the importance of these assumptions, additional calculations have been carried out to test the sensitivity of the relative effects to 1) levels of other trace gases, 2) seasonal and latitudinal dependencies and 3) assumed stratospheric transport processes.

### Sensitivity of ODPs to Other Trace Gas Levels

ODP values have all been based on calculated ozone changes in a modeled atmosphere assuming present day amounts of CFCs, CO<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O, Brx and other trace gases. Because it is important to quantify the effects of possible changes in the future trace gas concentrations on ODPs, calculations were performed to determine the sensitivity of the ODPs to trace gas concentration changes that may occur within the next century if current trends continue.

Trace gas concentrations were varied from current concentrations as shown in Table 6. These concentrations were changed both individually and as an ensemble in the sensitivity calculations. Calculated changes in ozone for tested CFCs and HCFCs are relative to an atmosphere including the assumed trace gas perturbation.

Two models were used to determine the sensitivity of atmospheric lifetimes and Ozone Depletion Potentials to trace gas concentrations. Calculations with the AER 1-D model assumed a background stratospheric chlorine content of 3 ppbv. Calculations with the Oslo 2-D model used a background chlorine amount of 5.2 ppbv. Prior calculations with the Oslo model indicate little effect on the derived ODPs from the assumed chlorine background amount.

**Table 6** Change in Ground Level Trace Gas Concentrations Assumed in Sensitivity Studies

Trace Gas	Normal	Perturbed
CO <sub>2</sub>	340 ppmv	680 ppmv
CH <sub>4</sub>	1.6 ppmv	3.2 ppmv
CO	100 ppbv	200 ppbv
N <sub>2</sub> O	300 ppbv	360 ppbv
Brx	20 pptv	40 pptv

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**Table 7** Sensitivity of Calculated Lifetimes to Changes in Trace Gas Values (based on AER 1-D results)  
LIFETIMES (years)

	CFC-11	CFC-12	HCFC-22	HCFC-123
Present day atmosphere	60	125	20	2.1
CO <sub>2</sub> (340 → 680 ppmv)	61	128	20	2.1
CH <sub>4</sub> (4.6 → 3.2 ppmv)	60	126	23	2.5
CO (100 → 200 ppbv)	60	125	25	2.7
N <sub>2</sub> O (300 → 360 ppbv)	59	123	20	2.1
CH <sub>3</sub> Br (20 → 40 pptv)	59	125	20	2.1
All changes combined	60	127	26	2.9

Table 7 shows the calculated changes in atmospheric lifetimes of CFC-11, CFC-12, HCFC-22 and HCFC-123 for the various sensitivity calculations. The largest effects are evident for the HCFCs in the cases where CH<sub>4</sub> and CO concentrations are perturbed. Both CH<sub>4</sub> and CO strongly influence tropospheric HO<sub>x</sub> chemistry, therefore OH concentration, and consequently the primary destruction of the HCFCs are affected resulting in the expected impact on atmospheric lifetimes. The relatively minor changes in lifetimes of the CFCs are primarily a result of increased photolysis rates for the trace gas perturbed atmospheres.

Table 8 presents ODPs resulting from these calculations. For both the AER 1-D model and the Oslo 2-D model, the largest sensitivity in the ODP for CFC-12 occurs for the assumed concentration change in N<sub>2</sub>O. As expected, ODPs for the HCFCs are affected most by changes in CH<sub>4</sub> and CO levels.

**Table 8** Sensitivity of Ozone Depletion Potentials to Changes in Trace Gas Values

<b>1. AER 1-D Model</b>				
	CFC-11	CFC-12	HCFC-22	HCFC-123
Present day atmosphere	1.0	0.92	0.057	0.019
CO <sub>2</sub> (340 → 680 ppmv)	1.0	0.93	0.051	0.018
CH <sub>4</sub> (1.6 → 3.2 ppmv)	1.0	0.93	0.069	0.023
CO (100 → 200 ppbv)	1.0	0.93	0.070	0.024
N <sub>2</sub> O (300 → 360 ppbv)	1.0	1.01	0.071	0.019
CH <sub>3</sub> Br (20 → 40 pptv)	1.0	0.92	0.055	0.019
All changes combined	1.0	0.95	0.076	0.026
<b>2. Oslo 2-D model (all calculations with 5.2 ppbv Cly)</b>				
	CFC-12	HCFC-22	HCFC-123	HCFC-124
Present day atmosphere	0.92	0.046	0.013	0.018
CO <sub>2</sub> (340 → 600 ppmv)	0.94	0.049	0.016	
CH <sub>4</sub> (1.6 → 3.2 ppmv)	0.93	0.058	0.016	
N <sub>2</sub> O (300 → 360 ppbv)	0.97	0.042	0.015	
Brx (18 → 33 pptv)	0.91	0.051	0.016	0.020
All changes combined	0.96	0.062	0.018	0.020

The calculated sensitivities to background trace gas concentrations can be explained as follows. First, changes in atmospheric lifetimes will affect the ODP in that as the lifetime increases/decreases, more/less of the CFC or HCFC is accumulated in the atmosphere at steady state for the same mass emitted. Secondly, the response of ozone to increases in chlorine can be different in the future atmosphere. However, this change in response will only affect the ODP estimates if the response of individual CFCs or HCFCs are different from that of CFC-11.

In conclusion, both lifetimes and derived ODPs are moderately sensitive to significant changes in background trace gas concentrations. However, for the scenarios examined, the range in sensitivity of the ODPs is well within the overall uncertainty range for model-determined ODP values. Possible systematic errors, perhaps due to missing chemistry or other processes, may provide a much more significant impact on the derived ODP values.

Sensitivity of ODPs with Latitude and Season

The ODPs derived from two-dimensional model results are analyzed in this section in terms of the variations of the ODP values as a function of latitude and season. These values were determined by comparing ozone changes calculated for each gas relative to changes calculated for the same mass of CFC-11 at all latitudes of the earth and seasons of the year in an approach analogous to the globally-averaged ODPs.

Figures 6 through 13 show results from the four two-dimensional modeling groups. Figure 6 shows

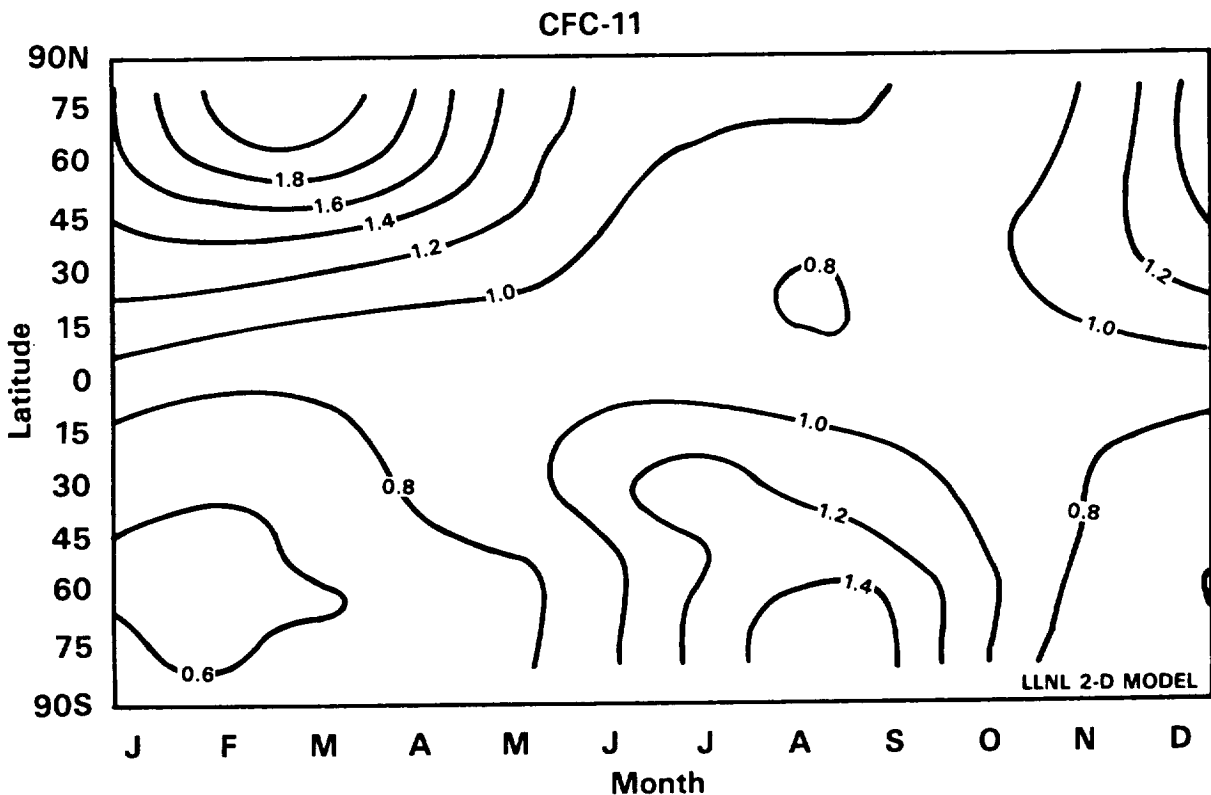
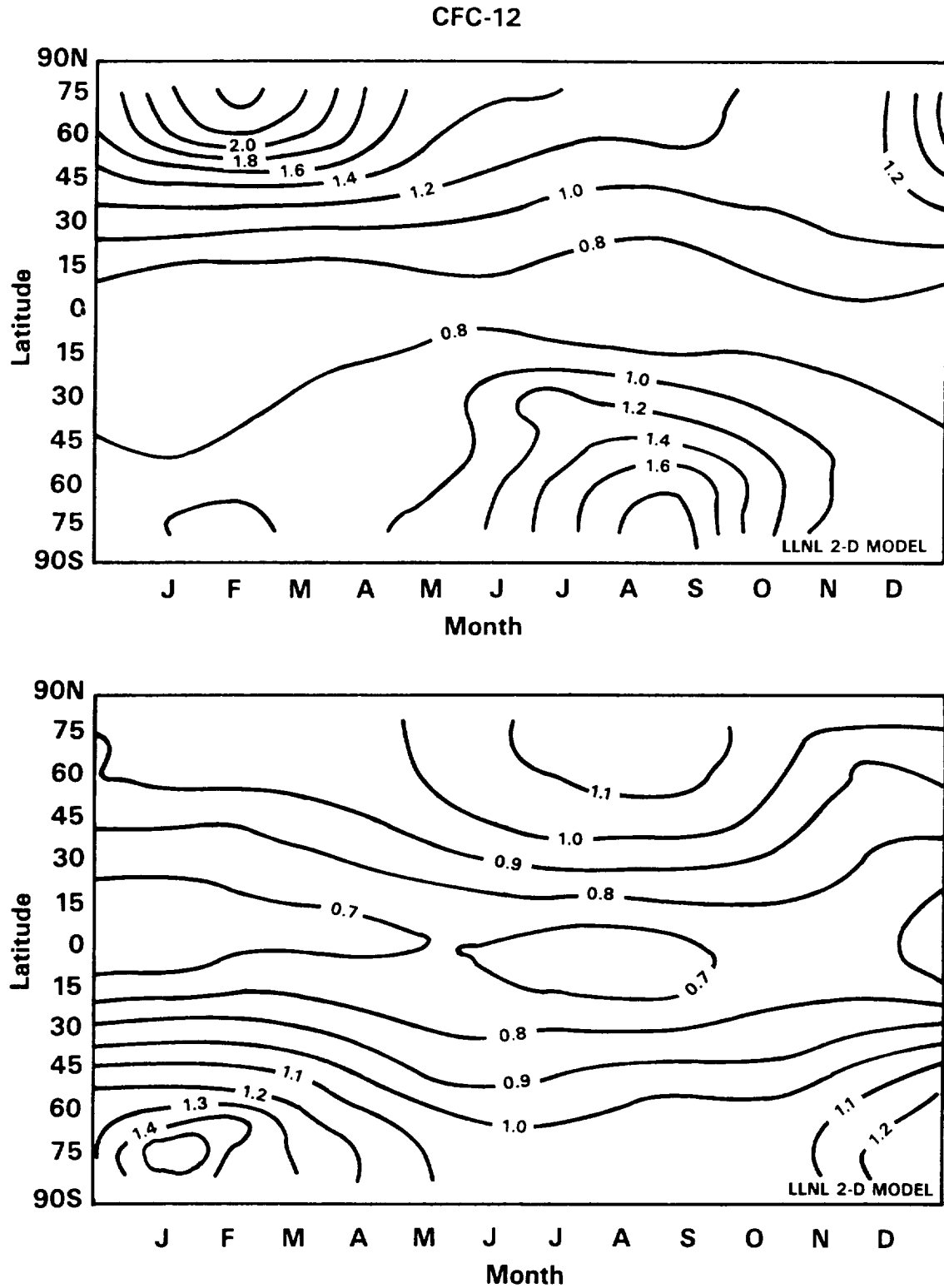


Figure 6. Calculated Latitudinal and Seasonal Steady-State Ozone Change from Emission of CFC-11 (LLNL 2-D).

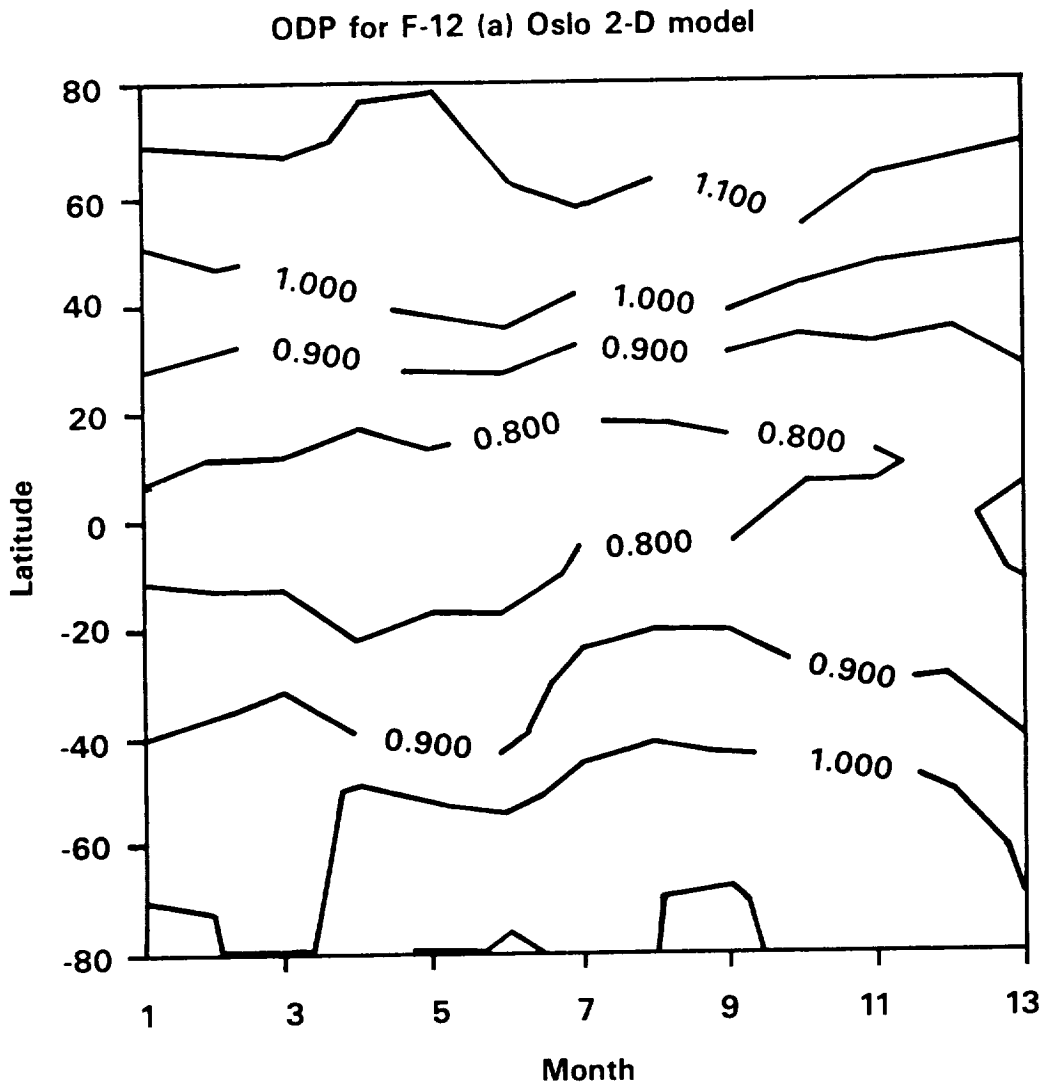
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**Figure 7A.** Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of CFC-12 (LLNL 2-D).

the calculated change in total ozone as a function of latitude and season for CFC-11 perturbation as calculated in the LLNL 2-D model; this calculation, designed with assumed emissions to give a global ozone decrease of 1%, acts as the comparison reference for the following discussion of latitudinal/seasonal ODPs. Consistent with previous 2-D model analyses of CFC effects on ozone (e.g., WMO, 1986), the largest changes in ozone occur at the poles in late winter to early spring. Figures 7 through 13 give the calculated latitude/season variations in ODPs from the four models (when available) for the following species: CFC-12, HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b and methyl chloroform. Also for each case, the calculated changes in total ozone are shown for the LLNL model assuming emission rates sufficiently large to give an approximate 1% global ozone decrease; as with CFC-11, maximum changes in total ozone are calculated to occur near the poles in late winter for all species.

Once the calculated changes are compared relative to CFC-11 and adjusted for differences in assumed emission rates, the resulting values indicate a generally variable dependency on latitude and generally weaker



**Figure 7B.** Calculated Latitudinal and Seasonal Relative Ozone Depletion of CFC-12 (Oslo 2-D).

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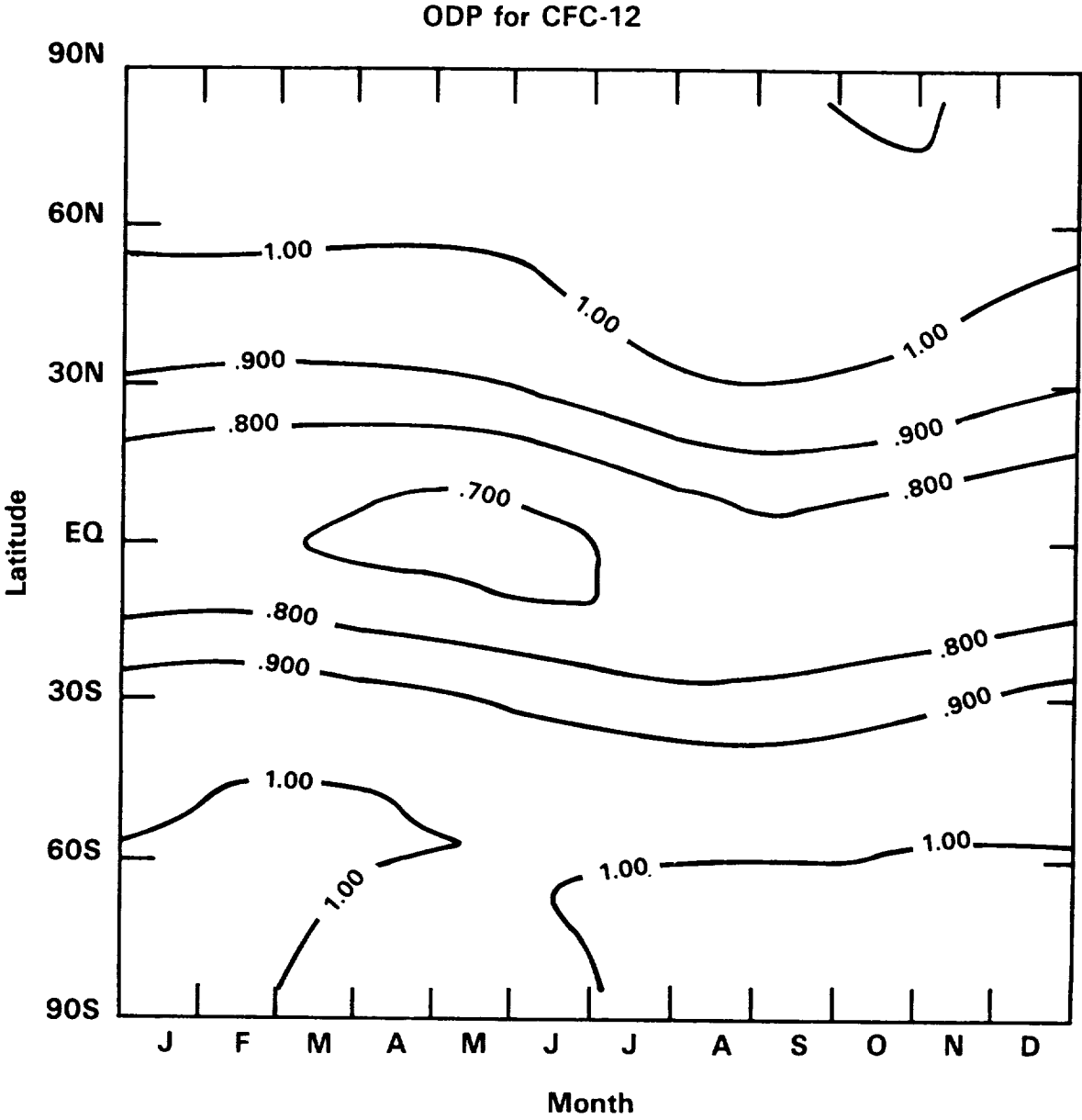
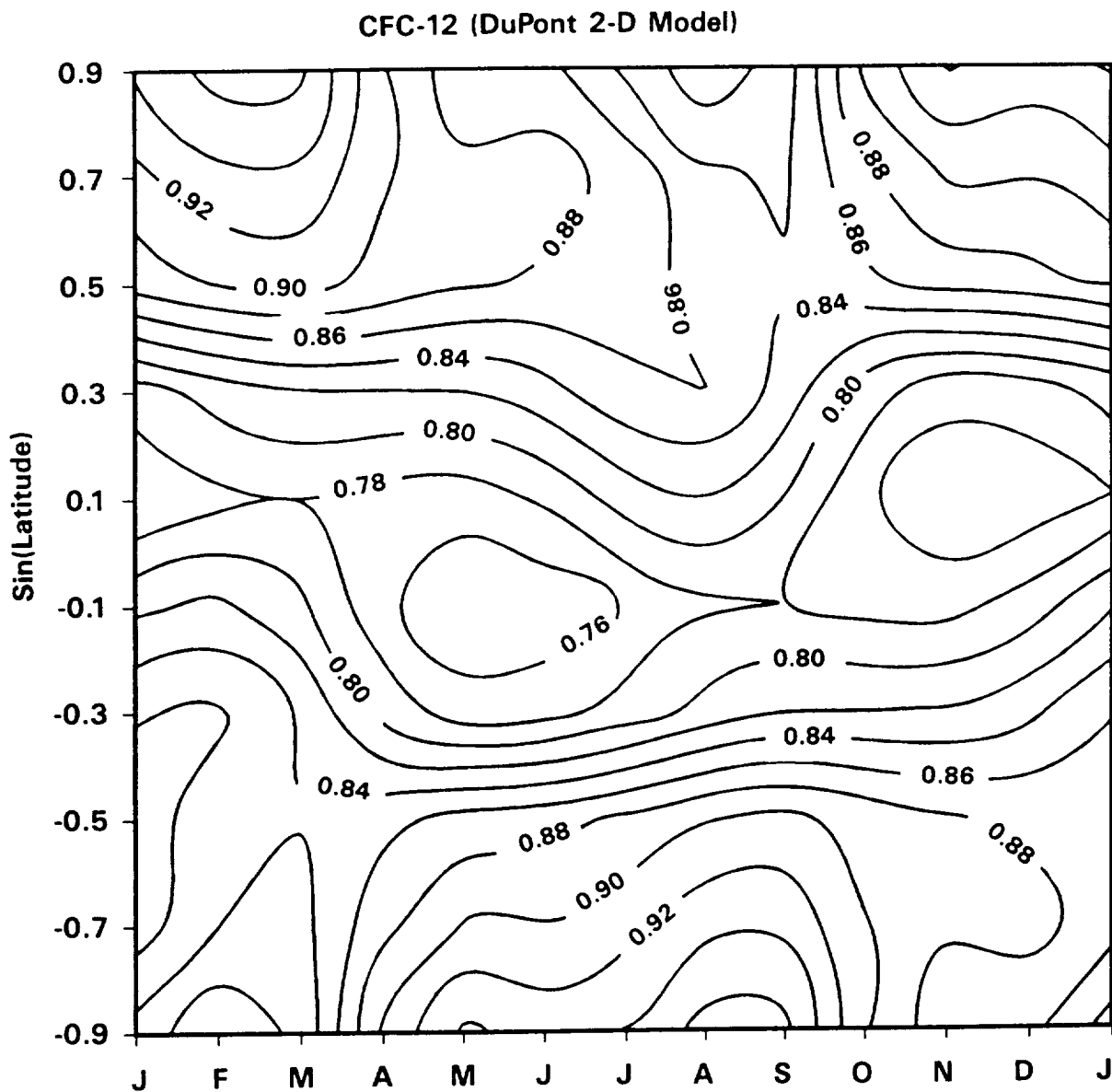


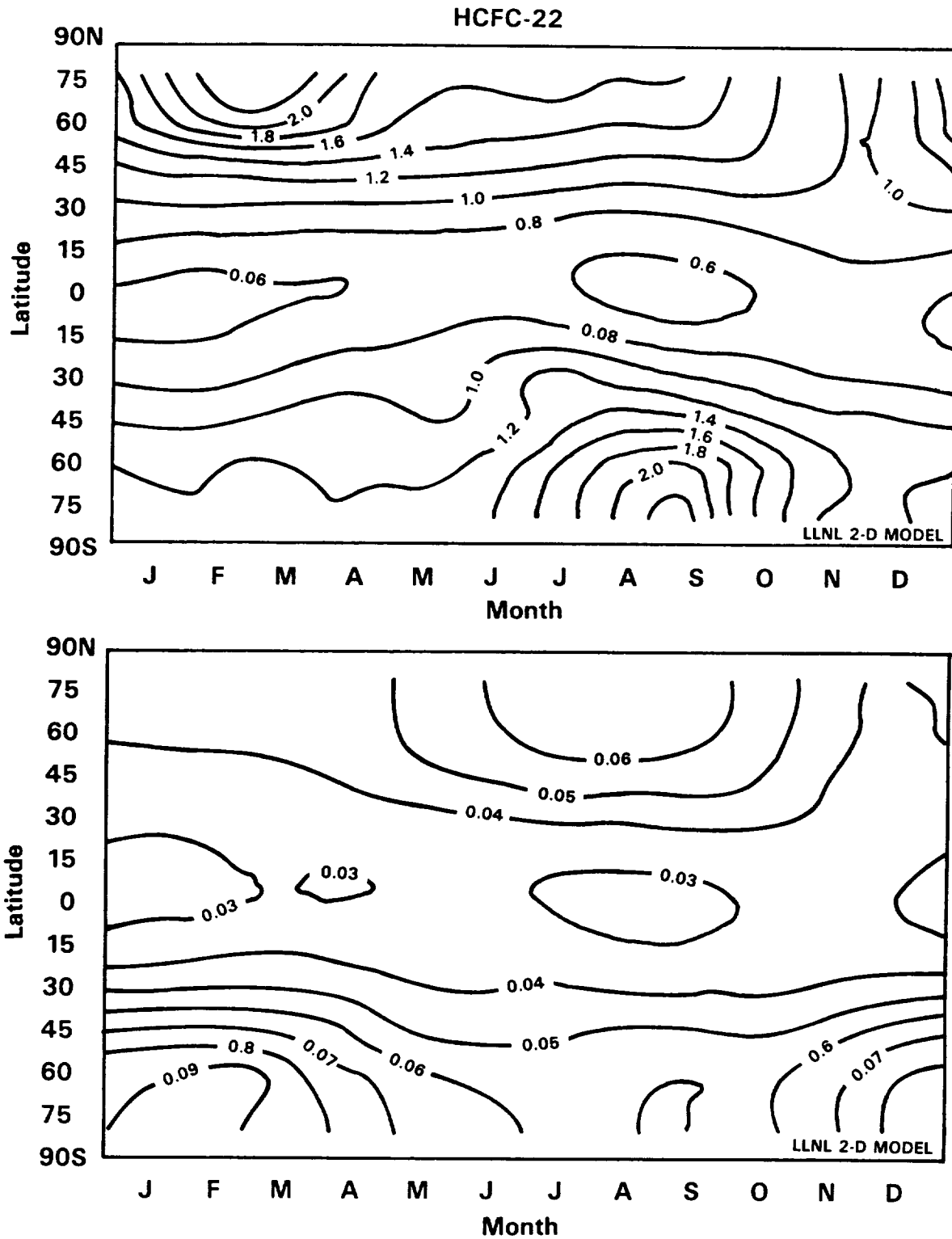
Figure 7C. Calculated Latitudinal and Seasonal Relative Ozone Depletion of CFC-12 (AER 2-D).





