Svensson, B.H. & Söderlund, R. (eds.) 1976.
Nitrogen, Phosphorus and Sulphur – Global
Cycles. SCOPE Report 7.
Ecol. Bull. (Stockholm) 22:23–73

THE GLOBAL NITROGEN CYCLE

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☆ Contribution No. 326 from the Department of Meteorology, University of Stockholm, Sweden.

ABSTRACT

A consistent picture of the global nitrogen cycle, mainly based on a comprehensive literature survey, is presented. The annual flows between the terrestrial, aquatic and atmospheric reservoirs are considered, the rates given referring to 1970. The cycle is presented in four parts: molecular nitrogen – nitrous oxide, ammonia compounds, compounds of odd nitrogen oxides (NO_x), and organic nitrogen compounds.

Atmospheric inventories and natural fluxes of NO_x through the atmosphere were shown to be smaller than those generally accepted. No great differences to earlier anthropogenic flows estimated were obtained, and they thus play a greater role in the atmospheric cycle than previously believed. Recent reports on the biochemistry of the nitrogen fixing enzyme system are regarded as supporting the possibility of biological sinks for nitrous oxide within the terrestrial and aquatic systems.

Nitrogen fixation in the aquatic system was found to be 20–120 Tg (million metric tons) annually. The nitrogen fixation in sediments was estimated to be approximately 10 Tg N yr^{-1}, a flux hitherto overlooked in budget considerations for the global system. The man-made contribution to the amount of nitrogen annually fixed was about 20 %. This part of the nitrogen fixation is expected to rise rapidly owing to the high demand for nitrogen fertilizers and to the increased use of fossil fuels.

The net transport of nitrogen compounds to the oceans through river runoff was estimated at 13–24 Tg and a transfer of 38 Tg org.-N is estimated to be permanently trapped in sediments. A range of 10–20 Tg org.-N yr^{-1}, within the total range of 10–100 Tg org.-N yr^{-1} in wet deposition on land, was regarded as being of oceanic origin.

INTRODUCTION

The biosphere contains a complex mixture of nitrogen compounds. The large number of compounds with different physical and chemical properties makes the picture for nitrogen flows and conversions very complex and variable (Table 1). Some of the compounds studied have a short turnover time in the various reservoirs, especially in the atmosphere, and for this reason, large local and regional deviations from the estimated global mean values for the fluxes as well as for the concentrations of these various forms of nitrogen must be expected, both in space and time.

Man-induced changes in the nitrogen cycle are primarily of regional and local character. The introduction of agricultural activity increased the turnover rate of nitrogen in the biosphere via leaching and losses to the atmosphere as compared with conditions under a natural system without agricultural practices. With the development of industry, the emission rates of acid substances to the atmosphere – including oxides of nitrogen, NO_x – increased considerably, giving rise to regional environmental problems. Acid sulphur compounds have almost exclusively been taken into account in connection with the acidification of lakes and rivers, and little attention has so far been paid to acid nitrogenous compounds. Irrigation and the intensive use of industrial fertilizers have led to local increases in the nitrate content to toxic levels in groundwater, making it unsuitable for human consumption and for domestic purposes (Commoner, 1970; Kumm, 1976).

Table 1. Nitrogenous compounds, their water solubility and processes accounted for in the present paper.

Compound		Solubility in water	Processes participated in
Molecular nitrogen	N_2	slightly soluble	Biol. & abiol. nitrogen fixation Denitrification
Ammonia/Ammonium	NH_3/NH_4^+	readily soluble	Nitrification Leaching and river runoff Decomposition of organic matter Dry and wet deposition Fertilizer production Combustion Reactions in the troposphere Plant uptake Volatilization
Nitrous oxide	N_2O	slightly soluble	Denitrification Reactions in the stratosphere
Nitric oxide	NO	slightly soluble	Dry deposition Reactions in the atmosphere Combustion
Nitrogen dioxide	NO_2	readily soluble	Nitrite reduction in acid soils Reactions in the atmosphere Combustion
Nitrous acid/Nitrite Nitric acid/Nitrate	HNO_2/NO_2^- HNO_3/NO_3^-	readily soluble	Nitrification Denitrification Dry and wet deposition Plant uptake Leaching and river runoff Reactions in the atmosphere
Organic nitrogen		readily soluble – insoluble	Production of biomass Dry and wet deposition Volatilization Decomposition of organic matter

On a global scale, a source of major concern is the extent to which human activities have increased the emission of nitrous oxide into the atmosphere (Crutzen, 1972). The nitrous oxide partly reaches the stratosphere, where it plays an important role in regulating the earth's ozone shield against UV radiation. The attainment of a better understanding of the processes involved in regulating the loss of nitrous oxide from the biosphere is therefore a matter of high priority (Eriksson & Rosswall, 1976). This was also emphasized by the WMO (1976) report entitled "Statement on modification of the ozone layer due to human activities and some possible geophysical consequences". The report placed high priority on a better understanding for the total nitrogen cycle.

The high energy required to break the N-N bond and the inability of most living species to utilize molecular nitrogen result in a high demand for already fixed forms of this essential element. Ecological systems are therefore, to a great extent, adapted to the recycling of the more easily available forms. Globally, 90–97 % of the nitrogen content of net primary production of plant biomass derives from the recycling of forms other than N_2, leaving only about 3–10 % as annually fixed from the molecular nitrogen pool (Rosswall, 1976).

Another distinctive feature of the nitrogen cycle consists in the time characteristics of various nitrogen compounds in the reservoirs. The short turnover time of atmospheric ammonia – of the order of days – compared with the turnover time of atmospheric molecular nitrogen – of the order of some millions of years – clearly shows the large variation in cycling rates of different components in the cycle. The uncertainty of estimates over time of the nitrogen content in terrestrial and aquatic reservoirs makes it impossible to ascertain if there is a balance or imbalance in the total system.

The literature contains several papers giving distribution and flows of nitrogen on a global scale. Many of the recent estimates of the behaviour of nitrogen in nature are based, directly or indirectly, on the vast compilation of data on geochemically cycled compounds made by Clarke (1924). Hutchinson (1954) obtained a rough quantitative picture by making a budget for the different parts of the biogeochemical cycle of nitrogen. This pattern was used by Eriksson (1959a), when discussing atmospheric nitrogen flows. He introduced the atmospheric transport of nitrogenous organic matter as an important pathway of the cycle, and suggested that the sea-surface was a major source for this type of nitrogen deposited over land areas. Several articles by Robinson & Robbins (1970a,b; 1975) also focussed on atmospheric flows. They stressed the predominance of natural sources of atmospheric NO_2 and NO over anthropogenic ones.

The model by Hutchinson (1954) was the basis for the global nitrogen cycles presented by Delwiche (1970) and Burns & Hardy (1975). These two articles concentrated on biological activities involving nitrogen. Delwiche (1970) emphasized the energy aspects of microbial conversions of various nitrogenous compounds. The magnitudes of the fluxes given by Hutchinson (1954) were slightly modified by Burns & Hardy (1975). They recalculated the global biological nitrogen-fixation on the basis of an extensive literature survey. Other atmospheric flows were only briefly dealt with in these two articles.

Because of the vague presentation of data bases and calculations in many earlier works, it was felt that a new compilation concentrating on the quantitative aspects of the cycle would be valuable and would enable current knowledge in this field to be determined.

The biogeochemical cycle of nitrogen presented here (Fig. 1) is the result of an interdisciplinary approach, which was believed necessary for this type of work. The magnitudes of most of the atmospheric flows and inventories and of the nitrogen fixation in the sea differ substantially from those given in earlier works. Most other compilations summarize uncertainties in flows and distributions in terms, such as, "the values may well be out by a factor of 10" without discussing or giving any reason for the factor of uncertainty stated. In the present article, however, a range was mostly applied for each value to indicate the uncertainty.

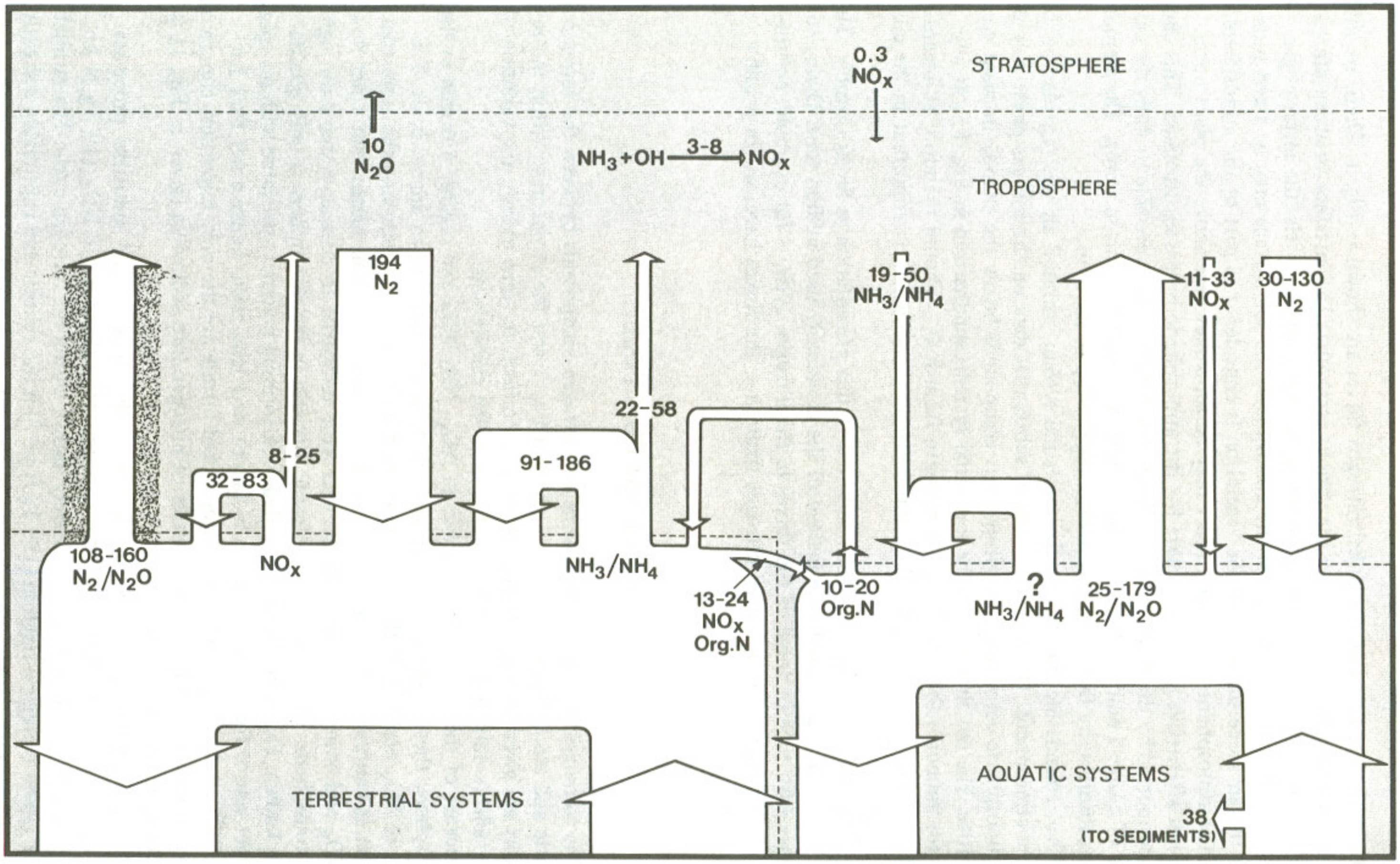

Figure 1. The global nitrogen cycle. The rates are given as Tg N yr^{-1}. The flows of N_2/N_2O are obtained when balancing the terrestrial and aquatic systems.

