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

REFERENCES AND NOTES
1. See examples and discussion in Z. Griliches, J. Politi. Econ. 66, 419 (1958); E. Mansfield, J. Rapoport, A. Romeo, S. Wagner, G. Beardsley, Q. J. Econ. 91, 221 (1977); R. E. Evenson, P. E. Waggoner, V. W. Kutan, Science 208, 1101 (1979).
2. M. N. Bailey [Science 234, 443 (1986)] attempts to do just that.
3. J. Schmooler, Invention and Economic Growth (Harvard Univ. Press, Cambridge, MA, 1986).
4. E. M. Schirer, Rev. Econ. Stat. 64, 627 (1982).
5. Z. Griliches, Ed., R&D, Patents, and Productivity (Univ. of Chicago Press, Chicago, 1984).
6. Z. Griliches, A. Pakes, B. H. Hall, Natl. Bur. Econ. Rev. Working Pap. 2083 (1986).
7. See F. M. Schirer in (5), p. 917.
8. A. Jaffe, Am. Econ. Rev. 76, 984 (1986).
9. M. Shachter and A. Pakes, Econ. J. 96, 1082 (1986).
10. Z. Griliches, Econ. Lett. 7, 183 (1981); A. Pakes, J. Polit. Econ. 93, 390 (1985).
11. Z. Griliches, Bell J. Econ. 10, 92 (1979).
12. It was not until 1986 that an allowance was made in the national income accounts for the improving quality of electronic computers [Varo. Carri. Bus. 66, 41 (1986)].
13. Z. Griliches, in Science and Technology in Economic Growth, B. R. Williams, Ed. (Macmillan, London, 1983), p. 89.
14. C. W. Cobb and P. H. Douglas, Am. Econ. Rev. Suppl. 18, 139 (1928); M. Nerlove, Estimation and Identification of Cobb-Douglas Production Functions (Rand McNally, New York, 1965).
15. Z. Griliches, Am. Econ. Rev. 76, 141 (1986).
16. These numbers differ from Fig. 1 both because they refer to the specific sample used by Griliches (15) and because they are averages of ratios rather than ratios of totals.
17. Here and subsequently, all statements about statistical "significance" should not be taken literally. Besides the usual issue of data mining clouding their interpretations, the "samples" analyzed come close to covering completely the relevant population. Tests of significance are used here as a metric for discussing the relative fit of different versions of the model. In each case, the actual magnitude of the estimated coefficients is of more interest than their precise "statistical significance."
18. E. Mansfield [Am. Econ. Rev. 70, 863 (1980)] and A. N. Link (ibid. 71, 1111 (1981)] present similar results based on somewhat smaller samples.
19. Z. Griliches, in New Developments in Productivity Measurement, J. W. Kendrick and R. Viscara, Eds. (Univ. of Chicago Press, Chicago, 1980), p. 419.
20. Z. Griliches and F. Lichtenberg in (5, p. 465); Rev. Econ. Stat. 66, 324 (1984).
21. F. M. Schirer (4) obtained similar results.
22. Derived from National Science Foundation, Science and Technology in Economic Growth, 1984 (Washington, DC, 1984), pp. 84-311 and earlier issues. Numbers refer to all of manufacturing rather than to the samples of firms considered in (15).
23. I am indebted to the National Science Foundation and the National Bureau of Economic Research for research support and to B. H. Hall for research assistance and collaboration.

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 (O₃) 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 O₃ 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 O₃.

The absorption of solar energy is the cause of the stratospheric vertical temperature gradient. Finally, because O₃ molecules absorb radiation at UV, visible, and infrared wavelengths, atmospheric O₃ affects the earth's energy budget and temperature.

Solar UV radiation of wavelengths less than 240 nm is absorbed by atmospheric O₃ and O₂, but for wavelengths between 240 and 320 nm only O₃ 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 O₃ permit disproportionately large amounts of UV radiation to penetrate through the atmosphere. For example, with overhead sun and typical O₃ amounts, a 10% decrease in O₃ 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 O₃, O₂, and photosynthesizing plants was probably intimately linked (3).