**Figure 7D.** Calculated Latitudinal and Seasonal Relative Ozone Depletion of CFC-12 (DuPont 2-D).

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**Figure 8A.** Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of HCFC-22 (LLNL 2-D).

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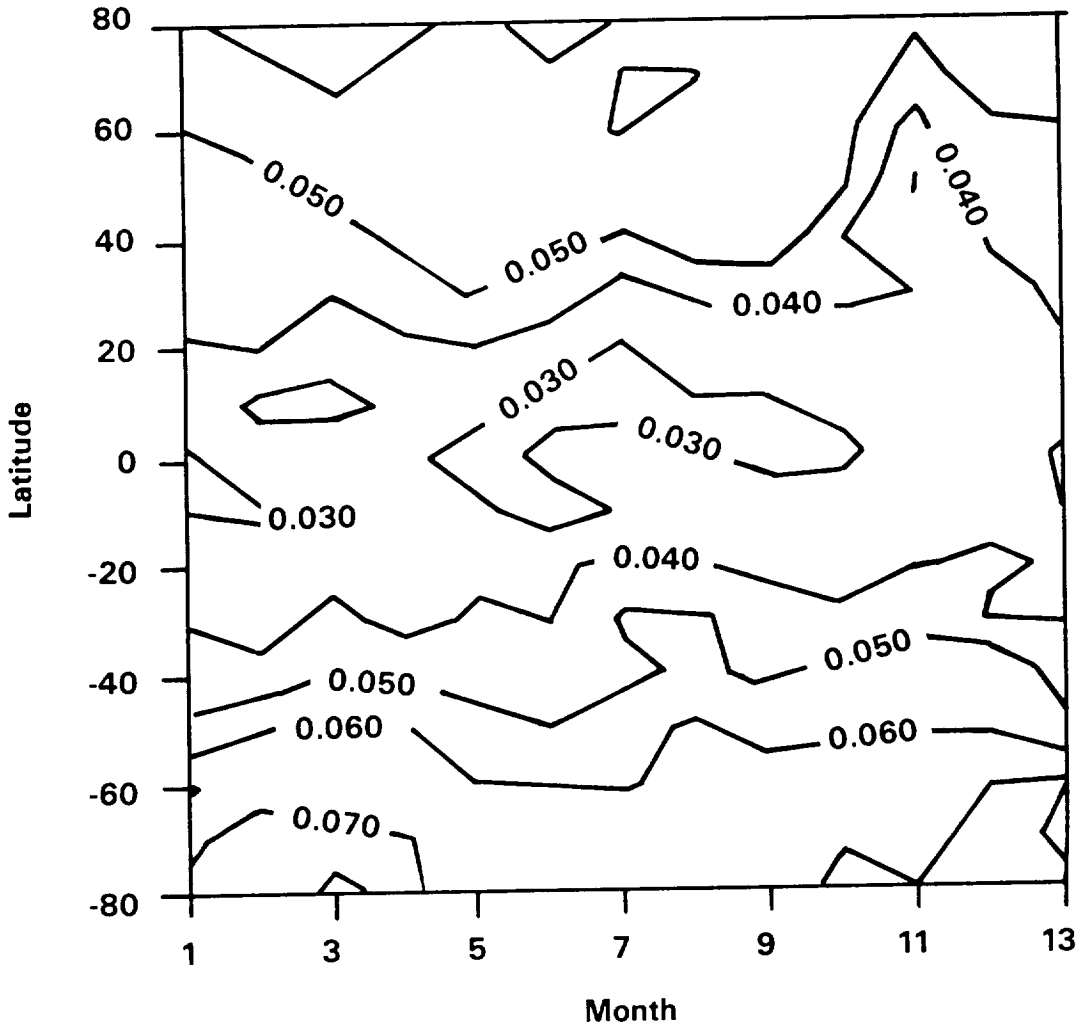


Figure 8B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 2 of Transport Sensitivity Study] (AER 2-D).

STRATOSPHERIC OZONE

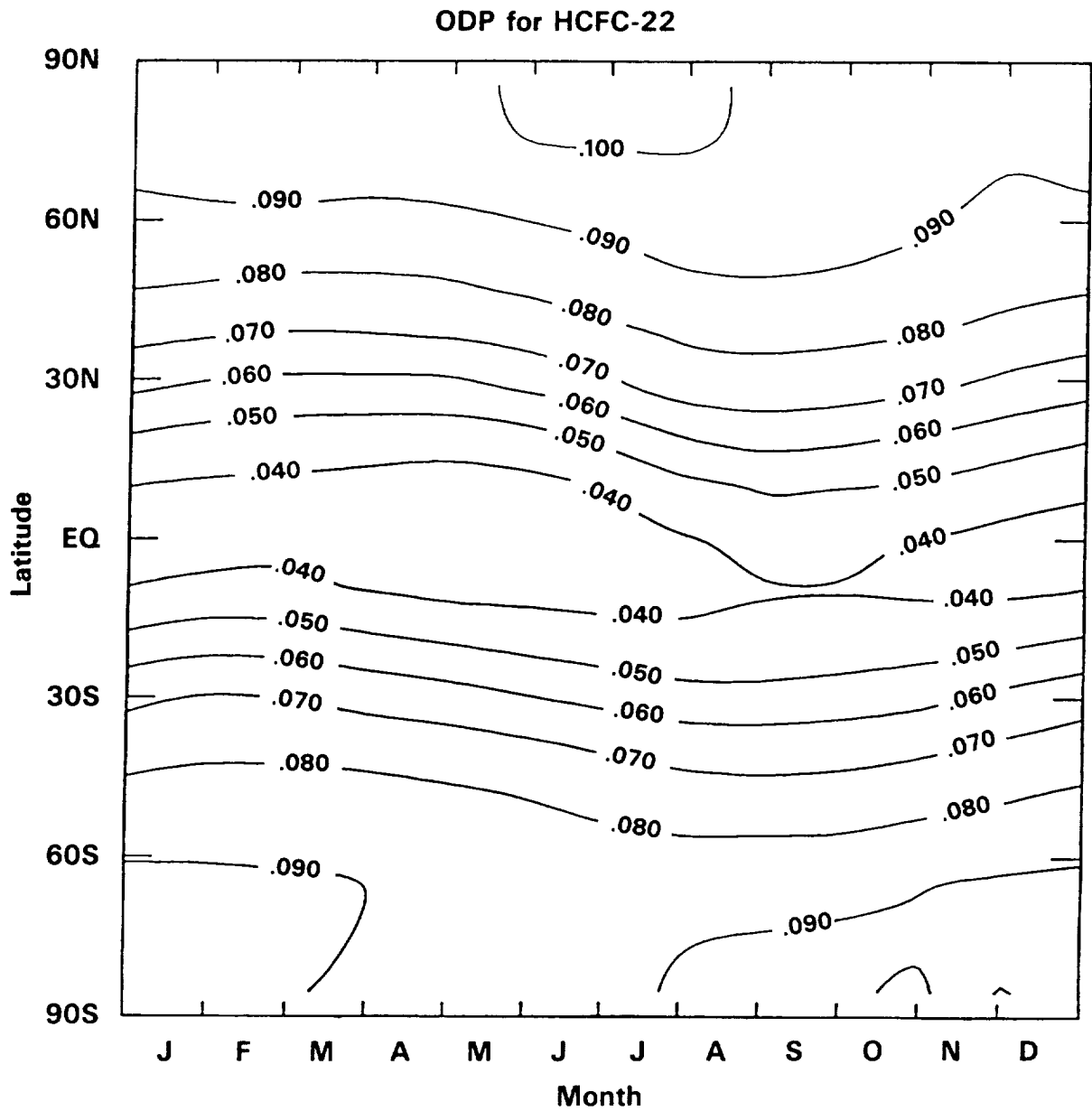


Figure 8C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 (AER 2-D).

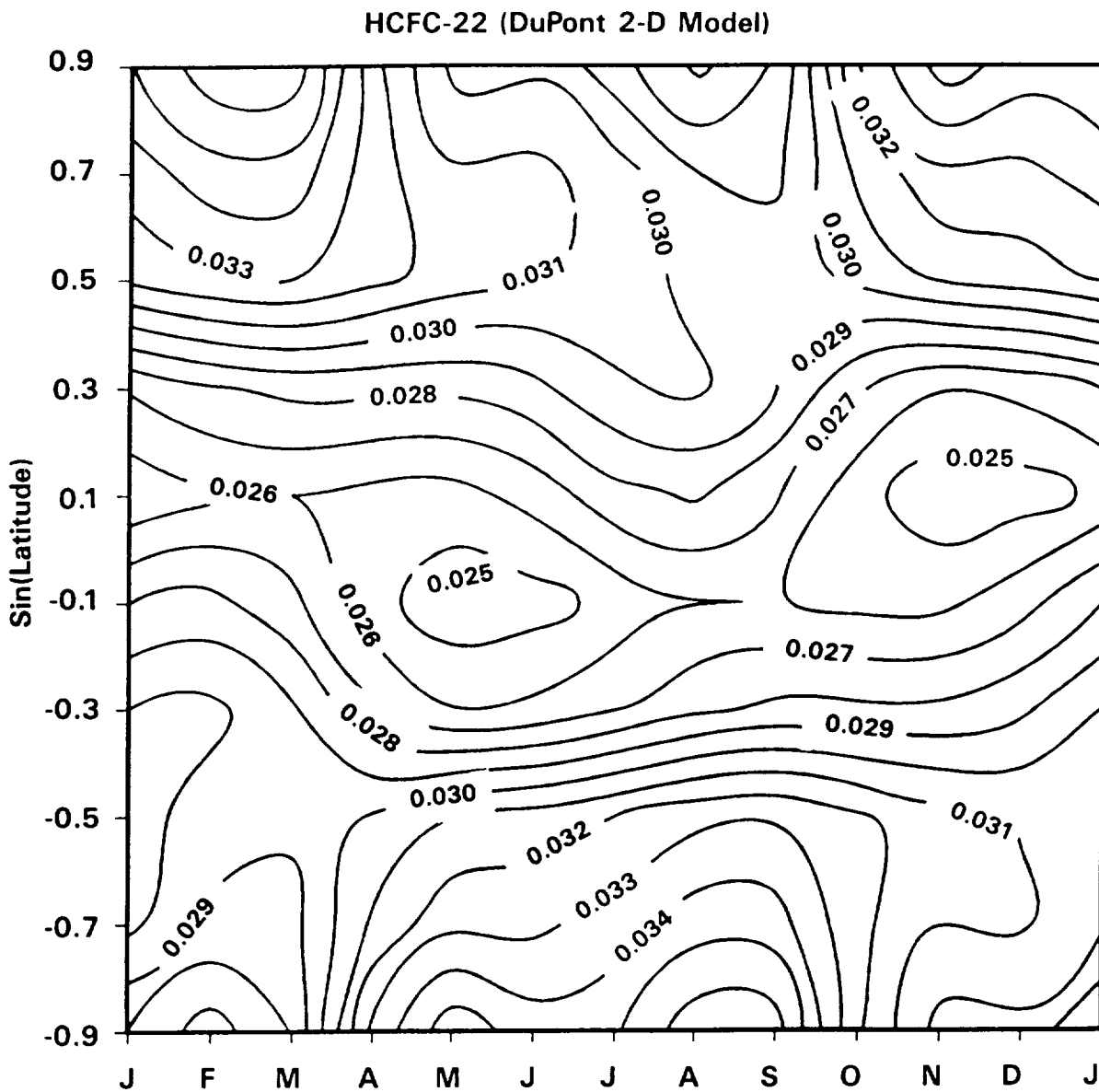
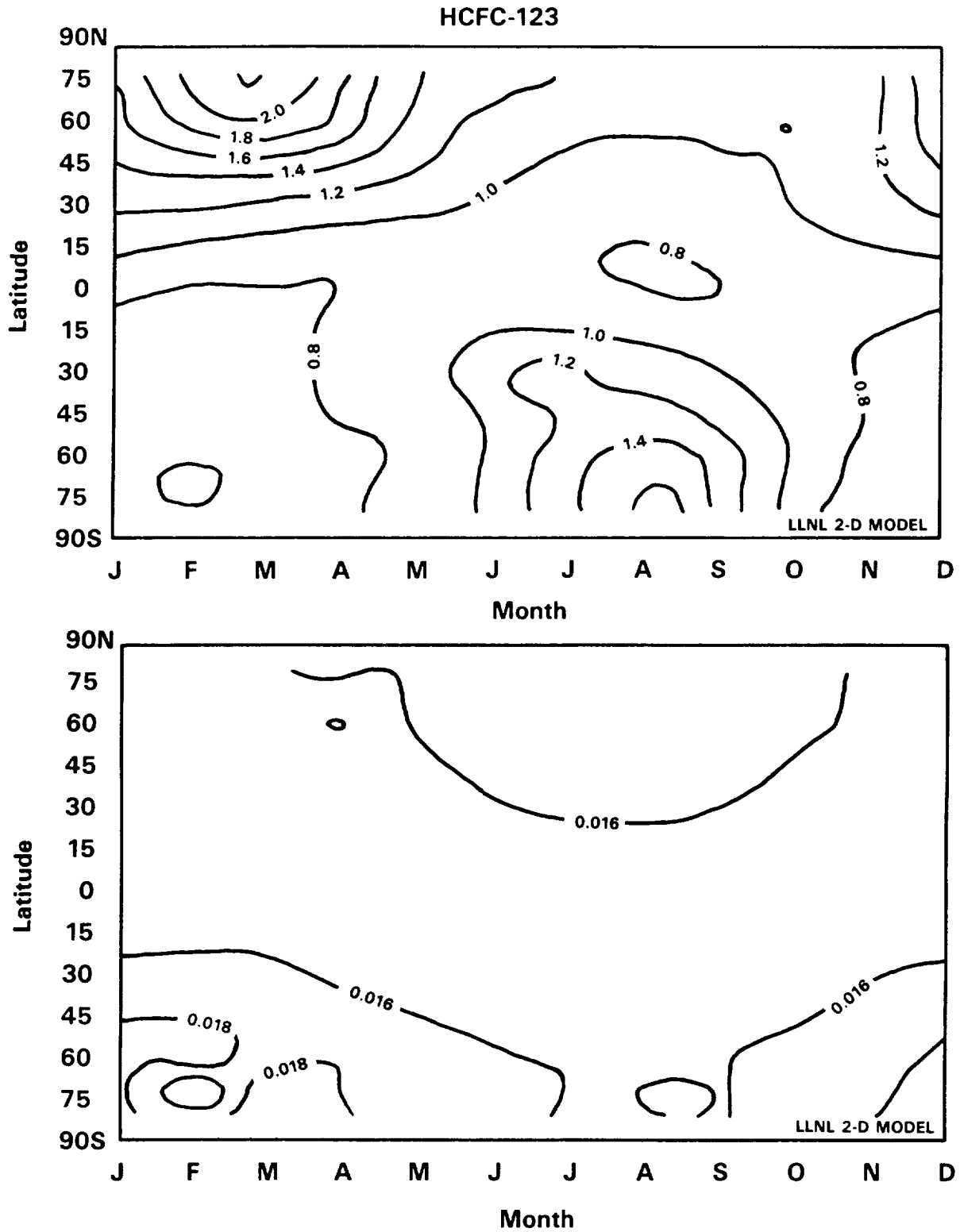


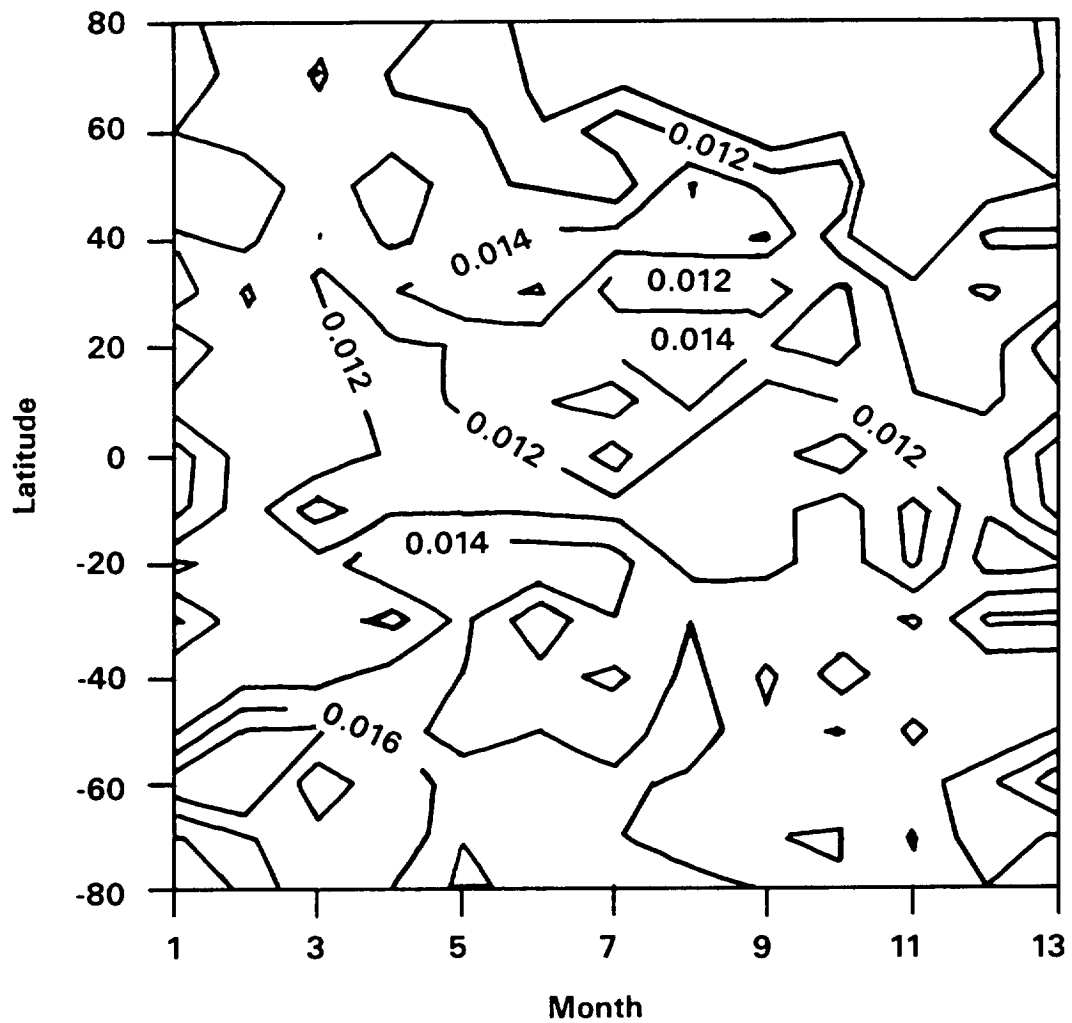
Figure 8D. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 (DuPont 2-D).

STRATOSPHERIC OZONE



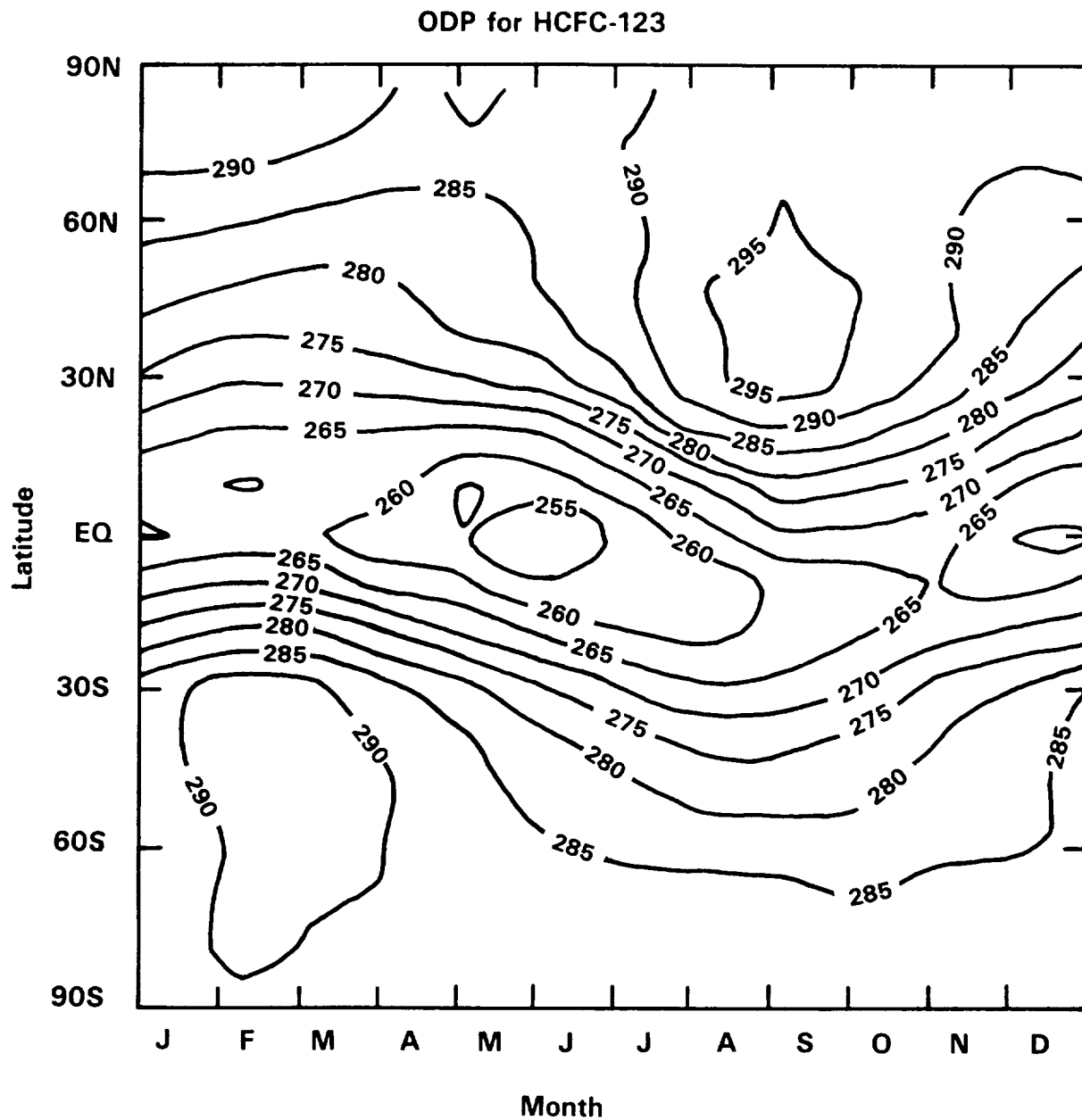
**Figure 9A.** Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of HCFC-123 (LLNL 2-D).

## ODP for F-123 (o) Oslo 2-D model



**Figure 9B.** Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-123 (Oslo 2-D).

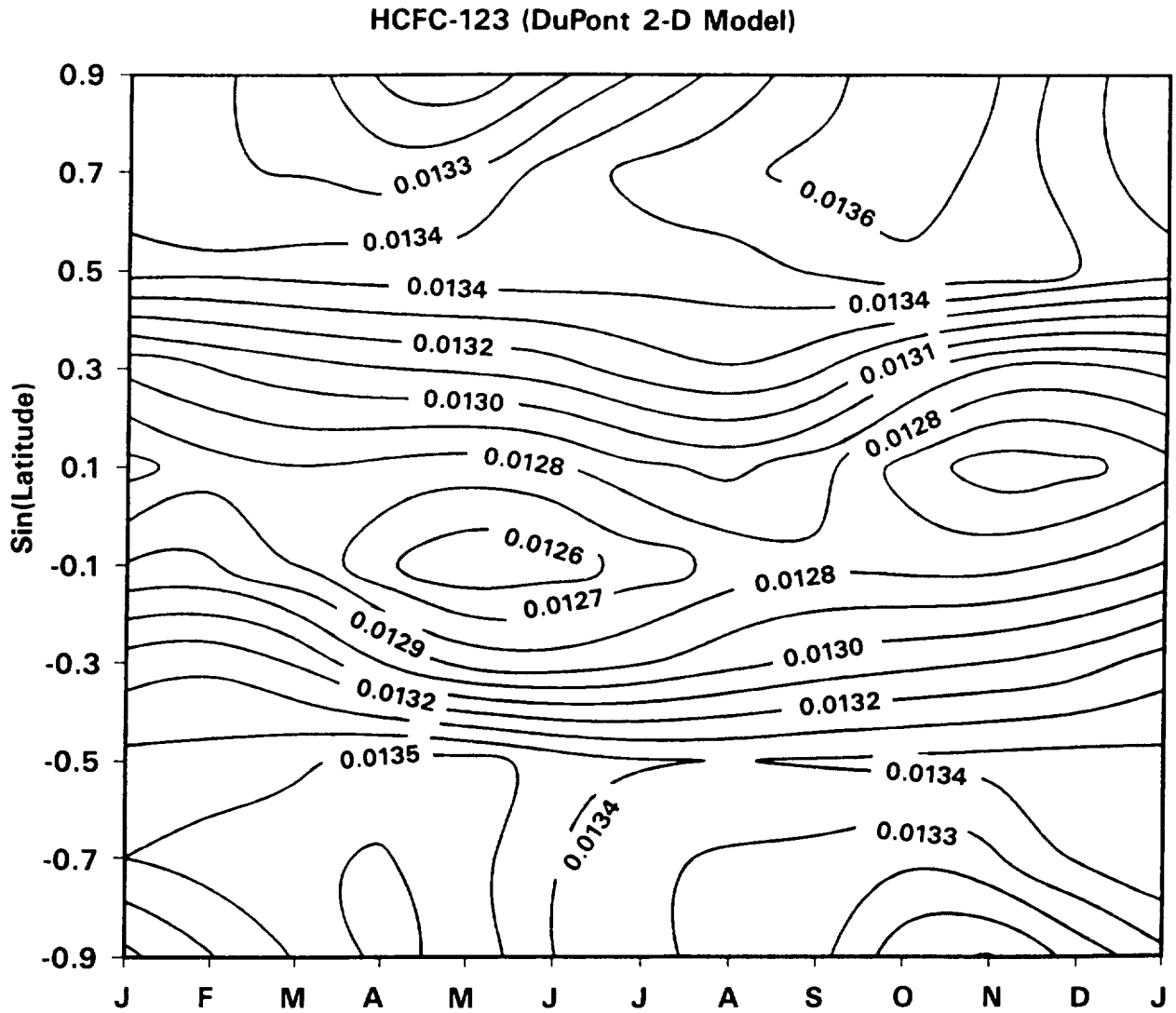
STRATOSPHERIC OZONE



**Please Note:**  
**Contours Labels are Multiplied by 1,000**

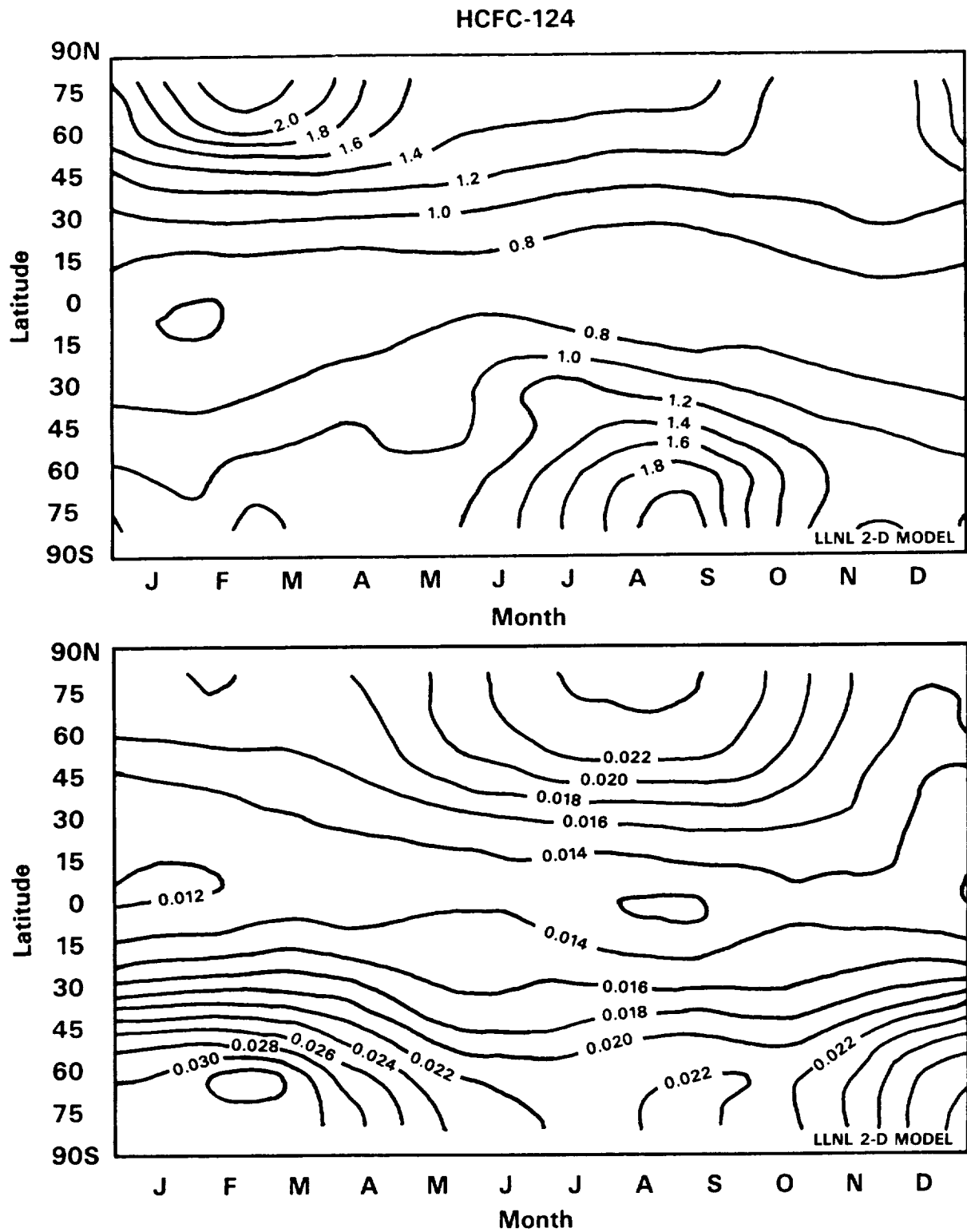
**Figure 9C.** Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-123 (AER 2-D).