Only the net flows of the global nitrogen fluxes are shown in Fig. 1. There are difficulties in assigning boundaries to the various reservoirs. The interface between atmospheric and terrestrial systems can be set at various arbitrary levels: the intrasoil gas phase may be regarded as part of the atmosphere; the soil surface may be fixed such that the air space surrounding the vegetation is considered as part of the atmosphere, and the atmospheric/terrestrial border may be set somewhere above the plant cover. The last alternative was chosen here for the atmospheric processes discussed. This choice was supported by the findings of Denmead *et al.* (1976), who were able to show the existence of a large ammonia flux from soil into the air between plants in a crop. The ammonia was reabsorbed by the plants before reaching the top of the crop.

When considering transfers in the terrestrial system, intrasoil air was regarded as part of the atmosphere. This is due to lack of substantial data on the soil gas phase and also on atmospheric conversions of nitrogenous compounds below the canopy in plant communities. The net fluxes from the terrestrial systems summarized in Fig. 1 – at any rate for ammonia, NO_x and organic nitrogen from soils – should therefore be regarded as the fraction of the large local "intraterrestrial" flows which is important in the context of atmospheric chemistry.

The SI system of units has been followed in this presentation as far as possible. The unit Tg (= 10^{12} g) is used here instead of the commonly used million tons. Owing to changes with time of some of the fluxes in the nitrogen cycle – for example, anthropogenic emissions and industrial nitrogen-fixation – the fluxes have, where possible, been adjusted to 1970.

A BALANCED CYCLE?

The summarized global flow scheme for nitrogen compounds between the terrestrial, aquatic and atmospheric reservoirs is given in Fig. 1 and the inventories within the reservoirs are given in Table 2. The ranges given reflect, to some extent, the variation of the available data and also the uncertainty in the calculations.

Because of the short turnover times of NO_x, NH_3/NH_4^+ and organic nitrogen in the atmosphere, these flows may be considered in steady states on an annual basis. The sinks of NO_x and NH_3/NH_4^+ have therefore been balanced by regarding the terrestrial system as containing missing sources for these compounds. This means that a net flow of NO_x and ammonia compounds prevails from terrestrial to oceanic systems through the atmosphere. The behaviour of organic nitrogen in the atmosphere is only qualitatively known. Eriksson (1959a) regarded slick-forming material associated with sea-spray as a net source for organic nitrogen in fallout over land areas, hence a net flow has been indicated in Fig. 1. Organic nitrogen and nitrate are the only important compounds in river discharge, while the net transfer of nitrogen into sediments (given in Fig. 1) is due to organic compounds.

The terrestrial nitrogen-fixation includes both biological and industrial processes. The magnitude of the latter and the emission of anthropogenic NO_x (19 Tg N yr^{-1}) to the atmosphere are the most accurately known within the nitrogen cycle. The estimate of the global biological fixation (139 Tg N yr^{-1}) is less reliable and is probably a slightly conservative value. Much research needs to be done on nitrogen fixation in marine environments before an accurate value can be assigned to that flow. The figures given are regarded as reflecting the potential sedimental (10 Tg N yr^{-1}) and pelagic fixation (20–120 Tg N yr^{-1}).

The most acute lack of data was found in the case of denitrification processes giving rise to flows of molecular nitrogen and nitrous oxide into the atmosphere. It was possible to make crude estimates for the latter compound for both terrestrial and aquatic systems, while the lack of data made it impossible to estimate the flow of nitrogen gas *per se*.

Despite the fact that no further information is given to a system when assigning a steady state and balancing the flows (Eriksson & Rosswall, 1976), this method was adopted in order to obtain possible magnitudes for denitrification rates (Fig. 1). .The terrestrial and aquatic systems were treated separately. The inputs were 204–214 Tg N yr^{-1}, and 73–237 Tg N yr^{-1} for terrestrial and aquatic systems, respectively. The corresponding outputs excluding denitrification were 43–107 Tg N yr^{-1} and 48–58 Tg N yr^{-1}. Terrestrial denitrification may therefore be within the range of 108–160 Tg N yr^{-1} of which 16–69 Tg N yr^{-1} should be released as nitrous oxide, while the corresponding values for aquatic systems were 25–179 Tg N yr^{-1} overall and 20–80 Tg N yr^{-1} as nitrous oxide.

The independent estimates of the fluxes of N_2O from the terrestrial and aquatic systems indicate minimum rates of 16 and 20 Tg N yr^{-1} respectively. These rates compared with the maximum denitrification values indicate that at least 10 % of the total amount of nitrogen denitrified is in the form of N_2O. No other sinks, apart from the flow to the stratosphere, are known for nitrous oxide. There are, however, some support for soil and water systems acting as sinks for nitrous oxide.

The denitrification rates obtained by balancing the systems are affected by the likelihood of the soil or water systems being sinks for nitrous oxide, which would increase the nitrogen flows from both, and by higher nitrogen fixation rates. Such changes will also affect the fraction of nitrous oxide evolved related to the total amount of nitrogen denitrified in these two systems.

GLOBAL INVENTORIES OF NITROGEN

The global nitrogen content in various reservoirs have been recalculated in this paper with a few exceptions, where earlier literature estimates were accepted (Table 2).

Terrestrial nitrogen

Terrestrial biomass and litter

Bazilevich (1974) estimated value of $2.4 \cdot 10^6$ and $1.9 \cdot 10^5$ for global plant biomass and litter with a mean nitrogen content of 0.6 and 1.7 % respectively. For the same pools Whittaker (1975) reported $1.8 \cdot 10^6$ and $1.1 \cdot 10^5$ Tg. A proportional difference exists for the net primary production figures given by the two authors. Lieth (1975) discussed the possibility that his net primary production value (about the same as that given by Whittaker, 1975) might have to be raised in the future in the light of

Table 2. **Global inventories of nitrogen in the terrestrial, oceanic and atmospheric systems given in Tg N.**

TERRESTRIAL:		
Plant biomass	$1.1-1.4 \cdot 10^4$	This compilation
Animal biomass	$2 \cdot 10^2$	Delwiche (1970)
Litter	$1.9-3.3 \cdot 10^3$	This compilation
Soil:		
organic matter	$3 \cdot 10^5$	This compilation
insoluble inorganic	$1.6 \cdot 10^4$	This compilation
soluble inorganic	?	
microorganicms	$5 \cdot 10^2$ *	This compilation
Rocks	$1.9 \cdot 10^{11}$	Stevenson (1965)
Sediments	$4 \cdot 10^8$	Stevenson (1965)
Coal deposits	$1.2 \cdot 10^5$	Donald (1960)
OCEANIC:		
Plant biomass	$3 \cdot 10^2$	This compilation
Animal biomass	$1.7 \cdot 10^2$	Delwiche (1970)
Dead organic matter		
dissolved	$5.3 \cdot 10^5$	This compilation
particulate	$0.3-2.4 \cdot 10^4$	This compilation
N_2 (dissolved)	$2.2 \cdot 10^7$	Delwiche (1970)
N_2O	$2 \cdot 10^2$	This compilation
NO_3^-	$5.7 \cdot 10^5$	Emery *et al.* (1955)
NO_2^-	$5 \cdot 10^2$	This compilation
NH_4^+	$7 \cdot 10^3$	This compilation
ATMOSPHERIC:		
N_2	$3.9 \cdot 10^9$	Robinson & Robbins (1970a)
N_2O	$1.3 \cdot 10^3$	Schütz *et al.* (1970)
NH_3	0.9	This compilation
NH_4	1.8	This compilation
NO_x	1–4	This compilation
NO_3^-	0.5	This compilation
Org.-N	1	This compilation

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* This amount is inevetably included in the figure for organic nitrogen in the soil.

better information on tropical rain forests. The same situation will therefore probably be true for the biomass and litter inventories. The nitrogen content was therefore believed to be within the ranges of $1.1-1.4 \cdot 10^4$ Tg N for the plant biomass and $1.9-3.3 \cdot 10^3$ Tg N for the terrestrial litter.

The figure for the nitrogen content in animal biomass (200 Tg) was taken from Delwiche (1970). The value seems reasonable as compared with the total carbon content (460 Tg) for the land pool estimated by Whittaker (1975). The global nitrogen pool within terrestrial microorganisms was calculated from the average nitrogen content of 4 g m^{-2} given by Rosswall (1976) and the figure for land areas of $133 \cdot 10^{12}$ m^2 given by Bazilevich (1974). The value obtained, $5 \cdot 10^2$ Tg N, is already contained in the value for nitrogen in soil organic matter.

Soil nitrogen

Bohn (1976) estimated the carbon content in world soils (to 1 m depth) using the FAO–Unesco soil map and other recent soil data. His value was $3 \cdot 10^6$ Tg C, and taking a C/N ratio of 10 for humus, $3 \cdot 10^5$ Tg N should be bound in soil organic matter. The values of 7.6 and $8.2 \cdot 10^5$ Tg N given respectively by Stevenson (1965) and Delwiche (1970) were calculated in the same manner from older, not very accurately made, compilations of soil organic matter. The value presented here was thus regarded as the most correct available.

Many difficulties are involved in estimating the soluble and insoluble inorganic pools in soils. Delwiche (1970) proposed $1.4 \cdot 10^5$ Tg N for the inorganic pool on land, without supplying any information as to how this figure was calculated. Burns & Hardy (1975) rounded this figure off to 10^5 Tg without indicating any reason for this manipulation. They assumed that the soluble inorganic nitrogen in soil was 1 % of the insoluble pool.

Nömmik (1965) reviewed values for fixed NH_4^+ in soils given by Bremner (1959), Stevenson (1959) and Young (1962). The values ranged from 1.7 to 7.9 % of total nitrogen in surface soils and from 9 to 47.2 % in subsurface soils. This fraction of insoluble, inorganic nitrogen together with organic nitrogen, constitutes the main nitrogen pool in soil. As a conservative estimate the average global, insoluble, inorganic fraction of nitrogen in soil was assumed to be 5 % of the total nitrogen content in soil. This resulted in $1.6 \cdot 10^4$ Tg, which was used in the present work. The authors of the present paper were not able to find any mean content for soluble inorganic nitrogen in soil, and it was left with a question mark in Table 2.

Nitrogen in rocks and coal

Stevenson (1965) estimated the nitrogen content in rocks and sediments at $1.9 \cdot 10^{11}$ Tg N and $4 \cdot 10^8$ Tg N respectively. Nitrogen bound in coal deposits was calculated to be of the order of $1.2 \cdot 10^5$ Tg N by Donald (1960). These values were adopted for the present compilation.

Nitrate, nitrite and nitrous oxide

Emery *et al.* (1955) reported a nitrate content of $5.7 \cdot 10^5$ Tg in world oceans. The figure was estimated by integration of the nitrate concentration profiles given by Sverdrup *et al.* (1942) for the depth of the Atlantic, Pacific and Indian Oceans. Sverdrup *et al.* (1942) emphasized the profiles as being qualitative.

Considerable amounts of nitrite occur, mostly at the compensation point and in anoxic waters, while other parts of the ocean seem to be devoid of this substance. Sverdrup *et al.* (1942) gave a range of 0.1–50 μg NO_2^--N l^{-1}, which is about one-tenth of the nitrate concentration range. Because of the distribution with depth, compared with nitrate (Riley & Chester, 1971), the inventory becomes even less. The profiles of nitrite from the Sargasso Sea and the East Tropical Ocean given by Riley & Chester (1971) were used to obtain a range for the nitrite content of the oceans (Table 3). It is apparent that at least 180–360 Tg of nitrite is available in the oceans. The true figure is probably higher because of the influence of anoxic areas, and for this reason, about 500 Tg was estimated in this compilation. The value obtained by extrapolating the anoxic part of the East Tropical Pacific to the whole ocean (Table 3) was regarded as much too high.

Table 3. Nitrite in the oceans. Concentrations obtained from Riley & Chester (1971) were integrated over the most concentrated band of nitrite for the whole ocean ($3.61 \cdot 10^{14}$ m^2).

