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Greenhouse Effects due to Man-Made Perturbations of Trace Gases

Anthropogenic gases may alter our climate by plugging an atmospheric window for escaping thermal radiation.

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It is well recognized that the thermal structure of the earth's atmosphere is influenced by the presence of small quantities of water vapor, carbon dioxide, ozone, and aerosols (*1*, *2*). The main radiative effect of the gases is through absorption of upward-moving thermal radiation and reradiation at the local temperature; this blanketing leads to an increase in the surface temperature, the so-called greenhouse effect. Aerosols may either heat or cool the surface, depending on their optical properties for both incident solar radiation and emitted thermal radiation (*3*, *4*). These phenomena, which have been well analyzed in the context of planetary atmosphere studies, almost certainly played a major role in the evolution of our own atmosphere as well as those of Venus and Mars (*5–7*).

The atmosphere also contains a large number of trace gases with strong infrared absorption bands; examples are N_2O, CH_4, NH_3, HNO_3, C_2H_4, SO_2, CCl_2F_2, CCl_3F, CH_3Cl, and CCl_4. Despite the small amounts of these gases, they can have a significant effect on the atmosphere's thermal structure because they have absorption bands within the 7- to 14-μm (700 to 1400 cm^{-1}) atmospheric window which transmits most of the thermal radiation from the earth's surface and lower atmosphere (Fig. 1). In this article we discuss the nature and climatic implications of possible changes in the concentrations of N_2O, CH_4, NH_3, and HNO_3; we also include computations of the greenhouse effect for the other trace gases listed above. The greenhouse effect of the chlorofluorocarbons (Freons) has already been studied by Ramanathan (*8*), and our computations for the Freons are included only for comparison. Similarly, to provide a further basis for comparison, we include computations of the changes in the atmospheric greenhouse effect which would accompany plausible or hypothetical modifications of the abundances of the primary gaseous radiative constituents—H_2O, CO_2, and O_3.

Sources and Sinks for Atmospheric Trace Constituents

The chemistry of N_2O, CH_4, NH_3, HNO_3, C_2H_4, SO_2, CCl_2F_2, CCl_3F, CH_3Cl, and CCl_4 has been extensively studied (*9–18*). The present status of our knowledge is summarized in Table 1. Nitrous oxide, methane, and ammonia appear to be produced mainly by decay of organic matter under anaerobic conditions. Their abundance in the present atmosphere must be the result of a delicate balance between bacterial activities and various removal mechanisms. Nitrous oxide (N_2O) is destroyed by photolysis (reaction J1) and reaction with $O(^1D)$ (K1), primarily in the stratosphere. There is, however, evidence for an additional tropospheric sink (L1), and the lifetime of N_2O may thus be as short as 10 to 30 years instead of the 130 years implied by reactions J1 and K1. Methane is removed from the atmosphere by reaction with the hydroxyl radical OH (K2), with small additional contributions due to photolysis (J2) and reaction with $O(^1D)$ (K3). The all-important hydroxyl radical involved in reaction K2 is mainly derived from

$$O(^1D) + H_2O \rightarrow 2OH \qquad (K10)$$

where $O(^1D)$ is formed by photolysis of ozone

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \qquad (J8)$$

The concentration of OH is limited by reaction K2 and by reaction with carbon monoxide

$$OH + CO \rightarrow CO_2 + H \qquad (K11)$$

We may note that CO itself is derived as a by-product in the oxidation of CH_4, with an additional contribution from combustion of fossil fuels. Our knowledge of the atmospheric chemistry of NH_3 is quite uncertain. The mixing ratio of NH_3 in the troposphere is highly variable, a consequence of its short lifetime; following McConnell (*12*), we use a mixing ratio 6×10^{-9}. Ammonia is readily attacked by OH or washed out by rain. The Freons are clearly anthropogenic in origin. They are destroyed by photolysis (J5 and J6) at altitudes above 25 kilometers.

As is clear from this discussion of Table 1, there is no reason to believe that the chemical composition of the atmosphere is immutable. In this article we focus on two major perturbations man is imposing on the global environment: stimulation of agriculture by chemical fertilizers, and combustion of fossil fuels (*9*, *18*). It is not possible at this time to accurately forecast the chemical evolution of the atmosphere accompanying these perturbations, so we simply point out the order of magnitude of effects that have been suggested.

The use of fertilizers provides the primary mechanism for man's influence on the nitrogen cycle, and it has recently been suggested that this perturbation could lead to an increase in atmospheric N_2O. There is a large range in the predictions of chemical modelers, with the

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higher estimates being as much as a factor of 2 by the year 2020 (*9, 18*). The corresponding effect on NH_3 has not been estimated, but it is probable that the source of NH_3 would scale with that of N_2O, and thus we would anticipate a potential increase in NH_3 of the same magnitude as that for N_2O.

