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TRACE GASES, AEROSOLS, AND SOLAR RADIATION
IN THE STRATOSPHERE -- EXPLORED AND UNEXPLORED
PROBLEM AREAS

by

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TRACE GASES, AEROSOLS, AND SOLAR RADIATION IN THE STRATOSPHERE-- EXPLORED AND UNEXPLORED PROBLEM AREAS

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Abstract

The Climatic Impact Assessment Program (CIAP) of the Department of Transportation is--among other things--faced with the task of providing a detailed review of the "undisturbed" stratosphere as it exists before the commencement of SST traffic. CIAP Monograph No. 1, presently in preparation, deals with this "natural stratosphere." Material for a rough draft of this volume was compiled by approximately 90 scientists during a workshop in Ft. Lauderdale from November 28 through December 1, 1972. This short review paper, based upon the draft of CIAP Monograph No. 1, points out the highlights of our present knowledge of the stratosphere, especially with respect to the O_3 , NO_x and H_2O problems, and also explores some of the deficiencies in this knowledge which will have to be overcome before a complete assessment of human impact on this atmospheric region can be made.

The Ozone Problem

Ozone, even though a minor constituent of the atmosphere (4×10^{-7} parts by volume average concentration), derives its eminent importance from its capability of blocking UV radiation at wavelengths $<3000 \text{ \AA}$. Dobson instruments (ca. 100 observation points globally) provide the major data source on total ozone. Detailed vertical structures have been detected from infrequent and intermittent balloon measurements. Rocket and aircraft data also are listed in the literature. Satellite data (Nimbus III and IV) carry great promise for global and detailed observations of total ozone. However insufficient funds and manpower are provided to analyze even the presently available data bank.

Latitudinal distribution

Lowest values during spring are observed at 5° to $10^\circ S$, and on an annual average close to the equator, but slightly south of the "meteorological equator". In the northern hemisphere highest total ozone values appear during spring in polar latitudes, in the southern hemisphere in middle latitudes (Figure 1). This is conclusive evidence that the photochemistry of ozone is strongly overshadowed by transport processes. If photochemistry alone were involved, both hemispheres should show the same seasonal behavior.

Seasonal variation

A maximum of total ozone is found in both hemispheres in middle latitudes during spring. Polar latitudes in the northern hemisphere also reveal a spring maximum of total ozone (Figure 1) indicating that horizontal and vertical large-scale

eddy transport processes in the lower stratosphere are supplying middle and high latitudes in the northern hemisphere with O_3 at a very efficient rate. In the southern hemisphere the eddy transport processes between middle and polar latitudes proceed slower, causing the time lag with which the ozone maximum is observed over the south pole.

Cyclone activity causes most of the ozone transport--vertically as well as horizontally--in middle latitudes. This can be shown from "ozone waves" that can be detected by satellites (Figure 2). These waves exhibit the same wavelengths, phase- and group-velocity characteristics as traveling cyclonic disturbances. A well developed planetary wave number 2 in the northern hemisphere stratosphere must be held responsible for the efficient transport of O_3 into north-polar regions during spring. In the southern hemisphere only planetary wave no. 1 (excentricity of the polar vortex) is reasonably well developed. The higher wave numbers 2 and 3 are rather insignificant there. This causes the O_3 transport by standing planetary waves in the southern hemisphere to be very much less significant than in the northern hemisphere. Lower transport efficiency of pollutants generated in the lower stratosphere (near 20 km) should be expected, therefore, in the south polar regions than in the north polar regions.

At this time we have only very sketchy information about the meridional extent of the aerosol layer near 15 - 20 km to polar regions. Some evidence exists that the aerosol layer is present near about 15 km over Alaska (Figure 3) (see Reiter 1971, Vol. 2, p. 198-211 for references). Major incursions of Mt. Agung debris into south polar regions, presumably also traveling in the major aerosol layer, occurred--nota bene--during December 1963 when, according to Figure 1 meridional transport processes in the stratosphere are best developed (Figures 4 and 5). It is questionable, however, whether the barrier to meridional transport processes that seems to exist near $60^\circ S$ (see Figure 1) allows a regular and persistent formation of such an aerosol layer over the Antarctic continent.

Hemispheric differences

Figure 6 presents one strong but "lopsided" ozone maximum over Antarctica in the Australian sector, whereas in the northern hemisphere the polar ozone maximum is better centered and a number of planetary waves, strengthened by the superposition of cyclone waves, are visible (Figure 7). (Lovill (1972) showed that strong meridional gradients of total O_3 exist near the position of the polar-front jet axis. The strength of this O_3 -gradient is proportional to the wind speed in the jet stream, i.e. to the intensity of the jet circulation). The O_3 maximum over Antarctica in

Figure 6--showing winter conditions--is located over the Antarctic highlands. Reiter (1969, p. 155; 1971, p. 151) postulates a significant and persistent sinking motion throughout the stratosphere and lower troposphere over this region, forced by katabatic outflow of cold air along the slopes of the highland. Such flow conditions are not characteristic for the north polar regions.

The katabatic outflow also gives rise to a mid-winter maximum of O_3 -concentrations in surface air of Antarctica (Figure 8). In the northern hemisphere all present indications are for a spring maximum of surface O_3 .