Photolysis of O₃ initiates much of stratospheric chemistry and includes processes, given by reactions 1a and 1b, that control O₃ amounts.

O₃ + hν → O(¹D) + O₂(³Σ) (1a)
→ O + O₂ (1b)

The high-energy branch (reaction 1a; λ < 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) + H₂O → 2OH (2)
O(¹D) + CH₄ → CH₃ + OH (3)
O(¹D) + N₂O → 2NO (4)
O(¹D) + CCl₂F₂ → reactive products such as ClO (5)

The absorption of solar UV and visible radiation by O₃ represents an important source of heat for the stratosphere. Absorption and emission of outgoing planetary and atmospheric infrared radiation by O₃ cools most regions of the stratosphere but heats the tropical lower stratosphere. The general circulation patterns of the strato-

The author is at the National Center for Atmospheric Research, Boulder, CO 80307.
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. \( O_3 \) 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

\[
O + O_2 + M \rightarrow O_3 + M \tag{6}
\]

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 \( O_3 \) 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 \( O_3 \) 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

\[
O_2 + h\nu \rightarrow O + O \tag{7}
\]

exceeds \( 2 \times 10^{10} \) 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. Photochemitical production of \( O_3 \) proceeds through reactions such as reaction 2 that are followed by reactions such as

\[
\begin{align*}
OH + CO & \rightarrow H + CO_2 \tag{8} \\
H + O_2 + M & \rightarrow HO_2 + M \tag{9} \\
HO_2 + NO & \rightarrow NO_2 + OH \tag{10} \\
NO_2 + h\nu & \rightarrow NO + O \quad \text{(near-UV light)} \tag{11}
\end{align*}
\]

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.

\[
\begin{align*}
O_3 + h\nu & \rightarrow O + O_2 \tag{1b} \\
O + O_2 & \rightarrow 2O_2 \tag{12}
\end{align*}
\]

Together with two other oxygen-only reactions,

\[
\begin{align*}
\text{Net reaction: } 2O_3 + h\nu & \rightarrow 3O_2 \tag{13}
\end{align*}
\]
reaction 12 is an important O₃ 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 O₃ concentration. In this way the effectiveness of these reactions in counterbalancing O₃ production increases with O₃ 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 O₃ catalytically through oxides of other elements.

Catalytic processes that destroy stratospheric O₃ are now thought to be very potent. Natural catalysts counterbalance O₃ production, and anthropogenic catalysts can be sufficiently active as to cause a net decrease in the amount of stratospheric O₃. Their inclusion into the scientific study of O₃ 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 O₃ through the following gas-phase catalytic cycle

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(16)}
\]

\[
\text{O}_3 + hv \rightarrow \text{O} + \text{O}_2 \quad \text{(1b)}
\]

\[
\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \quad \text{(17)}
\]

Net reaction: \(2\text{O}_3 + hv \rightarrow 3\text{O}_2\) \(\text{(18)}\)

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 NO₂—is determined by many other chemical reactions, some of which are shown below. For example, HNO₃ can be formed and transported downward to the troposphere (Fig. 2). This NO₃ cycle represents a major sink for O₃ that extends vertically throughout the stratosphere [see Johnston in (10)]. A second NO₃ catalytic cycle also destroys O₃ through reaction 16 followed by

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(19)}
\]

\[
\text{NO}_3 + hv \rightarrow \text{NO} + \text{O}_2 \quad \text{(20)}
\]

Net reaction: \(2\text{O}_3 + hv \rightarrow 3\text{O}_2\) \(\text{(18)}\)

When NO₃ is photolized to yield NO₂ + O (the dominant branch of this reaction), this latter NO₂+O reaction sequence does not consume O₃. Hydrogen oxides (HOₓ) also catalyze O₃ destruction. The following three reaction chains are significant.

\[
\text{HO} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{(21)}
\]

\[
\text{HO} + \text{O}_3 \rightarrow \text{HO} + \text{O}_2 + \text{O}_2 \quad \text{(22)}
\]

