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Instantaneous Photochemical Rates in the Global Stratosphere

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Abstract

Starting with the average, actual distribution of ozone (Dütsch, 1969) and temperature in the stratosphere, we have calculated the solar intensity as a function of wavelength and the instantaneous rates (molecules cm^{-3} sec^{-1}) for each Chapman reaction and for each of several reactions of the oxides of nitrogen. The calculation is similar to that of Brewer and Wilson (1968). These reaction rates were calculated independently in each volume element in spherical polar coordinates defined by $\Delta\Omega$ = 1 kilometer from zero to 50, $\Delta\theta$ = 5° latitude, and $\Delta\phi$ = 15° longitude (thus including day and night conditions). Calculations were made for two times: summer-winter (January 15) and spring-fall (March 22). As input data we take observed solar intensities (Ackerman, 1971) and observed, critically evaluated constants for elementary chemical and photochemical reactions; no adjustable parameters are employed. (These are not "photochemical equilibrium" calculations). According to the Chapman model, the instantaneous, integrated world-wide rate of formation of ozone from sunlight is about five times faster than the rate of ozone destruction, and locally (lower tropical stratosphere) the rate of ozone formation exceeds the rate of destruction by a factor as great as 1000. The global rates of increase of ozone are more than 50 times faster than Brewer and Wilson's (1968) estimate of the average annual transfer rate of ozone to the troposphere. The rate constants of the Chapman reactions are believed to be well-enough known that it is highly improbable that these

discrepancies are due to erroneous rate constants. It is concluded that something else besides neutral oxygen species is very important in stratospheric ozone photochemistry. The inclusion of a uniform concentration of the oxides of nitrogen (NO_x as NO and NO_2) averaging 6.6×10^{-9} mole fraction gives a balance between global ozone formation and destruction rates. The inclusion of a uniform mole fraction of NO_x at 28×10^{-9} also gives a global balance. These calculations support the hypothesis (Crtuzen, Johnston) that the oxides of nitrogen are the most important factor in the global, natural ozone balance. Several authors have recently evaluated the natural source strength of NO_x in the stratosphere; the projected fleets of supersonic transports would constitute an artificial source of NO_x about equal to the natural value, thus promising more or less to double an active natural stratospheric ingredient.

Introduction

Dütsch (1969) has published a review of global ozone distributions, the (Chapman, 1930) photochemical theory of ozone formation (equilibrium and non-equilibrium), and the role of lateral transport in the stratosphere in shaping the distribution of ozone in terms of latitude and season. The details of this review will not be repeated here, but certain stages of Dütsch's analysis will be copied down for ready reference.

Under conditions of the stratosphere Chapman's photochemical theory of ozone formation and destruction is given by four chemical equations

$$O_2 + h\nu \xrightarrow{f_2} O + O \tag{1}$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M$$

$$O_3 + h\nu \xrightarrow{f_3} O_2 + O$$

$$O + O_3 \xrightarrow{k_3} O_2 + O_2$$

The reaction rates for each chemical reaction are respectively

$$-\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[O]}{dt} = f_2[O_2] \tag{2}$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] \tag{3}$$

$$-\frac{d[O_3]}{dt} = f_3[O_3] \tag{4}$$

$$-\frac{d[O_3]}{dt} = k_3[O][O_3] \tag{5}$$

Dütsch gave a clear explanation of the meaning of the photochemical rate coefficients f_2 and f_3. Also he pointed out that oxygen atoms very rapidly (seconds) attain a steady-state concentration with respect to the local ozone

$$[O]_s/[O_3] = f_3/k_2[O_2][M] \tag{6}$$

Ozone, on the other hand, has a characteristic time that is highly variable with elevation. Ozone is potentially capable of attaining a steady-state concentration

$$\frac{[O_3]_s}{[O_2]} = \left(\frac{f_2\ k_2[M]}{f_3\ k_3}\right)^{1/2} \tag{7}$$

The relaxation time (time for half-restoration to equilibrium) is given as

$$\tau = \frac{1}{4}\left(\frac{k_2[M]}{f_2\ f_3}\right)^{1/2} \tag{8}$$

Dütsch's Table I lists these half-times as a function of latitude, season, and elevation. Typically the times are a few hours at 45 km, a few days at 35 km, a few months at 25 km, and many years at 15 km. Air motions in the stratosphere are much faster than photochemistry in the lower stratosphere, but the photochemical reactions are fast in the upper stratosphere so the photochemical steady state should be very closely approximated above 35 km.

As noted by Dütsch (1969): "There is complete disagreement between theory and observation with respect to seasonal and latitudinal variations...it has become clear that the redistribution of ozone by air motions produces the above-mentioned discrepancies."

The purpose of this paper is to re-examine (in light of recent laboratory results) the question as to whether the Chapman model is adequate to predict the observed values for the total ozone content if averaged over the globe and over the year. In making this comparison it is desirable, so far as possible, to get around the difficult problem of air motions and air transport inside the stratosphere. There is relatively little transport in one second, and thus we have calculated instantaneous (one second), world-wide rates of elementary chemical reactions based on observed ozone distributions. Integration over the entire volume of the stratosphere cancels out the effect of transport from one part of the stratosphere to another, and thus we integrate the instantaneous photochemical rates over the global stratosphere. Recently there have been significant improvements in the laboratory determinations of k_2 and k_3 and redeterminations of solar intensities and ultraviolet absorption cross sections. The actual ozone distributions and the parameters of the four Chapman reactions are now so well known that a sharp test of the global sufficiency of the Chapman model should be possible.

Computational Method

The computational method is similar to that of Brewer and Wilson (1968). We start with the measured, average distribution of ozone (Dütsch, 1969), between 75°N and 75°S and from 0 to 40 km. Dutsch's values of ozone were extrapolated to the poles, and they were extended to 50 km from profiles obtained in rocket flights by Johnson, Purcell, and Tousey (1954). The global ozone distributions for March 22 and January 15 are given as Figures 1 and 2. A standard temperature distribution for March 22 (Crutcher, 1969; Handbook of Geophysics, 1960) is given by Figure 3, and a temperature distribution for January 15 was obtained from Standard Supplemental Atmospheric

Data (Sissenwine, 1969). The distribution of oxygen and total gas was obtained from Sissenewine (1969). We set up an extensive grid over the globe (every 5° latitude, every 15° longitude, and every kilometer from 0 to 50), and we assume uniform composition, temperature, and photochemical rate constants inside each of the 43000 volume elements. We let a planar wave of sunlight (Ackerman, 1971) impinge on the spherical earth. We calculate the radiation density for each nanometer of solar radiation above 190 nm in each volume element, taking account of all overhead absorbing species. We calculate the steady-state oxygen-atom concentration, Figure 4, according to Equation (6). When the oxides of nitrogen, NO and NO_2, are assumed to be present, their dominant reactions are:

$$NO_2 + h\nu \xrightarrow{f_4} NO + O \tag{9}$$

$$NO + O_3 \xrightarrow{k_4} NO_2 + O_2$$

$$NO_2 + O \xrightarrow{k_5} NO + O_2$$

and these reactions rapidly (restoration half time is a few minutes) determine the steady-state ratio of NO and of NO_2 to the total NO_x

$$\frac{[NO]_s}{[NO_x]} = \frac{f_4 + k_5[O]}{f_4 + k_4[O_3] + k_5[O]} \tag{10}$$

$$\frac{[NO_2]_s}{[NO_x]} = \frac{k_4[O_3]}{f_4 + k_4[O_3] + k_5[O]} \tag{11}$$

Atmospheric input data are the observed distribution of T, $[O_2]$, [M], $[O_3]$, and sunlight above the atmosphere; and also input data

may be an assumed concentration of NO_x. Laboratory input data are: (1) light absorption cross sections and quantum yields for O_2, O_3 (Ackerman, 1971), and NO_2 (Leighton, 1961; Graham, 1972) and (2) rate constants for reactions 2, 3, 4, and 5 listed above and for the further, minor reactions

$$NO_2 + O_3 \xrightarrow{k_6} NO_3 + O_2 \qquad (12)$$

$$NO_3 + h\nu \xrightarrow{f_5} NO + O_2 \quad \text{(day)}$$

$$2NO + O_2 \xrightarrow{k_7} 2NO_2$$

$$NO + O + M \xrightarrow{k_8} NO_2 + M$$

The rate constants for the chemical reactions with references are given in Table 1.

In each volume element of the atmosphere, we calculate the concentration of oxygen atoms (Equation 6), the ratio of NO to NO_2, and the photon flux. The photon flux is that appropriate for the given elevation and longitude (local hour of day). The ozone and oxygen concentrations are the observed, average values. Then we calculate a world-wide, instantaneous (one second) rate for each of the 12 elementary reactions listed as Equations (1), (9) and (12). (Also, we have calculated rates of singlet oxygen atoms, hydroxyl radicals, nitric acid reactions, etc, but these reactions do not affect the present argument.) These instantaneous rates are independent, uncoupled, and relatively unaffected by atmospheric motions. We carry out a zonal average of these rates, integrating over longitude for fixed latitude and elevation. These results

are presented as contour lines on maps of latitude versus elevation. This procedure was carried out for the entire globe for the average conditions on January 15 (winter-summer) and March 22 (spring-fall). Note specifically that we did not determine the average light intensity and then find the zonal average rate; rather, we calculated the light flux and reaction rates in each volume element corresponding to each of the local 24 hours and then carried out the appropriate summations. Also note specifically that these are <u>not</u> "equilibrium" photochemical calculations for ozone.

Further integration over elevation from the tropopause to the stratopause gave vertical column rates, and integration over latitude gave hemispherical or global stratospheric rates.

Chapman Reactions Alone

The instantaneous rate of global photolysis of oxygen is given as Figure 5. This reaction is rapidly and quantitatively followed by the formation of ozone

$$O_2 + h\nu \xrightarrow{f_2} O + O$$

$$\underline{(O + O_2 + M \xrightarrow{k_2} O_3 + M) \text{ twice}}$$

$$\text{Result: } 3O_2 + h\nu \rightarrow 2O_3$$

At all locations in the stratosphere the second reaction is much faster than the first. The net effect of the photolysis of oxygen is the formation of two molecules of ozone. The <u>gross</u> instantaneous rate of formation of ozone is twice the rate of the elementary reaction given by Figure 5:

$$h\nu + O_2 \xrightarrow[\text{slow}]{f_2} 2O \xrightarrow[\text{fast}]{O_2} 2O_3 \tag{13}$$

The rate of photolysis of ozone

$$O_3 + h\nu \xrightarrow{f_3} O_2 + O$$

which is essentially equal to the rate of its reformation

$$O + O_2 + M \xrightarrow{k_2} O_3 + M$$

is given by Figure 6. A comparison of Figure 6 with Figure 5 shows that throughout the stratosphere, ozone is photolyzed very much faster than oxygen is photolyzed.

The rate of ozone destruction according to the Chapman reactions is $k_3[O][O_3]$, and this rate can be found by multiplying k_3 times $[O]$ times $[O_3]$ in each volume element. The more interesting quantity, however, is the net rate of production of odd oxygen, which is the net rate of production of ozone in the stratosphere

$$\frac{d([O_3] + [O])}{dt} = 2f_2[O_2] - 2k_3[O][O_3] \tag{14}$$

The difference given by Equation (14) is referred to as the <u>net</u> rate of ozone production, whereas the term $2f_2[O_2]$ alone is the <u>gross</u> rate of ozone production. The net rate of ozone production for spring-fall conditions is given by Figure 7. Where this quantity is positive, ozone is produced photochemically faster than it is being destroyed by the Chapman reaction; a positive net rate is often referred to as indicating a "source region" for ozone with respect to transport to other locations. A negative sign in Figure 7 indicates a region where ozone is destroyed by the reaction $O + O_3$ faster than it is being formed photochemically.

