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"N_2O Fluxes at the Soil-Atmosphere Interface in Various Ecosystems, and the Global N_2O Budget"

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The overall purpose of this research task is to study the effects of soil properties and ecosystem-variables on nitrous-oxide (N_2O) exchanges at the soil-atmosphere interface, and to assess their effects on the globle N_2O budget. Experimental procedures are implemented in various sites to measure the source/sink relations of N_2O at the soil-atmosphere interface over prolonged periods of time as part of the research of biogeochemical cycling in terrestrial ecosystems. A data-base for establishing quantitative correlations between N_2O fluxes and soil and environmental parameters that are of potential use for remote sensing, is being developed.

Specific activities within this project, during the period October 10, 1985-June 30, 1987 were:

1. The development of methods for accurate measurements of N_2O fluxes in the field was continued. A field sampling and laboratory analysis procedure was field-tested in the comparative study of adjacent desert- and cultivated-soil sub-sites in the Jordan Valley (see below).

2. A field station was constructed and measurements of N_2O dynamics were conducted in a desert soil in the Jordan Valley (near the Dead Sea), under two extreme cultivation regimes: The virgin, sterile soil and a reclaimed plot growing corn under intensive cultivation. Nitrous oxide concentration-gradients in the atmosphere and in the soil, and N_2O fluxes at the soil-atmosphere interface, were measured simultaneously during the growth period of the corn. Significant differences between the fluxes in the two adjacent sub-sites were observed and possible sink activities in the desert soil were identified. The data is now being analyzed, to statistically assess the trends and quantify the differences between the two sub-sites, with particular emphasis on the question of the possible role of desert soils as N_2O sinks.

3. An invited lecture was presented at the International Conference on "Man's Role in Changing the Global Environment" (Venice, October 1985), under the title: "Global Budget of N_2O: The role of soils and their change and degradation in terrestrial ecosystems". A paper was published in the proceedings of the conference. A reprint is attached as Appendix to this report.

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GLOBAL BUDGET OF N_2O: THE ROLE OF SOILS AND THEIR CHANGE

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ABSTRACT

The atmospheric concentration of nitrous oxide is increasing. A gross analysis of the global sources and sinks of this gas identifies soils as being a major source which is presently unconstrained quantitatively. The need to address atmospheric N_2O trends in the next 20-30 years, in view of its many faceted effects on atmospheric chemistry, the global thermal budget and biospheric processes, dictates the need for a concerted effort to study, analyze and monitor N_2O emissions from soils in all the terrestrial ecosystems.

INTRODUCTION

A trend showing an increase in the concentration of nitrous oxide (N_2O) in the troposphere has been established by careful studies over the last decade (1,2). The rate of increase is 0.2-0.5% per year amounting to a net addition to the atmosphere of 2.8-5.6 Tg N_2O-N per year. This perturbation increasingly affects stratospheric chemical cycles, the thermal balance of the Earth, the biosphere in general and human environment in particular.

ATMOSPHERIC DYNAMICS OF N_2O

Nitrous oxide has a complex atmospheric chemical cycle (3,4,5). Because it is stable and thus inert in the lower atmosphere (troposphere), it is carried into the stratrosphere where it is photolytically oxidized to nitric oxide (NO) by the following reaction:

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

The NO gas, which is much more reactive, catalytically converts ozone to molecular oxygen (6):

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (2)$$

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

$$\overline{O_3 + O \rightarrow 2\,O_2 \quad \text{(net)}}$$

Hence any increase in the N_2O flux into the stratosphere may be expected to result in ozone loss. In addition to its chemical effects, N_2O absorbs radiation in the infrared range, (peaks of absorption at 7.78, 8.56 and 17.0 μm), adding to the Greenhouse Effect of other trace gases in the atmosphere. Recently, it was estimated that an increase of 25% in atmospheric N_2O will cause a global average temperature rise of 0.1K (5), and reduce the average global ozone column by 3-4% (7,8). A 1% decrease in ozone was estimated to increase the incidence rates of various skin cancers by 2-10% with the higher effects being at the lower geographical latitudes (9).

It is thus evident that the cumulative effects on global climate and biosphere, resulting from a continuing increase of N_2O in the atmosphere, may be significant. We are then faced with the question: Will the recently observed trend of increase in atmospheric N_2O, continue in the next 2-3 decades? The answer requires a better understanding of the global cycles and processes of N_2O.