Combustion of fossil fuel is a significant source of atmospheric CO and must be responsible for the observed threefold enhancement of CO concentration in the mid-latitudes of the Northern Hemisphere as compared to similar latitudes in the Southern Hemisphere (*9*). Bolin (*19*) estimates that by the year 2020 the world's demand for fossil fuel will be twice what it is today. The chemical consequences of an increase in this source of CO will not be pursued in detail here, but it would be expected to lead, through reaction K11, to a decrease in OH and thus, through reaction K2, to an increase in CH_4. For our calculations of temperature perturbations we assume that this factor could conceivably be of the order of 2.

It is clear that the concentrations of C_2H_4 and CH_3Cl may increase too, since, like CH_4, they are removed mainly by reactions with OH (K7 and K9). An increase in atmospheric HNO_3 may be caused by the speedup of the nitrogen cycle discussed earlier and by combustion. Combustion is also expected to provide a large source of SO_2. The potential variation of CCl_4 in the future is difficult to assess, because of our lack of knowledge of the relative importance of natural and anthropogenic sources. For our present calculations we assume that these gases are potentially variable by factors of the order of 2.

Table 1. Major sources and sinks for several atmospheric trace constituents. The symbols J*i*, K*i*, and L*i* denote photodissociation, homogeneous reactions, and heterogeneous reactions, respectively; Reac., reaction

Species	Major source	Major sinks	Reac.	Lifetime
N_2O	Anaerobic decay	$N_2O+h\nu \rightarrow N_2+O$	J1	130 years
		$N_2O+O(^1D) \rightarrow 2NO \rightarrow N_2+O_2$	K1	
		Unknown sink	L1	10 to 30 years?
CH_4	Anaerobic decay	$CH_4+OH \rightarrow CH_3+H_2O$	K2	
		$CH_4+h\nu \rightarrow CH_2+H_2 \rightarrow CH_3+H$	J2	3 to 7 years
		$CH_4+O(^1D) \rightarrow CH_3+OH$	K3	
NH_3	Anaerobic decay	$NH_3+OH \rightarrow NH_2+H_2O$	K4	
		$NH_3+h\nu \rightarrow NH_2+H$	J3	~ 10 days
		Washout by rain	L2	
HNO_3	$NO_2+OH+M \rightarrow HNO_3+M$ (K5)	$HNO_3+OH \rightarrow NO_3+H_2O$	K6	
		$HNO_3+h\nu \rightarrow OH+NO_2$	J4	~ 10 days
		Washout by rain	L2	
C_2H_4	Anaerobic decay	$C_2H_4+OH \rightarrow$ products	K6	1 day
		$C_2H_4+O_3 \rightarrow$ products	K7	
SO_2	Oxidation of H_2S; combustion	Washout by rain	L2	~ 10 days
CCl_2F_2	Anthropogenic release	$CCl_2F_2+h\nu \rightarrow CClF_2+Cl$	J5	68 years
CCl_3F	Anthropogenic release	$CCl_3+h\nu \rightarrow CCl_2F+Cl$	J6	45 years
CH_3Cl	Decay of marine biological organisms	$CH_3Cl+OH \rightarrow$ products	K9	1 year
CCl_4	Natural or anthropogenic release	$CCl_4+h\nu \rightarrow$ products	J7	30 to 50 years

Table 2. Characteristics of the atmospheric model employed as a standard for comparison. These characteristics lead to a surface temperature of 287.67°K. In addition to the indicated infrared absorbers, the model contains present-day abundances of CH_2Cl_2, $CHCl_3$, C_6H_6, and peroxyacetyl nitrate (PAN), but these were found to have a negligible greenhouse effect (see Table 3).

Characteristic	Value
Surface pressure (P_0)	1013.25 mbar
Surface albedo	
Solar radiation	0.105
Thermal radiation	0
Solar "constant"	1.958 ly min^{-1}
Maximum tropospheric lapse rate	-6.5°K km^{-1}
Cloud cover	50 percent
Cloud-top height	5.5 km
H_2O vapor abundance	
$Q = P/P_0 \leq 0.02$	3×10^{-6} g per gram of air
$Q = P/P_0 > 0.02$	$q = 0.75\,(Q - 0.02)/(1 - 0.02)$*
CO_2 abundance	330 ppmv
O_3 column amount (*32*)	3.43 mm STP
HNO_3 column amount (*33*)	4.87×10^{-3} mm STP
NO_2 column amount	2.35×10^{-3} mm STP
N_2O abundance†	$f_0 = 0.28$ ppmv, $z_0 = 15$ km; $H = 10$ km
CH_4 abundance†	$f_0 = 1.60$ ppmv, $z_0 = 10$ km, $H = 30$ km
NH_3 abundance†	$f_0 = 6$ ppbv, $z_0 = 8$ km, $H = 1$ km
C_2H_4 abundance†	$f_0 = 0.2$ ppbv, $z_0 = 2$ km, $H = 1$ km
SO_2 abundance†	$f_0 = 2$ ppbv, $z_0 = 2$ km, $H = 1$ km
CCl_2F_2 abundance†	$f_0 = 0.1$ ppbv, $z_0 = 12$ km, $H = 3$ km
CCl_3F abundance†	$f_0 = 0.1$ ppbv, $z_0 = 12$ km, $H = 3$ km
CH_3Cl abundance†	$f_0 = 0.5$ ppbv, $z_0 = 12$ km, $H = 3$ km
CCl_4 abundance†	$f_0 = 0.1$ ppbv, $z_0 = 12$ km, $H = 3$ km