A striking feature of Figure 7 is that it is positive over almost all of the stratosphere. At each volume element the balance of rates may be expressed as

$$\frac{d([O_3]+[O])}{dt} = 2f_2[O_2] - \begin{matrix}\text{chemical}\\ \text{loss}\end{matrix} - \begin{matrix}\text{transport}\\ \text{loss}\end{matrix} \qquad (15)$$

To analyze the vertical and horizontal transport of ozone for each volume element is an exceedingly difficult job. However, transport out of one volume element contributes transport into neighboring volume elements, and for some considerations the integral of Equation (15) over the entire stratosphere is simpler than the individual terms. The integral over all of the stratosphere may be interpreted as

$$\begin{matrix}\text{Global rate of}\\ \text{ozone change}\end{matrix} = \int \begin{matrix}\text{gross rate}\\ \text{of } O_3 \text{ formation}\end{matrix} - \int \begin{matrix}\text{chemical}\\ \text{loss}\end{matrix} - \int \begin{matrix}\text{transport to}\\ \text{troposphere}\end{matrix} \qquad (16)$$

Each term in Equation (16) can be evaluated, except for the integral of chemical destruction, which can then be inferred by difference.

The "integrated gross rate of O_3 formation", in Equation (16) is the integral of $2f_2[O_2]$ over longitude, latitude, and elevation. This integral was evaluated for each hemisphere, for the globe, as of January 15, and as of March 22. These data are given as the first line in Table 2. These gross rates of formation are about 500×10^{29} molecules sec^{-1} for the world.

The "global rate of ozone change" in Equation (16) can be evaluated as the slope of a plot of total observed ozone against the months of the year, or the hemispherical rate of ozone change

can be found as the slope of a similar plot for each hemisphere. Brewer and Wilson (1968) evaluated just the desired terms for the northern and southern winter hemispheres from the data for 1966, and their values are entered for January 15 in Table 2. The total ozone in the northern hemisphere--derived from Dobson (1968)--was plotted as a function of the month of the year, Figure 8. The slope of the function at March 22 in Figure 8 is entered in Table 2 as the "global rate of ozone change" for the northern hemisphere on March 22, and the slope of the function on September 22 is entered in Table 2 as an approximation to the southern hemisphere for March 22. The rate of change of the global ozone inventory is the order of magnitude of $\pm 4\times10^{29}$ molecules sec^{-1}, which is less than one percent of the gross rate of ozone formation (The net rate of ozone formation according to the Chapman model is indicated by the slope of the arrows in Figure 8; the unbalanced ozone formation rate is far faster, steeper slope, than the seasonal rates of change).

The volume integral of ozone transport over the entire stratosphere is simply the surface integral of the flux across the boundaries. It is assumed that the flux of ozone across the stratopause is negligible in that region of fast photochemical reactions and presumably a photochemical steady state. Thus the last term in Equation (16) is the total transport of ozone across the tropopause into the troposphere. This quantity has been estimated several times in the meteorological literature. For example, Paetzold (1959) estimated the average flux of ozone across the tropopause to be between $(0.1 \text{ and } 1)\times10^{11}$ molecules cm^{-3} sec^{-1}, or $(0.5 \text{ to } 5)\times10^{29}$ molecules sec^{-1} for the globe. Brewer and

Wilson (1968) estimate about 6×10^{29} molecules sec^{-1} as the mean destruction rate over the year for the entire troposphere. We adopt Brewer and Wilson's value of 6×10^{29} molecules sec^{-1}. This rate is slightly larger than one percent of the gross rate of ozone formation.

Brewer and Wilson (1968) also estimated the flux of ozone between the northern and southern hemisphere, and these quantities are also given in Table 2. They vary between $(-4 \text{ to } 4)\times10^{29}$ molecules sec^{-1}.

The "actual rate of chemical loss" of stratospheric ozone is calculated in Table 2 as the difference between the gross rate of formation, the loss to the troposphere by air motions, and the seasonal change. The rate of chemical loss of ozone according to the Chapman mechanism is the integral of twice the rate of the reaction $O + O_3 \rightarrow O_2 + O_2$, and the integrals of these instantaneous rates are also given in Table 2. For the entire globe, these integrated rates are about 90×10^{29} molecules sec^{-1}, which is very much less than the inferred "actual rate of chemical loss" of ozone. The ratio of the total instantaneous chemical loss of ozone to the loss according to the Chapman mechanism is about 5 for each hemisphere. The chemical destruction of ozone by chemical processes other than the Chapman reactions are about 400×10^{29} molecules sec^{-1}, over 80% of the total chemical destruction rate.

The discrepancy between the total chemical destruction of ozone and that brought about by the Chapman reactions is a major effect. "Something else"--besides pure air--destroys ozone 5 times faster than ozone is destroyed by pure air species. "Something else"

destroyes ozone over 50 times faster than transport to the troposphere and the seasonal variation rate.

This problem has been encountered many times in the past. When the problem first appeared about 15 years ago, the laboratory chemical results were uncertain and represented long temperature extrapolation, Dütsch (1961). By the mid 1960's the laboratory results had enough force to call for a careful scrutiny of the problem. The "water reactions" were considered by several investigators, for example, Hunt (1965, 1966). Recent laboratory work by Langley and McGrath (1971) shows that the water reactions are insufficient (by a large margin) to explain the discrepancy.

Brewer and Wilson (1968) were able to explain the integrated global discrepancy by simultaneously including the water reactions, reducing the solar flux to the lowest probable value, and assuming values for the rate constant ratio k_3/k_2 that was five times larger than current laboratory values. However, Brewer and Wilson were dissatisfied with the resultant distribution of ozone sources and sinks in the stratosphere. In view of recent redeterminations of the rate constant, k_2 and k_3, Brewer and Wilson's rate constants are no longer acceptable, and thus their global balance would be unsatisfactory, as well as the local distribution.

Crutzen (1970, 1971) and Johnston (1971) proposed that the discrepancy could be explained by the oxides of nitrogen. In the next section, we ask how much oxides of nitrogen are required to remove the discrepancy between global, instantaneous ozone production and destruction.

Oxides of Nitrogen

When oxides of nitrogen are considered in addition to the Chapman reactions, the rate equation for odd oxygen is

$$\frac{d([O_3] + [O])}{dt} = 2f_2[O_2] + f_4[NO_2] \tag{17}$$

$$- (2k_3[O][O_3] + k_4[NO][O_3] + k_5[O][NO_2])$$

Since $[O] << [O_3]$ everywhere in the stratosphere, the rate of production of odd oxygen is essentially equal to the rate of production of ozone. The "odd oxygen ratio", Γ, as defined as

$$\Gamma = \frac{\text{rate of production of odd oxygen}}{\text{rate of destruction of odd oxygen}} \tag{18}$$

$$= \frac{2f_2[O_2] + f_4[NO_2]}{2k_3[O][O_3] + k_4[NO][O_3] + k_5[O][NO_2]}$$

$$\approx \frac{\text{gross rate of ozone production}}{\text{gross rate of ozone destruction}}$$

When Equation (17) is positive or Equation (18) is greater than one, locally more ozone is produced than destroyed. Conversely, a negative value to Equation (17) or a value less than one for Equation (18) indicates a region where ozone is being destroyed chemically faster than it is being created photochemically.

The addition of oxides of nitrogen to the stratosphere increases the rate of chemical destruction of ozone by the catalytic cycle

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (19)$$

$$NO_2 + O \rightarrow NO + O_2$$

$$\text{net: } O + O_3 \rightarrow O_2 + O_2$$

We wanted a simple one-dimensional variation function for the amount of NO_x (NO and NO_2) to be assumed. We used two such functions: (a) We assume that the stratosphere from tropopause to stratopause and from pole to pole has the same uniform mole fraction of NO_x

$$\alpha = [NO_x]/[M] \qquad (20)$$

and we assume a wide range of values of α. (b) As a second series of calculations, we assume that the entire stratosphere has a uniform concentration of NO_x, and we assume a wide range of values of $[NO_x]$. For each assumed α or $[NO_x]$, we made the complete set of calculations carried out with the Chapman reactions alone, including the integrated, world-wide, net rate of ozone formation. Figure 9 gives the variation of global ozone rate with added mole fraction of NO_x. It turns out that the global net ozone rate decreases linearly with NO_x. The global production rate is reduced to the rate of transport to the troposphere (6×10^{29} molecules sec^{-1}) by 28×10^{-9} mole fraction of NO_x uniformly distributed. For linear variation of the concentration of the oxides of nitrogen, the global production rate is reduced to the transport rate by 4.2×10^{9} molecules NO_x cm^{-3}. This uniform concentration corresponds to a column-average (15 to 45 km) mole fraction of 6.6×10^{-9}. Thus it requires only one-fourth as much NO_x to reduce the ozone discrepancy to

zero if it is distributed with a uniform concentration than if it is distributed with a uniform mole fraction. This calculation shows again (compare Johnston 1971a, Figure 2) that the distribution of NO_x in the stratosphere is almost as important a variable as the magnitude of NO_x. For a uniform concentration of NO_x of 4.4×10^9 molecules cm^{-3}, which is sufficient to produce a global balance of ozone under conditions of January 15, the rates of the elementary reactions of the oxides of nitrogen are presented graphically: $NO + O_3$, Figure 10; $NO_2 + h\nu$, Figure 11; and $NO_2 + O$, Figure 12.

The odd-oxygen ratio, Equation (18), is a sensitive indication of local source and sink regions. The ratio of ozone formation to ozone destruction is given by Figure 13, for the Chapman reactions. In the lower tropical stratosphere there is a large region where the Chapman reactions indicate that ozone is produced one hundred times faster than it is destroyed, with a maximum value above 1000. A very large part of the stratosphere indicates a formation rate of ozone 10 times as great as the destruction rate, according to the Chapman mechanism.

The addition of a uniform 28×10^{-9} mole fraction of NO_x reduces the global ozone discrepancy to zero (Figure 9), and it gives local formation/destruction ratios as shown in Figure 14. The great anomaly of Figure 13 in the lower tropical stratosphere is removed, and most of the stratosphere is within 50 per cent of photochemical equilibrium (Γ between 0.67 and 1.5). There are strong source regions high above the two poles, and these source regions appear to be unrealistic. However, these regions are entirely within the range of the extrapolated data; and they occupy (by virtue

of cosine factors) only a very small volume of the stratosphere. This model indicates a sink region for ozone between 20 and 35 km, whereas the region 25 to 35 km is almost certainly a source region.

The addition of a uniform concentration of NO_x, 4.2×10^9 molecules cm^{-3}, also reduces the global discrepancy to zero (Figure 9), but it sets up a rather different detailed distribution of points of balance and unbalance, Figure 15. In this case the entire stratosphere is within 50 per cent of photochemical equilibrium. A small amount of NO_x removed the discrepancy factor of 1000 given by the Chapman model for the lower tropical stratosphere. A relatively small amount of NO_x is capable of rapidly setting up a situation very close to photochemical equilibrium in the lower stratosphere. The uniform concentration of NO_x, however, overshoots photochemical equilibrium in the uppermost stratosphere. Figure 15 (correctly) indicates an ozone source region between 25 and 35 km, but it incorrectly indicates a sink region above 40 km.

A comparison of Figure 14 and 15 show that neither is entirely satisfactory, although either one is a great improvement over the Chapman model. The model of uniform NO_x concentration, Figure 15, has too much NO_x above 40 km between 70°N and 70°S. The model of uniform mole fraction, Figure 14, has too much NO_x between 20 and 35 km and it does not have enough NO_x (or other mode of chemical ozone destruction) above 40 km. Some distribution intermediate between these two simplified models would very nearly give a balance of ozone throughout the stratosphere. The purpose of this paper is not to try to deduce the real, world-wide distribution

of NO_x in the stratosphere; rather the purpose is broadly to test for the sufficiency of the Chapman reactions and of oxides of nitrogen in explaining the global ozone balance when the effect of atmospheric motions is included.

It should be emphasized that the quantities of NO_x referred to here apply to the species NO and NO_2. These calculations refer to NO and NO_2, as such. To the extent that odd nitrogen is tied up as nitric acid, HNO_3, or other forms, the total odd nitrogen would be greater than NO_x, as the term is used here. In particular, nitric acid is both formed and destroyed by hydroxyl radicals (Johnston et al, 1953)

$$HO + NO_2 \xrightarrow{M} HNO_3$$

$$HO + HNO_3 \rightarrow H_2O + NO_3$$

Under conditions of the lower stratosphere, these two reactions alone indicate that NO_2 is about 10 percent of HNO_3, and photolysis of nitric acid

$$HNO_3 + h\nu \text{ (below 325 nm)} \rightarrow HO + NO_2$$

would increase the fraction of NO_2, especially at higher elevations. We expect HNO_3 to be about equal to NO_x (NO and NO_2) where we sum from 15 to 50 kilometers.