GLOBAL SOURCES AND SINKS

One way to approach this question is by studying the global sources and sinks of N_2O in a framework of an annual global budget of N_2O. A simple, 3-compartment budget-model was developed recently by Banin et al. (7) for the global N_2O balances at the end of the 1970's on the basis of 1984 data. The three compartments considered are the atmosphere, the ocean and the land. The current estimates of the source and sink terms for each global compartment are shown in Table 1, and discussed below.

TABLE 1. Estimated annual production, consumption and accumulation of N_2O in the three global compartments. (Data for the late 1970's. Based on Banin et al. (7)).

COMPARTMENT	Flux, Tg N_2O-N yr^{-1}
ATMOSPHERE	
Sources	
Lightning	<0.01
Power-line corona	0.02-0.5
Excited species chemistry	0-20(?)
Sinks	
Stratospheric photolytic decomposition	6-11
Accumulation	
0.2-0.4% per year	2.8-5.6
OCEAN (including estuaries)	
Sources	2-10
Sinks	-
LAND	
Sources	
Natural soils and ecosystems	2.6-25.0
Cultivated soils	
Fertilizer N-conversions	0.1-1.5
Organic matter decay	1.5-3.8
Biomass burning	1-2
Fossil fuel combustion	1-2
Waste-water treatment	1-2
Sinks	
Desert sands, anaerobic soils	?

The atmosphere

Sources in the atmosphere are believed to be small; mainly resulting from N_2O production by lightning and coronal discharges (10). A recent suggestion by Prasad (11), of a mechanism for N_2O production by reactions of various excited chemical species in the atmosphere, has led to some controversy (e.g., 12) with estimates of its global magnitude varying widely (3). The atmospheric (stratospheric) sink, due to the photolytic decomposition reaction shown in Equation 1, is now quantitatively constrained, as is the rate of accumulation in the troposphere (Table 1).

The Earth-Surface

Basic processes: In the major part, N_2O production on land and in the oceans results from biologically mediated nitrogen conversions, which are either part of natural biospheric processes or anthropogenically enhanced activities such as nitrogen-fertilization, biomass burning and waste-water treatment. Non-biological production by chemically driven natural nitrate reduction ("chemodenitrification") has been observed on a limited scale; However, most of the non-biological production is due to anthropogenic sources, including combustion processes and biomass burning.

The production of N_2O in biological nitrogen transformations has been observed during denitrification, nitrate reduction, and nitrification, as shown schematically in Fig. 1. These processes involve many groups of microorganisms, and N_2O, in most cases, is an intermediate in a series of sequential oxidation-reduction nitrogen transformations. The cause and effect relations of N_2O fluxes from the Earth surface into the atmosphere are complex, since N_2O emissions may result from nitrogen transformations occurring at "opposing" directions. Since the valency of nitrogen in N_2O is +1, it appears as an intermediate in both the oxidative conversion (nitrification) of ammonia nitrogen to nitrate ($N^{-3} \rightarrow N^{+5}$) and the reductive conversion (denitrification) of nitrate to dinitrogen ($N^{+5} \rightarrow N^{0}$). As an intermediate gaseous product, N_2O may "leak" to the atmosphere before being consumed and further converted. The multitude of pathways that lead to N_2O production have complicated the study of N_2O dynamics since variable results are observed under apparently similar environmental conditiions, both in the ocean and on land. Particularly in soils where microenvironments inside aggregates may grossly differ from the bulk of the soil, high spatial and temporal variability have been observed even when repetitive sampling was done on scales of few tens of centimeters (13). This resulted in conflicting views with regard to N_2O emission rates into the atmosphere and the parameters affecting them, that can not be completely resolved yet, and require further detailed studies (see for example reviews by Scranton (14) and Delwiche (15)).