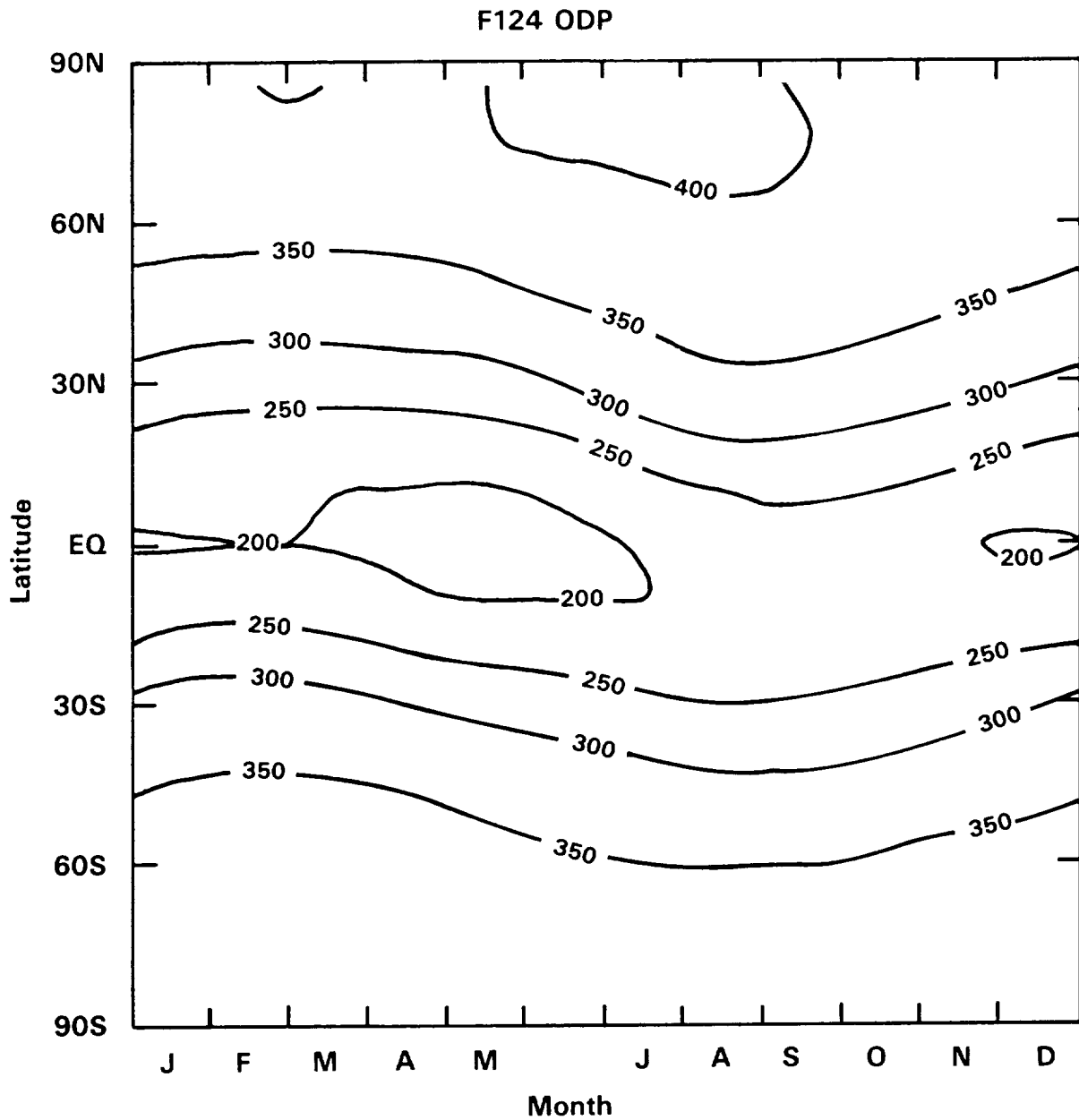
**Figure 9D.** Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-123 (DuPont 2-D).

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**Figure 10A.** Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of HCFC-124 (LLNL 2-D).

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Please Note:  
Contours are ODP X 10,000

**Figure 10B.** Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-124 (AER 2-D).

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HCFC-124 (DuPont 2-D Model)

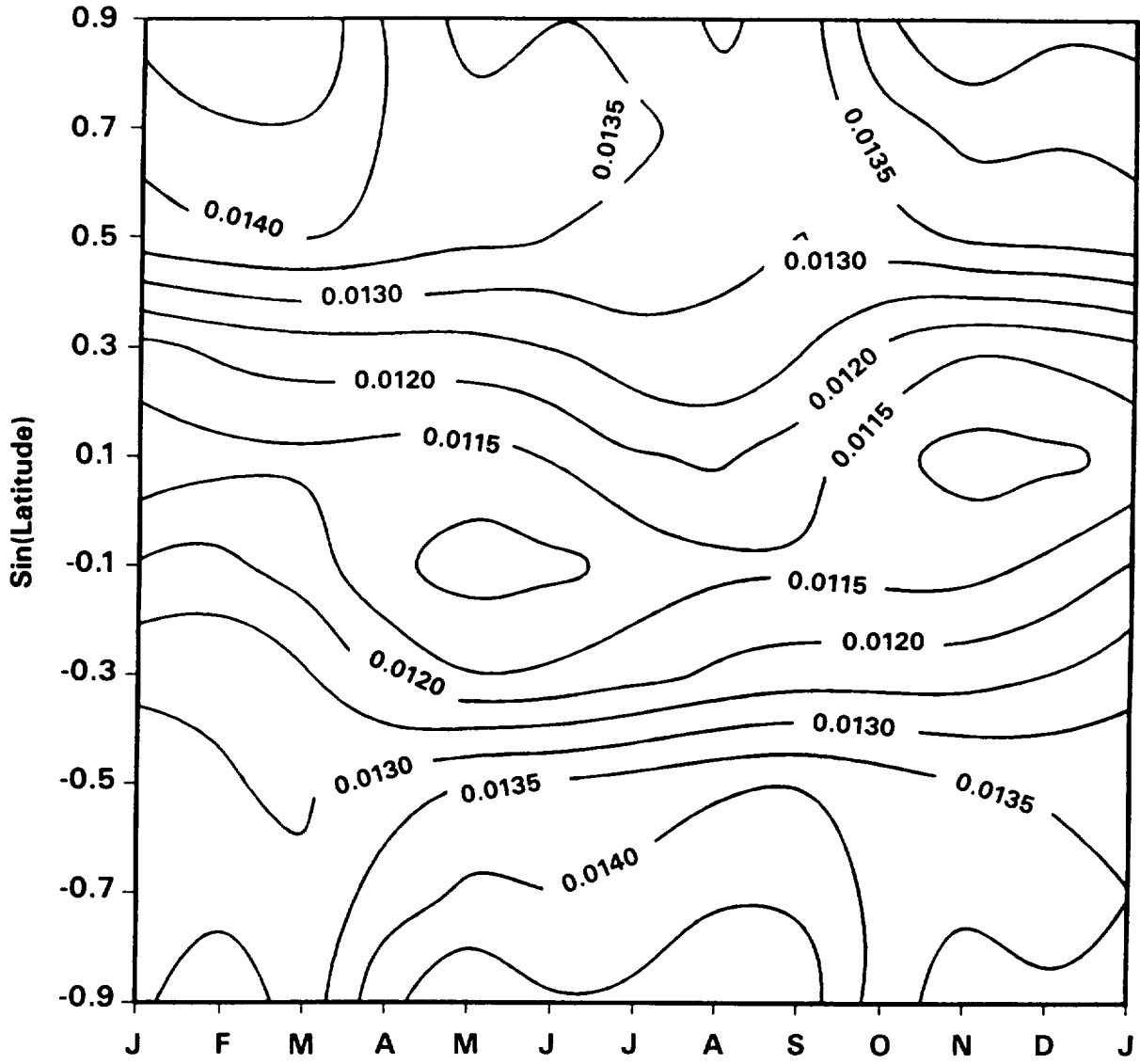


Figure 10C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-124 (DuPont 2-D).

HCFC-141b

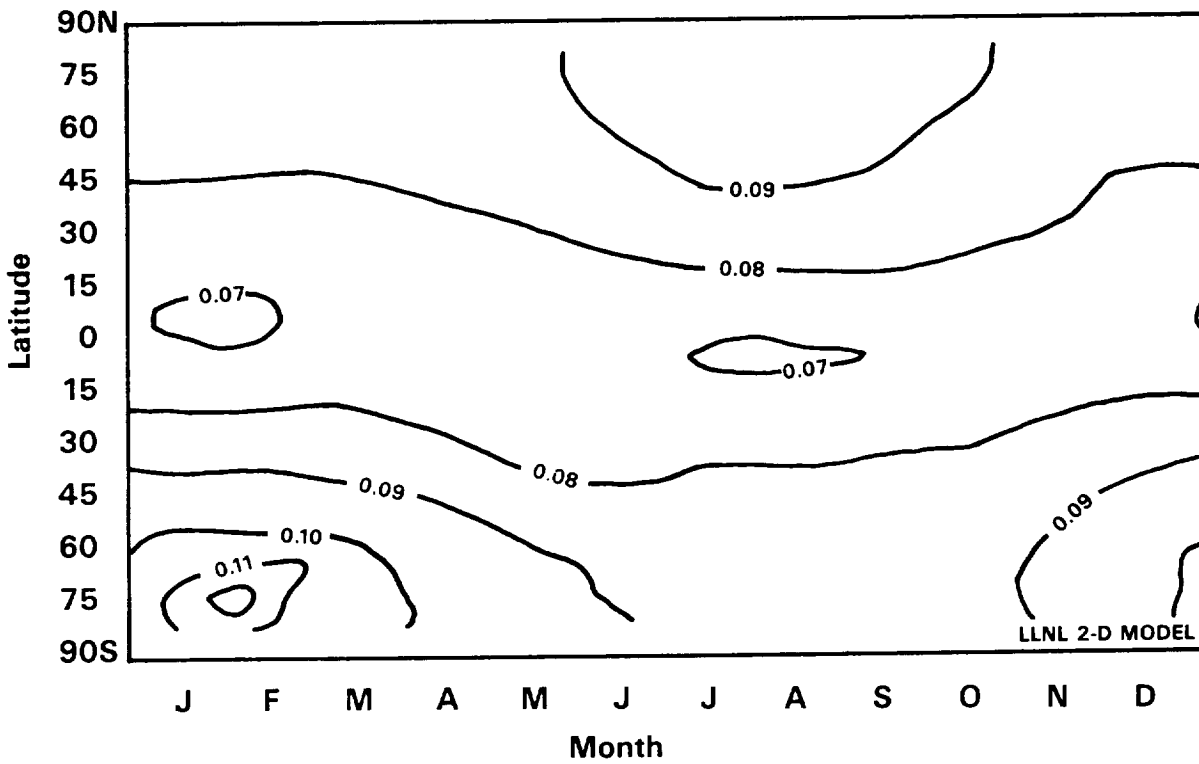
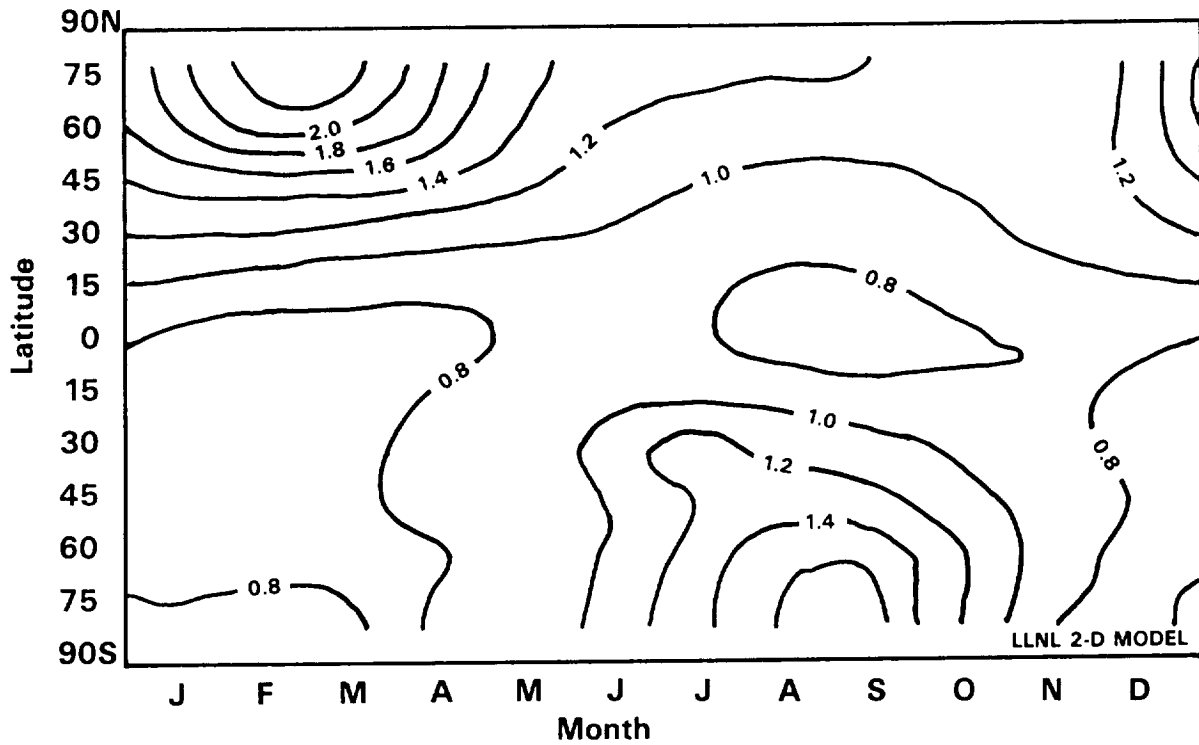


Figure 11A. Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Ozone Depletion from Emission of HCFC-141b (LLNL 2-D).

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ODP for F-141 (o) Oslo 2-D model

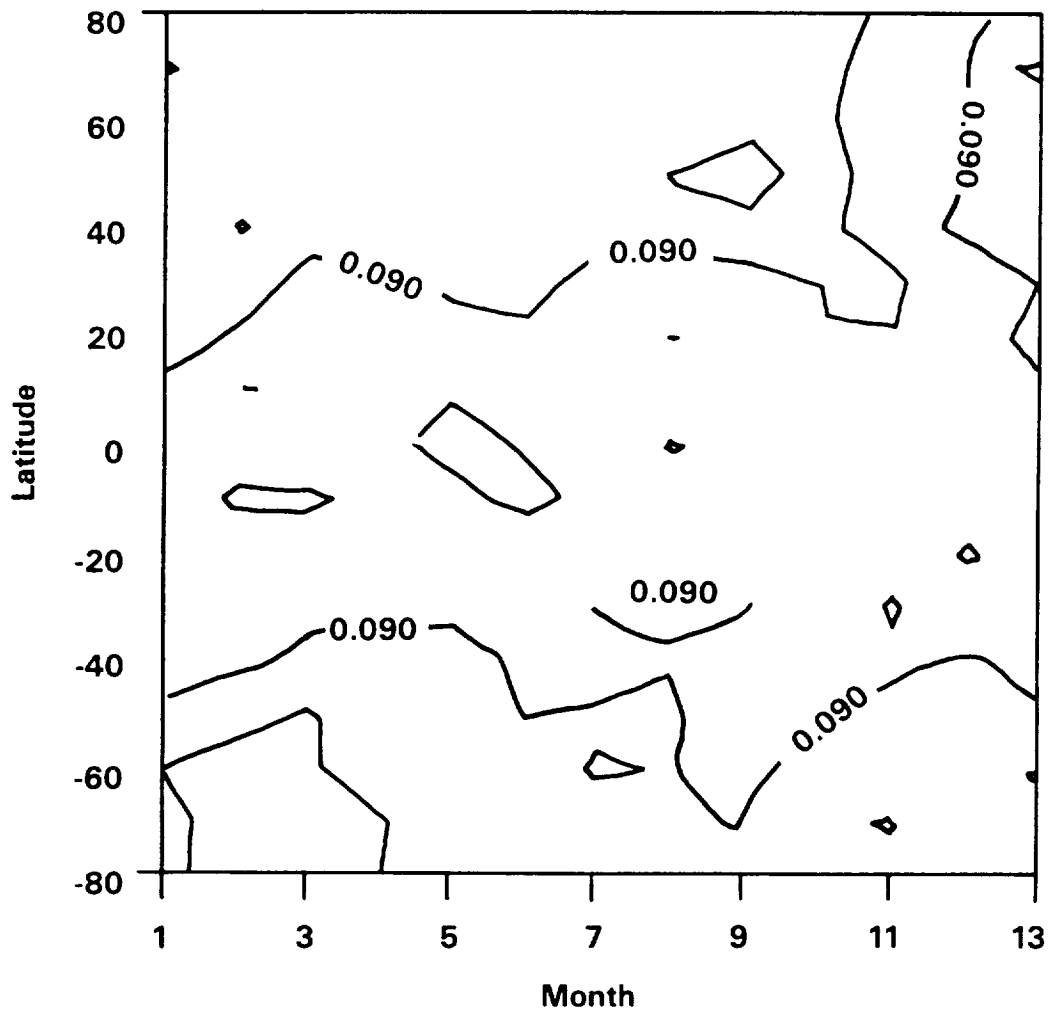


Figure 11B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-141b (Oslo 2-D).

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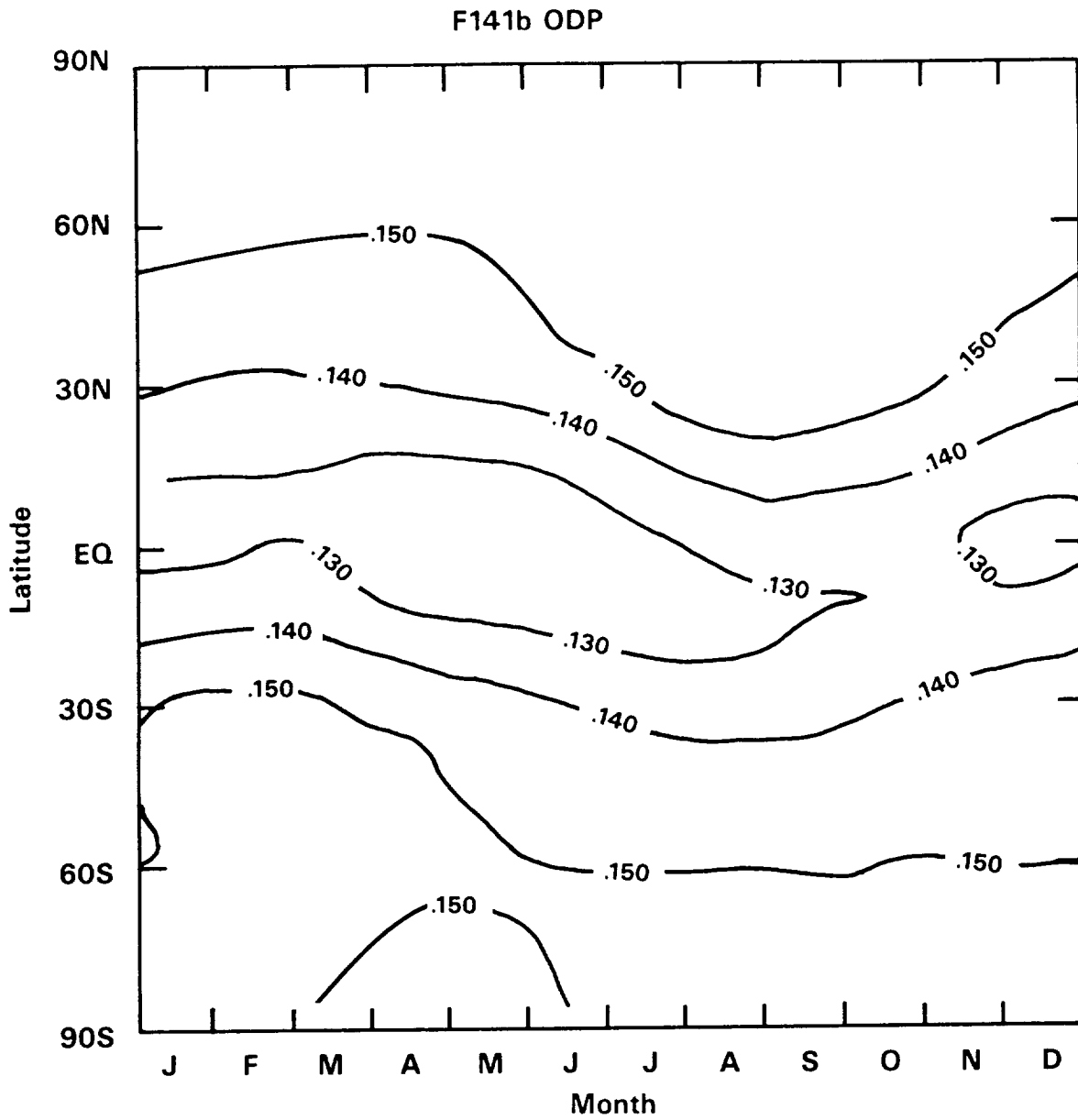


Figure 11C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-141b (AER 2-D).

