for the long-run growth of the world economy, correctly measured, is hard to overestimate.

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Changes in Stratospheric Ozone

RALPH J. CICERONE

The ozone layer in the upper atmosphere is a natural feature of the earth's environment. It performs several important functions, including shielding the earth from damaging solar ultraviolet radiation. Far from being static, ozone concentrations rise and fall under the forces of photochemical production, catalytic chemical destruction, and fluid dynamical transport. Human activities are projected to deplete substantially stratospheric ozone through anthropogenic increases in the global concentrations of key atmospheric chemicals. Human-induced perturbations may be occurring already.

THE OZONE (O_3) LAYER IS AN IMPORTANT COMPONENT OF the stratosphere, that part of the earth's atmosphere between altitudes of 10 and 50 km where temperature increases with altitude. Ozone serves as a shield against biologically harmful solar ultraviolet (UV) radiation, initiates key stratospheric chemical reactions, and transforms solar radiation into the mechanical energy of atmospheric winds and heat. Also, downward intrusions of stratospheric air supply the troposphere with the O_3 necessary to initiate photochemical processes in the lower atmosphere, and the flux of photochemically active UV photons [wavelength (λ) < 315 nm] into the troposphere is limited by the amount of stratospheric O_3. This absorption of solar energy is the cause of the stratospheric vertical temperature gradient. Finally, because O_3 molecules absorb radiation at UV, visible, and infrared wavelengths, atmospheric O_3 affects the earth's energy budget and temperature.

Solar UV radiation of wavelengths less than 240 nm is absorbed by atmospheric O_2 and O_3, but for wavelengths between 240 and 320 nm only O_3 is effective. Wavelengths less than 320 nm span the photoabsorption spectrum of DNA and can produce deleterious biological effects, including skin cancer (*1*). Reduced amounts of atmospheric O_3 permit disproportionately large amounts of UV radiation to penetrate through the atmosphere. For example, with overhead sun and typical O_3 amounts, a 10% decrease in O_3 results in a 20% increase in UV penetration at 305 nm, a 250% increase at 290 nm, and a 500% increase at 287 nm (*2*). Because of the apparent susceptibility of biota to UV radiation, the temporal evolution of paleoatmospheric O_2, O_3, and photosynthesizing plants was probably intimately linked (*3*).

Photolysis of O_3 initiates much of stratospheric chemistry and includes processes, given by reactions 1a and 1b, that control O_3 amounts.

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta) \tag{1a}$$

$$\rightarrow O + O_2 \tag{1b}$$

The high-energy branch (reaction 1a; $\lambda < 315$ nm; h, Planck's constant; ν, frequency) produces electronically excited oxygen atoms, $O(^1D)$, that in turn initiate the free-radical chemistry of the stratosphere (*4*) through reactions such as

$$O(^1D) + H_2O \rightarrow 2OH \tag{2}$$

$$O(^1D) + CH_4 \rightarrow CH_3 + OH \tag{3}$$

$$O(^1D) + N_2O \rightarrow 2NO \tag{4}$$

$$O(^1D) + CCl_2F_2 \rightarrow \text{reactive products such as ClO} \tag{5}$$

The absorption of solar UV and visible radiation by O_3 represents an important source of heat for the stratosphere. Absorption and reemission of outgoing planetary and atmospheric infrared radiation by O_3 cools most regions of the stratosphere but heats the tropical lower stratosphere. The general circulation patterns of the strato-

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sphere can be explained fairly well by diagnostic models that include only the interactions of O_3, O_2, and NO_2 with UV and visible radiation and the interactions of CO_2, O_3, and H_2O with infrared radiation (*5*).

Although reaction 1a is slower in the troposphere than in the stratosphere because less UV light is available, it proceeds and is followed by reaction 2, and thus tropospheric OH radicals are produced. The earth's atmosphere is oxidizing toward hydrocarbons, chlorocarbons, and various compounds of sulfur and nitrogen. This oxidation is initiated by gaseous species such as O_3, OH, and HO_2, not by O_2. The movement of stratospheric O_3 downward into the troposphere can initiate lower atmospheric photochemistry and even produce more O_3 (*6*).

The measured spatial and temporal distributions of stratospheric O_3 display patterns that are consistent with known photochemical production and consumption processes and the general circulation of the atmosphere, at least on the large scale (such as 15° belts of latitude), averaged seasonally. Figure 1 (*7*) displays vertically integrated O_3 amounts as a function of latitude and season. Vertical integrals (or total column amounts) can be measured by ground-based UV absorption techniques and are important because of the relation between O_3 and the flux of UV photons into the lower atmosphere.

Generally, O_3 column amounts increase with latitude, especially in winter and spring, although O_3 production rates are highest over the equator. Seasonal variations show the largest amplitudes at high latitudes. Ozone concentrations vary with altitude above the earth's surface; peak fractions of about 10^{-5} by volume are found between 25 and 35 km. The vertical column of O_3 is distributed roughly as follows: 0 to 10 km, 10%; 10 to 35 km, 80%; and above 35 km, 10%. These patterns and percentages are nominal; in reality the O_3 layer exhibits variability under the dynamic forces of chemical production and loss and fluid motions.

