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Stratospheric ozone destruction by man-made chlorofluoromethanes.

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Peer reviewed

## References and Notes

1. Key references include W. L. Bragg, R. W. James, C. H. Bosanquet, *Phil. Mag.* **44**, 433 (1922); R. J. Havighurst, *Phys. Rev.* **29**, 1 (1927); E. O. Wollan, *ibid.* **38**, 15 (1931). Corresponding studies by electron diffraction were first reported by L. S. Bartell and L. O. Brockway [*Phys. Rev.* **90**, 833 (1953)].
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6 May 1974

## Stratospheric Ozone Destruction by Man-Made

### Chlorofluoromethanes

**Abstract.** Calculations indicate that chlorofluoromethanes produced by man can greatly affect the concentrations of stratospheric ozone in future decades. This effect follows the release of chlorine from these compounds in the stratosphere. Present usage levels of chlorofluoromethanes can lead to chlorine-catalyzed ozone destruction rates that will exceed natural sinks of ozone by 1985 or 1990.

Chlorofluoromethanes ( $\text{CF}_x\text{Cl}_y$ ), principally  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$ , are being produced as aerosol propellants and refrigerants in large and growing amounts, and their atmospheric concentrations are increasing (1–3). These compounds have been considered valuable as tracers of atmospheric motions because they are relatively inert chemically with atmospheric lifetimes exceeding 10 years (4). Unlike  $\text{CCl}_4$  (1), they seem to have no natural sources or sinks in the troposphere; their lifetimes are controlled by diffusion into the stratosphere where they can be photodissociated by ultraviolet light (5). Molina and Rowland (5) have noted that this stratospheric sink for  $\text{CF}_x\text{Cl}_y$  also represents a potential sink for stratospheric  $\text{O}_3$ . This is so because the photodissociation of  $\text{CF}_x\text{Cl}_y$  releases chlorine atoms which can catalytically destroy  $\text{O}_3$  through reactions like those of the nitrogen oxides ( $\text{NO}_x$ ) with  $\text{O}_3$  (5–8). Because of the great importance of stratospheric  $\text{O}_3$  (9), we have reexamined this potential effect and its likely time evolution. We find that current  $\text{CF}_x\text{Cl}_y$  usage levels and trends can lead to chlorine-catalyzed  $\text{O}_3$  destruction rates exceeding all natural sinks of stratospheric  $\text{O}_3$  by the early 1980's. Stratospheric changes will continue long after ground-level emissions cease. For example, if emissions were curtailed now, the resultant  $\text{O}_3$  destruction would maximize around 1990 and would remain significant for several decades. Our calculations also indicate that the CIX concentrations (the sum of the concentrations of Cl, ClO, and HCl) will increase significantly in the stratosphere but not in the troposphere.

Hence, critical monitoring of this problem will require measurements in the stratosphere; tropospheric observations alone will not suffice.

After release,  $\text{CF}_x\text{Cl}_y$  molecules diffuse upward to be photolyzed by solar radiation (chiefly 175- to 220-nm ultraviolet wavelengths) in the stratosphere. On the basis of several atmospheric measurements (1–3) and known chemical properties of the chlorofluoromethanes, stratospheric photolysis ap-

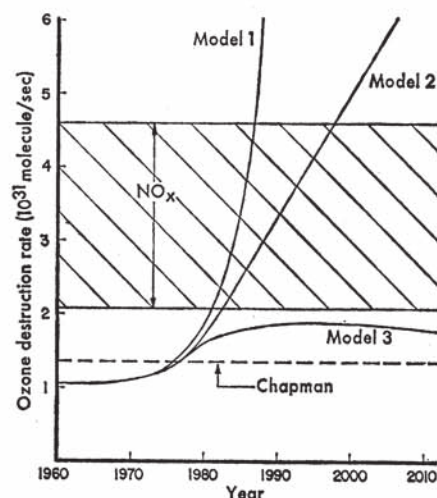
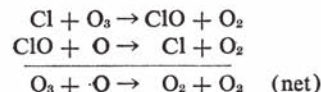


