Atmospheric Nitrous Oxide: A Critical Review

by

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(Z. Naturforsch. **32 a**, 190–214 [1977]; received December 15, 1976)

Observations, data and assessments concerning atmospheric N_2O are reviewed, in order to present the current state of knowledge on this subject. Background information from microbiology, soil science, and oceanography is provided to facilitate understanding of the complicated processes in soil and water which are responsible for the release of N_2O to the atmosphere. The problem of increasing use of industrial fertilizers and combustion of fossil fuels is discussed in so far as atmospheric N_2O is concerned.

Contents

Introduction

Recently, increasing interest has been focussed on nitrous oxide (N_2O) as a potential destructant of the earth's stratospheric ozone shield. Since all types of fixed (combined) nitrogen participate in global cycles, it is believed that a reduction of the stratospheric ozone may result from the increasing use of man-made nitrogen fertilizers in agriculture [1–12]. While there is general agreement that this problem should be carefully investigated, its urgency is open to question: imminent danger [7–9] or a longterm problem [3–6, 11, 12].

The discussion has centered on estimates of the turn-over time of N_2O in the troposphere and the role of the oceans in the life cycle of atmospheric N_2O [13–19]. In this paper, an attempt has been made to summarize what is known about the cycle of atmospheric N_2O. The validity of data when extrapolated to a global scale will be discussed.

1. Atmospheric Distribution of N_2O

Data on N_2O in ambient air [20–22, 13, 14, 16, 18, 23] show that at ground level atmospheric N_2O is relatively uniformly distributed throughout the two hemispheres, although the data collected from 1968 to 1973 over the Atlantic [21, 22, 14, 16, 18, 24] seem to indicate a certain latitudinal distribution of ground level N_2O. Lower mixing ratios (molar fractions) of N_2O where observed north of 60 °N, relatively high values between 50 °N and 30 °N, and low values between 30 °N and 10 °N increasing again as one proceeds southward. Since in the Pacific no such distribution was found [23], one may assume that the latitudinal distribution of ground level N_2O may be due to very active N_2O sources in the latitude belt between 50 °N and 30 °N and extremely low production in the Sahara desert. Except for areas with very active sources (e. g. the area of Mainz, W-Germany) or with very low net N_2O production, average values of measurements over more than a few days cover the range from 250 to 300 ppb N_2O by volume. It is interesting to note that the earliest measurements by Slobod and Krogh [25], Adel [26], and by Miller [27] yielded mixing ratios in ground level air of about 500 ppb(v). These early data seem to be somewhat high, as compared to values obtained in subsequent years using improved techniques. Birkeland [28] using infrared-absorption found values in Ohio (USA) ranging from 260 to 310 ppb(v) with 280 ppb(v) as the mean value. A set of 36 measurements carried out by Shaw [29] in Columbus (Ohio) over the period from July 1958 to February 1959 yielded an average N_2O mixing ratio of 280 ppb(v) with a range of scatter from 240 to 320 ppb(v). (In barns and greenhouses, the N_2O level was found to be significantly higher.) Beyond the relatively wide scatter of data, there seems to be no systematic trend. It should be pointed out, however, that recent data on ambient N_2O [23, 30–32] are rather at the high end of the range of scatter and in some cases even beyond this range. Since different analytical methods were used, it cannot be decided whether this indicates an increase in tropospheric N_2O or is due to calibration errors in the different methods used.

Trends in the variation of the tropospheric N_2O level will not only be obscured by the horizontal distribution and its possible variation but also by the occurrence of long-term fluctuations. Daily measurements in Mainz (W-Germany) over a 3 year period, which represent the largest set of consistent data on ground level N_2O available at present, revealed that tropospheric N_2O apparently undergoes longterm fluctuations [13]. This observation is supported by data from a mountain station in the Blackforest (W-Germany) and by data measured by Goody [33] in Milton, Mass. (USA). The long-term fluctuations appear to occur simultaneously over large areas, perhaps even world-wide, although there are obviously local components superimposed on them. The fluctuations are shown in Fig. 1 (taken from Schütz et al. [13]) for the area of Mainz (W-Germany), the Schauinsland mountain station (Blackforest, W-Germany), and the area of Milton (Mass.). Apparently, the fluctuations are not bound to the seasons and may amount to ±15 percent of the average value of 2 consecutive years. Comparizon of the curves indicates that local factors may be of the same order of magnitude.

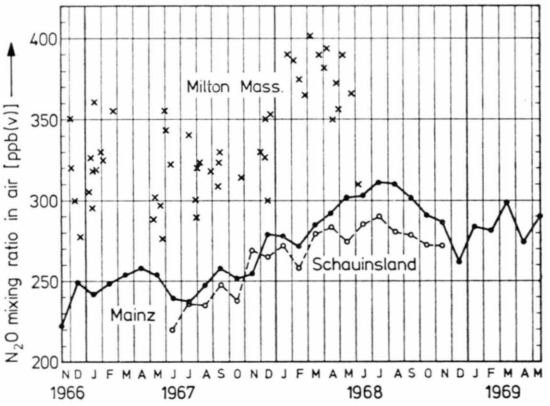

Fig. 1. Long-term fluctuations of tropospheric N_2O as measured in Mainz and Schauinsland (W.-Germany) and in Milton (Mass., USA). Crosses denote individual measurements, circles denote monthly average values.

At present, there is no explanation for these apparently irregular fluctuations. Possible causes may be short-term climatic changes affecting the N_2O production on the continents (in particular, variations in the amount of precipitation) and non-seasonal changes in the temperature of the sea surface water.

In a recent note, Newell and Weare [34] reported on a spatial and temporal correspondence between changes in Pacific sea surface temperature and changes in tropospheric CO_2 apparent from the data after seasonal trends had been removed. The authors suggested that in the case of reduced upwelling in the eastern tropical Pacific, the supply of nutrients and, therefore, photosynthesis is lower than average leading to a CO_2 supersaturation of surface water which becomes warm by radiation. Thus, CO_2 is released to the atmosphere. With increased upwelling, more nutrients are available for photosynthesis. This may lead to an uptake of atmospheric CO_2 by the ocean, if the loss of CO_2 due to increased photosynthesis exceeds the effect of warming the water on the solubility of CO_2.

We may extend this speculation to tropospheric N_2O, although the time span covered by continuous N_2O measurements is actually not long enough. The available data indicate a negative correlation of long-term fluctuations of tropospheric N_2O with the non-seasonal variation of the Pacific sea surface temperature as given by Newell and Weare [34]. Accepting Newell and Weare's idea, such a negative correlation might be explained as follows: In the case of reduced upwelling, we have less microbial production of N_2O in the water column (see chapter 3, section A) so that the surface water is less supersaturated with N_2O, despite a relative warming of the water, and less N_2O is released to the atmosphere. Conversely, with increased upwelling (lower temperatures of surface water) we have a larger microbial production of N_2O in sea water and, therefore, a higher N_2O supersaturation supported by an eventual warming of the upwelling water leading to a higher flux of N_2O into the atmosphere.

Recent N_2O measurements by Rasmussen et al. [32] in the eastern tropical Pacific showed sea water in areas with more upwelling to be substantially supersaturated with N_2O giving some support to these rather speculative assumptions. The atmospheric turn-over times of both CO_2 and N_2O are on the order of 5 – 15 years (see below). Thus, the good correlation between the modulation of atmospheric CO_2 and the (El Nino related) variation of the East Pacific ocean circulation would also suggest global effects on atmospheric N_2O, if the marine source of atmospheric N_2O in this area is sufficiently large. From the results obtained by Rasmussen and coworkers, one may conclude that this is indeed the case (see chapter 3, section B, paragraph b). The effect on atmospheric N_2O could, of course, be amplified by a simultaneous variation of the water circulation in other upwelling areas such as along the West African coast and by increased release of N_2O from soil due the unusually extensive rainfalls in productive areas of the continents.

The mean vertical distribution of atmospheric N_2O as a result of measurements by Schütz et al. [13], Murcray et al. [35], Harries et al. [36–37], Ehhalt et al. [38], and Ehhalt et al. [39] is given in Figure 2. The dashed lines exhibit the range of scatter. Within the troposphere, there is essentially no decrease of the N_2O mixing ratio with altitude, or to be more careful: the data available until now give little evidence for any mean gradient within the troposphere. The main decrease occurs above the tropopause, particularly 3 to 15 kilometers above the tropopause, and above 40 kilometers, Ehhalt et al. [38] found values lower than 10 ppb(v). The average tropospheric N_2O mixing ratio appears to be within the range 235 – 285 ppb(v) with 260 ppb(v) as the mean value. This value was obtained considering all measurements carried out in the troposphere and weighing the results with respect to the number of measurements performed at one geographical location. Assuming an average tropopause height of 16 km in latitudes $l < 30°$ and of 11 km in latitudes $l \geqq 30°$, these mixing ratios relate to a total tropospheric N_2O burden of $M = (1.70 \pm 0.20) \times 10^{15}$ g with an additional stratospheric burden of about 0.17×10^{15} g.

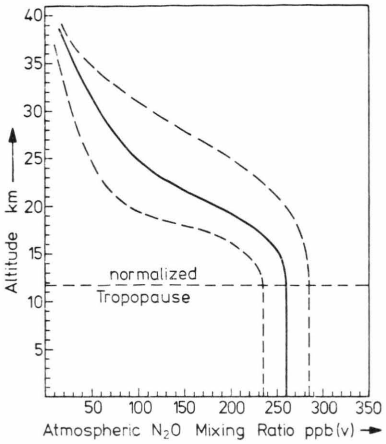

Fig. 2. Mean vertical distribution of atmospheric N_2O. Dashed lines indicate the scatter of data.

2. Tropospheric Turn-over Time of N_2O and Global Production Rate

A very important quantity in the cycle of atmospheric N_2O is it's residence time in the troposphere $T = \bar{M}/\bar{Q}$, where $\bar{Q}$ is the average global tropospheric source strength. According to Bolin and Rodhe [40], "turn-over time" is a more adequate term for this quantity. Under steady state conditions, $\bar{Q}$ is equal to the total tropospheric sink $\bar{S}$. Unfortunately, it is very difficult to obtain direct values for $\bar{Q}$, $\bar{S}$, or T. However, there are several ways to indirectly estimate the average tropospheric turn-over time of N_2O from the data available. These ways will be discussed in more detail:

1) If $Q(t)$ and $S(t)$ are the global tropospheric source and sink strengths at any time t, long-term steady state requires $\overline{Q(t)} = \overline{S(t)}$, where the bars denote average values for time periods Δt^* of several years. For time periods Δt considerably shorter than Δt^*, $M(t)$ will vary according to

$$\Delta M(t)/\Delta t = Q(t) - S(t) \, . \qquad (1)$$

Since $\Delta M(t)/\Delta t$ fluctuates about zero and $Q(t)$ and $S(t)$ are >0 and approximately equal to $\bar{M}/T$, we have

$$|\Delta M/\Delta t| < \bar{M}/T \quad \text{or} \quad T < |\Delta t\, \bar{M}/\Delta M| \qquad (2)$$

As mentioned above, the records of tropospheric N_2O from Mainz, the Blackforest, and Milton (Mass.) show similar trends over periods of 1/2 to 1 year. This quite certainly indicates more than regional and most likely hemispheric variations of M. Table 1

Table 1. Estimates for upper limits of the tropospheric N_2O turn-over time (T) on the basis of observed variations of the tropospheric N_2O mixing ratio.

Location	Time period ΔT	average N_2O mixing ratio ($\bar{r}$) (ppb)	Variation of N_2O mixing ratio (Δr) (ppb)	in Δt (years)	Upper limits of N_2O turn-over time (years)
Mainz (W.-Germany)	June 67 to July 68	271	73 (238 → 311)	13/12	4
Schauinsland (Blackforest) (W.-Germany)	June 67to July 68	262	70 (220 → 290)	13/12	4
Milton (Mass., USA)	August 67 to March 68	347	85 (309 → 394)	7/12	2.5
Mainz (W.-Germany)	July 68 to April 69	290	37 (311 → 274)	9/12	6

gives the relevant information on four time periods when uniform trends were apparent. Three of them are almost simultaneous in the three available records. The variations of M indicate that T should be smaller than about 6 years.

2) The total variance of a set of data σ_t^2 should be related to the variance due to methodical errors σ_m^2 and to the variance due to the data themselves σ_d^2 by the equation

$$\sigma_d^2 = \sigma_t^2 - \sigma_m^2 . \tag{3}$$

At the Blackforest station, where the 2 years average was close to the average tropospheric mixing ratio of 260 ppb(v) N_2O, the σ_t for the years 1967 and 1968 was found to be 9.2%. With this σ_t and a σ_m of 4.5%, a σ_d of 8% is obtained. Daily measurements of CO_2 in ambient air during the same time period and at the same location[41] yielded an average σ_d for CO_2 of 2.3%. This relates to an average photosynthetic turn-over time of tropospheric CO_2 of $10-15$ years[42]. Because in both cases the sources appear to have been located in that region and because the mixing processes in the atmosphere are the same for both gases, we can expect that the σ_d values are inversely proportional to the turn-over times of the respective gases. This results in values of $3-4$ years for T_{N_2O} in the troposphere. The monthly standard deviations of the Blackforest data were generally higher in the warm season and lower in the cold one. If we assume that the winter values are a better approximation to the mean global situation, because the local influences are smaller in winter, σ_d is found to be 4.3% leading to a turn-over time for tropospheric N_2O of $5-8$ years.