Production and Destruction of Ozone

To produce atmospheric O_3 it is necessary to break the O–O bond in O_2. Once released, oxygen atoms rapidly combine with O_2 to form O_3 by the reaction

$$O + O_2 + M \rightarrow O_3 + M \qquad (6)$$

where M is any third-body molecule, such as N_2 or O_2. The bond-dissociation energy for O_2 is 118 kcal $mole^{-1}$ and corresponds to a threshold wavelength of 242 nm for photodissociation. In the stratosphere O_2 is dissociated by solar radiation in the Schumann-Runge (SR) bands (175 to 205 nm) and the Herzberg continuum (HC, 190 nm to 242 nm). It is difficult and laborious to calculate the penetration of sunlight for wavelengths between 175 and 205 nm because of the rotational line structure in the SR absorption bands of O_2 (*8*). This SR radiation is absorbed by O_2 in the upper and middle stratosphere. Very little O_3 is produced through O_2 photodissociation below about 20 km, where the deepest penetration of HC radiation occurs. Production rates for O_3 reach 10^7 molecules cm^{-3} sec^{-1} near 40 km in the daytime; they taper off slowly with increasing altitude and rapidly at altitudes below 30 km.

A large amount of solar energy is used in producing stratospheric O_3. The global rate of UV energy that goes into breaking O_2 bonds through the reaction

$$O_2 + h\nu \rightarrow O + O \qquad (7)$$

exceeds 2×10^{10} kW, or is at least three times the worldwide human energy usage rate (*9*). Additional O_3 is produced by radiation at wavelengths below 175 nm above the stratosphere and by chemical means in the lower stratosphere and the troposphere. Photochemical production of O_3 proceeds through reactions such as reaction 2 that are followed by reactions such as

$$OH + CO \rightarrow H + CO_2 \qquad (8)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (9)$$

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (10)$$

$$NO_2 + h\nu \rightarrow NO + O \text{ (near-UV light)} \qquad (11)$$

These are then followed by reaction 6, where carbon monoxide (CO) is present because of natural and industrial sources and nitric oxide (NO) is present largely because of reaction 4 in the stratosphere.

How does nature counterbalance the production of O_3? The present view is that most O_3 is destroyed catalytically because of the gaseous oxides of nitrogen and hydrogen. There is an important direct process, however, identified more than 50 years ago by S. Chapman (*10*), that involves only oxygen allotropes and can be represented by reaction 1b followed by reaction 12.

$$O_3 + h\nu \rightarrow O + O_2 \qquad (1b)$$

$$O + O_3 \rightarrow 2O_2 \qquad (12)$$

$$\text{Net reaction: } 2O_3 + h\nu \rightarrow 3O_2 \qquad (13)$$

Together with two other oxygen-only reactions,

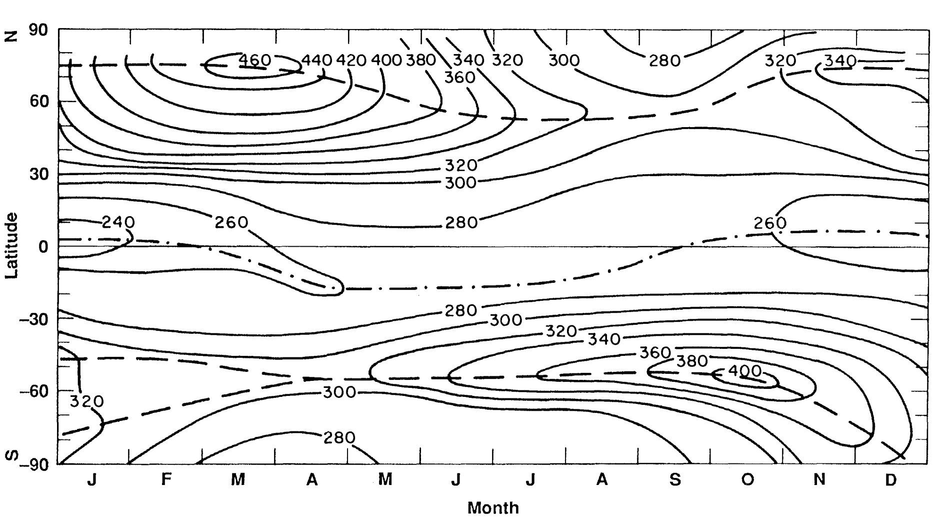

Fig. 1. Long-term average of the total amount of ozone (m-atm cm) as a function of latitude and season from ground-based data (1958–1980). The dashed lines show the maximum O_3 amount, and the dashed-dot line shows the maximum O_3 amount. [From (*7*). Courtesy of Van Nostrand Reinhold, New York]

$$O + O + M \rightarrow O_2 + M \qquad (14)$$

and

$$O(^1D) + O_3 \rightarrow 2O_2 \qquad (15)$$

reaction 12 is an important O_3 loss term from altitudes of 20 km through the upper reaches of the stratosphere and into the upper atmosphere. The bulk rates of reactions 12, 14, and 15 are essentially proportional to the square of the O_3 concentration. In this way the effectiveness of these reactions in counterbalancing O_3 production increases with O_3 concentration. These rates are limited by the availability of oxygen atoms produced by reaction 1. The requirement for oxygen atoms also characterizes most of the gas-phase processes that destroy O_3 catalytically through oxides of other elements.

Catalytic processes that destroy stratospheric O_3 are now thought to be very potent. Natural catalysts counterbalance O_3 production, and anthropogenic catalysts can be sufficiently active as to cause a net decrease in the amount of stratospheric O_3. Their inclusion into the scientific study of O_3 about 15 years ago has led to a much more complicated photochemical scheme than was summarized above (*10*) and to the realization that biological processes at the earth's surface influence the state of the global atmosphere.