Secular variations of total O_3

There is some indication of a slow increase of total O_3 in the 1960's (Figure 9). NO_x created by nuclear blasts had no visible effect on such a trend. As yet it is not clear whether volcanic eruptions, nuclear blasts or solar activity are the primary causes for such long-term trends in O_3 . It should be pointed out that Mastenbrook notes a secular increase of H_2O vapor in the stratosphere in the 1960's (Figure 10). To my knowledge, the photochemical implications of this secular trend of H_2O on total O_3 has not yet been explored. A possible interaction of these two trends should, however, be viewed as being of significant consequence to CIAP.

Short-term fluctuations

In middle latitudes these variations are strongest in winter and spring and are caused by cyclone activity (Figure 2). Vertical transport processes around jet streams of temperate latitudes produce the main "flushing" effect for the lower stratosphere (see Reiter, Vol. III, 1972). Since at these heights ozone is a quasi-conservative atmospheric constituent, we have to presume that other atmospheric admixtures introduced into the atmosphere at these levels would be subject to the same transport and mixing processes.

One may attempt to estimate qualitatively the effectiveness of such mixing processes (for more quantitative estimates one should turn to two- or three-dimensional stratospheric models). Figure 11 gives some clues. We note a general slope of the ozone peak from low to high latitudes, and from about 20 km to 16 km. (Equatorial peaks are located still higher. Photochemistry and upwelling motion in the equatorial stratosphere work together to create this effect). The downward slope of the ozone peak coincides well with our notion on the behavior of the Junge aerosol layer. The meridional transport processes responsible for the ozone flux in this layer belong quite significantly to the standing planetary waves, so dominantly present in the northern hemisphere winter stratosphere, especially above the 20 km level. Below this level transport by transient cyclone waves gains importance. The "secondary maxima" on the spring ozone profiles of mid-latitudes (Figure 11) attest to the effectiveness of this transport by cyclone waves: ozone-rich air is transported from the stratosphere into the troposphere within the stable layer underneath the jet-stream (the so-called "jet-stream front"). Ozone-poor tropospheric air flows back into the

stratosphere in the jet-core itself. It appears as a secondary ozone minimum on the middle- and high-latitude ozone profiles of spring in Figure 11a near the 15-km level. This level (15 to 16 km) obviously marks the limit in altitude to which the rapid flushing of the lower stratosphere in middle latitudes near jet stream systems proceeds. Stratospheric half-residence times (time required to remove $\frac{1}{2}$ of the observed concentration) of atmospheric mass and pollutants in this region below 15 km in the vicinity of jet streams has to be assumed to be of order of days to weeks, especially during the season of active jet stream systems, i.e. winter and spring. From evidence presented in Figure 1 we have to assume that this conclusion is valid for both hemispheres.

Above 15 km, and in the aerosol layer itself (15-20 km level, sloping upward from the pole towards the equator) half-residence times increase from weeks to months, perhaps a year, in middle latitudes. Pollutants injected above 20 km have longer half-residence times yet.

Approximately 70% of the stratospheric air is removed each year. This would include most of the air below 20 km. From the foregoing we can summarize, that the jet-stream systems of winter and spring take a very active part in removing and replenishing stratospheric air at a rapid pace. Between 15 and 20 km removal processes are slower, rely significantly on planetary-wave action (hence are probably weaker in the southern hemisphere, as discussed earlier), and on the mean meridional circulation in the Hadley cell. The seasonal imbalance between outflow from, and inflow into, the stratosphere coincides with the general shrinking and expanding of the stratosphere during spring and autumn, respectively. The expansion of the stratosphere during fall requires--by reason of mass continuity--an influx of ozone-poor tropospheric air. The ozone minimum observed in middle latitudes during October-November (Figure 1) substantiates this conclusion.

Detailed structure

Individual ozone soundings by balloons reveal great variations of ozone concentrations over shallow layers often less than 1 km thick (Figure 12). These variations may, at least in part, be ascribed to the superposition of gravity-inertia waves. The effect of such waves is also noticeable in the formation of "irregular" wind and temperature profiles. It should be noted, that with such irregularities in vertical shear and stability conditions one should expect relatively large variations in the vertical of the diffusive exchange coefficients. NO_x injected into the stratosphere and expected to react with ozone, therefore, will have to be considered together with a variety of possible ozone concentrations, but also with a variety of diffusion coefficients by which NO_x is diluted.

Photochemistry of O_3 and the NO_x problem

Reiter (1971, p. 59) lists 36 chemical reactions in the upper atmosphere. All these reactions, in some way or other, have a bearing on the photochemistry of ozone. They include water vapor and other hydrogen compounds, but not the nitrogen compounds. Consideration of the latter makes the chemistry and photochemistry of the upper atmosphere considerably more complicated. Not only is nitrogen important in the three-body collision postulated in

the Chapman equations of ozone formation, but the oxides of nitrogen play a very important role in the catalytic destruction of ozone. The chemistry and photochemistry of NO_x , therefore, will have to be considered very carefully when assessing the possible impact of the SST on the environment.

