

Increase and seasonal cycles of nitrous oxide in the earth's atmosphere

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ABSTRACT

Based on about nine thousand ground-level measurements at Cape Meares, Oregon (45° N), and Cape Grim, Tasmania (42° S), spanning three years, it is shown that nitrous oxide (N_2O) is increasing at about 0.9 p.p.b. yr^{-1} (0.6, 1.1) in the northern hemisphere, and at 0.7 p.p.b. yr^{-1} (± 0.2 p.p.b. yr^{-1}) in the southern hemisphere. It is also shown that N_2O concentrations vary with the season. On average, northern hemisphere concentrations are 0.8 p.p.b.v. higher during April, May, and June compared to the rest of the year, and southern hemisphere concentrations are about 0.5 p.p.b.v. lower during March, April, and May compared to the rest of the year. Based on the existing estimates of natural and anthropogenic sources of N_2O , the increase is explained by a sizeable anthropogenically-controlled land-based source. Mass-balance calculations also indicate that a natural land-based source, peaking in spring, would explain the main features of the observed seasonal cycle. The observed increase of N_2O is extrapolated into the future using a limited growth model and the results compared with exponential extrapolations which are sometimes used.

1. Introduction

It has been suspected for some time that human activities may be adding large quantities of nitrous oxide (N_2O) to the earth's atmosphere, particularly from increasing use of nitrogen fertilizers (McElroy et al., 1977; Crutzen, 1976; Liu et al., 1977) and also from combustion processes for the production of energy (Pierotti and Rasmussen, 1976; Weiss and Craig, 1976). Since N_2O is not easily removed from the atmosphere (lifetime $\tau \approx 100$ years), its concentrations may rise, ultimately altering the global environment. Increased levels of N_2O may add to the global warming already expected to occur from rising concentrations of carbon dioxide (CO_2) (Lacis et al., 1981; Donner and Ramanathan, 1980), and may also lead to destruction of ozone in the stratosphere (Luther et al., 1979). About two years ago, a NASA review summed up the situation by stating that: "The existence of a long-term trend is a key question." Reviewing the work of Goldan et al. (1979) and unpublished preliminary data of Weiss, the report

continued that: "In neither case is the data base adequate at the present time to accurately establish the magnitude of the increase." (Hudson and Reed, 1979.) Since then, several groups have analyzed their many years of atmospheric measurements and have observed an increasing trend. We have constructed Table 1 as a review of current and past studies on the increase of nitrous oxide. Except for one study, the observed rates of increase range from 0.2 to 0.4% yr^{-1} . This agreement is excellent considering that these studies were carried out by several independent groups, over different periods of time, and at different locations. This paper is based on the last item in Table 1, which refers to an extensive three-year data base consisting of 9000 measurements of N_2O at two mid-latitude locations, one in each hemisphere.

We describe the three years of measurements of N_2O and the experimental methodology used to obtain them. Based on these data the observed rates of increase in the two hemispheres are determined. The seasonal patterns which have emerged from this extensive data base are

Table 1. *Atmospheric studies on the increase of nitrous oxide*

Rate of increase $\hat{\beta}$ (% yr ⁻¹) ($\pm \delta\hat{\beta}$)	b (p.p.b.v. yr ⁻¹) (b_L, b_U)	$C(t_0)$ (p.p.b.v.)	n	Period covered by data base (and years)	Investigators
0.15 (—)	—	298.6	—	1966–1976 (10)	Craig et al. (1976)
0.6 (± 0.6)	1.8 (0, 3.8)	316.2	14	1976–1979 (3)	Goldan et al. (1980)*
0.4 (–0.3, +0.1)	1.2 (0.3, 1.5)	303.4	100	1975–1980 (4)	Rasmussen et al. (1981)
0.3 (± 0.2)	0.9 (0.3, 1.5)	303.2	500	1979–1981 (2)	Khalil and Rasmussen (1981)
0.2 (± 0.1)	0.5 (0.4, 0.6)	298.6	400	1976–1980 (4)	Weiss (1981)
0.3 (± 0.1)	0.8 (0.6, 1.0)	298.5	600	1977–1980 (3)	DeLuisi (Ed.) (1981)
0.4 (± 0.2)	1.5 (0.9, 2.1)	325.4	140	1978–1981 (3.5)	Cronn et al. (1982)
0.3 (± 0.1)	0.8 (0.6, 1.0)	302.1	9,000	1979–1982 (3)	Continuous measurements. This work.

