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# The Cycle of Atmospheric Nitrous Oxide [and Discussion]

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# The cycle of atmospheric nitrous oxide

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An attempt has been made to construct an $N_2O$ balance of the troposphere in order to demonstrate the state of knowledge of the cycle of atmospheric $N_2O$. This balance has been constructed considering the parameters relevant for atmospheric $N_2O$ as far as known such as the horizontal and vertical distribution in the atmosphere and in the oceans, the variation of the atmospheric mixing ratio with time, the fluxes in the air–sea and in the air–soil systems, and man-made fluxes. The total atmospheric burden of $N_2O$ appears to be in the range 1600–2100 Mt, the tropospheric turn-over time between 4 and 12 years.

Most of the atmospheric $N_2O$ seems to originate from microbial activities at the Earth's surface with the oceans apparently being the major source with about 35 % of the total source as obtained from the tropospheric $N_2O$ mass and turn-over time (range of uncertainty 5–100 %) followed by soil and fresh water with about 25 % of the total source (range of uncertainty 4–100 %) including the contribution of industrial nitrogen fertilizers with about 10 % of the total source (range of uncertainty 2–24 %). Direct man-made $N_2O$ sources seem to be relatively small with about 2 % of the total source (range of uncertainty 0.5–5 %), but may grow considerably in the future. The $N_2O$ production by chemical reactions in the troposphere itself (e.g. electrical discharges) is not known; a figure of between 3 and 70 % of the total source has been inferred from laboratory experiments.

The sinks of atmospheric $N_2O$ are poorly known. The only known major $N_2O$ destruction appears to occur in the stratosphere. The rate of transport into the stratosphere, however, limits this sink to about 10 % of the total amount of $N_2O$ to be destroyed under steady state conditions (range of uncertainty 3–22 %). The major problem of the cycle of atmospheric $N_2O$ is the unknown main sink. Since the stratosphere does not seem to come into question, the missing sink should be found somewhere in the troposphere, pedosphere, and/or hydrosphere.

## Introduction

The past decade has revealed that the stratospheric ozone layer is one of the most delicate features of the global environment. The ozone layer is important to life on Earth, because it absorbs potentially harmful solar radiation in the u.v. B range (280–320 nm) that otherwise would reach ground level. Small decreases in the thickness of this ozone shield may not only lead to increases in the incidence of human skin cancer, but may also have adverse effects on plant growth and animal life. Solar ultraviolet radiation can penetrate 10 m in clear water; and phytoplankton (the microscopic green plants which are the base of the aquatic food chain and one of the main sources of free oxygen) is sensitive to u.v. radiation. On the other hand, however, the latitudinal and temporal variability of the total vertical column density of ozone implies that there are rather effective biological repair mechanisms against permanent damage which may result from increased u.v. stress. It is difficult, if not impossible at present, to assess the ecological effects of long-lasting reductions in global ozone, nor can one predict the effects of a long-lasting global ozone reduction on climate (C.I.S.C. 1976).

Four different potential hazards to the ozone shield have been identified in recent years: nuclear weapon tests in the stratosphere, emissions from supersonic transports, upward diffusion of chlorofluoromethanes used mainly as aerosol propellants, and, last but not least, upward diffusion of nitrous oxide ($N_2O$). While the first three hazards are exclusively man-made, nitrous oxide is found to be a natural component of the Earth's atmosphere and appears to be responsible for the destruction of a major amount of the ozone formed in the stratosphere by photodissociation of molecular oxygen. The existing ozone layer is made of what is left over from ozone photolysis and reactions with OH and $HO_2$ radicals, with nitric oxide, and with natural halogen compounds such as methyl chloride. The nitric oxide mainly originates from $N_2O$ (Crutzen 1970; Johnston 1971). $N_2O$ may pose a threat to the existing ozone layer if its atmospheric level rises due to large-scale soil manipulations including development of virgin land and increasing fertilization with nitrogen-containing fertilizers. An increase in atmospheric $N_2O$ might also be brought about by increasing industrial production of nitric acid from ammonia Hahn (1975) and by increasing combustion of fossil fuels (McElroy *et al.* 1977; Hahn & Junge 1977).

For this reason, $N_2O$ has become a subject of major concern among atmospheric scientists. The discussion of the last two years has revealed how little we know about the cycle of atmospheric $N_2O$, despite the considerable effort made in the past (Goody 1969; Schütz *et al.* 1970; LaHue *et al.* 1970; Junge *et al.* 1971) and in recent years (see, for example, Murcray *et al.* 1973; Harries *et al.* 1974; Ehhalt *et al.* 1974; Hahn 1974, 1975; Yoshinari 1976; Rasmussen *et al.* 1976*a*, *b*; Schmeltekopf *et al.* 1977).