Nitrogen oxides are a central case. Once in the stratosphere, NO consumes O_3 through the following gas-phase catalytic cycle

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (16)$$

$$O_3 + h\nu \rightarrow O + O_2 \qquad (1b)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (17)$$

$$\text{Net reaction: } 2O_3 + h\nu \rightarrow 3O_2 \qquad (18)$$

Reactions 16, 17, and 1b constitute a catalytic cycle because the NO that is consumed in the first reaction is replaced in the final reaction. The chain length of this cycle—that is, the number of times the cycle is repeated before an intervening process somehow sequesters the NO or NO_2—is determined by many other chemical reactions, some of which are shown below. For example, HNO_3 can be formed and transported downward to the troposphere (Fig. 2). This NO_x cycle represents a major sink for O_3 that extends vertically throughout the stratosphere [see Johnston in (*10*)]. A second NO_x catalytic cycle also destroys O_3 through reaction 16 followed by

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (19)$$

$$NO_3 + h\nu \rightarrow NO + O_2 \qquad (20)$$

$$\text{Net reaction: } 2O_3 + h\nu \rightarrow 3O_2 \qquad (18)$$

When NO_3 is photolyzed to yield $NO_2 + O$ (the dominant branch of this reaction), this latter NO_2-NO_3 reaction sequence does not consume O_3.

Hydrogen oxides (HO_x) also catalyze O_3 destruction. The following three reaction chains are significant.

$$HO + O_3 \rightarrow HO_2 + O_2 \qquad (21)$$

$$HO_2 + O_3 \rightarrow HO + O_2 + O_2 \qquad (22)$$

$$\text{Net reaction: } 2O_3 \rightarrow 3O_2 \qquad (23)$$

$$HO + O_3 \rightarrow HO_2 + O_2 \qquad (21)$$

$$O_3 + h\nu \rightarrow O + O_2 \qquad (1b)$$

$$HO_2 + O \rightarrow HO + O_2 \qquad (24)$$

$$\text{Net reaction: } 2O_3 + h\nu \rightarrow 3O_2 \qquad (18)$$

$$O_3 + h\nu \rightarrow O + O_2 \qquad (1b)$$

$$HO + O \rightarrow H + O_2 \qquad (25)$$

$$H + O_3 \rightarrow HO + O_2 \qquad (26)$$

$$\text{Net reaction: } 2O_3 + h\nu \rightarrow 3O_2 \qquad (18)$$

Because of the rapidity of reaction 6, the loss of oxygen atoms in reactions 24 and 25 is equivalent to the loss of O_3 molecules. These three HO_x cycles are most important in the upper stratosphere, although reactions 21 and 22 can also be significant in the lower stratosphere and the troposphere (*10*).

Gaseous reactions that involve chlorine also destroy O_3. The importance of these reactions appears to be relatively small in the natural, unperturbed stratosphere but can be very large in a human-perturbed stratosphere. Key reactions are the following.

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (27)$$

$$O_3 + h\nu \rightarrow O + O_2 \qquad (1b)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (28)$$

$$\text{Net reaction: } 2O_3 + h\nu \rightarrow 3O_2 \qquad (13)$$

Other reaction sequences that involve Cl, ClO, HO_2, NO_2, HOCl, and $ClNO_3$ catalytically consume O_3, but reactions 27, 1b, and 28

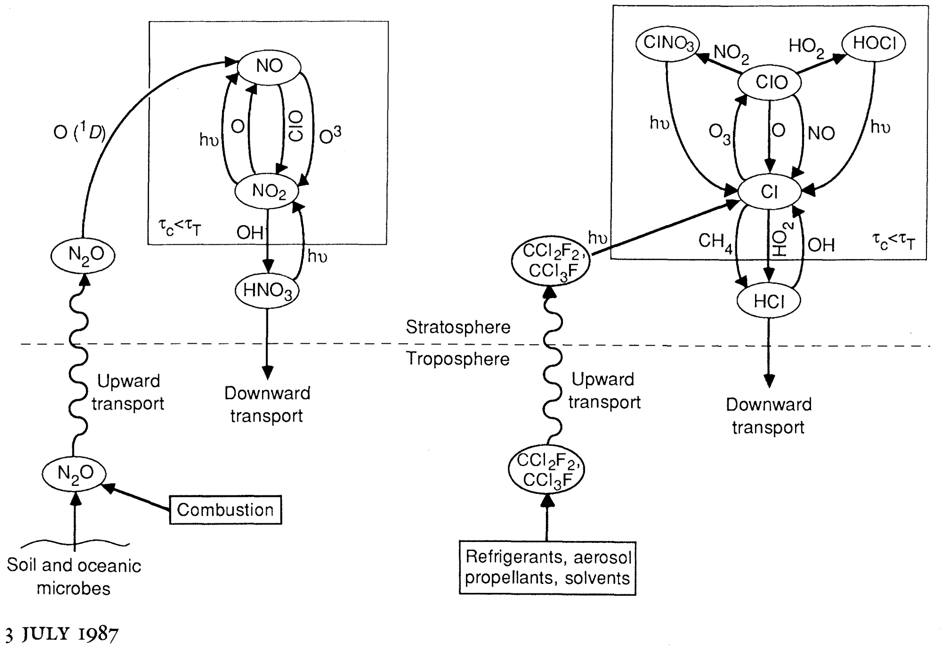

Fig. 2. Schematic depiction of how stratospheric source gases N_2O, CCl_2F_2, and CCl_3F originate at the earth's surface and are transported upward into the stratosphere, where they are irreversibly photo-oxidized to yield key gas-phase radicals. Reactants shown inside the boxes undergo reactions with time constants τ_c that are less than τ_T (the time required for significant vertical transport). Similarly, some CH_4 reaches the stratosphere, where it gives rise to H_2O, H_2, and HO_x.

make up the most important cycle.

