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The action of chlorine on the ozone layer as given by a zonally averaged two-dimensional model

by

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FOREWORD

The paper entitled "The Action of chlorine on the ozone layer as given by a zonally averaged two-dimensional model" has been presented at the IAGA / IAMAP meeting held in Seattle, Washington (August 1977) and has been submitted to PAGEOPH.

AVANT-PROPOS

Le texte intitulé "The Action of chlorine on the ozone layer as given by a zonally averaged two-dimensional model" résume une communication présentée à la réunion IAGA/IAMAP à Seattle, Washington en août 1977. Il a été soumis pour publication à la revue PAGEOPH.

VOORWOORD

De tekst, "The Action of chlorine on the ozone layer as given by a zonally averaged two-dimensional model" die voorgedragen werd tijdens de IAGA/IAMAP vergadering te Seattle, Washington (augustus 1977) is ter publikatie naar het tijdschrift PAGEOPH gezonden.

VORWORT

Dieser Text "The action of chlorine on the ozone layer as given by a zonally averaged two-dimensional model" resümiert ein Vortrag der zur IAGA/IAMAP Versammlung in Seattle, Washington, im August 1977 vorgetragen wurden. Dieses Artikel wird in der Zeitschrift PAGEOPH veröffendlicht.

THE ACTION OF CHLORINE ON THE OZONE LAYER AS GIVEN BY A ZONALLY AVERAGED TWO-DIMENSIONAL MODEL

by

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Abstract

In order to study the behavior of stratospheric minor constituents related to aeronomic processes and atmospheric transport in the meridional plane, a numerical two-dimensional model is established.

This model is applied to the study of chlorine compounds in the stratosphere. A special attention is devoted to the effect in the ozonosphere of an increase of ClX due to anthropogenic activities.

Résumé

Un modèle bidimensionnel de la stratosphère a été établi en vue d'étudier le comportement des constituants minoritaires dans cette région de l'atmosphère en relation avec les mécanismes aéronomiques et les phénomènes de transport.

Ce modèle est appliqué à l'étude particulière des composés chlorés de la stratosphère. L'action sur l'ozonosphère du chlore produit industriellement fait l'objet d'une attention spéciale.

Samenvatting

Met behulp van een tweedimensionaal numeriek model wordt het gedrag van de stratosferische minderheidsbestanddelen bestudeerd in verband met de aeronomische processen en het atmosferisch transport.

Dit model wordt toegepast op de studie van de chloor bestanddelen in de stratosfeer. In het bijzonder wordt de invloed van chloor te wijten aan de industriën, op de ozonosfeer onderzocht.

Zusammenfassung

Ein numerisches bi-dimensionales Modell für die minderwährtigen stratosphärische Konstituante die von aeronomische Reaktionnen und atmosphärischen Transport in der meridionalen Ebene abhängisch sind, is beschrieben worden.

Dieses Modell ist für die Chlorine Komponente in der Stratosphäre aufgelegt worden. Ein spezielle Aufmerksamkeit ist auf das Effekt des Cl_x in der Ozonosphäre gegeben.

1. INTRODUCTION

The stability of the atmospheric ozone layer has become an important problem since it has been recognized that the O_3 molecule could be destroyed by different stratospheric trace species [5], [11], [42]. In particular, it has been emphasized that the injection into the stratosphere of gases which are of anthrogenic origin, essentially nitrogen oxides [23] and halogen compounds [37], could lead to an ozone depletion and subsequently to an increase of the anaerobic UV radiation at ground level.

In order to study the potential effects of natural and artificial trace species on the ozonosphere, numerical models have been established extensively. Aeronomical models take into account the most important chemical and photochemical reactions and simulate the transport mechanisms using a very crude representation of the motions. The input data needed by these models are the chemical reaction rates and the absorption cross sections spectra, both obtained from laboratory investigations. Furthermore, the solar intensity spectrum in the UV range, the distribution of the mean temperature and the averaged transport parameters, which are supplied by observational studies, have to be specified. Finally a special attention has to be given to the boundary conditions. Output of these models are, besides the concentration profile of the minor constituents which are taken into account, several parameters, such as the production and destruction rates, the particle flux and its divergence. It should be remembered that the results provided by mathematical models are always related to the input conditions and should be interpreted as such.

The purpose of this paper is to present very concisely some results obtained by the steady state version of our model which has already been described in detail elsewhere [8], [9]. This work deals mainly with the action of chlorine compounds and its relations with ozone. However, the model also takes into account the influence of hydrogen and nitrogen species. With respect to our previous work, the chemical reaction rates and the solar flux spectrum have been updated according to the most recent and most reliable laboratory determination and observation.

2. SHORT DESCRIPTION OF THE MODEL

The version of our 2-D model described hereafter considers steady state conditions. In this case, the continuity equation of the ith constituent is written

$$\vec{\nabla}.\vec{\phi_i} = P_i - L_i \tag{1}$$

if $\vec{\phi_i}$ is the particle flux, P_i and L_i respectively the production and the destruction rate. In order to relate the flux to the volume mixing ratio $f_i = n_i/n(M)$, where n_i is the concentration of the ith constituent and n(M) the atmospheric concentration, a transport representation has to be specified. Since the detail of the atmospheric dynamics is not considered in this work, a simple parametrization of the large scale motions is adopted. According to the K theory, one writes the horizontal (y) and vertical (z) components of the flux as follows :

$$\phi_i^y = -n(M) \left[K_{yy} \frac{\partial f_i}{\partial y} + K_{yz} \frac{\partial f_i}{\partial z} \right] \tag{2.a}$$

$$\phi_i^z = -n(M) \left[K_{zy} \frac{\partial f_i}{\partial y} + K_{zz} \frac{\partial f_i}{\partial z} \right] \tag{2.b}$$

where K_{yy}, K_{yz}, K_{zy} and K_{zz} are the components of the tensor $\bar{\bar{K}}$ which is assumed to be symmetrical ($K_{yz} = K_{zy}$). These parameters have to be considered as purely phenomenological. Different authors [35], [18], [27], have derived stratospheric and tropospheric values of these coefficients. However, since the determination of the K's is not unique, there is no general agreement about the values that should be adopted. Therefore, it is necessary to scale the coefficients so that the meridional distribution of species, which are sensitive to the transport, is close to the mean observation. In order to oversimplify the conditions, we have adopted a constant value of $K_{yy} = 10^{10}$ cm^2 s^{-1} and $K_{zz} = 10^4$ cm^2 s^{-1} at all latitudes. K_{yz} has been adjusted in order to fit the observation of ozone in the meridional plane [26]. Fig. 1 represents the latitudinal variation of K_{yz} resulting from the calibration.