In this paper, an attempt has been made to summarize what is known about the processes which drive the cycle of atmospheric $N_2O$ and about the fluxes involved.

## PROCESSES OF $N_2O$ FORMATION AND $N_2O$ DESTRUCTION

Figure 1 shows a summary of the aspects of the global nitrogen cycle which are relevant for atmospheric $N_2O$. In order to avoid overcrowding, only major features are included. Reactions which may occur in the troposphere involving the oxidation of ammonia and the eventual formation of nitric oxide (NO) and/or $N_2O$ by lightning have been omitted.

The figure is made of a system of three interlinked concentric rings (8–7–9–10–11–10–9–7, 1–2–3–4–5–4–3–2, and 6) which represent biological and abiological processes. The wavy line separating the outer ring from the inner parts of the figure indicates the air–soil(–sea) boundary. Encircled by the wavy line are microbiological processes occurring in soil, fresh water, and sea water. The outer ring shows what happens to $N_2O$ in the stratosphere.

The total cycle consists of several subcycles each of which has its own rate. Subcycle I appears to be the slowest and proceeds via 1–2–3–7*a*–7*b*–9–11–1. The cycling time is primarily determined by the rate of $N_2O$ transport from the Earth's surface into the stratosphere (7*a*–7*b*) and the rate of the reverse transport of nitrate (11–1). Recent studies suggest an average cycling time on the order of 10 years. The same holds for the other branch of this subcycle (1–2–3–7*a*–7*b*–8*b*–8*a*–5–6–5–4–3–2–1) where again the transport in and out of the stratosphere (7*a*–7*b* and 8*b*–8*a*) should determine the cycling time.

Subcycle II proceeding via 1–2–3–7*a*–8*a*–5–6–5–4–3–2–1 appears to be faster. Here the cycling time is primarily determined by that part of subcycle II in which both higher plants and animals and various microorganisms participate (5–6–5). The average cycling time may be estimated to 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 average cycling time would be in the order of weeks. Both subcycle II and subcycle III should be fastest when only microorganisms are involved. The steps 5–6–5 actually form another subcycle which although it often operates separately may be considered to be part of the three subcycles mentioned.

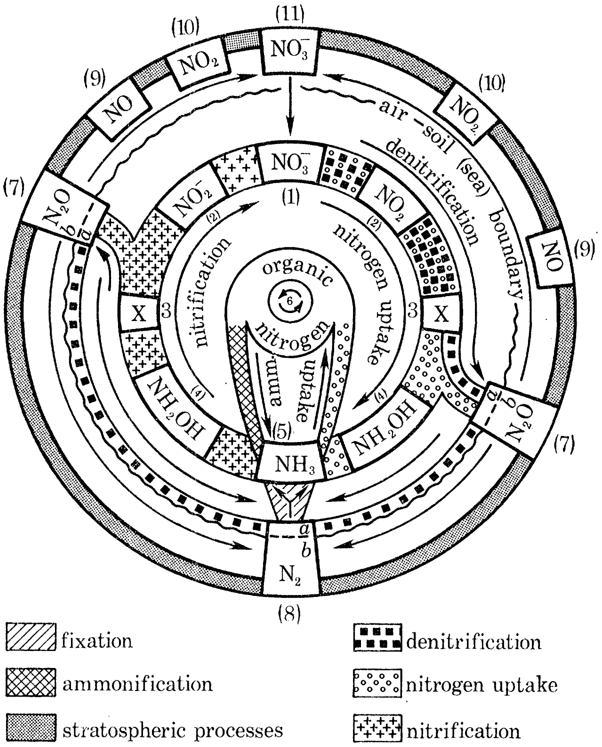

Figure 1. Global nitrogen cycle: features relevant for atmospheric $N_2O$. Wavy line separates processes in soil and in aquatic environments shown in the centre of the figure from atmospheric processes. Dashed line in the boxes of $N_2O$ and $N_2$ symbolizes exchange of $N_2O$ and $N_2$, respectively, across the air–soil(–sea) boundary layer. The reaction pathways of the various processes are marked by different symbols. (From Hahn & Junge 1977.)

$N_2O$ is formed in step 3–7*a* and is either lost to the atmosphere (7*a*–7*b*) or reduced to molecular nitrogen (7*a*–8*a*) which is again either lost to the atmosphere (8*a*–8*b*) or reduced to ammonia (8*a*–5) by nitrogen fixation and returned to the cycles of the inner part of the figure.

