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Agents and effects of ozone trends in the atmosphere

by

G. BRASSEUR and A. DE RUDDER

B E L G I S C H I N S T I T U U T V O O R R U I M T E A E R O N O M I E

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FOREWORD

This paper will appear in the proceedings of the NATO workshop held in Bad Windsheim (FRG), September 27-30, 1983, on "The impact of solar ultraviolet radiation upon terrestrial ecosystems. I. Agricultural systems". It will be published by Springer Verlag.

AVANT-PROPOS

Cet article figurera dans les comptes rendus du séminaire organisé par l'OTAN à Bad Windsheim (Allemagne Fédérale) du 27 au 30 septembre 1983 sur le thème "L'impact du rayonnement solaire ultraviolet (UV-B) sur les écosystèmes terrestres. I. Systèmes agricoles". Il sera publié par Springer Verlag.

VOORWOORD

Dit artikel zal verschijnen in de rapporten van de NAVO-werkvergadering gehouden in Bad Windsheim (Bondsrepubliek Duitsland)) van 27 tot 30 september 1983, over het thema "The impact of solar ultraviolet radiation upon terrestrial ecosystems. I. Agricultural systems". Het zal door Springer Verlag gepubliceerd worden.

VORWORT

Dieser Artikel wird erscheinen in den Rapporten der NATO-Tagung gehalten in Bad Windsheim (Bundessrepublik Deutschland) von 27 bis 30 September 1983, über dem Thema "The impact of solar ultraviolet radiation upon terrestrial ecosystems. I. Agricultural systems". Er wird durch Springer Verlag herausgegeben werden.

AGENTS AND EFFECTS OF OZONE TRENDS IN THE ATMOSPHERE

by

G. BRASSEUR and A. DE RUDDER

Abstract

Although it constitutes a very small proportion of the gases in the middle atmosphere, ozone plays a considerable role in this region. By absorbing the ultraviolet solar radiation, essentially in the 200-310 nm spectral range, it protects the biosphere and makes life possible at the Earth's surface.

Ozone is produced from the photodissociation of molecular oxygen by ultraviolet radiation ($\lambda < 242.4$ nm). It is destroyed by direct recombination with oxygen atoms. This recombination can be catalyzed by hydroxyl radicals, nitrogen and chlorine oxides. In other words, the ozone layer can be altered by species produced either by natural processes in the biosphere or by human activity in relation with agriculture or industry. As an example, man-made chlorofluorocarbons should reduce the ozone amount by a few percent if the present release into the atmosphere continues. On the other hand, an increase of carbon dioxide should cool the upper stratosphere and consequently increase the ozone concentration. This paper presents results from an interactive chemical/radiative/dynamic one-dimensional model with several coupled perturbation scenarios.

Résumé

Quoiqu'étant très peu abondant dans l'atmosphère moyenne, l'ozone joue cependant un rôle considérable dans cette région. En absorbant le rayonnement solaire ultraviolet, essentiellement dans la région spectrale de 200-310 nm, il protège la biosphère et rend possible la vie à la surface de la Terre.

L'ozone est produit par la photodissociation de l'oxygène moléculaire sous l'effet du rayonnement ultraviolet ($\lambda < 242.4$ nm). Il est détruit par la recombinaison directe avec des atomes d'oxygène. Cette recombinaison peut être catalysée par des radicaux hydroxyles, ainsi que par des oxydes d'azote et de chlore. La couche d'ozone peut donc être altérée par des composés produits naturellement dans la biosphère ou par des activités humaines en relation avec l'agriculture ou l'industrie. Par exemple, les chlorofluorocarbones fabriqués par l'homme devraient réduire la quantité d'ozone si le présent dégagement dans l'atmosphère continue. Par contre, une augmentation du dioxyde de carbone devrait refroidir la haute stratosphère et en conséquence augmenter la concentration d'ozone. Cet article nous donne les résultats d'un modèle uni-dimensionnel interactif, chimique, radiatif et dynamique, basé sur une série de scénarios prenant en compte différentes perturbations atmosphériques.

Samenvatting

Hoewel het slechts een klein gedeelte van de stratosfeer is, speelt ozon een aanzienlijke rol in het gebied. Door de ultraviolette zonnestraling te absorberen, voornamelijk in het spectraal gebied van 200-310 nm, beschermt het de biosfeer en maakt het leven op Aarde mogelijk.

Ozon wordt verkregen uit de fotodissociatie van moleculaire zuurstof door ultraviolette zonnestraling ($\lambda < 242.4$ nm). Het wordt vernietigd door directe recombinitie met zuurstofatomen. Deze recombinitie kan gekatalyseerd worden door hydroxylradicalen, stikstof- en chlooroxydes. De ozonlaag kan dus gewijzigd worden door soorten die, hetzij geproduceerd worden door natuurlijke processen in de biosfeer, hetzij door menselijke activiteiten m.b.t. de landbouw of de industrie. Zo zouden bv. door de mens gemaakte chloorfluorkoolstoffen het ozon-gehalte met enkele percenten moeten verlagen als de huidige loslating in de atmosfeer voortduurt. Anderzijds zou een verhoging van koolstofdioxide de hoge stratosfeer moeten afkoelen en bijgevolg de ozonconcentratie verhogen. Dit artikel geeft ons de resultaten van een interactief chemisch, radiatief, dynamisch één-dimensionaal model gebaseerd op een reeks scenario's van atmosferische storingen.

Zusammenfassung

Obschon es nur ein kleiner Teil der Stratosphäre ist, spielt das Ozon eine ansehnliche Rolle im Gebiet. Da das Ozon die ultraviolette Sonnenstrahlung absorbiert, vornehmlich im Spektralgebiet von 200-310 nm, schützt es die Biosphäre und mocht es möglich auf der Erde zu leben.

Das Ozon wird produziert aus der Fotodissoziation von Molekular-Sauerstoff durch ultraviolette Sonnenstrahlung ($\lambda < 242.4$ nm). Es wird vernichtet durch direkte Rekombination mit Sauerstoffatomen. Diese Rekombination kann katalysiert werden durch Hydroxylradikalen, Stickstoff- und Chloroxyden. Die Ozonschicht kann denn modifiziert werden durch Sorten die, sei est produziert werden durch naturliche Verfahren in der Biosphäre, sei est durch Menschen aktivitäten mit Bezug auf dem Ackerbau oder der Industrie. So würden z.B vom Mensch gemachte Chlorfluorkohlenstoffen der Ozon gehalt mit einzigen Prozenten vermindern müssen wenn die heutige Loslassung in der Atmosphäre fortdauert. Anderseits würde eine Erhöhung von Kohlensäure die höhe Stratosphäre erhalten müssen und folglich die Ozonkonzentration erhöhen. Dieser Artikel gibt uns die Resultaten eines interaktiven, chemischen radiativen, dynamischen eindimensionale Modelles basiert auf einer Szenarreihe von atmosphärische Störungen.

INTRODUCTION

Although its relative amount is only of the order of 5×10^{-7} , ozone is of great importance in the atmosphere. This gas, which is photochemically produced, is indeed a strong absorber of ultraviolet radiation with wavelengths shorter than 310 nm. It therefore protects the Earth surface from a series of potentially harmful biological effects of solar UV radiation. Moreover, ozone, which is confined essentially to the stratosphere, is responsible for the heating of the middle atmosphere and in particular for the temperature maximum at 50 km altitude. Ozone therefore is not only a protection for life on Earth, but it is also linked to the dynamic state of the atmosphere and finally to the terrestrial climate.

As indicated by Fig. 1 which shows an average vertical distribution of ozone below 100 km, the maximum O_3 concentration is located at an altitude of 20 to 25 km with a corresponding value of about $4 \times 10^{12} \text{ cm}^{-3}$. In the troposphere the ozone concentration is less than 10^{12} cm^{-3} and at the stratopause it is of the order of $5 \times 10^{10} \text{ cm}^{-3}$. The integrated concentration, also called the ozone column, is equal to about $9 \times 10^{18} \text{ cm}^{-2}$, corresponding to a layer at STP conditions of $0.35 \pm 0.05 \text{ cm}$. In fact, continuous observations show that the ozone column is rather constant in the equatorial regions (about 0.29 cm), but exhibits a great deal of diurnal and seasonal variability at higher latitude. An ozone maximum ($> 0.4 \text{ cm}$) occurs in the polar region at the end of the winter, suggesting a strong control of the ozone layer by dynamics (general circulation and waves). Figure 2 shows a time-latitude variation of total ozone resulting from the analysis of numerous observations made from ground level instruments.

The stability of the ozone layer has been a subject of great concern in the last 15 years since the destruction of the O_3 molecule is catalyzed by several radicals which are produced in fairly large amounts

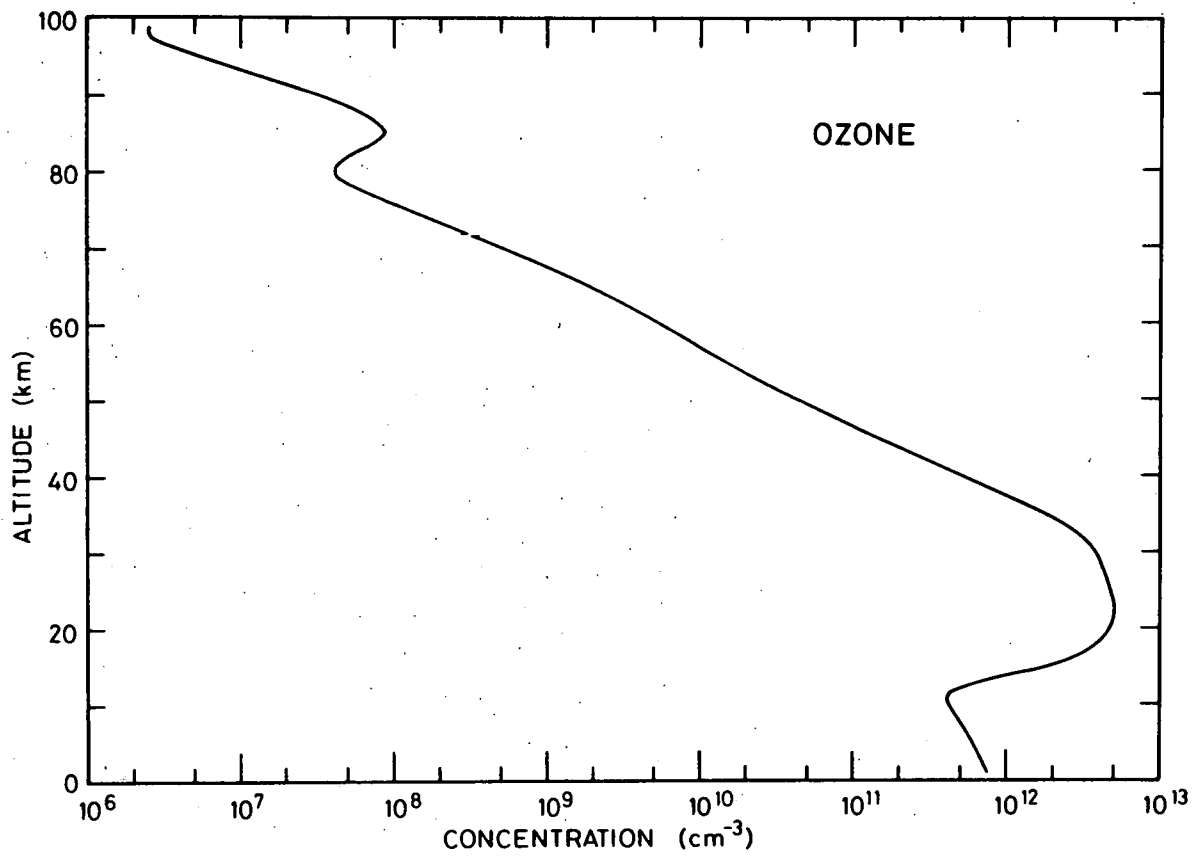


Fig. 1.- Calculated vertical distribution of the ozone concentration between 0 and 100 km altitude.