Most of the elementary chemical reactions listed here have been well characterized in laboratory studies; reaction rate constants and temperature dependencies have been studied, often by several independent methods (*11*). Thus it is clear that catalytic destruction of O_3 by chlorine, NO_x, and HO_x does occur. The effectiveness of this catalysis is a topic of current research.

There is room for research and speculation about other possible mechanisms of O_3 production and destruction. For example, bromine could be an efficient catalyst for destroying O_3 (*12*). Reaction sequences such as

$$Br + O_3 \rightarrow BrO + O_2 \qquad (29)$$

$$O_3 + h\nu \rightarrow O + O_2 \qquad (1b)$$

$$BrO + O \rightarrow Br + O_2 \qquad (30)$$

$$\text{Net reaction: } 2O_3 + h\nu \rightarrow 3O_2 \qquad (13)$$

and

$$Br + O_3 \rightarrow BrO + O_2 \qquad (29)$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (27)$$

$$BrO + ClO \rightarrow Br + Cl + O_2 \qquad (31)$$

$$\text{Net reaction: } 2O_3 \rightarrow 3O_2 \qquad (23)$$

could be important, especially in a bromine-perturbed stratosphere. The latter catalytic cycle is especially interesting because its rate is not limited by the ambient concentration of oxygen atoms, as it is for the key NO_x cycle (reactions 16 and 17), two of the HO_x cycles, and the main chlorine cycle (reactions 27 and 28). Thus reactions 29, 27, and 31 make up a cycle that could proceed at night (since no photons are required) and even in the lower stratosphere, where concentrations of oxygen atoms decrease with altitude. The chemical kinetics of bromine reactions, however, are less well studied than for chlorine (for example, reaction 31 may produce other products), and little is known about concentrations of bromine in the stratosphere.

The efficiency of each of these O_3-destruction processes depends on the fraction of time that the active chemicals exist as NO, NO_2, H, OH, HO_2, Cl, ClO, Br, and BrO compared to the time they exist in the form of inactive, reservoir species such as HNO_3, N_2O_5, HNO_4, H_2O_2, $ClNO_3$, HCl, and $BrNO_3$. Reservoir species such as $ClNO_3$ and HNO_3 are particularly interesting because through their formation reactions

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (32)$$

$$HO + NO_2 + M \rightarrow HNO_3 + M \qquad (33)$$

each sequesters O_3-active species from two chemical families. The flow of active chlorine and nitrogen species through reservoir species, and through the atmosphere, is partially sketched in Fig. 2.

All the O_3-destruction mechanisms outlined above derive from homogeneous gas-phase reactions. Recently, heterogeneous processes have been invoked because of the apparent inability of purely gaseous reactions to account for the observed rapid decreases in O_3 concentrations over Antarctica each September (*13, 14*). It has been suggested that heterogeneous processes liberate O_3-active species from reservoir species (*14*). These include

$$H_2O + ClONO_2 \xrightarrow{\text{surface}} HNO_3 + HOCl \qquad (34)$$

$$HCl + ClONO_2 \xrightarrow{\text{surface}} HNO_3 + Cl_2 \qquad (35)$$

and incorporation of gaseous HNO_3 and HCl into polar stratospheric cloud particles by condensation or ion-catalyzed condensation (or both). Although these processes are not well defined experimentally or theoretically, they could increase the efficiencies of chlorine and bromine attack on O_3 by regenerating more active species from reservoir species. Such possibilities are attractive because there are more cloud particles in the lower stratosphere over Antarctica than anywhere else. It is extremely important to deter-