3) Junge[19] showed that there is a pronounced inverse relationship between the mean standard deviation $\tilde{\sigma}_d$ for the whole troposphere and the turnover time T for all those tropospheric gases for which independent values of both quantities where available or could be estimated. The average relationship for all gases examined was $\tilde{\sigma}_d T = 0.14$ with $\tilde{\sigma}_d$ given in percent and T in years. Since it is clear that $\tilde{\sigma}_d$ does not only depend on T but also on the time and space distribution of the sources and sinks, it was pointed out that this relationship must be considered a stochastic one and that the constant 0.14 may be off in individual cases by a factor of 3 in either direction. Unpublished calculations with simplified transport models not only confirm the inverse relationship, but also the average value of the constant and its variations due to the distribution of sources and sinks up to a factor of 3 so that we may use this relation with good confidence. Junge[19] estimated T_{N_2O} to be 8 years by considerations similar to those under 1) and 2) and gave a $\tilde{\sigma}_d$ of 8% which was largely based on the long-term fluctuations observed in Mainz, the Blackforest, and in Milton (Mass.). Using the inverse relationship, the constant 0.14 would result in a T_{N_2O} of 1.8 years. If we consider that the value $\tilde{\sigma}_d = 8\%$ may be high due to the fact that all the observations were made in the northern hemisphere in areas with comparatively active sources, we may assume that the global value of $\tilde{\sigma}_d$ may be lower, perhaps by a factor of 2. If we in addition apply the above mentioned uncertainty factor of 3, we obtain a $T_{N_2O} \approx 1.8 \cdot 2 \cdot 3 = 11$ years as an upper limit which should not be greatly exceeded. Unfortunately, we do not have enough reliable long-term series of N_2O measurements to calculate a better $\tilde{\sigma}_d$ value. In particular, long-term series from the upper troposphere are lacking.

In Table 2, relevant data from series of N_2O measurements in air are compiled including recent data by Craig et al.[23], Craig et al.[30], and Rasmussen et al.[32, 43]. The table gives the locations of sampling, the time period, the number of measurements carried out over that time, the average N_2O mixing ratio obtained, the standard deviation of data σ_d, and the resulting tropospheric N_2O turn-over time calculated by using the σ_d-T-relationship given above. Further, the analytical method applied in each series of measurements is given. It should be pointed out, however, that the σ_d-T-relationship can be expected to hold only, if long-term averages of $\tilde{\sigma}_d$ (for the whole troposphere) are used. The series of measurements, which meet this requirement to some degree, are the series from Mainz, from the Blackforest, from Milton, and from the North and South Pacific. The smaller the number of measurements and the shorter the time period covered, the more accidentally local influences are reflected by the value calculated for the turn-over time. Since the N_2O sources seem to be chiefly located at the earth's surface and since they are certainly more variable in time and space over land than over the oceans (see next chapter), one may expect that the data collected over land give smaller values for the N_2O turn-over time in the troposphere than the data collected over the oceans. Also, data collected at ground level should give smaller values for the N_2O turn-over time than data collected in the upper troposphere. This is borne out by the values given in Table 2. With the exception of the data by Craig and co-workers who used a mass spectrometrical method to determine the ratio N_2O/CO_2 in the samples collected and who measured the amount of CO_2 using the infrared absorption method developed by Keeling (see e. g. Pales and Keeling[44]), the values given in Table 2 indicate that the true turn-

Table 2. Variation of tropospheric N_2O from available series of N_2O measurements in air.

Location	Time period	Number of measurements	Average mixing ratio ppb (v)	St. Dev. σ %	Turn-over time T (σ_d) years	Method	Reference
Mainz (W.-Germany) ground level	Nov. 66 to March 69	573	271	9.6	1.5	GC, heat cond. cell	Schütz et al.[13] [1970]
Blackforest (W.-Germany) ground level	June 67 to Nov. 68	456	266	8.9	1.6	GC, heat cond. cell	Schütz et al.[13] [1970]
Frankfurt-Tokyo, below tropop.	May 67 to May 68	43	252	6.1	2.3	GC, heat cond. cell	Schütz et al.[13] [1970]
Milton (Mass.) USA, atmos. mean	May 66 to June 68	79	330	8.9	1.6	spectrographic	Goody [1969][33]
N-Atlantic (Iceland-Faroe) sea level	June 70	56	252	1.8	7.8	GC, heat cond. cell	Hahn [1973][16]
NE-Atlantic sea level	June 71	30	273	1.8	7.8	GC, heat cond. cell	Hahn [1975][18]
Nebraska, Texas, Pacific upper troposph.	Aug. 71 to Sept. 73	24	241	5.0	2.8	MS. manometrical	Ehhalt et al.[33] [1975]
North and South Pacific sea level	Major part of 74	?	295	<0.5	>28	MS. IR	Craig et al.[25] [1976]
East. Equat. Pacific sea level	May 76	?	295	<0.5	>28	MS. IR	Craig et al.[30] [1976]
East. Equat. Pacific sea level	March 76	>1200	332	2.8	5.0	GC, EC detector	Rasmussen et al.[32] [1976 a]
Montana USA upper troposph.	March 76	40	331	0.8	17	GC, EC detector	Rasmussen et al.[32] [1976 a]
Missouri (USA) upper troposph.	June 76	16	333	1.1	13	GC, EC detector	Rasmussen et al.[43] [1976 b]

over time of tropospheric N_2O is smaller than 10 years. Until the data by Craig and co-workers have been published with all the relevant details, it is difficult to make any comments on this exception.

Although none of the estimates is very reliable by itself, the combined evidence is strong that the average N_2O turn-over time in the troposphere is between 4 and 12 years with 8 years as the mean value for both hemispheres.

With a total tropospheric burden of $\overline{M} = (1.70 \pm 0.20) \cdot 10^{15}$ g N_2O and this range of the turn-over time, we obtain for the likely range of global N_2O production $\overline{Q} = (125-475) \cdot 10^{12}$ g N_2O per year and a most likely value of $210 \cdot 10^{12}$ g N_2O per year ($135 \cdot 10^{12}$ g N_2O nitrogen per year).

The values for the average N_2O mixing ratio obtained from recent series of measurements are generally higher than those from previous series (see Table 2). As mentioned above, this cannot be taken to show a trend in the variation of tropospheric N_2O, because the data indicate not only that there are variations in time and space but that there is also a problem with the calibration of the analytical methods used. (For further work in this field, it appears highly desirable to intercalibrate the analytical methods in use.) If the data by Rasmussen et al.[32, 43] are correct and the average N_2O mixing ratio in the troposphere is 330 ppb (v) rather than 260 ppb (v), as we assumed, and the turn-over time of tropospheric N_2O is between 5 and 15 years (see Table 2), the likely range of global N_2O production $\overline{Q}$ is calculated to be $(127-482) \cdot 10^{12}$ g N_2O per year with a most likely value of $216 \cdot 10^{12}$ g N_2O per year which is very close to the values given above.

3. Sources and Sinks of Atmospheric N_2O

This chapter deals with the various sources and sinks of atmospheric N_2O. After a description of the processes leading to N_2O formation (A), the net production rates obtained from N_2O measurements are discussed (B). Following a paragraph on possible N_2O sinks (C), an attempt will be made to construct a N_2O balance of the troposphere by extrapolating net production and destruction rates to a global scale (D).

A) Processes of N_2O Formation

As was pointed out in a recent paper [18], there are 3 microbiological processes which seem to account for most of the atmospheric N_2O. These processes are bacterial denitrification, bacterial nitrification, and nitrogen uptake from nitrates and nitrites by phytoplankton and higher plants. In Fig. 3, the aspects of the global nitrogen cycle which are relevant for atmospheric N_2O are summarized. Only the major features are given. Reactions which occur in the troposphere itself involving the oxidation of ammonia and the eventual formation of NO or N_2O by lightning have been omitted. The location of the major sink of atmospheric N_2O is still unknown (see below). Therefore, this sink has not been taken into consideration in the figure. The reaction sequences of the inner cycles encircled by a wavy line (indicating the air/sea-soil boundary) represent microbiological processes in soil, fresh water, and sea water. It should be pointed out that these microbiological processes may be achieved by one species of micro-organisms (denitrification, non-symbiotic nitrogen fixation, nitrogen uptake from nitrate), two different species in turn (bacterial nitrification), or by a multitude of different micro-organisms (ammonification). The total cycle starting at (1) is a system of several subcycles each of which has its own rate.

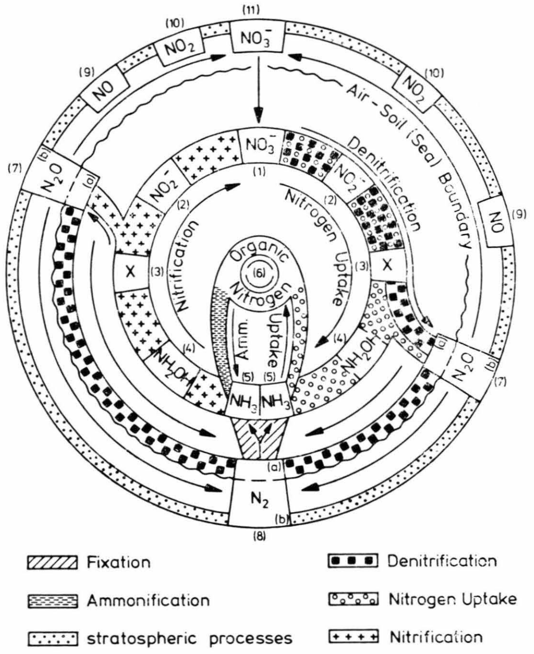

Fig. 3. The global nitrogen cycle. — Features relevant for atmospheric N_2O. Wavy line separates processes in soil and aquatic environments, shown in the center of the figure, from atmospheric processes. Dashed line in the boxes of N_2O and N_2 symbolizes exchange of N_2O and N_2, respectively, across the air/sea-soil boundary layer. The reaction pathways for the various processes are marked by different symbols.

Subcycle I is the slowest and partly proceeds via 1 – 2 – 3 – 7a – 7b – 9 – 10 – 11 – 1. The cycling time is determined primarily by the rate of N_2O transport from the earth's surface into the stratosphere (7a – 7b) and the rate of the reverse transport of NO_3^- (11 – 1). Recent studies suggest a cycling time on the order of 10 years. The same holds for the other part of this subcycle (1 – 2 – 3 – 7a – 7b – 8b – 8a – 5 – 6 – 5 – 4 – 3 – 2 – 1) where again the transport in and out of the stratosphere (7a – 7b and 8b – 8a) determines the cycling time.

Subcycle II proceeding via 1 – 2 – 3 – 7a – 8a – 5 – 6 – 5 – 4 – 3 – 2 – 1 is faster. In this case, the cycling time is largely determined by that section of subcycle II in which both higher plants and animals and various micro-organisms participate (1 – 2 – 3 – 4 – 5 – 6 – 5). The average cycling time should be on the order of months.

Subcycle III involving the steps 1 – 2 – 3 – 4 – 5 – 6 – 5 – 4 – 3 – 2 – 1 may be even faster than Subcycle II, because it is shorter. A conservative estimate of the cycling time would be on the order of weeks. Both Subcycle II and Subcycle III should be fastest when only micro-organisms are involved because of the rapid succession of generations.

N_2O is formed in step 3 – 7a and is either released to the atmosphere (7a – 7b) or reduced to molecular nitrogen (7a – 8a) which is again either released to the atmosphere (8a – 8b) or transformed to ammonia (8a – 5) and returned to the inner cycle. In the stratosphere, N_2O is destroyed by photolysis and/or chemical reaction with atomic oxygen $O(^1D)$. The reaction products are molecular nitrogen (8b) and nitric oxide (9). Nitric oxide reacts with ozone and ultimately forms NO_3^- (11) which is carried back into the troposphere where it is washed out by rain or returned to the earth's surface by dry deposition (11 – 1). Most of the nitrogen in ammonia (5) goes through the loop 5 – 6 – 5 and is trapped in the pool of organic nitrogen compounds (6) after transformation to amino acids, proteins, nucleic acids, humus substances, urea and others for various lengths of time (immobilisation of nitrogen). The pool of organic compounds comprises living matter in the form of micro-organisms, plants, and animal life, and dead organic matter in the form of humus or organic pellets (in the sea). Nitrogen uptake from ammonia by organisms and bacterial ammonification forms a fast secondary subcycle (5 – 6 – 5). The cycling time is again determined by the life cycle of the organisms involved which may be described with reproduction, feeding, excretion, and death. Bacterial ammonification produces ammonia from dead organic matter containing nitrogen. The nitrogen of ammonia is taken up again by organisms (5 – 6) or proceeds in subcycle III (5 – 4). With respect to N_2O production with nitrogen containing fertilizers as a substrate, this figure indicates that it does not make too much difference in what form combined nitrogen is added to the soil.