Net reaction: \(2\text{O}_3 + hv \rightarrow 3\text{O}_2\) \(\text{(18)}\)

\[
\text{O}_3 + hv \rightarrow \text{O} + \text{O}_2 \quad \text{(1b)}
\]

\[
\text{HO}_2 + \text{O} \rightarrow \text{HO} + \text{O}_2 \quad \text{(24)}
\]

Net reaction: \(2\text{O}_3 + hv \rightarrow 3\text{O}_2\) \(\text{(18)}\)

Because of the rapidity of reaction 6, the loss of oxygen atoms in reactions 24 and 25 is equivalent to the loss of O₃ molecules. These three HOₓ 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 O₃. 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.

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad \text{(27)}
\]

\[
\text{O}_3 + hv \rightarrow \text{O} + \text{O}_2 \quad \text{(1b)}
\]

\[
\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \quad \text{(28)}
\]

Net reaction: \(2\text{O}_3 + hv \rightarrow 3\text{O}_2\) \(\text{(13)}\)

Other reaction sequences that involve Cl, ClO, HO₂, NO₂, HOCl, and CINO₃ catalytically consume O₃, but reactions 27, 1b, and 28 are the most important.
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 O₃ by chlorine, NO₃, and HO₃ 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 O₃ production and destruction. For example, bromine could be an efficient catalyst for destroying O₃ (12). Reaction sequences such as

\[
\begin{align*}
\text{Br} + O_3 & \rightarrow \text{BrO} + O_2 \\
O_3 + hv & \rightarrow O + O_2 \\
\text{BrO} + O & \rightarrow \text{Br} + O_2 \\
\text{Net reaction: } 2O_3 + hv & \rightarrow 3O_2
\end{align*}
\]

(27)

and

\[
\begin{align*}
\text{Br} + O_3 & \rightarrow \text{BrO} + O_2 \\
\text{Cl} + O_3 & \rightarrow \text{ClO} + O_2 \\
\text{BrO} + \text{ClO} & \rightarrow \text{Br} + \text{Cl} + O_2 \\
\text{Net reaction: } 2O_3 & \rightarrow 3O_2
\end{align*}
\]

(29)

(28)

(31)

(32)

(33)

(32)

(34)

(35)

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 NO₃ cycle (reactions 16 and 17), two of the HO₂ 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 O₃-destruction processes depends on the fraction of time that the active chemicals exist as NO₃, NO₂, H₂O, HO₂, Cl₂, ClO₂, Br, and BrO compared to the time they exist in the form of inactive, reservoir species such as HN0₃, N₂O₅, HNO₄, H₂O₂, ClONO₂, ClO₂, HCl, and BrO. Reservoir species such as ClO₂ and HNO₃ are particularly interesting because through their formation reactions

\[
\begin{align*}
\text{ClO} + \text{NO}_3 + M & \rightarrow \text{ClONO}_2 + M \\
\text{HO} + \text{NO}_2 + M & \rightarrow \text{HNO}_3 + M
\end{align*}
\]

(32)

(33)

each sequesters O₃-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 O₃-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 O₃ concentrations over Antarctica each September (13, 14). It has been suggested that heterogeneous processes liberate O₃-active species from reservoir species (14). These include

\[
\begin{align*}
\text{H}_2\text{O} + \text{ClONO}_2 & \rightarrow \text{HNO}_3 + \text{HOCl} \\
\text{HCl} + \text{ClONO}_2 & \rightarrow \text{HNO}_3 + \text{Cl}_2
\end{align*}
\]

(34)

(35)

and incorporation of gaseous HN0₃ 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 O₃ 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 O₃ 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 N₂O and a 100% increase of CH₄. Changes in total O₃ 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 O₃ concentrations are shown in (B) and (D). The solid and dashed lines represent O₃ increases and decreases, respectively. [Adapted from (26). Courtesy of the American Geophysical Union, Washington, D.C.]](image-url)
mine the chemical composition and thermodynamic properties of these particles.