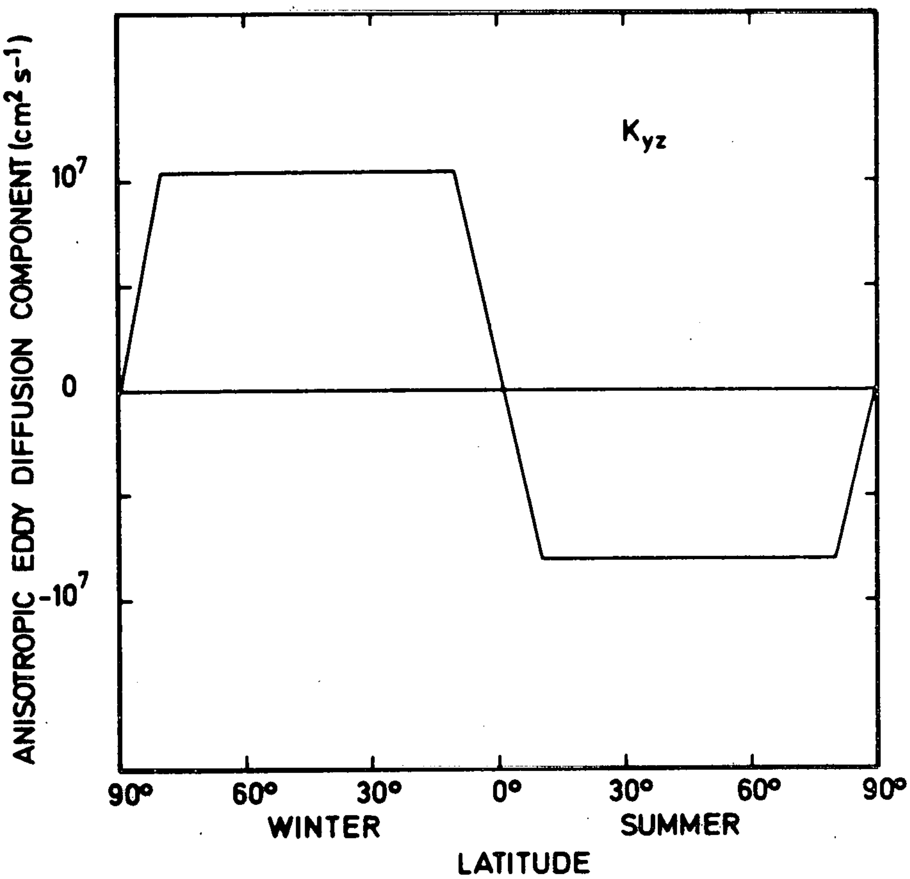

Fig. 1.- Latitudinal profile of K_{yz} adopted below 25 km. Above this altitude, the values have been multiplied by the factor exp(- 0.184 (z - 25)) where z is the altitude expressed in km.

The chemical and photochemical scheme adopted in the model results from the analysis of the aeronomical processes as made by Nicolet [29], [30], [31], [32]. Since a special attention is devoted to the chlorine chemistry, figure 2 represents a schematic graph indicating the most important reactions paths related to these compounds. It can be seen that odd chlorine (Cl, ClO, HCl and $ClONO_2$) is produced by dissociation of various halocarbons (CH_3Cl, $CFCl_3$, CF_2Cl_2, CCl_4...) which are injected at ground level either by natural or by industrial processes, and disappears by wash-out mechanisms in the tropospheric clouds. Table 1 gives the complete list of the aeronomical reactions which are considered and the corresponding rate constants. The distribution of the mean temperature adopted in this work is the same as the one used by Brasseur [8]. References concerning the adopted absorption cross sections of these molecules are also given in table 1. However, the attenuation of the UV flux due to molecular oxygen absorption in the Schumann-Runge bands is performed according to a numerical procedure established by Kockarts [25]. The spectrum of the solar radiation at the top of the atmosphere is taken from Simon [40].

Finally, it should be added that a constant mixing ratio of 5×10^{-7} is assumed for H_2, the corresponding value for CO being 5×10^{-8} in the stratosphere and 10^{-7} in the troposphere. In the case of H_2O, it is assumed at all latitudes that the volume mixing ratio decreases from 10^{-2} at ground level to 3×10^{-6} at 15 km and increases slightly to reach 5×10^{-6} at the stratopause. A working value of 1×10^{-12} is attributed to CH_3O_2.

The model ranges from the North Pole to the South Pole and from the ground to the stratopause level. It attempts to represent for mean solar illumination conditions the distribution of minor constituents in the steady state. The seasonal conditions are chosen in such manner that the winter hemisphere corresponds to the Northern hemisphere. In order to treat the problem numerically, the derivatives are approximated by finite-differences. The distance between the gridpoints in the meridional plane has been fixed to 1 km vertically and 5 degrees latitude horizontally. An alternating direction method is applied to compute the solutions. However, in order to avoid divergent oscillations due to the stiffness of the equations system and related to the large differences between the lifetime of the various constituents, some of the chemical species are grouped so that isolated or quasi isolated