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HCFC-141b (DuPont 2-D Model)

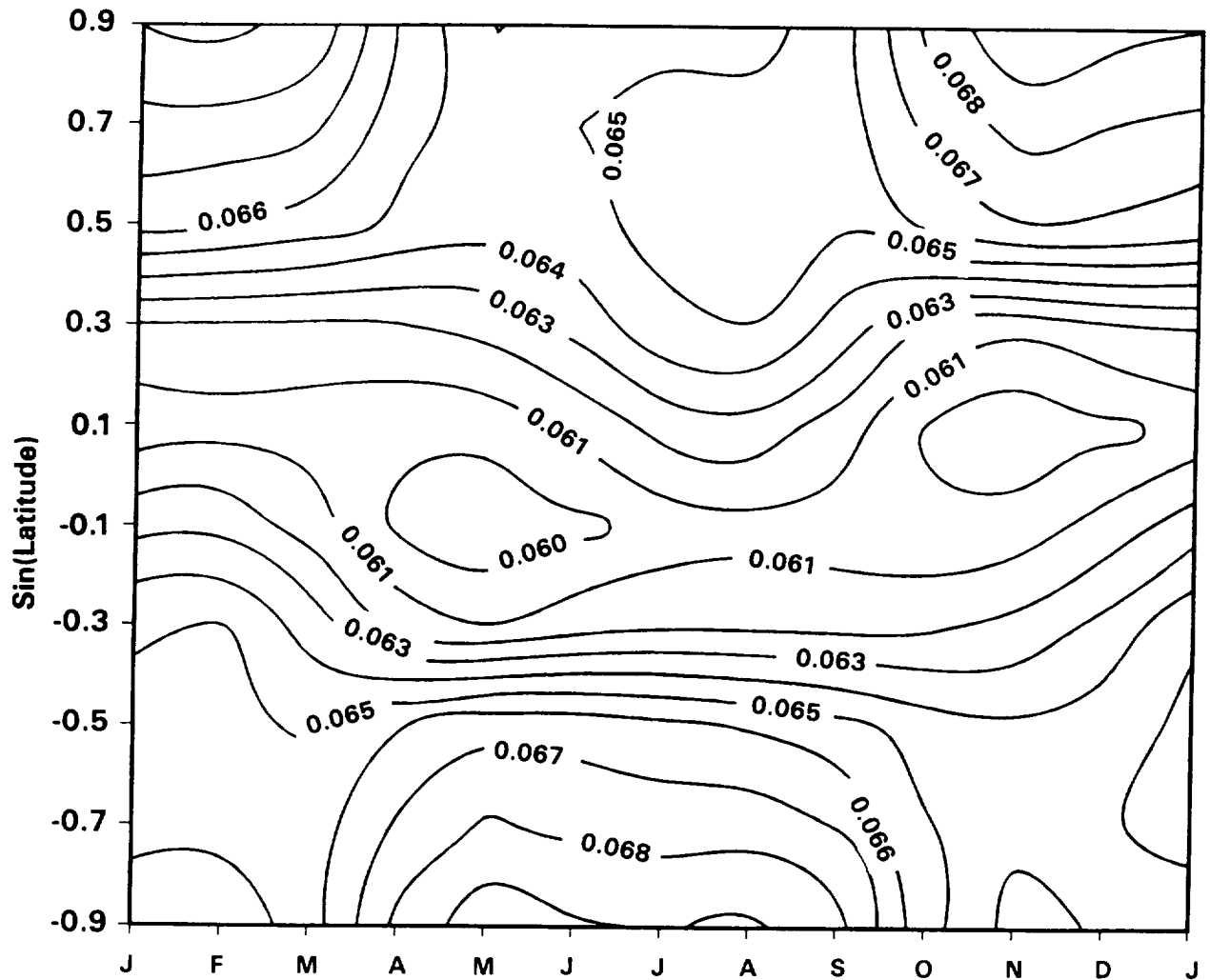
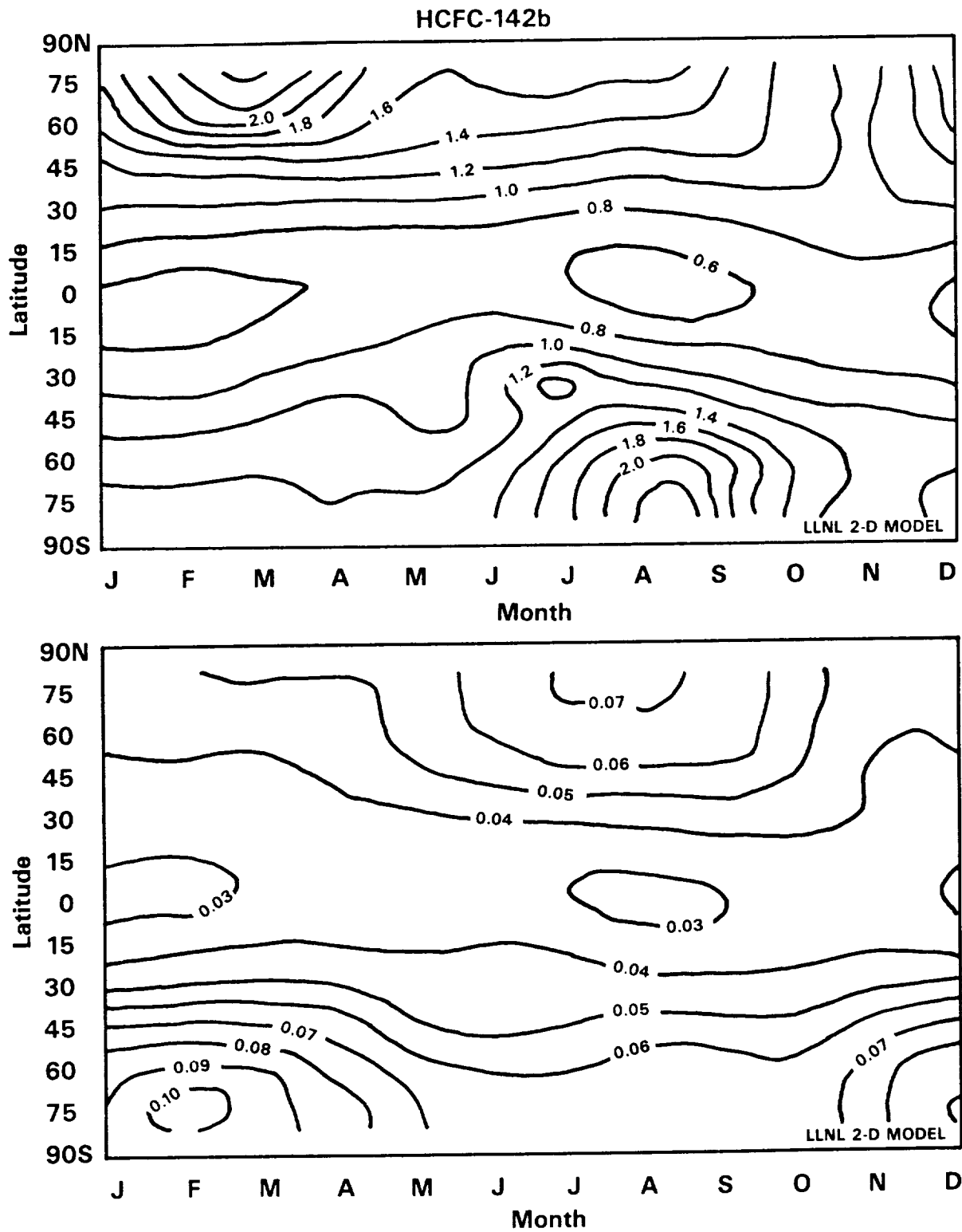


Figure 11D. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-141b (DuPont 2-D).





**Figure 12A.** Calculated Latitudinal and Seasonal Steady-State Ozone Change and Relative Depletion from Emission of HCFC-142b (LLNL 2-D).

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ODP for F-142b Oslo 2-D model

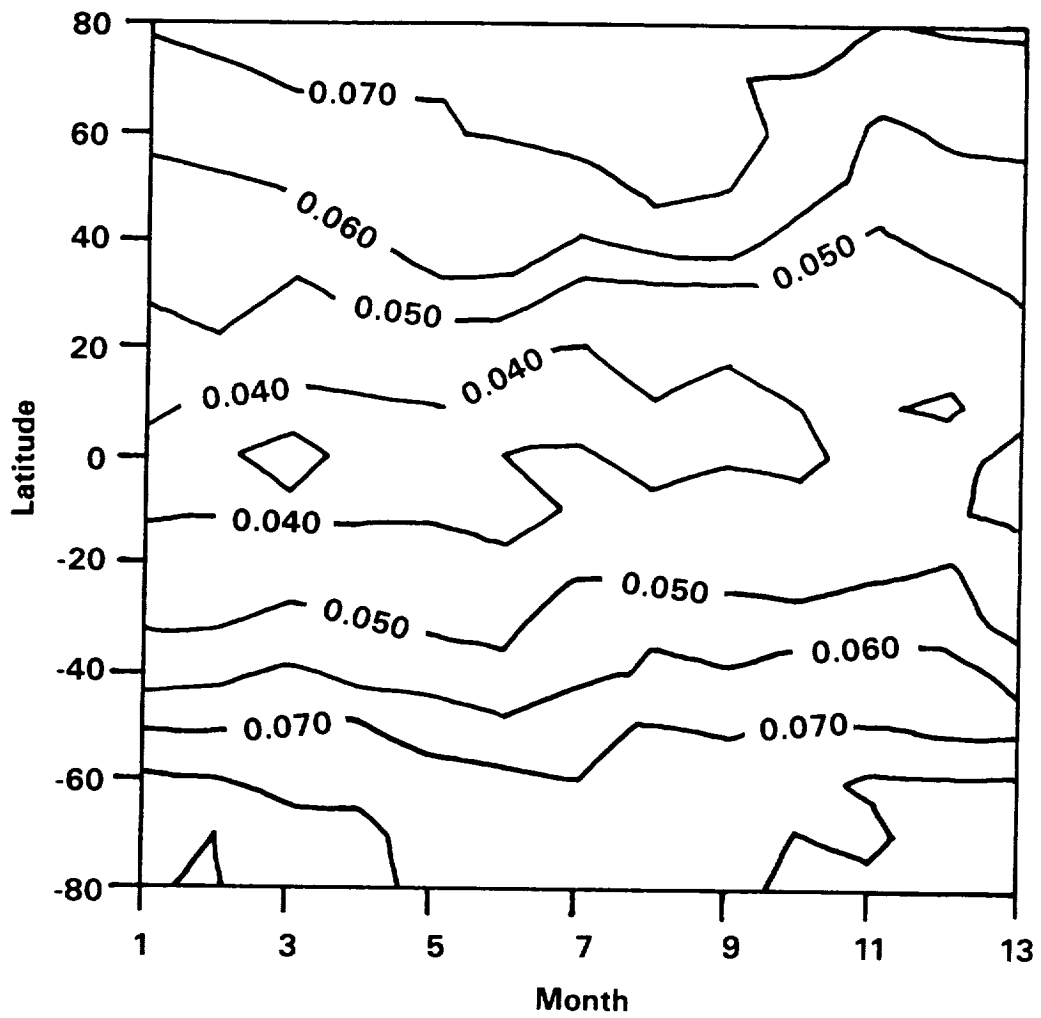


Figure 12B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-142b (Oslo 2-D).

STRATOSPHERIC OZONE

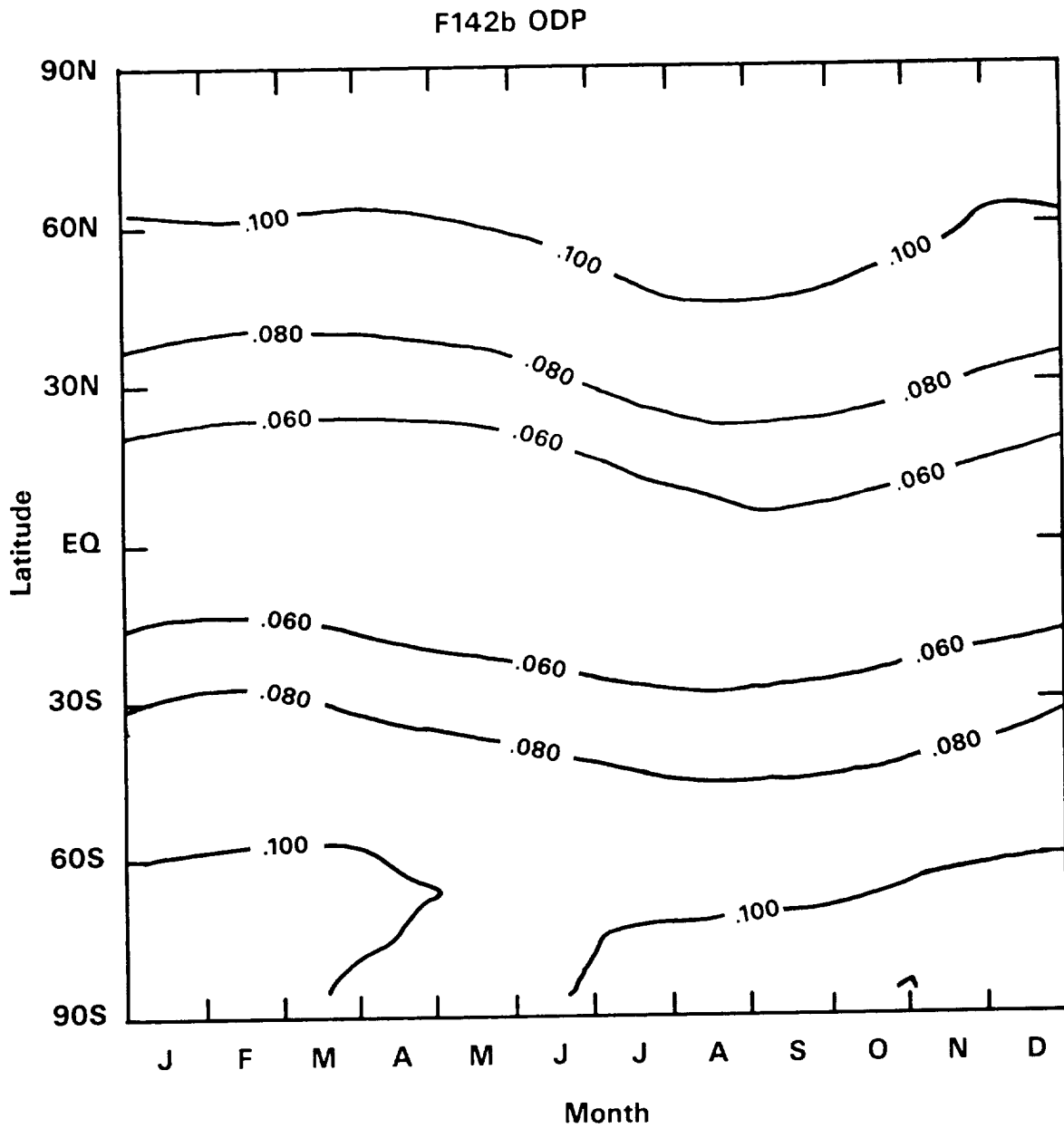
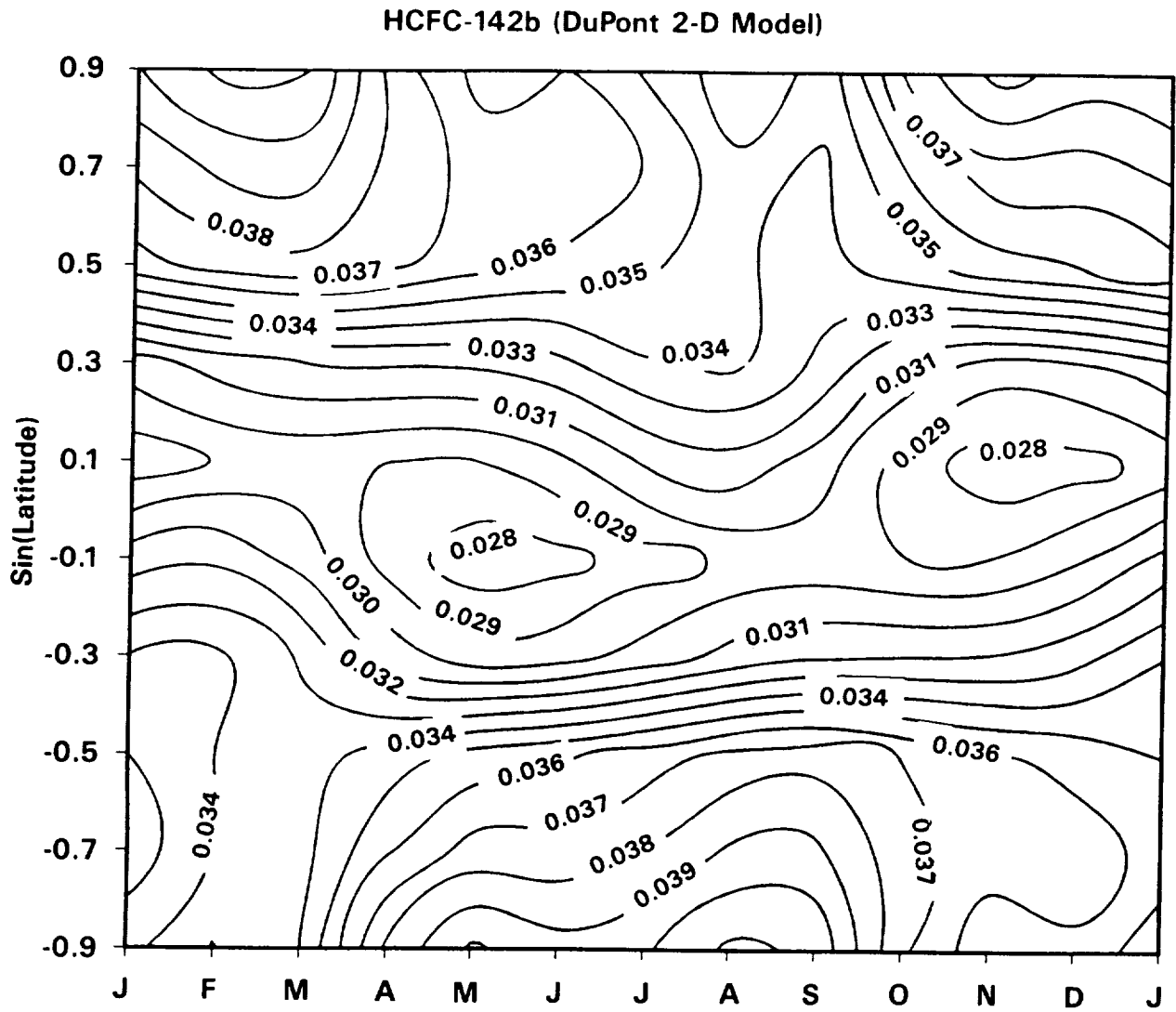


Figure 12C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-142b (AER 2-D).

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**Figure 12D.** Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-124b (DuPont 2-D).

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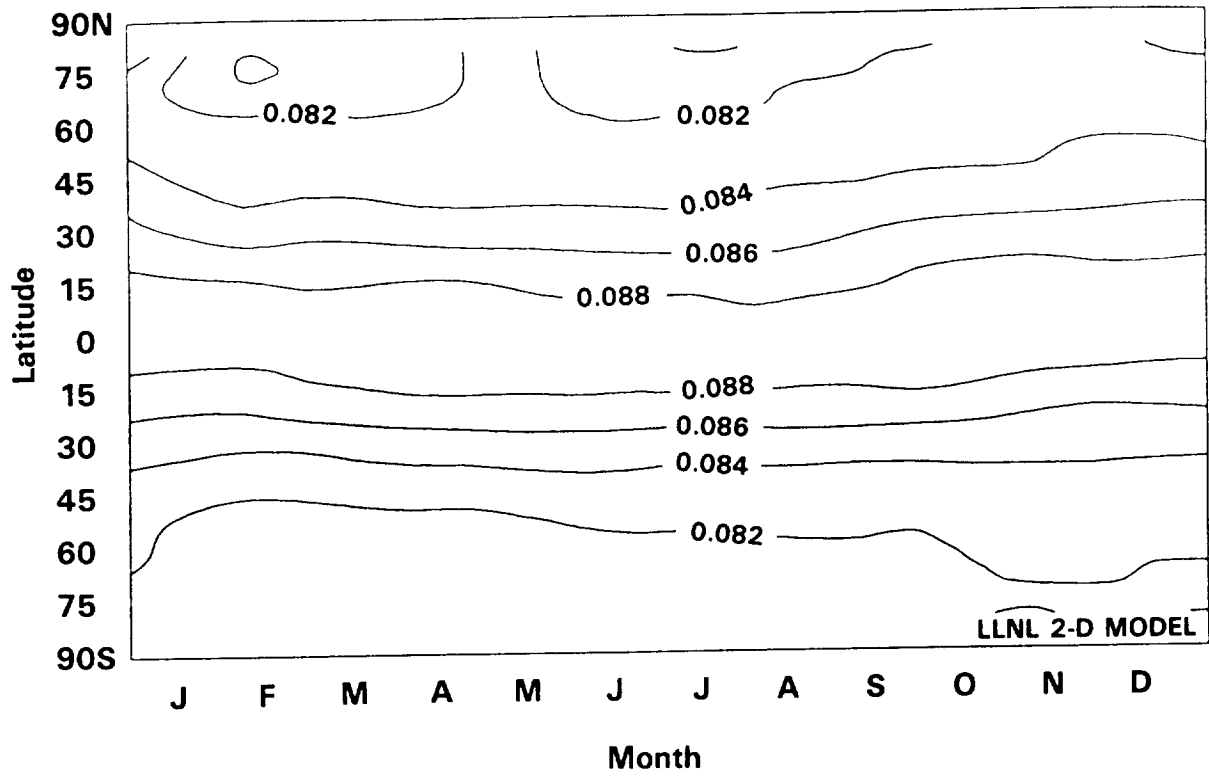


Figure 13A. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of Methyl Chloroform (LLNL 2-D).

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CH<sub>3</sub>CCl<sub>3</sub> ODP

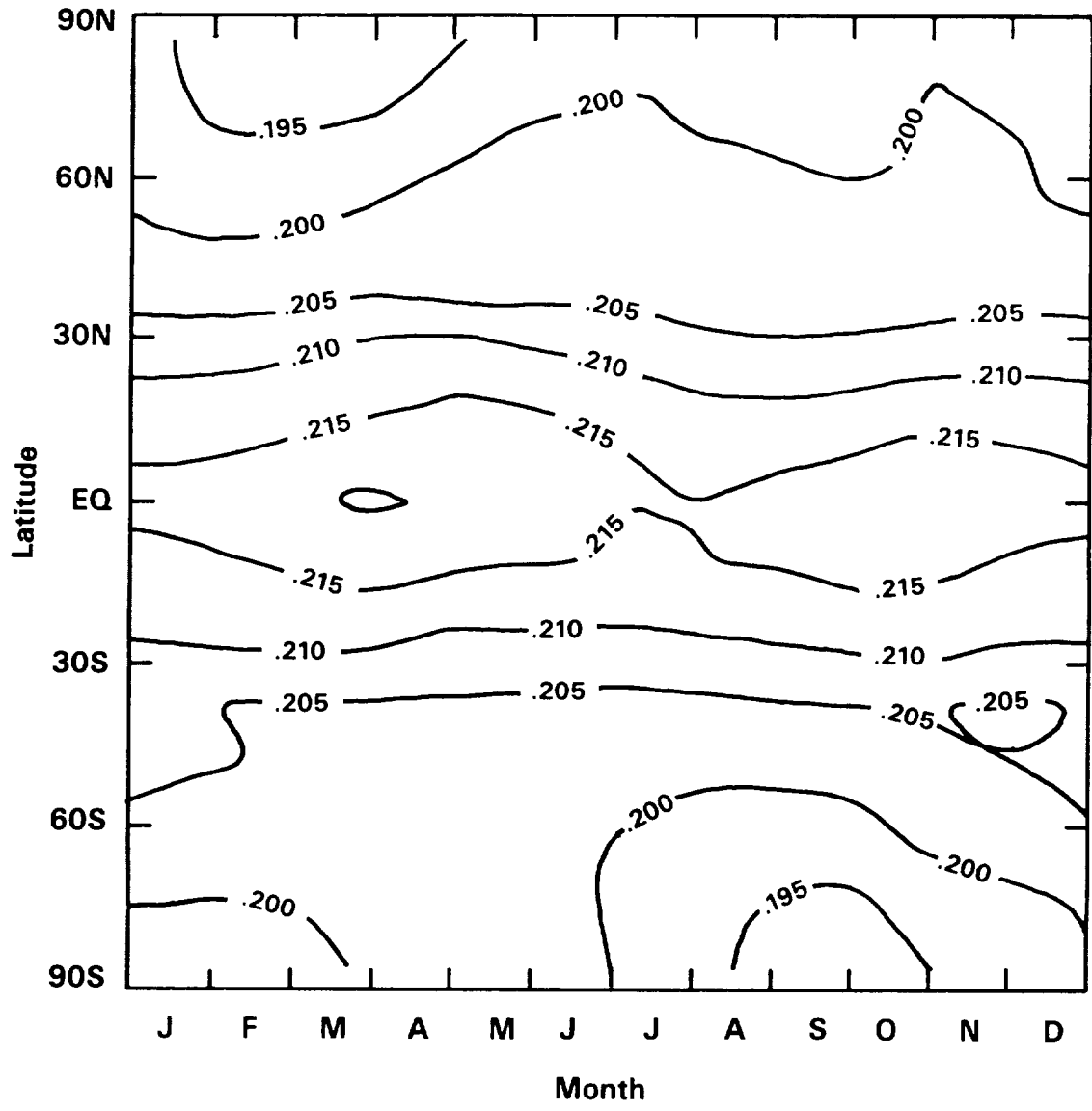


Figure 13B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of Methyl Chloroform (AER 2-D).

STRATOSPHERIC OZONE

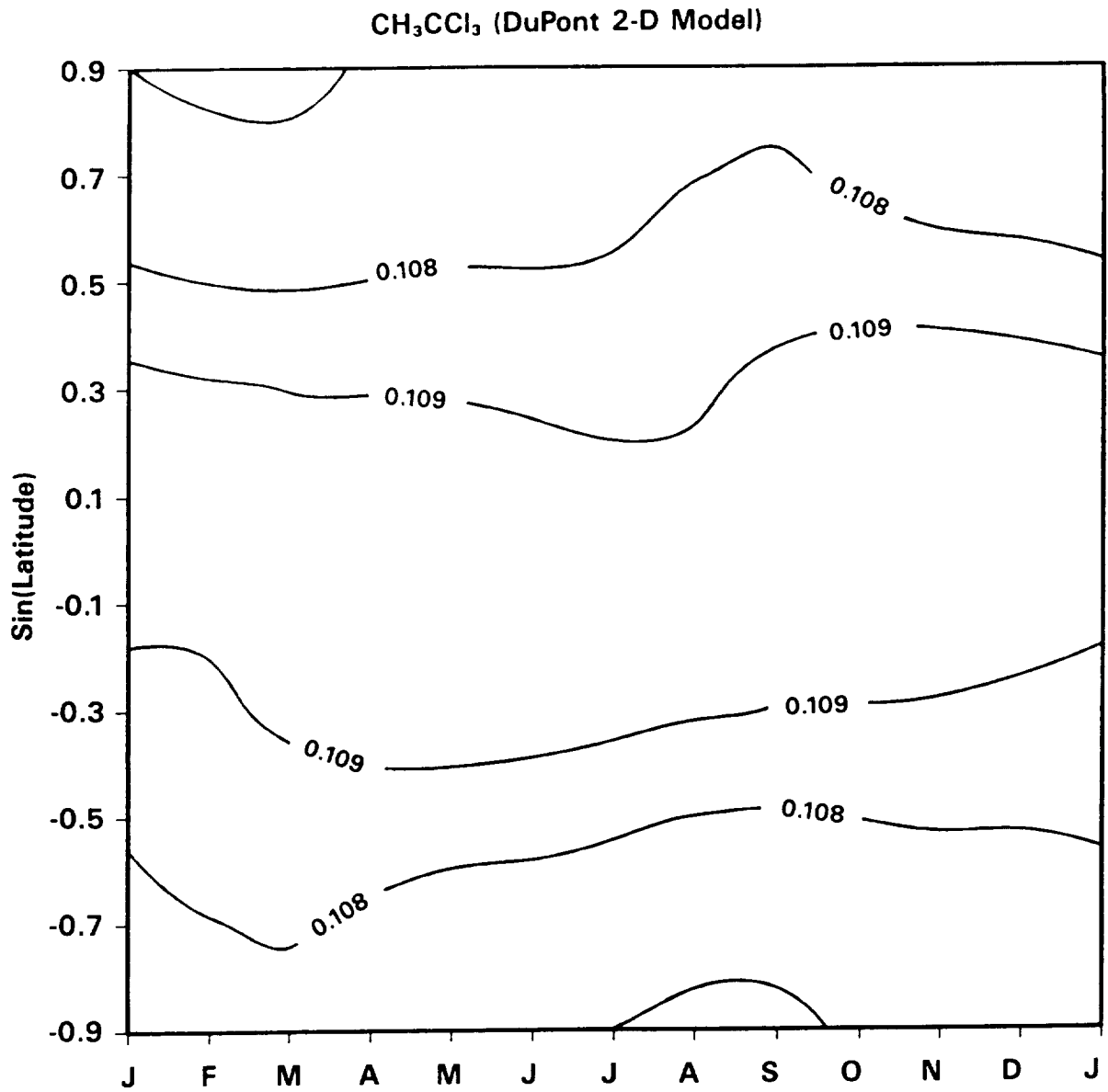


Figure 13C. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of Methyl Chloroform (DuPont 2-D).

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seasonal variations. In particular, the ODPs for CFC-12, HCFC-22, HCFC-124, and HCFC-142b have strong latitudinal variations, with the ODP increasing from lower tropical values to higher polar values by as much as a factor of three. Other species, such as HCFC-123, HCFC-141b, and CH<sub>3</sub>CCl<sub>3</sub> show little variation with latitude or season. The results from the four models are in good general agreement regarding this pattern, although the LLNL model shows slightly more seasonal response for some species than the other models, particularly at high latitudes in the Southern Hemisphere.

The strong latitudinal ODP variation of some species, in contrast to the weak variation determined for others, warrants further discussion. The distinguishing difference between the species categories is based on differences in the distributions of chlorine atoms which, in turn, depend on the altitudes for destruction of the respective species. Compounds that do not survive transport to the upper stratosphere for dissociation, and are therefore similar to CFC-11, show very little variation in their ODP with latitude and season. HCFC-123 is an example of such a species. On the other hand, species that persist into the upper stratosphere, (even if the dominant removal is at lower altitudes) show stronger latitudinal dependencies. CFC-12 and HCFC-22 are two examples that show a significant latitudinal dependency. CFC-12 is primarily dissociated at higher altitudes than CFC-11. HCFC-22, on the other hand, is primarily destroyed in the troposphere and lower stratosphere by reaction with OH radical, yet models predict that a fraction survives transport to the upper stratosphere and is dissociated through reaction with OH and O(<sup>1</sup>D) resulting in high altitude Cly generation.

