

# PREDICTION OF THE STATE OF THE OZONOSPHERE FOR DIFFERENT CFC EMISSION SCENARIOS BASED ON A 1-D PHOTOCHEMICAL MODEL

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*The problem of the destruction of the protective ozone layer by chlorofluorocarbons is studied. Alternative strategies for the industrial use of different freons are discussed. A number of scenarios of emission of chlorofluorocarbons into the atmosphere for the period up to the year 2050, which correspond to the strategies, is presented. Numerical experiments on the prediction of the changes in the total ozone content, the vertical distribution of ozone, and the accumulation of active chlorine in the atmosphere up to the year 2050 were performed based on a one-dimensional photochemical model of the atmosphere using the indicated scenarios. It is concluded that the industrial use of the any chlorine-containing freons is potentially dangerous from the standpoint of the effect on the ozonosphere.*

## INTRODUCTION

The emission of fluorochlorocarbons (CFCs) into the atmosphere is now thought to be potentially the most dangerous form of disturbance of the ozonosphere. The effects associated with the action of CFCs on atmospheric ozone are now being intensively studied in different countries using 1-D and 2-D photochemical models of the atmosphere (PCM).

There is no doubt that the existing qualitative and quantitative discrepancies in the model predictions of the future state of the ozonosphere also dictate different strategies for limiting the industrial use of CFCs. But there is now agreement regarding a number of the most important aspects of the problem.

Thus, for example, virtually all predictions based on PCMs showed that F-11 ( $\text{CCl}_3\text{F}$ ) and F-12 ( $\text{CCl}_2\text{F}_2$ ) play the dominant role in the destruction of the ozone layer. This is now used as a basis for prohibiting the industrial use of these chemicals to the end of

this century, as envisaged in the Montreal protocol. The question of the usefulness of alternative strategies, presupposing increased industrial use of F-22 ( $\text{CHF}_2\text{Cl}$ ),  $\text{CCl}_4$  or  $\text{CH}_3\text{CCl}_3$  as alternatives to the band F-11 and F-12, has not been studied as well. This paper is devoted to the analysis of this problem.

The numerical experiments were performed based on the 1-D PCM for altitudes in the range 0–60 km with an altitude step of 1 km in the troposphere and 2 km in the stratosphere.<sup>1</sup> The photochemical model is combined with a radiation block, where the photolysis rate constants are calculated based on an optimized  $\delta$ -Eddington scheme. The use of the  $\delta$ -Eddington scheme makes it possible to calculate correctly the diffuse component of the radiation field, which is of fundamental importance for modeling tropospheric photochemistry, while optimization of the computational procedure makes it possible to achieve a computational speed equivalent to the well-known simplified method of Ref. 2.

TABLE I.

*Preliminary scenario-surface boundary conditions ( $z = 0$ )*

Year	Concentrations of elements, ppb						
	$\text{N}_2\text{O}$	$\text{CH}_4$	F-11	F-12	F-22	$\text{CCl}_4$	$\text{CH}_3\text{CCl}_3$
1960	289	1255	0.011	0.033	0.001	0.075	0.005
1965	292	1316	0.027	0.064	0.004	0.080	0.030
1970	295	1375	0.060	0.121	0.010	0.085	0.055
1975	298	1450	0.116	0.207	0.027	0.090	0.080
1980	302	1525	0.173	0.297	0.054	0.095	0.105
1985	306	1600	0.220	0.375	0.080	0.100	0.130

### SCENARIOS EMPLOYED. PCM INITIALIZATION

It is obvious that the initial conditions determine the time scales of the reaction of the model to the emission of CFCs from the bottom boundary.

In order to have a common starting point, beginning in 1985, UNEP (89) recommended an initializing calculation for the 20 year period up to 1985.

The idea of the recommendations consists of bringing all the PCMs into a quasistationary regime, corresponding with respect to the vertical distributions of the most important gaseous components, to the real concentration level in 1985.

After the preliminary scenario (Table I) we employed in our computational experiments, starting with 1985, the surface boundary condition in the form of emissions. The data for F-11, F-12, and F-22 corresponded to the UNEP (89) scenario, while the data for CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> corresponded to Ref. 3 (see Table II).

The contribution of F-113, F-114, F-115, H-1211, and H-1301 was assumed to be negligibly small compared with F-11 and F-12 in accordance with earlier estimates.

### SCENARIO OF GROWTH AFTER 1985

In all scenarios the CH<sub>4</sub> concentration at the ground increased by 1% per year while the N<sub>2</sub>O concentration increased by 0.25% per year.

Scenario I. The emission of all CFCs in the period from 1985 to 2000 are constant and correspond to Table II: after 2000 the emission are zero.

Scenario II. Emissions of all CFCs from 1985 to 2000 are constant and correspond to Table II: after the year 2000 all emissions are halved.

Scenario III. All CFCs, including CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> are completely replaced with F-22, whose emission is equivalent - 1 metric megaton/yr., and is constant in magnitude throughout the entire period of the calculation. The calculations continue until the quasistationary state is established (50 model years).