Area	Band thickness (m)	Nitrite concentration (μg N l^{-1})	Total amount of oceanic nitrite (Tg)
Sargasso Sea	100	5	181
East Tropical Pacific	100–200	5	180–360
East Tropical Pacific (anoxic)	300	30	3 249

The inventory of nitrous oxide in the sea was calculated from the data of Hahn (1974) by extrapolation to the whole ocean down to 3000 m. The resulting estimate was about 200 Tg N as nitrous oxide in the sea. The figure may be low in view of the limited depth used for extrapolation. Indications of lower nitrous oxide concentrations in areas other than the Atlantic are suggested by the nitrate concentration profiles given by Sverdrup *et al.* (1942; see the oceanic denitrification below). The inventory for nitrous oxide given may therefore just reflect the order of magnitude.

Ammonium

The NH_4^+ concentration has a range of 5–50 μg N l^{-1} (Sverdrup *et al.*, 1942). The lower limit was used for offshore areas (deeper than 200 m), while the upper limit was applied for nearshore areas, resulting in 6800 and 137 Tg N respectively.

Thus these data indicate an NH_4^+ inventory of about 7000 Tg. Since the lower limit was set for the main part of the sea volume, the value is regarded as being on the conservative side.

Because of the old data used and the variation in concentration of inorganic nitrogen in the sea, the inventory figures given may simply indicate the respective orders of magnitude.

Biomass and dissolved and particulate detritus

Plant biomass in the sea, of which phytoplankton constitutes the main part, was estimated at $1.8 \cdot 10^3$ Tg C by Whittaker & Likens (1973). Using a C/N ratio of 6 for phytoplankton (Redfield *et al.*, 1963), the nitrogen content in plant biomass in the oceans works out to $3 \cdot 10^2$ Tg N. The value of $1.7 \cdot 10^2$ for nitrogen in sea animals was taken from Delwiche (1970).

The concentrations for dissolved organic matter in seawaters (Table 4) given by Riley (1973) and the mean C/N ratio of 2.7 for dissolved organic matter in deep waters (below 200 m) given by Duursma (1961) result in $5.2 \cdot 10^5$ Tg N. According to Duursma (1961), the C/N ratio for surface waters is generally higher than for deep waters. Hence the figure used by Emery *et al.* (1955) (C/N = 10) was applied for the upper layers. These waters will thereby contribute $0.1 \cdot 10^5$ Tg N.

Table 4. Concentrations of dissolved and particulate organic matter in the sea as given by Riley (1973).

	Particulate ($\mu g\ C\ l^{-1}$)	Dissolved ($mg\ C\ l^{-1}$)
Surface layer	25–300	1.36
Deep waters	12– 50	1.11

Using the C/N ratio of 6 for particulate organic matter (Redfield *et al.*, 1963) and the concentration of particulate organic matter in Table 4, a range of $0.3–2.4 \cdot 10^4$ Tg N was obtained for this fraction of dead organic matter in the oceans. This range will obviously only have a marginal influence on the total amount of dead organic nitrogen in the sea. As indicated by Eppley *et al.* (1973), this C/N ratio may be too high for the North Pacific Ocean, where 2.6 was obtained. Hence this inventory may be somewhat underestimated.

The total amount of dead organic matter in the sea was estimated by Gerlach (1971) at $1.5 \cdot 10^6$ Tg C. Using the C/N ratios of 6 and 2.7, this gives an organic nitrogen content in the range of $2.5–5.6 \cdot 10^5$ Tg. The value of $3.4 \cdot 10^5$ Tg estimated by Emery *et al.* (1955), which is often referred to, was based on a single value from the Atlantic Ocean.

The higher value of about $5 \cdot 10^5$ Tg N given above seems likely, since the mean C/N ratio given by Duursma (1961) was at the lower limit of the range (2.5–6.5) for deep waters, which constitute the main part of the oceans. Despite the possible underestimation of particulate organic nitrogen in the sea this fraction of dead organic matter will only contribute marginally to the total inventory.

Atmospheric nitrogen

A large number of papers and reports deal with the ambient concentration of nitrogenous gases and particulate matter in the atmosphere. The great paucity of data from the southern hemisphere nevertheless makes the estimates of the total content rather uncertain, especially for substances of terrestrial origin and with a short transfer time in the atmosphere. The estimates of inventories from literature values in the present work are much smaller for NO_x and ammonia than the generally accepted ones given by Robinson & Robbins (1970a,b; 1975).

Ammonia/Ammonium compounds

Lodge *et al.* (1974) reported a mean value of 9.4 μg N m^{-3} of ambient ammonia and ammonium compounds for tropical areas, without stating the ratio of particulate to gaseous ammonia. For temperate regions. Georgii & Müller (1974) investigated the vertical and seasonal variation of ammonia and ammonium. They observed a sharp decrease in concentration with height hence ground-based measurements were taken as representative of the lower part of the troposphere in this paper. Different mixing heights for different regions were used owing to geographical difference in intensity of the vertical exchange rates (Table 5).

Table 5. The values used and results of the calculations of the atmospheric global ammonia/ammonium inventories. CMH in the table heading = characteristic mixing height.

	Area (10^{12} m^2)	CMH (km)	NH_3 (ppb(v))	NH_4^+-N (μg m^{-3})	NH_3-N (Tg)	NH_4^+-N (Tg)	ΣN (Tg)
Ocean areas	361	1	0.4	0.4	0.07	0.12	0.19
Tropical land areas	56	2	(6–)12	2	0.66	0.17	0.83
Other land areas	94	1.5	(1–)2	3	0.08	0.33	0.41
Upper troposphere	511		0.1	0.7	0.12	1.16	1.28
Total					0.9	1.8	2.7

Widely occurring acid aerosols would react rapidly with the ammonia, and the latter would more likely be found in particles rather than in the gaseous phase. Observations of such acid aerosols in temperate and other climatic zones were reported by Brosset *et al.* (1975) and Mészáros & Vissy (1974). The range of observations for ground-based measurements of ammonia and ammonium in the temperate zone was 0.4–10 ppb(v) (Healy *et al.*, 1972; Breeding *et al.*, 1973; Georgii & Müller, 1974; J.R. Freney, pers. comm.). Mean values of 2 ppb (v) and 3 μg m^{-3} for surface air in all terrestrial areas except the tropics were adopted for ammonia and ammonium nitrogen respectively.

In accordance with the findings of Tsunogai (1971), the lower values of 0.4 ppb(v) and 0.4 $\mu g\ m^{-3}$ were respectively used for ammonia and ammonium nitrogen for surface air over the aquatic system, resulting in 0.19 Tg N. This author measured both ammonia and particulate ammonium, and a large particulate fraction (up to 80 %) of total ammonium was indicated in the surface oceanic environment. These findings are supported by the qualitative identification of the acidic ammonium hydrogen sulphate (NH_4HSO_4) and sulphuric acid in remote oceanic locations by Mészáros & Vissy (1974). The equilibrium pressure for ammonia over ammonium hydrogen sulphate is less than 0.1 ppb(v) and over sulphuric acid the equilibrium pressure is even smaller.

Using spectroscopic techniques in high-altitude measurements in southern Europe, Kaplan (1973) could not find any significant amounts of ammonia in the gaseous phase when integrating over the upper troposphere and the stratosphere. He stated that the ambient concentration of ammonia at the level investigated (3000 m) was less than 0.09 ppb(v). Estimates of 0.1 ppb(v) and 0.7 $\mu g\ m^{-3}$ for ammonia and ammonium nitrogen were respectively used for the upper troposphere, amounting to 1.28 Tg N overall (Table 5).

NO and NO_2

Background measurements of NO and NO_2 in ambient non-locally polluted air at different geographical locations have been performed by, among others, Junge (1956), Fisher *et al.* (1968), Ripperton *et al.* (1968), Breeding *et al.* (1973) and Moore (1974). The reported values indicated a latitudinal variation and the inventory was calculated by assuming different mean concentrations of NO_2 for different climatic zones. Recent spectroscopic measurements of NO_2 by Noxon (1975) indicated lower values; a range of 0.1–0.2 ppb(v) for NO_2 was found in most cases in a remote area of the Rocky Mountains in the USA. This range was adopted for NO and NO_2 in the upper troposphere in Table 6.

Table 6. **Atmospheric inventory of NO, NO_2 and NO_3^-.**

Zone	Area ($10^{12}\ m^2$)	NO, NO_2 (ppb(v))	Part NO_3^--N ($\mu g\ m^{-3}$)	ΣN (Tg)
Polar	8	0.5	0.1	0.01
Temperate	85	4	0.1–0.4	0.4–0.5
Tropical	55	0.8	0.1–0.4	0.07–0.1
Ocean	361	0.3	0.02	0.15
Upper troposphere	510	0.1–0.2	0.1–0.2	0.5–1.1
Total				1.1–1.9

For oceanic areas, the value of 0.3 ppb(v) for NO + NO_2 reported by Kühme (1968) was used. No other data were found in the literature. The total NO and NO_2 inventory thus ended up in a range of 1.2–1.8 Tg N.

HNO_3 and N_2O_5

Photochemical models predict that atmospheric NO_x exists mostly in the form of HNO_3 and N_2O_5 (McConnell & McElroy, 1973; Crutzen, 1974b). One of the reasons for this statement is the reaction:

$$3NO_2(g) + H_2O(g) \rightleftharpoons 2HNO_3(g) + NO(g).$$

Robbins *et al.* (1959) found an equilibrium constant of 0.004 atm^{-1} for this reaction. In view of the large excess of water present in the atmosphere, NO_x should mainly be present in the form of HNO_3 if the reaction is not too slow, thus enabling equilibrium to be reached.

Other important reactions influencing the composition of NO_x involve OH radicals and ozone:

$$\begin{aligned} OH &+ NO_2 \rightarrow HNO_3 \\ NO_2 &+ O_3 \rightarrow NO_3 + O_2 \\ NO_3 &+ NO_2 \rightleftharpoons N_2O_5 \end{aligned}$$

For further details of this complex pattern of photochemical reactions see, for example, Levy (1974) and Cox (1974).

Crutzen (1974b) estimated the ratio of HNO_3 to total NO_x to be 0.75 in the troposphere. By using this ratio and the value given in Table 6, a total inventory of 8 Tg of NO_x-N was calculated. A more conservative value in the range of 1–4 Tg of NO_x-N was estimated in this work, since the amount of HNO_3 in the upper troposphere was probably included in the measurements for particulate nitrates (Table 2).

Particulate nitrate

Particulate nitrate concentrations from Scandinavian areas, as found by monthly sampling (IMI, 1976), were in the range of 0.01–0.4 μg NO_3-N m^{-3}. Measurements in the lower part of the troposphere for different parts of the USSR, reported by Selezneva *et al.* (1967), were within the same range. A mean value of 0.2 μg NO_3-N was reported by Reiter *et al.* (1974) from measurements at a mountain station in southern Germany over a four-year period. Junge (1963) gave a mean value of 0.02 μg NO_3-N m^{-3} from measurements at Hawaii and 0.09 μg NO_3-N m^{-3} for a location in Florida. Prahm *et al.* (1975) found a background level of nitrates as low as 1 ng NO_3-N m^{-3} for samples collected at the Faroe Islands under extremely clean air conditions. Collection of particles in the upper part of the troposphere, followed by wet chemical analysis for nitrogen compounds, was performed by Gillette & Blifford (1971). The concentration of nitrate was found to be in the range of 0.1–0.2 μg NO_3-N m^{-3}. When doing the calculation, ground-based measurements were taken as representative of the lower 20 % of the troposphere. The amounts of NO_x calculated from available measurements are given in Table 6.

The calculation of the organic nitrogen in the atmosphere is given below in the section dealing with turnover times in the atmosphere.

THE NITROGEN FIXATION – DENITRIFICATION CYCLE

The compounds considered in this part of the nitrogen cycle are gaseous molecular nitrogen and nitrous oxide (N_2O). Two biological conversions involve molecular nitrogen: fixation of nitrogen gas by bacteria and blue-green algae into organic compounds, and the reduction of some oxidized forms of nitrogen (NO_3^-, NO_2^-, N_2O) by denitrifying bacteria to nitrogen gas. Nitrous oxide is produced under certain circumstances by biological reduction of nitrates and nitrites. Molecular nitrogen is also converted to ammonia by industrial fixation and to oxides by combustion. The flows are summarized in Fig. 2.