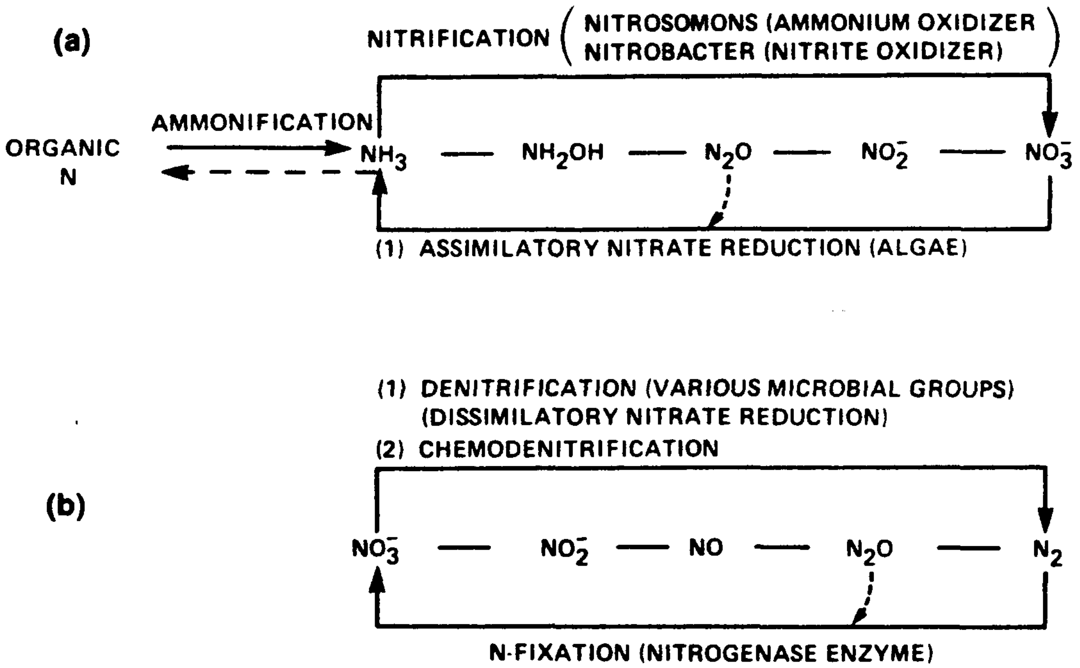

Fig. 1. Schematic description of nitrogen conversions involving N_2O: (a) The nitrification sequence, (b) The denitrification sequence.

The oceans: Estimates of the oceans' contribution to the global N_2O budget have been continuously decreasing since the mid-1970's. This is the result of intensive measurement program over the last decade or so, and in no small part, due to technical improvements and increased precision and reproducibility of N_2O analyses by gas chromatography.

Early works (16,17) have reported high supersaturation (up to 230% saturation in the ocean mixed layer) of the north and tropical Atlantic, and the ocean was identified as a major source emitting, on the global scale, about 85 Tg N_2O-N yr^{-1} (17). However, a series of studies later showed lower or no supersaturation of the mixed ocean layer, and an undersaturation of deep ocean waters (18,19,20).

An extensive series of measurements by Weiss (21) established that in general the surface layer of the ocean is in equilibrium with the atmosphere, except for upwelling locations where the water is frequently supersaturated with respect to N_2O. The latter finding was confirmed by Elkins et al. (22) and by Pierotti and Rasmussen (23). The emission of N_2O in upwelling areas may be locally significant but is not believed to be an important contributor to the global N_2O budget (3). Furthermore, since the findings show that the surface layer of the ocean is generally in equilibrium with the atmosphere or slightly supersaturated, it is not likely that the ocean is a major global sink for N_2O, though localized absorption may take place where anoxic conditions prevail (24). Denitrification is, however, an important process in maintaining the steady state concentration of nitrogen in the sea, and it is estimated that about 10-70 Tg N yr^{-1} are lost to the atmosphere by this process (25). However, it appears that most of this loss is in the form of N_2 and not N_2O, probably due to complete conversion of nitrogen by the oceanic denitrifiers to N_2, while this does not always happen during denitrification in soils on land. In fact, several reports have suggested that the source of whatever N_2O being released from the ocean is the nitrification process rather than denitrification (19,20,22,24). Although it is still debated what is the prevailing mechanism(s) of N_2O production in the ocean (14), it is believed now that the ocean is, grossly speaking, a closed compartment or possibly a small source with respect to nitrous-oxide on the global scale.

<u>The land</u>: It thus appears that the possible sources(s) for the observed increase in atmospheric N_2O concentration are land-based and largely anthropogenic. The land-based sources include emission from soils, combustion processes, biomass burning and waste-water treatment operations. Emission from soils has been identified as being by far the largest, and quite likely the least understood source. It is highly variable in space and time, and varies with moisture, temperature, nitrogen content and organic carbon content of the soil. These are modulated by vegetation, climate and cultivation intensity (4,7,15). In numerous field studies, mostly conducted in cultivated soils,

emission of N_2O was observed in the majority of cases (26-33), whereas uptake was seldom measured (28,34). The emission rates varied from 0.5-1.0 Kg N_2O-N ha^{-1} yr^{-1} in non-fertilized soils (27), to 6-40 Kg N_2O-N ha^{-1} yr^{-1} in heavily fertilized and frequently irrigated fields (35) and up to 100-200 Kg N_2O-N ha^{-1} yr^{-1} in cultivated organic soils (27). These values are based on relatively short periods of measurement that always showed a large scatter of emission rates both temporally and spatially. This is so because, unlike the ocean environment, the top layer of soils is extremely heterogeneous, and the redox, thermal and chemical conditions in it vary considerably in space, and rapidly in time, leading to gross uncertainties in flux estimates for fields, let alone for whole regions.