TABLE II.

Element	Emission metric kilotons/yr	References
F-11	350	UNEP(89)
F-12	450	»
F-22	140	»
CCl <sub>4</sub>	66	[3]
CH <sub>3</sub> CCl <sub>3</sub>	474	[3]

Scenario Ia. Growth of emission of CCl<sub>4</sub> from the 1985 level (Table II) by 5% per year up to 200 and 10% per year there after, is added to the scenario I.

Scenario Ib. Analogous to Ia with CCl<sub>4</sub> replaced by CH<sub>3</sub>CCl<sub>3</sub>.

Scenario Ic. Analogous to Ia with CCl<sub>4</sub> replaced by F-22.

Scenario I<sub>b</sub><sup>1</sup>. Analogous to Ib with the OH atmospheric content reduced by 30%.

Scenario I<sub>b</sub><sup>2</sup>. Analogous to Ib with the OH atmospheric content reduced by 60%.

Scenario III<sup>1</sup>. Analogous to III with the OH atmospheric content reduced by 30%.

Scenario III<sup>2</sup>. Analogous to III with the OH atmospheric content reduced by 60%.

The choice of scenarios corresponded to the following physical concepts:

since the lifetime of CFCs in the atmosphere is long (from 10 to 100 years) the scenario I permits estimating the relaxation time of the system to the background state and the character of this relaxation after emissions stop.

Scenario II simulates the strategy with 2 time higher emissions of all CFCs up to the year 2000.

Scenario III corresponds to the starting assumptions of Ref. 3 for estimating the possible effect on the ozonosphere in the case when all CFCs are replaced by F-22.

The scenario Ia, b, and c examine the alternative replacement of all CFCs by CCl<sub>4</sub>, CH<sub>3</sub>CCl<sub>4</sub> and F-22 separately with the same growth of emissions.

The scenarios I<sub>b</sub><sup>1</sup>, I<sub>b</sub><sup>2</sup>, III<sup>1</sup>, and III<sup>2</sup> take into account the fact that together with photolysis in the stratosphere for CH<sub>3</sub>CCl<sub>3</sub> and F-22 there exists a significant tropospheric sink in reactions with the hydroxyl radical (OH).

### DISCUSSION

Figure 1 shows the changes in the total ozone content based on the results of the numerical experiments performed compared with the data of 2-D<sup>3</sup> and 1-D<sup>4</sup> modeling, obtained by other authors. The curve 1 (scenario I), which agrees well with the calculations based on the OSLO 2-D model<sup>3</sup> under the assumption that the complete system of measures for limiting emissions, as envisaged by the Montreal protocol, is implemented, shows that the time scale of the relaxation of the ozonosphere to the background state after all perturbations cease is equal to several decades and by the year 2040 the deficit of the total ozone can be kept to 3-4%. All other curves in this figure (I<sub>a,b,c</sub>, I<sub>b</sub>, 1, 2, and 3), corresponding to various alternatives for using CFCs, exhibit only an insignificant quantitative discrepancy; this underscores the most important conclusion - the total ozone content can drop by 8-10% without the introduction of stringent measures to limit the emission of chlorine-containing CFCs.

Figure 2 contains information about the accumulation of active chlorine (Cl<sub>y</sub>) in the stratosphere in different scenarios. According to our numerical experiments the strongest accumulation of Cl<sub>y</sub> in the stratosphere is observed in the scenario I<sub>b</sub><sup>2</sup>; this underscores the need for studying in greater detail the OH concentrations in the stratosphere.

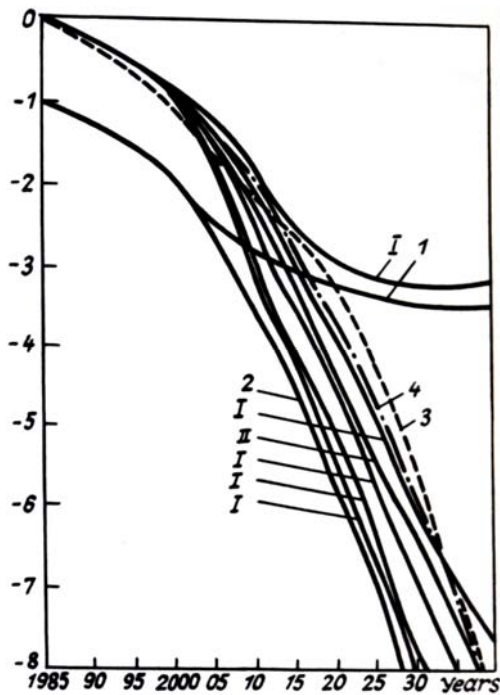


FIG. 1. The decrease in the total ozone content (as a percent of the 1985 level) for scenarios of CFCs emission. 1) results of 2-D calculations<sup>3</sup> with complete cessation of emission of CFCs by 1990; 2) results of 2-D calculations<sup>3</sup> with existing rates of growth of use of CFCs; 3) results of 1-D calculations (high scenario);<sup>4</sup> 4) results of calculations based on the scenario Ia with CCL<sub>4</sub> emission increasing by 2% per year. The remaining curves are numbered in accordance with the scenarios of CFCs emissions (see text).