*The value q is the relative humidity taken from (*2*). †These constituents are assumed to be uniformly mixed with relative abundance f_0 from the ground to altitude z_0, above which the relative abundance decreases exponentially with scale height H; that is, $f = f_0 \exp[-(z - z_0)/H]$.

Atmospheric Model

Quantitative evaluation of the changes in the earth's climate that would accompany a particular change in atmospheric composition is even more difficult to achieve than prediction of atmospheric chemical evolution. Climate modeling is at a primitive stage and is not yet capable of reproducing interannual and long-term climate variations. The primary difficulty is the large number of physical processes that come into play for time scales longer than the radiative time constant of the atmosphere, which is of the order of 1 month. These processes, involving the atmosphere, ocean, cryosphere, and land surface, are particularly complex because of the significant interactions and feedback effects that occur among them over climatic time scales. On the other hand, the long time scales involved in climate also mean that the external boundary conditions and the radiative forcing of the system must be principal determinants of climate, as opposed to the internal dynamical processes that account for the specific motions of the atmospheric eddies representing global weather patterns; this provides some hope for eventual deterministic climate modeling.

A first step toward achieving a realistic climate model can be taken by modeling specific aspects of the full climatic system. In particular, for evaluating the effect of a perturbation of atmospheric radiative constituents, a one-dimensional radiative-convective model of the atmospheric thermal structure is a useful tool. Although such models exclude horizontal transports and a number of other mechanisms, they do at least make it possible to compare the relative importance of different radiative perturbations. It is conceivable that one-dimensional models even provide a good first-order estimate of the effect of the assumed perturbation on the earth's average thermal structure, but it is difficult to be confident of that in the absence of reliable fully interactive climate models. For example, available climate models indicate that there is a feedback between snow or ice, albedo, and temperature which is strongly positive, implying that the actual change in the average surface temperature would be significantly larger than that obtained with a one-dimensional model; current global estimates for this feedback factor are ~ 1.5 (*20, 21*), with considerably larger values for high latitudes. There are many other potential feedbacks—for example, between temperature and cloud properties—which are very difficult to estimate quantitatively at this time.

In our one-dimensional radiative-convective model the atmosphere is allowed to reach an equilibrium thermal structure with a time-marching computational procedure (*22*). For the assumed atmospheric composition and initial temperature distribution, the local radiative heating and cooling rates for solar and thermal radiation are computed at each altitude, with the net heating used to determine the local temperature at time $t + \Delta t$. The relative humidity of the atmosphere is kept fixed; thus, if a change in the abundance of an atmospheric constituent increases the temperature, the absolute humidity also increases, causing a substantial positive feedback effect (*23*). At any altitude where the computed temperature lapse rate is steeper than a preassigned maximum value (-6.5°K per kilometer) it is assumed that convection occurs with a vertical energy flux just sufficient to yield that preassigned maximum lapse rate. Interaction through the time-marching procedure is continued until energy balance is achieved at each level in the atmosphere; after the atmospheric composition is perturbed, typically 300 to 450 simulated days are required to reestablish equilibrium to an accuracy of 0.01°K. Averaging over clear and cloudy regions, each assumed to cover 50 percent of the earth, is performed at each time step before computing the energy balance. Because of our inability to predict cloud feedback effects, we make computations with two different assumptions for the cloud-top altitude: fixed cloud-top height and fixed cloud-top temperature. The latter assumption seems more plausible (*24*), but by considering both cases we obtain an indication of the sensitivity of the results to that assumption. Other characteristics of the standard global average atmosphere that we employed are listed in Table 2.

Table 3. Infrared bands of trace atmospheric constituents, and the greenhouse effects arising from the indicated changes in concentrations of single species. The greenhouse effects obtained by doubling present-day abundances of CH_2Cl_2, $CHCl_3$, C_6H_6, and PAN were negligible (< 0.01°K). These mixing ratios are the values at the surface. The assumed vertical profiles are given in Table 2.