Fig. 1. Globally integrated  $\text{O}_3$  destruction rates for three model time histories of  $\text{CF}_x\text{Cl}_y$  emission. Corresponding rates appear for the natural  $\text{O}_3$  sinks due to pure oxygen (labeled "Chapman") reactions and  $\text{NO}_x$  reactions. The width of the  $\text{NO}_x$  band is due mostly to a lack of knowledge of the natural  $\text{NO}_x$  abundance and altitude distribution. All quantities were computed on the basis of present-day atmospheric background and have been integrated to 60-km altitude. The stratospheric  $\text{O}_3$  production rate, integrated globally, is about  $6 \times 10^{31} \text{ sec}^{-1}$ . Above 50 km the hydrogen oxides can also destroy  $\text{O}_3$ .

pears to be the major sink for  $\text{CF}_x\text{Cl}_y$  (5). Several other possible sinks have been suggested but appear to be negligible (10). After release of the first chlorine atom by a solar photon, chemical reactions will probably remove the remaining chlorine and fluorine atoms from the  $\text{CF}_x\text{Cl}_{y-1}$  radical, temporarily forming phosgene-type molecules (5). Once free in the stratosphere, chlorine atoms can catalyze the recombination of  $\text{O}_3$  and atomic oxygen. The key reactions are (5–8)



Eventually, the chlorine released from  $\text{CF}_x\text{Cl}_y$  should reach the ground through downward diffusion and tropospheric rainout (6–8).

We have quantitatively estimated globally averaged rates of  $\text{O}_3$  destruction due to the chlorine atoms released in the initial photodissociation from man-made  $\text{CF}_x\text{Cl}_y$ . Figure 1 displays the altitude integral of these rates for three presumed time histories of  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  (11): model 1, exponentially increasing with a doubling time of 3.5 years, the current pattern; model 2, exponential increase from 1960 to 1975, then constant at the 1975 rate; and model 3, exponential increase from 1960 to 1975, then immediate cessation. Figure 1 also presents globally integrated  $\text{O}_3$  destruction rates due to the chemical reactions of oxygen alone (labeled "Chapman") and for the  $\text{NO}_x$  catalytic cycles. These two  $\text{O}_3$  sinks are currently believed to control stratospheric  $\text{O}_3$  concentrations (8, 12). Models 1 and 2 yield rapidly increasing  $\text{O}_3$  destruction rates that will equal the natural sinks by about 1982 and 1986, respectively. Model 3 shows that, if  $\text{CF}_x\text{Cl}_y$  emissions were curtailed now, the ensuing  $\text{O}_3$  destruction rates would maximize around 1990 at a rate comparable to major natural cycles and would persist for several decades. Even larger effects may be possible because in our calculations we consider only the first chlorine atom released from each  $\text{CF}_x\text{Cl}_y$  molecule; in reality, all four halogen atoms may be freed (13).

Important parameters in calculations leading to Fig. 1 appear in Table 1. To account for vertical transport in our time-dependent, one-dimensional (altitude) model we adopted and smoothed the relatively high eddy diffusion coefficient ( $K$ ) profile of Wofsy and McElroy (14). To compute photodissociation coefficients,  $J$ , for  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  we used available laboratory



photoabsorption data (15). We evaluated the O<sub>3</sub>-destroying effect of the chlorine oxides (ClO<sub>x</sub>) by using the photochemical reaction scheme of Stolarski and Cicerone (6) after adding the reactions ClO + NO → Cl + NO<sub>2</sub> and H<sub>2</sub> + Cl → HCl + H (16). In the calculations we assumed an atmospheric background of O, O<sub>3</sub>, CH<sub>4</sub>, OH, NO, and H<sub>2</sub> that was constant in time. A constant O<sub>3</sub> profile representing present conditions is probably not consistent with the large O<sub>3</sub>-destroying rates of ClO<sub>x</sub> of Fig. 1, but through its use we can compare the effect of the CF<sub>x</sub>Cl<sub>y</sub> to the present natural O<sub>3</sub> sinks. Other procedures and input data are discussed in (17).

The accumulation (mixing ratio) of CF<sub>x</sub>Cl<sub>y</sub> molecules is shown as a function of altitude and time in Fig. 2, predicted from emission history model 2. Corresponding profiles are also shown for ClX. Because the relevant photochemical processes are fast relative to the transport processes, one may calculate the amounts of Cl, ClO, and HCl present at each altitude from the ClX concentration and the equations of photochemical equilibrium (6–8). The time evolution of the ClX profiles show large increases above 20 km and virtually no change below 15 km. The precise ClX concentration predicted for a given altitude and time depends on several computational parameters, especially *K*, but the profile shapes clearly indicate the effects of a mid-stratospheric source (see the *Q*<sub>Cl</sub> values in Table 1), slow transport below 25 km, and eventual loss to the ground.