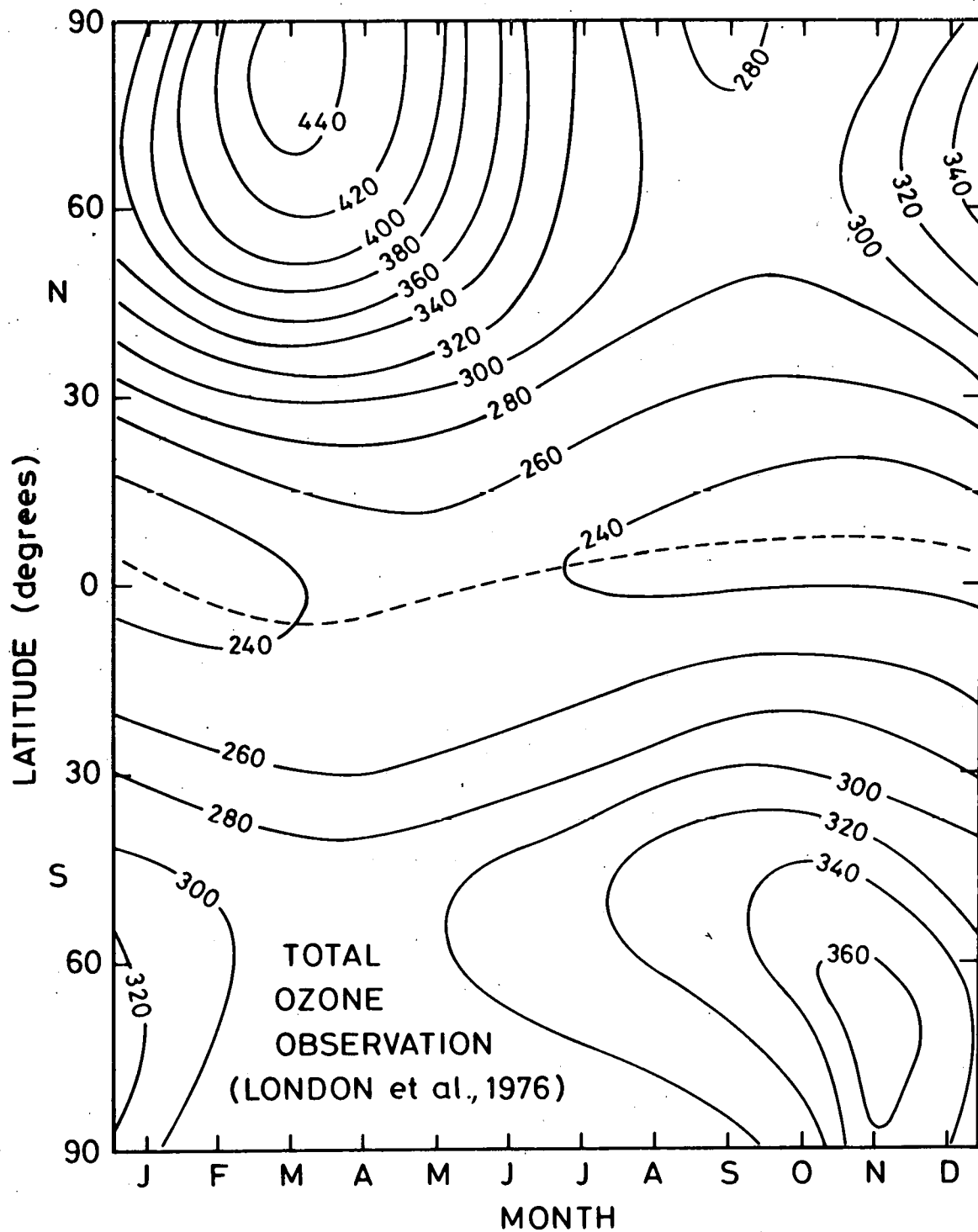


Fig. 2.- Seasonal variation of the ozone column (expressed in Dobson units) as a function of latitude (London et al. 1976).

as a result of human activity. For example, nitrogen oxides can be injected in the atmosphere directly from aircraft engines or produced from the N_2O molecules which are released when nitrogen fertilizers are used in agricultural practices. These NO and NO_2 molecules are involved in the catalytic destruction of ozone (Crutzen 1970) and would be the agents of a possible effect of aircraft emissions (Johnston 1971; Crutzen 1972) or nitrogen fertilizers (McElroy et al., 1976) on the ozone layer. Moreover, ozone can be depleted by halogen compounds such as chlorine (Stolarski and Cicerone 1974) which are produced from the man-made chlorofluorocarbons (Molina and Rowland 1974a, b).

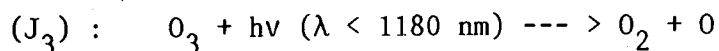
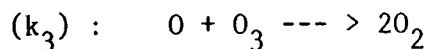
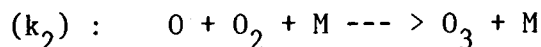
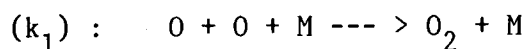
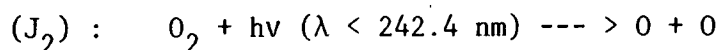
The estimation of the possible ozone depletion and the related increase in the UV penetration due to agricultural, industrial and domestic activity is usually based on theoretical models. These models take into account the most important chemical and photochemical reactions and are usually coupled with a radiative transfer code. The transport of the long-lived species and of heat has to be somewhat parameterized since a full three-dimensional calculation of the mean circulation and the waves requires prohibitive computer resources for most applications. Two-dimensional models assume a zonal symmetry and they parameterize the meridional transport either by the eulerian mean circulation and by eddy diffusion processes (Rao-Vupputuri 1973, 1979; Harwood and Pyle 1975; Crutzen 1975; Brasseur 1978; Miller et al., 1981) or by eulerian residual meridional wind components (Dunkerton 1978; Pyle and Rogers 1980; Garcia and Solomon 1983; Tung 1983).

One-dimensional models assume complete horizontal mixing and derive the globally averaged vertical distributions of the species concentrations and in some cases the temperature. The vertical exchanges are parameterized by a phenomenological eddy diffusion coefficient (K). Although these models are highly simplified from the dynamic point of view, they usually contain a rather detailed chemical and photochemical scheme and they are appropriate to study the direct couplings between chemistry, radiation and temperature. These models are commonly used

to estimate the global impact of several types of chemical perturbations (Logan et al. 1978; Wuebbles 1983; Wuebbles et al. 1983; Nicoli and Visconti 1983).

OZONE PHOTOCHEMISTRY IN A PURE OXYGEN ATMOSPHERE

A simple theory of ozone photochemistry has been given by Chapman, considering a pure oxygen atmosphere in which the following reactions take place :



The recombination of atomic oxygen by reaction (k₁) can, however, be neglected below the mesopause (85 km) so that, in the stratosphere and in the mesosphere, the kinetic equation which can be derived for odd oxygen (O_x = O₃ + O) is given by

$$\frac{dn(O_x)}{dt} + 2k_3 n(O) n(O_3) = 2J_2 n(O_2) , \quad (1)$$

if n(X) represents the concentration of species X (see Nicolet 1971 or Brasseur 1982). The ratio between the atomic oxygen and the ozone concentrations can be derived from the photoequilibrium equation

$$\frac{n(O)}{n(O_3)} = \frac{J_3}{k_2 n(M) n(O_2)} \quad (2)$$

The lifetime of odd oxygen, which is given by

$$\tau(O_x) = \frac{0,275 n(O_x)}{J_2 n(O_2)} \quad (3)$$

is of the order of 1 hour at the stratopause (50 km) but increases gradually with decreasing altitude to reach more than 5 years below 20 km. Since the dynamic time constant is of the order of 2 years in the stratosphere, ozone is controlled by dynamics only (general circulation and waves) below say 25 km and by photochemistry only above 30 km or so. In the intermediate layer both chemistry and transport have to be considered to explain the behavior of ozone. It should be noted that in the troposphere ($z < 12$ km) the chemistry again becomes more active with regard to O_3 and could even play the major role at low altitude.

When photochemical equilibrium conditions apply, the ozone concentration in a pure oxygen atmosphere is given by

$$n(O_3) = \left[\frac{J_2}{J_3} n(M) n^2(O_2) \frac{k_2(T)}{k_3(T)} \right]^{1/2} \quad (4)$$

The value of the rate constants k_1 , k_2 and k_3 are given in Table 1 and the averaged physical parameters which enter into the calculation of O_3 are specified in Table 2. The exact determination of the photodissociation frequency of O_2 and O_3 is not straightforward since it requires a detailed knowledge of the solar irradiance spectrum [see Brasseur and Simon (1981)] and of the absorption cross section of O_2 and O_3 [see Nicolet (1981) or Simon and Brasseur (1983) for a discussion]. In particular, one has to determine quantitatively the penetration of the solar radiation taking into account absorption and scattering processes. Indeed the solar irradiance ϕ at level z for a zenith angle of the sun χ and at wavelength λ is given by

$$\phi(\lambda; z, \chi) = \phi_\infty(\lambda) \exp. - [\tau_a(\lambda; z, \chi) + \tau_s(\lambda; z, \chi)] + \int_{4\pi} L(\lambda; z, \omega) d\omega \quad (5)$$

if $\phi_{\infty}(\lambda)$ is the solar irradiance at the top of the atmosphere, $L(\lambda; z, \omega)$ the radiance in direction ω due to the multiple scattering of the light, $\tau_a(\lambda; z, \chi)$ the optical depth due to the absorption, essentially by O_2 and O_3 :

$$\tau_a(\lambda; z, \chi) = [\sigma(O_2; \lambda) N(O_2; z) + \sigma(O_3; \lambda) N(O_3; z)] \sec \chi \quad (6)$$

where σ is the absorption cross section and N the vertically integrated concentration of the absorber (O_2 and O_3 , respectively) above altitude z . The optical depth due to the Rayleigh scattering is given by

$$\tau_s = \sigma_R n(M)$$

where $n(M)$ is the atmosphere concentration,

$$\sigma_R = \frac{8\pi^3}{3} \frac{(\mu^2 - 1)}{\lambda^4 n^2(M)} D \quad (7)$$

the corresponding cross section, μ the air refractive index, $D \cong 1.06$ the depolarization factor and χ the solar zenith angle. Moreover, the amplification factor of the solar irradiance at ground level due to scattering and the Earth's albedo in the 310-400 nm range, that is the factor by which the direct solar flux has to be multiplied to account for a given surface albedo and the multiple scattering processes, is shown in Fig. 3 (Nicolet et al., 1983). The photodissociation coefficient of a species X is then derived from

$$J(X; z, \chi) = \int_{\lambda} \sigma(X; \lambda) q(\lambda; z, \chi) d\lambda \quad (8)$$

if $q = \phi/h\nu$ is the photon flux and $h\nu$ the photon energy at frequency ν . A variation in the ozone column $N(O_3; z)$ consequently modifies the solar irradiance value in the atmosphere and at ground level and changes the photodissociation rates of the molecules which absorb in the same spectral range as O_3 . The thermal structure of the atmosphere is also modified.