Natural and Artificial Sources of Stratospheric Oxides of Nitrogen

Figure 9 indicates that an increase of the concentration of the oxides of nitrogen beyond 4.2×10^9 would result in a global decrease of ozone.

These calculations of global instantaneous rates in the stratosphere are part of a large effort (Climatic Impact Assessment Program) to understand the probable effect of supersonic transports (SST) on the ozone of the world. The present inventory of NO_x in the stratosphere is a balance between all the photochemical and transport processes that constitute the natural sources and sinks of stratospheric NO_x. The principal source of natural NO_x in the stratosphere is now believed to be the reaction of nitrous oxide with singlet oxygen atoms. Nitrous oxide, N_2O, is produced in small amounts from soil bacteria under anaerobic conditions. Although inert in the troposphere, nitrous oxide is destroyed both photochemically and chemically in the stratosphere (Bates and Hayes, 1967)

$$O_3 + h\nu \text{ (below 310 nm)} \rightarrow O_2 + O(^1D)$$

$O(^1D)$ deactivated in many ways

$$O(^1D) + N_2O \rightarrow N_2 + O_2$$
$$\rightarrow NO + NO$$

This source of natural stratospheric NO_x has been evaluated by Crutzen (1971), by Nicolet and Vergison (1971), and by McElroy and McConnell (1971). Their results are given in Table 3.

A simple statement of the currently expected role of artificial NO_x from supersonic transports is indicated by the

following propositions: (1A) Nitrogen oxides in the global stratosphere are naturally produced in quantities about (1.7 to 7.7)$\times 10^{26}$ molecules sec^{-1} (Table 3). (2A) These natural oxides of nitrogen in the stratosphere are subjected to complicated patterns of air motions, chemistry, and photochemistry. (3A) These natural oxides of nitrogen destroy ozone 4 or 5 times faster than all other factors put together (Table 2). (1B) Artificial oxides of nitrogen from full scale operation of fleets of SST are expected to constitute global stratospheric sources of NO_x of about 2.4×10^{26} molecules sec^{-1} (Concorde) to 7.5×10^{26} molecules sec^{-1} (proposed American SST), about the same as the natural input (Table 3). (2B) These artificial oxides of nitrogen in the stratosphere will be subjected to complicated patterns of air motions, chemistry, and photochemistry. (2C) These artificial oxides of nitrogen should be expected to have the same effect on stratospheric ozone as the natural oxides of nitrogen, until and unless positive knowledge to the contrary is developed.

Summary

Considerations of instantaneous photochemical rates show that the Chapman model predicts a continuous, worldwide production of ozone five times faster than its destruction, and it indicates a large local region where the formation rate is more than 1000 times the destruction rate. At present, laboratory rate constants are well enough known that it is regarded as improbable that the

world-wide factor of 5 (much less the local factor of 1000) discrepancy can be ascribed to erroneous rate constants. The net production rate inferred from the Chapman model is about 50 times greater than the rate of transfer of ozone to the troposphere as estimated by Brewer and Wilson (1968). These considerations provide strong evidence that something else besides neutral oxygen species is very active in destroying stratospheric ozone. It is shown that a world-wide uniform concentration of 4.2×10^9 molecules of NO_x per cm^3 is sufficient to balance the global discrepancy. This study gives additional evidence that the oxides of nitrogen are important substances in the natural ozone balance of the stratosphere. It is again pointed out that the current estimates of the natural source strength of NO_x in the stratosphere are about the same as current estimates of the artificial flux of NO_x from full scale operation of supersonic transports.

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References

Ackerman, M., 1971. Ultraviolet solar radiation related to mesospheric processes. Mesospheric Models and Related Experiments edited by G. Fiocco. D. Reidel Publishing Company, Dordrecht-Holland. pp. 149-159.

Australian Academy of Sciences Report No. 15, Atmospheric Effects of Supersonic Aircraft (1972).

Bates, D.R. and Hayes, P.B., 1967. Atmospheric nitrous oxides. Planet. Space Sci. 15:189-197.

Baulch, D.L., Drysdale, D.D., and Horne, D.G., 1970. Critical Evaluation of Rate Data for Homogeneous Gas Phase Reactions Volume 5. The University, Leeds, England.

Brewer, A.W. and Wilson, A.W., 1968. The regions of formation of atmospheric ozone. Roy. Meteorol. Soc. Quart. Jour. 94:249-265.

Brinkman, R.T., Green, A.E.S., and Barth, C.A., 1966. A digitalized solar ultraviolet spectrum. NASA Technical Report No. 32-951. Jet Propulsion Laboratory, Pasadena, California.

Chapman, S., 1930. A theory of upper-atmosphere ozone. Mem. Roy. Meteorol. Soc. 3:103.

Climatic Impact Assessment Program, research program by the Department of Transportation, 1972-1974.

Crutcher, H.L., 1969. Temperature and humidity in the troposphere. World Survey of Climatology Volume 4, edited by D.F. Rex. Elsevier Publishing Company, Amsterdam-London-New York. pp. 45-83.

Crutzen, P.J., 1970. The influence of nitrogen oxides on the atmospheric ozone content. Quarterly Jour. Roy. Meteorol. Soc. 96:320-325.

Crutzen, P.J., 1971. Ozone production rates in an oxygen-hydrogen-nitrogen atmosphere. Jour. Geophys. Res. 76:7311-7237.

Davis, D.D., 1972. Absolute rate constants for the reaction $O + O_2 + M \rightarrow O_3 + M$ over the temperature range 200-346K. Jour. Phys. Chem. October 1972.

Dobson, G.B.M., 1968. Exploring the Atmosphere, The Clarendon Press, Oxford, p. 126.

Dütsch, H.U., 1961. Chemical reactions in the lower and upper atmosphere, International Symposium, Stanford Research Institute.

Dütsch, H.U., 1969. Atmospheric ozone and ultraviolet radiation, World Survey of Climatology Volume 4, edited by D.F. Rex. Elsevier Publishing Company, Amsterdam-London-New York. pp. 383-432.

Graham, R., 1972. Measurements in this laboratory.

Hunt, B.G., 1965. The need for a modified photochemical theory of the ozonosphere. Jour. Atmospheric Sci. 23:88-95.

Hunt, B.G., 1966. Photochemistry of ozone in a moist atmosphere. J. Geophys. Res. 71:1385-1398.

Johnson, F.S., Purcell, J.D., and Tousey, R., 1954. Studies of the Ozone Layer Over New Mexico. Rocket Exploration of the Upper Atmosphere. Pergamon Press, London. pp 189-199.

Johnston, H.S. and Yost, D.M., 1949. The kinetics of the rapid gas reaction between ozone and nitrogen dioxide. Jour. Chem. Phys. 17:386-392.

Johnston, H.S., Foering, L., and Thompson, R.J., 1953. Kinetics of the thermal decomposition of nitric acid vapor. II. Mechanism. Jour. Phys. Chem. 57:390-395.

Johnston, H.S. and Crosby, H.J., 1954. Kinetics of the fast reaction between ozone and nitric oxide. Jour. Chem. Phys. 22:689-692.

Johnston, H.S., 1968. Kinetics of Neutral Oxygen Species, U.S. Department of Commerce, National Standard Reference Data System, National Bureau of Standards, Volume 20.

Johnston, H.S., 1971. (a) Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust. Science 173:517-522. (b) The same material in a much fuller form: Lawrence Radiation Laboratory Report UCRL-20568 TID-4500.

Kaufman, F. and McCrumb, J.L., 1972. Kinetics of the $O + O_3$ reaction. Jour. Chem. Phys. 57:1270-1276.

Langley, K.R. and McGrath, W.D., 1971. The ultraviolet photolysis of ozone in the presence of water vapour. Planet. and Space Sci. 19:413-418.

Leighton, P.A., 1961. Photochemistry of Air Pollution, Academic Press, New York and London.

McElroy, M.B. and McConnell, J.C., 1971. Nitrous oxide: a natural source of stratospheric NO. J. Atmosph. Sci. 28:1095-1098.

Nicolet, M. and Vergison, E., 1971. L'Oxyde azoteux dans la stratosphere. Aeronom. Acta 90:1-16.

Paetzold, H.K., 1959. Vertical atmospheric ozone distribution _Ozone Chemistry and Technology_, Advances in Chemistry No. 21 (American Chemical Society) pp. 209-220.

Sissenwine, M., 1969. Standard and supplemental atmospheres, in _World Survey of Climatology_ Volume 4, edited by D.F. Rex. Elsevier Publishing Company, Amsterdam-London-New York. pp. 5-44.

Table 1. Rate Constants for Chemical Reactions

Rate constant	k(T)	Units	Reference
k_2	$1.10\times10^{-34}\exp(502/T)$	a	Davis (1972) Johnston (1968)
k_3	$1.33\times10^{-11}\exp(-2100/T)$	b	Kaufman (1972) Johnston (1968)
k_4	$1.33\times10^{-12}\exp(-1250/T)$	b	Johnston and Crosby (1954)
k_5	9.2×10^{-12}	b	Davis (1972) Baulch *et al* (1970)
k_6	$9.8\times10^{-12}\exp(-3500/T)$	b	Johnston and Yost (1949)
k_7	$3.33\times10^{-39}\exp(527/T)$	a	Baulch *et al* (1970)
k_8	$2.9\times10^{-33}\exp(940/T)$	a	Baulch *et al* (1970)

a. cm^6 $molecule^{-2}$ sec^{-1}.

b. cm^3 $molecule^{-1}$ sec^{-1}.

Table 2. Evaluation of Individual Terms in Equation 16, Global Instantaneous Rates of Change of Ozone (Rates in Units of 10^{29} molecules sec^{-1})

	January 15			March 22		
	North Hemi.	South Hemi.	Global	North Hemi.	South Hemi.	Global
Integrated gross rate of O_3 formation	168	332	500	242	244	486
Global rate of O_3 change	5	-2	3	3	-2	1
Transport to troposphere, average	3	3	6	3	3	6
North to South transport	-4	+4	0	0	0	0
Actual rate of chemical loss (by difference)	164	327	491	236	243	479
Rate of chemical loss from Chapman mechanism (twice rate 3)	30	56	86	48	41	89
Ratio of actual chemical loss to chemical loss by the Chapman model	5.5	5.8	5.7	4.9	5.9	5.4
Rate of chemical loss of ozone from chemical processes other than the Chapman reactions	134	261	405	188	202	390

Table 3. Comparison of Natural and Artificial Sources of Nitric Oxide in the Stratosphere. Global, Instantaneous Rates in Units of 10^{26} Molecules Sec^{-1}

Calculated natural flux	Reference
1.5 to 7.5	Crutzen (1971)
2.5 to 12.5	Nicolet and Vergison (1971)
1.2 to 3.3	McElroy and McConnell (1971)
1.7 to 7.7	average
Estimated artificial flux	
Concorde (1985)	
2.4	Austr. Acad. Sci. (1972)
American SST	Johnston (1971)
7.5	

Titles to Figures

Figure 1. Global observed ozone mole fraction expressed as zonal average (parts per million).

Figure 2. Average concentration of ozone in molecules cm^{-3}. 5(E11) means 5×10^{11}.

Figure 3. Average temperature with approximate height of tropopause indicated by dashed line.

Figure 4. Steady state concentration of oxygen atoms, $O(^3P)$, as calculated by Equation 6, March 22.

Figure 5. The rate of photolysis of oxygen, Equation 2. This figure may be interpreted as one-half the gross rate of formation of ozone, Equation 13, March 22.

Figure 6. The rate of photolysis of ozone, Equation 4.

Figure 7. The net rate of production of ozone on the basis of the Chapman model, Equation 14, March 22.

Figure 8. Total ozone in the northern hemisphere as a function of time of year. The slope of the vectors represent the instantanteous rate of hemispherical ozone production (Figure 7) according to the Chapman model.