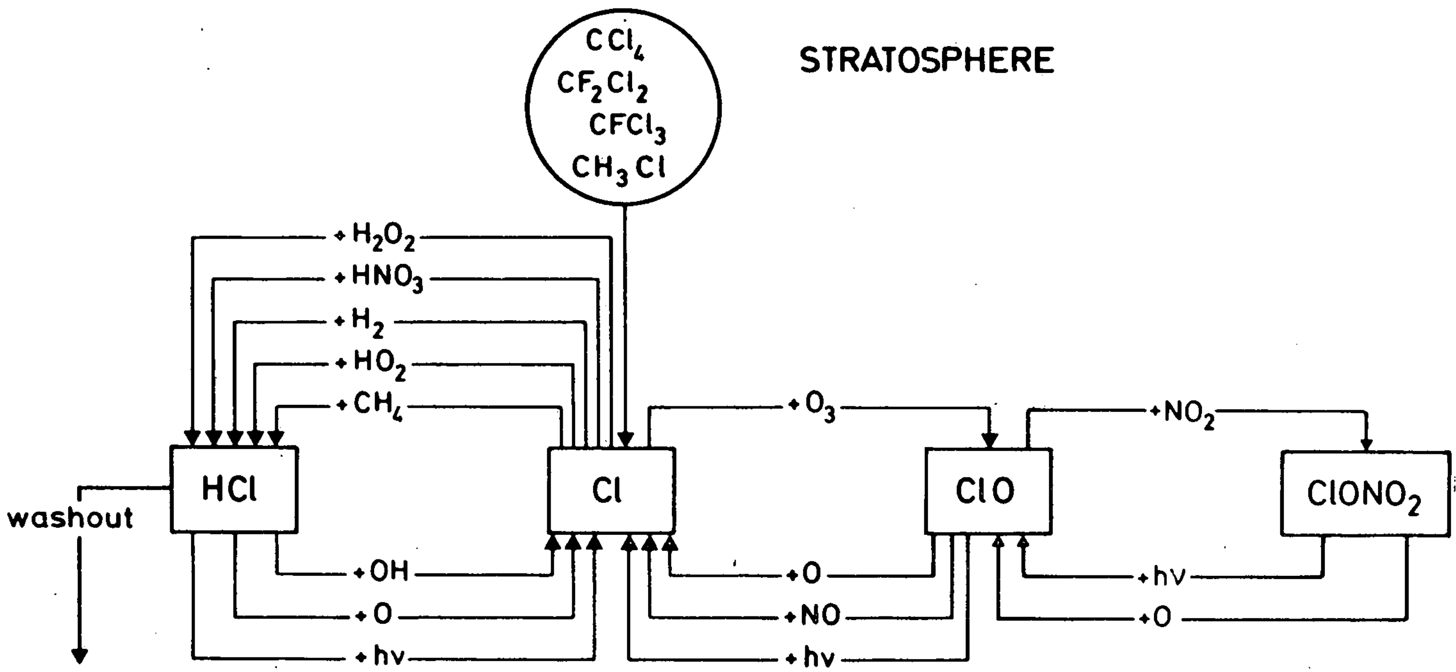

Fig. 2.- Schematic graph of the most important chlorine reactions in the stratosphere.

TABLE 1 : The reactions and their rates used in this work.

Reaction	Rate constant ($cm^3 s^{-1}$)	Reference
$O(^3P) + O_2 + M \rightarrow O_3 + M$	$k_2 = 1.1 \times 10^{-34} e^{510/T} n(M)$	Huie *et al.* [21]
$O(^3P) + O_3 \rightarrow 2O_2$	$k_3 = 1.05 \times 10^{-11} e^{-2150/T}$	Davis *et al.* [12)
$O(^1D) + M \rightarrow O(^3P) + M$	$k_q = 5 \times 10^{-11}$	Nicolet [29]
$H + O_2 + M \rightarrow HO_2 + M$	$a_1 = 2.1 \times 10^{-32} e^{290/T} n(M)$	Wong and Davis [45]
$H + O_3 \rightarrow OH + O_2$	$a_2 = 2.6 \times 10^{-11}$	Phillips and Schiff [34]
$OH + O \rightarrow H + O_2$	$a_5 = 4 \times 10^{-11}$	Nicolet [32]
$OH + O_3 \rightarrow HO_2 + O_2$	$a_6 = 1.6 \times 10^{-12} e^{-1000/T}$	Anderson and Kaufman [3]
$HO_2 + O_3 \rightarrow OH + 2O_2$	$a_{6b} = 1.0 \times 10^{-13} e^{-1250/T}$	Nicolet [32]
$HO_2 + O \rightarrow OH + O_2$	$a_7 = a_5$	Working value
$OH + OH \rightarrow H_2O + O$	$a_{16} = 2 \times 10^{-12}$	Westenberg and de Haas [44] Clyne and Down [10]
$OH + HO_2 \rightarrow H_2O + O_2$	$a_{17} = 3 \times 10^{-11}$	Hudson [20]
$HO_2 + NO \rightarrow NO_2 + OH$	$a_{26} = 8 \times 10^{-12}$	Howard and Evenson [19]
$OH + CO \rightarrow CO_2 + H$	$a_{36} = 1.25 \times 10^{-13}$	Greiner [17] Davis *et al.* [13]
$NO_2 + O(^3P) \rightarrow NO + O_2$	$b_3 = 9.2 \times 10^{-12}$	Davis *et al.* [14]
$NO + O_3 \rightarrow NO_2 + O_2$	$b_4 = 2.1 \times 10^{-12} e^{-1450/T}$	Hudson [20]
$NO_2 + O_3 \rightarrow NO_3 + O_2$	$b_9 = 1.3 \times 10^{-13} e^{-2450/T}$	Nicolet [32]

TABLE 1 : The reactions and their rates used in this work (cont. 1)

Reaction	Rate constant ($cm^3\ s^{-1}$)	Reference
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$b_{12} = 2.8 \times 10^{-30}\ n(M)$	Baulch *et al.* [6]
	$b_{12\infty} = 3.8 \times 10^{-12}$	Limiting value
$NO_2 + OH + M \rightarrow HNO_3 + M$	$b_{22} = 2 \times 10^{-30}\ n(M)$	Anderson and Kaufman [2]
	$b_{22\infty} = 5 \times 10^{-12}$	Limiting value
$HNO_3 + OH \rightarrow NO_3 + H_2O$	$b_{27} = 9 \times 10^{-14}$	Smith and Zellner [41]
$N_2O_5 + M \rightarrow NO_2 + NO_3$	$b_{32} = 2.2 \times 10^{-5}\ e^{-9700/T}$	Baulch *et al.* [6]
		Niki [33]
$N_2O + O(^1D) \rightarrow N_2 + O_2$	$b_{38} = 6 \times 10^{-11}$	Schiff [39]
$N_2O + O(^1D) \rightarrow 2NO$	$b_{39} = 9 \times 10^{-11}$	Schiff [39]
$H_2O + O(^1D) \rightarrow OH + OH$	$a^*_{1a} = 2.1 \times 10^{-10}$	Schiff [39]
$H_2 + O(^1D) \rightarrow OH + H$	$a^*_{1b} = 1.3 \times 10^{-10}$	Schiff [39]
$CH_4 + O(^1D) \rightarrow CH_3 + OH$	$a^*_{1c} = 1.3 \times 10^{-10}$	Schiff [39]
$CH_4 + OH \rightarrow CH_3 + H_2O$	$c_2 = 3.5 \times 10^{-12}\ e^{-1800/T}$	Greiner [17]
		Davis *et al.* [13]
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	$c_5 = 5 \times 10^{-13}$	Working value
$CH_3Cl + OH \rightarrow CH_2Cl + H_2O$	$d_1 = 2.2 \times 10^{-12}\ e^{-1141/T}$	Watson [43]
$Cl + O_3 \rightarrow ClO + O_2$	$d_2 = 2.7 \times 10^{-11}\ e^{-257/T}$	Watson [43]
$ClO + O \rightarrow Cl + O_2$	$d_3 = 7.7 \times 10^{-11}\ e^{-130/T}$	Watson [43]