Even less well characterized are the emissions from non-cultivated soils. The few recent reports for forests, surprisingly showed high emission rates: 0.4-40 Kg N_2O-N ha^{-1} yr^{-1} from temperate forest soil in Michigan (13) and 0-13 Kg N_2O-N ha^{-1} yr^{-1} in a tropical forest soil in the Amazon Basin (36). These high values, if representative of forest soils in general, may suggest the possibility that soils in natural ecosystems are major global sources of N_2O. Additional measurements in field and forest soils, for prolonged periods of time, are needed, however, before this can be conclusively shown.

Estimates of the magnitude of the contribution of soils to the global N_2O budget have been varied within wide limits. In 1982, Soderlund and Rosswall (37) estimated emissions from the earth surface to be 100 Tg N_2O-N yr^{-1} (with uncertainty limits of 35 to 350) of which soils contributed 45 (10-100) Tg N_2O-N yr^{-1}. More recently, Crutzen (38) revised drastically the estimates for earth-surface emissions to balance them against the better established stratospheric decomposition rate of 6-15 Tg N_2O-N yr^{-1}. He did not assign any value for emission from natural soils, and a value of just 1-3 Tg N_2O-N yr^{-1} to cultivated lands. Addressing the same problem at about the same time, Stedman and Shetter (3) assigned to soils a global source term of 38 Tg N_2O-N yr^{-1} and a sink term of 50 Tg N_2O-N yr^{-1} (net sink of 12 Tg N_2O-N yr^{-1}). Both these views are somewhat difficult to reconcile with the many observations of measurable emissions of N_2O from both cultivated and natural soils.

For their recent global budget, Banin et al. (7), calculated emission from natural soils on the basis of flux estimates for various ecosystems, multiplied by their respective area, and obtained an estimated global source of 14(3-25) Tg N_2O-N yr^{-1}. For cultivated soils two sources were considered by Banin et al. (7): N-fertilizer transformations and organic matter decay. These sources are better constrained than those of natural soils on the basis of a relatively large number of measurements in cultivated fields, conducted mainly between 1975 and 1980, and are estimated to be 3.5 (1.6-5.3) Tg N_2O-N yr^{-1}(Table 1). However, changes of agricultural regimes and activities such as increased fertilization in intensive agricultural areas in the developing countries and an increasing tendency for adopting zero-tillage practices over large agricultural areas may increase N_2O emission; It is thus imperative that follow-up studies will be conducted in cultivated lands to assess the long-term trends in nitrogen transformations and their effect on N_2O emissions. Even a more important long-term effect may be due to soil acidification in forests as a result of acid-rain and acid-dry deposition, since low soil pH favors N_2O as the end product of denitrification (39). We know practically nothing of the changes of N_2O emission in acidified forest soil under acid-deposition stress.

THE GLOBAL BUDGET

A concise annual global budget of N_2O, based on the estimates of sources and sinks given in Table 1 is presented in Table 2. The presently available data, using conservative emission rates for the land-based sources as done here, show an apparent global "surplus" of up to 50 Tg N_2O-N yr^{-1}. This discrepency will be resolved either by changing the estimates of the magnitude of the atmospheric sink and accumulation terms or by putting better constraints on the values of emissions from soils, and identifying additional sinks on land. Brief reports have suggested the possibility of N_2O decomposition by a thermal-catalytic process upon interaction with "desert-soils" (40, 41). Since the values for the two atmospheric terms are based on atmospheric chemistry models and calculations that have been experimentally validated over the last few years, it is not expected that they will be grossly modified (4). The terms related to soils are those that need further evaluation.

TABLE 2. The global atmospheric N_2O budget sheet; concise form, based on data in Table 1. (Following Banin et al. (7)).