In the stratosphere (outer ring of the figure), $N_2O$ is destroyed by photolysis and reaction with atomic oxygen $O(^1D)$. The products of this reaction are molecular nitrogen (8*b*) and NO (9). NO reacts with ozone and ultimately forms nitrate (11) which is transported 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 ammonia nitrogen (5) goes through the loop 5–6–5 and is trapped in the pool of organic nitrogen compounds (6) for various lengths of time. The pool of organic nitrogen compounds contains living matter in the form of microorganisms, plants, and animals, and dead organic matter in the form of humus, various excreta, and particulate and dissolved organic matter in aquatic environments.

The microbiological processes relevant for the production of $N_2O$ are symbolized by the steps 1–2–3–7*a*–8*a*, representing the process of bacterial denitrification, 5–4–3–(7*a*)–2–1, representing the process of bacterial nitrification, and 1–2–3–(7*a*)–4–5–6, representing nitrogen uptake from nitrates by phytoplankton. These three processes seem to produce most of the $N_2O$ present in the atmosphere; bacterial denitrification is commonly believed to be the main source. In bacterial denitrification, $N_2O$ may be taken to be an obligatory intermediate (Hahn & Junge 1977). Depending on the environment, changing amounts of $N_2O$ and molecular nitrogen are formed. In the other two processes, $N_2O$ seems to be a by-product, as is indicated in the figure. Very little is known about $N_2O$ formation during bacterial nitrification, and virtually nothing about $N_2O$ formation during nitrate uptake by phytoplankton.

As far as man-made perturbation of the cycle of atmospheric $N_2O$ is concerned, the figure contains an important piece of information: whenever the size of any of the various boxes (reservoirs) is increased, there is more net $N_2O$ production, unless there is feedback between the atmospheric $N_2O$ level and the production rate, which is not too likely. This holds for all of the boxes except for box (8) and parts of the boxes (6) and (1). The atmosphere is the largest reservoir of molecular nitrogen. The size of this reservoir is no limiting factor to nitrogen fixation. Part of the reservoir of organic nitrogen, i.e. nitrogen incorporated in soil humic matter in temperate and boreal climate zones, exhibits a relatively long turn-over time. The same holds for nitrate found in the deep sea. The global average of the turn-over time of nitrogen in natural soil is estimated to be on the order of 400 years. In agricultural soil, however, the turn-over time of nitrogen is much shorter. Measurements by various authors suggest an average of about 50 years (McElroy *et al.* 1977). The turn-over time of the deep sea is on the order of 1000 years. Fertilizer nitrogen, regardless of the form in which it is applied to the soil, has little chance to get into the reservoirs with long turn-over times (Hahn & Junge 1977). This is good for the farmer, but cause for concern for the atmospheric scientist.

Except for the production of $N_2O$ by microorganisms, some atmospheric $N_2O$ may be formed by lightning, as was suggested by Zipf (1975) and by Delwiche *et al.* (1977). Some $N_2O$ is also produced during industrial ammonia oxidation, as was mentioned above, and during the combustion of fossil fuels (Pierotti & Rasmussen 1977).

The sinks of atmospheric $N_2O$ are poorly known. The only major sink known so far is photolysis and chemical reaction with atomic oxygen, as already mentioned. For reasons which will be discussed, there have to be additional destruction processes somewhere in the troposphere, hydrosphere or pedosphere. Soil and sea water do not seem to come into question as major sinks of atmospheric $N_2O$ because of problems with transport to anoxic sites where $N_2O$ could be consumed by microorganisms. Assimilation of atmospheric $N_2O$ by nitrogen fixing organisms is apparently also an inefficient sink, since $N_2O$ has to compete with molecular nitrogen as a substrate, and molecular nitrogen is always present in large excess, even in water. Thus we are left with abiological destruction processes. Homogeneous reactions in the troposphere studied so far appear to destroy only small amounts of atmospheric $N_2O$. We know virtually nothing about heterogeneous destruction processes of $N_2O$ in the troposphere or at the Earth's surface. Photolysis of $N_2O$ absorbed on atmospheric particles is a conceivable destruction process, as was suggested by P. J. Ausloos (1977, private communication), but further proof is awaited.