The 3 microbiological processes important for the generation of atmospheric N_2O are symbolized by the steps:

1 – 2 – 3 – 7a – (7b) – 8a	bacterial denitrification
5 – 4 – 3 – (7a – 7b) – 2 – 1	bacterial nitrification
1 – 2 – 3 – (7a – 7b) – 4 – 5 – 6	nitrogen uptake from nitrates

Bacterial denitrification occurs in anoxic habitats in soil, fresh water, and sea water, and in the upper layers of sediments. It is brought about by the activity of a variety of micro-organisms [45–51]. Starting with nitrate, the sequential products of bacterial denitrification seem to be nitrite, an unknown intermediate ("X" in Fig. 3), nitrous oxide, and molecular nitrogen. It was thought that hyponitrite could be the unknown intermediate [50], but since there was no positive evidence found in favor of this compound, some people now believe that nitric oxide could come into question [52]. As long as there is sufficient oxygen in the medium, micro-organisms preferentially use this for respiration and biochemical oxidation of organic matter. If the oxygen level drops to low values (less than 5% by volume in the soil atmosphere, for example), the microbial population may use both free oxygen and combined oxygen in the form of nitrate at the same time. Under such conditions, N_2O seems to be the main product of denitrification [53]. In a truly anoxic environment, denitrification exhibits the fastest rates with molecular nitrogen being the final product and N_2O only an intermediate. Obviously, there is a certain oxygen concentration in the medium which is optimal for N_2O production during bacterial denitrification (e. g. in soil at 1 – 5% by volume oxygen in the soil atmosphere).

It is still not established whether N_2O is an obligatory intermediate or not – in Fig. 3, it was assumed for the sake of simplicity that N_2O is an obligatory intermediate – although it can be shown that, in a medium without free oxygen or nitrate and nitrite, N_2O is readily utilized by micro-organisms as a hydrogen acceptor. Further, in a recent paper, Yoshinari and Knowless [54] reported that acetylene specifically inhibits N_2O reduction and causes stoichiometric accumulation of N_2O during reduction of nitrate or nitrite by *Pseudomonas perfectomarinus, P. aeruginosa,* and *Micrococcus denitrificans.* In the absence of acetylene there was no or only transient accumulation of N_2O observed. This suggests that, at least for the organisms mentioned, N_2O is an obligatory intermediate.

Another parameter critical for bacterial denitrification is the pH value of the medium. The rate of bacterial denitrification in soil is fastest at pH values between 7 and 8, while the percentage of N_2O in the gaseous products is largest at pH values below 5 [50, 55]. Both the oxygen partial pressure and the pH value in soil are determined by such parameters as soil type and structure, moisture content, and the content of organic material. It is obvious, therefore, that a great variety of ecological conditions with respect to N_2O production prevail at the earth's surface.

In sea water, the pH value at all depths is always near the optimum for denitrification. However, denitrification occurs only when the concentration of free dissolved oxygen drops below a certain threshold. This threshold is commonly believed to be 0.2 – 0.3 ml O_2 per liter sea water which is less than 3 percent of the saturation concentration at 10 °C [56–59]. If the observation by Mechsner and Wuhrmann [51] is correct, this threshold does not apply to all species of denitrifying bacteria. These authors found strains of denitrifiers which were extremely sensitive even to very low oxygen concentrations and others which reduced nitrite at 1.4 to 2.0 percent O_2 by volume in the medium nearly as fast as under anaerobic conditions. There was even one strain which reduced nitrite with maximal rate under true aerobic conditions as long as there was glucose available as a hydrogen donator. Also, it is conceivable that denitrification may proceed in anoxic micro-environments (fecal pellets) with the bulk of sea water being more or less saturated with oxygen [60].

Previous investigations in the eastern tropical Pacific ocean where oxygen concentrations of less than 0.3 ml O_2 per liter sea water are common at depths between 100 and 800 meters [61–63] failed to show N_2O as a product of the marine denitrification process [64–66]. Obviously this was so, because the analytical methods used at that time were not sensitive enough. Very recently, Rasmussen et al. [32] found relatively high N_2O concentrations in the sea water of this region. (In the North Atlantic ocean, the N_2O concentration in sea water seems to be typically in the range $0.3 - 0.8\ \mu g$ N_2O per liter sea water as was measured by Junge et al. [14], Hahn [16, 17], and Yoshinari [31], while Rasmussen et al. [32], found values up to $5\ \mu g$ N_2O per liter sea water.)

Bacterial nitrification appears to occur in both the soil and the water column together with the uppermost sediment layers in lakes, rivers, and the sea. It is achieved by certain chemo-authotrophic bacteria. There are 7 genera of nitrifying chemo-authotrophs with Nitrosomonas and Nitrobacter being the most frequent ones in soil [50]. The oxidation of ammonia to nitrate is performed in 2 steps: transformation of ammonia to nitrite by Nitrosomonas species and subsequent formation of nitrate by *Nitrobacter*. Since nitrite is rarely found in soil, it is commonly believed that the formation of nitrate is very rapid. When the habitat becomes unfavorable for nitrifying bacteria, ammonia accumulates, because ammonification (see below) is less sensitive to environmental changes. Just as with the denitrification process, the oxygen content and the pH of the habitat determine the nitrification rate to a large extent. The presence of free oxygen is necessary for the nitrification process. In the total absence of free oxygen (true anoxic conditions), there will be no production of nitrite or nitrate. In soil, moisture controls the aeration regime. The moisture content, therefore, has a great effect on nitrate production. In waterlogged soil, nitrification is greatly suppressed, while in arid soils, at the other extreme, bacterial growth is not retarded by the supply of available oxygen, but by the lack of water, so that nitrification is enhanced by irrigation in such soils. Optimum moisture contents vary with different soils, but seem to be in the range from 1/2 to 2/3 of the field capacity [50]. The p_H value of the soil is another important ecological parameter for the nitrification process. A limiting p_H value cannot be given, because various factors will alter any specific boundaries in soil. Typically, a pronounced drop in the rate of nitrification can be noted below a p_H of 6, and below 5 the rate is very slow, although nitrate may occasionally be found in soil down to p_H values of 4 or even lower. The acidity influences not only the nitrification itself but also the number of nitrifying micro-organisms in the habitat, neutral to alkaline soils having the largest populations. Therefore, except for reactions near optimum conditions, addition of lime has a marked effect on nitrification in acidic soils.

Similar to denitrification, nitrification is markedly affected by temperature. Below 5 °C and above 40 °C, the rate appears to be very slow, but there seems to be low nitrate production almost down to the freezing point, an important fact for the cycle of soil nitrogen in boreal climates, where leaching and denitrification may occur during fall and winter, and for the nitrogen cycle in tundra soils where denitrification may chiefly occur in summer. The optimum temperature for nitrification is generally between 30 and 35 °C [50].

In the ocean, it seems that nitrification is most efficient in subsurface water layers (usually below 200 meters). Here nitrifying micro-organisms (e.g. *Nitrosocystis oceanus)* may compete more successfully for the limited amount of available ammonium, since phytoplankton is absent and the supply of organic matter to support heterotrophic micro-organisms is smaller [67].

Uptake of nitrogen from nitrates is achieved by phytoplankton and by higher plants. Phytoplankton uses nitrate ion as the source of inorganic nitrogen when living in the lower part of the euphotic zone. In general, the euphotic zone is the surface layer of the oceans (or any other water body) in which the net rate of photosynthesis of phytoplankton is positive. The depth of this zone is governed by the mean amount of solar radiation penetrating the water surface and by the transparency of the water. It varies in the oceans from about 15 meters in moderately turbid coastal waters to 100 meters in the clearest part of the open sea. When primary biological production is low in the sea, the euphotic zone extends below 50 – 60 meters, and the lower part or at least the bottom of the euphotic zone is within the discontinuity layer formed by the thermocline. Usually, there are more nutrients in the water within or below a discontinuity layer than in surface water [68]. Oceanic phytoplankton can live on both ammonium and nitrate nitrogen. (The blue-green alga *Trichodesmium* can even utilize molecular nitrogen.) Phytoplankton living near the surface generally prefers ammonium as the inorganic nitrogen source because of the ease of uptake and incorporation into amino acids (for the uptake of nitrate or molecular nitrogen, phytoplankton must synthezise enzymes: nitrate reductase or nitrogen hydrogenase, respectively). Phytoplankton species inhabiting a discontinuity layer above the compensation depth (the depth where oxygen production is just balanced by oxygen consumption) use nitrate to a greater extent than ammonium nitrogen [68–70]. The uptake of nitrate becomes a significant process, when the seasonal thermocline breaks down in winter and circulation subsequently reaching the permanent thermocline in intermediate water layers (800 – 1,000 meters) mixes nitrate and other nutrients upwards causing a spring bloom of diatoms (e. g. in the Sargasso Sea). As Dugdale and Goering[71] pointed out, one should distinguish between the relative importance of ammonia and nitrate as sources of nitrogen for the life and reproduction of the algal cell and as nitrogen sources for the growth of the algal population as a whole. For the phytoplankton cell, ammonia serves to maintain the cell in a healthy state and provides much of the nitrogen used in reproduction when nitrate levels in sea water are low. Under quasi-steady-state conditions, ammonia may circulate indefinitely as long as there are no losses of diatoms by sinking and mixing or by predation by zooplankton. (Losses of ammonia to the marine atmosphere are still a matter of discussion.) Losses must be compensated by nitrogen fixation (see below) and by nitrogen uptake from nitrates which are supplied by upward circulation of deep water, by bacterial nitrification, and to a lesser extent by precipitation. (In the Bermuda region, for example, the contribution of combined nitrogen in rain, both ammonia and nitrate, was estimated by Dugdale and Goering[71] to be on the order of 20% or less of the new production of organic matter calculated from nitrate uptake data.) Also, nitrate uptake and nitrogen fixation are the most important parameters regarding nitrogen limitation of primary productivity in the ocean.

Nitrate uptake by higher plants is an important process on land. The plants assimilate nitrate ions through the root system as supplied by rain fall, nitrification, and fertilisation. Nitrate is then gradually reduced in the plants, apparently in the same way as in phytoplankton cells, to ammonia which in turn is used for the buildup of proteins and nucleic acids. Conditions for nitrate uptake are identical with those for plant growth.

While it was definitely ascertained that N_2O is a product of bacterial denitrification, direct proof for the N_2O generation during bacterial nitrification in a natural habitat or during uptake of nitrogen from nitrates by phytoplankton or higher plants is still lacking. As shown in Fig. 3, bacterial nitrification and nitrate uptake may be considered to be inverse processes in terms of biochemistry. Bacterial denitrification seems to partly proceed along the reaction pathway used in nitrate uptake (up to step "X"). Very little is known about the nature of the intermediate named "X" in Figure 3. Since this intermediate seems to play a key role in N_2O formation, it would be highly desirable to learn more about this compound. As mentioned above, it could possibly be identical with hyponitrous acid $H_2N_2O_2$. If this should actually be the case, then it is obvious that N_2O can be formed in all of the 3 processes presented above, because $H_2N_2O_2$ (or even HNO) is unstable and decays to N_2O and water. In the case of denitrification in a slightly oxic environment or in the presence of inhibitors of N_2O reduction such as azide, cyanide, DNP, acetylene a. o.[52, 54], unstable hyponitrous acid ($H_2N_2O_2$ or HNO) would be the final product of the biochemical degradation of nitrate ion (with subsequent decay to N_2O and water). In the processes of nitrification and nitrate uptake it would be a true intermediate acting as a N_2O leak in subcycle III (see above). Of course, this is speculative but, at least for the nitrification process, there is some evidence in favor of these assumptions: in the effluents of the process of catalytic ammonia oxidation (industrial production of nitric acid), Leithe and Hofer[20] found 900 ppm(v) N_2O. This shows that N_2O is indeed formed during the oxidation of ammonia, although the reaction pathway must not necessarily be the same as in the nitrification process (biochemical oxidation of ammonia). From our N_2O measurements in the open North Atlantic ocean where, for all seasons and latitudes, the sea water shows an oxygen saturation well above the threshold for denitrification, it seems probable that bacterial nitrification and nitrate uptake by phytoplankton must be considered significant marine N_2O sources. Bacterial denitrification, however, cannot be fully excluded as mentioned above. Further evidence for N_2O production during nitrification may be derived from the work of Yoshida and Alexander[72] and the work of Ritchie and Nicholas[73] who found that the nitrifying bacterium *Nitrosomonas europaea* oxidizes ammonia to nitrite with N_2O as a by-product. (Under anaerobic conditions, this bacterium reduces nitrite to N_2O.) At present, it is difficult to say which of the 3 processes mentioned produces most of the atmospheric N_2O on a global basis. In soil, it seems that most of the N_2O is generated by bacterial denitrification[74].