	Tg N_2O–N yr^{-1}	
	Range	Mean
SOURCES (SO)		
Land		
Natural	3–25	14
Anthropogenic	5–11	8
Oceans	2–10	6
Atmosphere	0–21(?)	2(?)
Total Sources	10–67	30
SINKS (SI)		
Atmosphere	6–11	8
ACCUMULATION (AC)		
Atmosphere	3–6	4
BALANCE (B)		
B=SO–(SI+AC)	-1– +51	18

CONCLUSIONS

On paper, the global N_2O budget still appears to be grossly unbalanced, with a surplus of documented sources over sinks of up to 50 Tg N_2O–N yr^{-1}, an amount only slightly smaller than the world's annual industrial nitrogen fixation for production of N-fertilizers. While atmospheric and oceanic source–sink terms in the global N_2O cycles are relatively well constrained, those of soils in terrestrial ecosystems are not. This is the major loophole in our documentation of the N_2O fluxes on Earth and a major block in the attempts to predict future atmospheric changes of this gas. There is a definite need to evaluate the effects of prolonged use of soils, increasing intensification of agricultural activity, deforestation processes, soil acidification and organic matter decay, on the budget and dynamics of this trace, partly oxidized nitrogen gas in soil-air and in the atmosphere.

REFERENCES

1 R.F. Weiss, The temporal and spatial distribution of tropospheric nitrous oxide, J. Geophys. Res., 86 (1981) 7185-7195.

2 M.A.K. Khalil and R.A. Rasmussen, Increase and seasonal cycles of nitrous oxide in the earth's atmosphere, Tellus, 35B (1983) 161-169.

3 D.H. Stedman and R.E. Shetter, The global budget of atmospheric nitrogen species, in S.E. Schwartz (Ed.), Trace Atmospheric Constituents, Adv. Environ. Sci. and Technol., Vol. 13, John Wiley and Sons, New York, 1983, pp. 411-454.

4 R.C. Whitten, A. Banin and J.G. Lawless, Terrestrial N_2O cycles and atmospheric effects. AIAA 84 (Proc. AIAA 22nd Aerospace Sciences Meeting) Paper AIAA-84-0190, pp. 1-9.

5 V. Ramanathan, R.J. Cicerone, H.B. Singh and J.T. Kiehl, Trace gas trends and their potential role in climate change, J. Geophys. Res., 90 (1985) 5547-5566.

6 P.J. Crutzen, The influence of nitrogen oxides on the atmospheric ozone content, Quart. J. Roy. Meteorol. Soc., 96 (1970) 320-325.

7 A. Banin, J.G. Lawless and R.C. Whitten, Global N_2O cycles - Terrestrial emissions, atmospheric accumulation and biospheric effects, Adv. Space Res., 4 (1984) 207-216.

8 A.J. Owens, C.H. Hales, D.L. Filkin, C. Miller, J.M. Steed and J.P. Jesson, A coupled one-dimensional radiative convective chemistry-transport model of the atmosphere, 1. Model structure and steady state perturbation calculations, J. Geophys. Res., 90 (1985) 2283-2311.

9 National Research Council, Causes and Effects of Stratospheric Ozone Reduction, National Academy of Sciences, Washington, DC, 1982.

10 R.D. Hill, R.G. Rinker and A. Coucouvinos, Nitrous oxide production by lightning, J. Geophys. Res., 89 (1984) 1411-1421.

11 S.S. Prasad, Excited ozone is a possible source of atmospheric N_2O, Nature, 289 (1981) 386-388.

12 E.C. Zipf and S.S. Prasad, Nitrous oxide formation by metastable $N_2(A^3\Sigma)$ chemistry: a new perspective on its prospects, J. Geophys. Res., in press, 1985.

13 G.P. Robertson and J.M. Tiedje, Denitrification and nitrous oxide production in old growth and successional Michigan forests. Soil Sci. Soc. Amer. J., 48 (1984) 383-389.

14 M.I. Scranton, in E.J. Carpenter and D.J. Capone (Eds.), Nitrogen in the

Marine Environment, Academic Press, New York, 1983, pp. 37-64.

15 C.C. Delwiche (Ed.), Denitrification, Nitrification, and Atmospheric Oxide, Wiley-Interscience, New York, 1981.

16 C. Junge and J. Hahn, N_2O measurements in the North Atlantic, J. Geophys. Res., 76 (1971) 8143-8146.

17 J. Hahn, The North Atlantic Ocean as a source of atmospheric N_2O, Tellus, 26 (1974) 160-168.

18 T. Yoshinari, Nitrous oxide in the sea, Mar. Chem., 4 (1976) 189-202.

19 Y. Cohen and L.I. Gordon, Nitrous oxide in the oxygen minimum of the eastern tropical North Pacific: Evidence for its consumption during denitrification and possible mechanisms for its production, Deep-Sea Res., 25 (1978) 509-524.