Sources of Stratospheric Chemicals

The scientific effort to understand stratospheric O3 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 CH4, N2O, CH3Cl, 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 N2O 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 N2O is decomposed through

\[ N_2O + hv \rightarrow N_2 + O(1D) \]  (36)

but about 5% produces NO through

\[ N_2O + O(1D) \rightarrow 2NO \]  (37)

as indicated in Fig. 2. Similarly, the synthetic chlorofluorocarbons CCl2F2 and CCl3F are swept upward into the middle stratosphere, where UV photolysis dissociates them to yield chlorine atoms. As with N2O, there are no known tropospheric sinks for CCl2F2 and CCl3F, so that nearly 100% of the molecules released at the earth's surface reach the stratosphere. Atmospheric tracer data and spatial patterns of N2O, 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 N2O, CCl2F2, and CCl3F, 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 (CH4), is not depicted in Fig. 2. Methane is not as inert in the atmosphere as nitrous oxide (N2O) or CFCs. Rather, it is oxidized through the reaction

\[ CH_4 + OH \rightarrow H_2O + CH_3 \]  (38)

Perhaps 85 to 90% of the CH4 released at the earth's surface is consumed by reaction 38 in the troposphere. The remaining 10% to 15% (approximately 6 x 1012 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 CH4 gives rise to important quantities of water vapor and to OH and HO2 radicals.

The upper boxes of Fig. 2 show some of the important reactions that control stratospheric O3 concentrations, including some of the reactions 16 through 37. Chain reactions that are carried by radicals destroy O3 and perform other transformations; these chains are terminated by radical-radical reactions that produce relatively stable species such as HNO3 and HCl. Although NO2 and chlorine atoms can be regenerated from HNO3 and HCl, the time constant \( \tau \) for each of these reactions is long enough for downward transport into the troposphere to occur. When polar, soluble species such as HNO3 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\(^{-}\), and Cl\(^{-}\). Thus at steady state the amount of nitrogen from NO\(^{-}\) ions deposited annually would equal the amount of nitrogen released as NO in the stratosphere from N2O if there were no other sources of NO\(^{-}\) ions (such as pollution from combustion).

It is important to know the release rates of N2O, CH4, and CFCs because of the control over O3 exerted by the decomposition products of these source gases. Also, N2O, CH4, and several CFCs are potent clatamic “greenhouse” gases (as is O3) that trap outgoing planetary heat in the earth-atmosphere system, and their atmospheric concentrations are increasing (15). For N2O we have only semiquantitative information. Aerobic microbial nitrification and anaerobic microbial denitrification produce N2O both in soils and in water bodies (16). Consumption of fuels, especially nitrogen-rich fuels, also produces N2O. Temporal trends and spatial distributions of N2O 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 CH4 sources. Methanogenesis (an anaerobic process) in ruminant animals, rice-paddy soils, swamps and marshes, and perhaps termite guts furnishes the bulk of CH4, and CH4 is also released from natural gas exploration and transmission and coal mining (16). Microbial CH4 oxidation also limits the flux of CH4 from some soils and the oceans into the atmosphere.

Although our knowledge of microbial production rates of N2O and CH4 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

\[ TAS = \iint X(r)L(r)dr \]  (39)

where \( r \) is the spatial coordinate, \( L \) is the local atmospheric photochemical loss rate for gas X, and the integration is over the entire atmosphere. For N2O, solar UV radiation (\( \lambda < 250 \) nm) and attack by stratospheric O(1D) constitute \( L \), and the total annual source (sink) of N2O is calculated to be \( 11 \pm 2 \times 10^{12} \) g of nitrogen as N2O (16, 18). This steady-state argument is improper, because N2O concentrations are increasing (17) and 3 x 10\(^{12} \) g of nitrogen as N2O is needed annually in addition to the steady-state source to account for the increase. Thus the present sources of atmospheric N2O add to about 14 x 10\(^{12} \) g of nitrogen as N2O.
Equation 39 yields more uncertain results when applied to CH₄ because the atmospheric loss term L for CH₄ 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 CH₄ source is 450 (±150) x 10¹² g. In addition, the atmospheric burden of CH₄ has increased about 1% annually in recent years, which implies that a 50 x 10¹² to 60 x 10¹² g CH₄ source increase or sink decrease (or both) operates annually. There are indications from CH₄ data that 80% or more of the total CH₄ source is recent biological activity.