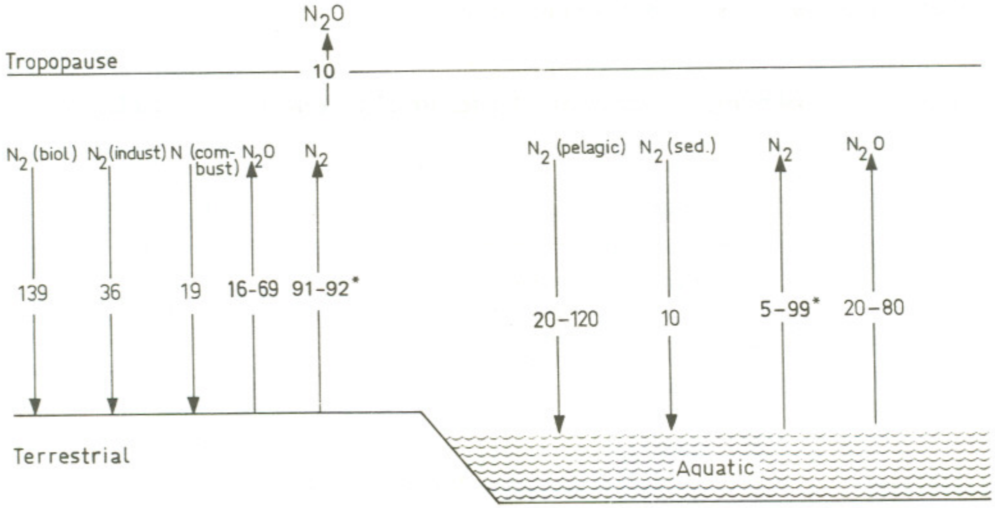

Figure 2. Global flows of N_2 and N_2O (Tg N yr^{-1}). The values for flows of N_2 to the atmosphere (*) are balanced (see text).

Nitrogen fixation

Fixation of molecular nitrogen, biologically or abiologically, into other compounds constitutes the primary input of nitrogen to the biosphere, which affects the entire biogeochemical cycle of nitrogen. The fixation process requires energy; biological systems utilize chemically bound energy in organic matter (symbiotic and asymbiotic non-photosynthesizing bacteria) or light energy (blue-green algae and photosynthetic bacteria; Stewart, 1973a,b; Fogg, 1974). For abiological fixation, energy is derived from fossil fuels and man-made sources for attaining the high pressures and temperatures needed. In all other biological conversions between nitrogenous compounds, except nitrate assimilation, energy is released and is available for the cells involved (Delwiche, 1970).

In this compilation, nitrogen fixation will be considered in different terrestrial ecosystems, aquatic ecosystems (including freshwater) and their sediments, industrial fixation and fixation by combustion.

Terrestrial fixation

A compilation of biological nitrogen fixation on a global scale was recently made by Burns & Hardy (1975). They mainly considered nitrogen fixation in terrestrial habitats, using literature data to obtain averages for the main types of ecosystem (Table 7). Their value of 139 Tg N yr^{-1} is higher than those previously presented (see, for instance, Hutchinson, 1954; Delwiche, 1970). As pointed out by Burns & Hardy (1975), this increase seems to be due to the more extensive literature survey made and also to the wider information available today as a result of the use of the acetylene reduction technique (Stewart *et al.*, 1967; Hardy *et al.*, 1968; 1973). The data may be subject to revision if conversion factors used in the C_2H_2 reduction assay (3:1 for $C_2H_2:N_2$ reduction) differ markedly in different systems. However, there is increasing evidence that in most *in vivo* systems this ratio is valid.

Table 7. Global nitrogen fixation rates for terrestrial systems (Burns & Hardy, 1975).

System		Rate ($Tg\ yr^{-1}$)
Agriculture:	legumes	35
	rice	4
	other crops	5
	grasslands	45
Forest		40
Others		10
Total		139

There is no reason to believe that any change in the biological fixation of nitrogen gas has occurred during the past 25 years (Hardy & Havelka, 1975). The value given by Burns & Hardy (1975) can thus be regarded as valid for 1970, the year to which all estimates were related in the present compilation.

Aquatic fixation

The data for pelagic fixation of nitrogen are very scanty. Goering *et al.* (1966) reported a fixation rate of 320 ng N l^{-1} h^{-1} for a bloom of *Trichodesmium* in the tropical Atlantic Ocean. They also reported fixation rates by the same algae under non-blooming conditions, from the surface down to a depth of 30 m, averaging 1 ng N l^{-1} in autumn and 5 ng N l^{-1} hr^{-1} in spring, both values with a standard deviation of more than 100 %. These average values were calculated from the tables of Goering *et al.* (1966). Accepting these values as generally valid down to the depths measured, and taking an active light period of 12 hr d^{-1}, gives 0.13 g m^{-2} yr^{-1} and 0.66 g m^{-2} yr^{-1} nitrogen fixed for autumn and spring respectively. Gundersen (1974) determined an annual average fixation rate of 0.69 g N m^{-2} in the North Central Pacific near Hawaii. The samples contained a mixed flora of algae, mainly *Trichodesmium* and diatoms containing endosymbiotic *Richelia*.

There are difficulties in scaling these data over all oceanic areas since the blooms of *Trichodesmium* are only of localized occurrence and, as noted by Carpenter & Price (1976), the rates may vary depending on the environmental conditions with *Trichodesmium* being much less active in turbulent waters. But by extrapolating the rates given above, a possible range for tropical oceanic waters (about one third of the world's ocean) of 15–80 Tg N yr^{-1} was obtained. Since no observations seem to be available for pelagic nitrogen fixation in temperate and cold waters, a conservative estimate was made on the assumption that the rate is about one-fourth of that in the tropical waters. As the area is twice as large, another 40 Tg yr^{-1} may be fixed in temperate and cold waters. The total rate range was estimated to be 20–120 Tg N yr^{-1} and believed to reflect the potential for pelagic nitrogen fixation.

Nitrogen fixation in the ocean also occurs in sediments, coral reefs and organisms attached to rocks and vegetation (Table 8). The data base for sedimental fixation is very small, so far dealing only with nearshore areas. In order to obtain a possible order of magnitude for this type of fixation, the rates given in Table 8 were scaled with the areas of reefs and algal beds ($0.6 \cdot 10^{12}$ m^2), estuaries ($1.4 \cdot 10^{12}$ m^2) and the continental shelf ($26.6 \cdot 10^{12}$ m^2), given by Whittaker & Likens (1973). Half of the estuarine areas were assumed to have sediments as active as the intertidal zone (Table 8). The continental shelf and the rest of the estuaries were assumed to be comparable with the shallow water sediment (Table 8). The very approximate sedimental nitrogen-fixation rate obtained in this way was about 60 Tg N yr^{-1}. Since this value was estimated for about 8 % of the total oceanic areas, the total value for oceanic sediments may be higher. By taking the shallow water sediment value (Table 8) as valid for the three regions given above, a rate of about 10 Tg yr^{-1} was obtained. This value was believed to be a lower limit for sedimental fixation. Blake & Brown (unpubl.) were not able to detect sedimental nitrogen fixation in Atlantic oceanic sediments (W.D.P. Stewart, pers. comm.) which supports the omission in this work of nitrogen fixation in deep sediments.

Biological fixation rates in some freshwater systems are compiled in Table 9. Since freshwaters are mainly oligotrophic, the contribution from freshwater systems seems to be minor in comparison with oceanic areas.

Table 8. **Rates of non-pelagic nitrogen fixation in ocean habitats given in the literature ($g\ N\ m^{-2}\ yr^{-1}$).**

Shallow water sediment near Florida (Brooks *et al.*, 1971)	0.4
Sediment of intertidal zone, Scotland (Herbert, 1975)	35*
Coral reef (Mague & Holm-Hansen, 1975)	40
Rocky shores with *Calothrix* (Stewart, 1970)	2.5
Bacteria in association with marine angiosperms (Patriquin & Knowles, 1972)	10–50

* Recalculated from the given rate of 0.7 kg N $(ton\ sed.)^{-1}\ yr^{-1}$, assuming 50 % water content of the sediment and a density of 2 kg dm^{-3} and using the depth down to which cores were sampled as the active layer of the bottom.

Table 9. **Fixation rates in lakes and lake sediments obtained by scaling over the total lake and stream area of $2 \cdot 10^{12}\ m^2$ given by Bazilevich (1974).**

System		Rate ($Tg\ yr^{-1}$)
Water:	Eutrophic (Stewart *et al.*, 1971; Granhall & Lundgren, 1971)	0.5–6.0
	Oligotrophic (Horne & Fogg, 1970)	0.1–0.6
Sediments:	Eutrophic (MacGregor *et al.*, 1973)	0.2–0.4
	Oligotrophic (MacGregor & Keeney, 1973)	0.02–0.4*

* This range was converted from 1–4 g N $(ton\ sed.)^{-1}\ yr^{-1}$ by assuming 50 % water content, a density of 2 kg dm^{-3} and an active layer of 0.02 m.

Fixation in industry and by combustion

According to UN statistics (UN, 1975), 33 Tg nitrogen was fixed by the world production of nitrogenous fertilizers in 1970. According to the same source, there was an annual increase of 7–9 % in the rate of growth, indicating 48 Tg in 1975. The industrial fixation of nitrogen for other purposes (plastics, nylon etc.) in highly industrialized areas (Europe, USA, and Japan) amounts to 15–30 % of the total nitrogen fixed for 1970 (OECD, 1973). This fraction is, no doubt, lower on a global scale –probably about 10 %. Accepting this crude estimate gives an overall industrial fixation of 36 Tg N for 1970 and 53 Tg for 1975. According to D.R. Keeney (pers. comm.) the UN statistics on fertilizer production are low. The worldwide NH_3-N production in 1973/74 was stated by the US Fertilizer Institute to be 62 Tg, hence the values used above may be low.

The nitrogen fixed as oxides of nitrogen by the combustion of fossil fuels was estimated at 19 Tg for 1970 (see the NO_x cycle below).

The total abiological nitrogen fixation therefore ends up at 55 Tg yr^{-1} in 1970. With an annual increase of 4 % for combustion and the previously mentioned figure for industrial fixation, a value of 76 Tg yr^{-1} seems plausible for 1975.

The chemical fixations in the atmosphere by ozonization and lightning presented in other compilations (see Burns & Hardy, 1975; Hardy & Havelka, 1975) are not significant (see the NO_x cycle below).

In Table 10, which summarizes the nitrogen fixation rates in different systems, the industrially fixed nitrogen is the most accurate value. The global nitrogen fixation rate for the natural terrestrial system (Burns & Hardy, 1975) is believed to be a reasonable estimate, while that for the aquatic system is uncertain. The 1970 figure for nitrogen fixation in the terrestrial system amounts to 194 Tg yr^{-1}, while the rate for 1975 will be at least 215 Tg yr^{-1}. Adding the range of 30–130 Tg yr^{-1}, estimated for pelagic and sedimental fixation in the oceans gives a global nitrogen fixation of 224–324 Tg N yr^{-1}.

Table 10. Summary of global nitrogen fixation.

Process	Rate (Tg N yr^{-1})
Biological:	
Terrestrial	139
Aquatic, pelagic	20–120
sedimental	10
Abiological:	
Industrial	36
Combustion	19
Total	224–324

Denitrification

The main conversion known by which molecular nitrogen is released as an end product is denitrification, which is carried out by several genera of facultative anaerobic bacteria. These bacteria are able to switch from oxygen to nitrate as electron acceptor for their respiration, reducing nitrate to molecular nitrogen, when oxygen starts to be limiting in their environment. Such denitrifying bacteria are widespread in nature. Payne (1973a) reviewed the physiology and biochemistry of these organisms in an extensive article, to which the reader is referred for further information.