The 1985 chlorine production rate, *Q*<sub>Cl</sub> for 1985 in Table 1, is 5 × 10<sup>6</sup> cm<sup>-2</sup> sec<sup>-1</sup>, integrated over altitude. Under steady-state conditions this figure will grow to 2 × 10<sup>7</sup> cm<sup>-2</sup> sec<sup>-1</sup> if only one chlorine atom is taken from

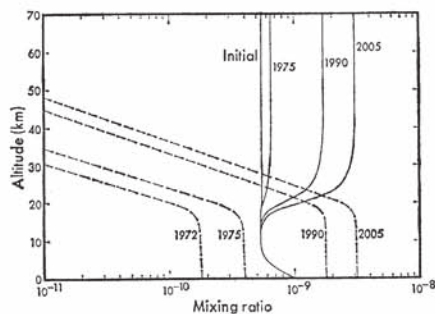


Fig. 2. Calculated fractional concentrations [mixing ratios (volume-volume)] of atmospheric CF<sub>x</sub>Cl<sub>y</sub> (dashed curves) and those for ClX (solid curves). In the calculations we employed emission history model 2 with a rapid temporal accumulation of CF<sub>x</sub>Cl<sub>y</sub>, resulting in a similar increase of stratospheric ClX. Ground-level CF<sub>x</sub>Cl<sub>y</sub> concentrations computed for the present are in good agreement with measured values (1–3). Also, the computed initial ClX profile is not inconsistent with available measurements (17).

each CF<sub>x</sub>Cl<sub>y</sub> and model 2 (constant) emissions are assumed. This man-made ClX source is comparable to the projected NO<sub>x</sub> input due to large supersonic transport (SST) fleets, and it appears that ClO<sub>x</sub> destroys O<sub>3</sub> more efficiently than NO<sub>x</sub> (6). McElroy *et al.* (12) find that O<sub>3</sub> depletion from SST NO<sub>x</sub> is sensitive to the injection altitude. The O<sub>3</sub> effect due to added ClX will be difficult to evaluate, but current models (6–8) indicate that ClX added above 25 km is much more important than that added below.

We have not attempted to predict O<sub>3</sub> concentrations or their changes due to increasing amounts of ClX from CF<sub>x</sub>Cl<sub>y</sub> usage. Predictions of O<sub>3</sub> concentrations and trends due to perturbations are still the subject of considerable debate (18). However, Fig. 1 indicates that, regardless of the precise magnitude of the effect of increasing destruction rates on O<sub>3</sub> content, chlorine atom produc-

tion from present or exponentially increasing CF<sub>x</sub>Cl<sub>y</sub> concentrations will eventually convert the O<sub>3</sub> layer from NO<sub>x</sub> to ClO<sub>x</sub> control. Uncertainties in the initial ClX profile, conversion rates to chlorine, or catalytic efficiency do not alter the basic conclusion, only the time of passage to ClO<sub>x</sub> control. Studies should be pursued with more complex interactive photochemical models to assess the impact of these large predicted increases in O<sub>3</sub> destruction on the O<sub>3</sub> content. In addition to continued careful monitoring of O<sub>3</sub>, other key stratospheric trace constituents must be measured. For example, the stratospheric concentrations of OH radicals and atomic oxygen, although central to questions of stratospheric chemistry, have not, to our knowledge, been measured. The present stratospheric abundance of gaseous chlorine, natural or otherwise, must also be determined.

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11. Worldwide rates of production of CF<sub>2</sub>Cl<sub>2</sub> and CFCl<sub>3</sub> are currently about 0.45 × 10<sup>6</sup> and 0.27 × 10<sup>6</sup> kg, respectively (R. L. McCarthy, personal communication). Between 1960 and the present, this production grew exponentially with a doubling time of 3.5 years; see also (2, 4).
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Table 1. Input data at several altitudes: *K*, the eddy diffusion coefficient; the NO concentration; *J*, the photodissociation coefficients for CFCl<sub>3</sub> and CF<sub>2</sub>Cl<sub>2</sub>, respectively; *Q*<sub>Cl</sub>, the predicted release rate of chlorine atoms assuming a model 2 emission time history. The *J* values were computed for a solar zenith angle of 60° and were divided by 2 to represent a diurnal average. Note: 1.5(4) means 1.5 × 10<sup>4</sup>.