If $C = C_0 + bt$, then $\hat{\beta}$ (% yr⁻¹) $\approx b/C_0$; $\pm \delta\hat{\beta}$ are the approximate 90% confidence limits; $C(t_0)$ is the concentration extrapolated to January 1975; n is the approximate number of samples.

* The numbers reported here have been recalculated from the data in the reference using non-parametric methods (Hollander and Wolfe, 1973).

delineated in Section 3. A global mass balance model, with estimates of the anthropogenic sources and the seasonal cycles of natural sources, is used to quantitatively explain both the increase and the occurrence of seasonal cycles. In Section 4 the observed increase is extrapolated into the future by a limited growth model.

2. Atmospheric increase of nitrous oxide

2.1. Data

Results of continuous automated measurements of nitrous oxide are shown as monthly averages and 95% confidence limits in Fig. 1. 5643 measurements of N₂O at Cape Meares, Oregon (45° N), and 3349 measurements at Cape Grim are summarized in the figure. The solid line is calculated from global mass balance equations and will be discussed later in Sections 2.2 and 3.

Care is taken to sample only clean background tropospheric air by placing the stations far from cities and other local anthropogenic sources of atmospheric trace gases. The air is sucked in periodically with a Metal Bellows Corp. MB-41 pump which has been tested in the laboratory and shown not to contaminate the air sample. Before being analyzed, the air is dried with a type 815 Nafion dryer. The atmospheric measurements of nitrous oxide are made with a microprocessor-controlled, dual-channel Hewlett-Packard gas chromatograph equipped with an electron capture

detector (EC/GC). Every ambient measurement is alternated with a measurement of N₂O from gas contained in a carefully maintained calibration tank. The chromatographic peaks are measured with an electronic integrator and the concentration obtained by comparison with the analysis of the standard is stored on magnetic tape. These tapes are read by a PRIME 350 computer and the data are managed with the aid of this computer. A detailed account of the experimental equipment, construction of standards, calibration experiments, and the stability of N₂O in calibration tanks will be given in a paper of Rasmussen et al. (1982) on the results of the Atmospheric Lifetime Experiment (ALE).

Other data shown in Table 1 were taken directly from the references; however, the uncertainties were recalculated to be comparable to the results of our continuous measurements and to each other. The data from Goldan et al. (1981) have been re-evaluated to arrive at the entry in Table 1. Specifically, we selected seven data points which represented tropospheric air over Laramie, Wyoming (41° N). Other data were from various separated locations or from the stratosphere. In all, Table 1 contains results from eight independent studies; and although there is still disagreement among investigators on the absolute concentration of N₂O in the atmosphere, there now appears little doubt that the concentration of N₂O is steadily increasing on a global scale, probably at a rate between 0.2 and 0.4% per year.