In Figure 13 the ratio of O_3 formation to O_3 destruction is shown for the Chapman equations. It is quite obvious that these equations alone cannot account for a photochemical equilibrium, since in the lower stratosphere approximately 1000-times more ozone would be produced than destroyed. Introduction of 4.2×10^9 molecules/ cm^3 of NO_x throughout the stratosphere, according to Figure 14, would bring about a rather close photochemical equilibrium of ozone. NO_x , therefore, may appear as a rather intriguing "solution" to the ozone problem. It has to be pointed out, however, that Figure 14 has been derived for a motionless atmosphere. This does not conform to reality.

We know that O_3 is moved through the lower stratosphere by atmospheric motion systems of a variety of time and distance scales. From studies of detailed O_3 -measurements by balloon soundings, and from (isentropic) trajectory analyses, we find our conclusions confirmed that O_3 in the lower stratosphere behaves almost as a conservative tracer. It, therefore, does not seem to undergo appreciable chemical or photochemical reactions at altitudes of 20 km or lower. Atmospheric motions, thus, appear to be in direct competition with NO_x in explaining the ozone distribution in the stratosphere.

Furthermore, it should be pointed out, that the concentration of 4.2×10^9 molecules/ cm^3 assumed by Johnston (1973) to be uniform throughout the stratosphere does not conform to constant mixing ratio in meteorological terms. Because pressure is decreasing with height, a constant chemical concentration would mean mixing ratios (mg of NO_x per g of air) increasing linearly with decreasing pressure, or increasing with height as pressure decreases. Mixing ratio is conserved during atmospheric transport processes that occur without mixing of different air masses, but chemical concentration is not. This does not belittle the fact, that the chemistry and photochemistry of NO_x is of great importance in the ozone region. But so are atmospheric transport processes. Something must happen to the NO_x which is present in the atmosphere even nowadays before the onset of SST traffic, that makes it less effective in destroying O_3 than would appear from Johnston's model. What are the natural sinks of NO_x ? Conversion to HNO_3 seems plausible. CH_4 may play a role in this conversion, so may the catalytic action of aerosols and ions of trace substances, about which we know hardly anything at all. There are, however, a lot of unsolved questions that make the removal rate of NO_x from the atmosphere an unknown quantity. Such removal possibilities will have to be studied in detail, however, if a credible estimate of the disposal of additional NO_x produced by "unclean" types of SST engines should be made.

Radiation and O_3

Since O_3 is generated photochemically in the stratosphere it is not only affected by, but also has a profound effect upon, the radiation fluxes that permeate the atmosphere. Photochemical models

are based upon a certain balance between UV radiation fluxes and O_3 concentrations (as well as the concentrations of other chemical species). The important questions arise:

(a) whether or not any changes in ozone concentrations in a particular layer of the stratosphere will alter the photochemistry of lower layers in a significant way;

(b) whether or not any changes in total stratospheric ozone will change the UV spectrum and its intensity received at the earth's surface. The biological significance of such changes will have to be assessed separately;

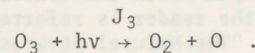
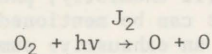
(c) whether or not changes in atmospheric O_3 concentrations may alter the radiation fluxes through the atmosphere, hence the heating rates, and thereby cause changes in climatic regimes.

A serious problem in trying to answer these questions arises from the fact that the transmissivity of the atmosphere as a function of radiation wave length is not precisely known, nor is the original solar brightness (as a function of wavelength) outside the earth's atmosphere. The problem is compounded by the fact that the sun is a variable star, with significant changes occurring in its UV spectrum between sun spot maximum and minimum. The composition of the atmosphere, especially with respect to aerosols and other trace materials, also cannot be considered as constant with time and space.

In the wave lengths effected strongly by ozone, centered at 210 nm, values of energy fluxes computed by Brewer and Wilson may be too low by a factor of four. Whether solar radiation changes cause changes in total ozone has not yet been determined unambiguously. Radiation changes of the sun are quite significant, especially in the X-ray region of the spectrum. The 11-year sunspot cycle and the 27-day rotation cycle play major roles in the solar radiation variability. One will have to allow for these changes in solar intensities when one attempts to answer questions (a), (b), and (c).

In estimating the balance between radiation intensities at a given level, and ozone generation and destruction, one runs again into the problem of the inadequacies of the simple Chapman model, and the relative effects of atmospheric motions and more complex photochemical reactions.

Between 296 nm and 222 nm there is almost complete extinction of UV radiation because of the Hartley continuum of ozone. This spectral feature, the so-called "Hartley Darkness", has important consequences on the dissociation rates J_2 and J_3 which govern the photochemical reactions



Suppose the amount of O_3 were reduced above level z . The Hartley Darkness, in this case, will brighten at level z , and due to the greater UV intensity the rate J_2 will increase at level z . J_3 , on the other hand, is dominated mainly by the optically thin Chappius band and will remain essentially unchanged. Thus J_2/J_3 will increase and so will the local O_3 concentration at level z . Thus, a decrease or increase of ozone above level z will result in an increase or decrease,

respectively, of ozone at level z . The total ozone, integrated over an air column from the ground to the top of the atmosphere, therefore, will remain essentially unchanged.