Species	Band center		Band designation	References for infrared properties	Assumed present concentration (ppmv)	Factor modifying concentration	Greenhouse effect (°K)	
	λ (μm)	ω (cm⁻¹)					Fixed cloud-top temperature	Fixed cloud-top height
N_2O	7.78 17.0 4.5	1285 588 2223	ν_1 ν_2 ν_3	(*34*)	0.28	2	0.68	0.44
CH_4	7.66	1306	ν_4	(*34, 35*)	1.6	2	0.28*	0.20
NH_3	10.53	950	ν_2	(*36*)	6×10^{-3}	2	0.12	0.09
HNO_3	5.9 7.5 11.3 21.8	1695 1333 850 459	ν_2 $\nu_3 + \nu_4$ $\nu_5 + 2\nu_9$ ν_9	(*37*)	See (*33*)	2	0.08	0.06
C_2H_4	10.5	949	ν_7	(*36*)	2×10^{-4}	2	0.01	0.01
SO_2	8.69 7.35	1151 1361	ν_1 ν_3	(*36*)	2×10^{-3}	2	0.03	0.02
CCl_2F_2	9.13 8.68 10.93	1095 1152 915	ν_1 ν_6 ν_8	(*38*)	1×10^{-4}	20	0.54	0.36
CCl_3F	9.22 11.82	1085 846	ν_1 ν_4	(*38*)	1×10^{-4}	20		
CH_3Cl	13.66 9.85 7.14	732 1015 1400	ν_3 ν_6 $\nu_2 + \nu_5$	(*39*)	5×10^{-4}	2	0.02	0.01
CCl_4	12.99	770	ν_3	(*40*)	1×10^{-4}	2		
H_2O	6.25 10 20 10–∞	1600 1000 500 0–1000	ν_2 Continuum Continuum Rotational	(*34*) (*41*) (*42*) (*34*)	See Table 2	2†	1.03	0.65
CO_2	15.0	667	ν_2	(*34*)	330	1.25	0.79	0.53
O_3	9.6	1042	ν_3	(*34*)	See (*32*)	0.75	−0.47	−0.34

*The greenhouse effect for CH_4 is 0.40°K, rather than 0.28°K, if the absorption data of Kyle are used rather than the data of Fox (*35*).

†The H_2O abundance change was a factor of 2 above 11 km, while it was determined by the condition of fixed relative humidity below that altitude.

Greenhouse Effects for Trace Atmospheric Constituents

Table 3 gives the equilibrium change in the surface temperature for the one-dimensional radiative-convective model when the abundance of each gas is modified by the indicated factor. A change in the global average surface temperature $\gtrsim 0.1$°K is potentially significant if it is maintained for a long time. Present climate models and paleoclimatic data both indicate that global average temperature perturbations are magnified several times for high-latitude regions (25). Major climatic changes are typically associated with average global temperature changes of the order of 1°K (25), and thus the potential climatic effects of N_2O, CH_4, NH_3, and HNO_3 warrant further consideration. Although a temperature perturbation such as that computed for HNO_3 may appear to be negligible, it is important to note that the combined greenhouse effects for such weak absorbers are essentially additive. For example, the net greenhouse effect for simultaneous doubling of the abundances of N_2O, CH_4, NH_3, and HNO_3 is 1.2°K. The Freons will also become significant if their abundances increase by an order of magnitude or more, and of course smaller percentage changes in the abundances of the primary radiative constituents (CO_2, O_3, and H_2O) also have substantial effects on the surface temperature.

Our primary objective here is to point out that several trace atmospheric gases may have a significant effect on atmospheric temperatures, and thus they should be included in analyses of man's impact on the environment. Previously their effects seem to have been either overlooked or underestimated. For example, in the World Meteorological Organization's report on climate and climate modeling (3) it is stated categorically that "minor constituents like N_2O, CH_4, etc. are present in such small concentration that their direct radiative effects are negligible" and that these trace gases "can have only an indirect effect on the energy budget of the planet (through participating in the photochemistry of ozone or the production of particulate matter)." This opinion leads to the recommendation in that publication that the abundances of these gases need to be measured only to the extent that they are useful for analyzing atmospheric chemistry. We believe, on the contrary, that N_2O, CH_4, and NH_3 should be accurately monitored to get a firm handle on the global trends of abundance, as is being done for CO_2 (3).