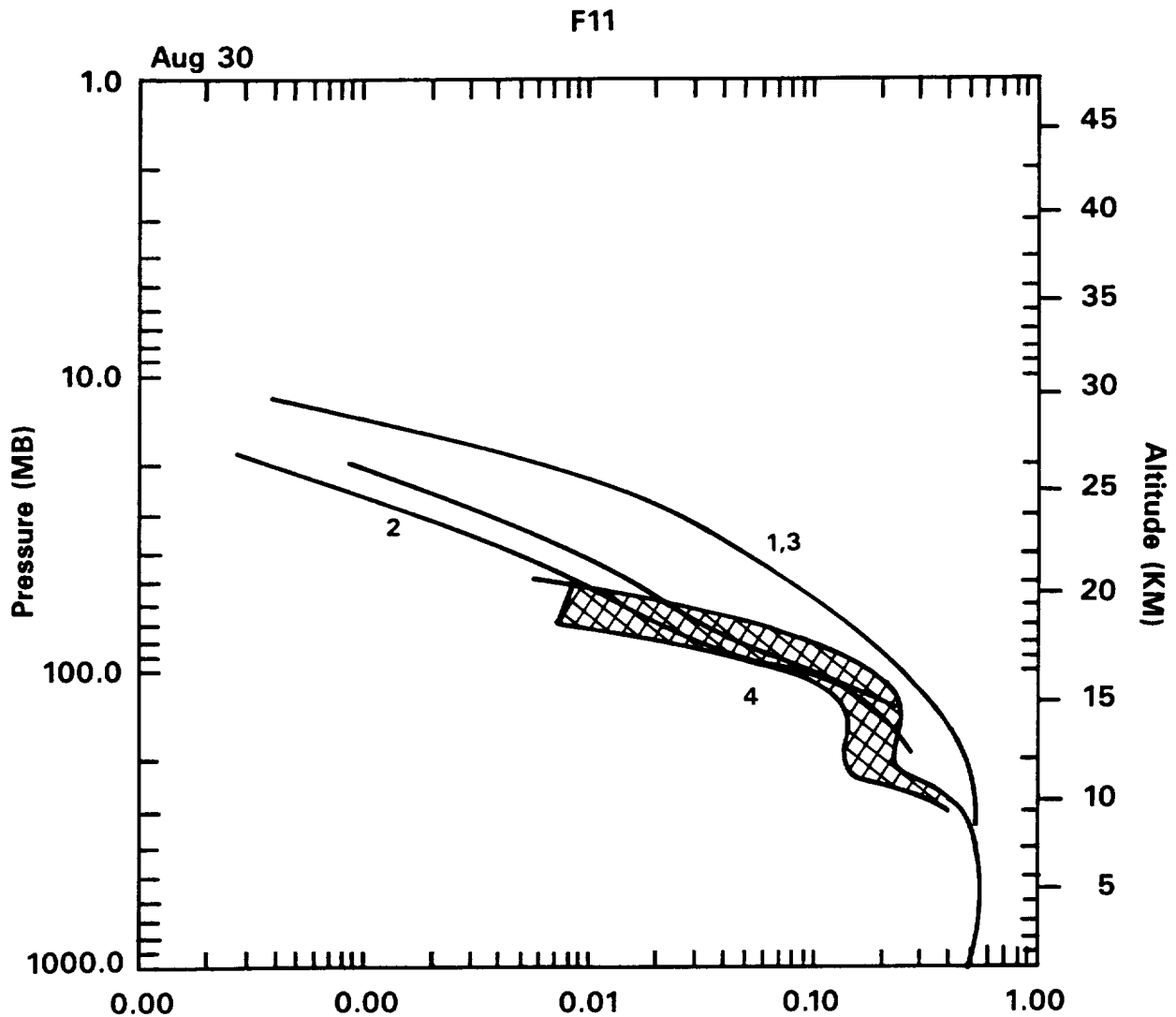
The resulting strong variations of ODPs with latitude occur in response to latitudinal differences in upper stratospheric chemistry on ozone destruction and the resultant effects of transport on both the ClO<sub>x</sub> produced and on the ozone being destroyed. The extent of these variations depends on the treatment and the strength of the modeled transport. It is not surprising, therefore, to find differences in the ODP variations with latitude and season between models.

### Sensitivity of ODP to Modeled Transport

The question can next be raised as to the sensitivity of ODP values to model parameters - primarily, transport processes. Model transport parameterization is a source of significant uncertainty in 2-D models. Modelers have used a combination of theoretical and empirical basics to derive expressions for circulation and dispersive fields for species transport in their models. As such, models yield good agreement of predicted profiles for key trace gases relative to measured values at low- and mid-latitudes. However, agreement at high latitudes is generally not as good. Modeled polar chemical profiles are keenly dependent on the representation of transport utilized in this region. Therefore, transport of chemical species is a source of significant uncertainties in atmospheric modeling.

Changing the model transport parameters would affect the ODP directly in three ways. First, the ODP values can change because of changes in lifetimes. Lifetime for CFC-11 is sensitive to the strength of the circulation in the stratosphere while the lifetime of HCFC-22, which is dominated by removal in the troposphere, is less sensitive. Second, changing transport parameters would affect the distribution of chlorine atoms in the stratosphere. The responses of each species differ according to where the chlorine atoms are released. Finally, change in transport can also affect the response of ozone to chemical perturbations.





**Figure 14.** Calculated CFC-11 Profiles from Transport Sensitivity Study at 75 Deg. South at Equinoc (AER-2D). AAOE Measurements Indicated by Cross Hatch Area.

Four sets of calculations were performed using different circulations and  $K_{yy}$  (latitudinal eddy diffusivity) values to define transport within the AER 2-D model. Calculated effects of CFC-1-1 and HCFC-22 were determined in each case. These cases are designated by:

	Circulation	$K_{yy}$
case 1	standard	standard ( $3 \times 10^9 \text{ cm}^2 \text{ s}^{-1}$ )
case 2	standard	small ( $1 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$ )
case 3	weak	standard ( $3 \times 10^9 \text{ cm}^2 \text{ s}^{-1}$ )
case 4	weak	small ( $1 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$ )

STRATOSPHERIC OZONE

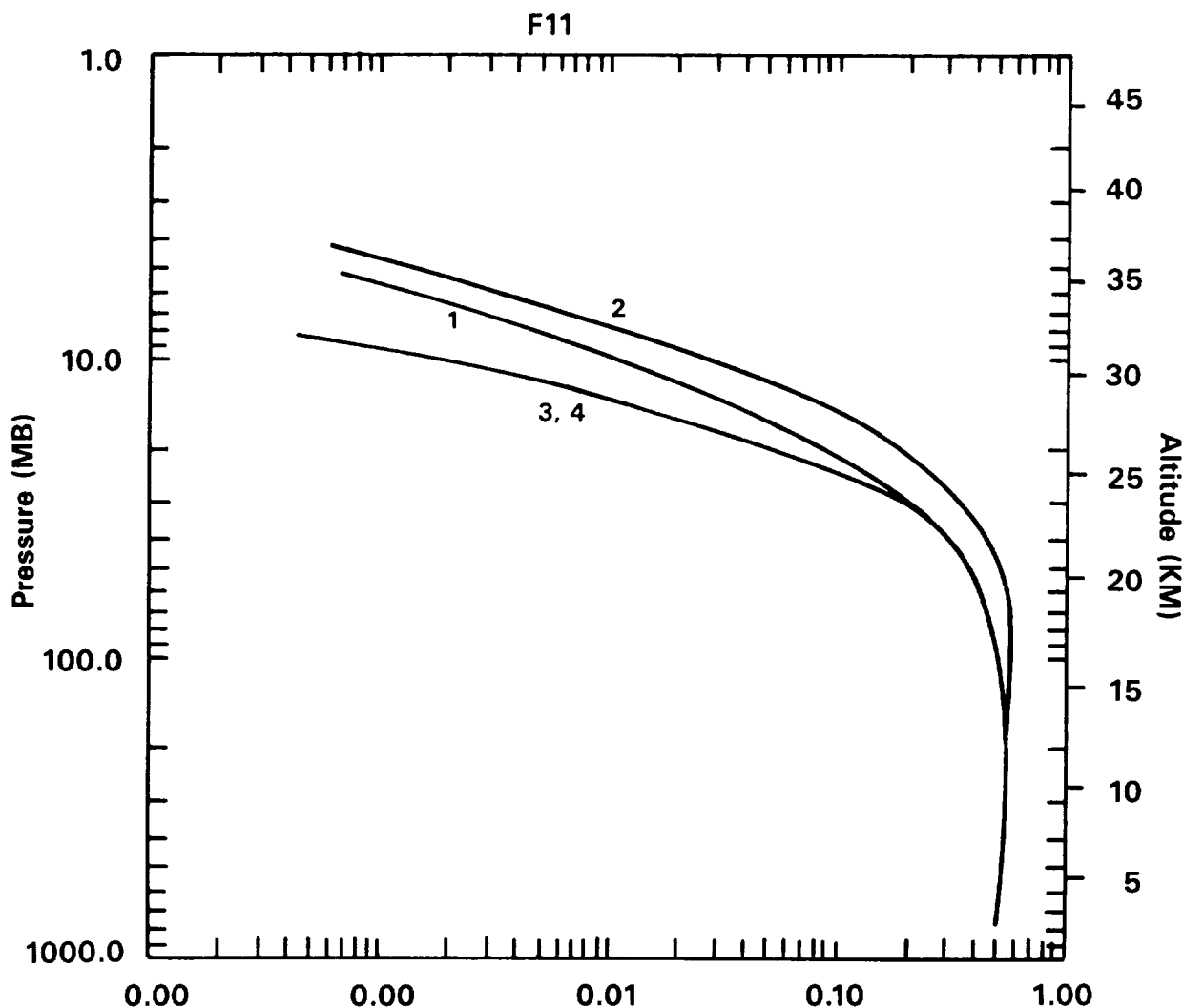


Figure 15. Calculated CFC-11 Profiles from Transport Sensitivity Study at Equator at Equinox (AER-2D).

The weak circulation for cases 3 and 4 is chosen to test the response of ODP for CFC-22 if a large portion of the CFC-22 is dissociated in the upper stratosphere. The circulation is adjusted so that the CFC-22 molecules spend more time in the upper stratosphere resulting in 90% dissociation of the molecules. Adopting smaller  $K_{yy}$  values for cases 2 and 4 represents an attempt to obtain lower concentrations for species such as  $N_2O$ , CFC-11 and CFC-12 in the polar lower stratosphere more in line with the observations obtained in the polar vortices during the Antarctic Airborne Ozone Experiment (AAOE) campaign. For simplicity, we have adopted the smaller value globally and year round. Clearly, if the smaller values are restricted to the high latitudes and limited to certain seasons, the response could be somewhat different. Finally, a more definitive test might be to utilize a transport scheme with stronger down-welling in the winter polar vortices.

Figure 14 shows calculated profiles of CFC-11 from the 4 cases for August at 75 deg. S compared to

**Table 9** Results of Transport Sensitivity Study (AER 2-D Model)

	Case 1	Case 2	Case 3	Case 4
CFC-11 lifetime	47 years	34 years	51 years	44 years
HCFC-22 lifetime	24 years	22 years	24 years	23 years
ODP	.07	.035	.055	.034
CLP	.27	.35	.25	.28
CEF	.26	.10	.22	.12

the AAOE measurements. The profiles at equinox for the equator are shown in Figure 15. The cases with small Kyy predict CFC-11 profiles that are in better agreement with observations at polar latitudes. At the same time, the concentration at the equator calculated under case 2 is large compared to case 1. Corresponding graphs for HCFC-22 are shown in Figures 16. Figures 17 shows the calculated column abundances of O<sub>3</sub> for the four cases. The results from cases 2 and 4 are distinctly different from observations with high columns predicted at high latitudes. Table 9 summarizes the calculated lifetimes and ODP values from the cases. Calculated lifetime of CFC-11 depends heavily on the transport field whereas the lifetime of HCFC-22 is less dependent. The ODP values for HCFC-22 for these cases reflects the impact of transport on the CFC-11 destruction process. Figure 18B shows that while there is an increase in ODP values at high latitudes for case 2 relative to case 1, the decrease at the tropics more than compensates for it in the global ODP value. Corresponding results for cases 3 and 4 are shown in Figures 18C and 18D. More discussion and analysis of these results as they relate to polar observations will follow in the next section.

In summary, the analysis presented here represents an attempt to quantify the sensitivity of the calculated ODP to model parameterization of transport. It is difficult to draw a definitive conclusion based on these limited number of simulations. Our attempts here to increase the ODP at high latitudes by using smaller Kyy lead to much smaller ODP at the tropics because of decreased eddy transport. We cannot be certain that there may not be other combinations of circulation and Kyy that would change the ODP results significantly. Our results did show that the same change in circulation would also have significant effects on the model simulated ozone and other trace gas profiles. Comparison of these simulated results with available observations would provide a way to validate the ODP values.

## 6. UNCERTAINTIES CONCERNING "OZONE HOLE" EFFECTS

None of the above Ozone Depletion Potential calculations consider the potential effects of heterogeneous chemistry in the lower stratosphere, particularly within the circulation vortex occurring at either pole during late winter and early springtime. Available observations indicate that the observed Antarctic ozone destruction is occurring as a result of heterogeneous reactions occurring on the surfaces of polar stratospheric clouds where free chlorine can be converted to activated forms that result in efficient chlorine-based catalyzed ozone destruction. Under these conditions, chlorine-induced ozone loss in the late winter-early spring-polar stratosphere is related to the total amount of available chlorine at the height of the polar stratospheric clouds, below approximately 25 km. Currently, inclusion of such effects in ODP calculations is prema-

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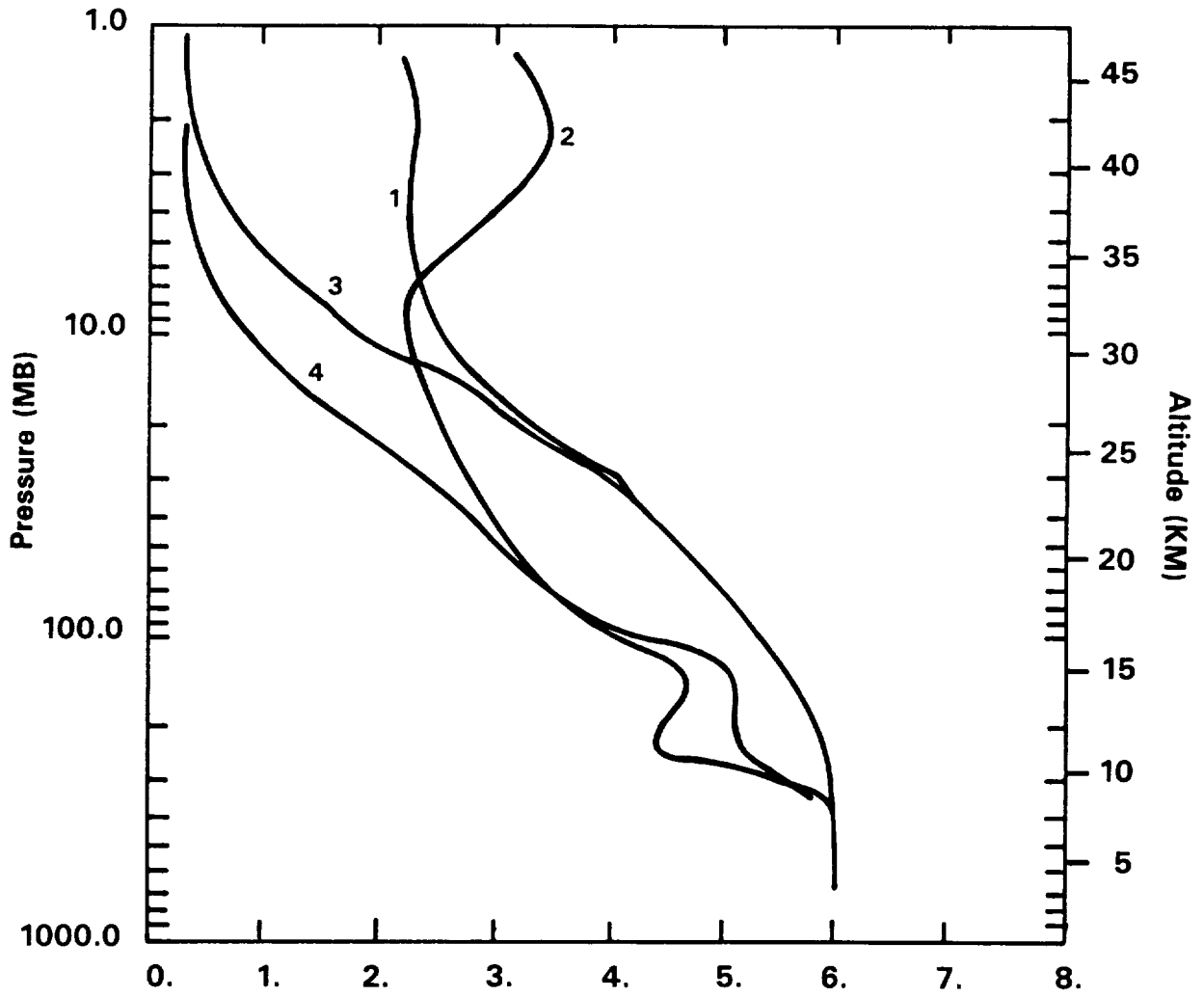


Figure 16A. Calculated HCFC-22 Profiles from Transport Sensitivity Study at 75 Deg. South Equinox (AER-2D).

STRATOSPHERIC OZONE

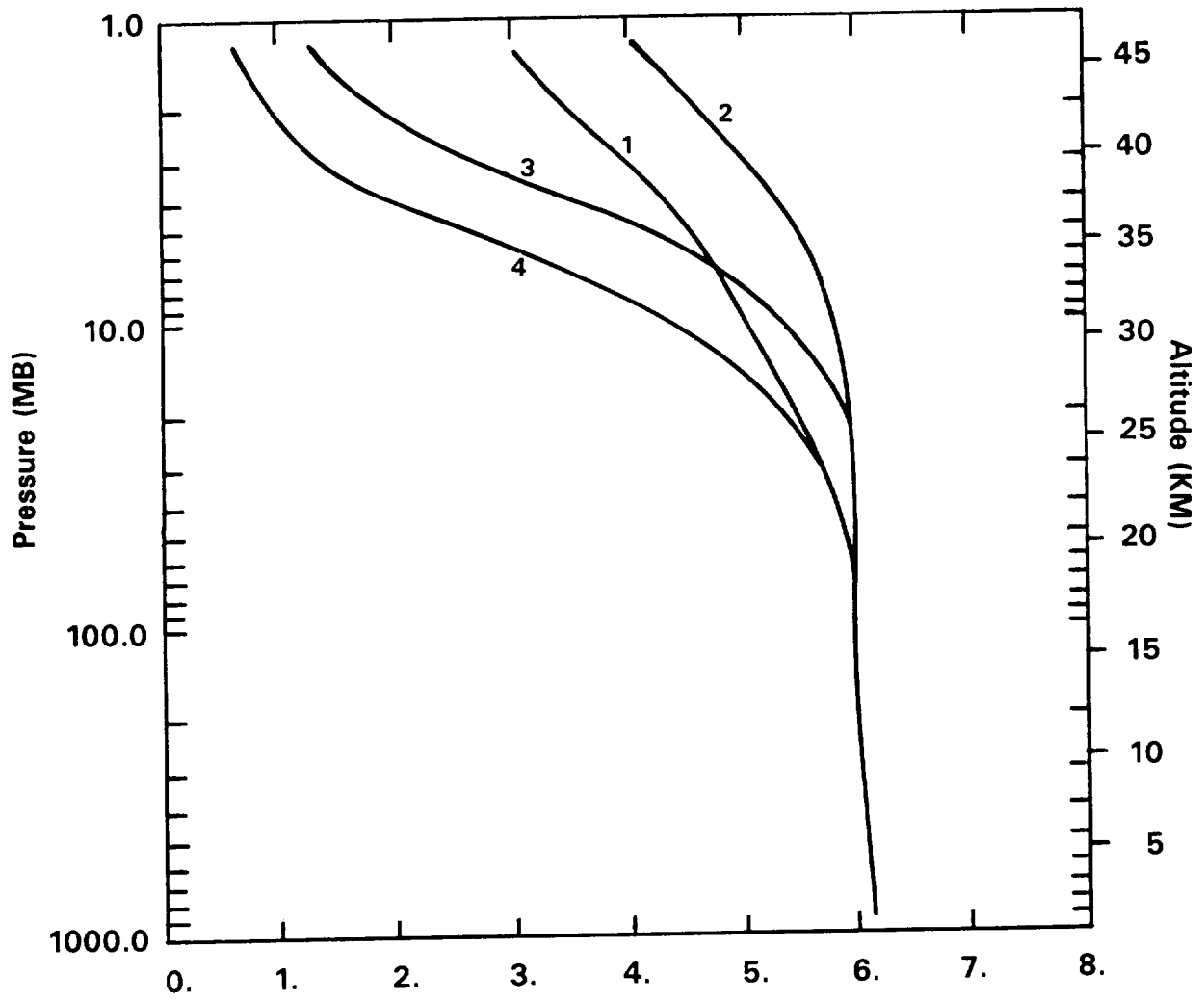
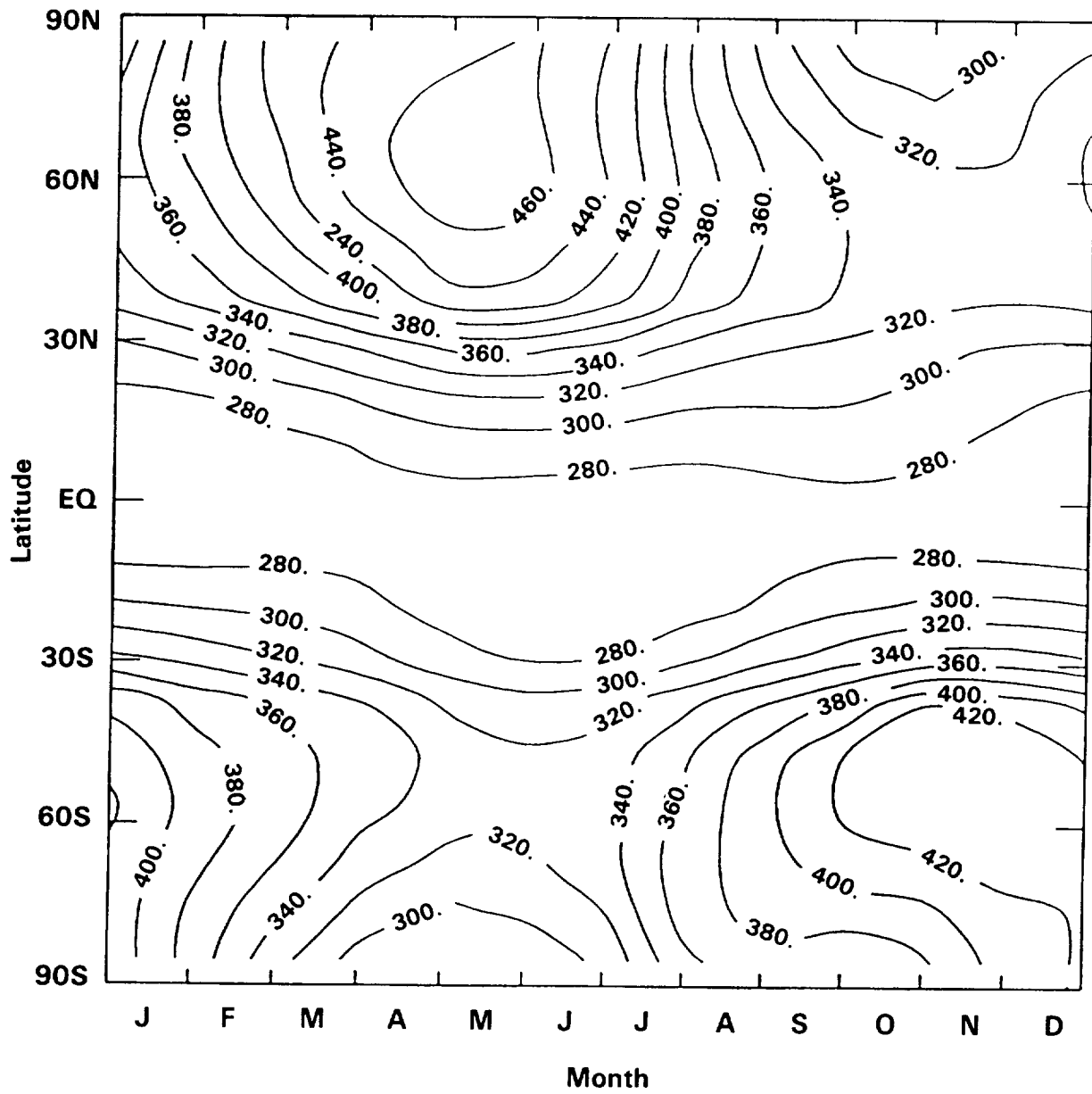


Figure 16B. Calculated HCFC-22 Profiles from Transport Sensitivity Study at the Equator at Equinox (AER-2D).

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**Figure 17A.** Calculated Ozone Abundance (Dobson Units) from Transport Sensitivity Studies [Case 2 of Transport Sensitivity Study] (AER-2D)

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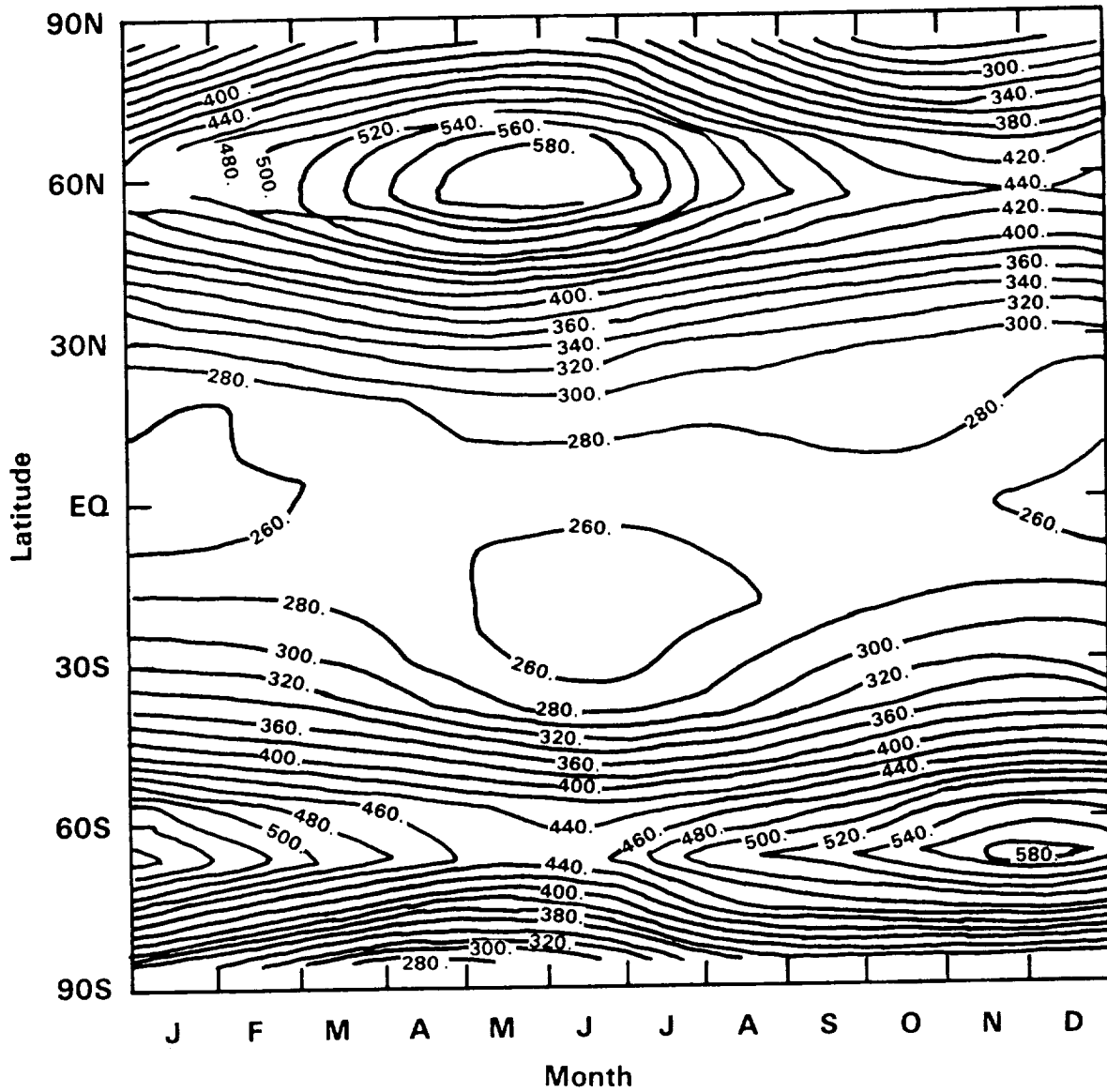


Figure 17B. Calculated Ozone Abundance (Dobson Units) from Transport Sensitivity Studies [Case 2 of Transport Sensitivity Study) (AER-2D).