This conclusion helps to answer questions (a) and (b):

(a) A loss of O_3 above a certain level is expected to yield an increase at and below this level.

(b) The net effect of these changes in the ozone layer--provided that they do not affect the whole ozone region, i.e. the whole stratosphere, in the same sense--will be rather negligible at the earth's surface.

This compensating effect, brought about by the Hartley continuum of ozone, makes it difficult to assess the virtues of one photochemical model of the atmosphere versus those of another. It should also be pointed out that there are still uncertainties in the dissociation rates J_2 and J_3 .

The heating rates in the stratosphere by O_3 in the UV and visible parts of the spectrum depend among other things on the mixing ratio of O_3 and on the photo-dissociation rate, J_3 . If, for some reason, the O_3 concentration were decreased above a certain level z , the heating rate T should decrease because of the decreased ozone mixing ratio. Below level z the ozone mixing ratio would increase, so would T , because of the mixing-ratio increase, but also because of the increased radiation energy that enters into the dissociation rate J_3 .

Thus, it appears that reduction of ozone in a confined layer of the stratosphere could lead to a slow destabilization because of the UV and visible-light heating rates. It will yet have to be estimated, probably from numerical models, whether this destabilization will proceed rapidly enough to enhance turbulent exchange in a significant way. This, again, would have to be considered a "self-healing" characteristic of the ozone layer.

The infrared radiation fluxes also tend to offset slightly the effects of UV and visible light on the heating rates. A decrease in O_3 concentration would lead to a decrease of infrared cooling in the stratosphere.

The presence of aerosols may change the radiation fluxes in the ozone layer significantly. Not enough is known about the optical properties and the distribution of stratospheric aerosols to permit detailed treatment of their effects on heating rates. In the infrared region a better knowledge of the refractive index of aerosols is even more crucial than in the UV and visible portion of the solar radiation spectrum.

Obviously, not all ongoing studies in the fields of stratospheric chemistry, photochemistry and radiation physics can be mentioned here. For more detail, and for an exhaustive summary of literature references upon which the statements made above are based, the reader is referred to CIAP Monograph Vol. 1, "The Natural Stratosphere" which is presently in preparation and will be available for general distribution early in 1974.

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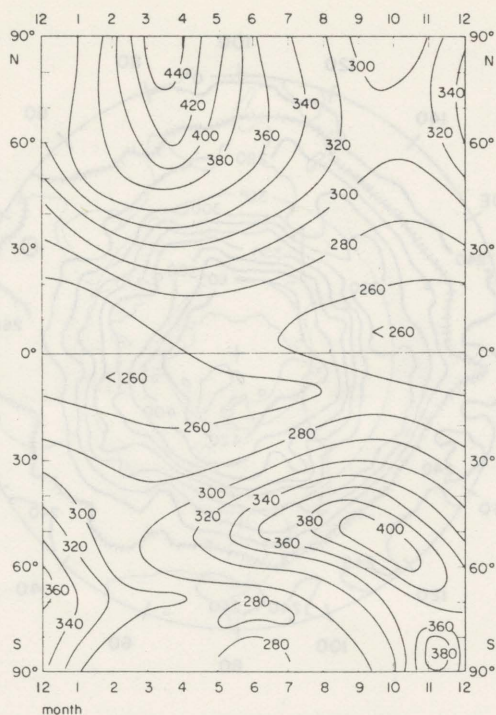


Figure 1. Total ozone as function of season and latitude in both hemispheres [From Dutsch, (1971), based upon data by London (1963), and Stickse (1970)].

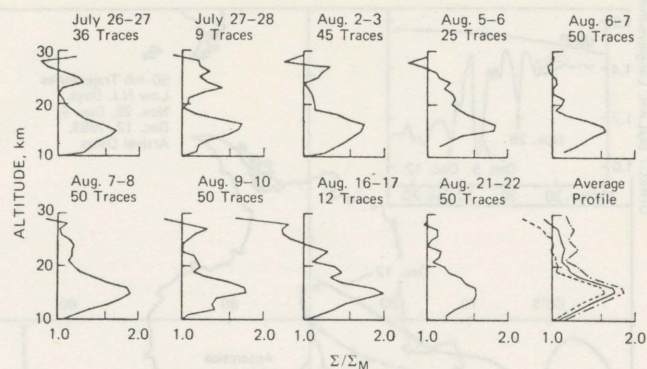


Figure 3. Profiles of the scattering ratio Σ/Σ_M of lidar returns obtained during summer 1964 in Alaska [From Grams and Fiocco, (1967)].

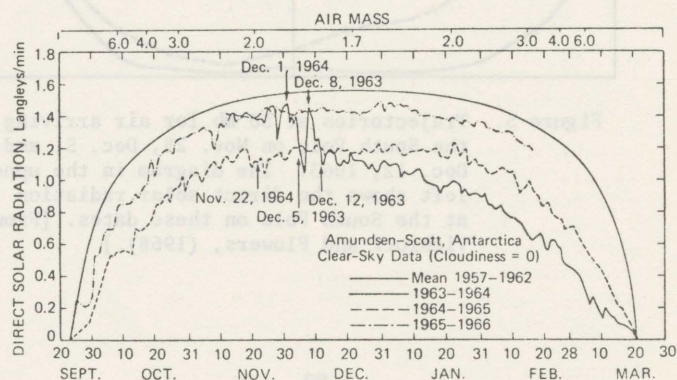


Figure 4. Direct solar radiation data for Amundsen-Scott (South Pole) station [From Viebrock and Flowers, (1968)].