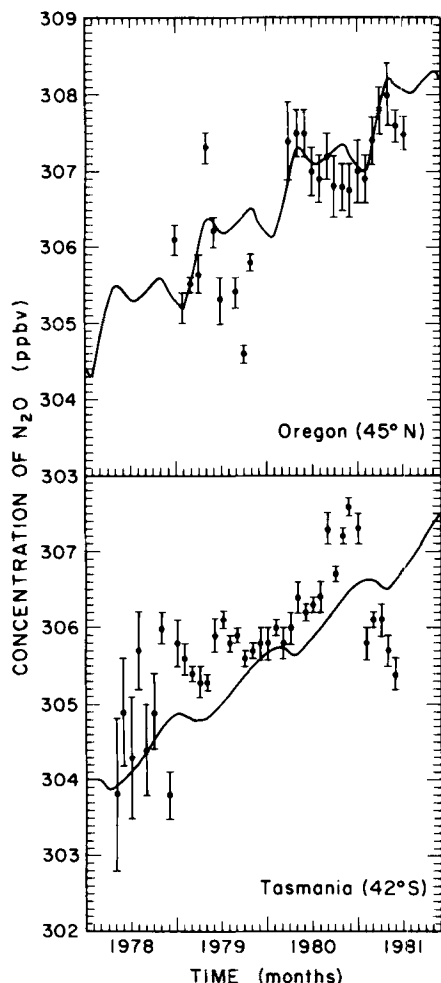


Fig. 1. Monthly average concentrations of nitrous oxide (N_2O at Cape Meares, Oregon ($45^\circ N$), and Cape Grim, Tasmania ($42^\circ S$). The horizontal bars are the 95% confidence limits of the average, and the solid line shows calculated concentrations based on a global mass balance model discussed in the text.

2.2. Global mass balance

Since the concentration of N_2O has long been known to be fairly uniform with latitude, we adopted a hemispherically average mass balance theory to investigate the increase, seasonal cycles, and possible future accumulations of N_2O . Such a model has been used often in the past (see for example Chang and Penner, 1978, and Weiss, 1981) and is represented by the following equation:

$$\frac{d}{dt} \begin{bmatrix} C_n \\ C_s \end{bmatrix} = \begin{bmatrix} S_n \\ S_s \end{bmatrix} - \begin{bmatrix} (\eta + \eta_T) & -\eta_T \\ -\eta_T & (\eta + \eta_T) \end{bmatrix} \begin{bmatrix} C_n \\ C_s \end{bmatrix}, \quad (1)$$

where C_n and C_s are the average concentrations of N_2O in the northern and southern hemispheres (in p.p.b.v.); S_n , S_s are the emissions in each hemisphere (p.p.b.v./yr); $\eta = 1/\tau$ where τ is the atmospheric lifetime; and $\eta_T = 1/\tau_T$, where τ_T is the inter-hemispheric transport time.

The global sources of N_2O are expressed as the sum of natural (S_{n0} , S_{s0}) and anthropogenic components; thus $S_n = S_{n0} + a \exp Bt$ and $S_s = S_{s0}$. We estimated the total yearly sources $S_n + S_s = S$ to be 29 Tg yr^{-1} , and took the lifetime of N_2O to be $\tau = 100$ years. 9 Tg yr^{-1} were assumed to come from the ocean, 13.4 Tg yr^{-1} from land-based sources, and 6.6 Tg yr^{-1} from human activities including combustion and agriculture. When the relative differences of land and ocean areas between hemispheres are taken into account, our estimates yield a northern hemisphere source of 13.4 Tg yr^{-1} (S_{n0}) and emissions of 9.6 Tg yr^{-1} (S_{s0}) in the southern hemisphere. The 6.6 Tg yr^{-1} related to anthropogenic activities is estimated for 1/1978 and assumed to be increasing at $3.5\% \text{ yr}^{-1}$ ($B = 0.035$) as also discussed by Weiss (1981). These estimates are drawn from papers published by McElroy (1980), Weiss and Craig (1976), Levy II and Mahlman (1980), Pierotti and Rasmussen (1976), Elkins et al. (1978), McElroy et al. (1977), Hudson and Reed (1979), Breitenbeck et al. (1980), Bremner et al. (1980), and Bremner and Blackmer (1978). The calculations based on eq. (1) of the expected concentration of N_2O according to the estimated sources and sinks discussed above are complicated by seasonal variations in emissions, especially from land-based sources and in transport between the hemispheres (Newell et al., 1969). These factors will be discussed later in this paper (Section 3). The solution of eq. (1) is shown in Fig. 1. The calculated atmospheric concentration is the sum of two components: an increasing trend arising from the anthropogenic component of S_n and a natural component undergoing seasonal variations. The trend component corresponds to an increase of about $0.9 \text{ p.p.b. yr}^{-1}$ in both hemispheres. This result agrees with the rate of increase in the observed concentrations of N_2O estimated by non-parametric statistical techniques (Hollander and Wolfe, 1973). In Table 2 the observed rate of increase and the increase calculated by the model of eq. (1) and shown as a solid line in Fig. 1 are summarized.