TABLE 1 : The reactions and their rates used in this work. (cont. 2)

Reaction	Rate constant ($cm^3\ s^{-1}$)	Reference
$ClO + NO \rightarrow Cl + NO_2$	$d_4 = 1.0 \times 10^{-11}\ e^{200/T}$	Hudson [20]
$Cl + CH_4 \rightarrow CH_3 + HCl$	$d_5 = 7.3 \times 10^{-12}\ e^{-1260/T}$	Watson [43]
$Cl + HO_2 \rightarrow O_2 + HCl$	$d_7 = 3 \times 10^{-11}$	Watson [43]
$HCl + OH \rightarrow Cl + H_2O$	$d_{11} = 3 \times 10^{-12}\ e^{-425/T}$	Watson [43]
$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$d_{22} = \dfrac{3.3 \times 10^{-23}\ T^{-3.34}\ n(M)}{1 + 8.7 \times 10^{-9}\ T^{-0.6}\ [n(M)]^{0.5}}$	Hudson [20]
$ClONO_2 + O \rightarrow$ products	$d_{32} = 3.0 \times 10^{-12}\ e^{-808/T}$	Watson [43]

Reaction	Photodissociation frequency (s^{-1})	Reference of absorption cross section
$O_2 + h\nu \rightarrow O + O$	J_{O_2} ($\lambda < 242.4$ nm)	Ackerman [1]
$O_3 + h\nu \rightarrow O(^3P) + O_2$	J_{O_3} ($\lambda > 310$ nm)	Ackerman [1]
$O_3 + h\nu \rightarrow O(^1D) + O_2$	$J^{*}_{O_3}$ ($\lambda < 310$ nm)	Ackerman [1]
$NO_2 + h\nu \rightarrow NO + O$	J_{NO_2} ($\lambda < 405$ nm)	Bass and Laufer [4]
$HNO_3 + h\nu \rightarrow NO_2 + OH$	J_{HNO_3} ($\lambda \leq 320$ nm)	Biaumé [7]
$N_2O + h\nu \rightarrow N_2 + O$	J_{N_2O} ($\lambda < 7420$ nm)	Johnston and Selwyn [24]
$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	$J_{N_2O_5}$ ($\lambda < 380$ nm)	Graham [15]

TABLE 1 : The reactions and their rates used in this work (cont. 3)

Reaction	Photodissociation frequency (s^{-1})	Reference of absorption cross sections
$CH_3Cl + h\nu \rightarrow CH_3 + Cl$	J_{CH_3Cl}	Robbins [36]
$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$	J_{CFCl_3} ($\lambda < 226$ nm)	Rowland and Molina [37]
$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$	$J_{CF_2Cl_2}$ ($\lambda < 215$ nm)	Rowland and Molina [37]
$CCl_4 + h\nu \rightarrow CCl_3 + Cl$	J_{CCl_4}	Rowland and Molina [37]
$HCl + h\nu \rightarrow H + Cl$	J_{HCl} ($\lambda < 220$ nm)	Inn [22]
$ClONO_2 + h\nu \rightarrow ClO + NO_2$	J_{ClONO_2}	Rowland *et al.* [38]

systems of constituents are formed. This method is used to determine the global behavior of $O_x = O_3 + O(^3P) + O(^1D)$, $HO_x = OH + HO_2$, $NO_y = NO + NO_2 + HNO_3 + ClONO_2$ and $ClX = Cl + ClO + HCl + ClONO_2$. The concentration of the individual constituents is derived by assuming equilibrium conditions between the various species belonging to a specified family. Other constituents, namely CH_4, N_2O, CH_3Cl, $CFCl_3$, CF_2Cl_2 and CCl_4, whose lifetime is rather long, are treated individually.

In order to specify the boundary conditions, one assumes no horizontal flux of any trace species at the North and the South Pole, so that the symmetry around the terrestrial axis is respected. At the ground and stratopause levels, a mixing ratio is specified as indicated in table 2. The lower condition related to the chlorofluoromethanes is representative of a 1977 situation. Most of the conditions on the upper boundary are based on the results provided by 1-D models which extend to higher altitudes.

3. RESULTS AND DISCUSSION

3.1. Chlorine in the atmosphere of 1977

The formation of odd chlorine in the stratosphere is related to the destruction of different chlorinated molecules which are released at ground level. The most important contribution [32] is due on the one hand to methylchlorides (CH_3Cl), whose origin is almost completely natural, and on the other hand to carbon tetrachloride (CCl_4), to trichlorofluoromethane ($CFCl_3$) and to dichlorofluoromethane (CF_2Cl_2) which are industrially produced. All these constituents whose mixing ratio is of the order of 10^{-10} to 10^{-9} in the troposphere [28] are injected into the stratosphere where they are photodissociated by UV radiation. Moreover, CH_3Cl reacts rather rapidly with hydroxyl radicals and is therefore partly destroyed in the troposphere. Figure 3 shows the vertical distribution of these species as given by our 2-D model at 30°N latitude (winter conditions). It appears that the mixing ratio of those constituents decreases rapidly in the stratosphere so that, for example, CCl_4 and $CFCl_3$ have almost completly disappeared above the altitude of 35 km. Figure 4

