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 (CF$_2$Cl$_2$), principally CF$_2$Cl$_2$ and CFC$_3$, 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 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 CF$_2$Cl$_2$ also represents a potential sink for stratospheric O$_3$. This is so because the photodissociation of CF$_2$Cl$_2$ releases chlorine atoms which can catalytically destroy O$_3$ through reactions like those of the nitrogen oxides (NO$_x$) with O$_3$ (5-8). Because of the great importance of stratospheric O$_3$ (9), we have reexamined this potential effect and its likely time evolution. We find that current CF$_2$Cl$_2$ usage levels and trends can lead to chlorine-catalyzed O$_3$ destruction rates exceeding all natural sinks of stratospheric 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 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, CF$_2$Cl$_2$ 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 appears to be the major sink for CF$_2$Cl$_2$ (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 CF$_2$Cl$_2$ radical, temporarily forming phosgene-type molecules (5). Once free in the stratosphere, chlorine atoms can catalyze the recombination of O$_3$ and atomic oxygen. The key reaction is

$$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$$

$$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$$

Eventually, the chlorine released from CF$_2$Cl$_2$ should reach the ground through downward diffusion and tropospheric rainout (6-8).

We have quantitatively estimated globally averaged rates of O$_3$ destruction due to the chlorine atoms released in the initial photodissociation from man-made CF$_2$Cl$_2$. Figure 1 displays the altitude integral of these rates for three presumed time histories of CF$_2$Cl$_2$ and CFC$_3$ (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 O$_3$ destruction rates due to the chemical reactions of oxygen alone (labeled “Chapman”) and for the NO$_x$ catalytic cycles. These two O$_3$ sinks are currently believed to control stratospheric O$_3$ concentrations (8, 12). Models 1 and 2 yield rapidly increasing O$_3$ destruction rates that will equal the natural sinks by about 1982 and 1986, respectively. Model 3 shows that, if CF$_2$Cl$_2$ emissions were curtailed now, the ensuing 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 CF$_2$Cl$_2$ 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 CF$_2$Cl$_2$ and CFC$_3$, we used available laboratory
photoabsorption data (15). We evaluated the O₃-destroying effect of the chlorine oxides (ClOₓ) by using the photochemical reaction scheme of Stolarski and Cicerone (6) after adding the reactions ClO + NO → Cl + NO₂ and H₂ + Cl → HCl + H (16). In the calculations we assumed an atmospheric background of O, O₃, CH₄, OH, NO, and H₂ that was constant in time. A constant O₃ profile representing present conditions is probably not consistent with the large O₃-destroying rates of ClOₓ of Fig. 1, but through its use we can compare the effect of the CFCl₃ to the present natural O₃ sinks. Other procedures and input data are discussed in (17).

The accumulation (mixing ratio) of CFCl₃ 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 CIX. 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 CIX concentration and the equations of photochemical equilibrium (6–8). The time evolution of the CIX profiles show large increases above 20 km and virtually no change below 15 km. The precise CIX 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 Ψ₁ values in Table 1), slow transport below 25 km, and eventual loss to the ground.

The 1985 chlorine production rate, Ψ₁ for 1985 in Table 1, is 5 × 10⁶ cm⁻² sec⁻¹, integrated over altitude. Under steady-state conditions this figure will grow to 2 × 10⁷ cm⁻² sec⁻¹ if only one chlorine atom is taken from each CFCl₃ and model 2 (constant) emissions are assumed. This man-made CIX source is comparable to the projected NO₃ input due to large supersonic transport (SST) fleets, and it appears that ClO₂ destroys O₃ more efficiently than NO₃ (6). McElroy et al. (12) find that O₃ depletion from SST NO₃ is sensitive to the injection altitude. The O₃ effect due to added CIX will be difficult to evaluate, but current models (6–8) indicate that CIX added above 25 km is much more important than that added below.

We have not attempted to predict O₃ concentrations or their changes due to increasing amounts of CIX from CFCl₃ usage. Predictions of O₃ 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 O₃ content, chlorine atom production from present or exponentially increasing CFCl₃ concentrations will eventually convert the O₃ layer from NO₃ to ClO₂ control. Uncertainties in the initial ClO₂ profile, conversion rates to chlorine or catalytic efficiency do not alter the basic conclusion, only the time of passage to ClO₂ control. Studies should be pursued with more complex interactive photochemical models to assess the impact of these large predicted increases in O₃ destruction on the O₃ content. In addition to continued careful monitoring of O₃, 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 CFC₁₁ and CFC₁₄ are currently about 0.45 × 10⁶ and 0.27 × 10⁶ 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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Methane Production in the Intertidal Waters of Sulfate-Depleted Marine Sediments

Abstract. Methane in the intertidal 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 intertidal 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 intertidal 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 intertidal 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 because of tidal fluctuations. Intertidal waters were sampled without coming into contact with air by transferring sediments from sealed core liners to a filter-press type squeezeer through an interlock flushed with CO₂ 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 intertidal water measurements by Reeburgh (11). Dissolved sulfate was measured by gravimetric analysis as BaSO₄. Blank corrections for precipitation of nonsulfate material led to uncertainties of ±0.5 mmole liter⁻¹ in dissolved sulfate concentrations.

Concentrations of methane and dissolved sulfate in the intertidal 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 mmole liter⁻¹ is consistent with reaching saturation with respect to methane. The solubility of methane calculated from the Setchenow relation by using solubility data from Winkler (12) and Atkinson and Richards (2) ranges from 1.1 to 2.3 mmole liter⁻¹ (25 to 51 ml liter⁻¹) for the temperature range (4° to 28°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 N₂ and Ar from intertidal waters in the sediments. We infer from the low concentrations of dissolved N₂ and Ar at station SC that this process may be taking place there (13).

The data in Fig. 1 show that in the intertidal 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

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\text{CH}_4 + \text{SO}_4^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + \text{CO}_2 + 2\text{H}_2\text{O}
\]