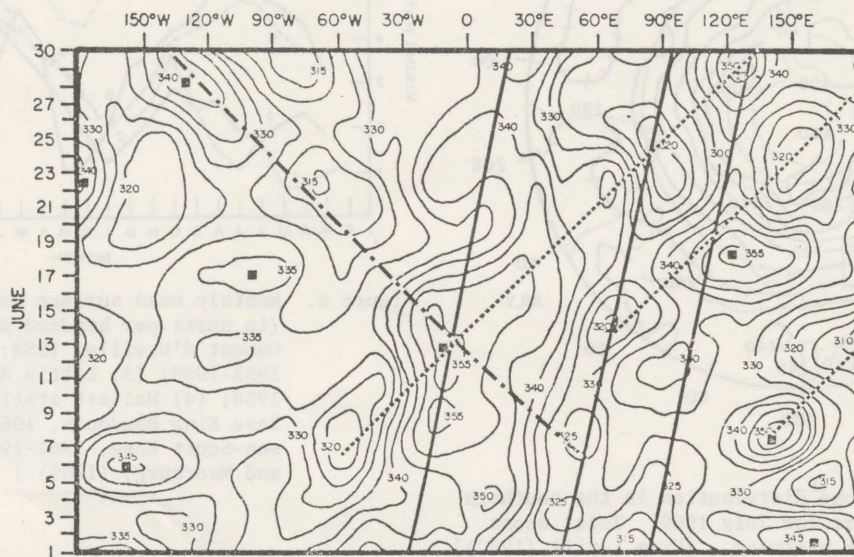


Figure 2. Time-longitude variations of the total ozone ($\text{m} \cdot \text{atm} \cdot \text{cm}$) during June 1969 at 40°N . Squares denote prominent ozone maxima. Solid lines are phase speeds of waves progressing eastward, dotted and dashed-dotted lines denote possible group-velocity propagation (From Reiter and Lovill, 1973).

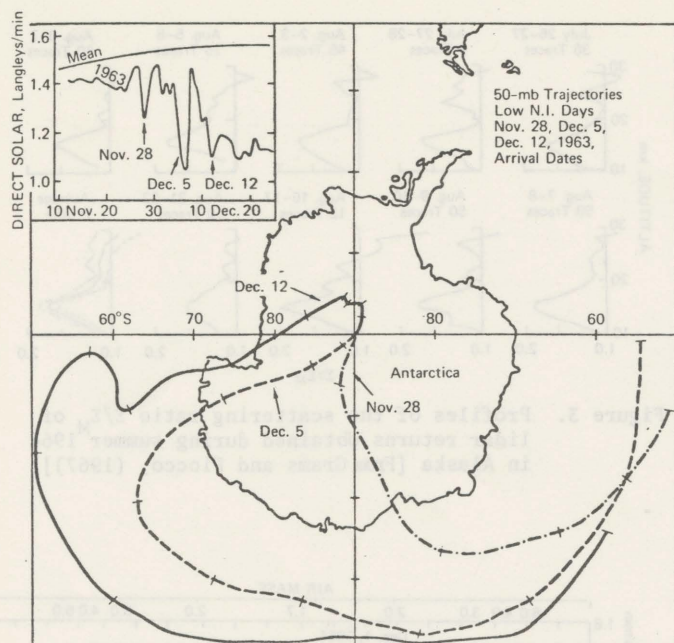


Figure 5. Trajectories at 50 mb for air arriving at the South Pole on Nov. 28, Dec. 5, and Dec. 12, 1963. The diagram in the upper left shows the direct solar radiation at the South Pole on these dates. [From Viebrock and Flowers, (1968).]

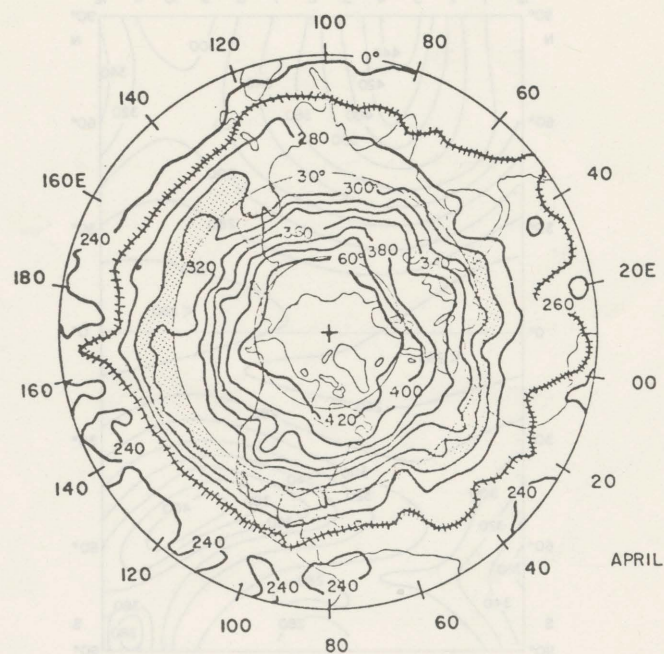


Figure 7. Total ozone distribution in the Northern Hemisphere for April 1969. (Total ozone values in $\text{m} \cdot \text{atm} \cdot \text{cm}$). [From Lovill (1972)].