In our calculations, the sources and sinks are of

Table 2. Results of the atmospheric measurements and mass balance calculations for the increase of nitrous oxide

	b (p.p.b.v. yr ⁻¹) (b_L, b_u)		β % yr ⁻¹ (β_L, β_u)		a (p.p.b.v.)		r	n	N
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.			
Northern Hemisphere (Oregon, 45° N)	0.9 (0.6, 1.1)	0.9 —	0.3 (0.2, 0.36)	0.3 —	305.5 305.6	305.6	0.76	25	5643
Southern Hemisphere (Tasmania, 42° S)	0.7 (0.5, 0.9)	0.9 —	0.2 (0.16, 0.30)	0.3 —	305.0 304.7	304.7	0.68	38	3349

b and β are the average rates of increase; (b_L, b_u) and (β_L, β_u) are 90% confidence limits calculated by non-parametric statistical techniques (Theil statistics; Hollander and Wolfe, 1973; Snedecor and Cochran, 1972). a = concentration during 1/1979. a_{obs} is the least squares estimate of the concentration; a_{calc} is based on the mass balance model; r = correlation coefficient between concentration and time; n is the number of months data were obtained, and N is the total number of measurements.

course not in equilibrium and thus, even if the rate of increase of the anthropogenic sources becomes zero ($B \rightarrow 0$), the atmospheric concentrations will continue to increase for some time. Because of this non-equilibrium of sources and sinks the calculated rate at which atmospheric concentrations are increasing is not very sensitive to errors in estimating the yearly increase of anthropogenic emissions (B), especially over two- to three-year periods over which data exist.

These calculations show that the slow, 0.2–0.4% yr⁻¹ increase of atmospheric N₂O can be explained by the existence of land-based sources controlled by human activities consisting of about 6 or 7 Tg yr⁻¹, and increasing at a rate of about 3 or 4% yr⁻¹. The estimated rate of increase is based on the analysis of coal and fuel oil consumption (Weiss and Craig, 1976).

3. Seasonal cycles

The data shown in Fig. 1 clearly show an upward trend, a feature also present in data obtained by Weiss (1981) and others listed in Table 1. In addition to this increasing trend, there may be other variations of concentrations with seasons reflecting changes in source and sink strengths or inter-hemispheric transport cycles. In this section we will refer to local seasons which are six months out of phase between the two hemispheres. Thus, reference to fall concentrations in the southern hemisphere is fall in Tasmania (which is spring-time in Oregon). We first removed the increasing trend from the monthly concentrations by

$$\bar{C} = C - bt. \quad (2)$$

Next we searched for repeating patterns in this modified data base consisting of $\bar{C}(t)$. At Cape Meares (45° N) the springtime concentration \bar{C} , observed during April, May, and June every year for the last three years, appeared to be about 0.8 p.p.b. higher on average than the concentrations (\bar{C}) during the rest of the year. Seasonal patterns in the southern hemisphere appear to be much weaker and qualitatively different from those at Cape Meares in Oregon. In March, April, and May (fall) average concentrations were about 0.5 p.p.b. less than during other times of the year. In addition to our data presented here, we also re-analyzed N₂O measurements published by Weiss (1981) according to the methods discussed above. Weiss' most extensive time series data were obtained from Pt. Barrow (71° N) in Alaska, and they too showed highest concentrations on average during April, May, and June compared to the rest of the year. A statistical analysis of average differences of concentrations during spring compared to the rest of the year in the northern hemisphere and fall compared to the rest of the year is shown in Table 3, wherein patterns of seasonal cycles are summarized.

The high spring concentrations in the northern hemisphere and the low fall concentrations in the southern hemisphere are the only seasonal features we are able to identify with some confidence. The features have been repeated over the three years of data. Other structure observed in the seasonal data (\bar{C}) was found not to be statistically significant. Consequently our goal in further investigating the seasonal cycles with mass-balance calculations was to explain the major identified features as shown in