Various oxides of nitrogen occur as intermediates in the biological reduction of nitrate and nitrite to molecular nitrogen (Nömmik, 1956; Payne, 1973a). Depending on local environmental conditions, gaseous oxides of nitrogen may be released. There is no doubt that the release of nitrogen is often accompanied by evolution of nitrous oxide (N_2O) and that, under certain conditions, the latter is the sole end product of denitrification (Nömmik, 1956; Stefanson, 1972a,b,c; Focht, 1974).

The evolution of nitric oxide (NO) is generally considered a plausible process in denitrification in acidic anaerobic systems. According to Nömmik (1956), Broadbent & Clark (1965) and Hauck (1968), this formation is considered to be the result of chemical nitrite reduction and negligible in most soils; nitric oxide production is low except when acid soils are exposed to large amounts of nitrite under anaerobic conditions (Nömmik, 1956). Such conditions are not likely to occur in natural systems, since nitrite rarely accumulates in great concentrations because of its intermediate position in the microbiological oxidation of ammonia to nitrate (nitrification) and in dentrification. According to Allison (1965), the formation and release of nitric oxide seems more likely in connection with ammonium fertilization and restricted nitrification.

Environmental factors not only influence the rate of nitrate reduction but also the proportions of the end products, mainly molecular nitrogen and nitrous oxide (Fig. 3; Stefanson, 1972a,b,c; Focht, 1974). Molecular nitrogen is the main product under true anaerobic conditions, while nitrous oxide predominates in slightly aerobic environments. The lower the pH, the greater is the proportion of nitrate reduction resulting in nitrous oxide, but at the same time the total rate decreases. High initial concentrations of nitrate give rise to more nitrous oxide than molecular nitrogen, while a good supply of energy in the form of easily metabolizable carbon compounds favours complete reduction to nitrogen gas.

Nitrous oxide is important in the regulation of the amount of ozone present in the stratosphere. Increasing attention has therefore been paid in recent years to the factors regulating the ratio of N_2O to molecular N_2 in denitrification. An increase of 1 % in the emission rate of nitrous oxide will cause a 0.2 % decrease in stratospheric ozone, influencing the penetration of ultraviolet light (Crutzen, 1974a).

Investigations concerning denitrification are dominated by studies on soil systems, especially those affected by agricultural activities. Information on denitrification rates in other terrestrial systems and in the oceans is scanty. Studies of agricultural soil systems, together with investigations of nitrate leaching, have mostly been performed with the aim of reducing nitrogen losses and thus optimizing the utilization of applied fertilizer by crops.

Soil denitrification

Nitrate is provided by microorganisms through autotrophic and heterotrophic nitrification, by precipitation and dry deposition, and by fertilization. The availability of nitrate for the denitrifying bacteria is influenced by plant uptake, leaching, and assimilatory reduction by bacteria, fungi and blue-green algae. The requisite anaerobic conditions are obtained when soil water content is increased, limiting the diffusion of oxygen within the soil pore space. Such a situation prevails when water is supplied by precipitation or irrigation. Growing plants also reduce the oxygen tension in soils because of the oxygen demand for root growth.

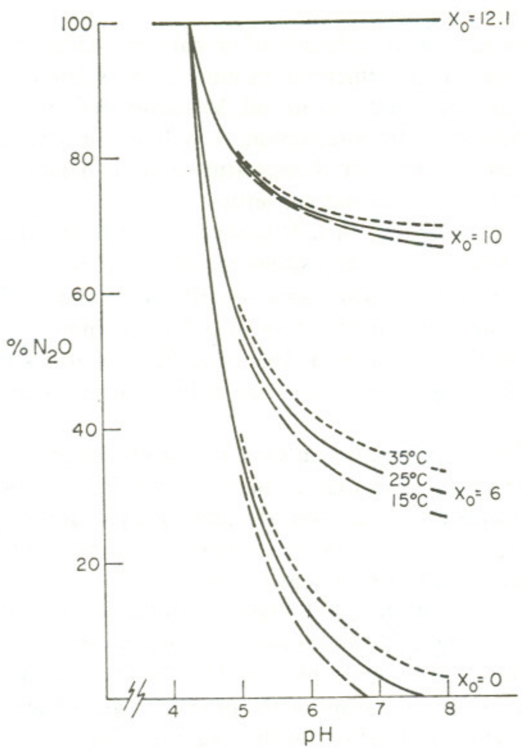

Figure 3. The proportion of N_2O of the total gaseous losses (N_2 + N_2O) as a function of pH, aerated pore space (X_0; %) and temperature. Adopted from Focht (1974); reprinted by permission.

The chemical energy necessary to provide electrons for the reduction of nitrate is taken from easily metabolized organic substances, which may be supplied as root exudates. An active rhizosphere flora of microoganisms with a high oxygen demand may also create anaerobic niches favouring denitrification.

Soil pH-values cover a wide range from down to 3 in bog and forest soils and up to about 10 in saline solonetz soils (Gerasimov & Glazovskaya, 1965). Both the nitrification and denitrification reactions are depressed at low pH-values compared with neutral or slightly alkaline ones. Soil temperature is also an important factor for denitrification rates. According to Nömmik (1956), the overall reaction rate of this process doubles with an increase in temperatures of 10°C (Q_{10} = 2) at 15°C and higher, while Q_{10} seems to be higher than 2 at lower temperatures. This is a common pattern observed for microbiological processes at low temperatures (Flanagan & Veum, 1974; Svensson *et al.*, 1975).

The denitrification kinetics have so far been regarded as a zero-order reaction (Focht, 1974). Bowman & Focht (1974) showed that Michaelis-Menten kinetics are applicable to denitrification and Focht (1974) claimed that the supplies of nitrate in many laboratory experiments were so high that maximal rates prevailed, thereby obscuring any relation to nitrate concentrations.

In order to make an appropriate estimate of global denitrification, estimates of nitrate concentrations and their annual fluctuations must be considered together with some kind of measure for anaerobic condtions in soil. Moreover, energy sources for the bacteria capable of dissimilatory nitrate reduction, as well as soil temperature and pH conditions, have to be taken into account. Temperature and pH data for soils are available in the literature on climatology and soil properties.

A high content of organic matter in soils is often found to stimulate denitrification (Stefanson, 1972a,b,c; Focht, 1974) and seems to be a measure of available energy. Data on the soil content of organic matter were compiled by Bohn (1975) from FAO-Unesco soil maps and other recent literature in order to obtain an estimate of the carbon content in world soils (see above). The anaerobic conditions for all soils and the nitrate availability in nonagricultural soils can only be qualitatively estimated at present.

Reliable rates for the fluxes of nitrogen gas and nitrous oxide to the atmosphere may be obtained in the future by (a) taking into account the influence of nitrate concentrations and energy sources on the rates, (b) making a global investigation of the moisture regime of different types of soil in response to rainfall, and (c) further developing the type of model proposed by Focht (1974).

Albrecht *et al.* (1970) and Burford & Stefanson (1973) estimated fluxes of nitrous oxide to the atmosphere using diffusion rates for the gas together with concentrations in soil profiles. The rate given by Albrecht *et al.* (1970) was an average value for one orchard soil, one garden soil and one soil with spruce and grass hummock amounting to 0.5 mg N m^{-2} d^{-1}. The investigation by Burford & Stefanson (1973) was made in an old cropped area, a recently cropped area and a pasture, all on red-brown earths. These areas were supplied with 112 kg $NaNO_3$-N ha^{-1} prior to the investigation and the losses were 26, 28 and 1 mg N m^{-2} d^{-1} respectively.

Since the data of Albrecht *et al.* (1970) indicated uniform seasonal activity, the whole year was used for extrapolation of global nitrous oxide fluxes to the atmosphere except for polar and boreal regions, and for agricultural areas under crop for which 90, 270 and 270 days were respectively chosen as the active season (Table 11). The choice of 365 days for the remaining parts of world soils is supported by the occurrence of nitrous oxide during the whole year in soils investigated by Dowdell & Smith (1974). The activity was limited to one-half of the year in the investigation by Burford & Stefanson (1973), for which reason their time limits were used, except for polar regions (90 days; Table 11). Their pasture value was used for estimating all fluxes except that for agricultural soil under crop, which was taken as the mean for the old cropped area and the recently cropped area.

The use of the higher value for agricultural areas is well founded, since many fields are heavily fertilized, and soil manipulations like ploughing etc. raise the nitrate content (Dowdell & Cannell, 1975). Barsdate & Alexander (1975) gave a total rate of 0.027 mg N m^{-2} d^{-1} for denitrification *in situ* for tundra areas (Barrow, Alaska). Extrapolating this figure to the whole polar region gives a rate of 0.02 Tg yr^{-1} – which is negligible. Hence it is likely that the rates for nitrous oxide production in this area may be overestimated.

Table 11. **N_2O flux from soils to the atmosphere in Tg N yr^{-1}. The areas are taken from Burns & Hardy (1975) and Bazilevich (1974). Rates in column 1 are based on data from Albrecht *et al.* (1970) and those in column 2 on Burford & Stefanson (1973). Figures in brackets are the length of season chosen (in days, see text).**

Zones	Area ($m^2 \cdot 10^{12}$)	1	2
Polar	8	0.4 (90)	0.7 (90)
Boreal	23	3.1 (270)	3.4 (150)
Agricultural (under crop)	14	2.0 (270)	56.7 (150)
Remaining (except arid regions, lakes, streams and ice-covered areas)	57	10.4 (365)	8.6 (150)
Total	102	15.9	69.4

In a recent report (CAST, 1976) another way of estimating the production of nitrous oxide from soils gave about 7 Tg N yr^{-1}. Here a certain rate obtained in California was regarded as valid for all cropland soils and 20 % of this rate was believed in for all other soils. To obtain a total denitrification rate a factor 16 for the N_2:N_2O ratio was applied. This means that about 6 % of the total nitrogen loss due to denitrification should be nitrous oxide.

It should be strongly emphasized that the data base used in the present paper is very small and that several assumptions had to be made in calculating the rates given. Moreover, as both investigations were made on soils where gas diffusion was obviously not inhibited, oxygen must certainly have been available in the soils, affecting the denitrification rates and the end products. Therefore the range of 16–69 Tg N yr^{-1} for nitrous oxide, based on the papers cited, most necessarily be regarded with caution.

Oceanic denitrification

In an early paper, Brandt (1899) advanced the hypothesis that denitrifying bacteria destroy nitrate in tropical seas and "hence prevent maximum phytoplankton growth". Silén (1965) stated that "at the present pH and E_h of sea water practically all N should be present as nitrate ions in sea water rather than as N_2 in the atmosphere" and postulated that "possibly some organism living in the upper layer of the ocean can destroy nitrate ions by reduction, even in the presence of oxygen".

It is evident from deviations from the normal NO_3^-/PO_4^{3-} ratio at certain depths and localities of the world's oceans (Thomas, 1966) and from O_2/NO_3^- relationships (Fiadeiro & Strickland, 1968; Gundersen & Mountain, 1973) that some of the nitrate previously formed by nitrificiation has been selectively removed from the water column. The areas of most dramatic nitrate deficiency are the oxygen-minimum zones under the highly productive surface waters of Central and South America (Brandhorst, 1959; Wooster *et al.*, 1965) and the Arabian Sea (Ivanenkov & Rozanov, 1961). These zones of low oxygen concentration (0.2 ml l^{-1} or less) are always accompanied by pronounced nitrite maxima. In addition to these large nitrate deficiencies, smaller nitrate deficiencies close to the ocean surface (150–300 m) are common in the tropical and subtropical ocean. These are associated with a nitrite band in the presence of considerable amounts of dissolved oxygen (Gundersen, 1974). Such anomalies have been considered to be due to bacterial denitrification in areas with a low oxygen content. The area most extensively investigated is the North East Tropical Pacific, for which total denitrification rates of 10 and 30 Tg yr^{-1} were calculated by Richards (1971) and Codispoti (1973) respectively.