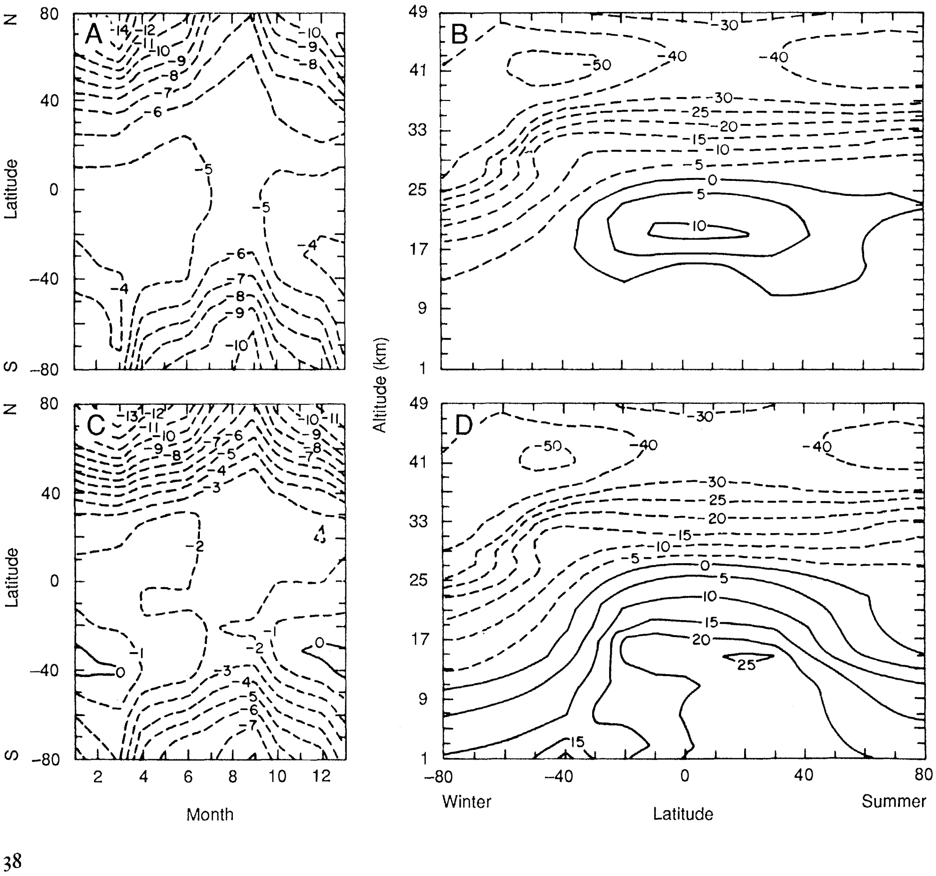

Fig. 3. Calculated changes in O_3 in percent due to (**A** and **B**) increased CFCs from continued usage at 1980 world rates and (**C** and **D**) the same CFC increases, but with a 40% increase of atmospheric N_2O and a 100% increase of CH_4. Changes in total O_3 columns as a function of latitude and time of year are shown in (A) and (C). The changes as a function of altitude and latitude of local O_3 concentrations are shown in (B) and (D). The solid and dashed lines represent O_3 increases and decreases, respectively. [Adapted from (*26*). Courtesy of the American Geophysical Union, Washington, D.C.]

mine the chemical composition and thermodynamic properties of these particles.

Sources of Stratospheric Chemicals

The scientific effort to understand stratospheric O_3 and human-induced perturbations is proceeding across disciplines and in several directions. One concern is the flow of chemicals into the stratosphere from natural and anthropogenic sources. Key species are gases that are relatively inert in the troposphere, such as CH_4, N_2O, CH_3Cl, synthetic chlorofluorocarbons (CFCs) and chlorocarbons, and certain organobromine compounds (Table 1).

Figure 2 displays examples of large-scale processes that produce and transfer source gases, which undergo irreversible photo-oxidation to yield important gaseous radicals, to the stratosphere. Thus N_2O from soil and oceanic microbes enters the lower atmosphere and, through large-scale motions (principally in the tropics), is transported upward to the stratosphere. Most N_2O is decomposed through

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad (36)$$

but about 5% produces NO through

$$N_2O + O(^1D) \rightarrow 2NO \qquad (37)$$

as indicated in Fig. 2. Similarly, the synthetic chlorofluorocarbons CCl_2F_2 and CCl_3F are swept upward into the middle stratosphere, where UV photolysis dissociates them to yield chlorine atoms. As with N_2O, there are no known tropospheric sinks for CCl_2F_2 and CCl_3F, so that nearly 100% of the molecules released at the earth's surface reach the stratosphere. Atmospheric tracer data and spatial patterns of N_2O, CFCs, and other gases indicate that, on average, it takes about 5 years for a gas emitted at the earth's surface from mid-latitudes of the Northern Hemisphere to travel upward to photochemically active altitudes (25 km and higher) in the stratosphere. Atmospheric residence times on the order of 100 years characterize N_2O, CCl_2F_2, and CCl_3F, because air at altitudes of 25 km and higher must be exchanged vertically many times to deplete the massive tropospheric reservoir of these species.

The activity of another important gas, methane (CH_4), is not depicted in Fig. 2. Methane is not as inert in the atmosphere as nitrous oxide (N_2O) or CFCs. Rather, it is oxidized through the reaction

$$CH_4 + OH \rightarrow H_2O + CH_3 \qquad (38)$$

Perhaps 85 to 90% of the CH_4 released at the earth's surface is consumed by reaction 38 in the troposphere. The remaining 10% to 15% (approximately 6×10^{13} g year^{-1}) reaches the stratosphere, where reaction 38 is once again the main sink; similar reactions with chlorine atoms and $O(^1D)$ atoms also occur. Stratospheric oxidation of CH_4 gives rise to important quantities of water vapor and to OH and HO_2 radicals.

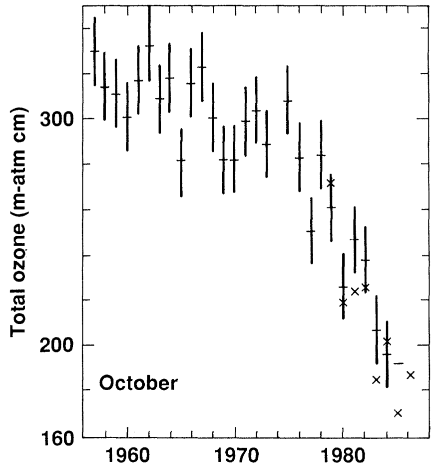

Fig. 4. Mean values of the total O_3 measured over Antarctica for the month of October for the years 1957 through 1986. BAS data, from Farman and colleagues (*13*), for 1957 through 1984 at Halley Bay (76°S) are shown as horizontal lines (mean values) through vertical bars (±1 standard deviation). An additional BAS point for 1985 (*35*) is also shown, but no measure of variance was reported, and BAS data for 1986 are not yet available. Ozone minimum values from NASA satellite data are shown as crosses for the years 1979 through 1986 (*36*). These are the lowest monthly means for any 2° latitude belt below 60°S. For clarity, no measures of variance are attached to the NASA data.

The upper boxes of Fig. 2 show some of the important reactions that control stratospheric O_3 concentrations, including some of the reactions 16 through 37. Chain reactions that are carried by radicals destroy O_3 and perform other transformations; these chains are terminated by radical-radical reactions that produce relatively stable species such as HNO_3 and HCl. Although NO_2 and chlorine atoms can be regenerated from HNO_3 and HCl, the time constant τ_c for each of these reactions is long enough for downward transport into the troposphere to occur. When polar, soluble species such as HNO_3 and HCl come into contact with condensed water and surfaces in the lower atmosphere, they can be deposited at the earth's surface, mostly as H^+, NO_3^-, and Cl^-. Thus at steady state the amount of nitrogen from NO_3^- ions deposited annually would equal the amount of nitrogen released as NO in the stratosphere from N_2O if there were no other sources of NO_3^- ions (such as pollution from combustion).