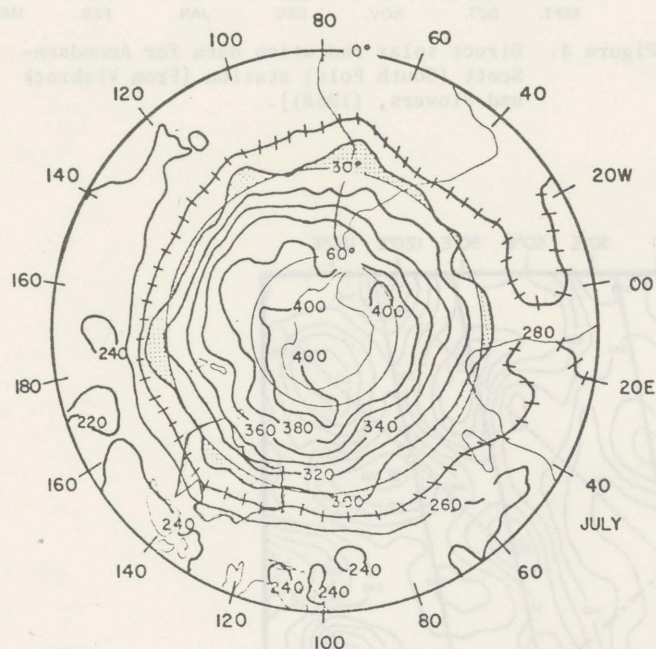


Figure 6. Total ozone distribution in the southern hemisphere for July 1969. Total ozone values in $\text{m} \cdot \text{atm} \cdot \text{cm}$. [From Lovill (1972)].

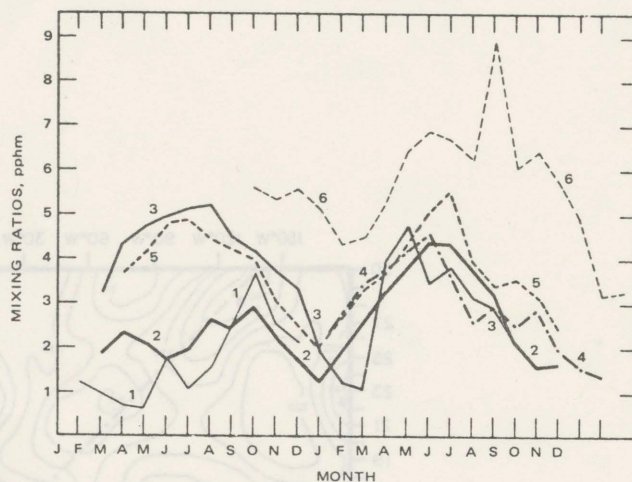


Figure 8. Monthly mean surface ozone mixing ratios (in parts per hundred million) for (1) Dumont d'Urville, 1958; (2) Halley Bay, 1958-1959; (3) Little America, 1957-1958; (4) Hallett station, 1962; (5) Base King Baudouin, 1965-1966; (6) Amundsen-Scott Base, 1961-1962. [From Wisse and Meerburg, (1969).]

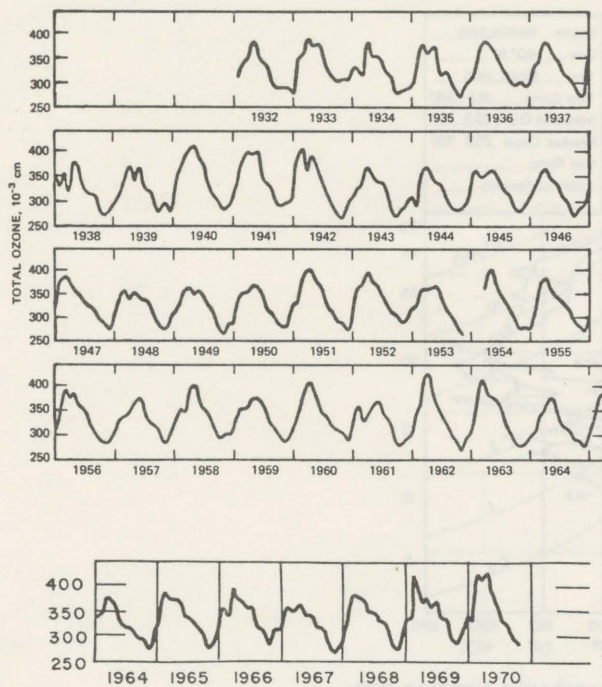


Figure 9. Monthly mean total ozone amounts at Arosa, Switzerland (46.5°N, 9.4°E) [Upper portion of diagram from Wallace and Newell (1966); lower portion: data courtesy of Dr. J. London].