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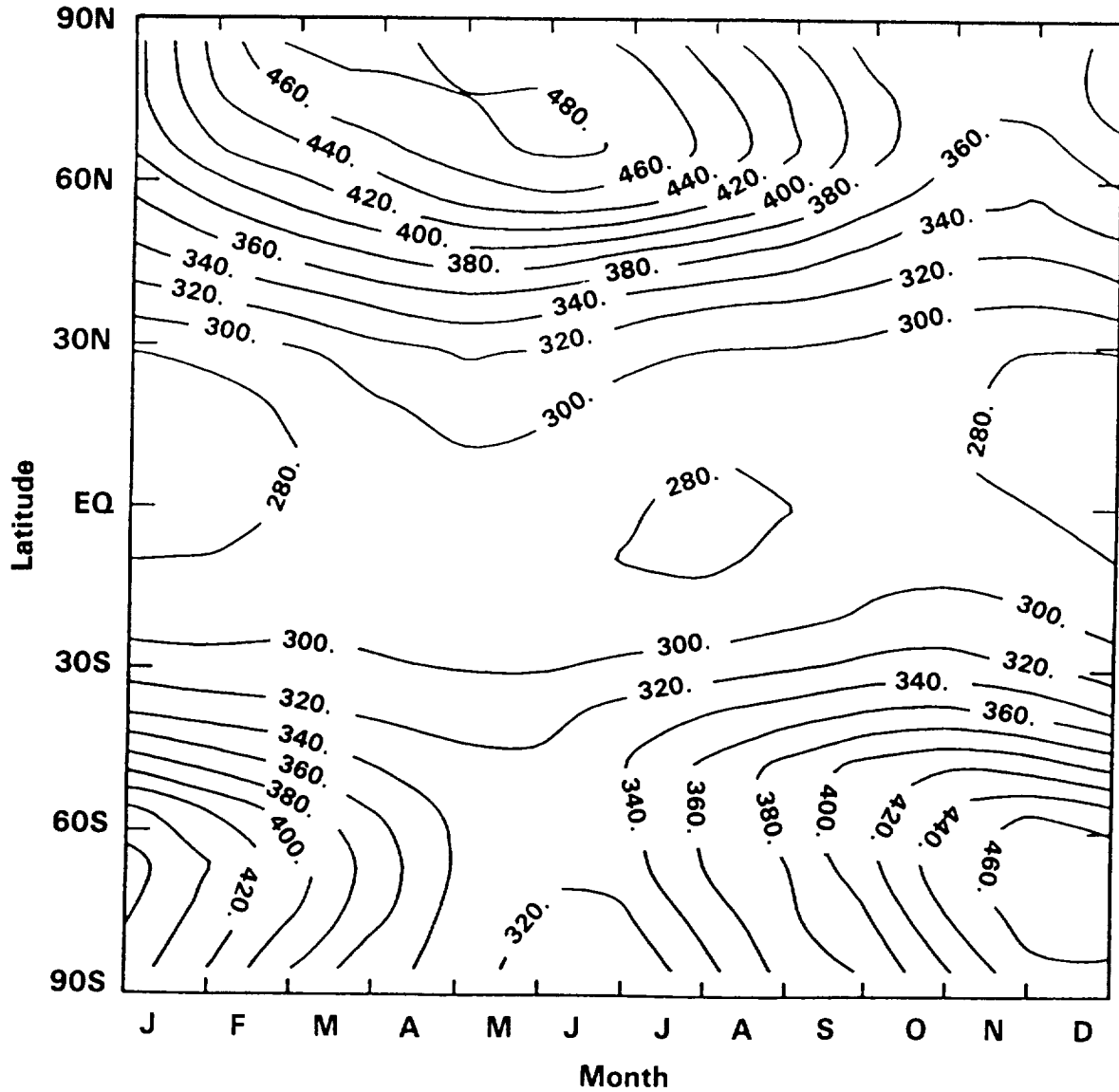


Figure 17C. Calculated Ozone Abundance (Dobson Units) from Transport Sensitivity Studies [Case 3 of Transport Sensitivity Study] (AER-2D).



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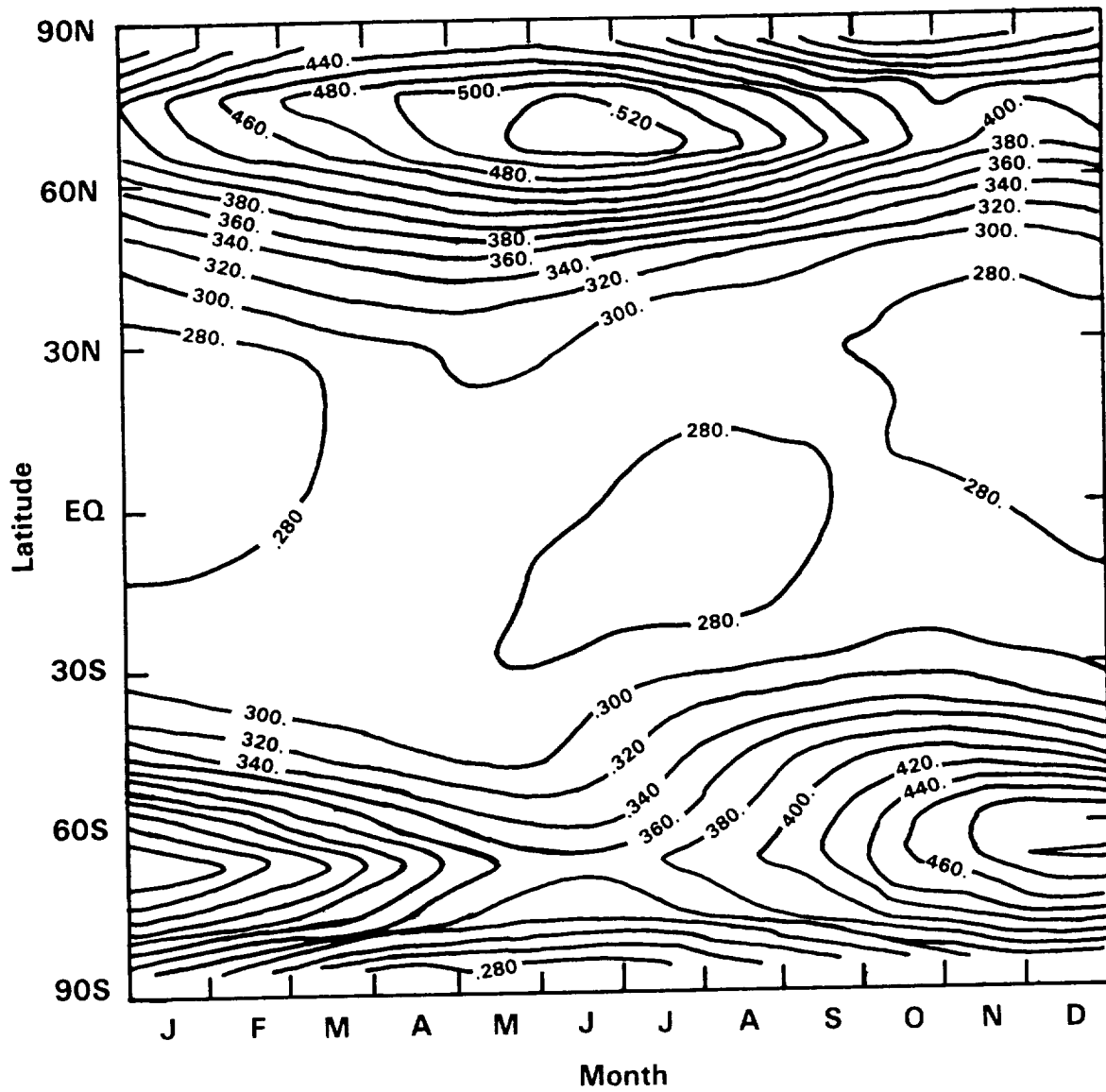


Figure 17D. Calculated Ozone Abundance (Dobson Units) from Transport Sensitivity Studies [Case 4 of Transport Sensitivity Study] (AER-2D).

STRATOSPHERIC OZONE

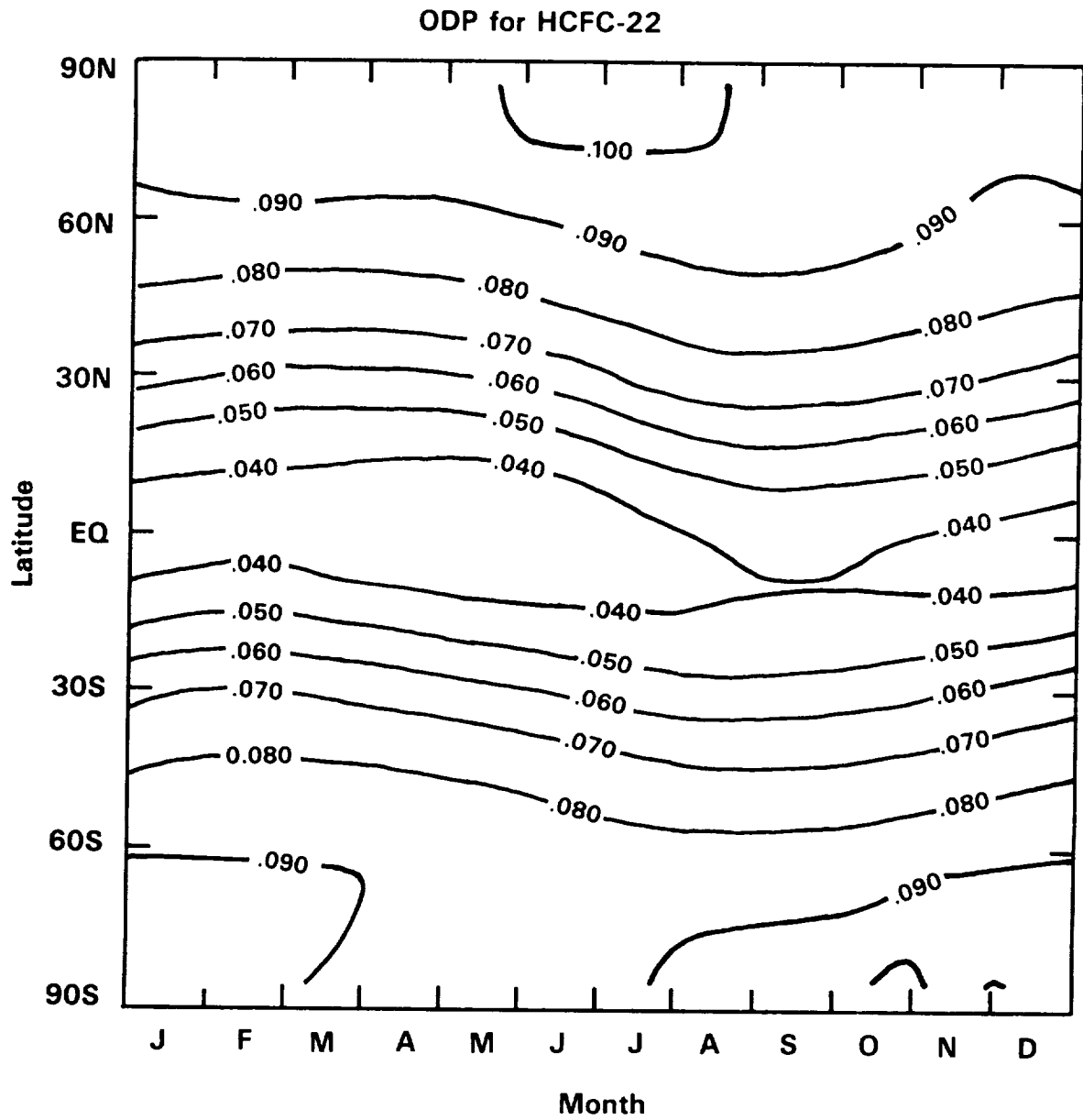


Figure 18A. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 1 of Transport Sensitivity] (AER 2-D).

STRATOSPHERIC OZONE

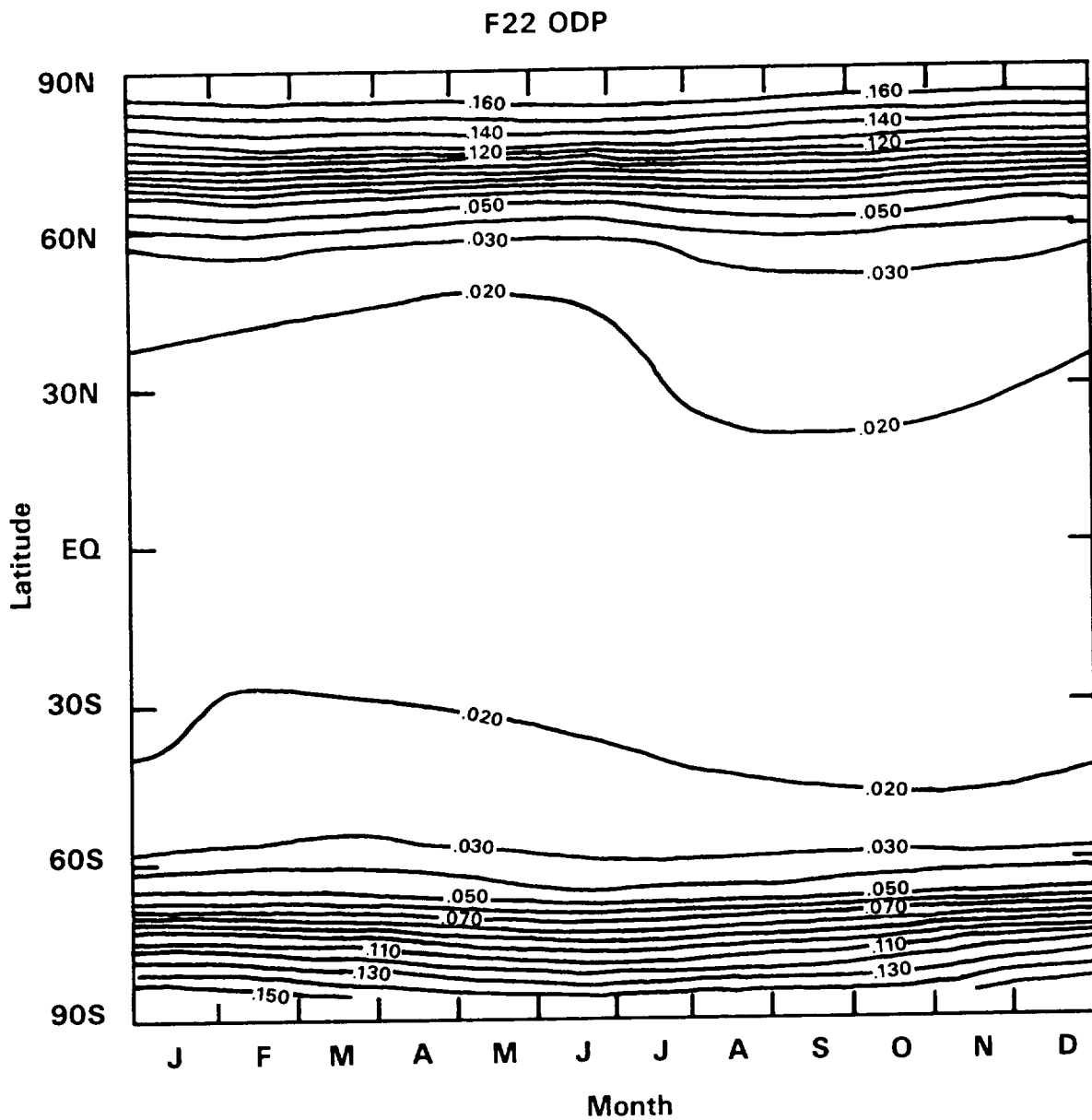
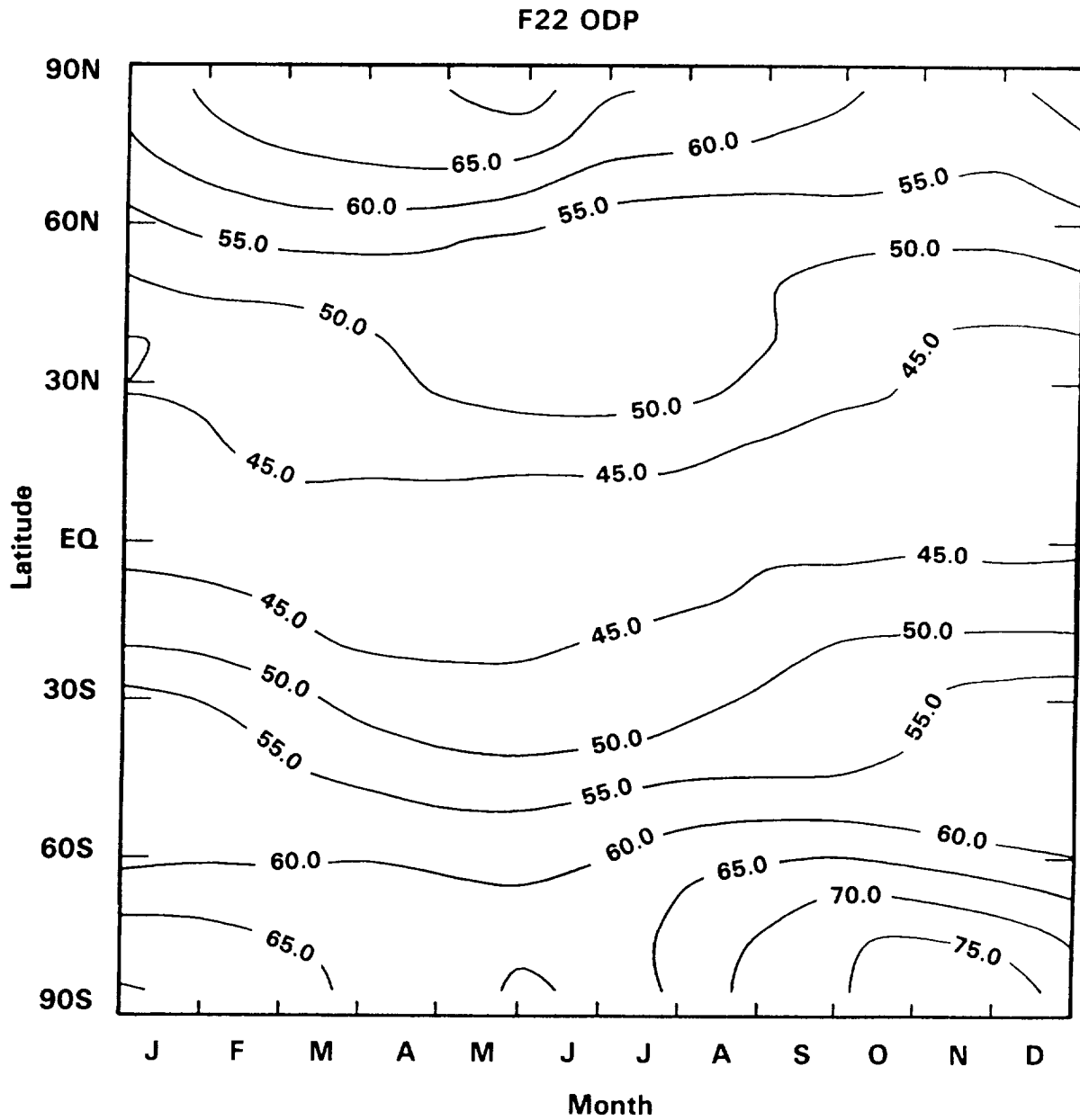


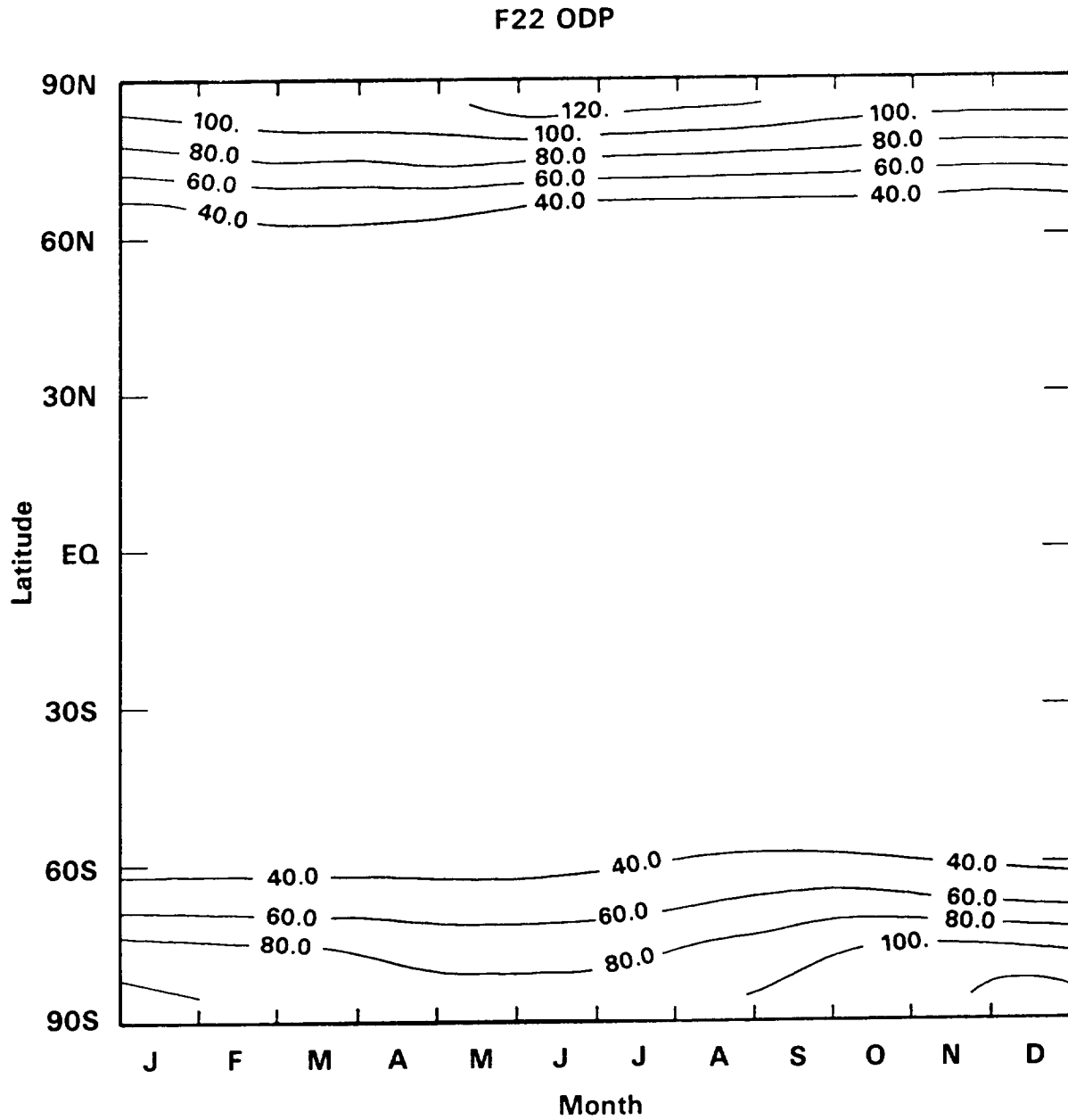
Figure 18B. Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 2 of Transport Sensitivity] (AER 2-D).

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**NOTE: Contours are ODP x 1000**

**Figure 18C.** Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 3 of Transport Sensitivity Study] (AER 2-D).



**NOTE: Contours are ODP x 1000**

**Figure 18D.** Calculated Latitudinal and Seasonal Relative Ozone Depletion from Emission of HCFC-22 [Case 4 of Transport Sensitivity Study] (AER 2-D).

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ture since modeling of heterogeneous chemistry in general, and the polar phenomena in particular are still in the early stages. Furthermore, increases in carbon dioxide and other greenhouse gases may impact on stratospheric cooling resulting in wider spread occurrence of polar stratospheric clouds.

The Ozone Depletion Potential concept is based on the annual-averaged changes in global ozone. Since the polar region constitutes a small percentage of the global area and since ODP is a relative measure of the effect on ozone, the overall impact of these phenomena on global ODP depends on, 1) the impact of polar processes on ozone at lower latitude either by dilution effects or by a "chemical processor" mechanism, and 2) the inter-species differences in the heterogeneous processes. The indirect impact on ozone at lower latitude is a subject of intense investigation yet to be resolved. Below, we focus on the species-to-species differences in the chlorine distribution that lead to differences in enhanced ozone depletion due to heterogeneous processing important in the polar regions.

### Chlorine Loading and ODP

In order to bracket the impact of this phenomena, we have estimated two limits for relative impact. First, a conservative estimate was determined based on chlorine transport to the stratosphere, and secondly, a less conservative estimate was made based on inorganic chlorine profiles from model output.

A conservative estimate for ODP can be derived based on the chlorine transported into the stratosphere. The relative effects on ozone and, therefore, on ODPs can be bracketed by the values indicated by the relative weighting of the total possible chlorine loading in the stratosphere.

Atmospheric models indicate that the steady state impact of an emitted CFC on ozone depends on both the distribution as well as the number of the chlorine atoms released by the CFC upon photodecomposition. At steady state, the expected chlorine loading (CL) from emission of a species is given by

$$CL \propto E \cdot T \cdot N / MW$$

where E is the mass emitted per year, T is the lifetime, N is the number of chlorine atoms in the molecule, and MW is the molecular weight. The constant of proportionality depends on the properties of the atmosphere and is independent of species. The quantity CL represents the asymptotic concentration of inorganic chlorine in or above the upper stratosphere where all the chlorine atoms have been released. The expression for CL is valid for species with atmospheric lifetime longer than one year so that the species is vertically well-mixed in the troposphere. Similar to the definition of the ODP, a chlorine loading potential (CLP) can be defined as the ratio of CL for the species to that of CFC-11 for the same emission, i.e.

$$CLP(x) = CL(x) / CL(\text{CFC-11})$$

The ratio of ODP to CLP is representative of the effect of the chlorine distribution on ozone and can be represented by a Chlorine Effectiveness Factor (CEF) ratio defined by

$$CEF = ODP / CLP$$

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**Table 10** Chlorine Loading Potentials (CLP) and Chlorine Efficiency Factors (CEF) from 2-D Models (HCFCs and HFCs scaled by lifetime of  $\text{CH}_3\text{CCl}_3 = 63.$ )

Species	Oslo		LLNL		AER		DuPont	
	CLP	CEF	CLP	CEF	CLP	CEF	CLP	CEF
CFC11	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
CFC12	1.325	0.694	1.465	0.594	1.531	0.575	1.939	0.459
CFC113	1.234	0.697	1.110	0.685				
CFC114	2.108	0.389	2.022	0.277				
CFC115	2.579	0.155	2.232	0.121	2.517	0.147		
HCFC22	0.152	0.303	0.171	0.273	0.215	0.268	0.197	0.220
HCFC123	0.017	0.766	0.018	0.919	0.025	0.883	0.022	0.815
HCFC124	0.041	0.432	0.045	0.408	0.058	0.420	0.052	0.338
HFC125	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HFC134a	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HCFC141b	0.104	0.852	0.114	0.781	0.148	0.764	0.132	0.661
HCFC142b	0.159	0.353	0.180	0.277	0.219	0.284	0.202	0.235
HFC143a	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HFC 152A	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$\text{CCl}_4$	1.036	1.159	1.077	1.022	1.013	0.938	1.031	1.135
$\text{CH}_3\text{CCl}_3$	0.108	1.295	0.124	1.058	0.138	1.170	0.140	1.061

The values for CEF can be calculated once the model simulated ODP and lifetimes are given. Table 10 shows the ODP, CLP and CEF as calculated by three 2-D models.