## NITROUS OXIDE BALANCE OF THE TROPOSPHERE

Available data show that in the troposphere $N_2O$ is well mixed throughout the two hemispheres. Based on older measurements, the average tropospheric mixing ratio of $N_2O$ was found to be $260 \pm 25$ parts/$10^9$ by volume (Hahn 1975; Hahn & Junge 1977). Recent measurements yielded values ranging from 280 to 340 parts $N_2O/10^9$ (see, for example, Rasmussen *et al.* 1976*a*, *b*; Yoshinari 1976; Weiss 1977; Singh 1977; Schmeltekopf *et al.* 1977; Brice & Penkett 1977; Cohen 1977). Although the precision of recent measurements is clearly better, the interlaboratory scatter of data has been still about 10 %. Apparently, this is primarily due to difficulties with calibration. Because of these difficulties and because the tropospheric $N_2O$ level seems to be subject to long-term variations (Hahn & Junge 1977), the seemingly obvious conclusion that the tropospheric $N_2O$ level has risen over the last decade cannot be drawn.

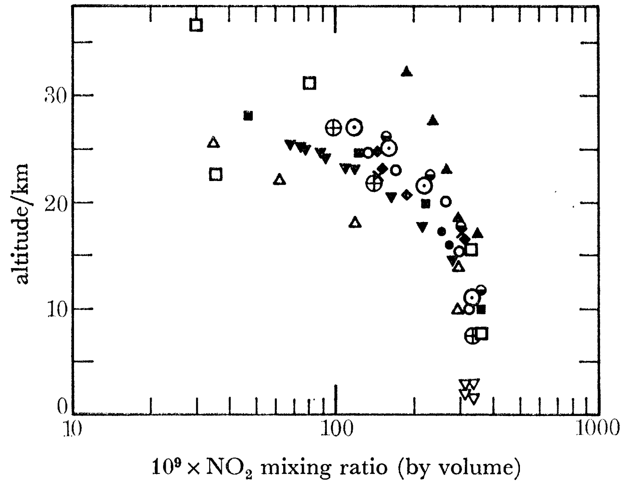

FIGURE 2. Atmospheric mixing ratio of $N_2O$ at various locations and altitudes (figure taken from Schmeltekopf *et al.* 1977). ⊖, Wyoming, June 1975; △, Saskatchewan, Canada, September 1975; ▽, Colorado, September 1975; ●, Wyoming, December 1975; ▼, Antarctic, January 1976; ×, New Mexico, March 1976; ▲, Panama, April 1976; ⊕, Wyoming, May 1976; □, Alaska, May 1976; ■, Alaska, May 1976; ○, Wyoming, July 1976; ⊙, Wyoming, July 1976; ◆, Wyoming, August 1976.

In agreement with the older measurements, the more accurate modern data show virtually no vertical gradient of the $N_2O$ mixing ratio in the troposphere and a pronounced decrease in the lower stratosphere. Vertical profiles recently obtained by Schmeltekopf and colleagues at five different latitudes are shown in figure 2 (taken from Schmeltekopf *et al.* 1977).

The profiles show that the $N_2O$ mixing ratio is remarkably constant within the troposphere. In the stratosphere above 17 km, however, the variability is substantial, indicating a strong dependence on both horizontal transport within the stratosphere and photochemistry. Compared with the profiles obtained at high latitudes in both hemispheres, the profile measured in the tropics (Panama) indicates that vertical transport into the stratosphere is relatively large at low latitudes, a finding which is important for the calculation of mean global eddy diffusion coefficients used in one-dimensional transport models. Schmeltekopf and colleagues found values 1.5–3 times larger than Hunten (1975) who had no data from the tropics at that time.

With 260 parts/$10^9$ by volume, the tropospheric $N_2O$ mass is 1700 Mt assuming an average height of the tropopause of 16 km in latitudes above 30° and of 11 km in latitudes below 30°.

Considering the precision of the measurements and the scatter data, the range of uncertainty is found to be 1700 ± 200 Mt. Based on recent data, a tropospheric $N_2O$ mass of 2000 ± 200 Mt is obtained.

As was discussed in a recent paper (Hahn & Junge 1977), we think that there is sufficient evidence to assume that the turn-over time of tropospheric $N_2O$ is relatively short. A value of 8 ± 4 years can be inferred from the older measurements. Rasmussen and coworkers' data (Rasmussen *et al.* 1976*a*, *b*), which represent the largest set of modern measurements within the troposphere, suggest a tropospheric turn-over of 10 ± 5 years.