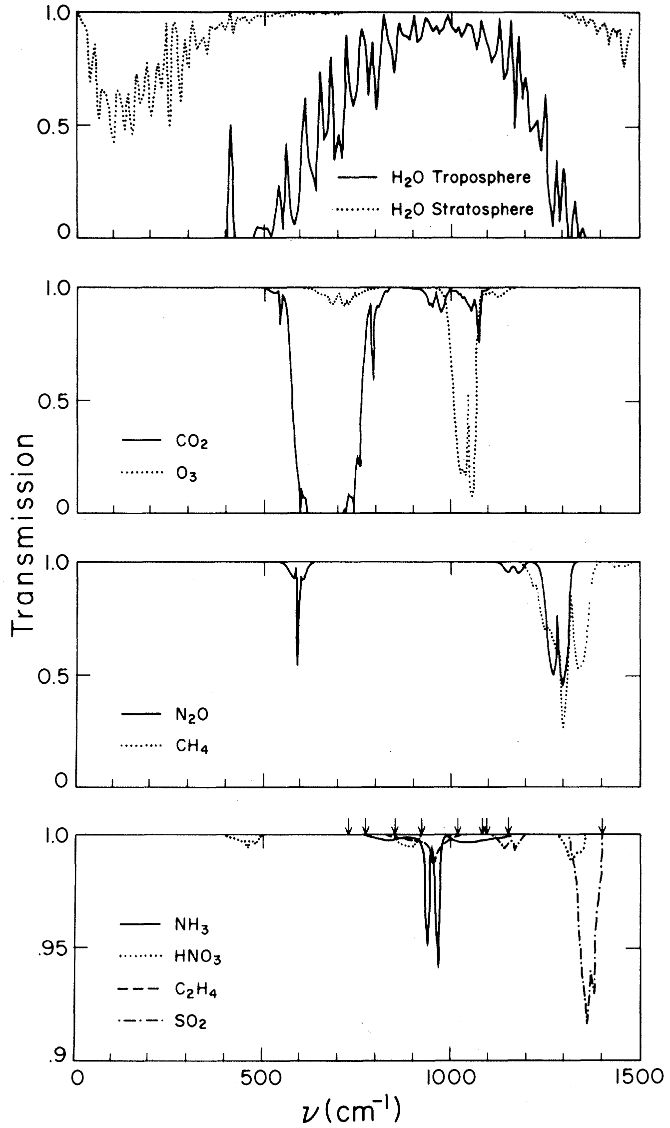

Fig. 1. Transmission of thermal radiation by atmospheric gases for present-day abundances. Water vapor effectively blocks emission from the earth's surface except for the "window," ~ 600 to 1300 cm^{-1}, which is narrowed somewhat by the strong CO_2 band. The O_3 band is particularly effective because of its location in the center of the window. The scale is expanded for the weak absorbers illustrated in the lowest panel. The arrows indicate the locations of the Freon and chlorocarbon bands, which are too weak to be visible.

In attempts to understand and predict man's impact on climate the greenhouse effect of trace constituents, such as N_2O, CH_4, and NH_3, and the factors influencing the abundance of these trace gases, such as the use of chemical fertilizers, should be included. Changes in their abundances of the order of 25 percent are required to significantly influence climate. The climatic effects of the Freons also must be reckoned with if the global Freon abundance increases an order of magnitude or more. However, the greenhouse effect of the Freons is smaller than reported by Ramanathan (8, 26). The possible climatic effects of Freons should be included in deliberations concerning possible restrictions on their commercial production, but in the context of the effects of other variable atmospheric constituents.

The warming effect of increased atmospheric CO_2 has been discussed by many authors, and our numerical results are in good agreement with the one-dimensional radiative-convective calculations of Manabe and Wetherald (20). The upward trend of global atmospheric CO_2 has been well documented, and projections of a global increase of the order of 20 percent by the year 2000 are probably reliable within a factor of 2 (3, 27). Thus we can anticipate that CO_2 will play a major role in future trends of the earth's radiation budget; perhaps it will have a dominant role, but it is certainly not possible to be categorical about that at this time.

The greenhouse effect due to a change in O_3 abundance is also substantial, as illustrated in Table 3. However, a single calculation is entirely inadequate for O_3 because the results depend strongly on its vertical distribution, which exhibits strong temporal and spatial variability. We thus do not consider the climatic effects of O_3 variations in detail here (28). However, our calculations have shown that the O_3 in the upper troposphere and lower stratosphere is the most efficacious in producing a greenhouse effect. The O_3 abundance at those levels is determined by atmospheric dynamics as well as chemistry. Thus, proper analysis of the climatic effects of O_3 involves complex considerations of radiative, dynamical, and chemical processes and their interactions, and particular regard must be paid to stratospheric-tropospheric exchange mechanisms.