#### Chlorine Distribution and ODP

The reader may wonder why the values of the chlorine loading potential CLP are often larger than the ODPs for the same species or alternatively why most CEF values are less than 1.0. If all sources of stratospheric chlorine were equivalent in the photochemical reactivity sense once they reached the stratosphere, ODP values would be identical to the CLP values. Two reasons account for the chlorine loading potential values being larger than the ODPs for many of the species. First, several of the CFCs and HCFCs, such as HCFC-22 and HCFC-142b, are incompletely dissociated within the stratosphere. Second, differences in the dissociation reactivity produce different chlorine distribution for the various gases.

Note that values of CEF are notably consistent among the models, to within 20% of each other for most species. In addition, the value for CEF can be larger than 1 as in the case of  $\text{CH}_3\text{CCl}_3$  for which a larger portion of the chlorine atoms is deposited in the lower stratosphere compared to CFC-11. The value for CEF can be related to the calculated chlorine distribution as follows. We will use HCFC-22 as an example in the following discussion. One can calculate the two steady state Cly distributions resulting from emissions of CFC's that maintain a surface mixing ratio of 1 ppbv for CFC-11 and 3 ppbv for HCFC-22 respec-

## STRATOSPHERIC OZONE

tively and define the ratio of the concentrations as the Normalized Chlorine Distribution (NCD). Note that NCD is a function of latitude and height. One expects the Cly distributions for CFC-11 and HCFC-22 to be different since the local loss frequencies for the two species are quite different and the chlorine atoms will be released in different regions of the stratosphere. If the stratospheric loss frequencies for both species were the same, the resulting distributions would be identical, and the values for NCD would be identically 1 everywhere (the factor of three in surface mixing ratio takes care of the fact that CFC-11 has 3 chlorine atoms while HCFC-22 only has 1) and  $CEF = 1$ .

A better estimate for the potential impact of polar ozone loss processes is perhaps possible based on the NCD. The difficulty for estimation of polar chemistry impact on local and global ODP from the local NCD arises for two reasons. First, the repartition of the chlorine species depends on the absolute amount of Cly in the atmosphere, a larger portion of the chlorine will be converted to ClO, the higher the concentration of Cly, Second, the  $O_3$  removal rate is approximately proportional to the square of the ClO concentration.

The 2-D NCD for HCFC-22 is shown in Figure 19A for January as calculated by the AER 2D model. The quantity CEF can be interpreted as a weighted average of NCD with the weighting determined by the response of ozone to the local chlorine concentration. Comparison of the latitudinal variation of the 2-D ODP for January (Figure 18A) with NCD (Figure 19A) indicates that the 2-D ODP is approximately

$$\text{local ODP} \sim \text{CLP} * \text{NCD} \text{ (in the lower stratosphere).}$$

Thus, it is reasonable that if the NCD in the polar lower stratosphere (NCDpl) is less than 1, then

$$\text{local ODP} \leq \text{CLP} * (\text{NCDpl})$$

holds even in the presence of heterogeneous conversion. With more chlorine available in the CFC-11 case, the response of  $O_3$  will be larger than that of the substitute compound with  $\text{NCDpl} \leq 1$ .

In estimating the effect of polar chemistry on the calculated global ODP, one must include the dilution effect away from the local effect (ozone hole) as well as the direct contribution from local effect. A simple estimate can be provided as follows. Noting that the ratio CEF for most substitute compounds are approximately equal to NCDpl, an argument can be put forward that if  $CEF, \text{NCDpl}$  and  $\text{NCD} \leq 1$

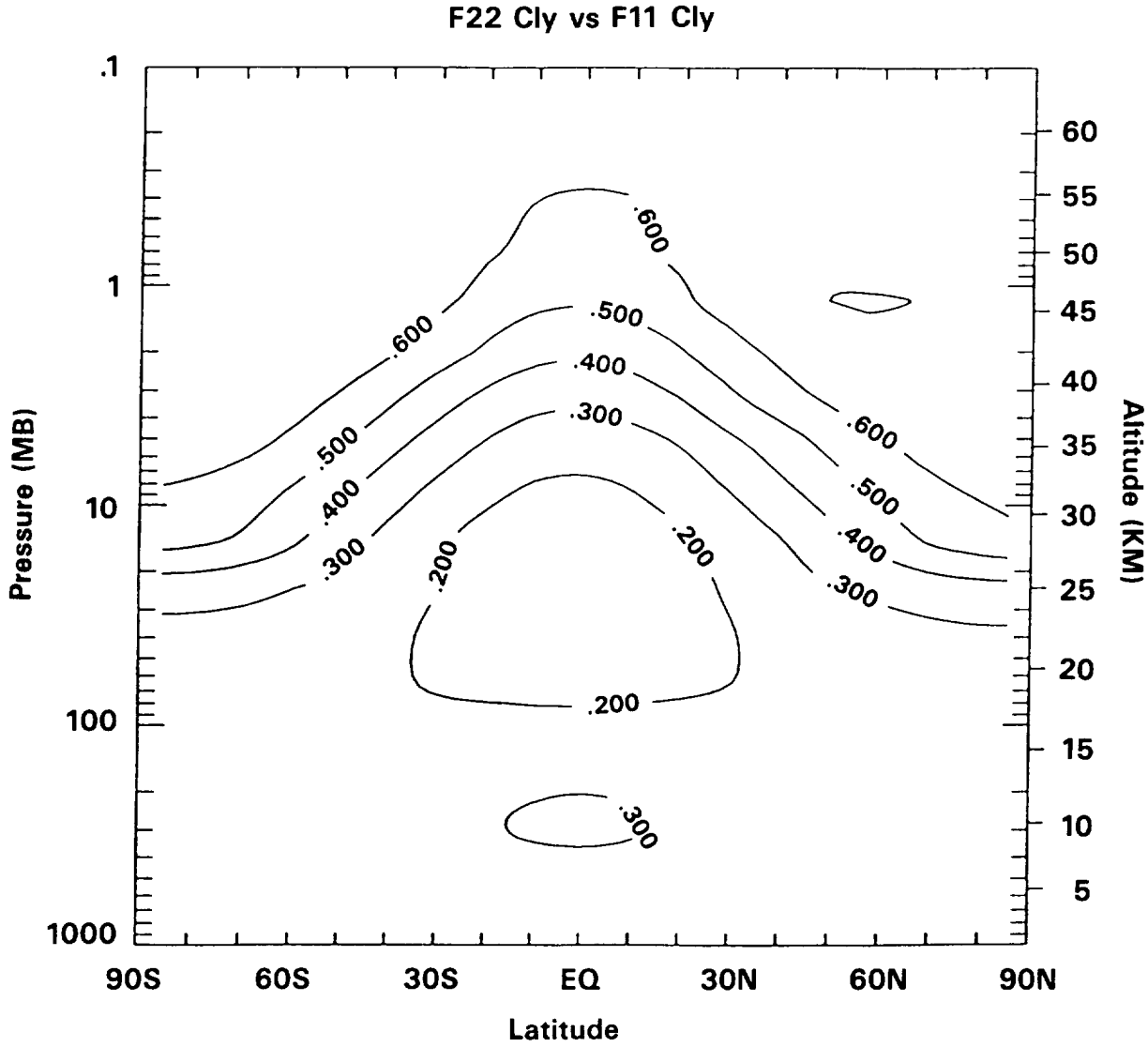
$$\text{then Global ODP} \leq \text{CLP} * (\text{NCDpl}).$$

in the presence of polar chemistry. The above conditions are satisfied for all HCFC's we have examined except for  $\text{CH}_3\text{CCl}_3$ . Thus for HCFC-22, this reasoning leads to an estimate bound of

$$\begin{aligned} \text{Global ODP(HCFC-22)} &\leq .27 * .500 \\ &\leq .135 \end{aligned}$$

which is approximately double the global ODP value calculated by AER, but only <50% of the CLP limit posed as the conservative estimate above.





**Figure 19A.** Normalized Chlorine Distribution (NCD) for HCFC-22 in January [Case 1 of Transport Sensitivity Study] (AER-2D).

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F22 Cly vs F11 Cly

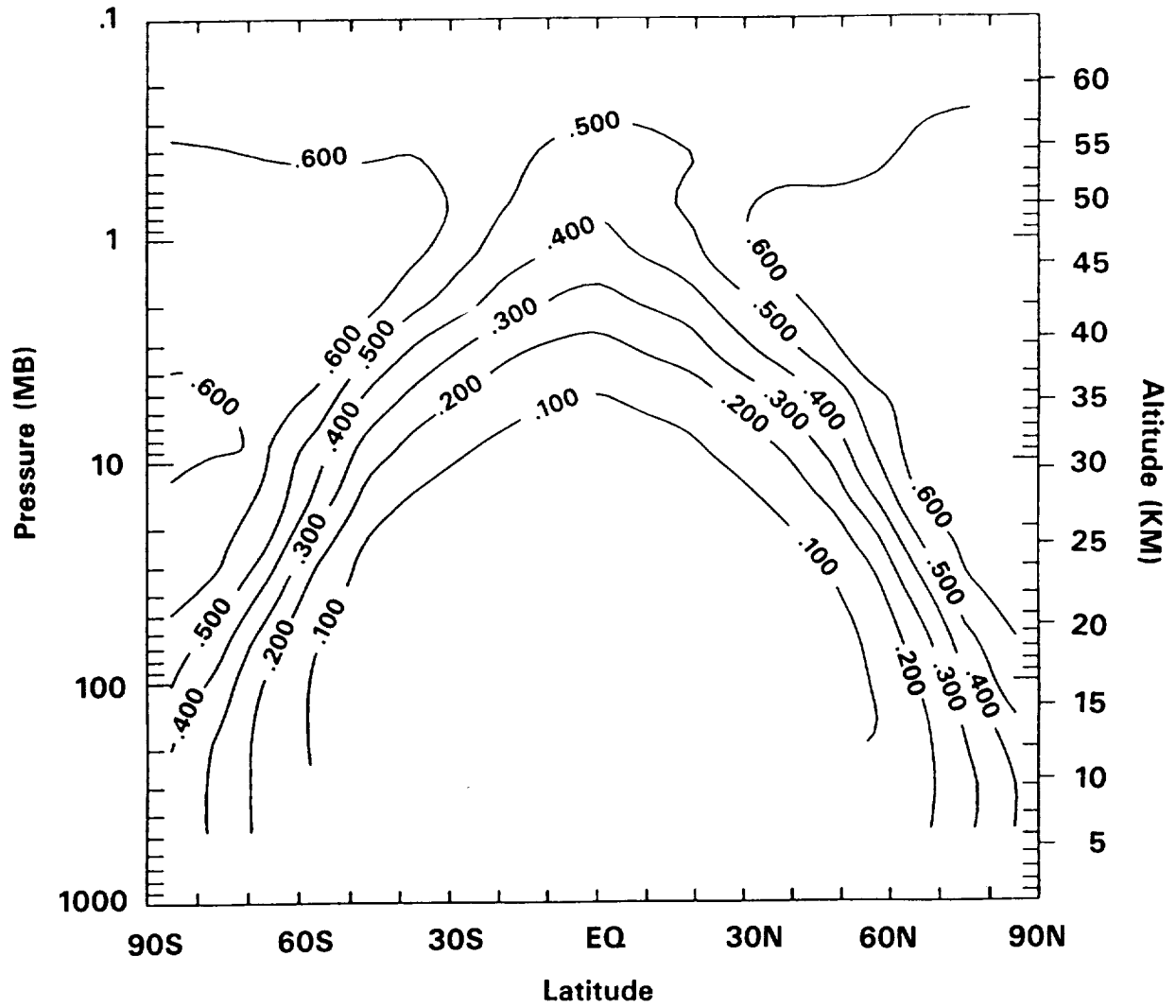


Figure 19B. Normalized Chlorine Distribution (NCD) for HCFC-22 in January [Case 2 of Transport Sensitivity Study] (AER-2D).

F22 Cly vs F11 Cly

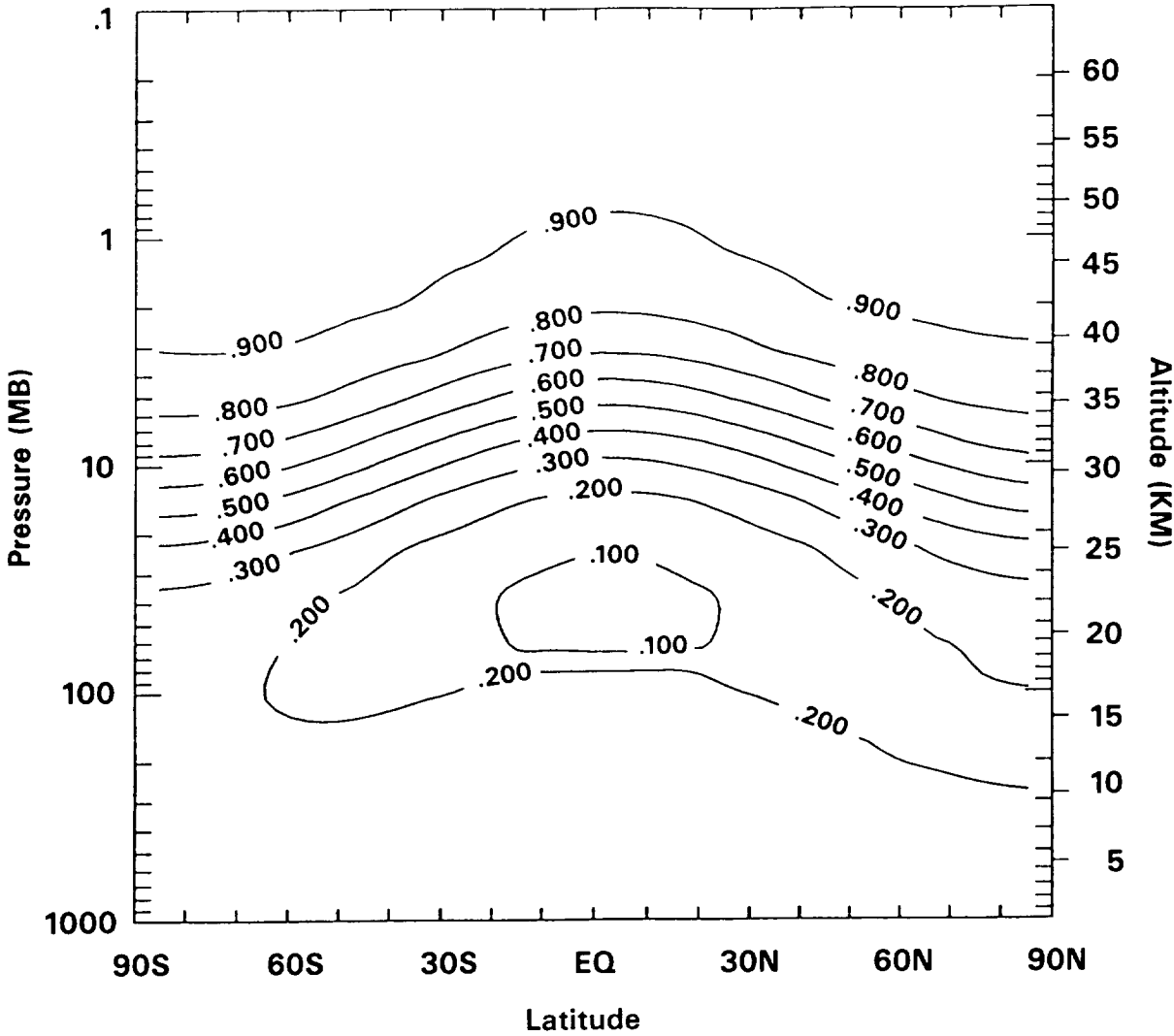


Figure 19C. Normalized Chlorine Distribution (NCD) for HCFC-22 in January [Case 3 of Transport Sensitivity Study] (AER-2D).

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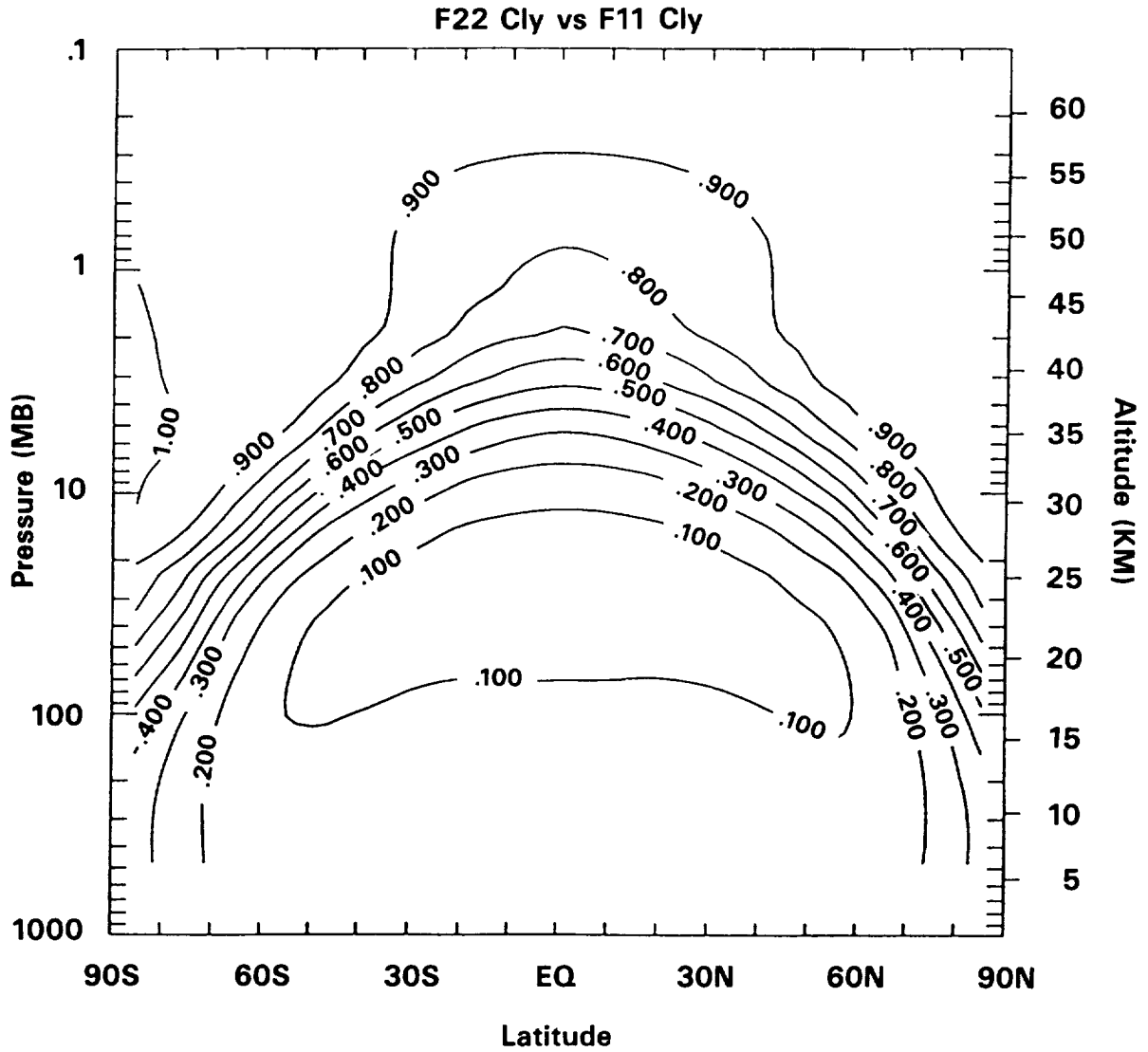


Figure 19D. Normalized Chlorine Distribution (NCD) for HCFC-22 in January [Case 4 of Transport Sensitivity Study] (AER-2D).

Because of apparent significant downward advection within the vortex (sufficient to explain the observed low concentrations of  $N_2O$ ,  $CH_4$ , and CFCs), it can be argued that active chlorine at all altitudes within the stratosphere and, perhaps, the mesosphere, may be available for affecting ozone within the polar vortex. The implication of this hypothesis on the derived ODPs is unknown.

At this time, until model studies of heterogeneous chemistry effects have been completed, we cannot conclude that using the ODP values in Table 4 is more definitive than using the chlorine loading potential values in Table 10. The answer to this open question depends on the maximum extent of the influence that polar springtime ozone destruction will have on global ozone, and on the extent of the downward transport within the Antarctic and Arctic polar vortices.

In summary, the impact of the unique polar chemistry on the relative effects can only be estimated quite crudely. The most conservative estimate is that the effects are bounded by a Chlorine Loading Potential which is substantially greater than the Ozone Depletion Potential for most chemicals. A less conservative estimate can be derived from the calculated profiles of inorganic chlorine distributions indicating that the relative effect may be substantially below the CLP values.

## **7. TIME-DEPENDENT RELATIVE OZONE DEPLETION**

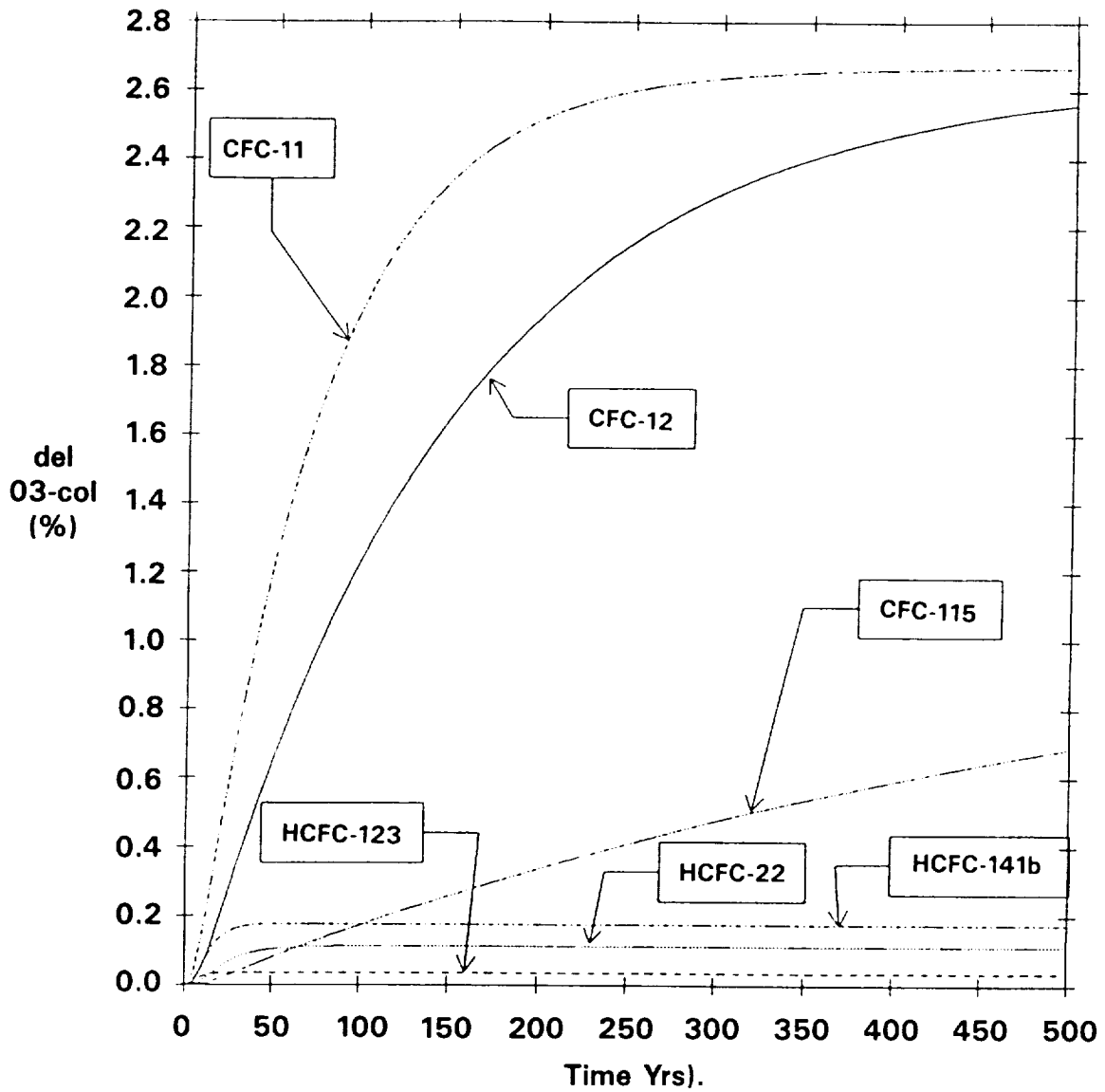
One of the limitations associated with the ODP parameter is that it is based on steady state perturbations; it does not consider the relative time-dependent effects of different constituents on ozone. While we have shown that ODP is equivalently a measure of the cumulative chronic effects of unit emitted mass of a gas over its life cycle in the atmosphere, we are also interested in the transient response at a constant emission level.

As mentioned in the first section, ODP values determined at steady-state are not expected to be representative of the relative transient effects expected for shorter-lived compounds during the early years of emission. During these early years, before one to two equivalent species lifetimes have passed, the ozone depletion per unit mass relative to CFC-11 can be much larger than the steady state ODP value for some of the short-lived constituents. We note from Figure 20, however, that the changes in ozone occurring, at these times are also relatively small compared to the steady-state ozone change.

The calculated time-dependent ozone depletions for several of the HCFCs following a step increase in emission level are shown in Figure 20. These results can be compared relative to CFC-11 to give relative ozone depletions. Results from the LLNL 1-D model are shown in Figure 21 and from the DuPont 1-D model in Figure 22 for a range of compounds. Results for the first few years are not shown because the derived changes in ozone were too small to be numerically accurate.