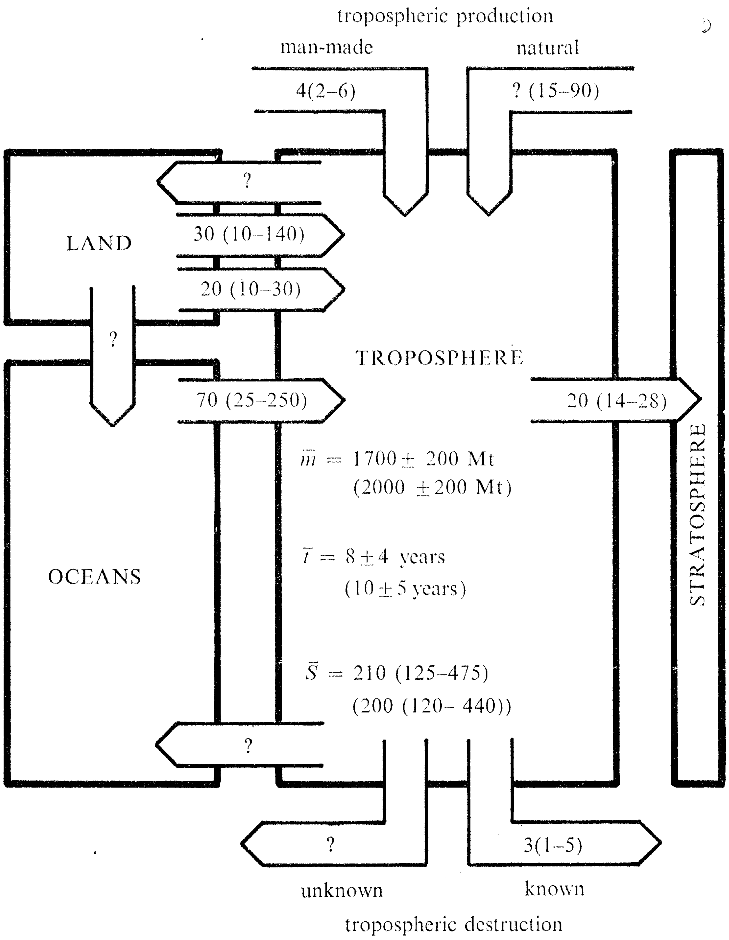

FIGURE 3. Nitrous oxide balance of the troposphere. Unless marked otherwise, all numbers given in the figure are in megatonnes $N_2O$ per year. $\overline{m}$ denotes the tropospheric mass of $N_2O$ averaged over a time period on the order of the tropospheric turn-over time $\overline{t}$. $\overline{s}$ is the total global source (sink) strength.

With a knowledge of the tropospheric mass ($\overline{m}$) and turn-over time ($\overline{t}$) of $N_2O$, the total flux ($\overline{s}$) into the troposphere and out of it, respectively, can be calculated ($\overline{m}/\overline{t} = \overline{s}$), if steady state is assumed. Considering, in addition, available data on $N_2O$ in sea water and fresh water (Junge *et al.* 1971; Hahn 1974; Yoshinari 1976; Rasmussen *et al.* 1976; Hahn & Junge 1977), on $N_2O$ in soil air (Arnold 1954; Albrecht *et al.* 1970; Schütz *et al.* 1970; Burford & Stefanson 1973; Rolston *et al.* 1976; Söderlund & Svensson 1976), and on $N_2O$ in exhaust gases of industrial plants for the oxidation of ammonia (Leithe & Hofer 1968) and those of power plants (Pierotti & Rasmussen

1976), one can try to estimate individual global fluxes and construct an $N_2O$ balance of the troposphere which appears to be the largest reservoir of $N_2O$. The result of such an effort is shown in figure 3.

Unless marked otherwise, all values given in the figure are in megatonnes $N_2O$ per year. The mean total flux ($\bar{s}$) in or out of the troposphere considering a time span on the order of the turnover time ($\bar{t}$) is found to be 210 Mt/a† (with a range of uncertainty of 125–475 Mt/a) based on the older measurements and 200 Mt/a (with a range of uncertainty of 120–440 Mt/a) on the basis of recent measurements, two values which agree very well. The fluxes between the different reservoirs are indicated by large arrows.

The fluxes from the land surface into the troposphere have been somewhat arbitrarily divided in this graph into natural fluxes and fluxes due to the application of nitrogen fertilizers, although the processes which generate $N_2O$ appear to be the same in both cases. The yield of $N_2O$, however may be different, (Hahn & Junge 1977). From measurements in soil air, a total global net $N_2O$ production of natural soil of 25 Mt/a can be inferred. The range of uncertainty of 10–100 Mt/a reflects the difficulties of this assessment. The large uncertainty is due to the limited number of data on the one hand, and to the large variety of ecological conditions for the $N_2O$ production in soil on the other hand. [In general, the microbial generation of $N_2O$ depends on the temperature, pH and aeration (availability of free oxygen) of the habitat. In soil, the availability of free oxygen and the pH are determined not only by the soil type and structure, but also by the moisture content and the content of organic matter.] With respect to net $N_2O$ production of fresh water, the situation is even worse. The only thing one can say at the moment is that this production rate must be somewhere between zero and 40 Mt/a (Hahn & Junge 1977). A first rough estimate would be about 5 Mt/a. This brings the natural production of the total land surface to about 30 Mt/a with a range of uncertainty of 10–140 Mt/a.