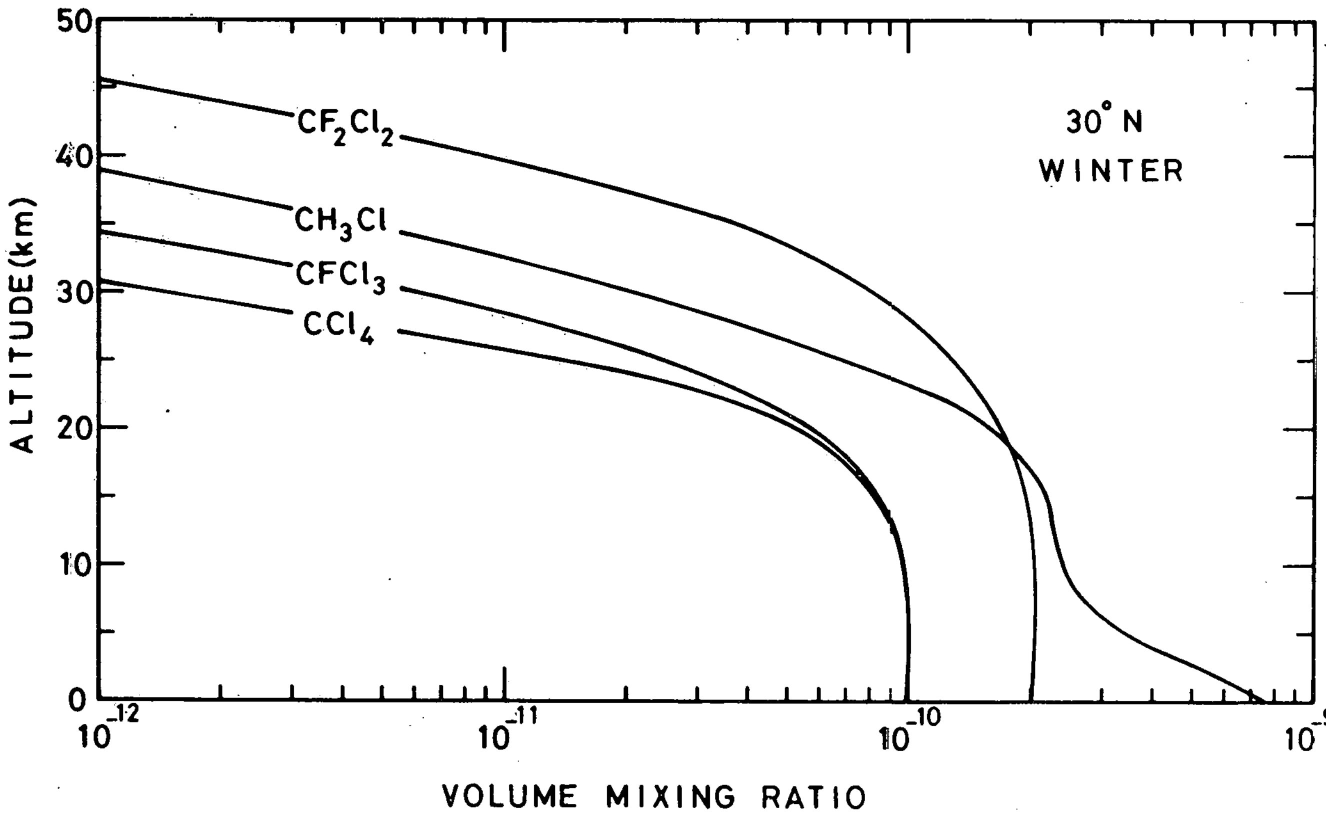

Fig. 3.- Vertical distribution of CH_3Cl, CCl_4, $CFCl_3$ and CF_2Cl_2 computed at 30°N for winter conditions.