For the same area, rates in the range 8.4–112 $\mu g\ N\ l^{-1}\ yr^{-1}$, estimated by Cline & Kaplan (1975), gave a range of 10–160 Tg N yr^{-1}. These estimates were from the upper and most active part of the profile and are probably not valid for the deeper parts, hence the mean value of 20 Tg N yr^{-1} obtained from the rates given by Richards (1971) and Codispoti (1973) was used for this area.

Estimates are lacking for the other known oxygen-minimum zones of the world's oceans, but the rates are probably similar to that given above for the North East Tropical Pacific. Hence that rate was used as a crude estimate in place of the missing ones (Table 12). Evidence also exists for denitrification in – mostly narrow zones and therefore in quantitatively less significant amounts – in some anoxic basins, fjords, bays and estuaries (Stewart, 1975).

Table 12. Total denitrification in the world oceans calculated from Gundersen's unpublished data for oxic waters and with the NE Tropical Pacific rate taken as an average for anoxic waters (Richards, 1971; Codispoti, 1973).

Oceanic region	Denitrification rate (Tg N yr^{-1})
NE Tropical Pacific	20
E Tropical Pacific	10
Arabian Sea	5
Other oxygen-minimum zones (W. Africa, Australia, Indian Ocean, Europe)	30
Anoxic basins, fjords, estuaries	5
Oxic tropical seas	7
Temperate and cold seas	14
Total	91

Bacteria capable of reducing nitrate to nitrite and gases have been found in large numbers in faecal pellets from copepods in the upper nitrate-deficient water column in the tropical ocean (K. Gundersen, unpubl.). These pellets might well represent miniature anoxic environments where conditions for denitrification are favourable. This may explain the occurrence of denitrification in waters of high oxygen content, and thereby the observed nitrate deficiencies. In order to explain nitrogen losses from the sea which were necessary to balance the nitrogen cycle for the oceans, Eriksson (1959b) claimed that denitrification occurs in oxygenated waters.

According to measurements made by Hahn (1974), an average supersaturation of nitrous oxide of about 180 % exists in the North Atlantic Ocean (38.5–48.5°N). By assuming this supersaturation as valid for the whole ocean, and a transport resistance in the laminar boundary layer in the sea as the factor which determines the flux to the atmosphere, an annual flow of 20–80 Tg N was extrapolated by Hahn (1975). He considered that the range covered uncertainties in the value for the thickness of the laminary boundary layer and in the assumption concerning nitrous oxide supersaturation in oceans other than the Atlantic, where actual measurements are available. The most pronounced saturation of nitrous oxide in the profiles was observed at depths below 200 m (Hahn, 1974), which are not influenced by any considerable seasonal changes. The measurements obtained for the North Atlantic in April and June may therefore be regarded as valid for the whole season. Cline & Richards (1972) could not detect any nitrous oxide in anoxic regions of the East Tropical Pacific Ocean. However, the limit of detection by their method was 22 $\mu g\ l^{-1}$ of nitrous oxide, while the concentrations obtained by Hahn (1974) were frequently about 0.4 $\mu g\ l^{-1}$. The possibility of the occurrence of nitrous oxide in these anoxic seawaters cannot be ruled out.

It is reasonable to believe that the occurrence of nitrous oxide in seawater is due to bacterial origin. Nitrous oxide maxima coincide with oxygen minima in the profiles measured (Hahn, 1974), implying nitrate reduction.

Craig & Gordon (1963) obtained a contradictory result for the South Pacific, indicating an undersaturation of nitrous oxide in these waters. They discussed both surface and deep waters but mentioned no sampling depths apart from 10 m. These data, although obtained by an analytical technique with lower reproducibility than the measurements by Hahn (1974), showed an average of 15 % higher ambient concentration of nitrous oxide in air than that reported by the latter author. Since the source strength calculated by Hahn (1974) is dependent on the ambient air concentration, the oceanic source of N_2O might have been overestimated, and the net flux may even turn out to be in the opposite direction when integrating over the entire ocean surface. According to Sverdrup *et al.* (1942), the vertical distribution of nitrate concentration in the Atlantic Ocean down to about 4000 m shows a deficit in comparison with the nitrate profiles in the Indian and Pacific Oceans. This may be an indication of a possibly higher denitrification rate in the Atlantic Ocean. The extrapolation of measurements in the Atlantic Ocean to other oceanic areas might be doubtful due to this observed deficit.

In view of the discussions above, the lower value of the range given for the nitrous oxide flux by Hahn (1975) were considered more likely. It should also be emphasized that the total denitrification rate estimated in Table 12 did not take the different end products into account. Since oxygen is present even in anoxic areas, the production of nitrous oxide may be favoured. This situation is suppressed by the alkaline pH of seawater.

Denitrification data for sea sediments seem to be even more scanty than for pelagic parts. Richards & Broenkow (1971) discussed sedimental denitrification for the Galápagos archipelago and roughly estimated a rate of 1.8 g N $m^{-2}\ yr^{-1}$. This indicates the possibility of considerable losses of nitrogen gas and/or nitrous oxide from sediments. Experiments by Goering & Pamatmat (1971) on sediments off the coast of Peru showed occurrence of denitrification, especially at the water-sediment interface. Their values were influenced by the investigation technique, and their rates may therefore be too high.

From the discussions above it is obvious that there is a lack of substantial data for denitrification in the oceans. The total nitrogen flux due to oceanic denitrification obtained as the residual when balancing the aquatic system (25–179 Tg N yr^{-1}) covers the value (91 Tg N yr^{-1}) estimated in Table 12. The latter value, although uncertain, together with the evidence for sedimental denitrification, makes it likely that future research in this field will show that marine denitrification is a much more widespread and important phenomenon than currently accepted, and will also reveal the extent played by nitrous oxide in this process.

Cycling of atmospheric N_2O

Sources of N_2O from the terrestrial and aquatic systems were estimated in the previous sections. The sinks for tropospheric N_2O that can be accounted for at present are much smaller than the estimated annual sources. It is not possible to judge whether there is a net accumulation in this part of the atmosphere or not. The rate at which N_2O diffuses into the stratosphere and is converted into oxygen, nitrogen and NO_x was estimated by Junge (1972). These calculations were based on measurements of nitrous oxide profiles in the lower stratosphere, together with assumptions on the eddy diffusivity at these altitudes, and gave a residence time of about 70 years. This value corresponds to a net flux of 18 Tg N yr^{-1} to the stratosphere. Recent model calculations indicate a somewhat lower figure – 10 Tg N_2O-N yr^{-1} – for this flux (P.J. Crutzen, pers. comm.). This value was accepted for the present paper. No photochemical reactions capable of destroying N_2O in the troposphere at any appreciable rate are known at present (P.J. Crutzen, pers. comm.).

In their discussion on alternative substrates for the nitrogenase enzyme system, responsible for nitrogen fixation, Burns & Hardy (1975) stated that the nitrogen fixation activity was competitively inhibited by nitrous oxide – i.e. nitrous oxide displaced molecular nitrogen as a substrate for the nitrogenase. Hardy & Knight (1966) demonstrated that, when supplied to the nitrogenase system, nitrous oxide was reduced to nitrogen gas and water; the nitrous oxide works as an electron acceptor during this reaction. From these findings it is evident that biological conversion of nitrous oxide to nitrogen gas may occur as soon as N_2O and organisms able to fix molecular nitrogen (certain bacteria and blue-green algae) appear in the same habitat. Such situations are common in nature.

Besides, the possibility of another bacterial sink in soils cannot be ruled out. In habitats with true anaerobic conditions and suitable pH (Fig. 3), where nitrate is quickly converted to nitrogen gas, reduction of nitrous oxide to molecular nitrogen may occur through the denitrification pathway (Payne, 1973b; Garcia, 1975a,b).

Nitrogen gas flow to the atmosphere

The flows of nitrogen gas and nitrous oxide are summarized in Fig. 2. In the absence of any direct data, the flows given for gaseous nitrogen from the terrestrial and aquatic parts are obtained by balancing all other flows to and from each of these systems and subtracting the estimated nitrous oxide losses (see above).

AMMONIA FLUXES AND CONVERSIONS

Ammonium is produced during the decomposition of nitrogenous organic matter in aquatic and terrestrial ecosystems. The major part of this ammonium is rapidly recycled and converted into amino acids and proteins within the systems. A large and fast internal circulation of ammonia within a crop was reported by Denmead *et al.* (1976), who observed a large production of ammonia near the ground and almost complete absorption within the plant cover. Only a fraction of the annually circulating amount of ammonia is released and transported through the atmosphere to any distance, returning to the ocean or land areas by precipitation (wet deposition), gaseous uptake by plants or physical absorption (dry deposition). Chemical conversions in the atmosphere also act as a sink for the ammonia transported through this reservoir (Fig. 4). In areas of dense animal population the redistribution of ammonia by the atmosphere can contribute as a major input of nitrogen to the surrounding areas (Wodehouse, 1974).

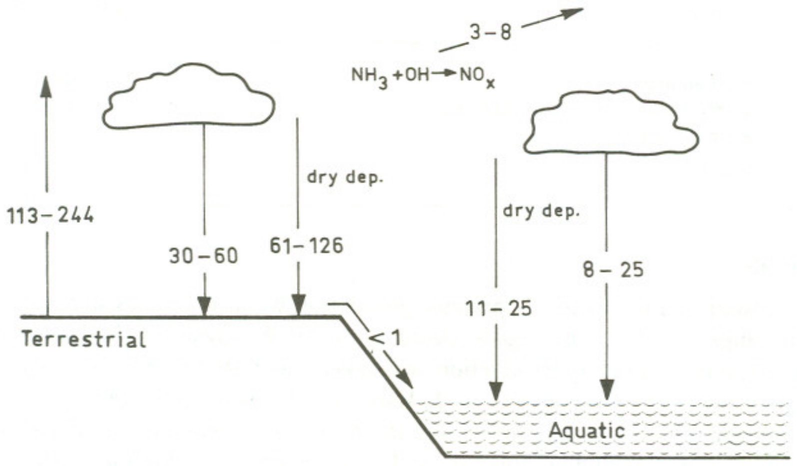

Figure 4. Ammonia/ammonium fluxes in Tg N yr^{-1}. The range for the flow from the terrestrial systems was obtained by balancing the other flows through the atmosphere.

Sources for atmospheric ammonia

Ammonia losses from grazed areas are frequently reported in the literature (Hutchinson & Viets, 1969; Loehr & Hart, 1970; Luebs *et al.*, 1973). Using micrometeorological methods, Denmead *et al.* (1974) found great losses from grass-covered pastures when grazed, but comparatively small losses for similar areas when ungrazed. This indicates the importance of animal urea as an important source of atmospheric ammonia. Similar results were reported from a calculation of a regional balance on ammonia and ammonium for the United Kingdom (Healy *et al.*, 1970).

The flux of ammonia to the atmosphere was calculated for the portion emanating from wild and domestic animals, using certain assumptions on the fraction of ammonia volatilized from excreta.The portion possibly emanating from the decompostion of dead organic matter other than excreta was taken as the difference between total sinks for atmospheric ammonia and the amount estimated from animals, coal combustion and volatilization of fertilizers. Other possibel direct sources are discussed separately below. The sources which could be directly accounted for are given in Table 13.

Table 13. Sources of ammonia/ammonium and their flows into the atmosphere.

Sources	Flow strengths (Tg N yr^{-1})
Wild animals	2– 6
Domestic animals and human beings	20–35
Burning of coal	4–12
Total	26–53

Wild animals

The consumption of world net primary production by wild animals was assumed to be in the range 3–10 %. The higher values, given by Woodwell (1970), is probably too high. World net primary production was taken from Rodin *et al.* (1974) and the world agricultural area given by Burns & Hardy (1975) was subtracted by assuming half of the agricultural area as tropical and the other half as equally distributed over other climatic zones, excluding polar areas. The net primary production calculated for non-agricultural areas amounted to 10^3 Tg dry matter. The ratio of urea to the excretion rate of dry matter for animals was reduced to 85 % of the figure given by Loehr & Hart (1970) of 6 mg of urea nitrogen per gram dry matter consumed, wild animals being assumed not to lose as much nitrogen as domestic animals. The proportion released to the atmosphere from animal urea (10 %) was taken from Healy *et al.* (1970). The range for the flux calculated in this way was 2–6 Tg of ammonia nitrogen annually.