So much for denitrification, nitrification, and nitrate uptake. Two processes were mentioned above which do not produce N_2O, but which are indirectly related to N_2O production as indicated in Figure 3. These two processes are biological nitrogen fixation (as opposed to anthropogenic and atmospheric nitrogen fixation) and bacterial ammonification. They are represented in Fig. 3 as one step (fixation 8a – 5, ammonification 6 – 5), although each of them comprises a series of discrete steps which are not yet fully known:

Biological nitrogen fixation is very important for the global nitrogen balance, since it returns the nitrogen lost to the atmosphere (due chiefly to denitrification) to the soil and the sea or other aquatic habitats. During biological nitrogen fixation, molecular nitrogen is transformed to ammonia which in turn is used to build up organic nitrogen compounds. This process is brought about by various bacteria and blue-green algae, which utilize N_2 by non-symbiotic means, and by symbiotic associations consisting of a micro-organism and a higher plant. The classical example of such a symbiosis is that between leguminous plants and bacteria of the genus *Rhizobium*. The symbiosis occurs within the nodules that appear on the plant roots. Nitrogen fixing organisms often produce more fixed nitrogen than they can use and excrete combined nitrogen in the form of amino acids through the roots. For more details see the literature on the subject[50, 75, 76]. A few observations should be pointed out here which show that N_2O or some related compound is formed in the metabolism of molecular nirogen indicating a biochemical relationship of biological nitrogen fixation to the processes presented above: N_2O is a competitive inhibitor of N_2 uptake by *Azotobacter* and *Clostridium*. Since growth on ammonia is not affected by the presence of N_2O, this effect must be considered specific for N_2. (Micro-organisms that fix nitrogen can also utilize ammonium. Actually, ammonium ion is used preferentially and often at a greater rate than molecular nitrogen so that the presence of ammonium, in effect, inhibits nitrogen fixation). On the other hand, N_2O is slowly metabolized by *Azotobacter vinelandii*, and the N_2O nitrogen subsequently appears in the microbial protoplasm. In other words: N_2O affects nitrogen assimilation, and conversely N_2 competitively inhibits N_2O uptake.

Bacterial ammonification converts organic nitrogen to the more mobile inorganic state by forming ammonium from organic nitrogen compounds. In a natural environment, the breakdown of proteins and other organic nitrogen compounds is the result of the metabolism of a multitude of microbial strains each of which have a specific function in the degradation pathway. There is a great variety of microorganisms that produce ammonium from organic nitrogen compounds. Almost all bacteria, fungi, and actinomycetes attack nitrogenous organic matter, however, the decomposition rate and the organic compounds utilized vary with species and genus. Ammonification occurs under the most extreme conditions, because so many physiologically dissimilar micro-organisms are involved. Under aerobic conditions, the major end-products of protein degradation are CO_2, ammonium, sulfate, and water, while the final products of anaerobic breakdown of protein-rich organic matter are ammonium, amines, CO_2, organic acids, indole, skatole, mercaptans, and hydrogen sulfide, hence the unpleasant smell associated with this process. The amount of ammonium which accumulates varies with the organisms, the substrate, the soil type, and the environmental conditions. Although, as mentioned above, ammonification is not too sensitive to environmental factors, its rate is markedly influenced by the environment. Optimum conditions in soil, for example, are moisture contents between 50 and 75% of the field capacity (but even in rice paddies ammonification is still rapid) and pH values of the medium between 7 and 8. In contrast to most microbiological processes, the optimum temperature for ammonification is above 40 °C, usually between 40 and 60 °C (ammonium accumulates, for example, in composts and manure piles maintained at 65 °C). For further details see e. g. Alexander[50].

Those points most important for the generation of N_2O may be summarized as follows:

1) Denitrification and nitrification appear to be the most important processes for the generation of N_2O in soil and in water achieved by a variety of microorganisms.

2) In nitrification, the main products are nitrites and nitrates. N_2O is the only gaseous by-product. The main product of denitrification is a mixture of N_2O and molecular nitrogen.

3) The p_H value of the medium and the content of free oxygen are parameters critical for both nitrification and denitrification. For both processes, optimal p_H values are between 7 and 8. In the products of denitrification, the percentage of N_2O is largest below a p_H value of 5. The rate of production, however, is slow.

With plenty of available oxygen, only nitrification seems to be possible, because denitrifying microorganisms preferentially use free oxygen for biochemical oxidation of organic matter. As the oxygen content of the medium decreases, nitrites and nitrates are used in increasing amounts. In total absence of free oxygen, nitrification is no longer possible, but denitrification exhibits the fastest rates. After the supply of nitrites and nitrates is exhausted, N_2O is attacked. The amount of free oxygen optimal for net N_2O production in soil appears to be between 1 and 5 percent O_2 by volume (in the soil atmosphere). The optimal concentration of free dissolved oxygen for net N_2O production in water is not known.

4) The rates of nitrification and denitrification depend not only on the p_H value and the concentra-

tion of free oxygen in the microbial habitat, but also on the temperature and on the supply of water, organic matter, and combined nitrogen. Thus, it is obvious that a great variety of ecological conditions prevail at the earth's surface with respect to N_2O production. This is particularly true for soil where the oxygen concentration and the p_H value are determined by the soil type and structure, the moisture content, and the content of organic matter.

5) Except for the biological processes mentioned, atmospheric processes (lightning) may eventually form another source of tropospheric N_2O. Also, some N_2O is apparently generated in industrial ammonia oxidation and in burning of fossil fuels.

B) Relative Importance of the Various Sources of N_2O

Several series of N_2O measurements were performed in the past, in order to get an idea of the N_2O source strength at the earth's surface.

a) N_2O measurements in soil air [13, 77] and in well water [78] in the area of Mainz (W-Germany) resulted in estimates of average fluxes of N_2O from the soil into the atmosphere of 3.4×10^{-12} g cm^{-2} s^{-1} for a pararendzina soil developed from loess (unploughed soil covered with grass, weeds, and some fruit trees), 0.4×10^{-12} g cm^{-2} s^{-1} for a pararendzina soil with low biological activity derived from sand dunes (covered with scattered grass and weeds and with some pine trees), and 0.5×10^{-12} g cm^{-2} s^{-1} for a natural humus soil in a mountaneous woodland above the region of agriculture (50 – 100 cm humus over gravel and rock). Recently, desert soil was examined on the island of Sal (Cape Verde Islands). It turned out that even this soil acted as a weak source of N_2O with a flux rate of less than 0.1×10^{-12} g cm^{-2} s^{-1} [24]. The flux values given are averages for one year. There seem to be seasonal variations with higher fluxes from May to June and December to February. Relatively low values were found from March to April and July to November [77]. This may be explained by the variation of parameters critical for the rates of bacterial nitrification/denitrification. As mentioned above, such parameters are the temperature, p_H value, and moisture content of the soil and the availability of organic compounds (dead organic matter and combined nitrogen). Large microbial food supply, high moisture contents (little aeration), high temperatures, and p_H values of 7 – 8 favor both nitrification and denitrification.

As was shown by Focht [55], there is a percentage of aerated pore space which is optimal for the net N_2O production in soil (in temperate zones). This is consistent with the results obtained by Cady and Bartholomew [53]. As long as there is sufficient aerated pore space (free oxygen), say more than 25 percent, no denitrification will occur. Under such conditions, N_2O can only by generated by nitrification. From the results obtained by Arnold [74], one may conclude that nitrification is less effective with respect to N_2O production in soil than denitrification. N_2O will, therefore, not be generated in larger quantities before denitrification begins at about 20 percent aerated pore space. Then under favorable soil reaction at p_H values between 7 and 8, the net production of N_2O increases rapidly with decreasing aeration of the soil, until the aerated pore space has dropped to about 10 percent. With less than 10 percent aerated pore space, the net N_2O production decreases, because the rate of N_2O reduction (to molecular nitrogen) increases faster than the rate of N_2O formation. In other words: The moisture content of the soil which regulates the percentage of aerated pore space is one of the most important parameters for the net N_2O production in soil. In a water-logged soil, where aeration is zero percent, there should be no net N_2O production, although the rate of denitrification is maximal. Although part of the soil source, the N_2O production with nitrogen containing fertilizers as a substrate will be treated under man-made sources (see below).

Nothing is known about the net N_2O production of fresh water. Some very preliminary measurements of Rhine water near Mainz (W-Germany) suggest that fresh water can release N_2O to the atmosphere. However, the Rhine is not representative of natural fresh water because of the high degree of pollution.

b) Simultaneous N_2O measurements in sea water and in marine air are a means to study the role of the oceans in the cycle of atmospheric N_2O. Only the N_2O concentration in the surface layer of the ocean is relevant to the question of whether the oceans act as net sources or net sinks of atmospheric N_2O. N_2O measurements were carried out by Craig and Gordon [79] in the South Pacific ocean, by Junge et al. [14], Hahn [16, 18], and by Yoshinari [31] in the North Atlantic, and by Rasmussen et al. [32] and by Craig et al. [30] in the eastern tropical Pacific.

Unfortunately, Craig and Gordon [79] were forced to combine samples collected at different geographical locations and at different depths into 3 groups, in order to get sufficient $CO_2 - N_2O$ gas to be analyzed. Thus, little can be said about the N_2O saturation of the South Pacific surface water. It seems from their results that, in tropical and subtropical latitudes of the South Pacific, the sea water from 10 to 2200 meters in depth is supersaturated with N_2O with respect to air, but that a high latitudes (45 to

70 °S), the mean N_2O saturation of the water column from 10 meters down to 1400 meters is less than 100 percent.

More detailed measurements were performed in the North Atlantic ocean. During 3 cruises of the German research vessel "Meteor", more than 40 water samples were collected from the sea surface besides other samples from deeper water layers down to 3000 meters. The analysis of these samples showed without any exception that the well mixed surface water layer of the North Atlantic was either supersaturated with N_2O with respect to air or at least saturated. It should be pointed out that the samples were collected from a large area of the North Atlantic without any preference for zones of unusually high biological productivity. Using the productivity map by Koblentz-Mishke et al.[80], McElroy and co-workers tried to prove that regions with a high biological productivity were deliberately picked out so that the data could not be taken to be representative for the North Atlantic. The reader may easily verify that this is not the case by looking up the corresponding figure in the paper by McElroy et al.[8]. Except for the measurements in the sea over the Iceland-Faroe ridge, samples were collected in areas with moderate or low biological productivity. The *lowest saturation values* were found just in the area of the Iceland-Faroe ridge where *biological productivity is high,* particularly in June when the measurements were made. The *highest* degree of N_2O saturation was observed in areas with *low* biological productivity in *tropical and subtropical* latitudes. The same holds for the data obtained by Craig and Gordon in the South Pacific[79].

At a later time, Yoshinari[31] also carried out N_2O measurements in the North Atlantic. His results confirmed these data. He found essentially the same N_2O concentrations in the North Atlantic sea water of comparable latitude, although his analytical method was different. Unfortunately, he did not collect simultaneous air and water samples. Instead, he took 20 samples of marine air in the open North Atlantic and in the Caribbean during March and April 1972 and found an average mixing ratio of 328 ppb(v) N_2O. We, however, found an average mixing ratio of 273 ppb(v) N_2O in the marine air over the NE Atlantic one year earlier. Since the results of N_2O measurements in sea water were nearly identical, and both of us used the same analytical method for air and water samples, this discrepancy should be real and not due to analytical errors. Unfortunately, there are no long-term records of the N_2O mixing ratio in air for the years 1971 and 1972 in the northern hemisphere. Thus, we cannot decide whether Yoshinari's value of the average mixing ratio of N_2O in North Atlantic air indicated a general rise of the atmospheric N_2O level or a rather temporary and local phenomenon. But even with 328 ppb(v) N_2O in marine air, Yoshinari found no significant N_2O undersaturation of surface water. In accordance with our results, his data exhibit a decrease in the N_2O supersaturation of surface water as one proceeds northward in the open North Atlantic with the highest N_2O supersaturation in the Caribbean and in the Sargasso Sea where biological productivity is apparently very low. Also, his data indicate that in coastal zones, the N_2O supersaturation of surface water may be higher than in the open ocean of the same latitude belt.