Figure 9. Instantaneous, global, rate of ozone production as a function of various amounts and two different distributions of the oxides of nitrogen ($NO_x = NO + NO_2$): a. Various uniform mole fractions of NO_x between 1 and 60×10^{-9} distributed throughout the stratosphere; b. Various uniform concentrations of NO_x, expressed in units of average mole fraction (the column of NO_x divided by

column of M from 15 to 45 kilometers). The transport balance refers to Brewer and Wilson's estimate of the average rate of transport of ozone from the stratosphere to the troposphere (6×10^{29} molecules sec^{-1}). The axis with zero NO_x corresponds to the Chapman model.

Figure 10. Rate of the elementary reaction, $NO + O_3 \rightarrow NO_2 + O_2$, $[NO_x] = 4.4\times10^9$ molecule cm^{-3}, January 15.

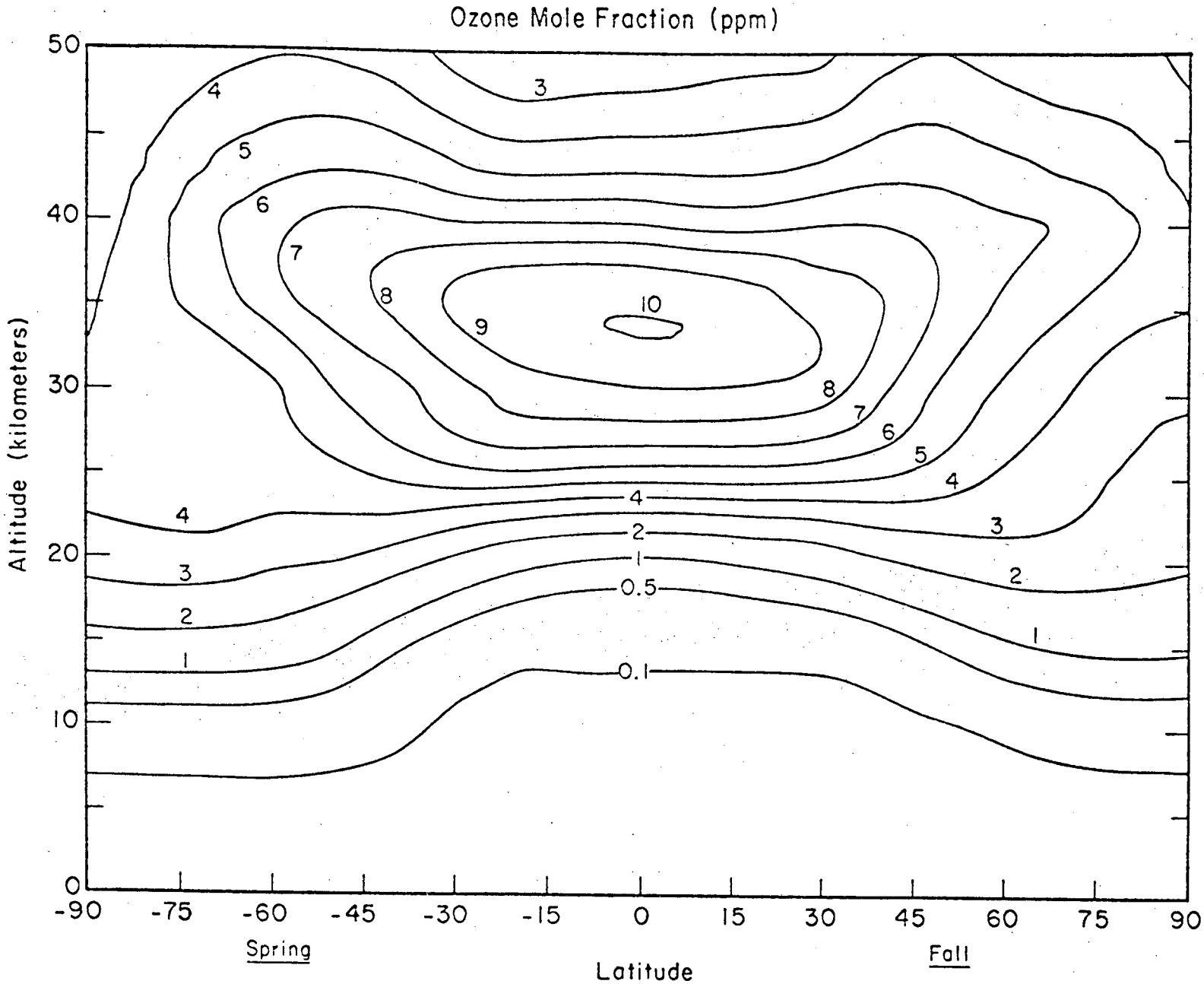
Figure 11. Rate of the primary photochemical reaction, $NO_2 + h\nu \rightarrow NO + O$. Same conditions as Figure 10.

Figure 12. Rate of the elementary reaction, $NO_2 + O \rightarrow NO + O_2$. Same conditions as Figure 10.

Figure 13. The ratio of the rate of photochemical production of ozone to its rate of photochemical destruction according to the Chapman model, the "odd oxygen ratio", Equation 18. Net ozone photochemical production is given by numbers greater than one; net destruction by numbers less than one, March 22.

Figure 14. The ratio of ozone production rate to destruction rate for the uniform mole fraction of NO_x, 28×10^{-9}, that gives a global ozone balance (Figure 9).

Figure 15. The ratio of ozone production rate to destruction rate for the uniform concentration of NO_x, 4.2×10^9 molecules cm^{-3}, that gives a global ozone balance (Figure 9).