Table 3. *Statistical analysis of seasonal cycles of N₂O*

Location	Cycle	α	$\Delta \pm \delta\Delta$ (p.p.b.v.)
Cape Meares, Oregon (45° N)	$C(\text{AMJ}) > C(\text{rest})$	0.01	0.8 (± 0.3)
Tasmania (42° S)	$\bar{C}(\text{MAM}) < \bar{C}(\text{rest})$	0.01	-0.5 (± 0.4)
Barrow, Alaska (71° N) (R. F. Weiss, 1981)	$\bar{C}(\text{AMJ}) > \bar{C}(\text{rest})$	0.01	1.4 (± 0.8)

$\bar{C}(\text{AMJ})$ = average concentration for April, May & June, $\bar{C}(\text{rest})$ = average concentration during the rest of the year. All concentrations $\bar{C}(\dots)$ are determined after the average trend has been subtracted. α is the level of significance at which the cycle was tested based on the *t*-statistic, and Δ is the average difference in p.p.b.v., $\bar{C}(\text{AMJ}) - \bar{C}(\text{rest})$, at northern latitudes, and $\bar{C}(\text{MAM}) - \bar{C}(\text{rest})$ at Tasmania. $\delta\Delta$ is the 90% confidence limit based on the *t*-statistic.

Table 3. We discovered that there was practically no published information to guide the calculations, although we suspect that N₂O production by microbial processes in soils may be greatest during spring, coming with renewed vigorous biomass productivity and rainfall. Similarly, we expected winter land-based sources to be small. There are sparse data on emissions of N₂O from agricultural lands, supporting a reduced land-based source during winter; however, greatest emissions occurred during summer (Bremner et al., 1980; Hutchinson and Mosier, 1979). The applicability of these studies to global scales is uncertain, especially since agricultural practices may affect N₂O production in summer. Based on the idea of high springtime productivity, we divided the land-based sources according to the following scheme: S_1 (spring) = 0.5 S_{IT} , S_1 (summer) = S_c (fall) = 0.25 S_{IT} , and S_1 (winter) = 0, where the subscript "1" refers to "land-based" source and S_{IT} are the total yearly emissions. Since the oceans are a smaller source and there is no definitive evidence on seasonal cycles of production, we assumed uniform release. These apportionment rules were applied to both hemispheres and thus, based on our estimated yearly emissions discussed earlier, we calculated the seasonal cycle of natural sources which is shown in Fig. 2.

The interhemispheric transport time was taken to be $\tau_T = 10$ months (0.8 yr); however, the transport was also apportioned among the four seasons according to the results of Newell et al. (1969), so that $\eta_T = 1/\tau_T$ turned out to be η_T (spring) = 0/mo; η_T (summer) = 0.17/mo; η_T (fall) = 0.09/mo; and

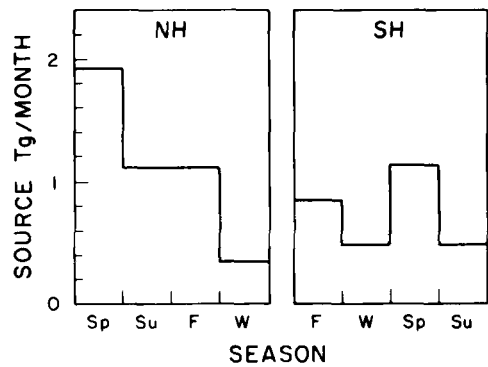


Fig. 2. Estimates of the combined natural emissions (Tg/month) of nitrous oxide from soils and oceans of the northern (NH) and southern (SH) hemispheres during each (local) season.

η_T (winter) = 0.14/mo, where the seasons are referenced to the northern hemisphere.

Eq. (1) was solved numerically with the seasonal cycles of sources and transport as discussed above. The results are shown in Figs. 1 and 3. In Fig. 3 the increasing trend has been removed from both the observed concentrations and the calculations based on the mass-balance equation. The average of \bar{C} (see eq. (1)) for each month during the three years of the experiment is shown as the solid dot. The vertical bars are the range of observed values. It is noteworthy that the assumption of a higher spring source accounts for the general features of the observed seasonal cycles, namely a spring maximum in the northern hemisphere and a weak fall minimum in the southern hemisphere. Although the spring source is a plausible explanation, there