TABLE 1a. Reaction rates adopted in the model

Reactions	Rate constants ($\text{cm}^3 \text{s}^{-1}$)
$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$k_1 = 4.7 \times 10^{-33} (300/T)^2 n(\text{M})$
$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	$k_2 = 6.0 \times 10^{-34} (300/T)^{2.3} n(\text{M})$
$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$	$k_3 = 1.5 \times 10^{-11} e^{-2218/T}$
$\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O}(^3\text{P}) + \text{N}_2$	$k_4 = 1.8 \times 10^{-11} e^{107/T}$
$\text{O}(^1\text{D}) + \text{O}_2 \rightarrow \text{O}(^3\text{P}) + \text{O}_2$	$k_5 = 3.2 \times 10^{-11} e^{67/T}$
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$a_1 = 5.5 \times 10^{-32} (T/300)^{-1.4} n(\text{M})$
$\text{H} + \text{O}_3 \rightarrow \text{O}_2 + \text{CH}(v \ 9)$	$a_2 = 1.4 \times 10^{-10} e^{-470/T}$
$\text{CH} + \text{O} \rightarrow \text{H} + \text{O}_2$	$a_5 = 2.2 \times 10^{-11} e^{117/T}$
$\text{CH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	$a_6 = 1.6 \times 10^{-12} e^{-940/T}$
$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	$a_{6b} = 1.4 \times 10^{-14} e^{-580/T}$
$\text{HO}_2 + \text{O} \rightarrow \text{O}_2 + \text{CH}(v \ 6)$	$a_7 = 3.0 \times 10^{-11} e^{200/T}$
$\text{CH} + \text{CH} \rightarrow \text{H}_2\text{O} + \text{O}$	$a_{16} = 4.2 \times 10^{-11} e^{-242/T}$
$\text{CH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$a_{17} = 1.6 \times 10^{-11} e^{436/T}$
$\text{CH} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$	$a_{19} = 6.1 \times 10^{-12} e^{-2030/T}$
$\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$	$a_{23a} = 4.2 \times 10^{-10} e^{-950/T}$
$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	$a_{23b} = 4.2 \times 10^{-11} e^{-350/T}$
$\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}$	$a_{23c} = 8.3 \times 10^{-11} e^{-500/T}$
$\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$	$a_{24} = 8.8 \times 10^{-12} e^{-4200/T}$
$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$	$a_{26} = b_{29} = 3.7 \times 10^{-12} e^{240/T}$
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$a_{27} = 2.4 \times 10^{-13} e^{560/T}$
$\text{CH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$a_{30} = 3.1 \times 10^{-12} e^{-187/T}$
$\text{CH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	$a_{36} = 1.35 \times 10^{-13} (1 + P_{\text{atm}})$
$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	$a_1^* = 2.2 \times 10^{-10}$
$\text{O}(^1\text{D}) + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$	$a_2^* = 1.4 \times 10^{-10}$
$\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$	$a_3^* = 1.0 \times 10^{-10}$

Table 1a. (cont.)

Reactions	Rate constants (cm ³ s ⁻¹)
O(³ p) + NO ₂ → NO + O ₂	b ₃ = 9.3 x 10 ⁻¹²
O ₃ + NO → NO ₂ + O ₂	b ₄ = 2.2 x 10 ⁻¹² e ^{-1430/T}
N(⁴ S) + NO → N ₂ + O	b ₆ = 3.4 x 10 ⁻¹¹
N(⁴ S) + O ₂ → NO + O	b ₇ = 4.4 x 10 ⁻¹² e ^{-3220/T}
NO ₂ + O ₃ → NO ₃ + O ₂	b ₉ = 1.2 x 10 ⁻¹³ e ^{-2450/T}
NO ₃ + NO ₂ + M → N ₂ O ₅ + M	b ₁₂ } see Table 1b
NO ₂ + CH + M → HNO ₃ + M	b ₂₂ }
HO ₂ + NO ₂ + M → HO ₂ NO ₂ + M	b ₂₃ }
HNO ₃ + CH → H ₂ O NO ₃	b ₂₇ = 9.4 x 10 ⁻¹⁵ e ^{778/T}
HO ₂ NO ₂ + OH → H ₂ O+NO ₂ +O ₂	b ₂₈ = 20 x 10 ⁻¹² (1-0.9e ^{-0.0587PTorr})
N ₂ O ₅ + M → NO ₃ + NO ₂ + M	b ₃₂ = 2.2 x 10 x 10 ⁻⁵ e ^{-9700/T}
N ₂ O + O(¹ D) → N ₂ + O ₂	b ₃₈ = 4.9 x 10 ⁻¹¹
N ₂ O + O(¹ D) → 2NO	b ₃₉ = 6.7 x 10 ⁻¹¹
CH ₄ + OH → CH ₃ + H ₂ O	c ₂ = 2.4 x 10 ⁻¹² e ^{-1710/T}
CH ₃ + O ₂ + M → CH ₃ O ₂ + M	c ₄ : see Table 1b
CH ₃ O ₂ + NO → CH ₃ O + NO ₂	c ₅ = 4.2 x 10 ⁻¹² e ^{180/T}
CH ₃ O ₂ + HO ₂ → CH ₃ OOH + O ₂	c ₇ = 7.7 x 10 ⁻¹⁴ e ^{1300/T}
CH ₃ O ₂ + CH ₃ O ₂ → 2CH ₃ O + O ₂	c ₁₄ = 1.6 x 10 ⁻¹³ e ^{220/T}
CH ₃ OOH + OH → CH ₃ O ₂ + H ₂ O	c ₁₇ = 2.6 x 10 ⁻¹² e ^{-190/T}
C ₂ H ₂ + Cl → products	c ₂₀ = 1.0 x 10 ⁻¹²
C ₂ H ₂ + OH → products	c ₂₁ = 6.5 x 10 ⁻¹² e ^{-650/T}
C ₂ H ₆ + Cl → products	c ₂₂ = 7.7 x 10 ⁻¹¹ e ^{-90/T}
C ₂ H ₆ + OH → products	c ₂₃ = 1.9 x 10 ⁻¹¹ e ^{-1260/T}
C ₃ H ₈ + Cl → products	c ₂₄ = 1.4 x 10 ⁻¹⁰ e ^{40/T}
C ₃ H ₈ + OH → products	c ₂₅ = 1.6 x 10 ⁻¹¹ e ^{-800/T}
CH ₃ HN + OH → products	c ₂₉ = 5.86 x 10 ⁻¹³ e ^{-750/T}

TABLE 1a. (cont.)

Reactions	Rate constants (cm ³ s ⁻¹)
CH ₃ + OH → CH ₂ Cl + H ₂ O	d ₁ = 1.8 x 10 ⁻¹² e ^{-1112/T}
Cl + O ₃ → ClO + O ₂	d ₂ = 2.8 x 10 ⁻¹¹ e ^{-257/T}
ClO + NO → Cl + O ₂	d ₃ = 7.7 x 10 ⁻¹¹ e ^{-130/T}
ClO + NO → Cl + NO ₂	d ₄ = 6.2 x 10 ⁻¹² e ^{294/T}
Cl + CH ₄ → HCl + CH ₃	d ₅ = 9.6 x 10 ⁻¹² e ^{-1350/T}
Cl + H ₂ → HCl + H	d ₆ = 3.7 x 10 ⁻¹¹ e ^{-2300/T}
Cl + HD ₂ → HCl + O ₂	d ₇ = 1.8 x 10 ⁻¹¹ e ^{170/T}
Cl + H ₂ O ₂ → HCl + HD ₂	d ₈ = 1.1 x 10 ⁻¹¹ e ^{-980/T}
Cl + CH ₂ O → HCl + CHO	d ₁₀ = 8.2 x 10 ⁻¹¹ e ^{-34/T}
HCl + CH → Cl + H ₂ O	d ₁₁ = 2.8 x 10 ⁻¹² e ^{-425/T}
HCl + O(3P) → Cl + CH	d ₁₂ = 1.0 x 10 ⁻¹¹ e ^{-3340/T}
ClO + NO ₂ + M → ClONO ₂ + M	d ₂₂ = d ₃₁ : see Table 1b
ClONO ₂ + O → ClO + NO ₃	d ₃₂ = 3.0 x 10 ⁻¹² e ^{-808/T}
ClO + HD ₂ → HOCl + O ₂	d ₃₃ = d ₃₅ = 4.6 x 10 ⁻¹³ e ^{710/T}
CH ₃ CCl ₃ + CH → CH ₂ CCl ₃ + H ₂ O	d ₅₀ = 5.4 x 10 ⁻¹² e ^{-1820/T}

TABLE 1b. Three-body reactions. The rate constants of these reactions are expressed as follows :

$$\frac{k_o n(M)}{1 + n(M) k_o/k_\infty} \times 0.6 [1 + \log_{10}^2 (n(M)k_o/k_\infty)]^{-1}$$

with

$$k_o = k_o^{300} (T/300)^{-n} \text{ cm}^6 \text{ s}^{-1}$$

$$k_\infty = k_\infty^{300} (T/300)^{-m} \text{ cm}^3 \text{ s}^{-1}$$

Reactions	Name of the constants	Values of the parameters
$\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	b_{12}	$k_o^{300} = 2.2 \times 10^{-30}$ $n = 2.8$ $k_\infty^{300} = 1.0 \times 10^{-12}$ $m = 0$
$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	b_{22}	$k_o^{300} = 2.6 \times 10^{-30}$ $n = 2.9$ $k_\infty^{3300} = 2.4 \times 10^{-11}$ $m = 1.3$
$\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$	b_{23}	$k_o^{300} = 2.3 \times 10^{-31}$ $n = 4.6$ $k_\infty^{300} = 4.2 \times 10^{-12}$ $m = 0$
$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	c_4	$k_o^{300} = 1.8 \times 10^{-31}$ $n = 2.2$ $k_\infty^{300} = 2.0 \times 10^{-12}$ $m = 1.7$
$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	$d_{22} = d_{31}$	$k_o^{300} = 1.8 \times 10^{-31}$ $n = 3.4$ $k_\infty^{300} = 1.5 \times 10^{-11}$ $m = 1.9$