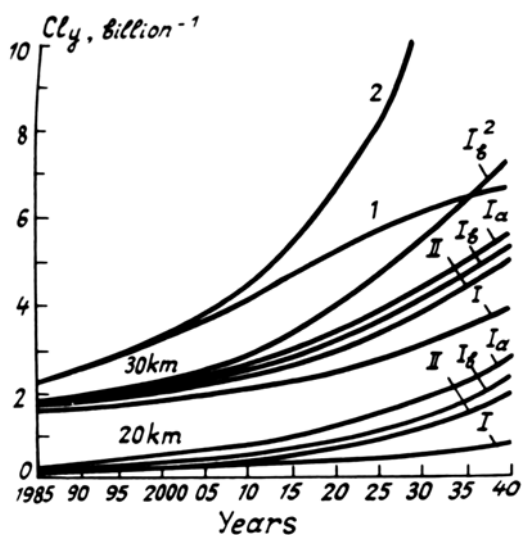


FIG. 2. The accumulation of active chlorine in the stratosphere based on results of numerical experiments. 1) 2-D results for the variant "no control"; 2) same with restrictive measures introduced in accordance with the Montreal protocol.

The very high content of chlorine in the stratosphere in the OSLO 2-D model for the "no control" variant is interesting.

Summarizing the results, including those presented in Fig. 1 and 2, we can draw the following conclusions.

1) Since the main sources and sinks of Cl<sub>y</sub> (CFCs emission and washing out of HCl by precipitation) are located in the troposphere, the regime of accumulation of active chlorine at stratospheric altitudes and therefore the depletion of the ozone layer will be determined by the effective flux of chlorine-containing components through the tropopause.

2) Currently the CFCs accumulated in the stratosphere will be sufficient for continued growth of the background level of the Cl<sub>4</sub> content at the altitudes of the ozonosphere for several decades even after emissions of freons stop completely (curve I in Fig. 2).

3) Since the destruction of ozone occurs in catalytic cycles without consumption of molecules of active chloring and the present background level of the Cl<sub>y</sub> content in the stratosphere can be characterized as being "precritical" at moderate latitudes and "critical" at polar latitudes, any alternatives connected with chlorine-containing substitutes are very dangerous.

Figure 3 demonstrates the loss of ozone at altitudes in the range 0-60 km in the quasistationary regime with a constant flux of F-22 from the surface of 1 metric megaton/yr (see the scenarios III, III<sup>1</sup>, and III<sup>2</sup>). The curve III<sup>F</sup> corresponds to the results obtained earlier by P. Fabian et al.<sup>5</sup> on the basis of a 1-D PCM with analogous initial data.

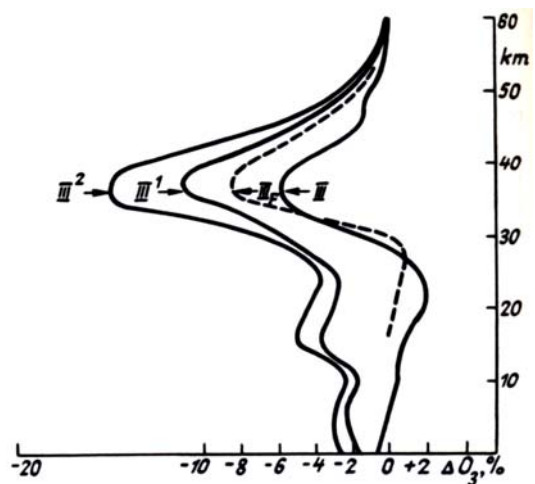


FIG. 3. The change in the ozone content at altitudes from 0 to 60 km with all CFCs replaced by F-22. The curve III<sup>F</sup> shows the results of the 1-D modeling.<sup>5</sup> The rest of the notation corresponds to the scenarios (see text).

We note the close qualitative and quantitative agreement between the results of Ref. 5 and our calculations (III and III<sup>F</sup>). The curves III<sup>1</sup> and III<sup>2</sup> correspond to 30 and 60% reduction of OH content. We stress that in these cases the effect with the

maximum in the layer 34–38 km is significantly amplified (the ozone deficit reaches 16%). This fact once again points to the fundamental role of tropospheric OH in the predictions made. At the present time the background level of OH in the troposphere falls in the range  $10^5$ – $10^6$  moles/cm<sup>3</sup> with clear variations (up to orders of magnitude) in time periods ranging from several minutes up to an entire season. The mechanisms by which the OH concentrations in the troposphere decrease can be related with the following: a) screening of UV radiation by clouds; b) washing out of H<sub>2</sub>O<sub>2</sub> – an important reservoir of OH – in clouds and precipitation; and, c) heterogeneous annihilation of OH and HO<sub>2</sub> on the surface of tropospheric aerosol.

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