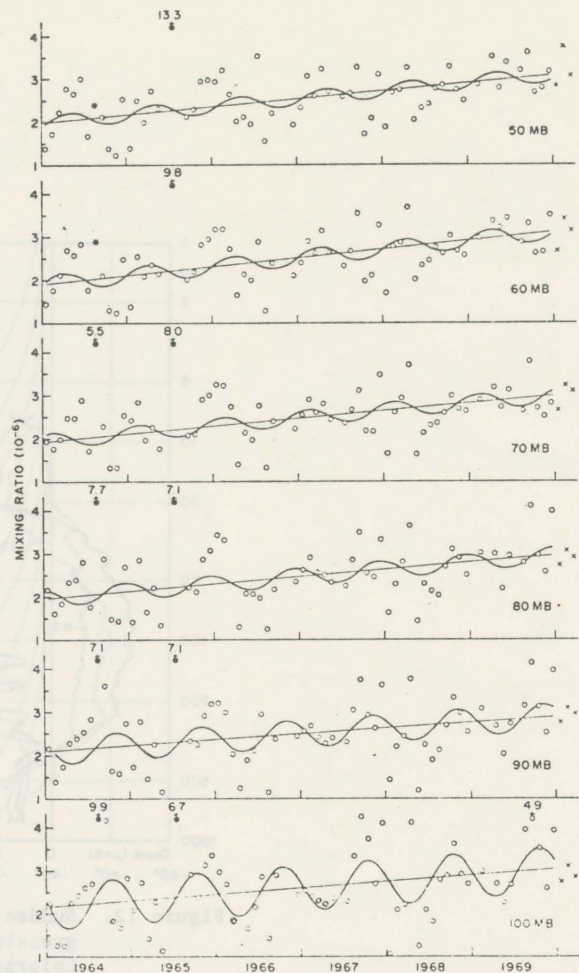


Figure 10. Time-series analysis of mixing-ratio data for selected levels. The curves for each level represent the best fit of a linear trend and an annual cycle. Open circles and crosses are data used for this analysis. Closed circles represent rejected data. [From Mastenbrook, (1971)].

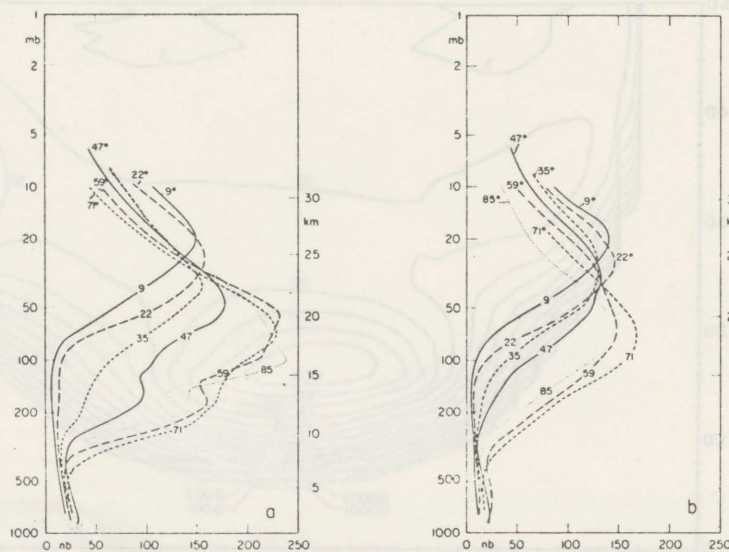


Figure 11. Mean vertical distribution (direct soundings) at different latitudes: (a) spring (mean of March and April); (b) fall (mean of October and November); 71°N is the mean from observations at Thule (76°N) and Fairbanks (65°N). [From Dütsch (1971)].

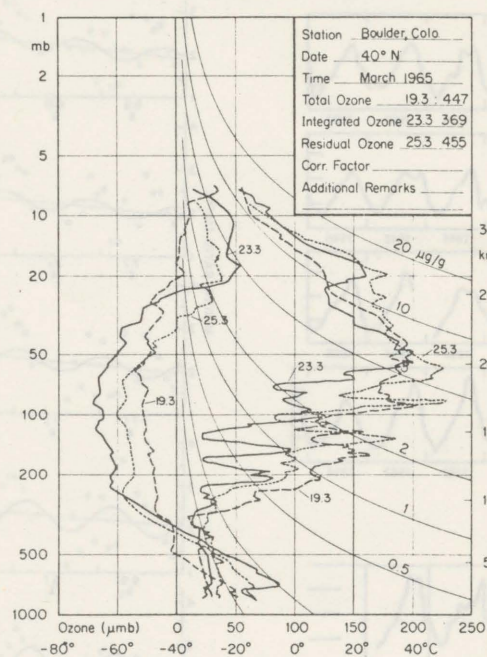


Figure 12. Sudden stratospheric warming progressing downward over Boulder, Colorado. Comparison between the ozone variations in the middle and the lower stratosphere shows that the changes are much more regular (i.e., on a larger scale in space and time) at the higher level. [From Dütsch (1971)].