Domestic animals and human beings

The source magnitude from domestic animals and the human population was calculated in the following way. Excretion rates for the different species of domestic animals were taken from Lengdén (1951) and Loehr & Hart (1970). For the human population the excretion rate was taken from Engwall (1972). The numbers of human beings and different animals were taken from UN and FAO statistics (UN, 1975; FAO, 1975). Depending on the method used for breeding domestic animals, whether intensively or extensively, nitrogen losses vary greatly. High ammonia losses to the atmosphere (approximately 50 % of the nitrogen content in manure) appear in intensive animal breeding (Eriksson, 1959a). The world sheep, buffaloes and half the cattle population were regarded as extensively bred. The proportion of total urea releseased as ammonia into the atmosphere from extensively bred animals (10 %) was given by Healy *et al.* (1970).

Half of the annual amount of human excrement (about 10 Tg N) was regarded as either treated in sewage treatment plants or directly transferred into the aquatic system, not giving rise to any considerable losses of ammonia to the atmosphere. The other half was believed to be transferred onto the soil surface. The same proportion of the nitrogen content released to the atmosphere as for the extensively bred livestock was used for this type of excrement (see above). The minor contribution (approx. 1 Tg) from human sweat was calculated from data by Healy *et al.* (1970). Atmospheric ammonia from the excrement of human beings and domestic animals was thereby found to be within a range of 20–35 Tg ammonia-N annually.

Ammonia from coal

Combustion of coal as a source of atmospheric ammonia has been suggested by many authors (Russel & Richards, 1919; Eriksson, 1952; Georgii, 1963). Ammonia gas is a surprisingly stable compound and strongly oxidizing agents or catalysts have to be used for the industrial conversion of ammonia into oxides of nitrogen. The nitrogen content of coal varies between 1–2 %. No coal has been found which does not contain nitrogen. Younger coals usually contain more nitrogen than older ones (Hill, 1945).

Until the development of the Haber-Bosch process, the major industrial source of ammonium was recovery in coke manufacture. By high-temperate carbonization, 15–20 % of the total nitrogen in coal appears in the crude gas a ammonia (Powell, 1945). In the industrial process an average yield of 2.8 kg ammonia per ton coal processed was reported by the same author. The yields increased with higher oxygen content of the coal in the carbonization process. World consumption of hard coal in 1970 was 2100 Tg (UN, 1975), of which 400 Tg was coked, ammonia presumably being recovered in the process.

By using the mean nitrogen content and the range for yields of ammonia previously mentioned, the amount of ammonia released to the atmosphere was calculated to be in the range 2–7 Tg N yr^{-1}. To this figure 2–5 Tg N yr^{-1} has to be added for the burning of 800 Tg of brown and pitch coals, which are not included in the figures for hard coal.

Sinks for atmospheric ammonium compounds

Precipitation and dry deposition, together with the conversion of ammonia into NO_x, constitute the main sinks. The latter flow is considered in the section on NO_x (see below).

Wet deposition

The wet deposition of 8–25 Tg N yr^{-1} of ammonium compounds over the ocean was taken from the estimate by Söderlund (1976). Two extensive compilations of precipitation chemistry data have appeared in the literature (Eriksson, 1952; Steinhardt, 1973). These compilations were used for land areas in the present calculation. The earth was divided into 30° latitudinal zones and the maximum and minimum wet deposition values were scaled with the land area within each zone. No account was taken of the low precipitation in desert areas, which would tend to lower this estimate by approximately 15 %. The range for the flux calculated in this way amounted to 20–80 Tg N yr^{-1}. Another calculation was made using the latitudinal deposition given by Robinson & Robbins (1970a,b), which was taken as representative of land areas and scaled with land areas between the parallels. The amount calculated in this way was 36 Tg, which is within the range calculated by the previous method. A most likely value for the range of the wet deposition over the terrestrial system is estimated at 30–60 Tg N yr^{-1}. Eriksson (1959a) estimated this flux at 44 Tg N yr^{-1} and Robinson & Robbins (1970a,b; 1975) at 150 Tg N yr^{-1}.

Dry deposition

Since there seem to be no data on dry deposition velocities for ammonia, they were assumed to be the same as for sulphur dioxide. The dry deposition of SO_2 has been investigated at a number of sites with different surface characteristics, especially those with smooth surfaces. An average value of $8 \cdot 10^{-3}$ m s^{-1} for the dry deposition velocity of SO_2 is frequently reported (Prahm *et al.*, 1975). This value was used for the dry deposition of ammonia in this compilation. For permanently dry deserts the mechanism of dry deposition for removal of atmospheric ammonia was considered ineffective.

Dry deposition of particulate ammonium compounds was calculated using a lower deposition velocity of $3 \cdot 10^{-4}$ m s^{-1} as suggested by Chamberlain (1975). Dry deposition of particulate matter is not an efficient way of transporting material from the atmosphere to either the terrestrial or the aquatic system, especially when the particles are small. Particulate atmospheric ammonium is mainly found in particles of less than 1 μm diameter (Junge, 1963), which supports the choice of this low deposition velocity.

The same deposition velocity for dry deposition of ammonia and particulate ammonium compounds as used for the terrestrial system was used for the aquatic system. The concept of dry deposition velocity implies the assumption that the surface is a sink for the compounds studied. Lau & Charlson (1975) performed a calculation based on Henry's law, using observed concentrations of ammonium in seawater. The equilibrium pressure of ammonia over the sea areas obtained in this way is within the range for the global average value of ammonia estimated for the oceanic atmosphere. Therefore, the assumption that the sea acts solely as a sink for ammonia is questionable. The ocean most likely acts both as a source and a sink for atmospheric ammonia. The calculated figures should therefore be regarded as a high estimate for this flux. A conservative estimate for the flux was subjectively chosen at half this value and the range thereby given is 10–20 Tg N yr^{-1}. The results from the calculations of dry deposition for the terrestrial and aquatic systems are given in Table 14.

Table 14. Dry deposition of gaseous ammonia and particulate ammonium compounds. The areas were taken from Rodin *et al.* (1974) and the concentration from Table 5.

Zones		Concentrations		Deposition rates	
	Area	NH_3(g)	Particulate	Gaseous	Particulate
	(10^{12} m^2)	(ppb(v))	($\mu g\ m^{-3}$)	(Tg N yr^{-1})	
Land areas (tropical without deserts)	50	6–12	2	45–90	1–3
Other land areas (non-tropical without deserts)	78	1–2	3	12–24	2–7
Deserts (tropical)	6	12	2	0	0.1–0.4
Deserts (non-tropical)	15	1.2	3	0	0.4–1.5
Total terrestrial				57–114	4–12
Ocean areas	361	0.4	0.4	10–20*	1–5
Total				67–134	5–17

* Half the calculated range (see text).

Conclusions and perspectives

Owing to the short turnover time of ammonium and ammonia in the atmosphere, the global sources and sinks must be balanced on an annual basis. The sources calculated in the paragraphs above (26–53 Tg N yr^{-1}) cannot supply the amounts needed to balance the total annual deposition. Other sources must therefore exist and the magnitude of these should be in the range of 87–191 Tg N yr^{-1}.

Measurements of the ambient concentration of ammonia in Australia gave high values when bush fires were frequent (J.R. Freney, pers. comm.), and it is very likely that forest fires and bush fires volatilize large amounts of ammonia. Another possible source is the ocean, where during the cold season rather high concentrations of NH_4^+ (up to 50 mg m^{-3}) were reported by Horne (1969), which would increase the equilibrium pressure of ammonia in the air above the oceans. Therefore a transport of ammonia to the terrestrial system could occur periodically. In addition, there may be losses of ammonia from fertilizers during manufacture, storage, handling and use.

Decomposition of organic matter other than animal excreta is another probable source, the magnitude of which could not be directly estimated. In tropical areas, where the ambient ammonia concentrations in air are obviously higher (Lodge *et al.*, 1974; see Table 14) than in other areas, litter may be the source of atmospheric ammonia. In other climatic zones, this process may contribute to a smaller extent to the ammonia fluxes into the atmosphere because of the slower turnover of litter (Table 15).

As an indiciation of the geographical differences in the possible supply of atmospheric ammonia from decomposition of litter, the turnover times of nitrogen for this pool in the different bioclimatic zones were calculated from data given by Bazilevich

(1974), and shown in Table 15. The authors are aware that there is no linear relation of the turnover times and the amounts released into the atmosphere. The supplies are most likely large in areas with high decomposition rates but in areas with slow turnover these processes are probably insignificant as a source of atmospheric ammonia.

Table 15. Litter nitrogen inventory and turnover in different bioclimatic zones, based on values given by Bazilevich (1974).

Zones	Area ($m^2 \cdot 10^{12}$)	Litter nitrogen inventory ($g\ N\ m^{-2}$)	Estimated litter nitrogen turnover time (yr)
Polar	8.1	106	66
Boreal	23.2	76	12
Subboreal	22.5	11	1
Subtropical	24.3	12	0.4
Tropical	55.4	6	0.2
Total	133.5	26	1.3

NO_x FLUXES AND CONVERSIONS

The generic formula NO_x includes nitric oxide (NO) and nitrogen dioxide (N_2O) in their mono-, di- and polymolecular forms, as well as mixtures of these oxides and their corresponding acids. In this work, both gaseous, liquid and solid states of NO_x were generally included in NO_x, unless otherwise stated. The flows are shown in Fig. 5.

The main pathway for the annual turnover of NO_x is the large circulation within the biologically active parts of the terrestrial and aquatic systems. Only small losses from the terrestrial system to the atmosphere occur as gaseous NO_x, while the losses from the aquatic systems into the atmosphere are insignificant. The terrestrial losses of gaseous NO_x to the atmosphere are believed to originate from the chemical decomposition of nitrate.

Anthropogenic emissions were considered an important source for tropospheric NO_x. These, together with minor contributions from lightning, inflow from the stratosphere and from chemical conversion of atmospheric ammonia within the troposphere are the known sources.

The sinks for atmospheric NO_x are wet deposition and dry deposition; river runoff is a process accounting for a flux of NO_x from terrestrial to aquatic systems.

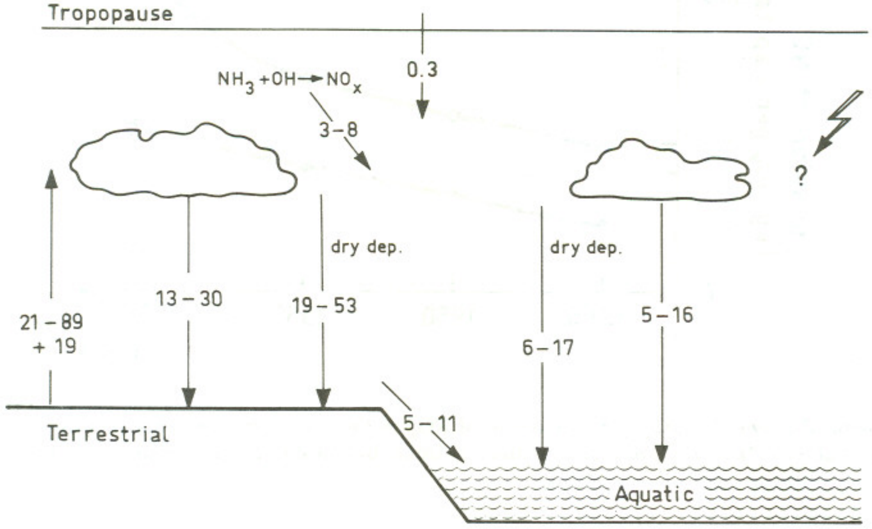

Figure 5. Simplified flow diagram for NO_x compounds in Tg N yr^{-1}. The possible input due to lightning is indicated with a flash. The output range from the terrestrial part was obtained as a residual source for the flows through the atmosphere and the direct anthropogenic contribution added is indicated (+).