XBL 728-6742

Fig. 1

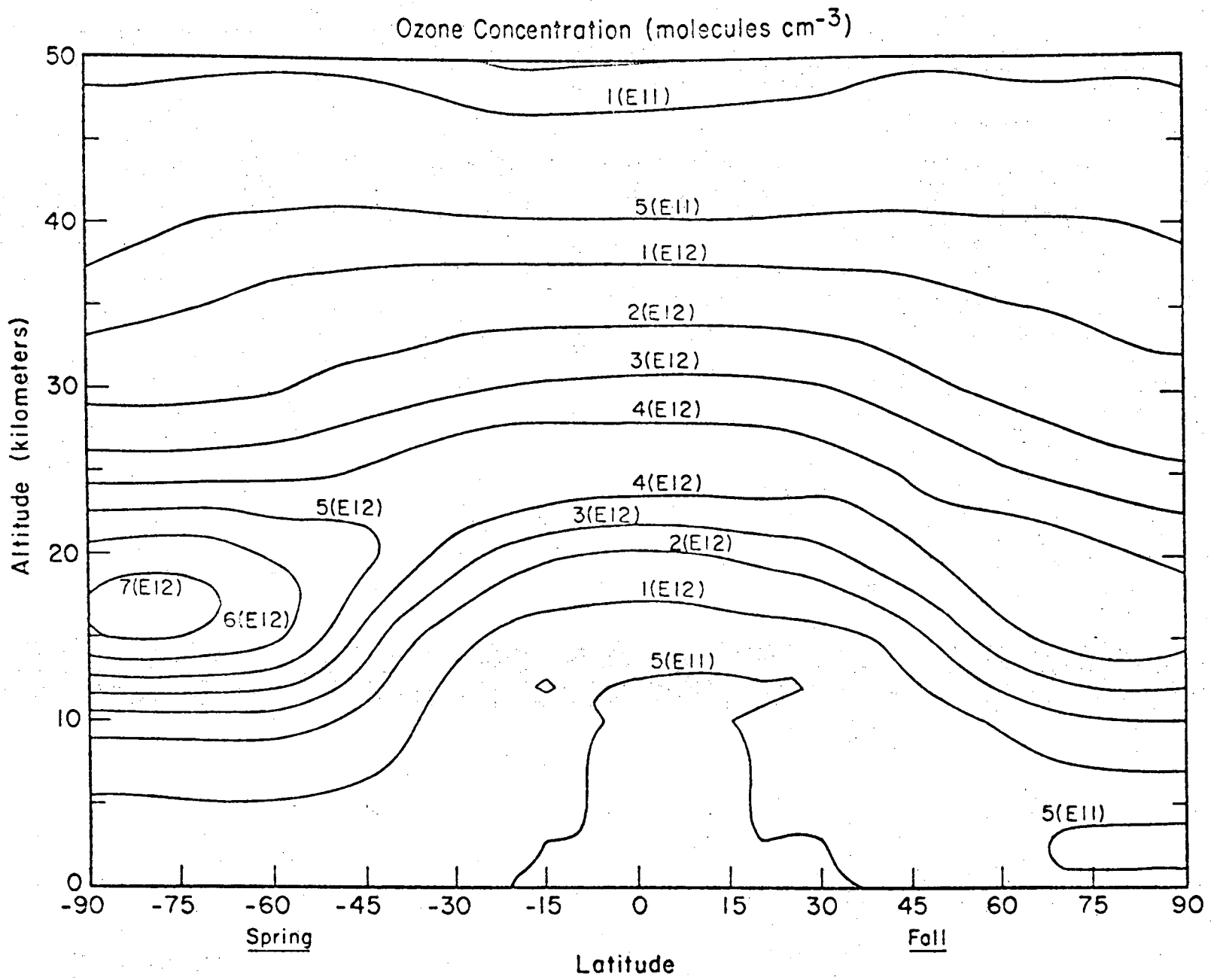


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Fig. 2

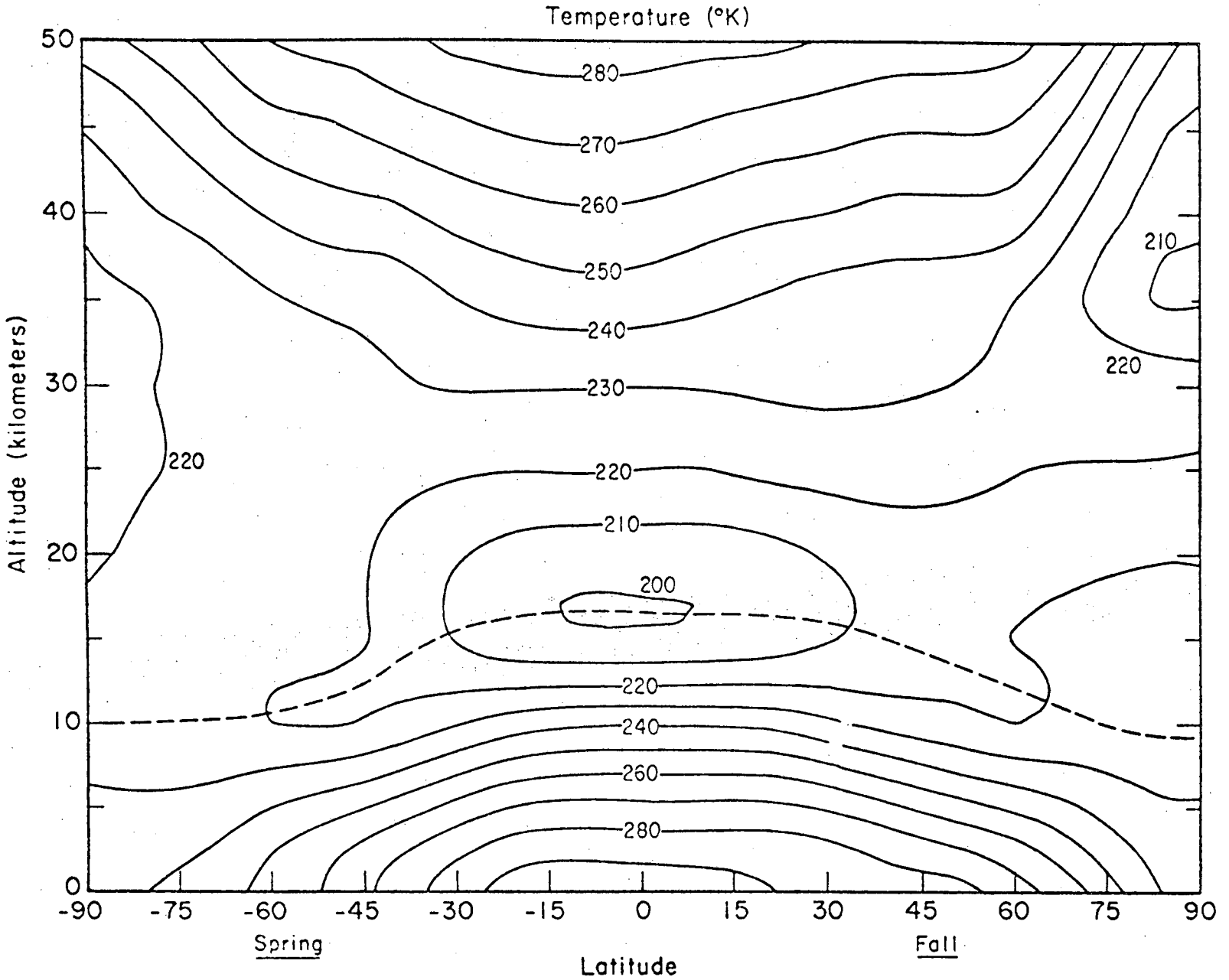

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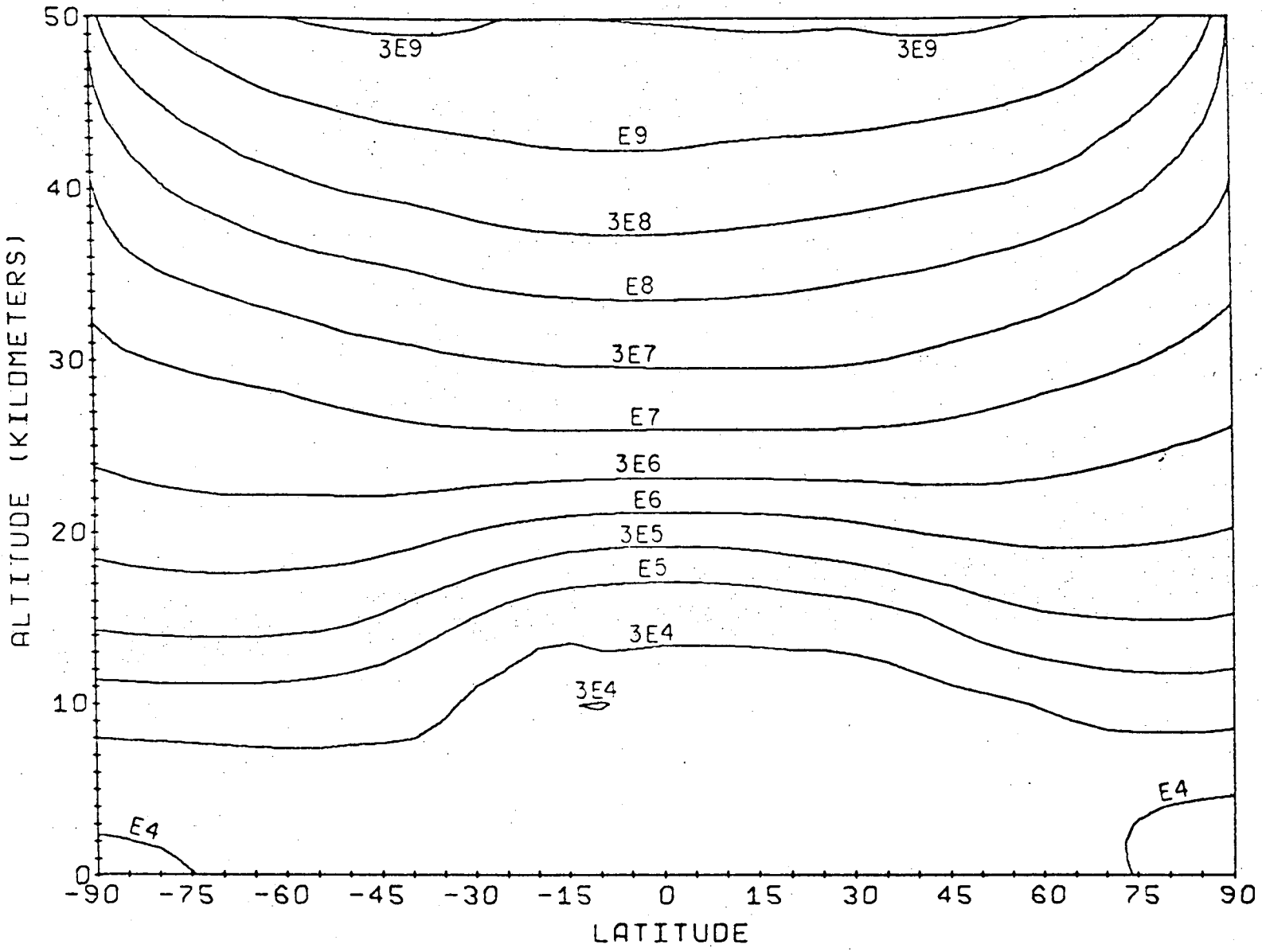
Fig. 3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-75
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-45
-30
-15
0
15
30
45
60
75
90
LATITUDE
3E9
3E9
E9
3E8
E8
3E7
E7
3E6
E6
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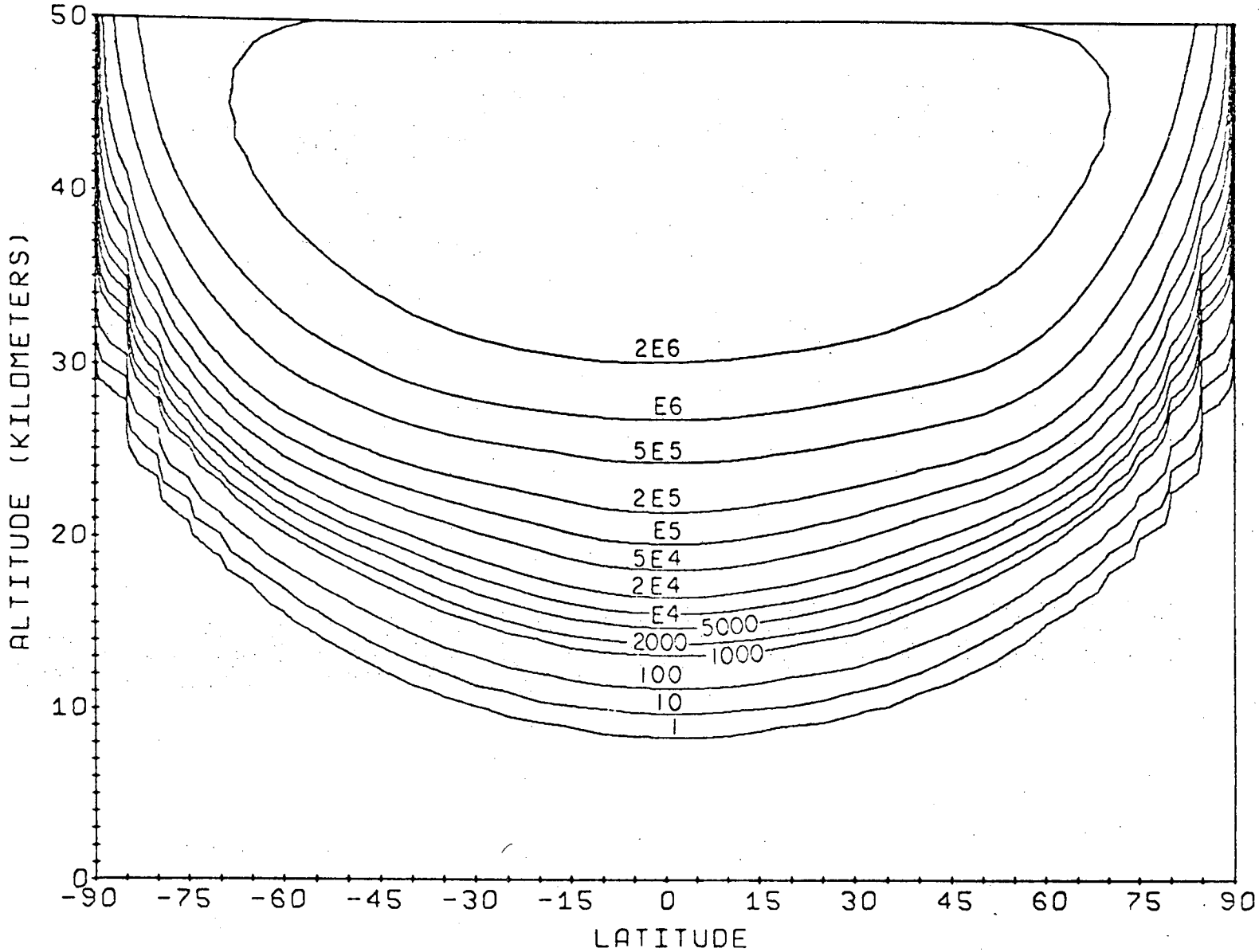
3E4
E4
E4

Fig. 4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0
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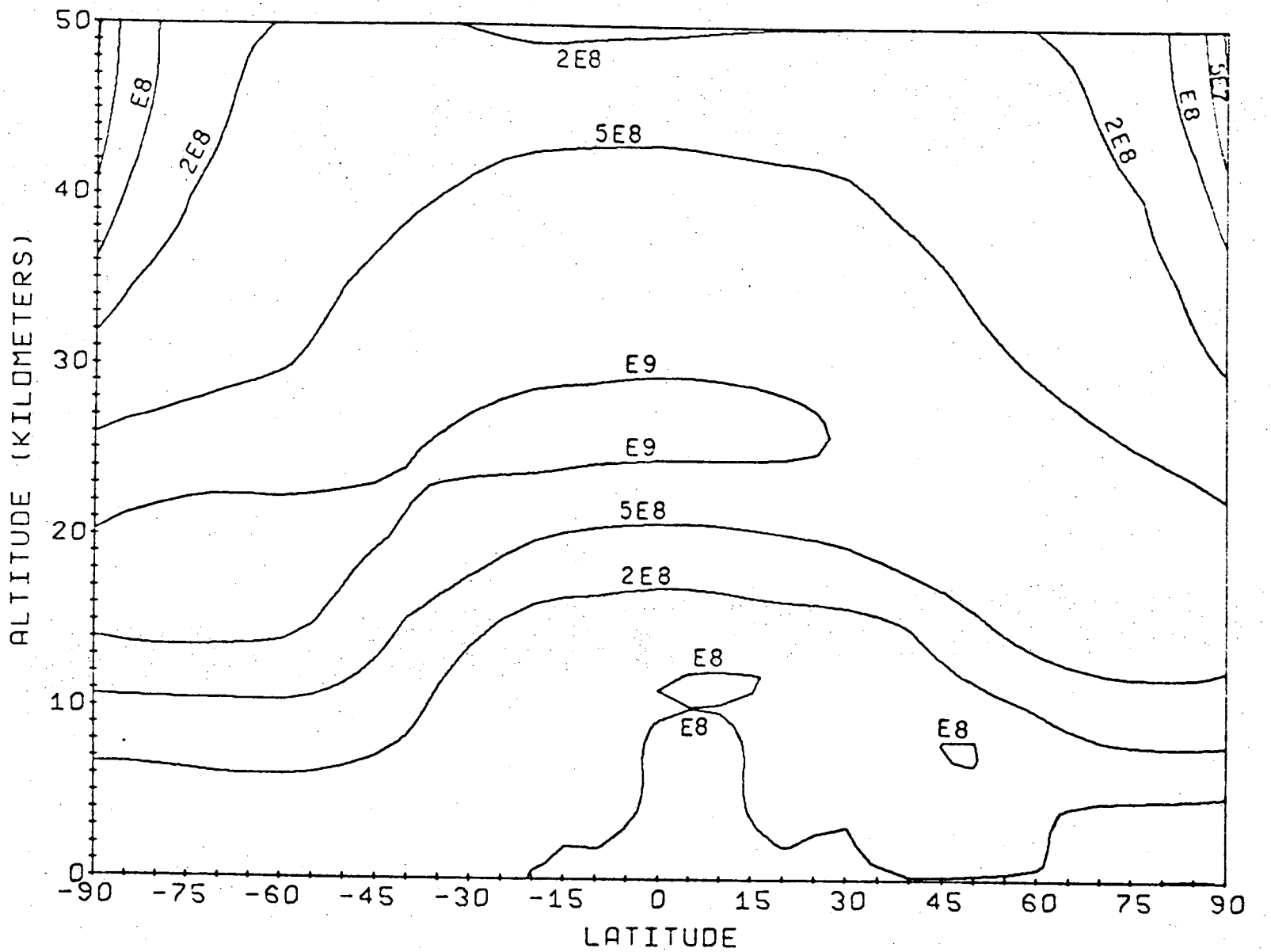
30
45
60
75
90
LATITUDE
2E6
E6
5E5
2E5
E5
5E4
2E4
E4
5000
2000
1000
100
10
1