TABLE 1c. Photochemical reactions considered in the model

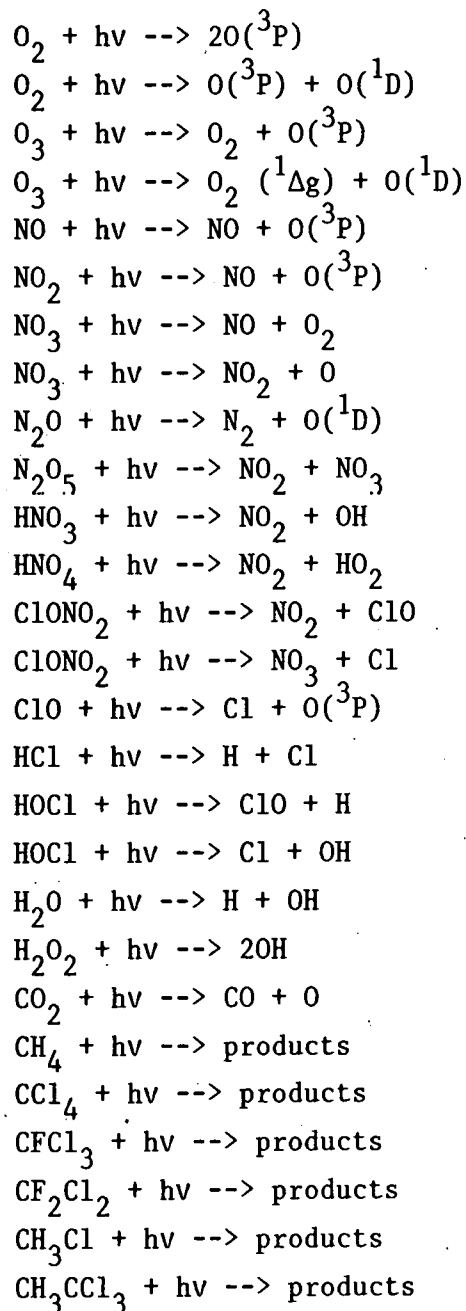


TABLE 2. Temperature, pressure, atmospheric and molecular oxygen concentration as a function of altitude between 0 and 120 km (US Standard Atmosphere 1976).

Altitude (km)	Temperature (K)	Pressure (mb)	Total concentration (cm ⁻³)	Molecular oxygen concentration (cm ⁻³)
0	288	1013	2.55 x 10 ¹⁹	5.33 x 10 ¹⁸
5	246	540	1.53 x 10 ¹⁹	3.20 x 10 ¹⁸
10	223	265	8.60 x 10 ¹⁸	1.80 x 10 ¹⁸
15	217	121	4.05 x 10 ¹⁸	8.47 x 10 ¹⁷
20	217	55.3	1.85 x 10 ¹⁸	3.87 x 10 ¹⁷
25	222	25.5	8.33 x 10 ¹⁷	1.74 x 10 ¹⁷
30	227	12.0	3.83 x 10 ¹⁷	8.01 x 10 ¹⁶
35	237	5.75	1.76 x 10 ¹⁷	3.68 x 10 ¹⁶
40	250	2.87	8.31 x 10 ¹⁶	1.74 x 10 ¹⁶
45	264	1.49	4.09 x 10 ¹⁶	8.55 x 10 ¹⁵
50	271	7.98 x 10 ⁻¹	2.14 x 10 ¹⁶	4.47 x 10 ¹⁵
55	261	4.25 x 10 ⁻¹	1.18 x 10 ¹⁶	2.47 x 10 ¹⁵
60	247	2.20 x 10 ⁻¹	6.44 x 10 ¹⁵	1.35 x 10 ¹⁵
65	233	1.09 x 10 ⁻¹	3.39 x 10 ¹⁵	7.09 x 10 ¹⁴
70	220	5.22 x 10 ⁻²	1.72 x 10 ¹⁵	3.60 x 10 ¹⁴
75	208	2.39 x 10 ⁻²	8.30 x 10 ¹⁴	1.74 x 10 ¹⁴
80	199	1.05 x 10 ⁻²	2.84 x 10 ¹⁴	8.02 x 10 ¹³
85	189	4.46 x 10 ⁻³	1.71 x 10 ¹⁴	3.57 x 10 ¹³
90	187	1.84 x 10 ⁻³	7.12 x 10 ¹³	1.48 x 10 ¹³
95	188	7.60 x 10 ⁻⁴	2.92 x 10 ¹³	5.83 x 10 ¹²
100	195	3.20 x 10 ⁻⁴	1.19 x 10 ¹³	2.15 x 10 ¹²
105	209	1.45 x 10 ⁻⁴	5.02 x 10 ¹²	7.65 x 10 ¹¹
110	240	7.10 x 10 ⁻⁵	2.14 x 10 ¹²	2.62 x 10 ¹¹
115	300	4.01 x 10 ⁻⁵	9.68 x 10 ¹¹	9.65 x 10 ¹⁰
120	360	2.54 x 10 ⁻⁵	5.11 x 10 ¹¹	4.40 x 10 ¹⁰

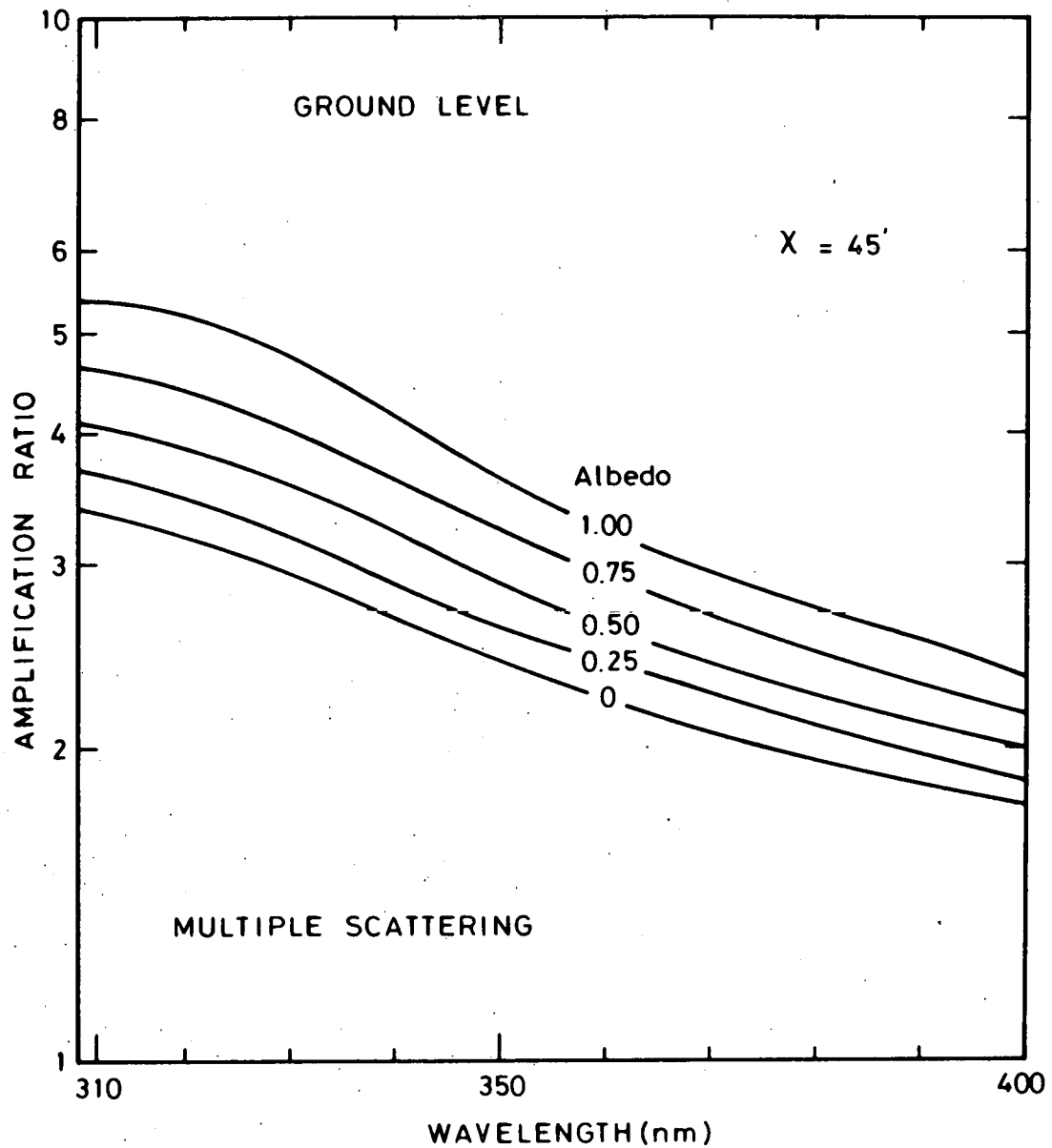


Fig. 3.- Amplification ratio of the solar radiation at ground level for wavelength between 310 and 400 nm and for different values of the surface albedo. The amplification ratio is defined by q_1/q_0 where q_1 is the irradiance calculated including multiple scattering and albedo and q_0 is the irradiance of the direct solar radiation only.

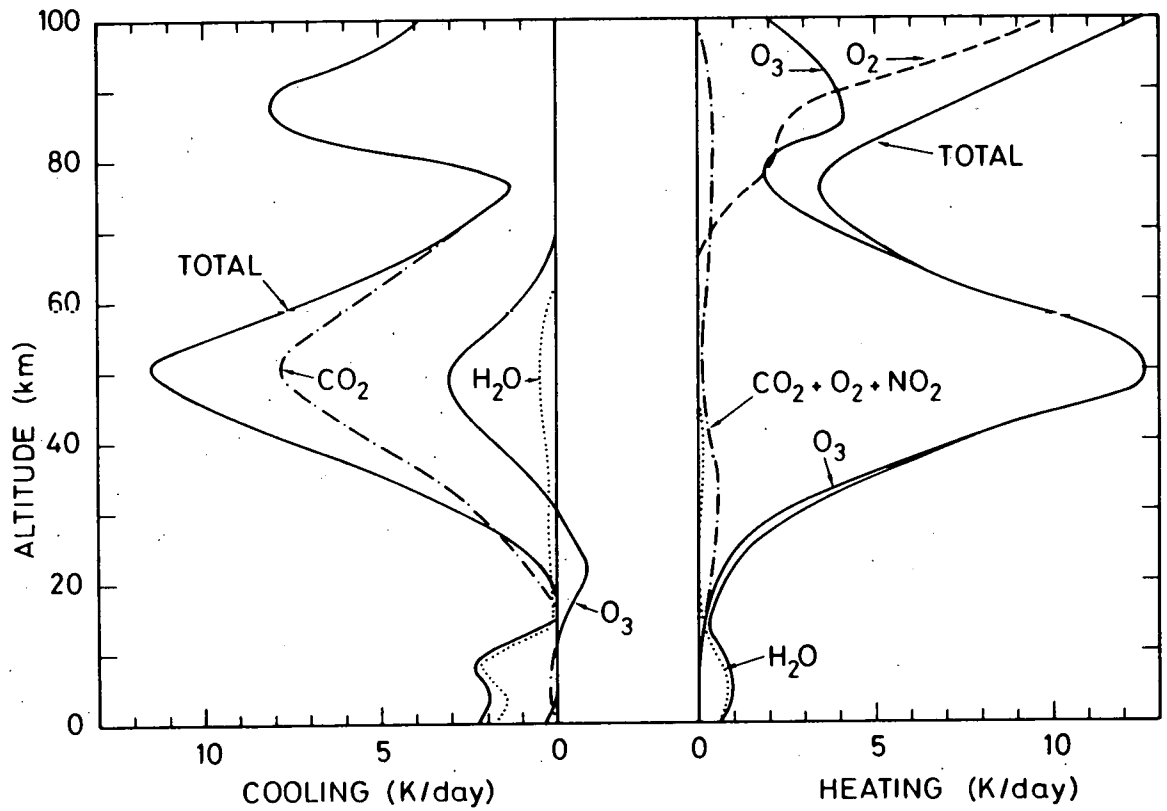


Fig. 4.- Vertical distribution of the heating and the cooling rates due to several atmospheric species (London 1980).