In March 1976, Rasmussen et al.[32] carried out N_2O measurements in air and sea water in the eastern tropical Pacific during a cruise of the Alpha Helix research vessel from San Diego, California, to San Martin, Peru. The data obtained are very interesting, because they give the first information on marine N_2O in a region where high surface productivity induced by upwelling and a sluggish water circulation maintain conditions favorable for the reduction of nitrate and nitrite. Previously, it was believed that such regions could possibly act as sinks of atmospheric N_2O (see below) because of the high rates of denitrification found to occur in the water column beneath the strong permanent thermocline and because of the extreme depletion of combined nitrogen in the water layers between thermocline and the surface. The data by Rasmussen and co-workers, however, show that in the oligotrophic waters off Southern Mexico and Central America, where a thick layer of water with very low oxygen concentration (<0.25 ml O_2 per liter sea water) between 200 and 800 meters indicates very high denitrification rates, the N_2O saturation of surface water was relatively low as compared to the adjacent areas but never significantly below 100 percent. (The saturation values given by Rasmussen and co-workers are too low due to a miscalculation of the N_2O equilibrium concentration in sea water with respect to air.) In the adjacent areas in the North and South where the rates of upwelling are generally higher and the oxygen concentration in the upper water layers is not so extremely low, the N_2O saturation of surface water reached values up to 280 percent! These are the highest N_2O saturation values found in surface water up to now. The highest values we found in the tropical North Atlantic were around 250 percent saturation[14].

Recent N_2O measurements by Craig et al.[30] performed in May 1976 during the Pleiades Expedition in the eastern tropical Pacific largely confirmed the results of Rasmussen and co-workers.

We may assume, therefore, that the North Atlantic ocean and wide parts of the Pacific act as net sources of atmospheric N_2O. Using the stagnant film model [81, 82] the flux into the atmosphere can be calculated according to

$$\mathrm{FLUX} = D\frac{C^{\mathrm{w}} - \alpha(T,S)\,\varrho\,P}{Z} = \frac{D}{Z}\,(C^{\mathrm{w}} - C^{\mathrm{w}}_{\mathrm{eq}}) \qquad (4)$$

where D is the molecular diffusion coefficient of N_2O in sea water, Z the thickness of the air-sea boundary layer (film thickness), C^{w} the concentration of N_2O in sea water at the base of the stagnant film, $\alpha(T,S)$ the solubility of N_2O in sea water, ϱ the density of N_2O gas, and P the partial pressure of N_2O in air above the sea's surface. The N_2O equilibrium concentration in sea water with respect to air is $C^{\mathrm{w}}_{\mathrm{eq}} = \alpha(T,S)\,\varrho\,P$. The film thickness in the Atlantic ocean was determined by Broecker and Peng [83–84] by means of radon measurements. From their results, they derived an average Z value of $63 \pm 30\ \mu$. Taking into account a possible variation of the film thickness with wind speed [82], one should expect average Z values between 40 and 60 μ for the time period of the measurements in the North Atlantic ocean. For the time period of Rasmussen and co-workers' measurements in the eastern tropical Pacific, one may assume an average Z of 50 μ.

Fluxes of N_2O from the sea's surface into the atmosphere obtained from our measurements in this way are listed in Table 3. The range of uncertainty and the average flux are given for all measurements. The Z values used in the calculation of fluxes were 40 and 60 μ. Considering all uncertainties such as the standard error of the measurements, the range of uncertainty for the film thickness, and the range of uncertainty for the N_2O solubility in sea water (± 7 percent), an overall range of uncertainty for the calculated fluxes was obtained as indicated in the fourth column of the table. The largest fluxes were found to occur in the tropical North Atlantic ocean with a general tendency for lower values as one proceeds northward. The relatively high value at 30 °W/10.3 °N may be due to the fact that the N_2O concentration here was not measured right at the surface but at a depth of 50 meters. Supporting the observations of the 1969 cruise, the smallest fluxes were obtained from the data collected in the area of the Iceland-Faroe ridge. Although the accuracy of the analytical method was improved as compared to the 1969 measurements, the small fluxes in the area of the Iceland-Faroe ridge exhibit a relatively broad scatter which might be due to the peculiar current pattern in the sea of this region (overflow phenomenon). The fluxes calculated from the 1971 data were lower in general than the value obtained from the 1969 data for approximately the same latitude belt (36.6 °N). The 1969 data were collected in April when in subtropical latitudes of the North Atlantic a bloom of the blue-green alga Trichodesmium occurs, because the winter thermocline breaks down at that time and water rich in nutrients is mixed upward. This might be the reason for the higher value obtained from the 1969 data for subtropical latitudes. The relatively large fluxes in tropical latitudes may in part be due to the upwelling along the W-African coast which mixes nutrients upward to the surface with water relatively rich in N_2O (from a depth of 200 – 300 meters).

Using 50 μ for the average film thickness Z, the data by Rasmussen et al. [32] collected in the eastern

Table 3. N_2O fluxes from the sea into the atmosphere.

	Number of measurements	Sea surface temperature (°C)	Film thickness (μ)	Values of N_2O flux range (10^{-12} g cm^{-2} s^{-1})	mean
Cruise no. 16 April 1969 (along 30 °W)					
0.6 °N	1	27	40–60	0.82–1.66	1.21
10.3 °N	1	26	40–60	1.00–2.25	1.51
25.6 °N	1	22.5	40–60	0.40–1.25	0.74
36.6 °N	1	18	40–60	0.26–0.99	0.55
59.9 °N	1	10	40–60	0.05–0.66	0.29
Cruise no. 23 June 1971					
Lisbon – 44 °N/43 °W 44 °N/43 °W – Hamburg	15	15–18	40–60	0.14–0.45	0.26
Cruise no 20 June 1970					
Iceland-Faroe	11	9–11	40–60	0.01–0.30	0.13
ridge	8	4– 7	40–60	0.05–0.37	0.17

tropical Pacific yield fluxes of N_2O from the sea's surface into the atmosphere ranging from essentially zero in the region of the Central American coast to 2.0×10^{-12} g N_2O $cm^{-2} s^{-1}$ south of the equator with a mean value of 0.58×10^{-12} g N_2O $cm^{-2} s^{-1}$.

c) Direct manmade sources of atmospheric N_2O are found in industrial processes involving the oxidation of ammonia and/or organic nitrogen compounds, particularly in plants for the production of nitric acid and in power plants where coal or other fossil fuels including natural gas are burned. These N_2O sources appear to be currently of minor importance, although they may represent point sources of considerable strength. A plant producing nitric acid by catalytic oxidation of ammonia at a rate of 10 tons nitric acid nitrogen per day would release approximately 0.1 tons of N_2O per day to the atmosphere according to measurements by Leithe and Hofer[20]. This is equivalent to the net production of 230 km^2 of natural woodland soil as measured in the area of Mainz. Pierotti and Rasmussen[85] found the stack gases of 3 different power plants, 2 burning gas and the third burning coal, enriched in N_2O by a factor of from 10 to 100 with respect to ambient air. The exhaust gases from the coal-fired power plant were found to be considerably higher in N_2O than those from the gasburning power plants.

Indirect manmade sources of atmospheric N_2O are found in polluted fresh waters and in industrial fertilizers containing combined nitrogen. In January 1971, the Rhine river in the area of Mainz carried between 33 an 36 μg N_2O per liter water[78]. This is about a hundred times the N_2O concentration found in the North Atlantic sea water and gives a flux of N_2O into the atmosphere of about 70×10^{-12} g $cm^{-2} s^{-1}$. Most of this N_2O is very likely due to the heavy pollution of the Rhine water.

Industrial fertilizers contain combined nitrogen in the form of nitrate, ammonium, and/or organic nitrogen compounds. They are used predominantly for the fertilization of arable soil (some fertilizer is applied to pasture) and entering the cycle of soil nitrogen add to the substrate for denitrification, nitrification, and nitrogen uptake (see Figure 3). Immediately after application of fertilizer or after the first rainfall following the application (when the soil is dry), high fluxes of N_2O from the soil into the atmosphere were found to occur. Burford and Stefanson[86] examined Urrbrae redbrown earth (Australia) after application of 112 kg $NaNO_3$ nitrogen per hectare which represents a relatively moderate rate of fertilization and found N_2O fluxes up to 1.8×10^{-12} g $cm^{-2} s^{-1}$ for a pasture, 47×10^{-12} g $cm^{-2} s^{-1}$ for an old cropped area, and 50×10^{-12} g $cm^{-2} s^{-1}$ for a recently cropped area. These fluxes occurred after rain had fallen and lasted for a few days.

More recently, Rolston et al.[87] determined N_2O fluxes from alluvial Yolo loam soil at Davis (California) after application of 300 kg KNO_3 nitrogen per hectare. The soil-water content was high (44 percent by volume water; 3 percent aerated pore space). For the first 10 days after application of the KNO_3 fertilizer, extremely high N_2O fluxes of up to 480×10^{-12} g $cm^{-2} s^{-1}$ were found with a sharp decrease after the 10th day. The release of molecular nitrogen, however, increased further and reached its maximum by the 18th day at a rate of more than 1350×10^{-12} g N_2 $cm^{-2} s^{-1}$.

C) Sinks of Atmospheric N_2O

The sinks of atmospheric N_2O are poorly defined. The only significant sink known at present is in the stratosphere. Stratospheric N_2O is destroyed by either photolysis

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

or reaction with $O(^1D)$

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

$$N_2O + O(^1D) \rightarrow N_2 + O_2. \qquad (2\,b)$$

Nitric odixe formed in (2a) acts as a catalyst for the destruction of stratospheric ozone[88, 89]

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (4)$$

$$\overline{O + O_3 \rightarrow 2\,O_2} \qquad (5)$$

Although about 60% of the photochemically produced ozone is destroyed by these reactions[90], the stratospheric N_2O sink is far too small to balance the N_2O net production at the earth's surface, since the rate of N_2O destruction is limited by the velocity of N_2O transport from the troposphere into the stratosphere.

In the troposphere, there seems to be very little N_2O degradation. In contrast to the results of the study by Bates and Hays[91], Johnston and Selwyn[92] and Stedman et al.[93] found the photolytic destruction rate of N_2O in the troposphere to be negligibly small ($j_{N_2O} < 1 \cdot 10^{-11}\,sec^{-1}$). Although very fast, the reaction with $O(^1D)$ can also be neglected, because the tropospheric concentration of $O(^1D)$ is only between 1 and 2×10^{-2} molecules cm^{-3}[94]. The reaction of N_2O with atmospheric negative ions forms no significant sink of tropospheric N_2O either, as was shown by Fehsenfeld and Ferguson[95]. Further possibilities of N_2O destruction in the troposphere are the reactions of N_2O with OH or HO_2 radicals

$$N_2O + OH \rightarrow N_2 + HO_2\,, \tag{6}$$

$$N_2O + HO_2 \rightarrow N_2 + O_2 + OH\,, \tag{7 a}$$

$$N_2O + HO_2 \rightarrow 2\,NO + OH\,. \tag{7 b}$$

Recently, Biermann et al.[96] measured the rate constant k_1 for reaction (6) at 298 °K to be $(3.8 \pm 1.2) \times 10^{-17}$ cm^3 molecule^{-1} sec^{-1}. With about 10^6 molecules cm^{-3} OH radicals[94], this is too slow for a significant N_2O destruction in the troposphere. The tropospheric concentration of HO_2 radicals is about 200 times higher (about $2 \cdot 10^8$ molecules cm^{-3}; Levy[94]) than the OH concentration. Unfortunately, the rate of the reactions (7a) and (7b) is not known, but one might expect that these reactions are slower by a factor of approximately 100 compared to reaction (6) so that the tropospheric N_2O destruction rate due to reactions (7a) and (7b) should be on the same order of magnitude as the destruction rate due to reaction (6).

Since all of these atmospheric reactions together are apparently only capable of destroying relatively small amounts of the N_2O formed at the earth's surface, one might be tempted to conclude that a major sink of atmospheric N_2O is located in the hydrosphere or pedosphere where micro-organisms could conceivably assimilate N_2O instead of N_2. As mentioned above, assimilation of atmospheric N_2O by microorganisms or higher plants cannot be expected to represent a major sink of atmospheric N_2O, because N_2O has to compete with molecular nitrogen as a substrate for nitrogen fixation. In addition, molecular nitrogen is always present in large excess, even in water. Experiments with plants and ambient air supported this view[97]. In these experiments, parts of living plants (leaves) were encased in a glass bulb and ambient air of known N_2O content was very slowly drawn through the bulb. No evidence was found for any net uptake of N_2O. During the 1969 cruise of the "Meteor" in the southern North Atlantic relatively low N_2O mixing ratios were measured in air masses which obviously originated from the Sahara desert[14]. McGregor[98], on the other hand, found that even if sufficient water is present to support increased microbial activity, desert soil produces rather than absorbs N_2O. The experiments with desert soil on the Island of Sal by Liebl[24] mentioned above confirmed this observation. Therefore, one may conclude that the Sahara does not act as a sink of atmospheric N_2O. The low N_2O mixing ratios found in Sahara air may be due to a very low N_2O production or even no N_2O production in the soil of the large area of the Sahara and to the presence of sinks in the neighbourhood of the Sahara (unknown tropospheric sinks?).