Fig. 5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60
75
90
LATITUDE
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E8
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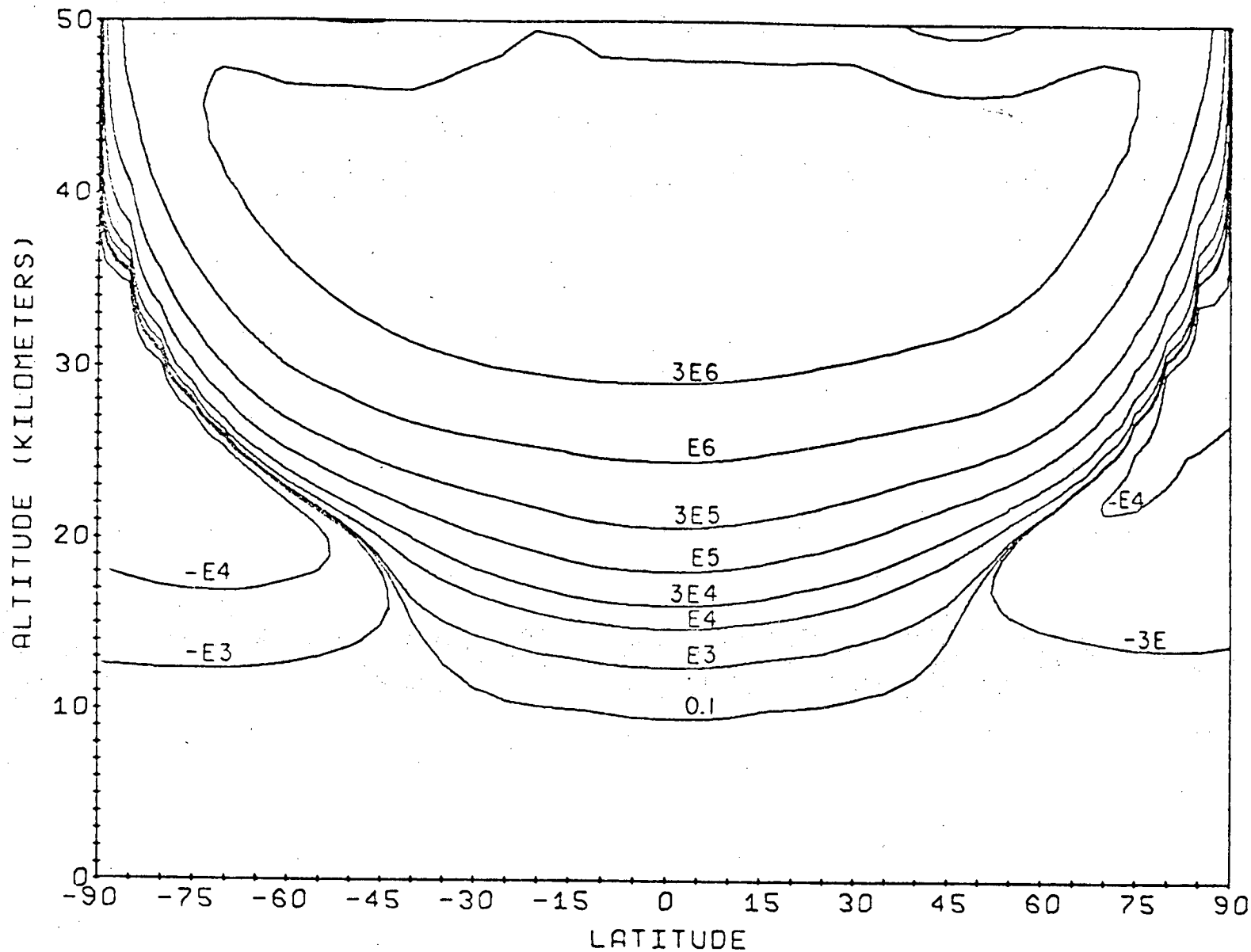
2E8
E8
5E7

Fig. 6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30
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60
75
90
LATITUDE
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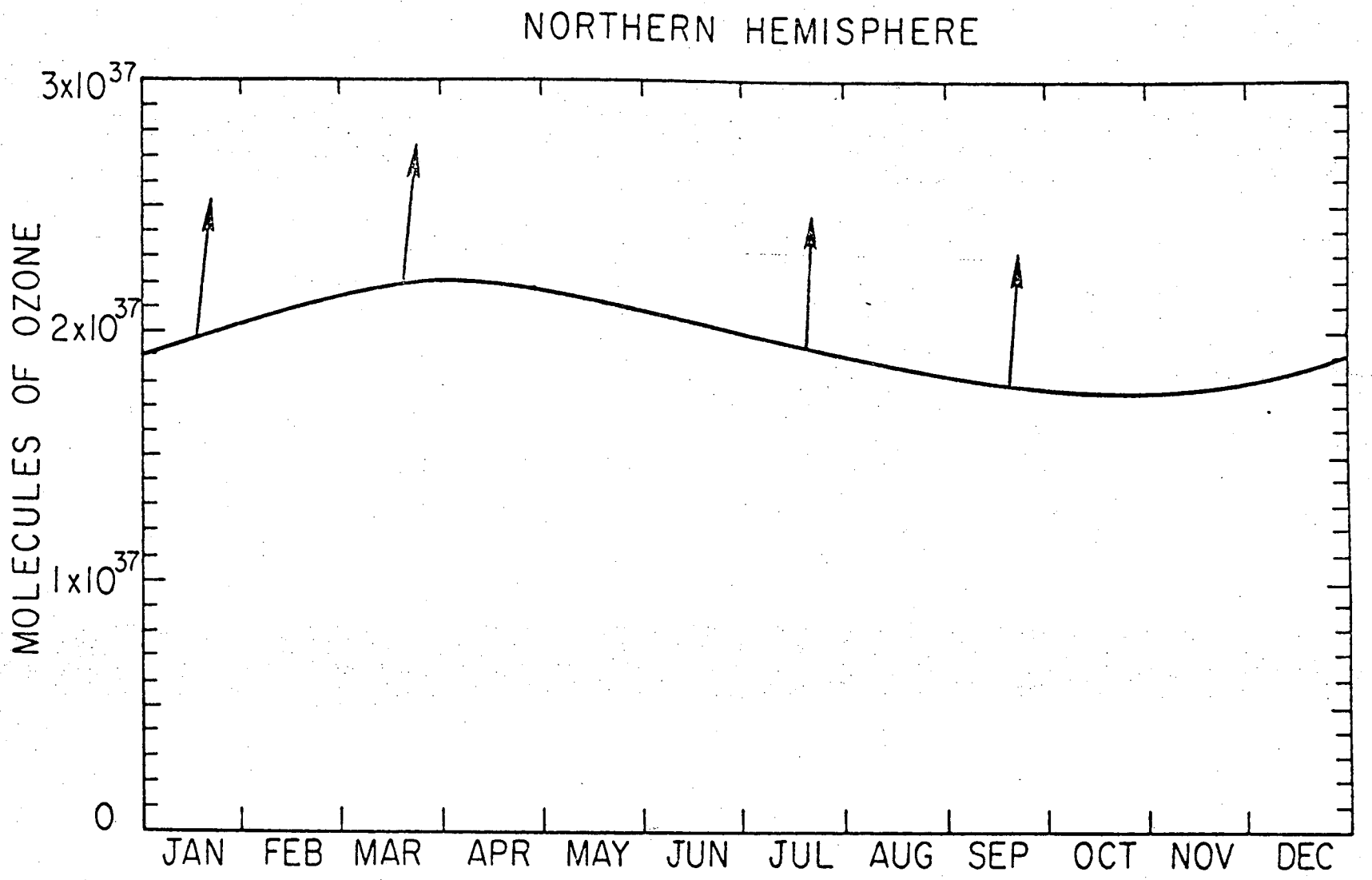
-E4
-3E

Fig. 7


NORTHERN HEMISPHERE
MOLECULES OF OZONE
3x10^37
2x10^37
1x10^37
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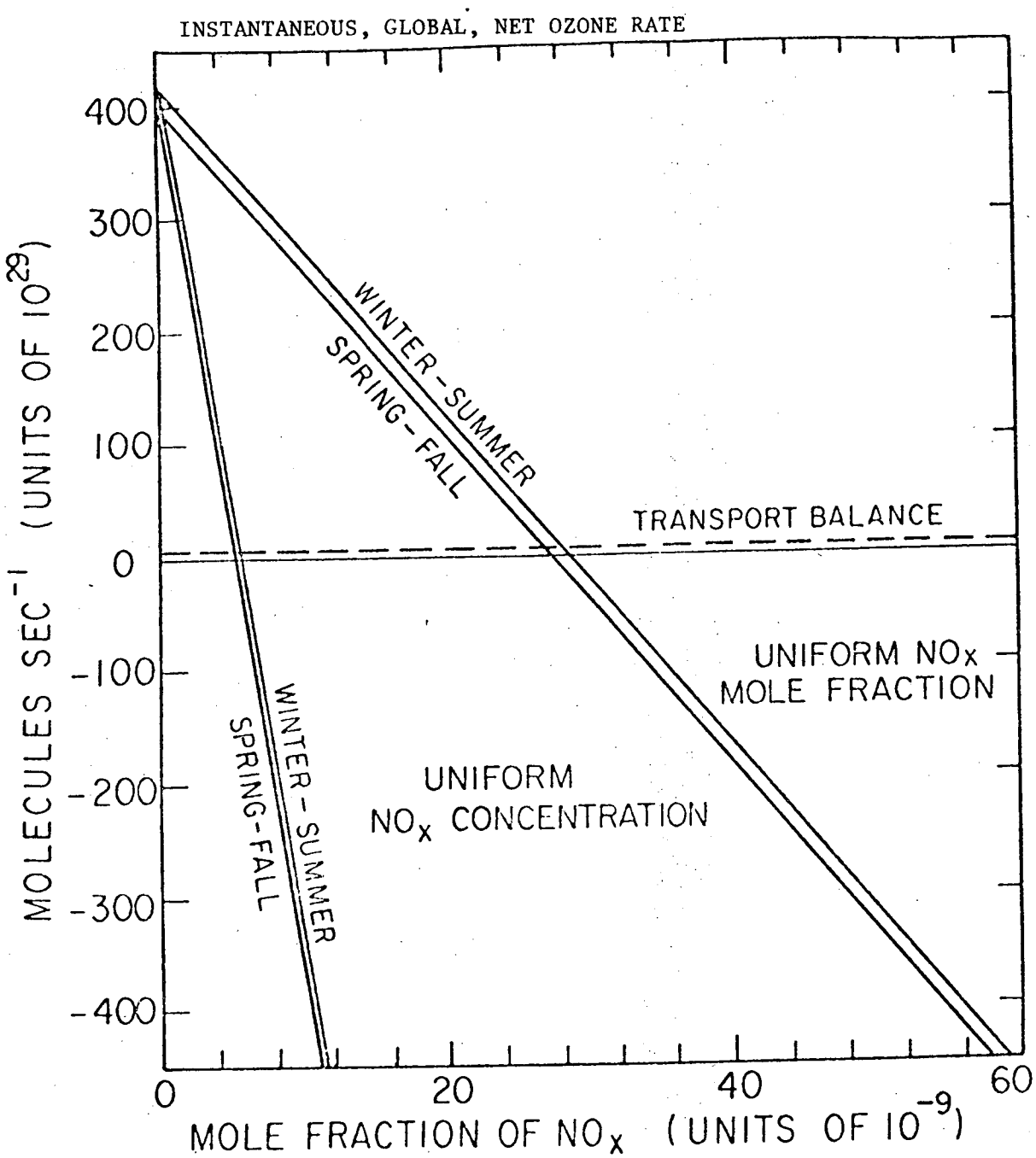
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC

Fig. 8


INSTANTANEOUS, GLOBAL, NET OZONE RATE
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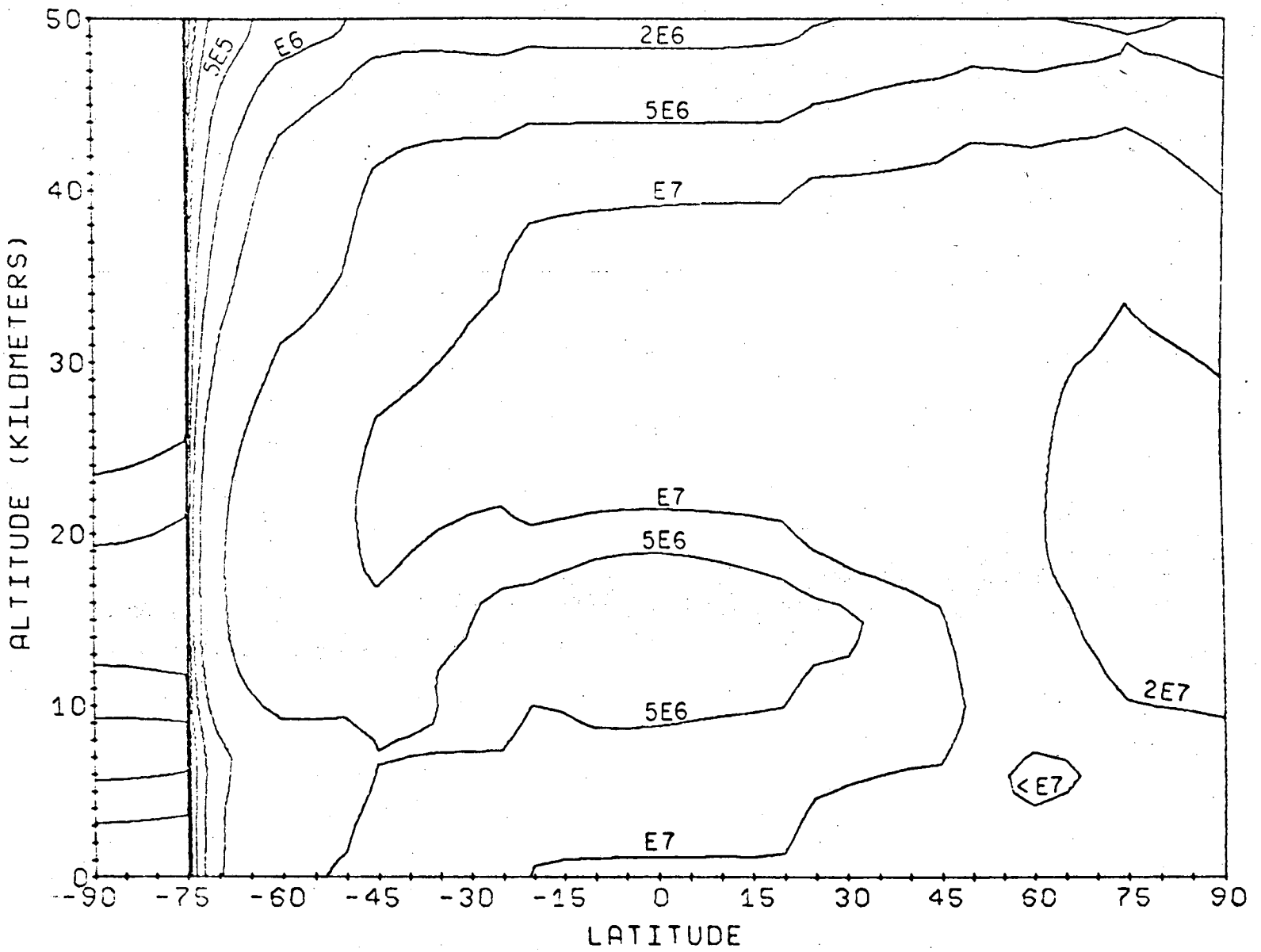
200
100
0
-100
-200
-300
-400
MOLECULES SEC^{-1} (UNITS OF 10^{29})
WINTER-SUMMER
SPRING-FALL
TRANSPORT BALANCE
UNIFORM NOx MOLE FRACTION
UNIFORM NOx CONCENTRATION
WINTER-SUMMER
SPRING-FALL
0
20
40
60
MOLE FRACTION OF NOx (UNITS OF 10^{-9})

Fig. 9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-90
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-15
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15
30
45
60
75
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E6
2E6
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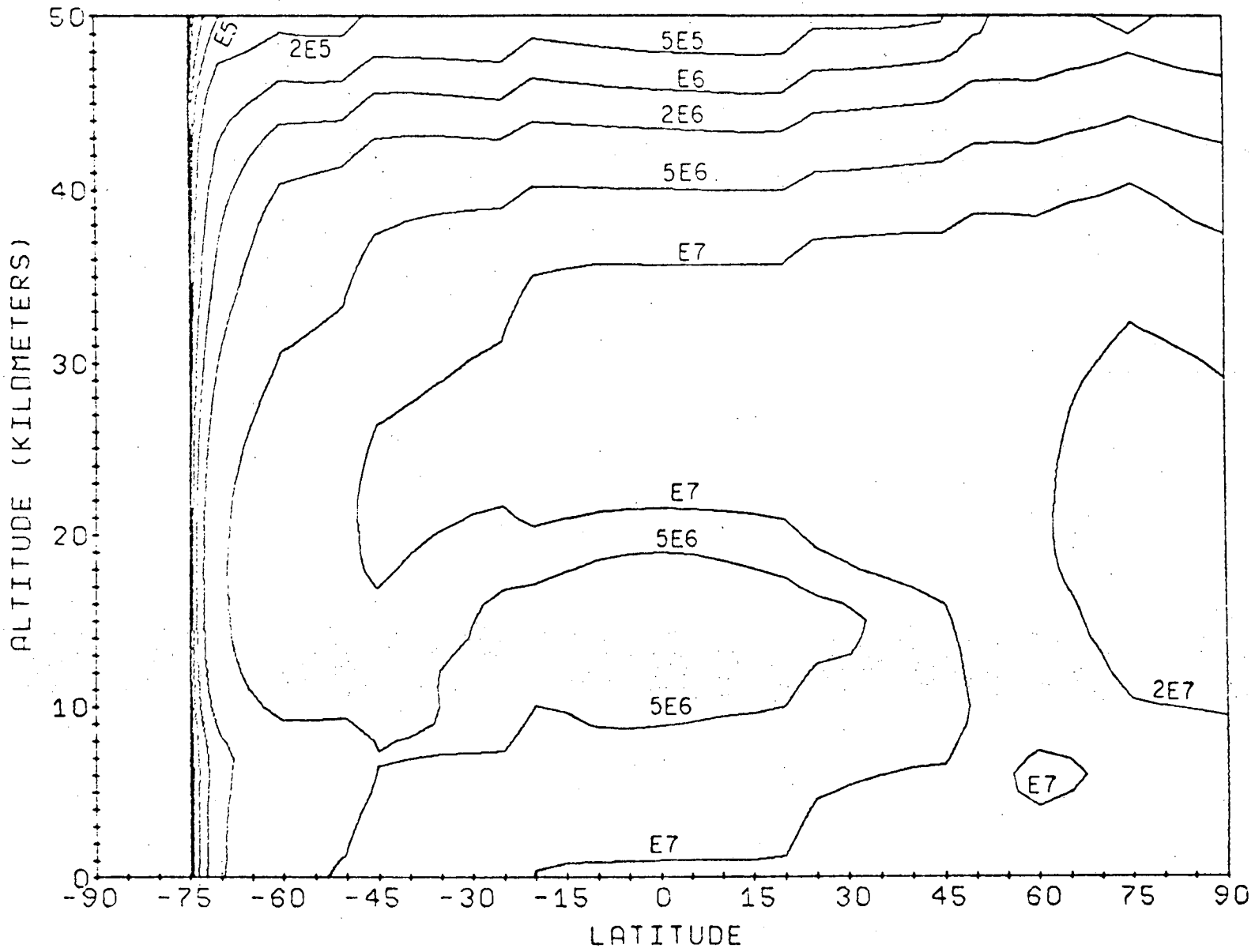
E7
E7
5E6
5E6
E7
2E7
< E7

Fig. 10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0
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30
45
60
75
90
E5
2E5
5E5
E6
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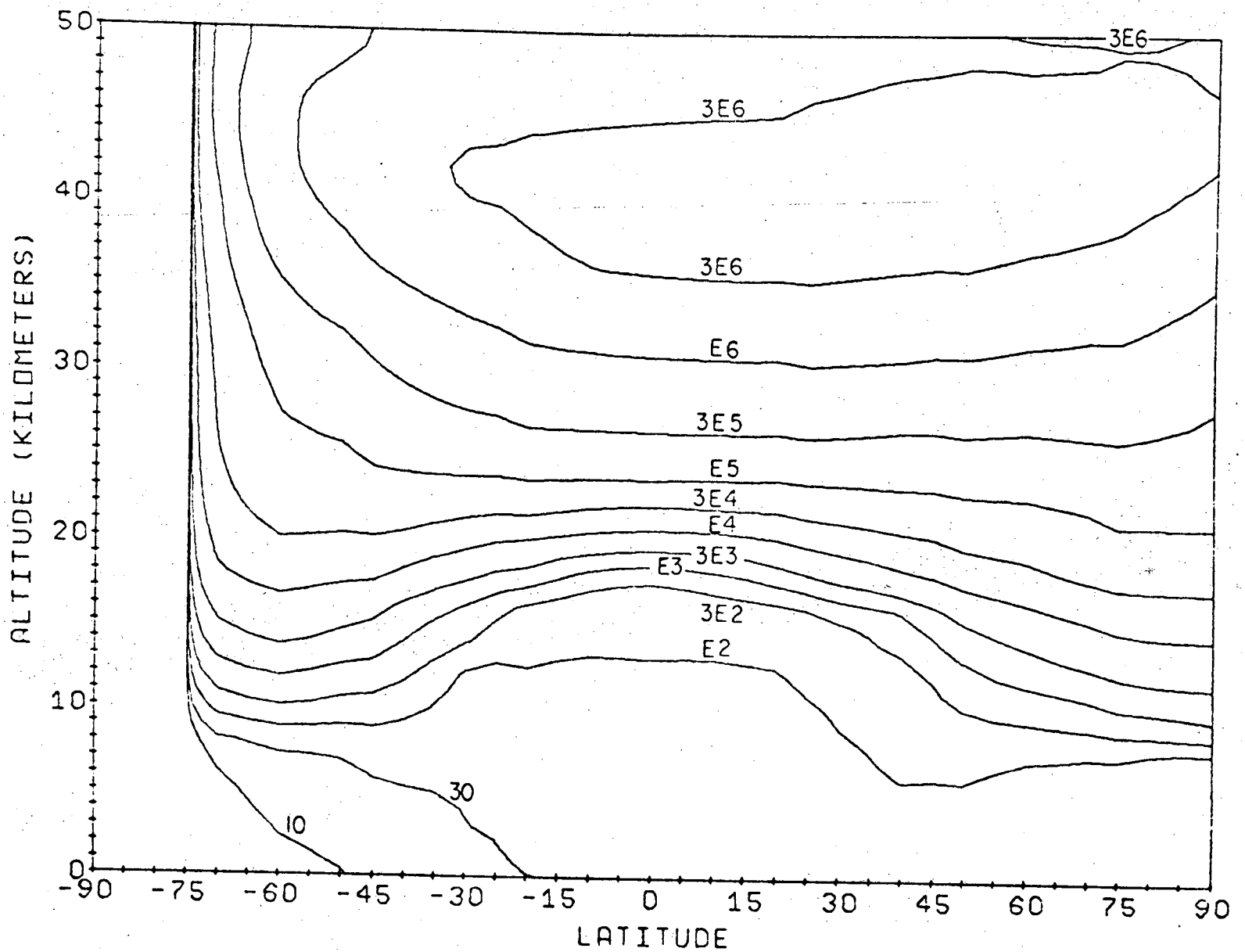
E7
E7
5E6
5E6
E7
2E7
E7