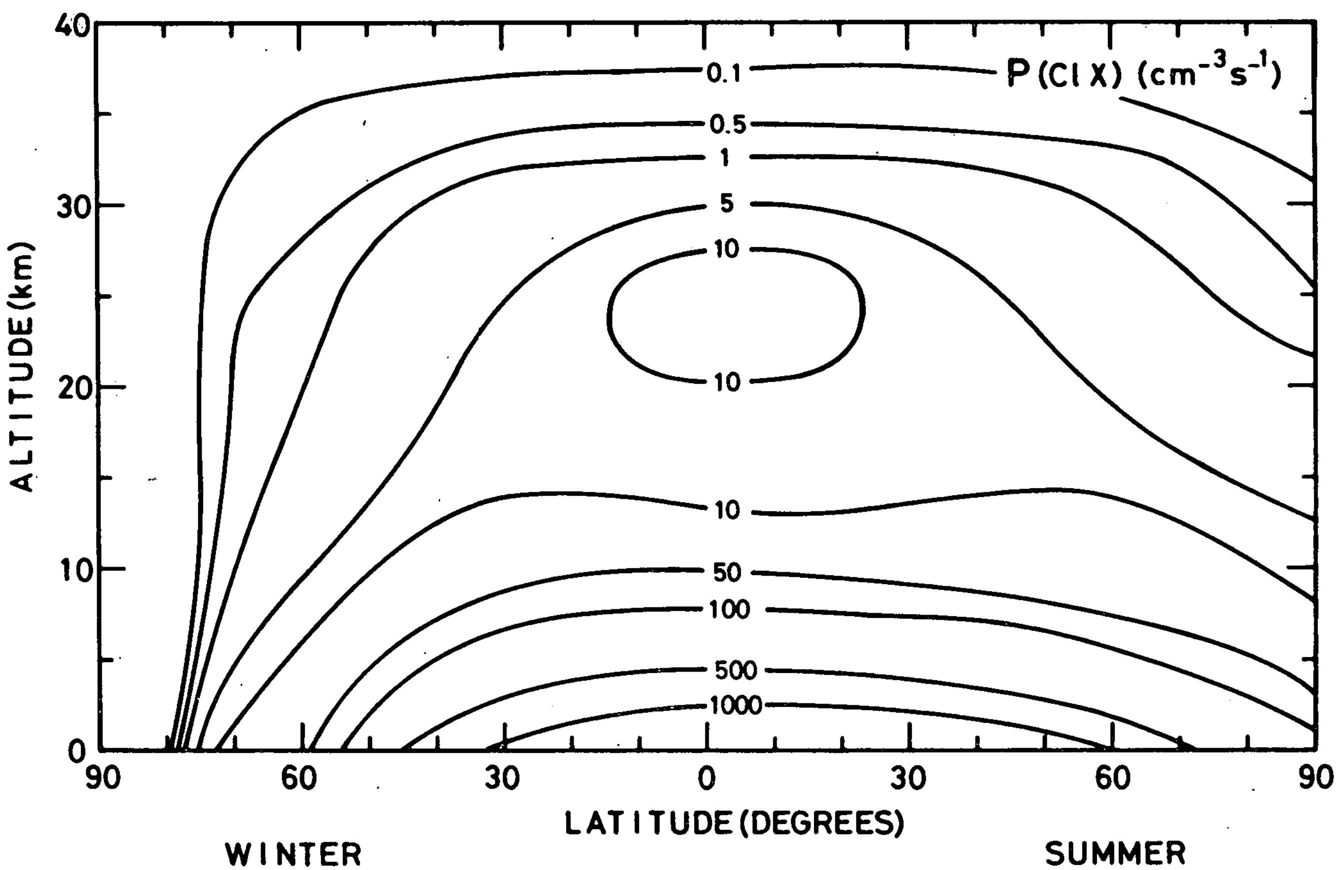

Fig. 4.- Production rate of odd chlorine in the meridional plane assuming that all chlorine atoms present in the halocarbons are converted into ClX.

TABLE 2 : Boundary conditions (volume mixing ratio).

	0 km	50 km
O_3	2.6×10^{-8}	photochemical equilibrium
N_2O	3×10^{-7}	1×10^{-10}
NO_y	1×10^{-9}	6×10^{-10}
CH_4	1.5×10^{-6}	2×10^{-8}
CH_3Cl	8×10^{-10}	2×10^{-14}
$CFCl_3$	1×10^{-10}	0
CF_2Cl_2	2×10^{-10}	5×10^{-13}
CCl_4	1×10^{-10}	0
ClX	1×10^{-9}	1.5×10^{-9}

represents the production rate of ClX in the meridional plane assuming that all the chlorine atoms present in the halocarbons are converted into odd chlorine. The production rate reaches values of the order of 10 to 1000 cm^{-3} s^{-1} in the troposphere due to the destruction of CH_3Cl by OH but these chlorine atoms are quickly washed out. In the stratosphere the production rate reaches a maximum of about 10 cm^{-3} s^{-1} in the equatorial region at about 22 km. This formation is due to the photodissociation of the different halocarbons.

The vertical distribution at 30° N (winter) of Cl, ClO, $ClONO_2$ and HCl is shown on figure 5. According to the model, hydrogen chloride is the most abundant constituent at all altitudes but its concentration is very close to the concentration of chlorine nitrate between 20 and 30 km and is not far from the concentration of ClO between 40 and 46 km. Further theoretical and observational investigations are needed in order to establish the atmospheric value of the ClO/HCl ratio which is of particular importance to determine the effective loss of ozone by chlorine species. As a matter of fact, the loss rate of ozone is proportional to the concentration of ClO and therefore the complete distribution of this molecule in the meridional plane is represented on fig. 6.

3.2. Sensitivity of ozone to an increase of ClX

In order to investigate in a simplified way the effect of an increase of ClX related to anthropogenic activities, the amount of the actual chlorine resulting from the computation described in the previous section has been multiplied at all altitudes and all latitudes by 5 and 10 respectively. The corresponding relative ozone variation as a function of the altitude calculated for winter mid-latitude conditions is represented on fig. 7. The graph shows that the largest ozone depletion occurs between 35 and 50 km with a maximum at about 43 km. The relative reduction is rather large (60 to 80 percent) at these heights but the absolute ozone concentration at these altitudes contributes only slightly to the total ozone column. On the other hand, the depletion is the smallest where the ozone concentration is the largest. According to our computation, one finds even a slight increase of the local concentration around 30 km. In the lower stratosphere, the reduction is of the order of 10 - 20 percent. Finally, the computation provides a global ozone depletion of 9 and 17 percent