The uptake of atmospheric N_2O by denitrifying micro-organisms cannot be a relevant degradation process either, because the zone where the rate of N_2O destruction is faster than the rate of N_2O production (true anoxic, no free oxygen available) is commonly overlain by a zone where the production rate of N_2O is faster than the destruction rate (low concentration of free oxygen). Only in such environments where the "biological pressure" for denitrification[53] is so high that even in the top layer which is in contact with the atmosphere there is nothing left but N_2O for he biochemical oxidation of dead organic matter, one may expect uptake of atmospheric N_2O. Such environments may occur in rice paddies, in stagnant black waters in tropical latitudes, and possibly in Tundra soils in the warm season. They don't seem to occur in the open ocean, except for areas with extremely high biological productivity as found in the eastern tropical Pacific, in the Indian ocean, and in the Arabian Sea. From the data collected by Rasmussen et al.[32] in the eastern tropical Pacific, one should conclude, however, that the relevance of these areas for the degradation of atmospheric N_2O is very questionable.

D) Global Estimates of the Sources and Sinks of Atmospheric N_2O

On the basis of global estimates of the sources and sinks of atmospheric N_2O, an attempt was made to construct a N_2O balance of the troposphere as shown in Table 4. The various fluxes are given in million metric tons (Mt) N_2O per year and in million metric tons (Mt) N_2O nitrogen per year. The sources of N_2O are listed in the left part, and the sinks of N_2O in the right part of the table. The first column in both parts of the table gives the most likely values and the second column the range of uncertainty of the estimates.

As was discussed above, the global net production of N_2O is estimated to be between 125 and 475 million metric tons (Mt) N_2O per year with 210 Mt N_2O per year as the most likely value (row III). It should be emphazised that this value is the most reliable and accurate estimate in the global N_2O budget at present. All the other estimates based on N_2O measurements in soil air or in sea water are clearly less reliable.

When extrapolated to a global scale, the N_2O fluxes determined for the North Atlantic ocean (see Table 3) gave a global marine net production of N_2O of 135 Mt per year (86 Mt N_2O nitrogen per year) considering the variation of the air-sea boundary layer thickness Z with wind speed according to

Table 4. N_2O balance of the Troposphere.

Sources		likely value	range		Sinks	likely value	range	
		(10^6 metric tons per year)				(10^6 metric tons per year)		
I a)	N_2O:	70	25 – 250	marine sources	II a)	20	14 – 28	stratospheric processes (reaction with $O(^1D)$ and photolysis)
	N_2O-N:	45	16 – 160			13	9 – 18	
b)	N_2O:	25	10 – 100	land sources (soil)				
	N_2O-N:	16	6 – 65					
c)	N_2O:	20	10 – 30	industrial N fertilizers	b)	3	1 – 5	tropospheric processes (photolysis and reaction with $O(^1D)$, negat. ions, OH, and HO_2)
	N_2O-N:	13	6 – 20			2	1 – 3	
d)	N_2O:	4	2 – 6	direct man-made sources				
	N_2O-N:	2.5	1 – 4					
e)	N_2O:	5	0 – 40	fresh water (lakes and rivers)	a+b)	23	15 – 33	sum
	N_2O-N:	3	0 – 25			15	10 – 20	
f)	N_2O:	?	15 – 90	lightning	c)	?	(110 – 440)	unknown sinks
	N_2O-N:	?	10 – 55			?	(70 – 280)	
a – f)	N_2O:	>125	60 – 515	all known sources				
	N_2O-N:	>80	40 – 330					
III)	N_2O:	210	125 – 475	total source (independent estimate)	III)	210	125 – 475	total sink (independent estimate)
	N_2O-N:	135	80 – 300			135	80 – 300	

the results by Kanwisher [82] and the variation of the N_2O supersaturation of surface water and of the ratio sea/land with latitude [17]. This value was estimated to be correct within one order of magnitude (45 – 450 Mt N_2O per year). This estimate assumed that all oceans are similar to the North Atlantic with respect to N_2O production. If we consider the fluxes found during April 1969 in subtropical latitudes to be restricted to the season of Trichodesmium bloom, the annual average of the N_2O flux into the atmosphere should be lower in this latitude than the value found in April 1969 (see Table 3). Using the fluxes obtained from the 1971 data for a correction, 125 instead of 135 Mt N_2O per year is obtained for the global marine net production. This shows that such a seasonal phenomenon has little effect on the global estimate.

A greater effect is obtained, when the value of the mean film thickness Z used in the calculation of fluxes is altered. For our previous assessment, we used a Z value of 28 μ assuming a variation of the film thickness with wind speed as given by Kanwisher [82]. As mentioned above, recent radon measurements by Broecker and Peng [83, 84] suggest a mean film thickness Z of $63 \pm 30\ \mu$. If we allow for a moderate variation of film thickness with wind speed and use Z values as indicated in Table 3, a global marine net N_2O production of 45 – 120 Mt per year with a most likely value of about 75 Mt N_2O per year is obtained by extrapolating the fluxes given in Table 3 to a global scale.

Extrapolating the fluxes calculated from the data by Rasmussen et al. [32] to a global scale (with a mean film thickness of $Z = 50\ \mu$), a global marine net production of maximal 230 Mt N_2O per year with a mean value of 66 Mt N_2O per year is obtained.

Craig et al. [30] extrapolating their results from the eastern tropical Pacific to a global scale arrived at a global marine net production of mximal 70 Mt N_2O per year.

Considering the additional uncertainty brought in by extrapolation to a global scale, one may assume that a conservative estimate of the global marine net production of N_2O should be in the range of 25 to 250 Mt per year. Until more data are available – it would be very desirable to obtain data not only from the upwelling zones along the West African coast, from the Indian ocean, and from the Arabian Sea, but also from the South Atlantic, Central Pacific, and South Pacific and from coastal areas where rivers put large quantities of nutrients into the sea – one may accept 70 Mt N_2O per year as the most likely value (Table 4, row Ia).

The N_2O net production rate of soil appears to range from essentially zero (dry desert soil) to about $4 \cdot 10^{-12}$ g N_2O cm^{-2} s^{-1} (rich pararendzina soil) as was mentioned above. When we use the rates given above to derive a figure for the global net N_2O production of soil, we have $3.4 \cdot 10^{-12}$ g cm^{-2} s^{-1} as the mean flux from arable soil (unploughed) and may assume a productive period of 8 months/year. For pasture, the net production rate is obviously smaller[86]. Tentatively, we may assume $1.7 \cdot 10^{-12}$ g N_2O $cm^{-2} s^{-1}$ (half the value for arable soil) and 8 months/year as the period of N_2O production. For woodland soil, we have $0.5 \cdot 10^{-12}$ g N_2O $cm^{-2} s^{-1}$ and again 8 months/year as the period of N_2O production, and for steppe and the like the production rate may be about $0.2 \cdot 10^{-12}$ g N_2O $cm^{-2} s^{-1}$ with N_2O production all over the entire year. For tundra soil, Söderlund and Svensson[99] gave a mean net production rate of about $1 \cdot 10^{-12}$ g N_2O $cm^{-2} s^{-1}$ with 3 months/year for the N_2O production period. The resulting global net production of the land surface of the earth except for lakes, rivers, and ice-covered regions is then 25 Mt N_2O per year. In view of the fact that we have only a few measurements from some soil types and that there is a great variety of ecological conditions for N_2O production in soil, this estimate may be considered to be correct within one order of magnitude at its best with a range of uncertainty of 10 – 100 Mt N_2O per year (Table 4, row Ib). The effect of fertilization with industrial nitrogen fertilizers has not been taken into account in this estimate.

The contribution of industrial fertilizers to the tropospheric N_2O budget may be estimated in the following way: For 1974, the amount of industrial fertilizer nitrogen applied world-wide to agricultural soil in the form of ammonia, ammonium, nitrate, or organic nitrogen compounds (urea) was estimated by Hardy and Havelka[76] as 40 Mt. Part of this combined nitrogen is lost to the atmosphere due to evaporation (as ammonia), volatilization (as wind-blown dust), and immediate denitrification within the first one or two weeks after application. This immediate loss of nitrogen was estimated by Fleige et al.[100] to be about 30 percent of the fertilizer nitrogen applied in middle Europe. For the USA, estimates range between 15 and 30 percent. Since losses due to evaporation and volatilization are included in these estimates, the loss due to nitrification and denitrification alone should be less than 30 percent. A conservative estimate of this loss would be 20 percent or 8 Mt fertilizer nitrogen per year. Fertilizer nitrogen which evaporates as ammonia or is volatilized as wind-blown dust is not lost, but is greatly returned to the soil within a relatively short time span. Thus, the amount of fertilizer nitrogen left over from the quantity initially applied to the soil in 1974 was about 30 Mt.

The leaching rate in arable soil may range from 10 to 50 percent of the fertilizer applied[101]. This portion, however, is not lost for N_2O production. It is washed down into the lakes and rivers where one may expect relatively high rates of nitrification and denitrification, particularly in the case of eutrophication. As was mentioned above, the Rhine water was found to contain, even in the cold season, about one hundred times more N_2O than the water of the open North Atlantic ocean, indicating substantially higher rates of net N_2O production (either a higher N_2O yield from nitrification and denitrification, or high rates of these processes, or both).

All nitrogen from fertilizers which is not lost due to nitrification and denitrification and leaching is incorporated in crop plants. Even that portion of nitrogen which might be left in soil later-on as crop residue is balanced by losses of soil nitrogen due to erosion. Buchner and Sturm[101] constructed a nitrogen balance of arable soil, woodland soil, and other soil in W-Germany for the year 1971. It turned out that the amount of nitrogen removed from all the soils in W-Germany by cropping, leaching, and nitrification/denitrification was larger by about 15 percent than what was put in as industrial nitrogen fertilizer, seed, manure, and combined nitrogen from precipitation and natural nitrogen fixation. For arable soil, the nitrogen balance was slightly negative (about 2 percent) despite addition of about 90 kg per hectare industrial fertilizer nitrogen and about 45 kg N per hectare as manure. Since it may be assumed that this is the normal situation in agriculture, one must not worry about the size and turn-over time of fixed nitrogen in the soil reservoir as Liu et al.[11] claimed. This is even more valid when less fertilizer nitrogen is added to the soil. What counts is the turn-over time of nitrogen in the crop plants and in the crop itself. Most of the crop plants are annual plants. Thus, nitrification and denitrification as the processes that return the nitrogen to the atmosphere may be delayed by one year or more as the plants are eaten and digested, and the plant nitrogen is incorporated in animal tissue. The turn-over time of this part of the fertilizer nitrogen once applied to the soil should be 15 years at most. This is very short as compared to the lag time assumed by Liu et al.[11].

Ultimately, fertilizer nitrogen which had been incorporated in plants and animals will show up in sewage and waste water treatment plants where the rate of denitrification is usually high. What is left over, goes into the rivers. Here the rates of nitrification and denitrification may be expected to be fairly high so that only a certain portion of the combined nitrogen which had entered the rivers may reach the sea. However, even this portion has little chance to reach the deep ocean where it would be out of circulation for a long time (about 1000 years). Coastal zones where biological productivity is usually high may be considered filters for combined nitrogen from river run-off. Since nitrogen is one of the limiting nutrients in the sea and since mixing between the upper water layers and the deep ocean is relatively slow, there is essentially zero chance for fertilizer nitrogen to get down into the deep water layers.

If we are cautious, we may assume that only two thirds of the fertilizer nitrogen which had been incorporated in crop plants or was washed out from the soil into the rivers are promptly released (within 10 years) to the atmosphere, while the remaining one third has a turn-over time of 20 – 50 years. Then, considering that less industrial fertilizer was used in the past, the substrate for N_2O production in 1974 which can be related to industrial fertilizers may have amounted to 20 Mt combined nitrogen plus 8 Mt combined nitrogen consumed in immediate nitrification and denitrification.

In nitrification, the main product is nitrate and N_2O is a by-product. In denitrification, the main product is a mixture of N_2O and molecular nitrogen, as was pointed out above. If we consider the gaseous products from both of these two processes, we may define the quantity A as the ratio of the amount of fertilizer nitrogen, which is released as N_2O nitrogen, to the total amount of fertilizer nitrogen in gaseous products

$$A = \frac{N_2O - N}{N_2O - N + N_2(+NO)} .$$

The value of A may vary from essentially zero to 1 depending on the p_H value and the moisture content of the soil and on the form of combined nitrogen applied to the soil. In experiments with sealed soil-plant systems and Australian Urrbrae red-brown earth, Stefanson[102] found A values ranging from 0.05 to 0.15 with ammonium sulfate as the substrate and soil water contents around 25 percent. With calcium nitrate as a substrate, A values between 0.10 and 0.90 were observed. Focht[55] used data obtained from two types of Scandinavian arable soil to develop a model for net N_2O production in soil. This model, for example, predicts A values of 0.3 – 0.4 when the p_H value is between 6 and 7 and the aerated pore space is 6 percent. Recently, Rolston et al.[87] examined alluvial Yolo loam soil at Davis (California) as mentioned above. They performed a very detailed study with laboratory and field experiments. After application of a pulse of KNO_3 to a field plot at a rate of 300 kg N per hectare (in November 1974), the soil immediately began to release N_2O and N_2 to the atmosphere. In the gas released, A values were found to vary with time from 0.25 the day after application of the nitrate to about 0.005 on the 18th day when the release of N_2 was found to be maximal. The aerated pore space of the soil was 3 percent during the experiment (soil-water content: 0.44 cm^3/cm^3). The average A value from two experiments for the total amount of nitrogeneous gas released from the soil within 30 days after application of KNO_3 was about 0.06. This result is comparable to what the model by Focht would predict. On the basis of Focht's model, the mean A value for the gaseous products of nitrification and denitrification in arable soil may be estimated to be in the range 0.20 – 0.60 for the time periods when fertilizer nitrogen is usually applied to the soil (late fall and early spring). Sze and Rice[103] assumed an A value of 0.3 for agricultural field conditions.