It is important to know the release rates of N_2O, CH_4, and CFCs because of the control over O_3 exerted by the decomposition products of these source gases. Also, N_2O, CH_4, and several CFCs are potent climatic "greenhouse" gases (as is O_3) that trap outgoing planetary heat in the earth-atmosphere system, and their atmospheric concentrations are increasing (*15*). For N_2O we have only semiquantitative information. Aerobic microbial nitrification and anaerobic microbial denitrification produce N_2O both in soils and in water bodies (*16*). Combustion of fuels, especially nitrogen-rich fuels, also produces N_2O. Temporal trends and spatial distributions of N_2O are well characterized (*16, 17*), but the relative roles of processes that cause its increase (microbiological sources that act on excess amounts of nitrogen fertilizer compared to combustion processes) are not clear (*16, 17*).

Microbiological processes are also central to the question of atmospheric CH_4 sources. Methanogenesis (an anaerobic process) in ruminant animals, rice-paddy soils, swamps and marshes, and perhaps termite guts furnishes the bulk of CH_4; and CH_4 is also released from natural gas exploration and transmission and coal mining (*16*). Microbial CH_4 oxidation also limits the flux of CH_4 from some soils and the oceans into the atmosphere.

Although our knowledge of microbial production rates of N_2O and CH_4 is inadequate, and although we know very little of the variations in these rates and their underlying mechanisms, we do know the global totals to which the various sources must add. For a gas X with no atmospheric sources and a steady-state global distribution, the total annual source (TAS) is given by

$$\mathrm{TAS} = \int\!\!\int\!\!\int X(\boldsymbol{r})L(\boldsymbol{r})d^3\boldsymbol{r} \qquad (39)$$

where $\boldsymbol{r}$ is the spatial coordinate, L is the local atmospheric photochemical loss rate for gas X, and the integration is over the entire atmosphere. For N_2O, solar UV radiation ($\lambda < 230$ nm) and attack by stratospheric $O(^1D)$ constitute L, and the total annual source (sink) of N_2O is calculated to be 11 (± 2) $\times 10^{12}$ g of nitrogen as N_2O (*16, 18*). This steady-state argument is improper, because N_2O concentrations are increasing (*17*) and 3×10^{12} g of nitrogen as N_2O is needed annually in addition to the steady-state source to account for the increase. Thus the present sources of atmospheric N_2O add to about 14×10^{12} g of nitrogen as N_2O.

Equation 39 yields more uncertain results when applied to CH_4 because the atmospheric loss term L for CH_4 is dominated by its tropospheric OH radicals (reaction 38). There are virtually no observational data for tropospheric OH, but if OH concentrations from theoretical models are used with Eq. 39 and additional lines of reasoning, the total annual steady-state CH_4 source is 450 (± 150) $\times 10^{12}$ g (*16*). In addition, the atmospheric burden of CH_4 has increased about 1% annually in recent years, which implies that a 50×10^{12} to 60×10^{12} g CH_4 source increase or sink decrease (or both) operates annually. There are indications from $^{14}CH_4$ data that 80% or more of the total CH_4 source is recent biological activity (*15*).

For CFCs, especially CCl_2F_2 and CCl_3F, the situation is simpler. From industrial production statistics and tariff data we know the amounts of these chemicals that have entered the atmosphere since their use became widespread in the 1960s. In recent years, the annual industrial production of CCl_2F_2 and CCl_3F has been 450×10^3 and 300×10^3 metric tons, respectively. After corrections for the amounts already destroyed in the stratosphere, for CFC storage times, and for amounts dissolved in oceans, the measured atmospheric concentrations agree closely with those expected from production data (*16*). In contrast, only semiquantitative information is available for sources of $C_2Cl_3F_3$, CCl_4, CH_3Cl, and organobromine gases.

Perturbations to Stratospheric Ozone

Stratospheric O_3 could be decreased by any process that can lead to increased stratospheric amounts of O_3-destroying catalysts (for example, oxides of nitrogen, chlorine, hydrogen, or bromine). Many possible stimuli have been proposed, principally NO_x from nuclear explosions (*19*), hypothetical fleets of supersonic aircraft (*20*), solar proton events (*21*), and increased atmospheric N_2O (*22*) and chlorine from continued use of CFCs (*23*), volcanoes, and space shuttle rocket exhaust (*24*). Also, increases in atmospheric CH_4 can lead to O_3 perturbations through interactions with NO_x and ClO_x cycles and through production of HO_x. Further, increases in carbon dioxide can lead to increases in O_3, not through direct chemical reactions but through enhanced radiative cooling of the middle and upper stratosphere. Such a cooling would hasten reaction 6 and decrease the concentration ratio of oxygen atoms to O_3 molecules. While it can be said that all these stimuli are now being applied to the atmosphere, the most definitive experiment to date concerns solar proton events. Observations that followed the large event of August 1972 showed that O_3 concentrations were reduced by about as much as theory predicted, at least in the upper stratosphere (*25*).

Attempts to predict the future effects of continued increases in stratospheric source gases (CFCs, N_2O, CH_4) have given rise to various mathematical models. Early models were one-dimensional (altitude), but in the last several years two-dimensional (altitude and latitude) models have become available. Some of these two-dimensional models include as many chemical reactions as the one-dimensional models and also treat atmospheric motions, latitude variations, and seasonal changes much more realistically. One hundred or more gas-phase reactions are included in modern models.