The net $N_2O$ production of soil and fresh water with fertilizer nitrogen as a substrate may be estimated to be currently in the range of 10–30 Mt/a with 20 Mt/a as the most likely value. We arrive at this number when we consider the trend in fertilizer use over the last decade with about 40 Mt fertilizer nitrogen applied to soil in 1974. The range of 10–30 Mt/a corresponds to a yield factor of 0.2–0.6 for the nitrogen return to the atmosphere in the form of $N_2O$ (Hahn & Junge 1977).

The most likely value for the net $N_2O$ production of all oceans is estimated to be about 70 Mt/a (Hahn & June 1977). The estimate is based primarily on our measurements in the North Atlantic ocean using the stagnant film model (Bolin 1960; Kanwisher 1963) for the calculation of fluxes through the air–sea boundary layer. Assuming a mean thickness of the air–sea boundary layer of 60 μm (Broecker & Peng 1971, 1974), the value of 70 Mt/a would mean that the mean saturation of the surface water of the world ocean with $N_2O$ should be between 150 and 160 % with respect to air (with 10 °C as the mean surface temperature of the world ocean). Values actually observed in the North Atlantic and in the Eastern Tropical Pacific range from 100 to 280 % saturation. In view of the fact that data on marine $N_2O$ are still lacking from seemingly very productive areas such as the West African coast, the Indian ocean, and the Arabian Sea, and also from the South Atlantic, Central and South Pacific, and from the polar regions, the value of 70 Mt $N_2O$/a given in the graph should be taken with caution. The correct value should certainly however, be greater than 25 Mt/a.

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† a = year.

Direct man-made sources of atmospheric $N_2O$ seem to be relatively small at present. Pierotti & Rasmussen (1977) recently estimated the global release of $N_2O$ to the atmosphere from the combustion of fossil fuels to be about 3.5 Mt/a. Considering additional input from other industrial processes, one arrives at about 4 Mt/a with 2–6 Mt/a as the range of uncertainty.

If the assessment by Dubin & Zipf (1977) is correct, lightning may be a significant source of tropospheric $N_2O$. From laboratory experiments, they inferred a figure of 15–90 Mt/a. Because of difficulties with the extrapolation of measurements carried out in the laboratory to the real atmosphere, it is felt that more experiments and measurements in the field are necessary to validate these numbers.

As already mentioned, the sinks of tropospheric $N_2O$ are not too well known. The only sink one can be fairly sure of is in the stratosphere. Assessments by Junge (1972), Crutzen (1976), McElroy *et al.* (1977) and Schmeltekopf *et al.* (1977) cover the range from 14 to 28 Mt $N_2O$/a. In figure 3, 20 Mt/a was considered to be the most likely value. Except for a minute amount of about 3 Mt/a which may be destroyed by homogeneous reactions in the troposphere, no other sinks of atmospheric $N_2O$ are known. This, however, should not lead us to conclude that there are no other sinks and that the tropospheric turn-over time of $N_2O$ must therefore be on the order of 100 years. The variation of the tropospheric $N_2O$ level with time strongly suggests a relatively short turn-over time as given in figure 3. At the present state of knowledge, it is hard to understand how the oceans and the soil can act as significant sinks of atmospheric $N_2O$. Assuming steady state in the troposphere, additional sinks totalling about 180 Mt $N_2O$/a remain to be found. As mentioned above, one should take a closer look into the possibility of $N_2O$ destruction by heterogeneous reactions in the troposphere itself or at the soil surface.

## References (Hahn)

Albrecht, B., Junge, C. & Zakosek, H. 1970 *Z. PflErnähr. Bodenk.* **125**, 205–211.

Arnold, P. W. 1954 *J. Soil Sci.* **5**, 116–128.

Bolin, B. 1960 *Tellus* **12**, 274–281.

Brice, J. A. & Penkett, S. A. 1977 *Measurements of nitrous oxide in the atmosphere via E.C.D. gas chromatography at Harwell.* U.K. Atomic Energy Authority, ERE-R8569. London: H.M.S.O.