Table 3 also indicates that a very large greenhouse effect arises from doubling the stratospheric water vapor, even though there is relatively little H_2O in the stratosphere. The reason for the predominance of water vapor as a greenhouse material is clear from Fig. 1, which includes the infrared transmittances for typical stratospheric and tropospheric amounts of water vapor. Although it is difficult to predict even the sense of future trends of stratospheric water vapor, we include this calculation for an H_2O perturbation for the following reasons.

1) Water vapor plays a predominant role in determining the atmospheric and surface temperatures, and thus assumptions about the response of the atmospheric water vapor distribution to any of the compositional perturbations under consideration are crucial. There is also the possibility that compositional perturbations could modify H_2O condensation processes, resulting in either a positive or a negative feedback effect on temperatures. Changes in cloud cover or cloud altitude strongly influence the radiation budget, so the constraints of fixed cloud properties that we have employed should be removed in more realistic modeling experiments. Earth is the water planet, and only with a quantitative understanding of the web of processes connecting water in its various forms—atmospheric vapor, clouds, ground hydrology, snow cover, land and sea ice, and the oceans themselves—can we hope to model climate.

2) Stratospheric perturbations can have a large effect on conditions in the troposphere and at the earth's surface, and understanding stratospheric-tropospheric exchange processes is of primary importance. Although it is plausible to assume that fixed relative humidity is a good approximation in the troposphere, there is little justification to support such an assumption for the stratosphere. It is possible, for example, that the stratospheric water vapor abundance is controlled primarily by the temperature at the tropical tropopause, where towering cumulus clouds inject tropospheric air into the stratosphere. However, chemical processes, such as the oxidation of CH_4, may also have a significant role in controlling stratospheric H_2O abundance. Again we are forced to conclude that reliable analyses must properly incorporate radiative, dynamical, and chemical processes and their interactions.

Discussion

The overall impression left by Table 3 is that anthropogenic perturbations of the gaseous atmospheric composition are likely to eventually warm the earth, a result that would be expected to have greatest consequences for mid- and high-latitude land areas in the Northern Hemisphere. That impression is supported by the likelihood that the potential countereffect of atmospheric aerosols (*1, 3, 4*) will be either sporadic (in the case of volcanic aerosols) or limited by the short lifetime of airborne particles subject to fallout and rainout (in the case of tropospheric anthropogenic aerosols) (*29*). Man-made thermal pollution and a suspected slow increase of the solar radiative output during the last three centuries (*30, 31*) work in the same sense as increasing trace gas abundances—that is, to warm the planet. However, the primitive status of today's atmospheric modeling capabilities, as indicated by the sampling of caveats discussed above, suggests that a reliable climate prognostication must await the development of improved climate models as well as the attainment of accurate measurements of the trends of atmospheric composition and solar radiative output. The primary value of the type of computations we have made is to provide order of magnitude estimates of surface temperature sensitivity to trace gases and a relative measure of several different potential perturbations.

Finally, we would like to emphasize the value of planetary atmosphere studies for the objective of understanding and predicting the climatic consequences of anthropogenic perturbations of atmospheric composition. Searing-hot Venus, Dry Ice–cold Mars, and our presently hospitable lukewarm Earth provide a striking range of conditions for testing climate models. Furthermore, recent photographs from the Viking spacecraft support the belief that Mars was once a warm planet with plentiful rivers and oceans, and although we do not yet have the data to test the theories, it has been suggested by Ingersoll (*6*) and by Rasool and De Bergh (*7*) that an earlier clement Venus was brought to its present state by a runaway greenhouse effect. There can be little doubt that the compositions of these planetary atmospheres have undergone substantial evolution and that major temperature and climate changes accompanied the evolving composition. By studying and reaching a quantitative understanding of the evolution of planetary atmospheres we can hope to be able to predict the climatic consequences of the accelerated atmospheric evolution that man is producing on Earth.

Summary

Nitrous oxide, methane, ammonia, and a number of other trace constituents in the earth's atmosphere have infrared absorption bands in the spectral region 7 to 14 μm and contribute to the atmospheric greenhouse effect. The concentrations of these trace gases may undergo substantial changes because of man's activities. Extensive use of chemical fertilizers and combustion of fossil fuels may perturb the nitrogen cycle, leading to increases in atmospheric N_2O, and the same perturbing processes may increase the amounts of atmospheric CH_4 and NH_3. We use a one-dimensional radiative-convective model for the atmospheric thermal structure to compute the change in the surface temperature of the earth for large assumed increases in the trace gas concentrations; doubling the N_2O, CH_4, and NH_3 concentrations is found to cause additive increases in the surface temperature of 0.7°, 0.3°, and 0.1°K, respectively. These systematic effects on the earth's radiation budget would have substantial climatic significance. It is therefore important that the abundances of these trace gases be accurately monitored to determine the actual trends of their concentrations.