The transient values for relative ozone depletion and the time it takes to approach the steady state values depend on the time-dependent behavior of the calculated  $O_3$  decrease for the species and the reference gas CFC-11 which depends on the stratospheric lifetimes as well as the atmospheric lifetimes. Since the

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**Figure 20.** Time Response of Column Ozone Following Step Change in Release of Specified Gas at  $5.0 \times 10^8$  kg/yr. (DuPont 1-D Model)

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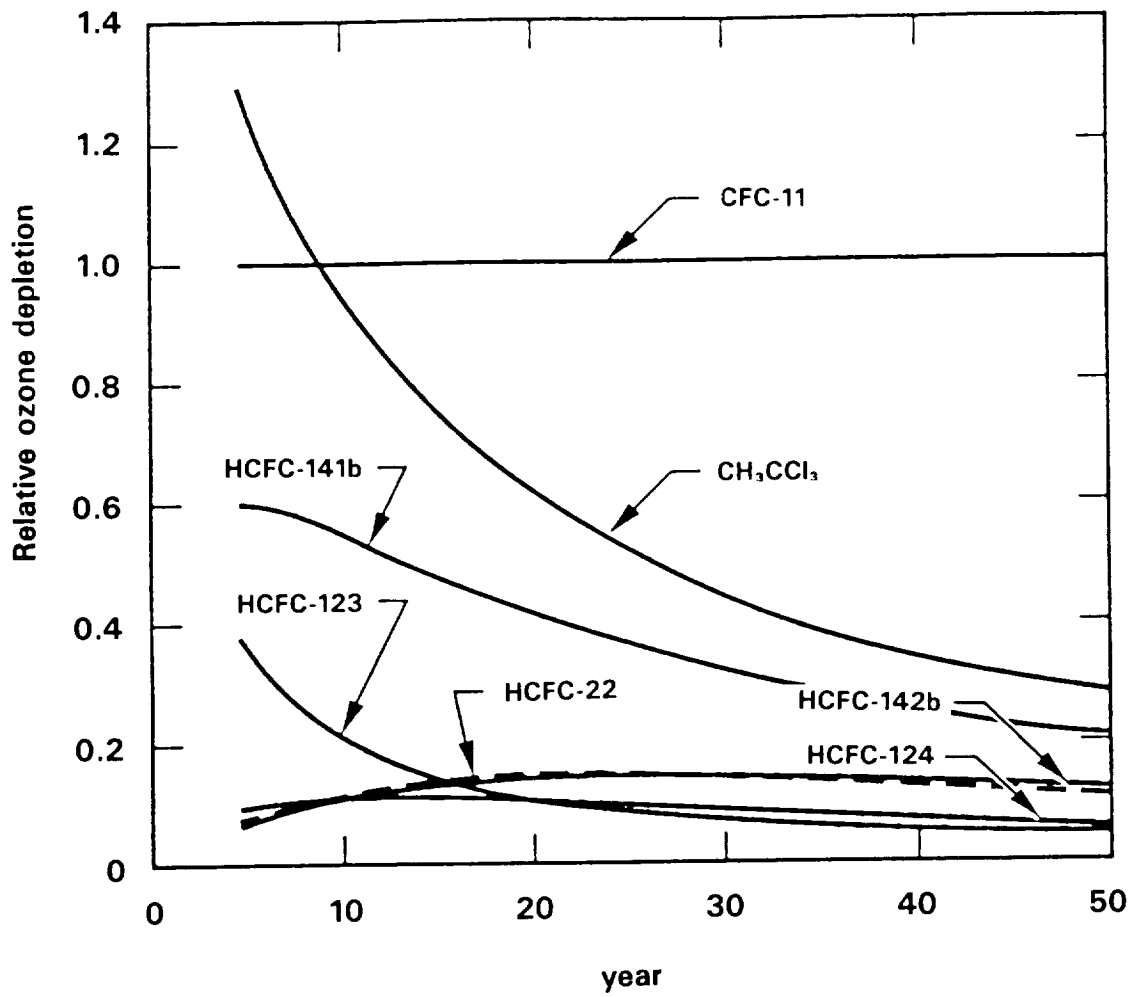


Figure 21. Calculated time-dependent change in relative ozone column depletion. (LLNL 1-D Model)

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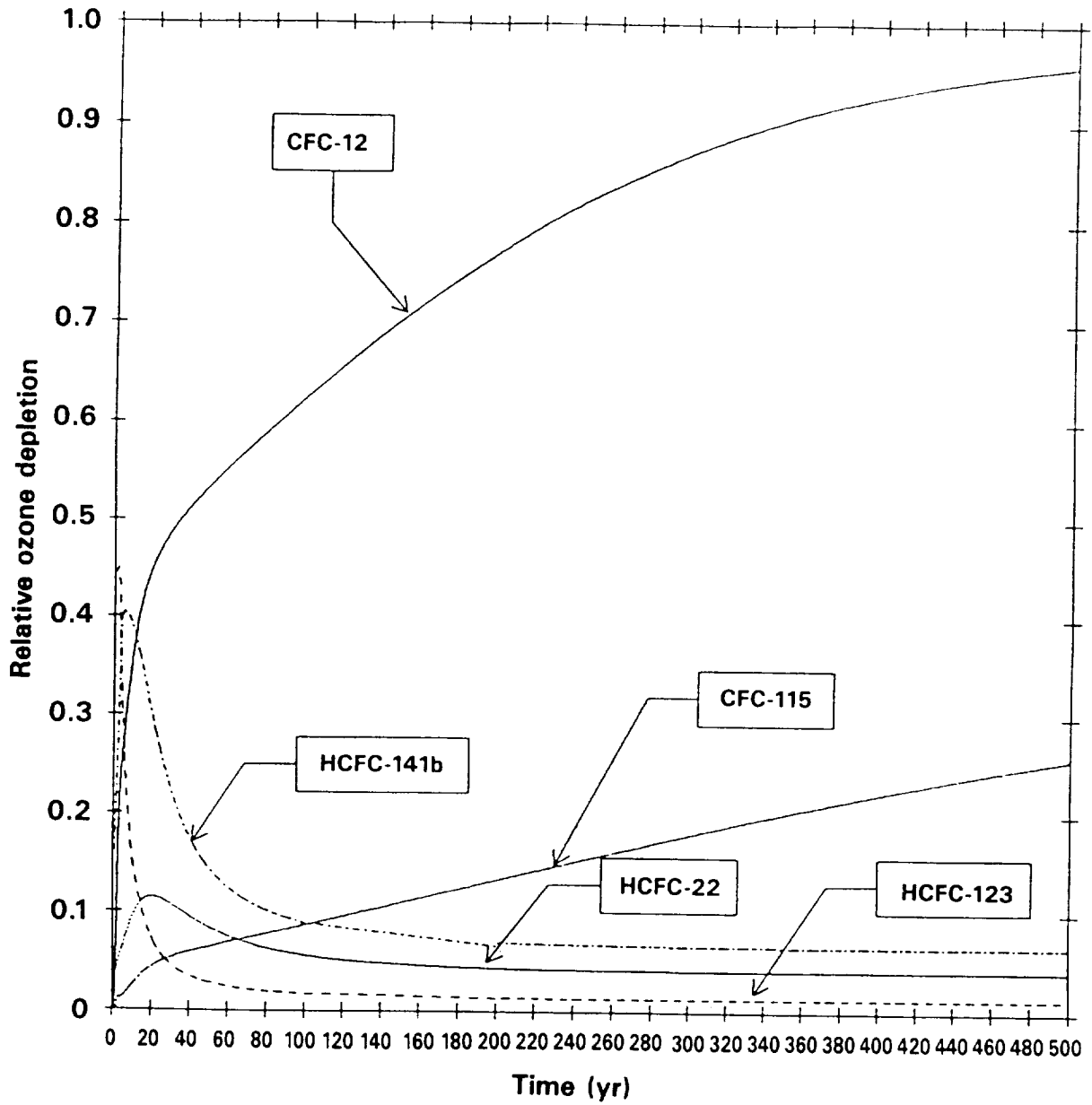


Figure 22. Calculated time-dependent change in relative ozone column depletion following a step change in emission of Halocarbons. (DuPont 1-D).



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atmospheric lifetimes of the HCFC's examined in this study are shorter than that of CFC-11, the time constant for exponential decay to the ODP asymptote is determined by the CFC-11 lifetime. The magnitude of the transient relative ozone depletion depends on the stratospheric lifetimes and how fast the chlorine atoms are released after transport into the stratosphere.

Several of the HCFCs, namely HCFC-123, HCFC-141b, and CH<sub>3</sub>CCl<sub>3</sub>, have much larger relative ozone depletions at early times compared to the Ozone Depletion Potential values. Each of these cases have relatively short reaction time constants within the stratosphere - compared to CFC-11. As a result, chlorine atoms are quickly released by these gases and the full effect on ozone is reached much sooner than CFC-11. At longer times the relative ozone depletions asymptotically approach the ODP value.

Other species, such as HCFC-22, HCFC-124, and HCFC-142b, have long reactive time constants in the stratosphere. The time-dependent relative ozone depletions have much different behavior for these species. The relative ozone depletion builds gradually to a maximum value for these species, reflective of their long stratospheric time constants and the amount of time needed to build-up stratospheric concentrations. After the first 2040 years, the relative ozone depletion for these species gradually decays to the ODP value.

For gases with longer lifetimes than the reference gas, no maximum in relative ozone depletion is noted. This can be seen by examining the results for CFC-12 and CFC-115 in Figure 22.

Of equal interest to many is the relative ozone depletions once emissions cease. Figure 23 shows the calculated change in ozone column when gases are emitted at a constant level of  $5.0 \times 10^8$  kg/yr, for 50 years and at which point emissions stop (Du Pont 1-D model). Calculated effects for the HCFCs fall to near zero at the end of the 100 year period whereas a significant fraction of the calculated effects for CFCs remain at the end of this period. The relative (to CFC-11) effect for each of the species is shown in Figure 24. Response during the first 50 years is the same as shown in Figure 22. Once emissions are curtailed, all of the curves for HCFCs drop significantly faster than during the emission period whereas the curves for CFC-12 and CFC-115 increase in slope. In other words, this reinforces the conclusion that it takes far less time for any residual effect from HCFCs to diminish than from CFCs once emissions are stopped.

Figures 25 and 26 show the relative time-dependent behavior of chlorine being transported through the tropopause for these same gases (taken relative to CFC-11). In all cases, the time-dependent stratospheric chlorine loading is much larger initially compared with their eventual steady-state relative Chlorine Loading Potential value (given previously in Table 10) if the lifetime of the species is less than the reference gas.

In summary, time dependent ozone depletion and chlorine loading values for species with lifetimes shorter than CFC-11 are generally larger than the ODP and CLP values defined at steady state. Time dependent relative ozone depletion and chlorine loading for CFCs with lifetimes longer than CFC-11 show a monotonic increase to the steady state ODP and CLP value.

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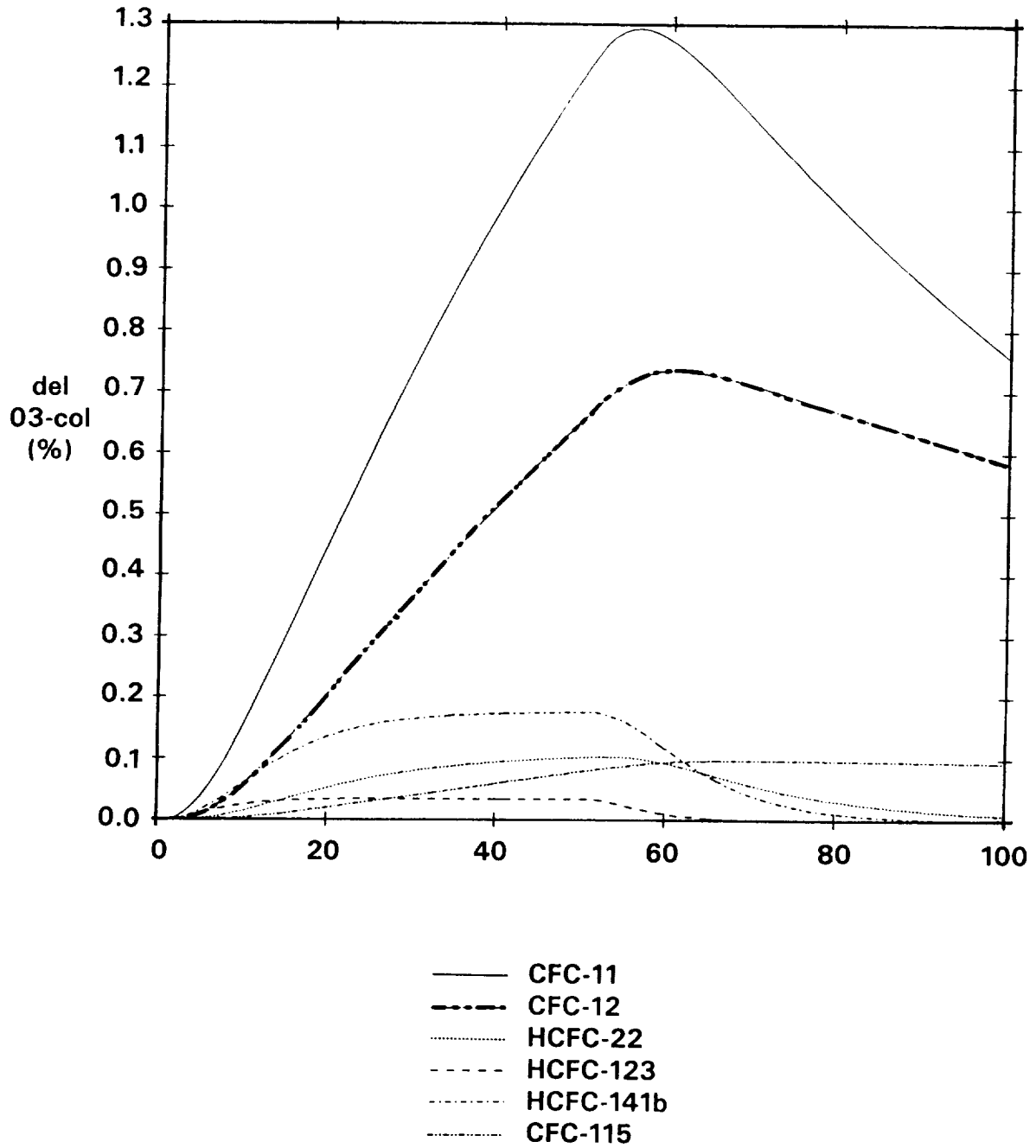


Figure 23. Column Ozone Change Following Step Emission Increase of Specified Gas of  $5.0 \times 10^8$  kg/yr for 50 years, and then Cut to 0 Emissions for Next 50 Years. [DuPont 1-D Model]

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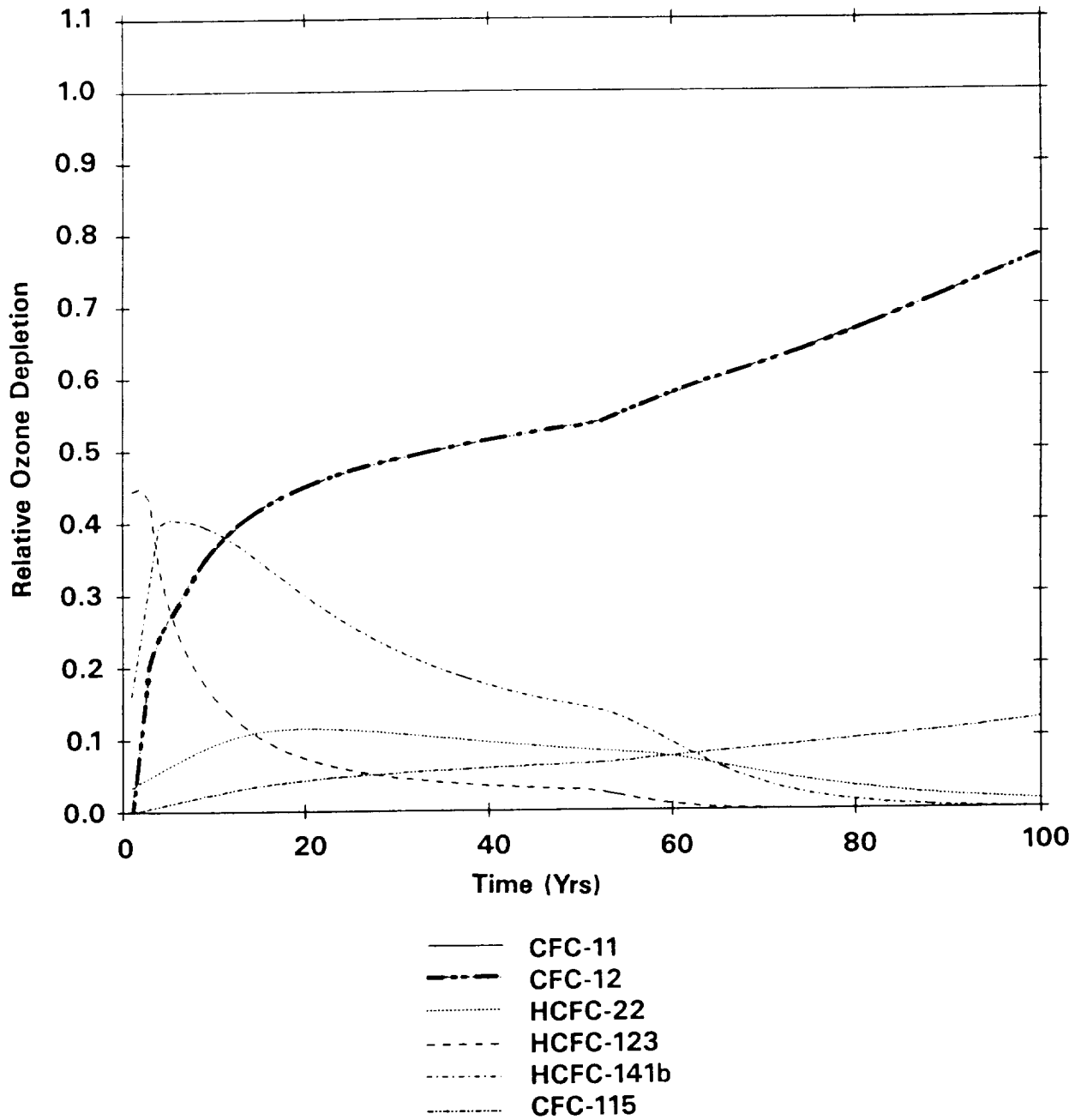


Figure 24. Relative Column Ozone Change Following Step Emission (of  $5.0 \times 10^{*8}$  kg/yr) Increase for Specified Gases for 50 Years, and then Cut to 0 Emissions for Next 50 Years. (Basis: CFC-11 = 1.0) [DuPont 1-D Model]

STRATOSPHERIC OZONE

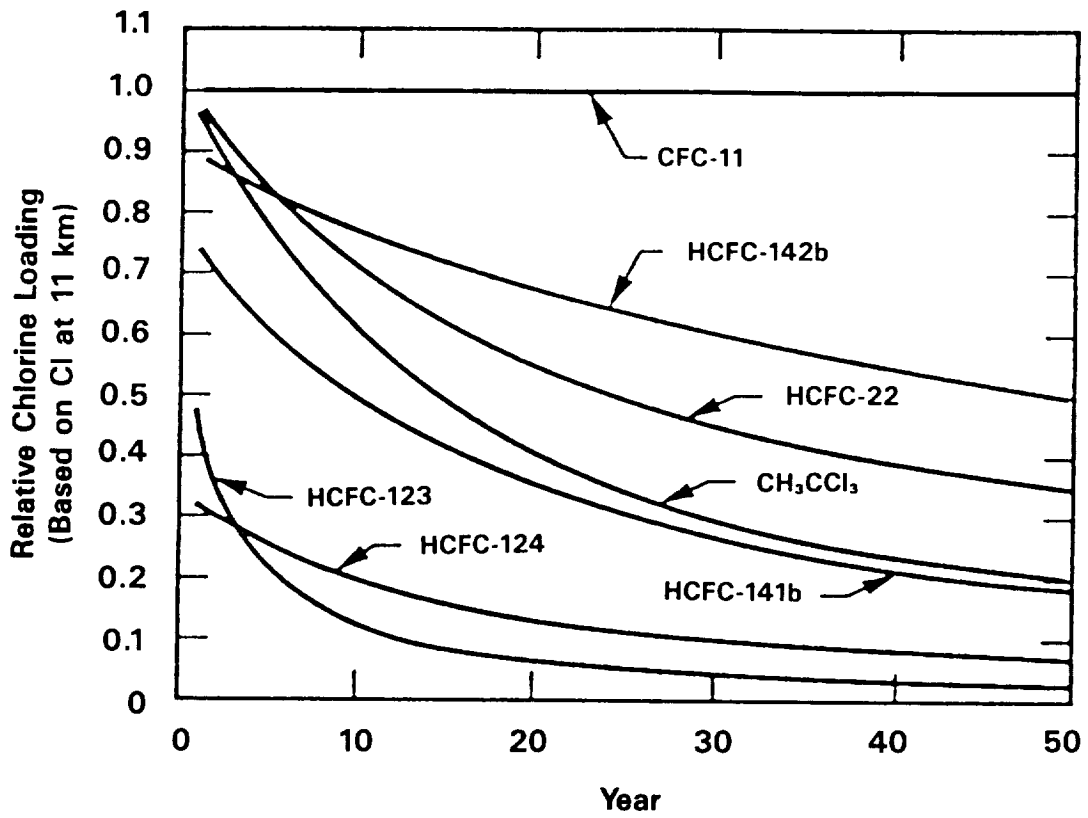


Figure 25. Calculated Time-Dependent Relative Chlorine Loading Following a Step Change in Emission of Halocarbons. (LLNL 1-D).

STRATOSPHERIC OZONE

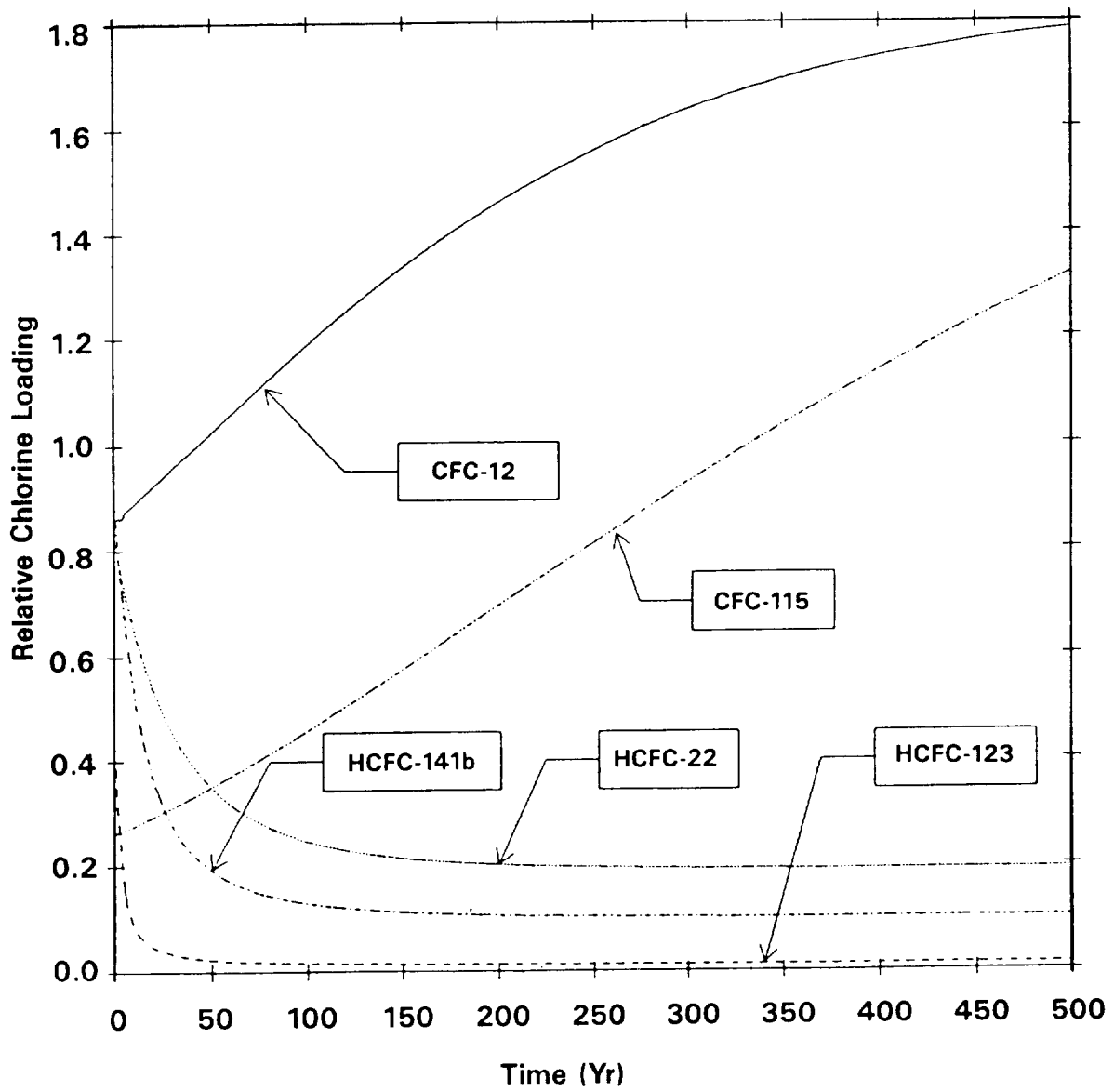


Figure 26. Calculated Time-Dependent Relative Chlorine Loading Following a Step Change in Emission of Halocarbons. (DuPont 1-D).

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### **8. ACKNOWLEDGMENTS**

The authors are grateful for the support received for this work from the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS). Additional funding was provided by the following companies: Allied-Signal Corporation, Atochem, E.I. du Pont de Nemours & Co., Hoechst Aktiengesellschaft, ICI Chemicals and Polymers Limited, and Montefluos SPA.

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**APPENDIX A: RELATIONSHIP BETWEEN FORMS OF ODP**

It is helpful to look at the various formulations for ODP and explore the background relationships between them. We have chosen our definition for ODP to be the column ozone change following a constant release of a given compound divided by the column ozone change resulting from the same mass release rate of CFC-11 at steady state. Subsequently, we showed, based on model exercises, that the ratio of cumulative effects following a one-time input of gases was virtually equivalent to ODP. The purpose of this section is to examine the background mathematical formulations in order to define the relationship(s) between the formulations.

Let  $G(t-t_0)$  be the response function [which in this example corresponds to the ozone column change] at time  $t = t_0$  to a stimulus  $S(t_0)$  [which in this example corresponds to a release of a set mass of chlorine containing gas into the atmosphere] at time  $t_0$ . We furthermore make the assumption that the response is linear so that it can be normalized to the source strength to Give:

$$g(t-t_0) = G(t-t_0)/S(t_0)$$

Properties of the function  $g(t)$  are that:

$$g(\infty) = 0 \text{ (i.e., the response decays to 0 at infinite time),}$$

In terms of physical processes, the function  $g(t-t_0)$  contains the results from the transport and chemistry within the reacting system (atmosphere) and is specific to one set of reaction parameters, and therefore is species specific.

**STEADY STATE**

Let us first examine the case of a steady-state response. If a stimulus started at time  $= 0$  and held constant at  $S = S_0$  until steady state is realized, then the steady-state response is reached at time  $T$  and is the integrated response from all gas released over history and is of the form:

$$G_{ss} = \int_{t_0=0}^{t_0=T} S_0 * g(T-t_0) dt_0$$

Since by definition of steady state, it is insensitive to starting time, so we could have started the release at time,  $t = -\infty$ . Thus,  $G_{ss}$  can be expressed, without loss of generality, as:

$$G_{ss} = \int_{t_0=-\infty}^{t_0=T} S_0 * g(T-t_0) dt_0$$

Therefore if we use the notation that  $G_{ss-x}$  is the steady state response for compound  $x$ , and  $G_{ss-11}$  is the corresponding response for CFC-11, then ODP(ss) can be expressed as:

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$$\text{ODP(ss)} = \frac{G_{ss-x}/S_0-x}{G_{ss-11}/S_0-11}$$

or,

$$\text{ODP(ss)} = \frac{\int_{-\infty}^T g_x(T-t_0) dt_0}{\int_{-\infty}^T g_{11}(T-t_0) dt_0} \quad (\text{A})$$

With a substitution of integration variables of  $t \rightarrow T-t_0$ , equation A becomes:

$$\text{ODP(ss)} = \frac{\int_0^{\infty} g_x(t) dt}{\int_0^{\infty} g_{11}(t) dt}$$

or,

$$\text{ODP(ss)} = \frac{\int_0^{\infty} g_x(t) dt}{\int_0^{\infty} g_{11}(t) dt} \quad (\text{B})$$

## PULSED INPUT

Now, let us focus on the ratio of integrated responses to a pulsed input. For a pulsed input of value PS at time  $t_0$ , the integrated resulting effect, GP, on the system over the ensuing period is:

$$\text{GP} = \int_{t_0}^{\infty} \text{PS} * g(t-t_0) dt$$

Since PS is constant, GP becomes:

$$\text{GP} = \text{PS} * \int_{t_0}^{\infty} g(t-t_0) dt$$



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We can again change the integration variable such that  $T = t-t_0$  and since the values for PS will be the same both in the numerator and the denominator, the ratios of integrated responses reduces to:

$$\frac{\text{GP-x}}{\text{GP-11}} = \frac{\int_0^{\infty} g_x(T) dT}{\int_0^{\infty} g_{11}(T) dT} \quad (\text{C})$$

Which is the same functional form as ODP expressed by equation B.

Therefore we have shown mathematical equivalence as long as we have linear relationships between release (stimuli) and ozone change (response). Real world interpretations as well as model exercises indicate that the relationships are not exactly linear. Therefore, discrepancies between ODP and ratio of responses to pulsed releases do exist but are caused by the (minor) non-linearities of the phenomena and/or numerical round-off errors associated with the numerical models.