Broecker, W. S. & Peng, T.-H. 1971 *Earth planet. Sci. Lett.* **11**, 99–108.

Broecker, W. S. & Peng, T.-H. 1974 *Tellus* **26**, 21–35.

Burford, J. R. & Stefanson, R. C. 1973 *Soil Biol. Biochem.* **5**, 133–141.

Cohen, Y. 1977 *Anal. Chem.* **49**, 1235–1237.

C.I.S.C. 1976 *Halocarbons: environmental effects of chlorofluoromethane release.* Washington, D. C.: Committee on Impacts of Stratospheric Change, National Academy of Sciences.

Crutzen, P. J. 1970 *Q. Jl R. met. Soc.* **96**, 320–325.

Crutzen, P. J. 1976 *Geophys. Res. Lett.* **3**, 169–172.

Delwiche, C. C., Bissell, S. & Virginia, R. 1977 In *Proc. Kearney Foundation Workshop on 'Nitrogen in relation to environmental quality'*, Lake Arrowhead, California, U.S.A., 31 January to 3 February. Academic Press.

Dubin, M. & Zipf, E. P. 1977 *Trans. Am. geophys. Un.* **58**, 646 (SA 131).

Ehhalt, D. H., Heidt, L. E., Lueb, R. H. & Roper, N. 1974 In *Proc. Third Conf. Climatic Impact Assess. Progr.* pp. 153–160. Washington, D.C.: U.S. Department of Transport.

Goody, R. M. 1969 *Planet. Space Sci.* **17**, 1319–1320.

Hahn, J. 1974 *Tellus* **26**, 160–168.

Hahn, J. 1975 *Meteor. Forsch.-Ergebn* A **16**, 1–14.

Hahn, J. & Junge, C. 1977 *Z. Naturf.* A **32**, 190–214.

Harries, J. E., Birch, J. R., Fleming, J. W., Stone, N. W. B., Moss, D. G., Swann, N. R. W. & Neill, G. F. 1974 *Proc. Third Conf. Climatic Impact Assess. Progr.*, pp. 197–212. Washington, D.C.: U.S. Department of Transport.

Hunten, D. M. 1975 *Proc. nat. Acad. Sci. U.S.A.* **72**, 4711–4715.

Johnston, H. S. 1971 *Science, N.Y.* **173**, 517–519.

Junge, C., Bockholt, B., Schütz, K. & Beck, R. 1971 *Meteor Forsch.-Ergebn.* B **6**, 1–11.

Junge, C. 1972 *Q. Jl R. met. Soc.* **98**, 711–729.

Kanwisher, J. 1963 *Deep Sea Res.* **10**, 195–207.

LaHue, M. D., Axelrod, H. D. & Lodge, J. P. 1970 *J. geophys. Res.* **75**, 2922–2926.

Leithe, W. & Hofer, A. 1968 *Allg. prakt. Chem.* **19**, 78–79.

McElroy, M. B., Wofsy, S. C. & Yung, Y. L. 1977 *Phil. Trans. R. Soc. Lond.* **277**, 159–181.

Murcray, D. G., Goldman, A., Murcray, F. H., Williams, W. J., Brooks, J. N. & Barker, D. B. 1973 *Proc. Sec. Conf. Climatic Impact Assess. Progr.*, pp. 86–98. Washington, D.C.: U.S. Department of Transport.

Pierotti, D. & Rasmussen, R. A. 1976 *Geophys. Res. Lett.* **3**, 265–267.

Rasmussen, R. A., Pierotti, D., Krasnec, J. & Halter, B. 1976*a* *Report on the cruise of the Alpha-Helix research vessel, March* 5–20, 1976. Air resources section, College of Engineering, Washington State University, Pullman, Washington, U.S.A.

Rasmussen, R. A., Krasnec, J. & Pierotti, D. 1976*b* *Geophys. Res. Lett.* **3**, 615–618.

Rolston, D. E., Fried, M. & Goldhamer, D. A. 1976 *Soil Sci. Soc. Am. J.* **40**, 259–266.

Schmeltekopf, A. L., Albritton, D. L., Crutzen, P. J., Goldan, P. D., Harrop, W. J., Henderson, W. R., McAfee, J. R., McFarland, M., Schiff, H. I., Thompson, T. L., Hofmann, D. J. & Kjome, N. T. 1977 *J. atmos. Sci.* **34**, 729–736.

Schütz, K., Junge, C., Beck, R. & Albrecht, B. 1970 *J. geophys. Res.* **75**, 2230–2246.