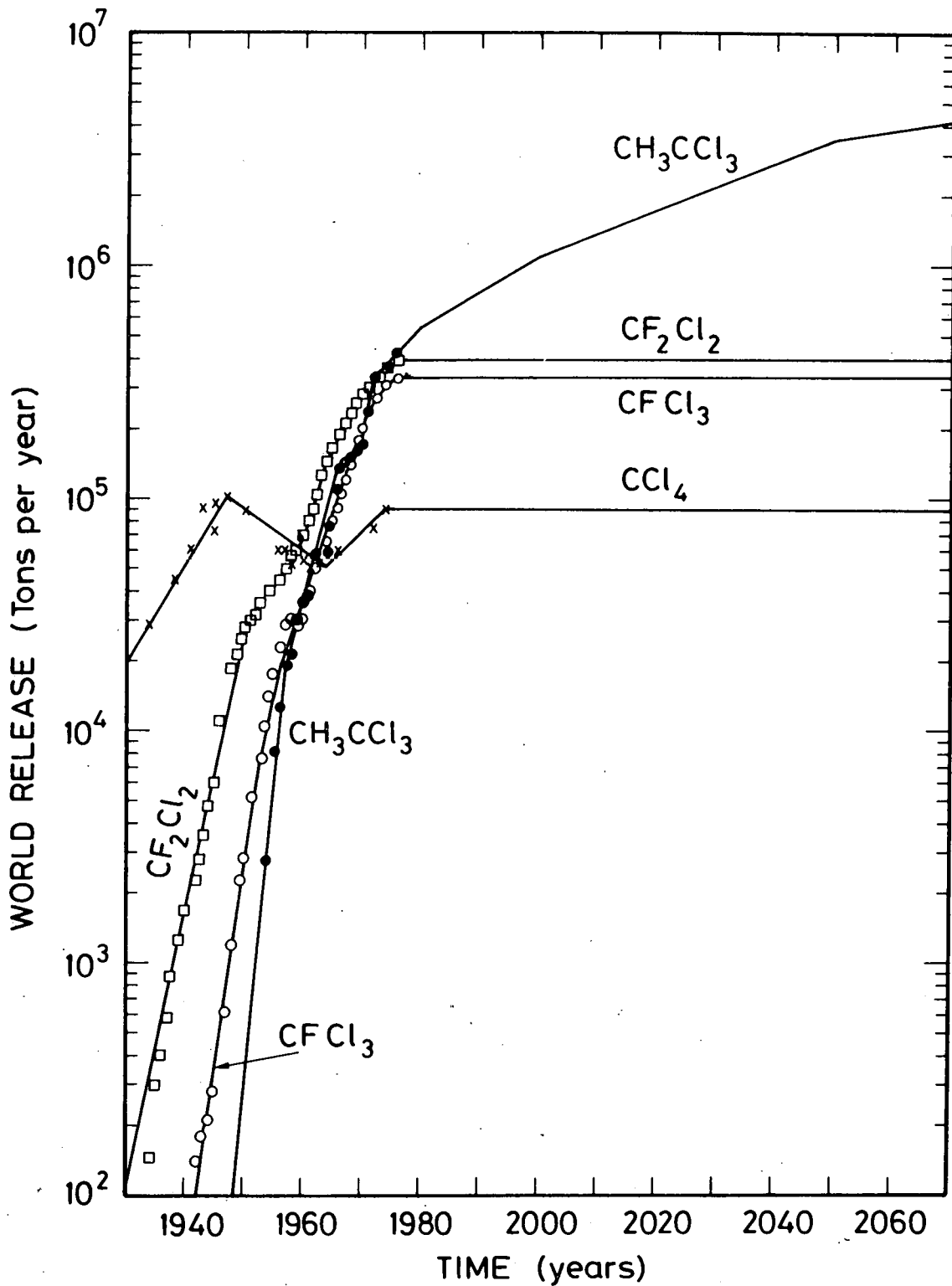


Fig. 5.- Historical release and assumed, future emission of different halocarbons adopted as scenario for the perturbation calculations (Logan et al. (1978).

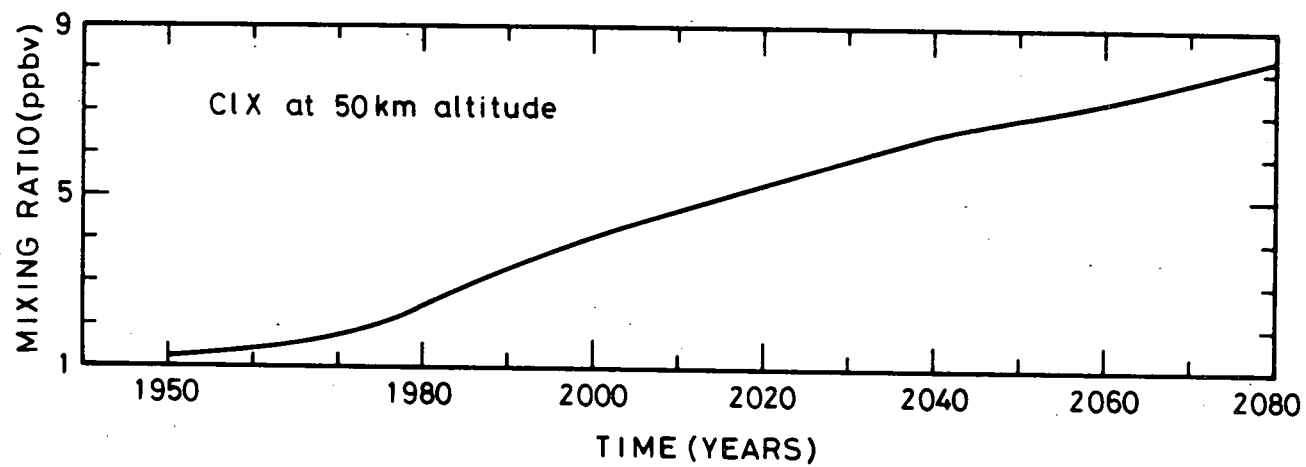


Fig. 6.- Variation of the ClX mixing ratio in the upper stratosphere derived for the halocarbon release shown in Fig. 5.

The Chapman scheme, which has been described previously, does not explicitly consider the electronic state of the oxygen atoms which are produced. When the wavelength of the incident radiation is shorter than 310 nm, the photodissociation of ozone leads to excited atomic oxygen O(¹D). The atoms are rapidly quenched by the major gases N₂ and O₂. However a small fraction of them react with several trace species and initiate several reaction chains which will be discussed hereafter.

OZONE AND TEMPERATURE

Assuming again a pure oxygen atmosphere, a relation between the ozone concentration and the temperature can be deduced from expression (4) by considering the numerical values of k₂ and k₃ as a function of the temperature, namely

$$\frac{\Delta n(O_3)}{n(O_3)} = -\frac{1400}{T^2} \Delta T \quad (9)$$

If the temperature at the stratopause (270°K) were increased by 10°K, the ozone concentration would be reduced by about 20 percent. This value however has to be considered as an upper limit since the introduction of a more detailed chemical scheme reduces the sensitivity of ozone to temperature. Nevertheless, when considering the action of ozone-depleting agents, the temperature feedback should be introduced in the computation. Since the heating rate is directly proportional to the amount of ozone (Fig. 4) expression (9) introduces a negative feedback mechanism which stabilizes ozone against several chemical agents. However, it introduces a relation between the O₃ and CO₂ amounts. This latter gas, which emits infrared radiation due to its 15 μm band, is responsible for most of the cooling in the vicinity of the stratopause (Fig. 4). The observed enhancement in the carbon dioxide concentration should lead therefore to an increase in the amount of ozone.

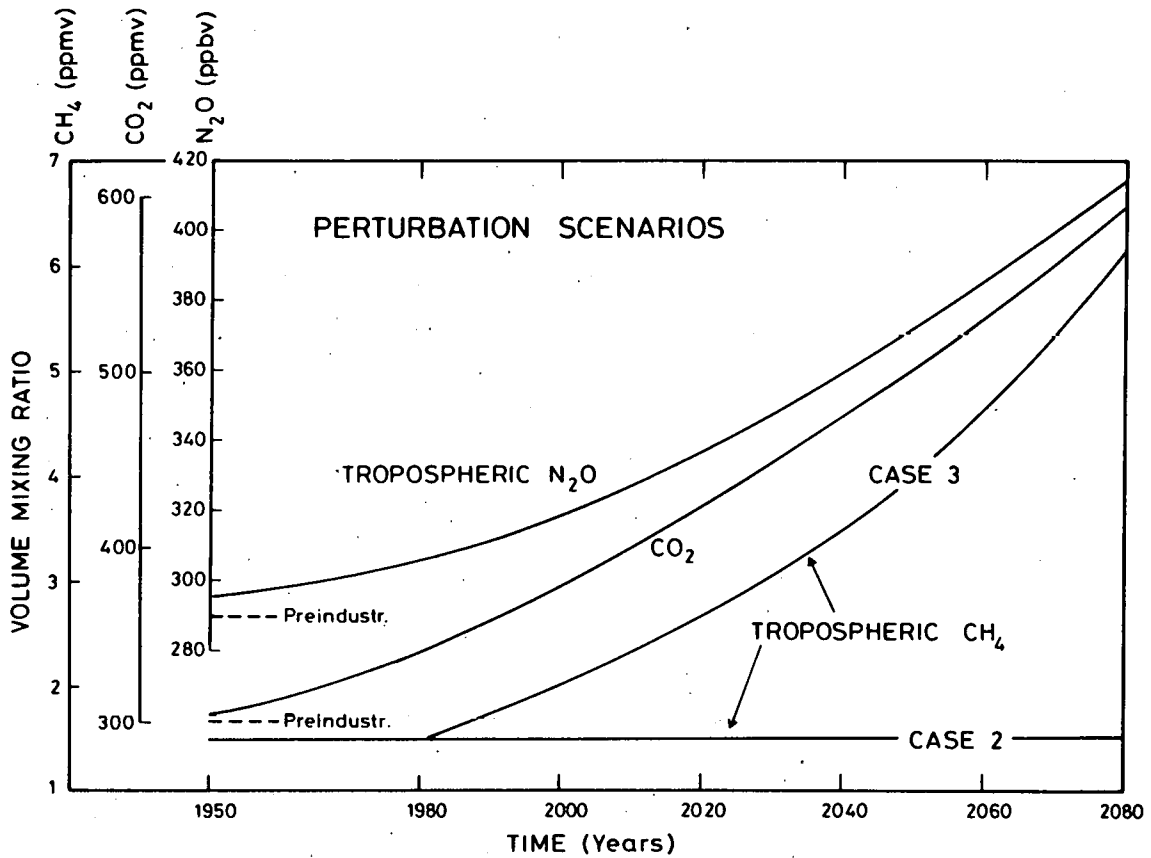
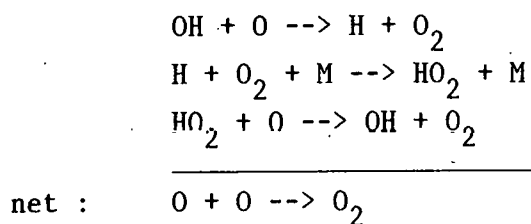