Figure 3 shows the results of calculations of future O_3 perturbations caused by continued CFC releases and the changes due to simultaneous CFC releases and increases in atmospheric N_2O and CH_4. These O_3 changes were calculated with a two-dimensional diabatic circulation model (*26*) that simulates known tracer fields very well but does not account for thermal and fluid dynamical changes due to O_3 changes. In these calculations, steady annual releases of 392×10^3 and 265×10^3 tons were simulated for CCl_2F_2 and CCl_3F, respectively, and the model was run to steady state. Similarly, N_2O and CH_4 concentrations at the lower boundary (zero altitude) were fixed at 1.4×305 parts per billion (ppb) and 2.0×1.6 parts per million, respectively. The steady-state results in Fig. 3 represent the atmosphere in approximately the year 2050.

Simulated CFC releases lead to O_3 column decreases at all latitudes in Fig. 3; local O_3 concentrations decrease greatly above altitudes of 35 km at all latitudes. Increases in local O_3 appear below 25 km in the tropics and are largely due to increased penetration of radiation at wavelengths less than 240 nm that produces new O_3. Larger O_3 column decreases are calculated for high latitudes (>40°) than for low latitudes. When the sustained CFC releases are accompanied by increases in N_2O and CH_4, similar spatial patterns are calculated but with sharper gradients. Calculated O_3 decreases are smaller at high altitudes, and O_3 increases are greater at low altitudes. The former is due to decreased attack of chlorine on O_3 because of the increased rates of reaction 32 and of the reaction

$$CH_4 + Cl \rightarrow HCl + CH_3 \tag{40}$$

both of which sequester chlorine atoms. At low altitudes there is increased troposphere-like O_3 production due to increased CH_4 and NO_x in the model, although other mechanisms also operate (*26*). The reference state for the perturbations of Fig. 3 was a stratosphere that included 2.4 ppb of inorganic chlorine, ClX; although this ClX value may characterize the present stratosphere, the earlier unperturbed stratosphere probably had less than 1 ppb of ClX.

The transient temporal approach to future O_3 perturbations is an important matter both for testing the scientific theory of atmospheric behavior and for more practical reasons, such as limiting future increases in UV radiation or evaluating climate change. Experimental and analytical efforts are under way to detect temporal changes in stratospheric O_3 and related species (*27*) and to compare the results to the time-dependent analogs of Fig. 3. Trend detection is a major goal of these efforts; existing models require additional verification, and early warnings of larger future O_3 changes are needed. No clear trend in the total column of stratospheric O_3 has been reported to date except for that over Antarctica (*27*). Some data show a decrease of O_3 concentrations in the upper stratosphere since 1970 (*27*); it is in the upper stratosphere where the largest and earliest O_3 decreases are expected.

Large O_3 decreases over Antarctica have been reported (*13*); this perturbation was not predicted, nor is there an accepted explanation at present. Figure 4 shows the measured monthly means of total O_3 measured each October over Halley Bay, Antarctica (76°S), from 1957 through 1984, after Farman and colleagues (*13*) of the British Antarctic Survey (BAS). A decrease of more than 35% has occurred since about 1970. Stolarski and co-workers (*13*) examined NASA satellite data on total O_3 and found that the phenomenon is regional in extent, not just local. The decrease occurs during September as the sun rises, and O_3 concentration reaches a minimum in mid-October. Eight years (1979–1986) of NASA's October minimum monthly means are plotted as crosses in Fig. 4; these are the lowest monthly means observed in any 2° latitude belt south of 60°S. The NASA analysis also shows a 30% decrease in the O_3 minimum and a 20% decrease in the surrounding O_3 maximum. It seems clear that, for O_3 column decreases of tens of percent to be achieved, O_3 must be decreased greatly in the lower and middle stratosphere, not just above. Stolarski and co-workers also found that the deep O_3 minimum follows the polar vortex, in which temperatures of the lower stratosphere are very low in winter and early spring (often below 190 K) and stratospheric clouds are much more prevalent than over the Arctic (*28*).

Table 1. Data that characterize four key stratospheric trace gases that enter the atmosphere at the earth's surface. Source designation: N, natural; A, anthropogenic; HC, under human control. For CH_4 only 10 to 15% of the total source enters the stratosphere, and the concentration decreases with altitude in the stratosphere. Concentrations are in parts per million (ppm), parts per billion (ppb), and parts per trillion (ppt) by volume. TAS, total annual source (see reaction 39 in text).

Gas	Concentration	Trend ($year^{-1}$)	Residence time (years)	Sources	TAS (10^{12} g)
N_2O	305 ppb	0.6 ppb	120	Microbial nitrification and denitrification (N) and accelerated rates thereof due to synthetic nitrogen fertilizer (HC)	
				Combustion (A)	15*
CH_4	1.66 ppm	17 ppb	10	Microbial methanogenesis in swamps, marshes, tundra, and termites (N) and in ruminant animals and rice-paddy soils (HC)	
				Natural gas transmission and mining (A)	500
CCl_2F_2	380 ppt	19 ppt	120	Aerosol spray propellants (outside United States), refrigerants, solvents, and foam blowing (A)	0.45
CCl_3F	220 ppt	11 ppt	70	Same as for CCl_2F_2	0.30

*As grams of nitrogen.