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22. The time-marching procedure and convective adjustment are basically the same as those employed by Manabe and Wetherald (*2*) and W. C. Wang and G. A. Domoto [*J. Appl. Meteorol.* **13**, 521 (1974)]. In our computations we specify gaseous absorption coefficients within a frequency interval $\Delta\nu$ by means of a probability distribution function, which is thus used for an implicit integration over wavelength. This function is obtained for each frequency interval and each gas by using the band model of W. Malkmus [*J. Opt. Soc. Am.* **57**, 323 (1967)]. The band model parameters for each interval are obtained by using data from the sources indicated in Table 3. The region of solar radiation is divided into 59 frequency intervals and the thermal spectrum into 49 intervals. The number of frequency intervals is sufficient to permit the spectral dependence of the cloud particle properties, which is relatively slowly varying, to be treated explicitly. Absorption by more than one gas within an interval $\Delta\nu$ is treated by assuming that their probability distribution functions are independent. For both solar and thermal radiation, multiple scattering is handled by using the doubling method within each layer and the adding method for combining these layers [see A. A. Lacis and J. E. Hansen, *J. Atmos. Sci.* **31**, 118 (1974)]. The inhomogeneous nature of the atmosphere is incorporated through the pressure and temperature dependence of the probability distribution functions. The resulting heating rates are accurate within a few percent, as demonstrated by comparisons with "line-by-line" calculations that we have made and will include in our theoretical paper (*28*).
23. The actual equilibrium response of the water vapor profile is one of the aspects that must be addressed in more realistic global modeling but, except perhaps in the stratosphere, the assumption of fixed relative humidity should be a realistic approximation; see (*2, 3, 20, 21*) and F. Möller [*J. Geophys. Res.* **68**, 3877 (1963)]. The greenhouse effect is one-third to one-half smaller for the case of fixed absolute humidity, but that assumption is clearly inappropriate for the troposphere; indeed, it is possible that the relative humidity could increase somewhat with an increase in the average temperature of the earth.
24. Consider the case of Venus, which has 100 percent cloud cover: the albedo for incident solar radiation is ~77 percent, requiring an effective radiating temperature of ~235°K. Thus, since the clouds are nearly black (perfect radiators) the cloud tops occur at the level where $T \sim 235°K$. For a planet with partial cloud cover the problem is more complex, but the cloud top temperature remains more fundamental than the cloud top altitude per se.
25. The difference between the present globally averaged sea-surface temperature and that during the last great (Wisconsin) ice age is ~2.3°K, for the area that was open water at both times. At high latitudes temperature differences of 10°K and larger occur [CLIMAP Project Members, *Science* **191**, 1131 (1976); W. L. Gates, *ibid.*, p. 1138].
26. Although we obtain a significantly smaller greenhouse effect for the Freons than the 0.9°K obtained by Ramanathan (*8*), this does not qualitatively modify Ramanathan's conclusion that a large increase in Freon abundance could have climatic consequences. The primary factors we can identify which may cause the quantitative difference between our result and that of Ramanathan are: (i) We employ the integrated band intensities for the Freons measured by Varanasi (*38*), which are ~13 percent smaller than those used by Ramanathan. (ii) Our standard atmosphere includes several gases not included in Ramanathan's computations (see Table 2); these reduce the greenhouse effect of the Freons by a few percent. (iii) Ramanathan's result is based on an empirical formula of M. I. Budyko [*Tellus* **21**, 600 (1969)] relating the surface temperature and the thermal radiative flux at the top of the atmosphere and on a one-dimensional radiative transfer model with approximate methods for integrating over wavelength and angle—these approximations, such as the use of a diffusivity factor of 2, apparently tend to increase the computed greenhouse effect. (iv) There are differences in our respective treatments of clouds; for example, in the cloud cover, cloud heights, and the methods of averaging over clear and cloudy regions. In one sense our results are still an upper limit since, in the absence of measured line widths for Freons, we employed the optically thin (weak line) assumption (as did Ramanathan); however, use of actual line widths is not likely to further reduce the computed greenhouse effect by more than a few percent.
27. W. S. Broecker, *Science* **189**, 460 (1975); L. Machta and K. Telegadas, in *Weather and Climate Modification*, W. N. Hess, Ed. (Wiley, New York, 1974), pp. 687–725.
28. In a paper in preparation we examine in detail the vertical distributions of O_3 and HNO_3 in the stratosphere and troposphere. We explicitly deal with the effects on O_3 and HNO_3 arising from potential increases in atmospheric N_2O and CH_4.
29. We do not mean to minimize the potential climatic significance of atmospheric aerosols. We have excluded from Table 3 results for changes in the amount of atmospheric aerosols only because such results depend on a number of parameters, such as global aerosol distributions and optical properties, for which we have inadequate data.
30. Eddy (*31*), partly on the basis of a paper by E. J. Öpik [*Irish Astron. J.* **8**, 153 (1968)], estimates that the solar constant was increasing at a rate of 0.5 percent per century in the first half of the present century. At this rate the solar constant would have been about 1.4 percent less than at present during the "Maunder Minimum" (1645–1715) of solar activity discussed by Eddy, which coincided with the coldest excursion of the "Little Ice Age." This magnitude of variation of the solar constant is consistant with the relationship between solar activity and solar energy deduced by K. Ya. Kondratyev, G. A. Ninolsky, D. G. Murcray, J. J. Kosters, and P. R. Gast [*Space Res.* **11**, 695 (1971)] from balloon measurements, which indicates an amplitude of ~2 percent for the solar energy variations with solar activity. Although measurements of variations of the solar constant are highly controversial, it is safe to say that the existing measurement precision does not exclude variations of that magnitude. With our one-dimensional radiative-convective model we compute a decrease (increase) of 0.8°K for a 0.5 percent decrease (increase) in the solar constant. It is interesting that these numbers are roughly consistent with the estimated increases in global temperature of 0.6°K between 1880 and 1940 and of a few degrees between 1700 and the present [W. L. Gates and Y. Mintz, Eds., *Understanding Climatic Change* (National Academy of Sciences, Washington, D.C., 1975)]. This reemphasizes our conclusion that there are a number of mechanisms capable of producing the small perturbations in the radiation budget required to cause climatic change. Study of past climatic data in conjunction with realistic climatic models should provide a means for gauging the nature of future man-induced accelerated climate change.
31. J. A. Eddy, *Science* **192**, 1189 (1976).
32. The vertical O_3 distribution is taken as