For CFCs, especially CCl₂F₂ and CCl₃F, 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 CCl₂F₂ and CCl₃F has been 450 x 10¹² and 300 x 10¹² 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 C₂Cl₃F₃, CCl₄, CH₂Cl, and organobromine gases.

**Perturbations to Stratospheric Ozone**

Stratospheric O₃ could be decreased by any process that can lead to increased stratospheric amounts of O₃-destroying catalysts (for example, oxides of nitrogen, chlorine, hydrogen, or bromine). Many possible stimuli have been proposed, principally NOₓ from nuclear explosions (19), hypothetical flights of supersonic aircraft (20), solar proton events (21), and increased atmospheric N₂O (22) and chlorine from continued use of CFCs (23), volcanoes, and space shuttle rocket exhaust (24). Also, increases in atmospheric CH₄ can lead to O₃ perturbations through interactions with NOₓ and ClO₃ cycles and through production of HO₂. Further, increases in carbon dioxide can lead to increases in O₃, 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 O₃ 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 O₃ 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, N₂O, CH₄) 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 O₃ perturbations caused by continued CFC releases and the changes due to simultaneous CFC releases and increases in atmospheric N₂O and CH₄. These O₃ 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 O₃ changes. In these calculations, steady annual releases of 392 x 10¹² and 265 x 10¹² tons were simulated for CCl₂F₂ and CCl₃F, respectively, and the model was run to steady state. Similarly, N₂O and CH₄ concentrations at the lower boundary (zero altitude) were fixed at 1.4 x 305 parts per billion (ppb) and 2.0 x 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 O₃ column decreases at all latitudes in Fig. 3; local O₃ concentrations decrease greatly above altitudes of 35 km at all latitudes. Increases in local O₃ 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 O₃. Larger O₃ column decreases are calculated for high latitudes (>40°) than for low latitudes. When the sustained CFC releases are accompanied by increases in N₂O and CH₄, similar spatial patterns are calculated but with sharper gradients. Calculated O₃ decreases are smaller at high altitudes, and O₃ increases are greater at low altitudes. The form is due to decreased attack of chlorine on O₃ because of the increased rates of reaction 32 of Cl₂O₃.
Theories that attempt to explain the Antarctic O₃ "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 O₃ 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 O₃, a prolonging of the time span of the polar vortex, reduction of the transport of O₃ 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 O₃ 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 O₃ decreases such as those observed over Antarctica, then our ability to detect other human-induced O₃ 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).

\[
\begin{align*}
2(\text{Cl} + \text{O}_3) & \rightarrow \text{ClO} + \text{O}_2 \quad (27) \\
\text{ClO} + \text{Cl} + \text{M} & \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \quad (41) \\
\text{Cl}_2\text{O}_2 + h\nu & \rightarrow \text{Cl} + \text{ClOO} \quad (42) \\
\text{ClOO} + \text{M} & \rightarrow \text{Cl} + \text{O}_2 \quad (42)
\end{align*}
\]

Net reaction: \(2\text{O}_3 + h\nu \rightarrow 3\text{O}_2\) (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 O₃ 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, OCIO (the symmetric form of chlorine dioxide). It is not yet clear whether this stratospheric OCIO is directly related to O₃ destruction, but it was observed in surprisingly large quantities during the austral spring O₃ decrease. The origin of this OCIO is unclear. A second branch of reaction 31 is known to form OCIO (33); surface reactions involving ClO and O₃ or CINO₂ and O₃ are possible (33); even isomerization of ClOO with O₃ is possible. Similar ground-based observations (34) have also demonstrated that the Antarctic stratosphere contains unusually small amounts of NO₂, which implies that solar-proton–produced nitrogen oxides act minimally (if at all) in the destruction of O₃ 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 O₃ 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.