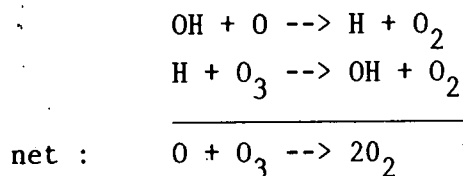
Fig. 7.- Assumed variations in the mixing ratio of N₂O, CO₂ and CH₄ from 1950 to 2080. Case 2 refers to a constant methane content and Case 3 to an increase of 1.5%/yr.

AGENTS OF OZONE DEPLETION

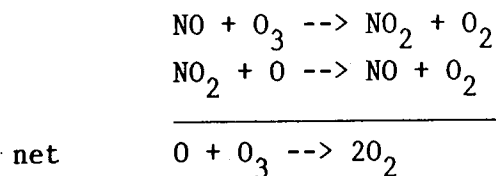
The loss of odd oxygen ($O + O_3$), namely the recombination of ozone and atomic oxygen ($O + O_3 \rightarrow 2O_2$) can be catalyzed in the presence of hydroxyl radicals (OH), nitric oxide (NO) and chlorine oxide (ClO). Different cycles have to be considered with specific efficiencies depending on the altitude. In the mesosphere the main destruction of odd oxygen is due to the hydrogen species :



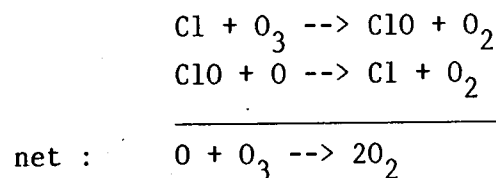
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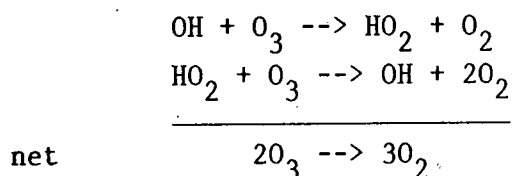
(Bates and Nicolet 1950; Nicolet 1971) while, in the stratosphere, the most efficient processes are



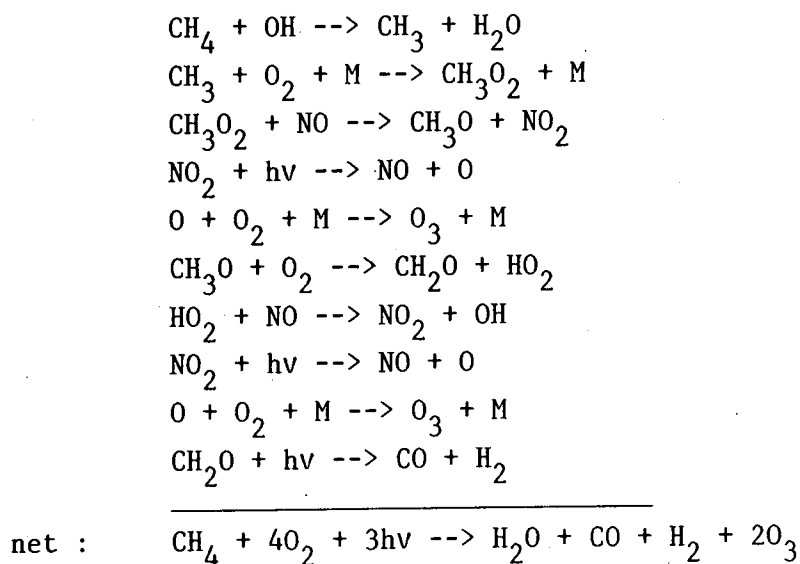
(Crutzen 1970; Johnston 1971; Nicolet 1971) or



(Stolarski and Cicerone 1974). In the lower stratosphere, and particularly near the tropopause, other cycles involving odd hydrogen have to be considered (Nicolet 1975), for example :



Supplementary reaction chains involving species such as NO_3 , N_2O_5 , HOCl , ClONO_2 , etc... can also be introduced (see Brasseur 1982 for a comprehensive review of these cycles), showing the complexity of the ozone chemistry in the stratosphere. Furthermore, in the troposphere and in the lower stratosphere, additional ozone resulting from the oxidation of methane in the presence of nitric oxide has to be considered. The reaction chain is



(Crutzen 1974; Nicolet 1975). The equilibrium concentration of ozone depends on the amount of catalytic agents which are present in the atmosphere. Above 30 km expression (4) can still be used if the k_3 coefficient is replaced by an effective recombination rate

$$k_{3A} = k_3 [1 + A] \quad (10)$$

where A is a correction factor which is given to a first approximation by

$$A = \frac{a_5 n(\text{OH}) + b_3 n(\text{NO}_2) + d_3 n(\text{ClO})}{k_3 n(\text{O})} \quad (11)$$

a_5 , b_3 and d_3 being the rate constants of reaction $\text{O} + \text{OH}$, $\text{O} + \text{NO}_2$ and $\text{O} + \text{ClO}$ (Nicolet 1971). In the middle and lower stratosphere where the transport can no longer be neglected, a general continuity equation must be used, namely

$$\frac{\partial n(\text{O}_3)}{\partial t} + \vec{\nabla} \cdot \vec{\phi} = 2J_2 n(\text{O}_2) + a_{26} n(\text{HO}_2) n(\text{NO}) + c_5 n(\text{CH}_3\text{O}_2) n(\text{NO}) - [2k_3 n(\text{O}) n(\text{O}_3) + a_5 n(\text{OH}) n(\text{O}) + a_6 n(\text{OH}) n(\text{O}_3) + a_{6b} n(\text{HO}_2) n(\text{O}_3) + a_7 n(\text{HO}_2) n(\text{O}) + 2b_3 n(\text{NO}_2) n(\text{O}) + 2d_3 n(\text{ClO}) n(\text{O})] \quad (12)$$

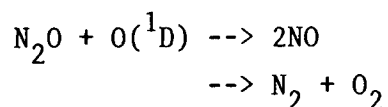
assuming that $n(\text{O}_x) \cong n(\text{O}_3)$ in this altitude range. The value of the individual rate constants is given in Table 1.

As shown by these latter expressions, a detailed understanding of the ozone balance requires a study of the processes which are responsible for the formation and the destruction of the radicals which are involved (Cariolle 1983). This problem is not yet completely solved since, as indicated by Schmailzl and Crutzen (this volume), some inconsistencies in the description of the ozone budget remain.

The major mesospheric source of odd hydrogen (H , OH , HO_2) is the photodissociation of water vapor while, in the stratosphere, the main production mechanism of HO_x is the oxidation of water vapor, methane and molecular hydrogen by the excited oxygen atom $\text{O}(^1\text{D})$.

Consequently an increase in the methane amount as a function of time should lead to an ozone reduction in the mesosphere and upper stratosphere where OH is the main depleting agent of O₃, and to an ozone increase in the troposphere where the reaction chain involving methane and nitric oxide (see previous description) plays a dominant role.

Nitric oxide in the stratosphere is also produced by the O(¹D) atoms which dissociate nitrous oxide as follows :



The N₂O molecules are produced at ground level by bacterial processes associated with complex nitrification and denitrification mechanisms in soils. Since the industrial fixation of nitrogen can no longer be neglected in comparison to the corresponding natural processes, it is now believed that the future anthropogenic production of N₂O, especially through nitrogenous fertilizers, combustion and organic wastes, could perturb the ozonosphere. Direct production of odd nitrogen (N, NO, NO₂, N₂O₅, HNO₃, HO₂NO₂) from aircraft engine emissions should also be considered in the future ozone balance.

Finally the atmospheric release of chlorofluorocarbons is responsible for an increase in the amount of odd chlorine (essentially Cl, ClO, HCl, ClONO₂) and consequently for a depletion in the stratospheric ozone (Molina and Rowland 1974). The most important sources of ClX are the dissociation of CCl₄ (or F-10), CFCl₃ (or F-11), CF₂Cl₂ (or F-12) and CH₃CCl₃, which are anthropogenically produced, and the destruction of the natural CH₃Cl by OH radicals and by sunlight.

MODEL CALCULATIONS OF THE OZONE RESPONSE TO CHEMICAL PERTURBATIONS

Theoretical models are currently used to predict the changes in ozone concentration and in temperature due to the intrusion into the atmosphere of several chemical constituents. These coupled chemical/radiative models have to be validated by comparing the calculated, current concentrations of the different species with the corresponding observed values (see e.g. Brasseur et al. 1982). Although a certain number of discrepancies remain, one should point out the difference in the calculated and observed vertical distribution of several source species such as CFCl_3 , CF_2Cl_2 , N_2O , CH_4 and H_2O , especially in the upper stratosphere. An incorrect treatment of the solar penetration in the O_2 Schumann-Runge bands region could partly explain these discrepancies. Moreover, models do not correctly reproduce the ClO and HNO_3 distribution in the upper stratosphere and results in ozone concentrations above 40 km which are somewhat smaller than the known observed values. These problems among others indicate that the predictions made by models, and especially by one-dimensional approaches, should be considered with care and are subject to quantitative changes as long as some important chemical or photochemical parameters are still inaccurately known.