Assuming A values between 0.20 to 0.60 for the total microbial degradation of combined nitrogen which was initially introduced as fertilizer nitrogen to arable soil and about 30 Mt combined nitrogen as a substrate (see above), the net production of N_2O from fertilizer nitrogen may be estimated to be currently 10 – 30 Mt per year with 20 Mt N_2O per year as a mean value (Table 4, row Ic).

Direct man-made sources of atmospheric N_2O appear to be currently of minor importance. On the basis of the measurements by Leithe and Hofer[20] and a global industrial production of about 70 Mt nitric acid per year, the total release of N_2O to the atmosphere from this source may be calculated to be about 0.2 Mt N_2O per year, a very minute amount compared to the other N_2O sources. The world-wide release of N_2O from the combustion of fossil fuels was recently estimated by Pierotti and Rasmussen[85] to be about 3.5 Mt N_2O per year. The total direct man-made production of atmospheric N_2O may, therefore, be assumed to be about 4 Mt N_2O per year (Table 4, row Id).

Because of the lack of measurements, one can only speculate about the contribution of fresh water to the tropospheric N_2O budget. Apparently, the Rhine river as a heavily polluted river represents one extreme in the net N_2O production of fresh water. Extrapolated to a global scale (with $2 \cdot 10^{16}$ cm^2 of fresh water surface), the flux rate given above yields 40 Mt N_2O per year. The other extreme must be set to zero. A rough estimate would give a mean value of about 5 Mt N_2O per year (Table 4, row Ie).

If Zipf[104] is right, lightning forms another source of N_2O in the troposphere itself. He assessed the production of oxides of nitrogen by lightning on the basis of laboratory experiments and arrived at a production rate of $(1-6) \cdot 10^{28}$ molecules of nitrogen oxides formed per second on a global basis which are predominantly N_2O. This would give an annual production of 15 – 90 Mt N_2O (Table 4, row If).

Adding up the various items in Table 4, a total net production of more than 125 Mt N_2O per year is obtained. This may be compared with the 210 Mt N_2O per year obtained from estimates of the tropospheric N_2O burden and turn-over time.

Our knowledge of the sinks of atmospheric N_2O is very poor. Junge[105] estimated the net flux into the stratosphere due to photolysis and reaction with $O(^1D)$ to be 28 Mt N_2O per year. Considering the cross sections of N_2O determined recently by Johnston and Selwyn[92], Crutzen[4] arrived at a rate of N_2O loss in the upper atmosphere of 14 Mt N_2O per year. Destruction of N_2O due to photolysis and reaction with $O(^1D)$ in the troposphere is apparently negligibly small (<0.5 Mt N_2O per year), and so is the N_2O destruction by reaction with tropospheric negative ions[95]. The reaction of tropospheric N_2O with OH radicals will not use up more than 2 Mt N_2O per year. The reaction of N_2O with HO_2 radicals should account for approximately the same amount of N_2O per year (see section C). Hence, the total rate of loss of N_2O in the troposphere due to photolysis and reaction with $O(^1D)$, negative ions, and with OH and HO_2 radicals should not exceed 5 Mt N_2O per year (Table 4, row IIb). Adding about 20 Mt N_2O per year which may be destroyed in the stratosphere, a major portion of the 210 Mt N_2O which should be destroyed annually under steady state conditions remains for unknown degradation processes (Table 4, row IIc). In other words: the main sink of atmospheric N_2O is still unknown.

In a recent paper[8], it was postulated that the missing sink of atmospheric N_2O may be found in the oceans. The tropospheric turn-over time of N_2O was somewhat arbitrarily assumed to be 20 years so that the total amount of atmospheric N_2O to be annually destroyed was substantially smaller than 210 Mt. It was further assumed that the global marine net production of N_2O was only 16 Mt per year and that, on the other hand, marine microorganisms in the surface water layer of the oceans eat 80 Mt atmospheric N_2O per year (50 Mt N_2O nitrogen per year). Although a marine N_2O sink of this size is not very likely for reasons discussed in section C, we can consider how this fits the data on marine N_2O available at present.

With the help of the "stagnant film" model (see section B) which is as good as any other model for the exchange of gases across the air/sea boundary layer, we may calculate what N_2O saturation (concentration) must be maintained in the surface water layer, at the base of the stagnant film and just beneath it, and in what area of the world ocean, in order to make 80 Mt of atmospheric N_2O per year go into the sea to be degraded. The variables may be chosen in favor of this hypothesis for maximum effect with 300 ppb(v) N_2O in marine air, 10 °C as the mean surface temperature of the oceans, and 40 μ as the average film thickness Z. Assuming, for simplicity, that marine sources and sinks are found in different geographical locations operating the whole year, it is obtained that the N_2O saturation of the surface water of 75% of the area of the world ocean (e. g. the total ocean area except for the Atlantic) must be lower than 44 percent (N_2O concentration lower than 0.2 μg per liter water). With 58 percent saturation (0.26 μg N_2O per liter water), one would need the entire ocean surface as a permanent sink of atmospheric N_2O.

We, however, never found saturation values below 100 percent in surface water (in surface water with temperatures around 10 °C, N_2O concentrations of 0.40 μg per liter water were common). Even the data by Yoshinari[31] and by Rasmussen et al.[32] with a relatively high N_2O mixing ratio in marine air (see above) showed the N_2O saturation of surface water to be in no case lower than 90 percent. The data on marine N_2O by Craig and Gordon[79] are less suitable for this consideration, because they represent average values of measurements at different locations and depths down to 900 meters with only a few measurements in surface water. However, since these data were used as a basis for the argument, we can take a closer look at these figures. The measurements in the high southern latitudes of the Pacific ocean yielded 68 percent N_2O saturation as an average for the upper 600 meters. This is the lowest reported N_2O saturation value. In tropical and subtropical latitudes however, Craig and Gordon found 125 percent N_2O saturation (as an average of the upper 900 meters)!

Things get worse, if we reject the estimate of the turn-over time of tropospheric N_2O as being too high and use a value of 8 years as given above. This would require the oceans to swallow about 180 Mt of atmospheric N_2O per year. From our calculations this is only possible, if 95% of the world ocean had the N_2O saturation of zero, or if the surface water of all oceans over the entire year had a N_2O saturation of 4 percent. This result needs no comment. Hence, the existing data give absolutely no support for the existence of a major marine N_2O sink. This does not mean that we entirely exclude the possibility of marine sinks of atmospheric N_2O. We think that such sinks can only be of a local character with limited significance for the tropospheric N_2O cycle.

Since for similar reasons other aquatic sinks of atmospheric N_2O cannot account for too much, and since in general the existence of a main N_2O sink at the earth's surface seems not to be too likely according to the present state of knowledge (see section C), an unknown tropospheric degradation process is what remains. Although there is no evidence in favor of it until now, a degradation process in the troposphere would be the most effective way for a major destruction of atmospheric N_2O, because there would be no problem with transport.

4. The Global Nitrogen Cycle

In 1970, Delwiche[106] published data on the global inventory and cycle of nitrogen, and although further results on this topic have been published in recent years[7–9, 11, 12, 107–109], there is still considerable uncertainty about the various elements of the nitrogen cycle.

In Table 5, estimates of different authors are compiled for the fluxes in and out of the land and sea reservoirs. It can be noted, that there is a tendency for increasing values with the estimates of the biological fixation rate and the denitrification rate (N_2+N_2O) as new information became available. As Hardy and Havelka[76] pointed out, industrial nitrogen fixation (Haber-Bosch process) amounted to 40 Mt nitrogen per year in 1974. The assessment for the total amount of fixed nitrogen deposited on the earth's surface is particularly uncertain for the contribution of dry deposition. While the uncertainty factor for most of the estimates listed in Table 4 is between 2 and 5, a factor of 10 may be involved with the assessment of the rate of dry deposition. Another very uncertain quantity of the nitrogen cycle is the contribution of NO_x in the different fluxes. In general, estimates for the fluxes in or out of the oceans are more uncertain than those for the fluxes in or out of the land surface (soil). Our estimates are given in column 8 of the table. The

Table 5. Nitrogen balance of the land and sea reservoirs.

Land (million metric tons per year nitrogen)								
Flux in from	1	2	3	4	5	6	7	8
1) N fixation, biological	—	44	30	175	170	139	200	180
2) N fixation, industrial	—	30	—	40	40	45	40	40
3) fixed N, precip.+dry dep.	—	4	—	—	220	120–340	160	160
4) atmospheric nitrous oxide	—	—	—	—	0	—	—	—
total	—	78	—	—	430	310–530	400	380
Flux out as								
1) N_2+N_2O	—	43	—	—	243	100–240	140	150
a) N_2	—	—	—	—	193	83–160	125	125
b) N_2O	—	—	—	—	50	20–80	8–25	25
2) NH_3	—	—	70	—	150	27–50	190	170
3) NH_4/NO_3/org. N	—	—	—	—	—	83–186		
4) NO_X	—	—	—	—	—	1–14	—	?
5) fixed N, river run-off	19	30	10	—	20	13–24	30	40
total	—	73	—	—	413	225–515	360	>360
Sea (million metric tons per year nitrogen)								
Flux in from	1	2	3	4	5	6	7	8
1) N fixation, biological	—	10	—	100	10	90–130	40	85
2) fixed N, precip.+dry dep.	59	3.6	—	—	20	25–67	60	40
3) fixed N, river run-off	19	30	10	—	20	13–24	30	40
4) atmospheric nitrous oxide	—	—	—	—	50	—		—
total	—	43.6	—	—	100	130–220	130	165
Flux out as								
1) N_2+N_2O	—	40	—	100	106	110–250	130	165
a) N_2	—	—	—	—	96	90–173	115	115
b) N_2O	—	—	—	—	10	20–80	7–25	45
2) NH_3	—	—	—	—	0	?	—	?
3) NH_4/NO_3/org. N	—	—	—	—	—	10–20	—	?
4) NO_X	—	—	—	—	—	—	—	?
total	—	40	—	—	106	120–270	130	>160

(References: (1) Emery et al.[126]; (2) Delwiche[106]; (3) Tsunogai[107]; (4) Hardy and Havelka[76], Piper and Codispoti[127], Gundersen[60]; (5) McElroy et al.[8]; (6) Scope report[109]; (7) Liu et al.[12]; (8) our estimates).

value of the biological fixation rate on land was adopted from Hardy and Havelka[76], while the marine nitrogen fixation rate was estimated from the scarce information which became available in recent years. Since we used the same sources of data, our estimate is close to the value of the fixation rate given by Gundersen[110] and the Scope report[109]. Our estimate is somewhat lower, because we neglected the nitrogen fixation in sediments and coral reefs. The value for the industrial fixation rate was again adopted from Hardy and Havelka[76]. The estimate on fixed nitrogen in precipitation was based on data by Egner and Eriksson[111, 112], Junge[113], Tsunogai and Ikeuchi[114], Menzel and Spaeth[115], Tsunogai[107], Jones[116], Ungemach[117], Georgii[118] and McConnell[119]. The values obtained are essentially identical to the assessments by Liu et al.[12]. The flux of fixed nitrogen by river run-off was estimated from water run-off data by Baumgärtner and Reichel[120] and from data on nitrogen compounds in river water, IRK[121], Williams[122], Gibbs[123], and Ungemach[117]. The value of the flux of (N_2+N_2O) from the land surface (soil) including the contribution of the industrial nitrogen fertilizers was obtained from our estimates of the N_2O net production of soil (16 Mt N_2O nitrogen per year) and of the fertilizer contribution (about 10 Mt N_2O nitrogen per year with an A value of 0.3). We applied A values of 0.15 and 0.30, respectively, which appear to be conservative estimates of the ratio $N_2O-N/(N_2O-N+N_2)$ in the gaseous products of nitrification and denitrification (see chapter 3, section D), although in the CAST[108] report A values of $5-10\%$ were reported. It can be noted that the resulting values are within the range covered by the estimates by McElroy et al.[8], the Scope report[109], and Liu et al.[12]. The value of the flux of NH_3, NH_4^+, NO_3^-, and organic nitrogen from the land surface was adopted from the Scope report[109]. No values are given for NO_x, since the data base is still too small. The fluxes of N_2 and (N_2+N_2O) from the sea's surface into the atmosphere were obtained in a way similar to those from the land surface assuming an A value of 30% for the marine nitrification and denitrification processes and 50 Mt N_2O nitrogen per year as the average marine N_2O net production. The A value was assumed to be higher for the marine environment because in the oceans, nitrification may play a comparatively important role in the production of N_2O, an assumption which, of course, needs further substantiation by detailed measurements. There is some evidence that in tropical latitudes, the sea is releasing ammonia to the atmosphere, but reliable data are still lacking. The amount of other nitrogen compounds released is also very uncertain. Therefore, we gave no number for the flux of fixed nitrogen other than N_2O from the sea's surface into the atmosphere. Inspite of the uncertainty of the estimates, one may conclude that there is sufficient fixed nitrogen supplied to both of the reservoirs to allow for a N_2O net production of the estimated size.