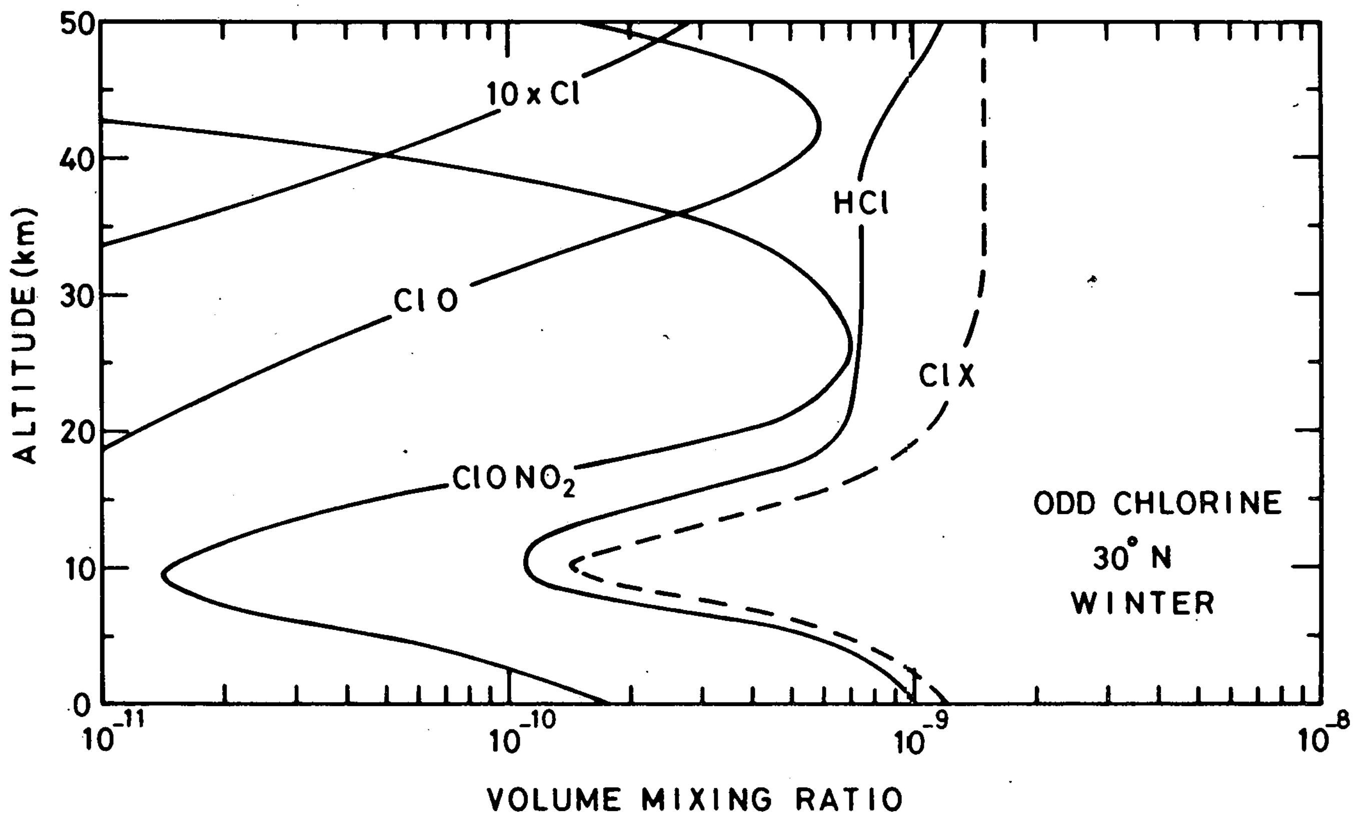

Fig. 5.- Vertical distribution of Cl, ClO, $ClONO_2$ and HCl computed at 30^0N for winter conditions.

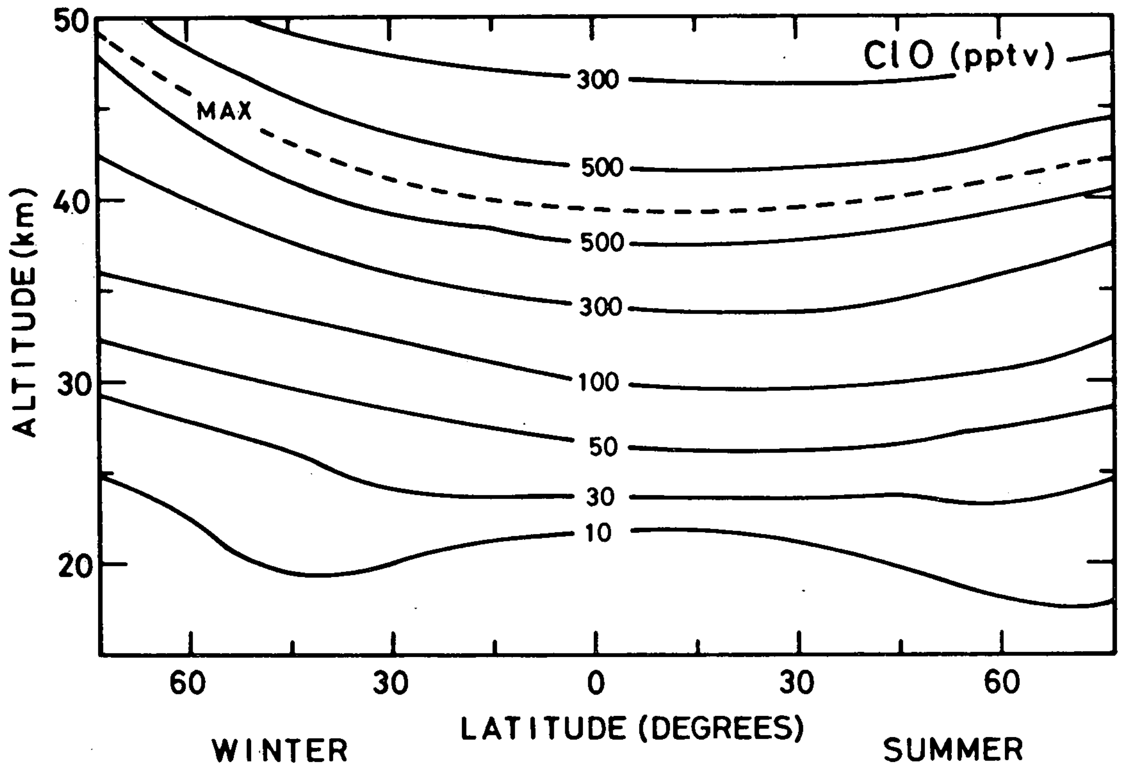

Fig. 6.- Distribution of the ClO mixing ratio in the meridional plane. The dashed line represents the altitude where the mixing ratio reaches its maximum value.