In order to study the sensitivity of the ozone layer to several chemical agents, a series of individual and coupled scenarios has been applied and the new equilibrium ozone concentration has been calculated. The CFC perturbation (P) corresponds to a constant emission of CFCl_3 (3.4×10^5 T/yr), CF_2Cl_2 (4.1×10^5 T/yr), CCl_4 (1.0×10^5 T/yr) and CH_3CCl_3 (3.6×10^5 T/yr). For the other species (CO_2 , N_2O and CH_4), the current concentration has been uniformly multiplied by two. Table 3 shows the resulting variation in the total ozone column. To estimate the importance of the temperature feedback, which is introduced in most model runs, a number of cases have been

computed using a fixed temperature profile. The results show that, with the presently adopted chemistry, the ozone depletion for a CFC perturbation lies between 3 and 3.5 percent. On the contrary, a doubling in the CO_2 amount leads to an ozone increase of 3.14 percent which is explained by a cooling of the stratosphere. Since the processes which are involved are highly non linear, the two perturbations applied simultaneously do not cancel. The combined effects lead to an ozone depletion of 1.3 percent. The reduction in the O_3 column when the amount of nitrous oxide is doubled, is of the order of 8 percent. When the methane concentration is multiplied by two, the total ozone amount is increased by 1 percent. Finally a combined perturbation of CFC's, CO_2 , N_2O and CH_4 leads to an ozone reduction of 3 percent which is comparable to the corresponding depletion when the sole action of CFC's is considered.

These results, when compared with values obtained previously (NASA 1979; NAS 1979), indicate a larger effect of nitrogen compounds and a smaller influence of the chlorofluorocarbons. These changes can be explained by smaller calculated concentration values of the OH radicals as a result of recent revisions in the reaction rates involved in the odd hydrogen destruction. Smaller OH amount lead to a smaller $n(\text{ClO})/n(\text{HCl})$ ratio and to a larger $n(\text{NO}_2)/n(\text{HNO}_3)$ value.

The perturbations which have been applied are useful to test the model but are rather arbitrary. To predict the future state of the atmosphere would require the introduction of a realistic scenario into the model. Because of the large uncertainties in the projected emissions of the pollutants, different scenarios have been considered. In case 1 only the CFC contribution to the pollution has been considered. Figure 5 shows the historical data and the projected values which have been used for the industrial sources of the several halocarbons which are released in the atmosphere (Logan et al. 1978). The corresponding ClX mixing ratio at the stratopause from year 1950 to year 2080 is reproduced in Fig. 6. The next two cases (2 and 3) consider, together

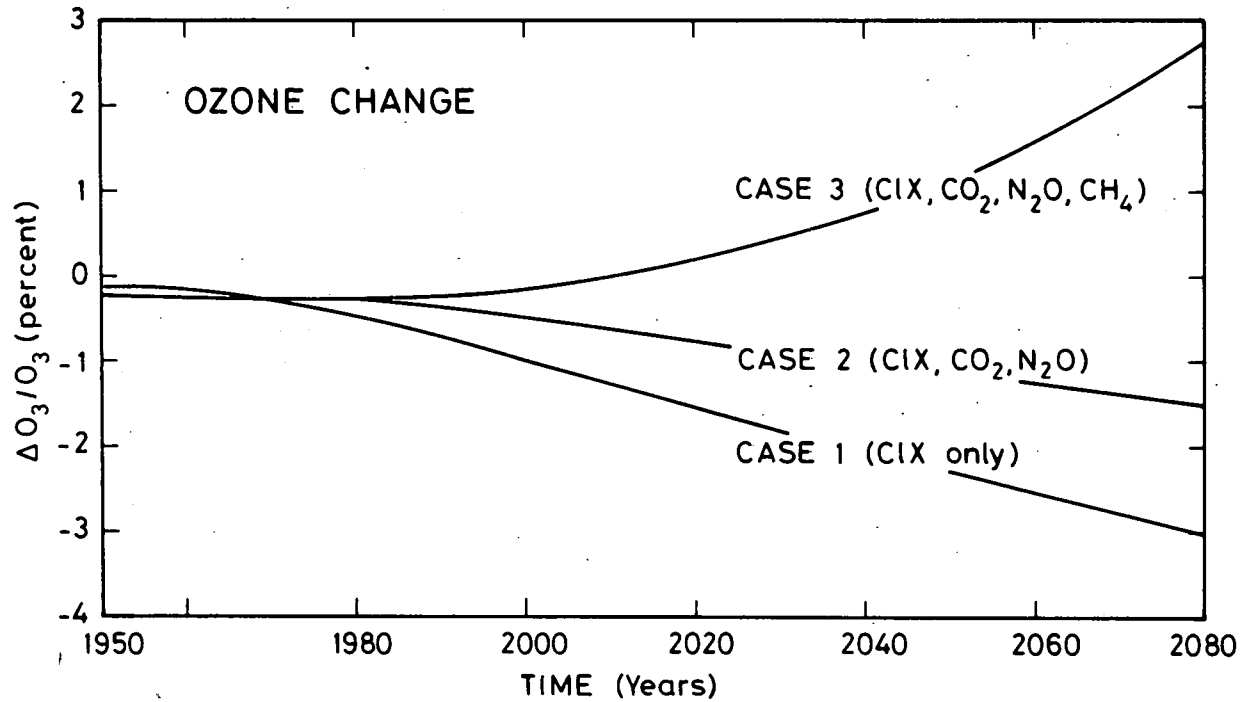


Fig. 8.- Calculated changes (expressed in percent) of the ozone column for three different scenarios. Case 1 refers to a perturbation by halocarbons only, Case 2 takes into account also the increase in the CO₂ and N₂O amount (fig. 7) and Case 3 considers the combined effects of halocarbons, carbon dioxide, nitrous oxide and methane.

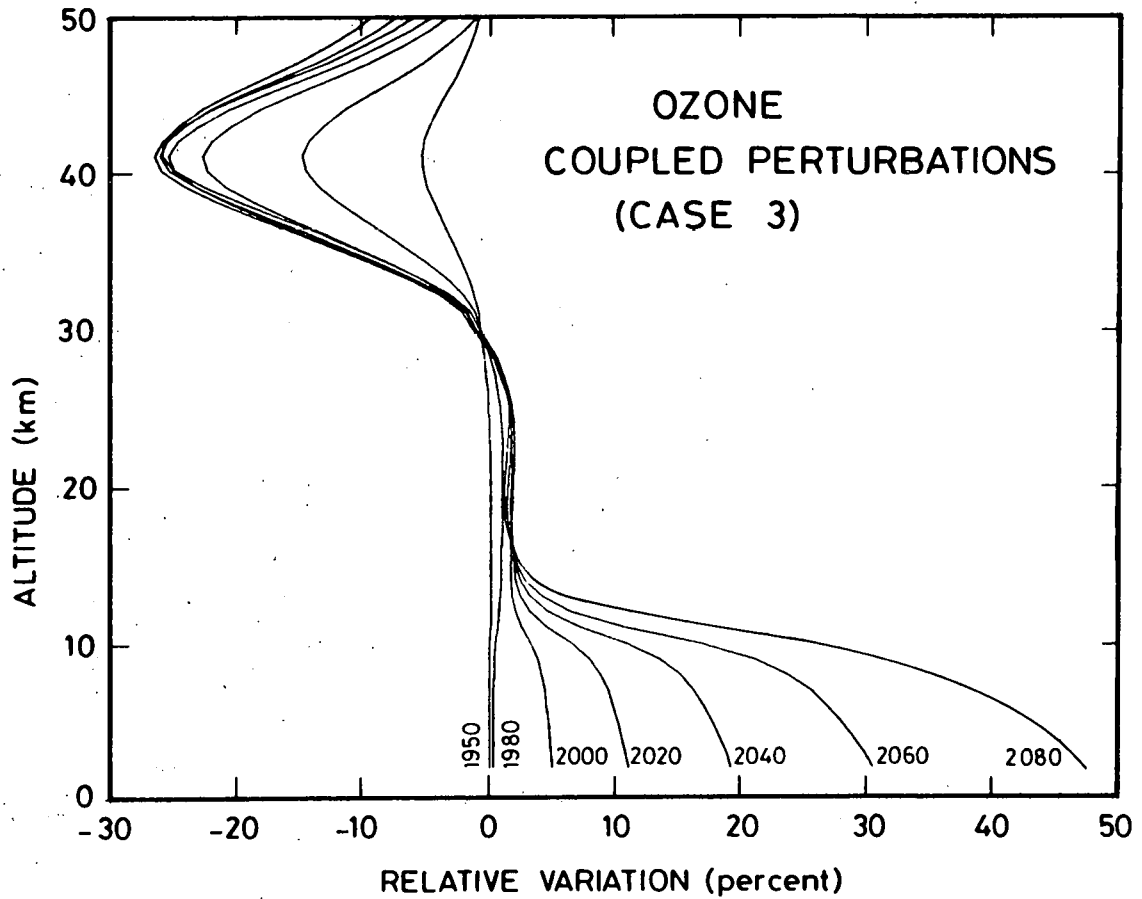


Fig. 9a. Relative variation of the ozone concentration as a function of altitude corresponding to Case 3 (ClX, CO₂, N₂ and CH₄ increase - see Figs. 6 and 7) between years 1950 and 1980.

TABLE 3. Perturbation of the ozone column

Case	CO ₂	N ₂ O	CH ₄	CFC's	Temperature feedback	$\frac{\Delta O_3}{O_3}$	%
A				P ^a	Yes	- 3.50	
A'				P	No	- 3.37	
B	x 2				Yes	+ 3.14	
C		x 2			Yes	- 7.79	
C'		x 2			No	- 8.92	
D			x 2		Yes	+ 0.97	
D'			x 2		No	+ 0.87	
E	x 2			P	Yes	- 1.30	
F		x 2	x 2	P	Yes	- 5.56	
F'		x 2	x 2	P	No	- 6.84	
G	x 2	x 2	x 2	P	Yes	- 3.06	

^a Emission of CFC's.

with the CFC emission, a gradual increase in the CO₂ and N₂O mixing ratio (Fig. 7).

A number of scenarios for the emission of carbon dioxide have been developed (see e.g. Niehaus 1976; Rotty 1977; Council of the Environmental Quality 1981) and are based on the projected fossil fuel usage. The projection adopted in this work is based on the expression suggested by Wuebbles et al (1983) :

$$f(\text{CO}_2) = 335.0 \exp [0.0056(t - 1979)]$$

where $f(\text{CO}_2)$ is the CO₂ mixing ratio expressed in ppmv and t the year. Such an expression leads to a doubling of the CO₂ amount at the end of the 21st century. The past evolution of carbon dioxide is based on historical records (WMO 1977).

Atmospheric measurements carried out in the last decade have shown a systematic increase in the N₂O concentration of about 0.25 percent per year (see e.g. Weiss 1981; Khalil and Rasmussen 1981, 1983). It has been assumed that such a growth rate will remain constant until 2080.

The existence of a systematic trend in the methane amount is subject to discussion. Analyzing a series of measurements made in the past decade and taking into account several corrections made for older data, Ehhalt (1983) does not derive any significant change in the CH₄ mixing ratio. However, continuous observations made in recent years by Rasmussen and Khalil (1981), Blake et al. (1982) and Rowland (1983) definitely show an increase of 1 to 2 percent per year. Because of the present difficulty in proposing a future trend in the CH₄ concentration, two scenarios have been considered : in Case 2 the amount of atmospheric methane remains constant (mixing ratio of 1.5 ppmv) while in Case 3 a continuous growth of 1.5 percent/year has been applied after 1970.