### References and Notes

1. R. B. Setlow, Proc. Natl. Acad. Sci. U.S.A. 71, 3363 (1974).
2. P. Catches, Science 184, 13 (1974). Actual amounts of UV radiation that reach the earth's surface depend on solar zenith angle, cloud characteristics, and multiple scattering.
3. J. C. Walker, Evolution of the Atmosphere (Macmillan, New York, 1977).
4. J. A. Davidson et al., J. Chem. Phys. 67, 5021 (1977).
5. J. T. Kiehl and S. Solomon, J. Atmos. Sci. 43, 1525 (1986).
6. W. Chameides and J. C. Walker, J. Geophys. Res. 78, 8751 (1973); P. J. Crutzen, Pure Appl. Geophys. 106–108, 1385 (1975).
7. J. London, Ozone in the Free Atmosphere, R. C. Whitten and S. S. Prasad, Eds. (Van Nostrand Reinhold, New York, 1985), chap. 1.
8. J. E. Frederick and R. D. Hudson, J. Atmos. Sci. 37, 1101 (1980).
9. For the method of calculating O₃ photolysis rates, see R. J. Cicerone, S. Walters, S. C. Lin, J. Geophys. Res. 88, 3647 (1983); energy-usage rates were taken from D. M. Gates, Energy and Ecology (Sinuera, Sunderland, MA, 1985), p. 377.
10. M. Nicol de Rev. Geophys. Space Phys. 13, 593 (1975) and H. S. Johnston (ibid., p. 637) present excellent critical reviews of O₂ layer research and history.
11. W. B. Demore et al., Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling (Publication 85-37, NASA Jet Propulsion Laboratory, Pasadena, CA, 1985).
12. R. T. Watson, in The Natural Stratosphere of 1974: Climatic Impact Assessment Program Monograph I (DOT-TST-75-S, Department of Transportation, Washington, DC, 1975), pp. 5–125–5–152; Y. L. Young, J. P. Peiser, R. T. Watson, S. P. Sanders, J. Atmos. Sci. 37, 339 (1980); M. J. Trattner, B. M. McElroy, S. C. WoIey, Nature (London) 312, 227 (1984).
13. J. C. Farman, B. G. Gardner, J. D. Shanklin, Nature (London) 315, 207 (1985).
14. R. S. Stolarski et al., ibid. 322, 908 (1986). More than 40 additional papers on the

### 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 CH₄ 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 (10¹² g) |
|--------------|---------------|----------------|------------------------|------------------------------------------------------------------------|--------------|
| N₂O          | 305 ppb       | 0.6 ppb        | 120                    | Microbial nitrification and denitrification (N) and accelerated rates thereof due to synthetic nitrogen fertilizer (HC) | 15*          |
| CH₄          | 1.66 ppm      | 17 ppb         | 10                     | Microbial methanogenesis in swamps, marshes, tundra, and termite (N) and in ruminant animals and rice-paddy soils (HC) | 0.45         |
| CCl₂F₂       | 380 ppt       | 19 ppt         | 120                    | Natural gas transmission and mining (A)                                | 500          |
| CCl₃F       | 220 ppt       | 11 ppt         | 70                     | Aerosol spray propellants (outside United States), refrigerants, solvents, and foam blowing (A) | 0.30         |

*As grams of nitrogen.
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 synaptic 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 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

M. F. Bear is an Alfred P. Sloan Research Fellow and assistant professor of neural science in the Center for Neural Science at Brown University; L. N. Cooper is Thomas J. Watson, Sr., Professor of Science in the Department of Physics at Brown University; and F. F. Ebner is professor of medical science in the Division of Biology and Medicine at Brown University. L. N. Cooper and F. F. Ebner are codirectors of the Center for Neural Science at Brown University, Providence, RI 02912.