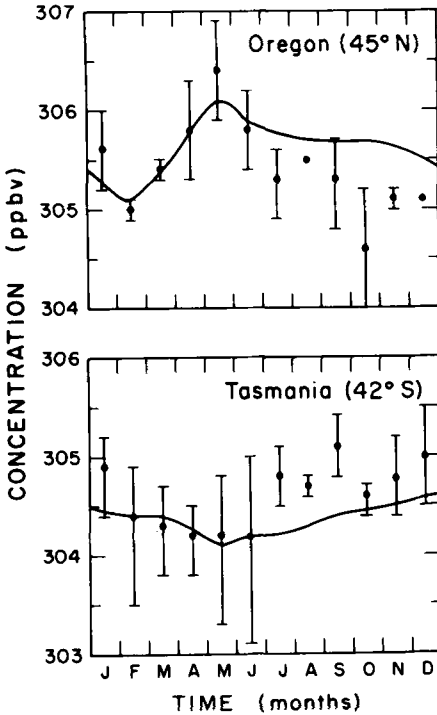


Fig. 3. Average concentrations during each month after subtraction of increasing trend (\bar{C}). The horizontal lines represent the observed range of concentrations during a given month. The solid line is calculated from the mass balance model discussed in the text.

are other natural variabilities which may also account for the observed seasonal cycles; these include seasonal cycles of lifetimes or oceanic and anthropogenic sources. With information currently available, we are unable to evaluate the role of such cycles.

The seasonal cycles, both observed and those obtained from the mass-balance model, imply that the interhemispheric difference also varies with season. At present there is little agreement on its value (DeLuisi, 1980; Weiss, 1981; this work), but further observations of the interhemispheric difference may provide a test of whether the current estimates of the sources and sinks or their seasonal cycles are accurate.

4. Projections into the future

The environmental effects of increased nitrous oxide are likely to be observed many years from

now after sufficiently high atmospheric concentrations have been reached. Therefore, it is of interest to extrapolate the observed increase of N_2O to the concentration expected in the future, although accuracy for such estimates is difficult to achieve. Weiss (1981) assumed an exponential growth model, which is often used for such projections and is founded on past observations and expected increases in human population, energy use, and agricultural needs. We adopted a logistic model for the increase of N_2O . Such a model is based on the same assumptions as the exponential model except that growth is perceived to be limited. The two approaches are nearly identical during initial phases of growth, but differ as the limits to growth are approached in the logistic model. The anthropogenic source (S_a) according to the two models is described by the following equations:

(exponential)

$$S_a = a_0 \text{ for } t < 0, \quad S_a = a_0 e^{\alpha t} \text{ for } t > 0; \quad (3)$$

(logistic)

$$S_a = \frac{A\bar{B}}{A - \bar{B}} \frac{e^{\alpha t}}{1 + \frac{\bar{B} e^{\alpha t}}{A - \bar{B}}} = S_{a0} F(t). \quad (4)$$

The latter expression is a solution of the differential equation for the source written as:

$$dS_a/dt = \bar{B} S_a (A - S_a), \quad (5)$$

where A is the upper limit of S_a and $\alpha = \bar{B}A$ which determines the rapidity with which S_a approaches its constant asymptotic value. For the purpose of this calculation, a global mass balance model was adopted as expressed by eq. (6):

$$\frac{dC}{dt} = S - \eta C. \quad (6)$$

The solutions of this equation with the exponential or logistic model of the anthropogenic source are:

(exponential)

$$C = S_0 \tau + \left[C_1 - \frac{a}{\alpha + \eta} \right] e^{-\eta t} + \frac{a}{\alpha + \eta} e^{\alpha t}; \quad (7)$$

(logistic)

$$C = S_0 \tau + C_1 e^{-\eta t} + S_{a0} e^{-\eta t} \int_0^t F(y) e^{\eta y} dy, \quad (8)$$