Singh, H. B. 1977 *Geophys. Res. Lett.* **4**, 101–104.

Söderlund, R. & Svensson, B. H. (eds) 1976 *Scope report* no. 7 and *Ecological Bulletins* no. 22. Stockholm: Swedish Natural Science Research Council.

Weiss, R. F. 1977 Unpublished work. Scripps Oceanographic Inst., La Jolla, California, USA.

Yoshinari, T. 1976 *Mar. Chem.* **4**, 189–202.

Zipf, E. P. 1975 Laboratory studies on the synthesis of $N_2O$ and $NO_2$, and on the destruction of $CF_2Cl_2$ by lightning. Paper presented at the A.G.U. Fall Annual meeting, San Francisco, California, U.S.A.

## *Discussion*

B. A. Thrush, F.R.S. (*University of Cambridge, Department of Physical Chemistry, Lensfield Road, Cambridge CB2 1EP, U.K.*). It has been suggested that the increased acidity of rain might increase the ratio of nitrous oxide to nitrogen in denitrification processes and that this could provide a positive feedback mechanism enhancing the ozone depletion which is expected to arise from greatly increased production of nitrate fertilizers. Could Dr Hahn comment on this suggestion?

J. Hahn. Although it appears to be fairly well established that with decreasing pH the ratio $N_2O:N_2$ in the products of bacterial denitrification increases, the effect of a decrease in the pH of rain water on the microbiological production of atmospheric $N_2O$ is hard to assess. There is the buffer capacity of soil and water bodies on one hand; on the other there is the observation that the rates of both nitrification and denitrification decrease with decreasing pH in the microbial habitat.

Soils with limited buffer capacity are found in areas with granitic bedrock and are common in Canada and in Scandinavia. On a global scale, however, soils derived from sedimentary bedrock containing large amounts of clay minerals and changing amounts of carbonates and humus predominate which have a very good buffer capacity. Soils typical of the humid parts of the temperate zones are the podzols and their relatives. Abundant vegetation makes the soil water acidic anyway (pH reaching 4.0–4.5 in the clay portion of the soil and as low as 3.5 in the humus) so that acidic rain water, as long as it is not pure sulphuric or hydrochloric acid, would not change too much in these zones as far as the acidity of the microbial habitats is concerned.

Even if the rain does change the pH in the microbial habitats, the effect would be that the nitrogen cycle in the systems affected by a decreasing pH would slow down more and more, very probably with decreasing rather than increasing net $N_2O$ production rates. Fixed nitrogen which is added to the soil in such areas and which is not incorporated into plants would either be trapped in the soil organic matter or leached out and carried off to where conditions are more favourable for nitrification and denitrification (ultimately to the sea with its extremely large buffering potential).

T. Nash (*Microbiological Research Establishment, Porton Down, Wilts., U.K.*). I suggest that the 'unknown main sink' for nitrous oxide, mentioned by Dr Hahn, is the photosynthetic cycle for the reduction of carbon dioxide. Nitrous oxide should be able to enter the cycle by being iso-electronic with carbon dioxide. There is a precedent here in the form of the acetylene reaction in nitrogen fixation. I further suggest that carbonic anhydrase should be able to hydrate nitrous oxide reversibly to hyponitrite, permitting biological reduction to ammonia.

J. Hahn. The possibility that photosynthesis and/or nitrogen fixation could act as main sinks of atmospheric $N_2O$ has been considered. However, there is as yet no support for this idea.

In higher plants, no evidence for any active assimilation of $N_2O$ could be detected. As far as microorganisms are concerned, studies have shown that *Azotobacter vinelandii* is able to metabolize $N_2O$ slowly and that the $N_2O$ nitrogen subsequently appears in the microbial protoplasm. Similar observations have been made in laboratory studies with certain soil–plant combinations. If one accepts the premise that these observations indicate a real assimilatory process and not a combination of local denitrification and subsequent $N_2$ fixation, one must conclude that $N_2O$ – if present in sufficiently large mixing ratio, i.e. in the percentage range rather than in parts/$10^9$ – is slowly taken up and reduced along the reaction pathway used in photosynthesis and/or along the reaction pathway used in nitrogen fixation. Nitrogen fixation would be more plausible, since it has been that $N_2O$ acts as a competitive inhibitor of $N_2$ uptake by microorganisms such as *Azotobacter* and *Clostridium*. Regardless of which is correct, a sink of atmospheric $N_2O$ on the basis of photosynthesis and nitrogen fixation can only be minor judging from what we know at present.