Altitude (km)	<i>K</i> (cm <sup>2</sup> sec <sup>-1</sup> )	NO concentration (cm <sup>-3</sup> )	<i>J</i> <sub>CFCl<sub>3</sub></sub> (sec <sup>-1</sup> )	<i>J</i> <sub>CF<sub>2</sub>Cl<sub>2</sub></sub> (sec <sup>-1</sup> )	<i>Q</i> <sub>Cl</sub> (cm <sup>-3</sup> sec <sup>-1</sup> )	
					1980	1985
15	1.5(4)	1.9(8)	0	0	0	0
20	2.5(3)	5.0(8)	3.0(-10)	2.7(-11)	0.14	0.24
25	7.6(3)	7.2(8)	2.1(-8)	2.2(-9)	1.2	2.06
30	3.5(4)	8.0(8)	3.6(-7)	4.0(-8)	2.4	4.14
35	6.5(4)	5.8(8)	2.0(-6)	2.3(-7)	1.5	2.68
40	1.0(5)	5.4(8)	4.6(-6)	5.0(-7)	0.4	0.82
45	1.6(5)	4.7(8)	6.4(-6)	7.5(-7)	0.12	0.23
50	2.5(5)	3.3(8)	7.6(-6)	9.5(-7)	0.03	0.06



- by reactions in the atmosphere. Although the fluorine atoms released by similar reactions can also destroy  $O_3$  catalytically, the reaction  $CH_4 + F \rightarrow CH_3 + HF$  will terminate the fluorine chains more quickly than  $CH_4 + Cl \rightarrow CH_3 + HCl$  does for chlorine. Further, reinitiation of fluorine chains will not proceed via  $HF + OH \rightarrow F + H_2O$ , whereas  $HCl + OH \rightarrow Cl + H_2O$  does reinitiate the chlorine chains.
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  16. Both D. D. Davis and D. D. Garvin (personal communication) have suggested that  $ClO + NO \rightarrow Cl + NO_2$ , which couples  $ClO_x$  and  $NO_x$  cycles, is important for stratospheric chlorine chemistry. This reaction and  $H_2 + Cl + HCl + H$  were subsequently included in model studies by Wofsy and McElroy (7).
  17. We computed photolysis rates for  $CFCl_3$  and  $CF_2Cl_2$  versus altitude and time through an implicit numerical solution of the diffusion equation with 10-day time steps and altitude steps  $\Delta Z$  of 1 km. These loss rates for  $CF_2Cl_2$  then served as chlorine production rates,  $Q$ , in the photochemical, vertical transport model for CIX. Table 1 shows an example of  $Q$  along with selected input data. The OH profile was taken from (12); the reaction rate for  $HCl + OH \rightarrow Cl + H_2O$  was  $2 \times 10^{-12} \exp(-335/T)$  (where  $T$  is the absolute temperature) (J. G. Anderson, personal communication). The remainder of the photochemical scheme and input data were adopted from (6). For the CIX calculations the boundary conditions were: zero flux at the upper boundary (80 km), ground upward flux of  $2 \times 10^{10} \text{ cm}^{-2} \text{ sec}^{-1}$  [see (7)], and diffusion to the ground at a velocity of  $0.4 \text{ cm sec}^{-1}$ . These conditions yield ground-level concentrations of 1 part per billion (ppb), consistent with data from C. Junge [*Tellus* **9**, 528 (1957)], an initial stratospheric concentration of 0.55 ppb, below the 0.8 ppb estimated for HCl at 16 km by C. B. Farmer (paper presented at the 3rd Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts, 27 February 1974). A 10-day rainout period (0 to 5 km), tapering to 100 days at 10 km, was assumed for HCl. The initial CIX profile, though not critical for the present problem, implies a column-integrated  $O_3$  destruction rate of  $2 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ .
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  19. We thank M. J. Molina and F. S. Rowland for several helpful discussions and for making available to us their not yet published laboratory data; we also thank D. D. Davis for ideas and criticism. Support provided by NASA through grant NGR 23-005-616 and by the Climatic Impact Assessment Program, Department of Transportation, through NSF grant GA-43326.