20 Y. Cohen and L.I. Gordon, Nitrous oxide production in the ocean, J. Geophys. Res., 84 (1979) 347-353.

21 R.F. Weiss, Nitrous oxide in the surface water and marine atmosphere of the North Atlantic and Indian Oceans, Trans. Amer. Geophys. Union, 59 (1978) 1101-1102.

22 J. W. Elkins, S.C. Wofsy, M.B. McElroy, C.E. Kolb and W.A. Kaplan, Aquatic sources and sinks for nitrous oxide, Nature, 275 (1978) 602-606.

23 D. Pierotti and R.A. Rasmussen, Nitrous oxide measurements in the eastern tropical Pacific Ocean, Tellus, 32 (1980) 56-72.

24 Y. Cohen, Consumption of dissolved nitrous oxide in an anoxic basin, Saanich Inlet, British Columbia, Nature, 272 (1978) 235-237.

25 A. Hattori, in E.J. Carpenter and D.J. Capone (Eds.) Nitrogen in the Marine Environment, Academic Press, New York, 1983, pp. 191-232.

26 A.R. Mosier, M. Stillwell, W.J. Parton, and R.G. Woodmansee, Nitrous oxide emissions from a native shortgrass prairie, Soil Sci. Soc. Amer. J., 45 (1981) 617-619.

27 J.M. Duxbury, D.R. Bouldin, R.E. Terry and R.L. Tate, Emission of nitrous oxide from soils, Nature, 298 (1982) 462-464.

28 J.C. Ryden, N_2O exchange between a grassland soil and the atmosphere, Nature, 292 (1981) 235-237.

29 D.E. Rolston, A.N. Sharpley, D.W. Toy and F.E. Broadbent, Field measurement of denitrification. III. Rates during irrigation cycles, Soil Sci. Soc. Amer. J., 46 (1982) 289-296.

30 G.L. Hutchinson and A.R. Mosier, Nitrous oxide emissions from an irrigated cornfield, Science, 205 (1979) 1125-1126.

31 R. Conrad and W. Seiler, Field measurements of the loss of fertilizer nitrogen into the atmosphere as nitrous oxide, Atmos. Environ., 14 (1980) 555-558.

32 R. Conrad, W. Seiler and G. Bunse, Factors influencing the loss of fertilizer nitrogen into the atmosphere as N_2O, J. Geophys. Res., 88 (1983) 6709-6718.

33 F. Slemr, R. Conrad and W. Seiler, Nitrous oxide emissions from fertilized and unfertilized soils in a subtropical region (Andalusia, Spain), J. Atmos. Chem., 1 (1984) 156-169.

34 J.C. Ryden, Denitrification loss from a grassland soil in the field receiving different rates of nitrogen as ammonium-nitrate, J. Soil Sci., 34 (1983) 355-365.

35 J.C. Ryden, L.J. Lund, J. Letey, and D.D. Focht, Direct measurement of denitrification loss from soils, II. Development and application of field methods, Soil Sci. Soc. Amer. J., 43 (1979) 110-118.

36 M. Keller, T.J. Goreau, S.C. Wofsy, W.A. Kaplan and M.B. McElroy, Production of nitrous oxide and consumption of methane by forest soils, Geophys. Res. Lett., 10 (1983) 1156-1159.

37 R. Soderlund and T. Rosswall, The nitrogen cycles, in D. Hutzinger (Ed.), Environmental Chemistry, Vol. 1, Part B, Springer-Verlag, Berlin, 1982, pp. 61-81.

38 P.J. Crutzen, Atmospheric interactions - homogeneous gas reactions of C, N, and S containing compounds, in B. Bolin and R.B. Cook (Eds.), The Major Biogenic Cycles and Their Interactions, SCOPE 21, Wiley, New York, 1983, pp. 65-113.

39 T.B. Parkin, A.J. Sexton and J.M. Tiedje, Adaptation of denitrifying populations to low soil pH, Appl. Environ. Microbiol., 49 (1985) 1053-1056.
40 R.E. Rebbert and P. Ausloos, Decomposition of N_2O over particulate matter, Geophys. Res. Lett., 5 (1978) 761-764.
41 D. Pierotti, L.E. Rasmussen and R.A. Rasmussen, The Sahara as a possible sink for trace gases, Geophys. Res. Lett., 5 (1978) 1001-1004.