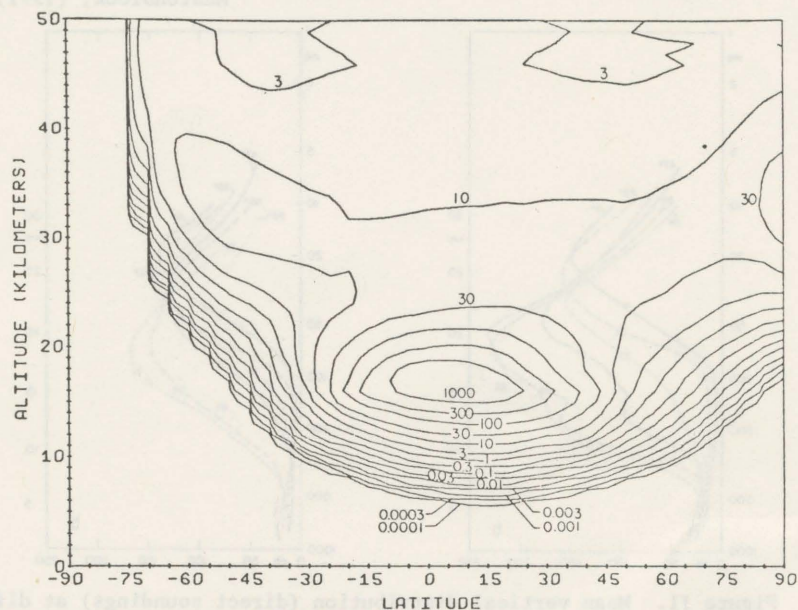


Figure 13. Ratio of ozone production rate to ozone destruction rate according to Chapman mechanism [From Johnston (1973)].

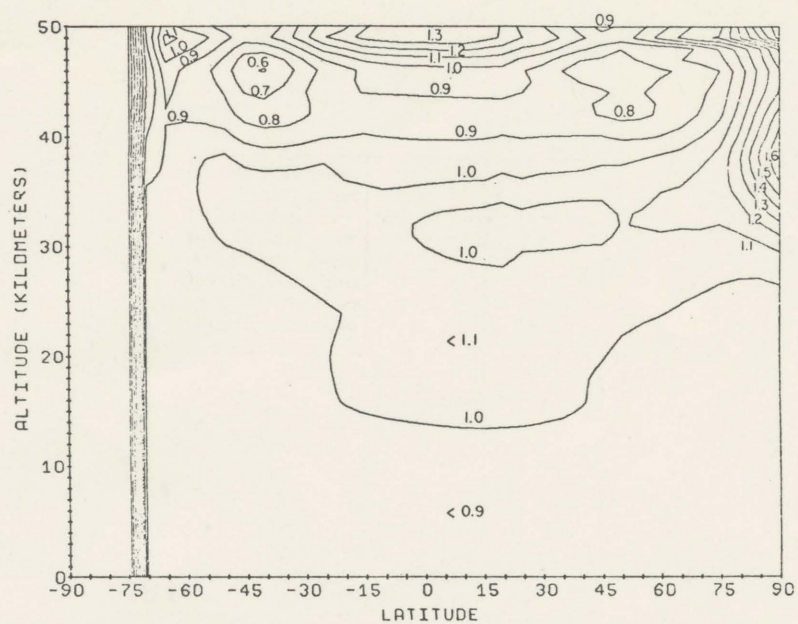


Figure 14. Same as Fig. 13, except 4.2×10^9 molecules/cm³ of NO_x added. [From Johnston (1973)].

-- NOTES --

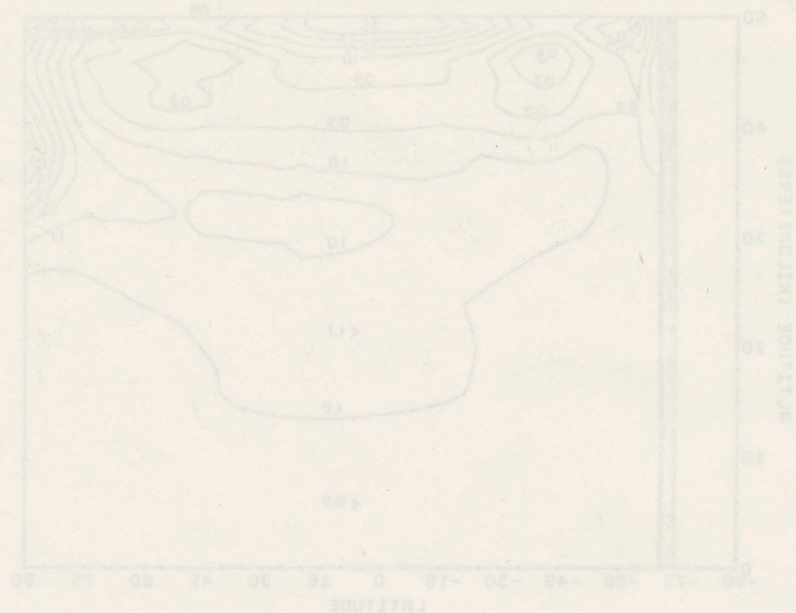


Figure 14. Same as Fig. 13, except 4.5×10^6 molecules/cm² of NO₂ added. [From Johnston (1972)].