Fig. 11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3E6
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E6
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3E4
E4
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E3
3E2
E2
30
10

Fig. 12

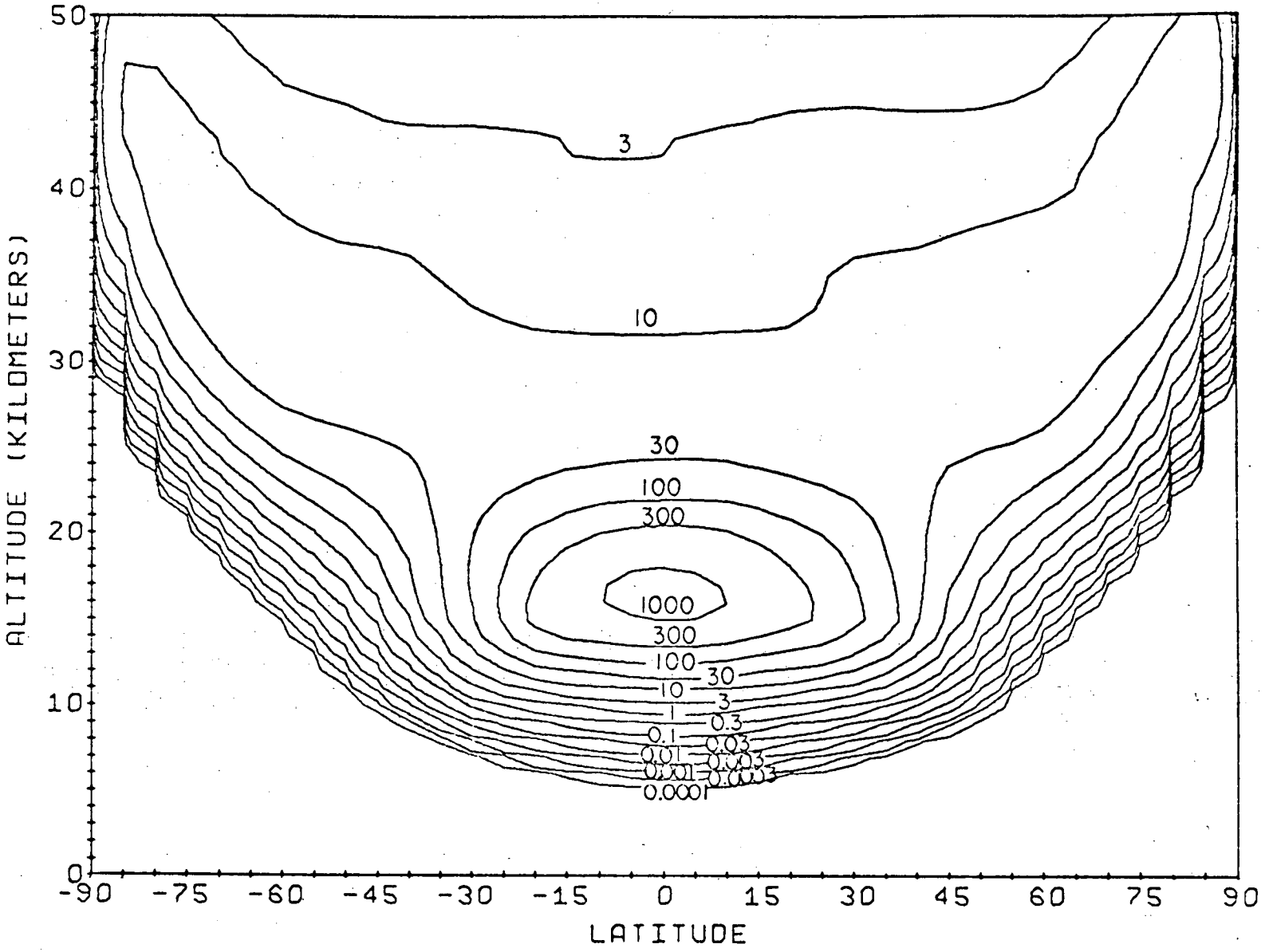
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Fig. 13

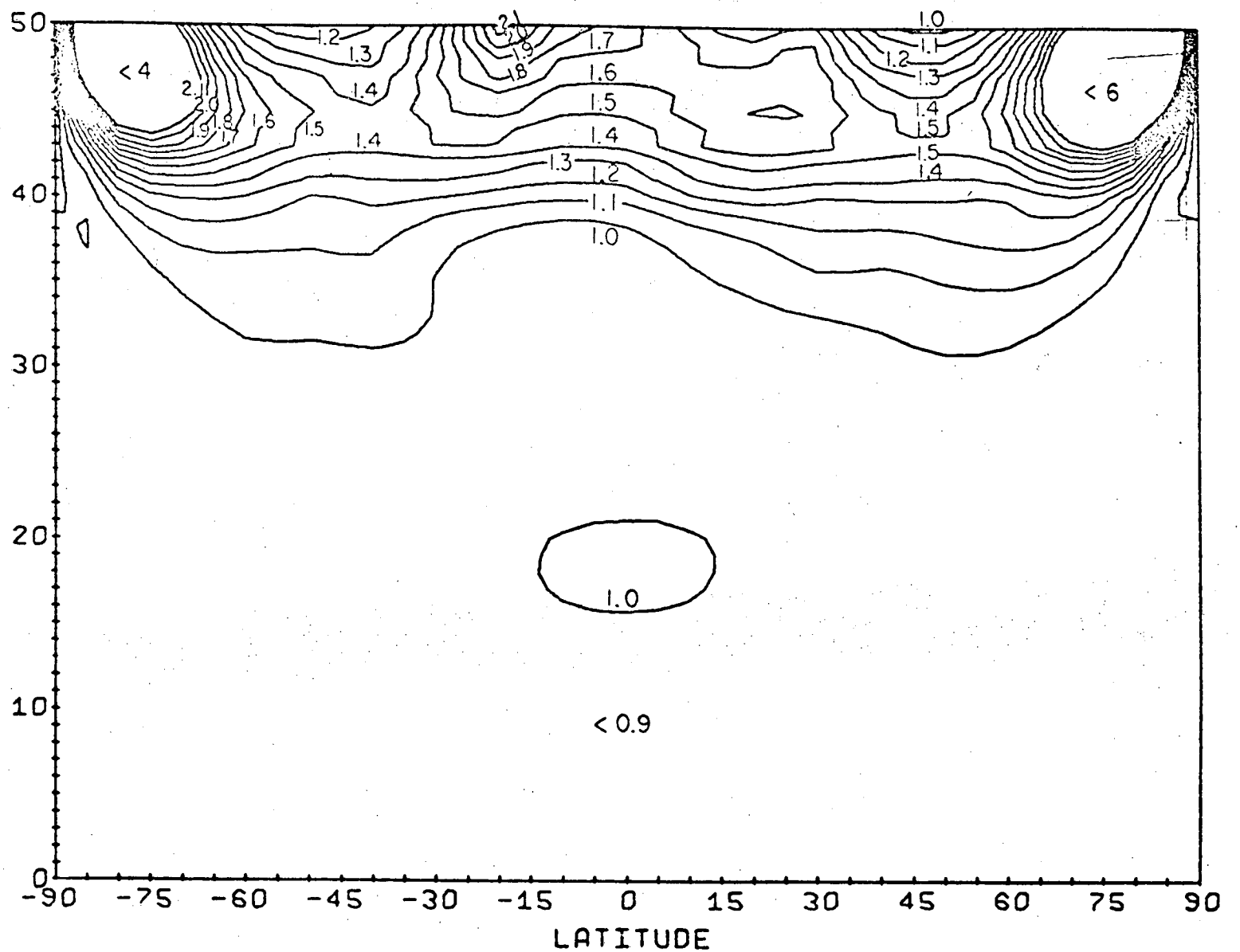
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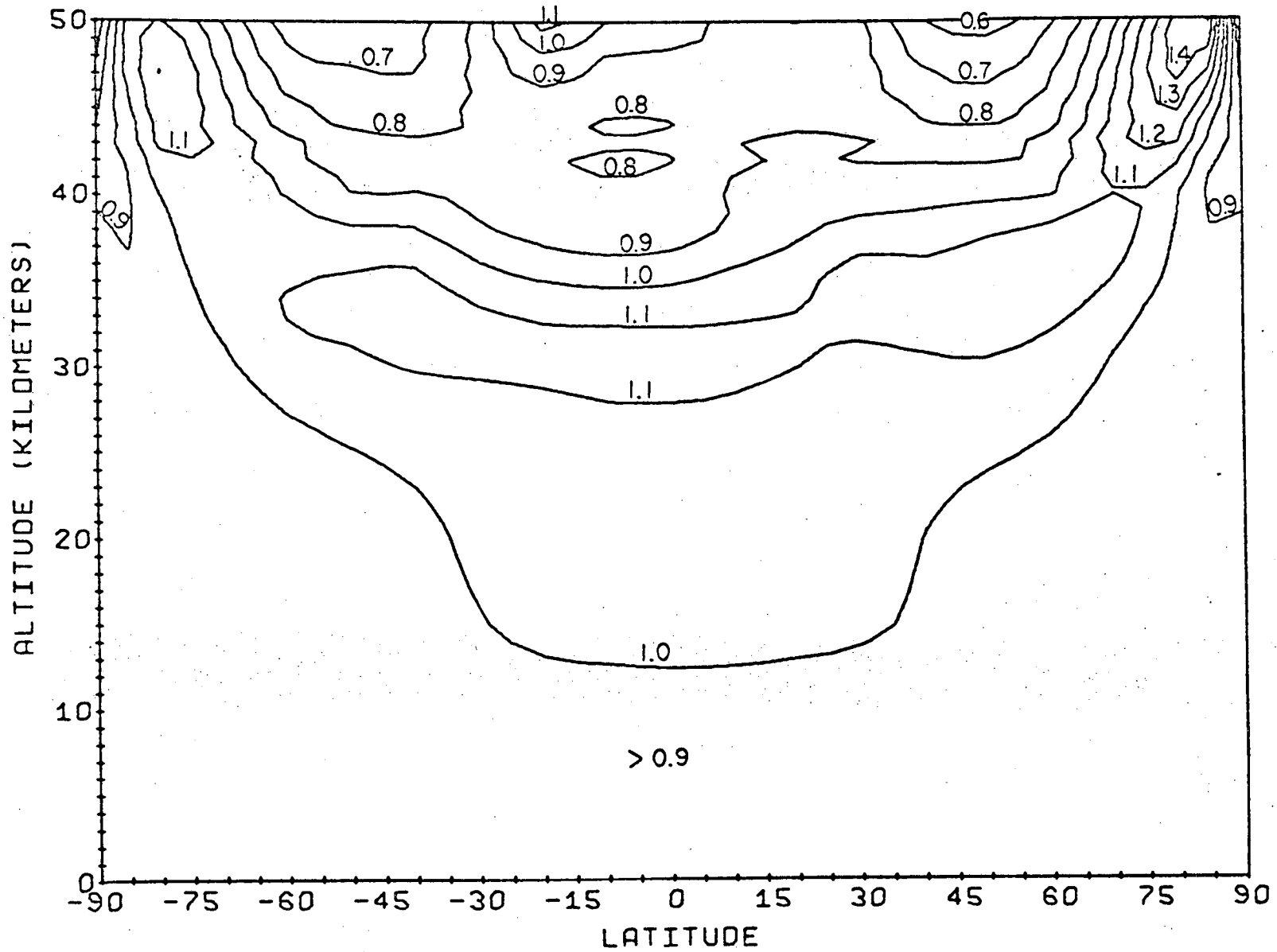
Fig. 14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1.0
0.9
0.8
0.7
0.6
1.4
1.3
1.2
> 0.9

Fig. 15

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