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## Methane Production in the Interstitial Waters of Sulfate-Depleted Marine Sediments

**Abstract.** Methane in the interstitial waters of anoxic Long Island Sound sediments does not reach appreciable concentrations until about 90 percent of seawater sulfate is removed by sulfate-reducing bacteria. This is in agreement with laboratory studies of anoxic marine sediments sealed in jars, which indicate that methane production does not occur until dissolved sulfate is totally exhausted. Upward diffusion of methane or its production in sulfate-free microenvironments, or both, can explain the observed coexistence of measurable concentrations of methane and sulfate in the upper portions of anoxic sediments.

Amounts of methane in the marine environment in excess of that resulting from equilibration with the atmosphere most frequently occur in anoxic waters such as those found in fjords (1, 2) and in the interstitial water of anoxic sediments (3-6). In the absence of sources associated with shipping and industrial activity or natural seeps from oil and gas reservoirs (7), most of this methane results from anaerobic bacterial decomposition of organic matter. Methane bacteria are readily found in anoxic environments, where they are terminal organisms in the microbial food chain (8); moreover, there is some evidence that methane is not produced until dissolved sulfate has been previously removed by sulfate-reducing bacteria (5, 6).

The interstitial waters of Recent organic-rich marine sediments are ideal for studying the relation between methane and dissolved sulfate distributions

because of the large concentration changes over short depth intervals that result from high bacterial activity. In this report we present the results of a study of methane and dissolved sulfate in the interstitial waters of Long Island Sound sediments which suggest that significant production of methane does not begin until dissolved sulfate concentrations approach zero. Results of laboratory studies of time-dependent changes in the chemistry of anoxic marine sediments indicate that sulfate reduction and methane production are mutually exclusive metabolic processes.

Gravity cores were collected at three stations in Long Island Sound. Station TH is located approximately 2 km south of the coastal town of Guilford, Connecticut, at a water depth of approximately 7 m. Stations BS and SC are located in two shallow harbors near Guilford. The water depths at these two stations ranged from 1.5 to 4 m be-

cause of tidal fluctuations. Interstitial waters were sampled without coming into contact with air by transferring sediments from sealed core liners to a filter-press type squeezer through an interlock flushed with  $CO_2$  or He (9). Dissolved methane was measured by liquid stripping techniques developed for measuring dissolved gases in seawater by Swinnerton *et al.* (10) and applied to interstitial water measurements by Reeburgh (11). Dissolved sulfate was measured by gravimetric analysis as  $BaSO_4$ . Blank corrections for precipitation of nonsulfate material led to uncertainties of  $\pm 0.5 \text{ mmole liter}^{-1}$  in dissolved sulfate concentrations.

Concentrations of methane and dissolved sulfate in the interstitial waters are plotted as a function of depth in Fig. 1. Differences in the depth of complete sulfate reduction at the three stations are probably a result of variations in sedimentation rates and the content of organic matter in the sediments. The leveling off of methane concentrations at station SC at about  $1.0 \text{ mmole liter}^{-1}$  is consistent with reaching saturation with respect to methane. The solubility of methane calculated from the Setchénow relation by using solubility data from Winkler (12) and Atkinson and Richards (2) ranges from 1.1 to  $2.3 \text{ mmole liter}^{-1}$  ( $25$  to  $51 \text{ ml liter}^{-1}$ ) for the temperature range ( $4^\circ$  to  $28^\circ C$ ) and salinity range (27 to 31 per mil) encountered in these sediments.

Reeburgh (4) has presented evidence of methane saturation in Chesapeake Bay sediments, which results in the formation of trapped methane bubbles that strip other dissolved gases such as  $N_2$  and Ar from interstitial waters in the sediments. We infer from the low concentrations of dissolved  $N_2$  and Ar at station SC that this process may be taking place there (13).

The data in Fig. 1 show that in the interstitial waters of Long Island Sound sediments high methane concentrations do not occur unless sulfate concentrations have been appreciably lowered. Only where dissolved sulfate concentrations approach zero do concentrations of methane attain saturation.

Four alternative hypotheses can be used to explain these results. The first is that methane is produced at roughly the same rate throughout the sediment column by methane bacteria but is consumed by sulfate-reducing bacteria through the reaction