where C_1 is the current level of N_2O contributed by anthropogenic sources, S_0 are the natural yearly sources, $\tau = 1/\eta$ is the global atmospheric life-time, a , α , S_{a0} , and $F(y)$ are defined by eqs. (3) and (4). The global sources estimated in Section 2 yield $S_0 = 2.82$ p.p.b. yr^{-1} , $C_1 = 15$ p.p.b.v. The lifetime τ is assumed to be 100 years, $\bar{B} = 0.72$ p.p.b. yr^{-1} , $A = 2.16$ p.p.b. yr^{-1} , and α is chosen to be 0.035 yr^{-1} and 0.06 yr^{-1} as also assumed by Weiss (1981). The solutions of eqs. (7) (dashed line) and (8) (solid line) are shown in Fig. 4 for A.D. 1978 to 2050. The lower lines are for $\alpha = 0.035$ yr^{-1} and the upper lines represent $\alpha = 0.06$ yr^{-1} . It can be seen that the two models show perceptible differences only after a decade from now or more. The major differences in these predictions occur after about fifty years. These differences are based on the assumed upper limit of the logistic model (here represented by A). Our choice of A ($= 2.16$ p.p.b. yr^{-1}) is scaled with the median expected growth of human population (Ehrlich et al., 1977). Thus, we believe that there are logical extensions of current observational data which suggest that N_2O concentrations may not rise as rapidly or reach as high concentrations as calculated by an exponential extrapolation. Still, the nearly 20% more N_2O expected to accumulate in the atmosphere over the

next fifty years according to the logistic model is sufficient to make a small contribution to global warming of about $0.1-0.2^\circ K$ (see Wang et al., 1976; Lacis et al., 1982). N_2O thus joins a growing class of atmospheric trace gases which, taken separately, do not each make a significant contribution to global warming, but together may overshadow the global warming effect of increased CO_2 expected in the future.

5. Some issues

Despite a decade of continued progress in research, there is still little that is known about the atmospheric behavior of nitrous oxide beyond reasonable doubt. It is agreed that N_2O is equally abundant throughout the troposphere at concentrations of about 300 p.p.b.v., although there is still some small disagreement about the absolute concentration. Based on the results summarized in Table 1, it is established that the concentration of N_2O is increasing slowly at 0.2 to 0.4% yr^{-1} . In the next category of qualitative knowledge, based on experimental studies, the concentrations appear to undergo weak seasonal cycles, the soils and waters

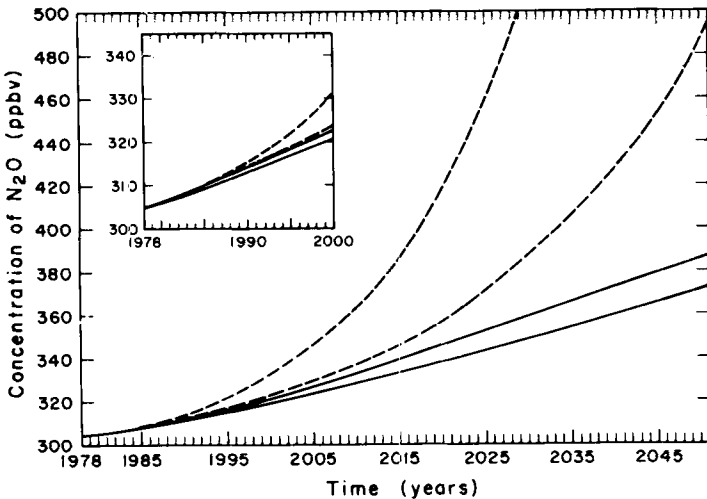


Fig. 4. Concentrations of N_2O expected in the future. Solid lines show calculations based on the logistic model, the upper one corresponding to a rate of increase of 6% yr^{-1} and the lower one to an increase of 3.5% yr^{-1} . The dashed lines were for the exponential model of the anthropogenic sources with rates of increase of 6% (upper) and 3.5% (lower) per year.

are natural sources, and combustion, agriculture, and disposal of human wastes provide anthropogenic sources. Chemical and photochemical reactions in the stratosphere are sinks. Sand and dust surfaces may provide pathways for tropospheric removal. The magnitudes of these sources and sinks are not at all well known at present, with the possible exception of the stratospheric sink. In addition, there is still insufficient evidence to exclude the possibility of major undiscovered sources or sinks. Because of these uncertainties, only a plausible case can be made for concentrations expected in the future and the causes of the increase of N_2O and its seasonal cycles. Slow increases or decreases, lasting over decades or even millenia, may occur due to natural causes alone.

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