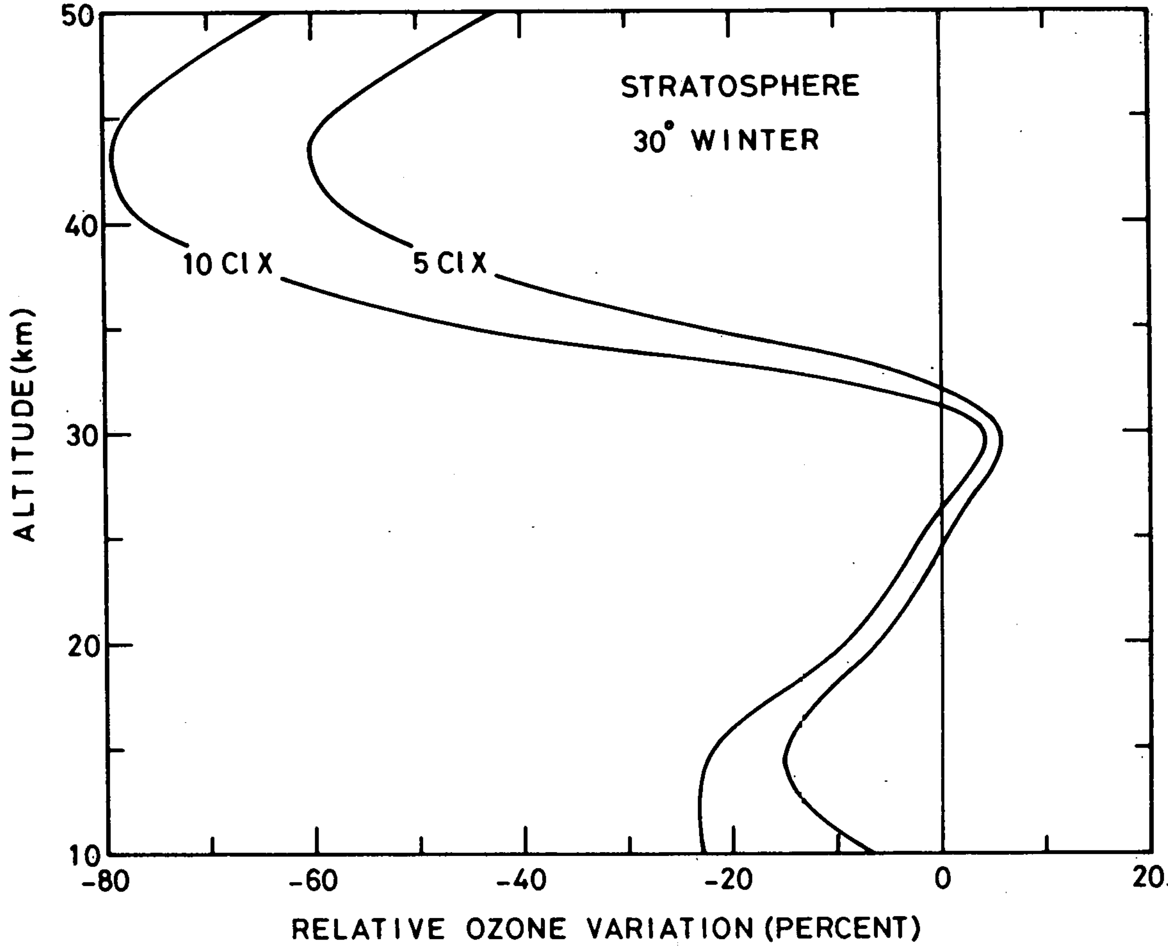

Fig. 7.- Relative variation of the ozone concentration as a function of the altitude when the actual ClX amount is uniformely multiplied by 5 and 10 respectively.

when the two different cases are considered. However, it should be noted, as shown on fig. 8, that the relative reduction appears to be slightly latitude dependent.

These results should be considered as numerical experiments more than final answers to the problems of the stratosphere. Many uncertainties in the input data (aeronomical and transport parameters) remain and further investigations are needed before it will be possible to consider such results as representative of reality.

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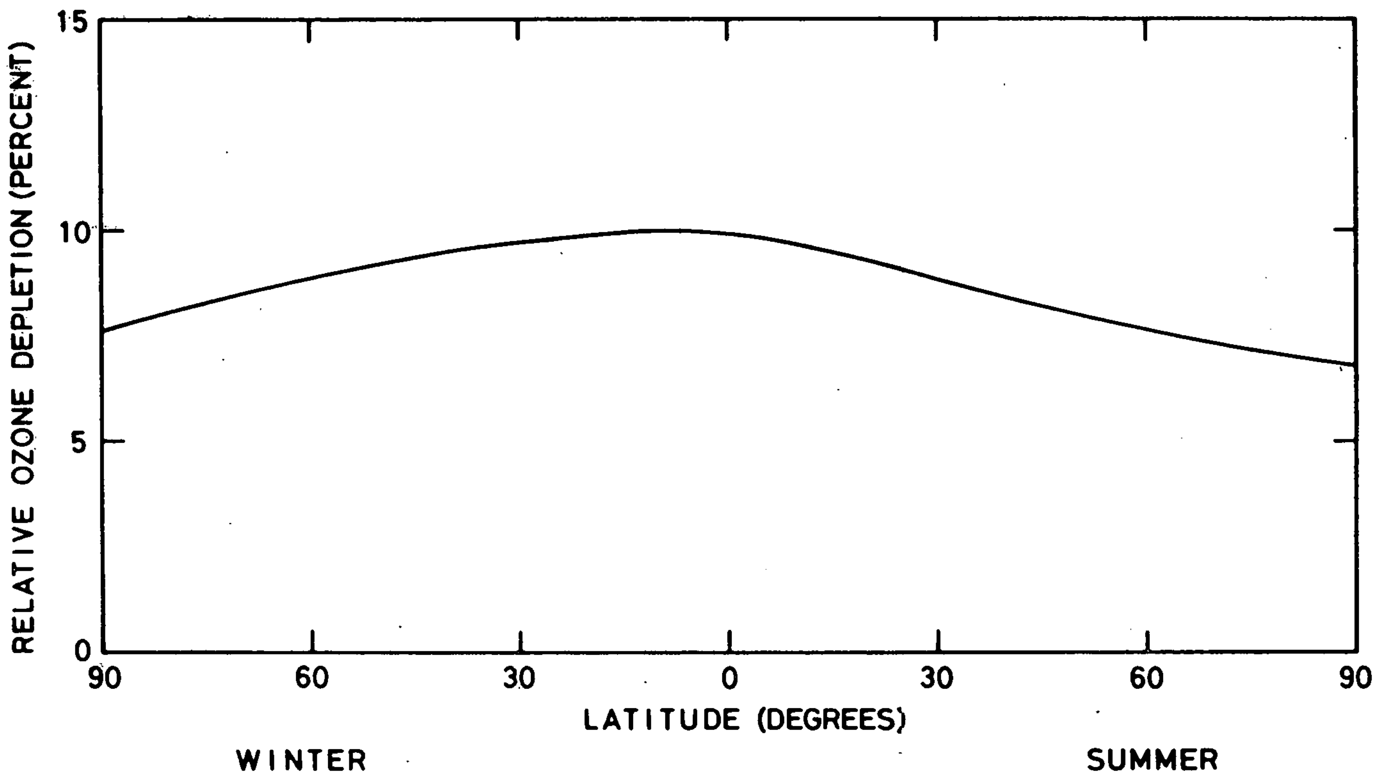

Fig. 8.- Relative variation of the ozone column as a function of the latitude when the actual ClX amount is uniformely multiplied by 5.

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