Theories that attempt to explain the Antarctic O_3 "hole," its timing, and its secular change are becoming numerous (*13, 14*). It is important to understand the chemical and physical mechanisms of this perturbation to be able to predict whether it will spread to lower latitudes and worsen, or dissipate and shrink. Atmospheric fluid motions, radiative energy exchange, and atmospheric chemistry are likely to be strongly linked in a successful explanation. From a mostly fluid-dynamical point of view, Mahlman and Fels (*29*) proposed a mechanism that could trigger many features of the Antarctic O_3 decreases. If a natural climatic process could substantially reduce the wintertime planetary-scale disturbance activity in the Southern Hemisphere troposphere, then several southern stratospheric responses would be expected (*29*): a reduction of wintertime polar O_3, a prolonging of the time span of the polar vortex, reduction of the transport of O_3 out of the middle stratosphere, and an increased possibility of polar rising motion shortly after the return of the sun to high latitudes. All these effects are in qualitative agreement with the observed O_3 changes, although the reasons for the hypothesized triggering events are not clear and the overall mechanism does not preclude independent chemical mechanisms. If natural dynamical mechanisms can cause secular O_3 decreases such as those observed over Antarctica, then our ability to detect other human-induced O_3 changes would be seriously challenged because more natural variability would have to be incorporated into our trend-detection schemes.

From the viewpoint of chemical perturbation, the Antarctic phenomenon is stimulating proposals of more complex chemical reactions and reactants than had been included in previous models. As noted above, condensed-phase and heterogeneous processes are being invoked to account for the release of more active chlorine, for example from less active chlorine reservoir species (*30*). If relatively high ratios of ClO to total inorganic chlorine concentrations do characterize the September and October Antarctic stratosphere, then new catalytic cycles could become significant. The following reaction sequence has been suggested (*30, 31*).

$$2(Cl + O_3 \rightarrow ClO + O_2) \qquad (27)$$

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \qquad (41)$$

$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO \qquad (42)$$

$$ClOO + M \rightarrow Cl + O_2 \qquad (42)$$

$$\text{Net reaction: } 2O_3 + h\nu \rightarrow 3O_2 \qquad (13)$$

A reaction sequence such as this could grow in importance as the square of the chlorine content in the stratosphere in the future (when more ClO will be present). To date, models of future global O_3 perturbations by CFCs have not included processes such as this that involve the higher oxides of chlorine.

Recent ground-based spectroscopic observations from Antarctica (*32*) have indeed detected a higher oxide of chlorine, OClO (the symmetric form of chlorine dioxide). It is not yet clear whether this stratospheric OClO is directly related to O_3 destruction, but it was observed in surprisingly large quantities during the austral spring O_3 decrease. The origin of this OClO is unclear. A second branch of reaction 31 is known to form OClO (*33*); surface reactions involving ClO and O_3 or $ClNO_3$ and O_3 are possible (*33*); even isomerization of ClOO with O_3 is possible. Similar ground-based observations (*34*) have also demonstrated that the Antarctic stratosphere contains unusually small amounts of NO_2, which implies that solar-proton–produced nitrogen oxides act minimally (if at all) in the destruction of O_3 during austral spring.

As global atmospheric change becomes a matter of fact rather than conjecture, it becomes even more important to advance the scientific study of stratospheric O_3 perturbations and our ability to predict them. A growing arsenal of experimental techniques is developing, and new instruments are being applied to characterize the atmosphere and its variations and to laboratory experiments in photochemistry and kinetics (*27*). It is to be hoped that the speed of acquisition of quantitative understanding and predictive skill exceeds the rate at which atmospheric change occurs.

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A Physiological Basis for a Theory of Synapse Modification

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The functional organization of the cerebral cortex is modified dramatically by sensory experience during early postnatal life. The basis for these modifications is a type of synaptic plasticity that may also contribute to some forms of adult learning. The question of how synapses modify according to experience has been approached by determining theoretically what is required of a modification mechanism to account for the available experimental data in the developing visual cortex. The resulting theory states precisely how certain variables might influence synaptic modifications. This insight has led to the development of a biologically plausible molecular model for synapse modification in the cerebral cortex.

ALTHOUGH ARISTOTLE IDENTIFIED HEART AS THE SEAT OF intellect, reserving for brain the function of cooling the head, it is now generally believed that it is brain that is the source of thought, the location of memory, the physical basis of mind, consciousness, and self-awareness: all that make us distinct and human. In recent years it has become increasingly fashionable to treat this complex system as a neural network: an assembly of neurons connected to one another by synaptic junctions that serve to transmit information and possibly to store memory.

Since the contents of memory must depend to some extent on experience, the neural network and, in particular, the synapses between neurons cannot be completely determined genetically. This evident reasoning has led to much discussion about possible modification of synapses between neurons as the physiological basis of learning and memory storage. To properly function, neural network models require that vast arrays of synapses have the proper strengths. A basic problem becomes how these synapses adjust their weights so that the resulting neural network shows the desired properties of memory storage and cognitive behavior.

The problem can be divided into two parts. First, what type of modification is required so that in the course of actual experience the neural network arrives at the desired state? The answer to this question can be illuminated by mathematical analysis of the evolution of neural networks by means of various learning hypotheses. The second part of this problem is to find experimental justification for any proposed modification algorithm. A question of extraordinary interest is: What are the biological mechanisms that underlie the nervous system modification that results in learning, memory storage, and eventually cognitive behavior?

One experimental model that appears to be well suited for the purpose of determining how neural networks modify is the visual cortex of the cat. The modification of visual cortical organization by sensory experience is recognized to be an important component of early postnatal development (*1*). Although much modifiability disappears after the first few months of life, some of the underlying mechanisms are likely to be conserved in adulthood to provide a basis for learning and memory. We have approached the problem of experience-dependent synaptic modification by determining theoretically what is required of a mechanism in order to account for the experimental observations in visual cortex. This process has led to the formulation of hypotheses, many of which are testable with currently available techniques. In this article we illustrate how the interaction between theory and experiment has suggested a possible

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