$$u(z) = \frac{a_1 + a_1\exp(-b/c_1)}{1 + \exp[(z - b)/c_1]} + a_2\exp(-z/c_2)$$

where $u(z)$ is the amount of O_3 (cm STP) above altitude z, a_1 and a_2 are 0.331 and 0.012 cm STP, b is 23 km, and c_1 and c_2 are 4.55 and 5.23 km. This distribution accurately fits the proposed standard midlatitude O_3 profile of A. J. Krueger and R. A. Minzner, *NASA Tech. Memo. TM X-651-73-22* (1973).

33. The HNO_3 profile is based on the midlatitude data given in *Climate Impact Assessment Program, Monograph 1* [(Report DOT-TST-75-51, Department of Transportation, Washington, D.C., 1975), pp. 1–20] with a maximum concentration of 10 parts per billion by volume (ppbv) in the stratosphere (at 25 km) and a concentration at the ground of 1 ppbv.
34. R. A. McClatchey, W. S. Benedict, S. A. Clough, D. E. Burch, R. F. Calfee, K. Fox, L. S. Rothman, J. S. Garing, *Air Force Camb. Res. Lab. Rep. AFCRL-TR-73-0096* (1973).
35. The CH_4 ν_4 absorption band data in the most recent compilation of McClatchey *et al.* (*34*) are based on computations of K. Fox [*Air Force Camb. Res. Lab. Rep. AFCRL 68-0521* (1968)]. Recent measurements of F. W. Taylor and A. D. Jones (*Icarus*, in press) are in close agreement with Kyle's data, so, as indicated in a footnote of Table 3, we computed the greenhouse effect of CH_4 with the older data of Kyle as well as with the current compilation of McClatchey *et al.*
36. C. B. Ludwig, R. Bartle, M. Griggs, *NASA Contract Rep. CR-1380* (1969).
37. A. Goldman, T. G. Kyle, F. S. Bonomo, *Air Force Camb. Res. Lab. Rep. AFCRL 70-0091* (1970); A. Goldman, F. S. Bonomo, W. J. Williams, D. G. Murcray, *J. Opt. Soc. Am.* **65**, 10 (1975).
38. P. Varanasi, *J. Quant. Spectrosc. Radiat. Transfer*, in press.
39. A. D. Dickson, I. M. Mills, B. Crawford, Jr., *J. Chem. Phys.* **27**, 445 (1957).
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41. D. E. Burch, *Aeronutronic Report U-4784* (Aeronutronic Div., Philco-Ford Corporation, Newport Beach, Calif., 1970).
42. K. J. Bignell, *Q. J. R. Meteorol. Soc.* **96**, 390 (1970).
43. We thank R. Jastrow for pointing out the paper by Eddy (*31*), which led to the computation reported in (*30*). We also would like to thank P. Varanasi, F. W. Taylor, and A. D. Jones for data supplied prior to publication, and V. Ramanathan, W. B. Pearson, B. Gay, and G. Orton for useful information.