5. Perturbation of Atmospheric N_2O by Man

From the discussion in the foregoing chapters, it is apparent that the level of atmospheric N_2O should have risen as man's agricultural activities increased, in particular after the large-scale developments of arable land began in the last century (unless man is unconsciously manipulating the sinks of atmospheric N_2O in such a way that the increased N_2O net production is just belanced by an additional anthropogenic N_2O destruction which is not too likely). Since atmospheric N_2O apparently undergoes long-term fluctuations (see chapter 1) which over-lie the general trend, a small increase over a longer period of time would be hard to detect, even if we would have enough long-term series of N_2O measurements. In the next $10-15$ years, however, a general increase of the atmospheric N_2O level might become noticeable due to increased application of industrial nitrogen fertilizers.

The fertilizers seem to be the main cause for a rising level of atmospheric N_2O. Hardy and Havelka[76] pointed out that in 1975, about 40 Mt fertilizer nitrogen were used in agriculture. They estimated the growth of fertilizer usage to be about 6% per year leading to about 200 Mt fertilizer nitrogen applied annually to arable soil by the year 2000. Assuming quasi-steady-state conditions with respect to the sources and sinks of atmospheric N_2O (sufficiently slow increase of atmospheric N_2O) until 1975, we may calculate what the future increase in atmospheric N_2O could be. With a constant N_2O turn-over time T, the total sink of atmospheric N_2O is defined by

$$S(t)=M(t)/T\,. \tag{5}$$

If $N(t)$ is the rate of nitrogen fixation, the total global source of atmospheric N_2O would be

$$Q(t)=A\,N(t) \tag{6}$$

with A being the fraction of fixed nitrogen which shows up as N_2O in the products of nitrification and denitrification. For quasi-steady-state conditions, this results in

$$\mathrm{d}M/\mathrm{d}t=A\,N(t)-M(t)/T\,. \tag{7}$$

If the application of fertilizer nitrogen to arable soil is increased according to $N_f(1+a)^t$, we obtain

$$\mathrm{d}M/\mathrm{d}t = A\,[N_n + N_f(1+a)^t] - M(t)/T \qquad (8)$$

where N_n is the amount of naturally fixed nitrogen per year and N_f the amount of fertilizer nitrogen used annually at $t=0$ (1975). Equation (8) gives the upper limits of the increase in atmospheric N_2O with time, since one cannot expect immediate balance of the input of fertilizer nitrogen by denitrification (see chapter 3, section D).

If there is no further increase in fertilizer use beyond the time t_1, a new steady state will be reached according to

$$\mathrm{d}M/\mathrm{d}t = A\,[N_n + N_f(1+a)^{t_1}] - M(t)/T\,. \qquad (9)$$

With $M = M_0$ and $\mathrm{d}M/\mathrm{d}t = 0$ at $t = 0$, the successive integrations of (8) and (9) yield for $t \leqq t_1$:

$$\Delta M = A\,N_f\,T\left[\exp\left\{\frac{-t}{T}\right\}\left(1 - \frac{1}{1 + T\ln(1+a)}\right) + \frac{(1+a)^t}{1 + T\ln(1+a)} - 1\right] \qquad (10)$$

for $t \geqq t_1$:

$$\Delta M = A\,N_f\,T\left[\exp\left\{-\frac{t}{T}\right\}\left(1 - \frac{1}{1 + T\ln(1+a)}\right) + \frac{(1-a)^{t_1}}{1 + T\ln(1+a)}\exp\left\{\frac{t_1 - t}{T}\right\} + (1+a)^{t_1}\left(1 - \exp\left\{\frac{t_1 - t}{T}\right\}\right) - 1\right] \qquad (11)$$

where $\Delta M = M - M_0$. The maximum increase in atmospheric $N_2O\,(t \to \infty)$ is then

$$\Delta M_\infty = A\,N_f\,T\,[(1+a)^{t_1} - 1]\,. \qquad (12)$$

The time t_b required to reach b percent of the maximal increase in atmospheric N_2O is

$$t_b = T\ln \cdot \left[\frac{[(1+a)^{t_1}\exp\{t_1/T\} - 1]\,T\ln(1+a)}{[100 - b]\,[(1+a)^{t_1} - 1]\,[1 + T\ln(1+a)]}\cdot 100\right]. \qquad (13)$$

Actually, this time will be longer, because the input of fertilizer nitrogen will not immediately be balanced by denitrification, as mentioned above. Also transport and mixing in the atmosphere will take some additional time.

Putting $a = 0.06$, $t_1 = 25$ years, $M_0 = 1200$ Mt N_2O nitrogen (1870 Mt N_2O) and, according to Hardy and Havelka[76], $N_f = 40$ Mt fertilizer nitrogen per year, $\Delta M/M_0$ according to (10) and (11) is shown in Fig. 4 for the range of the estimates of T (4 – 12 years) and A (0.2 – 0.5). As shown in the figure, there is still a broad range of uncertainty. The upper limits of the increase of atmospheric N_2O by the year 2000 are between 7 and 31.5 percent of the 1975 atmospheric N_2O burden, while the new steady state in the atmosphere will adjust at a N_2O level which is between 9 and 66 percent higher than in 1975. It may be noted that with higher values of A and T, a substantial portion of the total increase of atmospheric N_2O will occur after the year 2000 when the fertilizer use is no longer increasing. For $A = 0.5$ and $T = 12$ years, it is even the major portion of the total increase which occurs after the year 2000. According to (13), the time required to reach 90 percent ($b = 90\%$) of the maximal increase of atmospheric N_2O is about 29 years for $T = 4$ years, about 36 years for $T = 8$ years, and about 45 years for $T = 12$ years. In other words: it is possible that the maximal effect of the perturbation of atmospheric N_2O is felt 40 years after fertilizer use is no longer increasing.

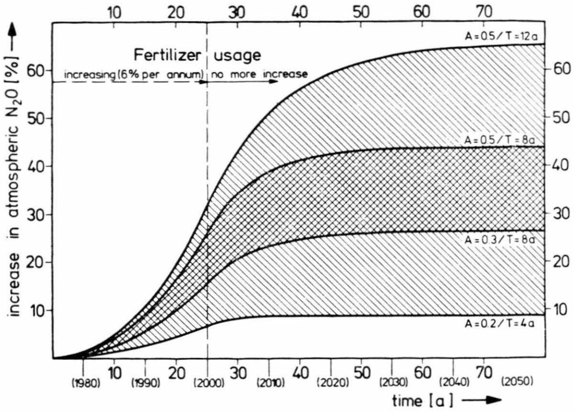

Fig. 4. Increase of atmospheric N_2O due to increasing use of industrial fertilizers as a function of time, for different values of the fraction of combined nitrogen, which shows up as N_2O in nitrification and denitrification (A), and of the tropospheric N_2O turn-over time (T). Cross-hatched area denotes the most likely range of increase.

As Johnston[6] pointed out, the number of possible combinations of A and T is restricted to certain pairs, because of the size of N_n (in Mt nitrogen per year)

$$M_0 = 1200 = A\,T\,(N_n + 40)\,. \qquad (14)$$

Table 6 shows values of N_n calculated according to Eq. (14) for various A and T values. The actual value of N_n, however, should be equal to the total amount of molecular nitrogen and N_2O nitrogen generated by micro-organisms and released to the atmosphere (assuming that the release of NO and NO_2 is negligibly small). As shown in Table 5, this

Table 6. Values of N_n in Mt nitrogen per year as a function of A and T [$N_n = (1200/A)\,T - 40$].

A	$T = 4$	$T = 8$	$T = 12$ years
0.1	2960	1460	960
0.2	1460	710	460
0.3	960	460	293
0.4	710	335	210
0.5	560	260	160
0.6	460	210	127

value should be somewhere between 250 and 500 Mt nitrogen per year, most likely between 300 and 350 Mt nitrogen per year. In Table 6, N_n values which fall into these ranges are enclosed by either a dashed line or a solid line. As can be noted, likely pairs of A and T are $0.2-12$, $0.3-12$, $0.3-8$, $0.4-8$, $0.5-8$, and $0.6-4$. All other combinations of A and T appear to be very unlikely. The most likely pairs seem to be $A = 0.3/T = 12$ years and $A = 0.4/T = 8$ years. Hence, the most likely increase of atmospheric N_2O may be found within the cross-hatched area of Fig. 4 with a maximal increase of $35-40$ percent of the current atmospheric N_2O burden.

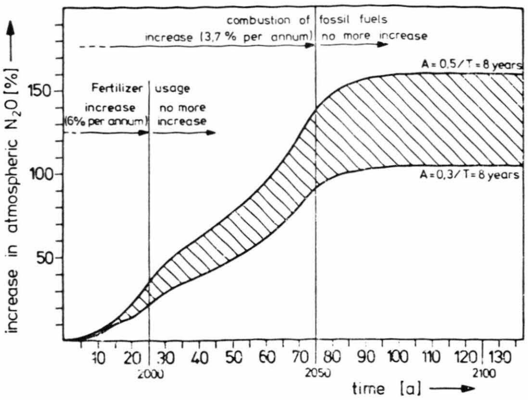

Fig. 5. Increase of atmospheric N_2O due to both increasing usage of industrial fertilizers and increasing combustion of fossil fuels as a function of time (most likely range).

Combustion of fossil fuels represents another source of atmospheric N_2O which may grow considerably with time. The combustion of coal, fuel oil, and gas is expected to increase by a factor of about 15 within the next 75 years[124] so that the direct production of N_2O due to combustion may possibly increase from the current 2.2 Mt N_2O nitrogen per year to reach a value of 33 Mt N_2O nitrogen per year by the year 2050. Besides this direct contribution to the global N_2O net production, combustion will indirectly affect the sources of N_2O at the earth's surface by increasing the amount of fixed nitrogen annually deposited so that the substrate for microbiological N_2O production will grow accordingly. Hardy and Havelka[76] estimated the nitrogen fixation rate due to combustion to 20 Mt nitrogen per year in 1974. This amount of fixed nitrogen was taken to be part of N_n in the above calculations. If we assume that the consumption of fossil fuel will increase at a rate of 3.7% per year[124, 125] until the year 2050, we may use equations (10) and (11) to calculate the upper limits of an increase of atmospheric N_2O with time due to increased NO_x production by combustion. In Fig. 5, the total increase of atmospheric N_2O due to both increasing usage of nitrogen containing fertilizers and increasing combustion of fossil fuels is shown. As opposed to Fig. 4, it may be noted that the atmospheric N_2O level will in no case reach a new plateau before the year 2050, but will continue to ascend through the first half of the 21st century. The most likely increase of atmospheric N_2O should be within the hatched area of the figure with maximal values between 100 and 160 percent of the current level. This result may be compared with the curves McElroy et al.[9] obtained from their model B 2. With a current mean tropospheric mixing ratio of 260 ppb (v) N_2O, one may expect tropospheric mean values between 520 and 680 ppb (v) N_2O by the year 2100.

Finally, it should be mentioned that this view may be expected to hold only, of course, if man is not unconsciously manipulating the sinks of atmospheric N_2O and if there is no feedback mechanism between the level of atmospheric N_2O and the N_2O generating processes. The problem of a potential destruction of the stratospheric ozone layer due to the increase of atmospheric N_2O is not discussed in this paper. Reference is made to several recent papers[3–7, 9, 11, 12] where this problem was treated with different assumptions for the rate of natural nitrogen fixation, the net production of N_2O, the tropospheric N_2O turn-over time, and the extent of ozone destruction in the stratosphere due to reactions (2a), (3), and (4) (see chapter 3, section C).

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft through its Sonderforschungsbereich 73: Atmosphärische Spurenstoffe.

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Verantwortlich für den Inhalt: A. Klemm
Satz und Druck: Konrad Triltsch, Würzburg