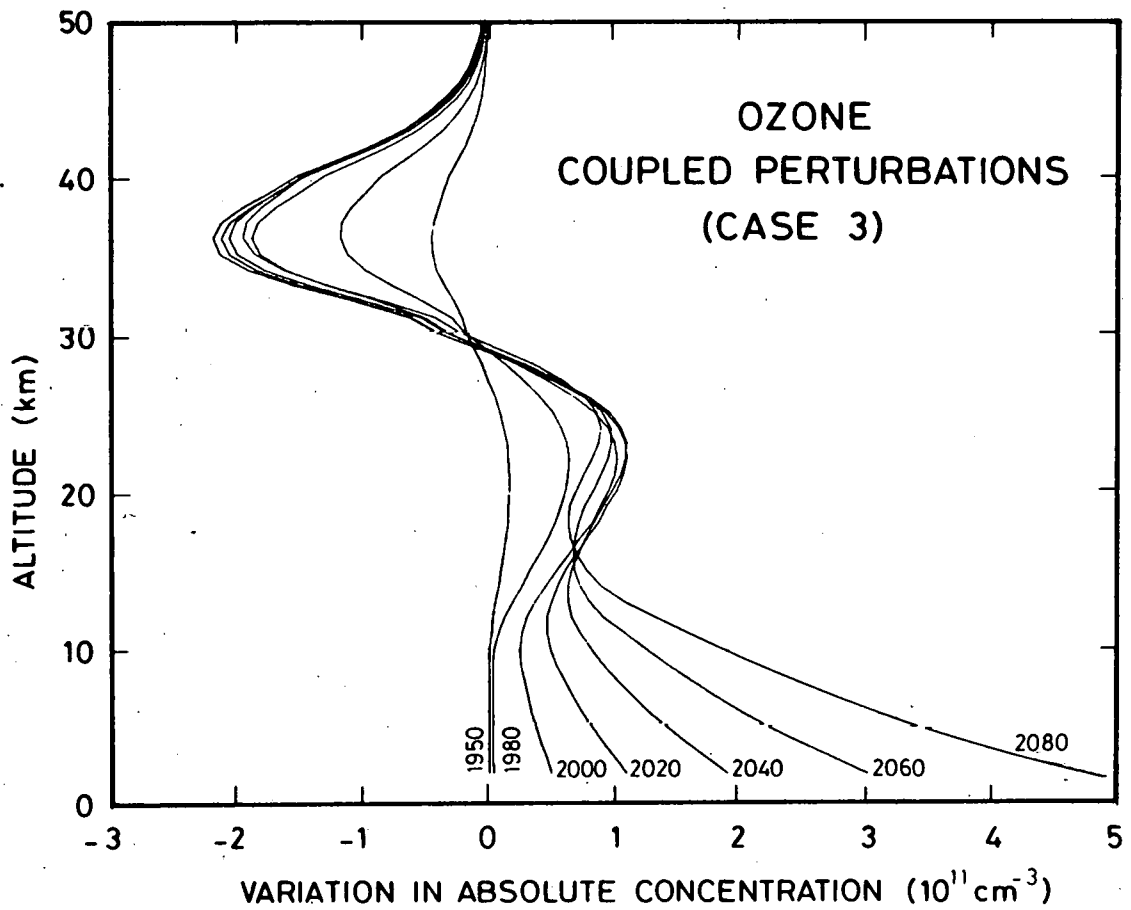


Fig. 9b.- Same as in Fig. 9a but for the absolute variation in the ozone concentration.

The response of ozone and temperature for these three scenarios has been determined by using a coupled chemical and radiative one-dimensional model. This model includes a detailed chemical and photochemical scheme taking into account the action of the oxygen, hydrogen, nitrogen, chlorine and carbon species (Brasseur et al. 1982). The vertical temperature profile is derived from a thermal scheme in which heating is calculated using the parameterization suggested by Schoeberl and Strobel (1978). The radiative transfer in the infrared is treated by determining the transmission function in four large spectral intervals. The upward and downward infrared flux, as well as the corresponding cooling rates, are obtained by solving the radiative transfer equation. An energy balance is achieved at the top of the atmosphere assuming a global earth-atmosphere albedo of 0.3. The model extends from 0 to 70 km. the vertical transport of the trace species and of heat (especially in the troposphere where convective instability appears) is parameterized by means of an eddy diffusion coefficient.

The change in the ozone column relative to a preindustrial atmosphere is shown in Fig. 8. When only a continuous injection of CFC's is considered (Case 1) the ozone amount decreases gradually and the corresponding depletion reaches 3 percent in year 2080. When the increase in CO_2 and N_2O is added to the CFC's emission (Case 2), the decrease in the ozone column is somewhat reduced (1.5 percent in year 2080). However, as shown by Fig. 9a and b, this enhancement results from an increase in the troposphere and a simultaneous decrease in the upper stratosphere. It should be noted however that, at these levels, the presence of a large quantity of methane prevents the chlorine species from depleting the ozone. This is explained by the fact that methane, when sufficiently abundant, converts the active chlorine atoms into inactive HCl molecules. Moreover, the simultaneous introduction of nitrogen and chlorine oxides leads to the formation of ClONO_2 in the middle and lower stratosphere. The ClONO_2 molecule acts as a temporary reservoir for both CIX and NO_x and its presence therefore

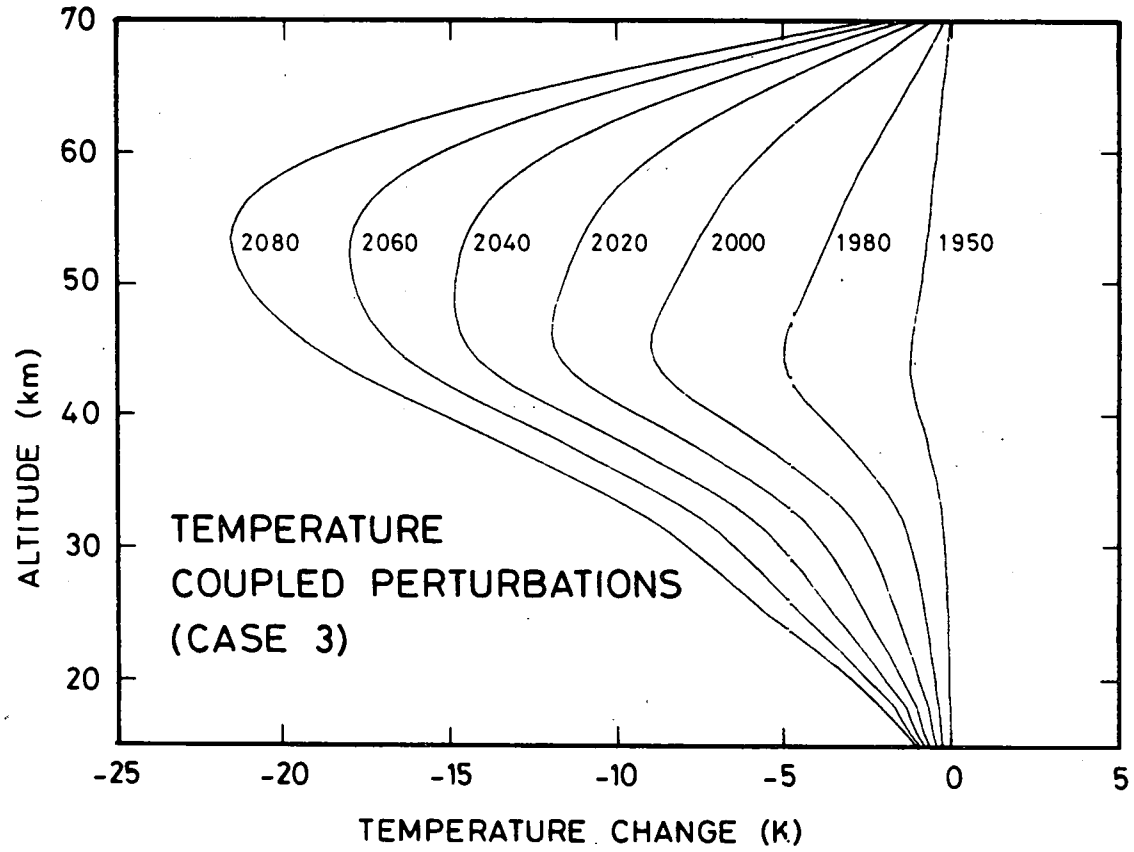


Fig. 9c.- Same as in Fig. 9a but for temperature.

introduces a nonlinear effect in the ozone depletion problem. Finally, the model calculations show that, in the presence of a large CIX concentration, the efficiency of CO_2 in increasing the ozone concentration by cooling the stratosphere is considerably reduced since the sensitivity of O_3 to temperature becomes very small when the loss rate of O_3 is reaction (d_3) instead of (k_3). Equation (9) must be modified when the correction factor A (Eq. 11) becomes equal to or greater than 1 (Haigh and Pyle 1982).

The calculated change in the stratospheric temperature corresponding to case 3 is shown in Fig. 9c. It results from both the reduction in the ozone concentration (less UV absorption and less heating) and the increase in the CO_2 amount (more IR emission and more cooling). These quantitative results depend on the scenarios which are adopted and on the relative contribution of O_3 and CO_2 in the cooling processes.

In the troposphere the introduction of molecular species such as CO_2 , N_2O , CH_4 and CFC's, which are optically active in the infrared, enhances the greenhouse effect and should somewhat increase the averaged temperature at ground level. These climatic changes, although very important for the world's future, will not be treated here. Most radiative-convective models suggest, for a doubling of CO_2 , a temperature increase at the Earth's surface of 1 to 3°K (see Ramanathan 1981). It is usually believed that in the future the combined effect of the other trace gases (N_2O , CH_4 and CFC's) could modify the temperature by a value which is comparable to that inferred by the CO_2 increase.

SUMMARY

Ozone drives a number of important mechanisms occurring in the atmosphere and involving chemical, radiative, thermal and dynamic processes. Since this gas is a strong absorber of UV radiation, its

depletion by several chemical agents leads to an increase in the abiotic radiation level at the Earth's surface. It is, for example, generally assumed (see NAS 1975) that the percentage change of the erythemal ultraviolet at ground level would be about twice the percentage ozone decrease. Agricultural and industrial activity is responsible for the emission of several gases which modify the morphology of the ozone layer and consequently the penetration of ultraviolet radiation. Determination of the quantitative ozone change requires complex models taking into account many interactive processes and feedback mechanisms. The models are based on laboratory data which are measured with a certain degree of uncertainty and on phenomenological parameters which are sometimes poorly known. Consequently the model results should be associated with an uncertainty which is difficult to determine because of the large number of processes which are involved.

ACKNOWLEDGEMENTS

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