Sources of tropospheric NO_x

Anthropogenic emissions

High-temperature combustion of fossil fuels leads to the formation of oxides of nitrogen. The major sources are transportation, energy production and preparation of petroleum products. Fig. 6 shows the *per capita* anthropogenic emission of NO_x in the USA during the past thirty years. The total emission rate and emission due to transport increased proportionally during the first part of this period, whereas sources other than transport seem to have grown at a faster rate in recent years. In a similar emission inventory for the UK by Derwent & Stewart (1973), the rates estimated were one-third and one-tenth for the total sources and sources due to transport emissions respectively, when compared with the *per capita* US rate.

An estimate of 19 Tg was obtained for the anthropogenic emission of nitrogen. This value refers to 1970 and was calculated by increasing the 1965 emissions, as given by Robinson & Robbins (1970a,b), by an annual increase in emission rate of 3.5 %. The growth rate figure is in good agreement with the increase of the emission rate inventory made by Cavender *et al.* (1973; Fig. 6) and Derwent & Stewart (1973) for the USA and UK respectively.

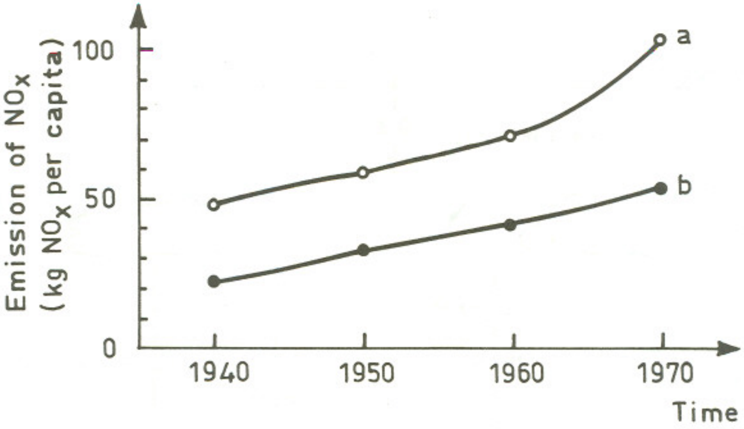

Figure 6. *Per capita* anthropogenic emissions of NO_x in the USA over three decades. Data from Cavender *et al.* (1973). The curves show a) total emission, b) emission due to transport activities.

Fixation by lightning

The idea that nitrogen is fixed by electrical discharges in the atmosphere was first advanced by Liebig (1827). The data by Finnel & Haughton (1931; 1932) on precipitation chemistry were reexamined by Hutchinson (1954), who concluded that less than half of the nitrate found in precipitation at the investigated location originated from lightning.

The correlation between the nitrate content in precipitation, collected on a daily basis, and the number of lightning flashes was investigated by Visser (1961). Only a very weak correlation was found and the contribution by lightning was concluded to be of minor importance for the nitrate content of rain. Junge (1958), when analyzing quarterly precipitation maps for the USA, concluded that the amounts of nitrogen fixed by lightning can only contribute 10–20 % of the amounts of nitrate found in rain. There is, however, no direct evidence for these figures.

A mechanism for the fixation of nitrogen by lightning was proposed by Ferguson & Libby (1971) in analogy with reaction mechanisms in the ionosphere, which can probably be used for calculating the amount of nitrogen fixed by this process.

Inflow from the stratosphere

A minor annual contribution for tropospheric NO_x as an inflow from the stratosphere, in the range of 0.3 Tg, is predicted by photochemical models (P.J. Crutzen, pers. comm.). The chemical forms for this addition of tropospheric NO_x are mainly expected to be NO_2 and HNO_3. The main source for this nitrogen is N_2O originating from denitrification processes in the biosphere (see above).

Chemical conversion in the troposphere

McConnell (1973) and Crutzen (1974b) suggested homogeneous gas-phase reactions as a source of NO_x from ammonia. The first step in the main reaction, whereby NO_x should be formed, involves OH radicals:

$$NH_3 + OH \rightarrow NH_2 + H_2O$$

The reaction rate ($k = 1.5 \cdot 10^{-19}$ m^3 s^{-1} $molecule^{-1}$) given by Levy (1974) was used in calculations together with the concentrations of ammonia for different parts of the troposphere (see Table 5). The OH radical concentration was set at $1.5 \cdot 10^{12}$ molecules per cubic metre, a value commonly used for tropospheric OH radicals (McConnell, 1973; Crutzen, 1974b). The possible quenching of the reaction according to:

$$NH_2 + NO \rightarrow H_2O + N_2$$

was not considered. A range of 3–8 Tg N yr^{-1} for the conversion of ammonia into NO_x, calculated in the way described, was considered likely.

Losses of gaseous NO_x from soils

A major source of NO_x in the atmosphere has been regarded to be losses from soils (Robinson & Robbins, 1970a,b; 1975). As previously discussed in the denitrification section, formation of NO in acidic soils can be explained by chemical decomposition of nitrite into nitric oxide. Nitric oxide is then rapidly oxidized to nitrogen dioxide under aerobic conditions. Release of nitrogen dioxide has been reported in laboratory experiments with soils having a pH within the range 4.8–7.8 (Nelson & Bremner, 1970). The losses at higher pH-values may be explained by small niches with a lower pH giving rise to nitrite decomposition.

Scanty measurements on the evolution of nitrogen dioxide from soil have been made. Makarov (1969) reported values in the range $0.3–7 \cdot 10^{-9}$ g NO_x-N m^{-2} s^{-1} in pot experiments and Kim (1973) gave figures in the range $1.7–4 \cdot 10^{-9}$ g NO_x-N m^{-2} s^{-1} by trapping gases from soil in the field. Both investigations were performed during the growing season covering May to September. Extending this period by three months and using the surface area of terrestrial ecosystems without glaciers, lakes, rivers and permanent deserts ($112 \cdot 10^{12}$ m^2) yields a possible range of 1–14 Tg NO_x-N yr^{-1}.

Summation of the abiological sources mentioned for NO_x in the troposphere gives a range of 23–29 Tg N yr^{-1}. Compared with the sinks (see below) there is a deficit of 21–89 Tg, when a steady state is assumed for the troposphere. This deficit is only partly covered by the estimated flows from the soils. Further data on the release from soil may show a greater contribution by these processes. This may also be the case when the contribution by lightning is better understood.

Tropospheric NO_x-sinks

Wet deposition

The nitrite content of atmospheric precipitation is generally low (Eriksson, 1952; Georgii, 1963), the predominant nitrogenous anion being nitrate. Wet deposition of nitrate was estimated analogously to the wet deposition of ammonium compounds. Scaling with the maximum and minimum deposition data from Eriksson (1952) and Steinhardt (1973) results in a range of 13–30 Tg NO_3-N yr^{-1} for the flux into the terrestrial system. Scaling with deposition rates from Robinson & Robbins (1970a,b) for land areas results in 24 Tg. The range of 13–30 Tg was adopted in this work for wet deposition of nitrate over terrestrial systems.

For wet deposition of nitrates over oceanic areas the estimate by Söderlund (1976) of 5–16 Tg NO_3-N was used.

Dry deposition

Dry deposition of NO_x (Table 16) was calculated by using a deposition velocity in the range $0.3–0.8 \cdot 10^{-2}$ m s^{-1} for the gaseous phase and $0.5–1.5 \cdot 10^{-3}$ m s^{-1} for the particulate phase. The estimated mean values for the ambient concentration of particulate and gaseous NO_x (Table 6) were used. The choice of deposition velocity was in analogy with the findings for sulphur compounds, as no other information seemed to be available in the literature. Permanent deserts were assumed to be inefficient for the trapping of gaseous compounds and for this reason no gaseous sink was taken into account for these regions.

Table 16. Calculated dry deposition rates of gaseous and particulate NO_x. The areas were taken from Bazilevich (1974).

Zones	Area (10^{12} m^2)	Concentrations Gaseous NO_x (ppb(v))	 Particulate ($\mu g\ m^{-3}$)	Deposition Gaseous (Tg N yr^{-1})	 Particulate (Tg N yr^{-1})
Polar areas	8	0.5	0.1–0.4	0.2–0.6	0.01–0.2
Temperate areas (excluding deserts)	70	4	0.1–0.4	16–43	0.1 –1.3
Tropical areas (excluding deserts)	50	0.8	0.1–0.4	2.3–6.2	0.1 –0.9
Desert areas	21	–*	0.1–0.4	0	0.03–0.4
Total terrestrial areas	149			19–50	0.2 –2.8
Oceanic areas	361	0.3	0.02	6–17	0.1

* Since permanent deserts were assumed inefficient as gaseous sinks, no concentration is given.

The somewhat higher deposition velocity chosen for the nitrate particulate matter compared with ammonium reflects the fact that nitrates are more abundant in larger particles than in smaller ones, and are thus more effectively scavenged than submicron particles (Junge, 1963). Even with this higher deposition velocity for nitrate particulate matter compared with ammonia, it is evident that the predominant sink processes for NO_x in the atmosphere are wet deposition and gaseous dry deposition, while deposition of nitrate particulate matter is only of small importance. Besides, if the lower troposphere contains substantial amounts of $HNO_3(g)$ – which is predicted from photochemical models (see above) – an additional amount of NO_x as HNO_3 is expected to be effectively scavenged by gaseous dry deposition, at any rate in humid and temperate areas, owing to its water solubility and strongly acidic character.

Nitrate in river runoff

Ahl & Odén (1972) made a regional division of the annual river discharges of inorganic-N in Sweden into the surrounding seawaters into a northern and a southern area. For the northern area, with low agricultural and urban influence, the inorganic-N discharge was 28 mg N m^{-2} yr^{-1} while for the southern area, with higher agricultural and urban activities, it was 152 mg N m^{-2} yr^{-1}. Sewage discharges from coastal cities were not included in the figures given. Wiklander & Vohtras (1975) showed that only 1 % of the inorganic-N leached from soil was NH_4^+-N even though the soil was fertilized with ammonia nitrogen. In accordance with these findings, the major part of inorganic-N discharged was regarded as NO_3-N, which is further supported by analysis of river runoff.

Rodin *et al.* (1974) estimated tropical areas as covering $55.9 \cdot 10^{12}$ m^2 and other vegetational zones – excluding desert and polar areas – $41.1 \cdot 10^{12}$ m^2. Burns & Hardy (1975) considered $44.0 \cdot 10^{12}$ m^2 as global agricultural land. By taking half of the agricultural area as situated in tropical zones and the other half in the other climatic zones, the non-agricultural areas of these zones become 33.9 and $19.1 \cdot 10^{12}$ m^2 respectively. The discharge values from northern Sweden were regarded as valid for non-agricultural areas and those from southern Sweden for agricultural areas, which resulted in 8.1 Tg N yr^{-1} for the flow of nitrate from terrestrial to aquatic systems (Table 17). By scaling the concentration measured by Williams (1968) for the Amazon river to the annual world river runoff, 5 Tg was obtained. Similarly, using the value given by Horne (1969) for the Mississippi-Missouri area, a somewhat higher value of 11 Tg was obtained. An average of 8 Tg ranging from 5 Tg to 11 Tg seems likely for river discharge. This range is in agreement with a global mean value of 0.2 mg NO_3-N l^{-1} for river runoff (Livingstone, 1963) and with the recent estimate of the annual world runoff of $39.7 \cdot 10^{12}$ m^3 yr^{-1} made by Baumgartner & Reichel (1973).

Table 17. Global river discharge of nitrate nitrogen excluding polar and desert areas.

Origin	Area (10^{12} m^2)	Rate (mg N m^{-2} yr^{-1})	Amount (Tg N yr^{-1})
Agricultural	44.0	152	6.7
Non-agricultural tropical	33.9	24	0.9
Non-agricultural other than tropical	19.1	24	0.5
Total	97.0		8.1

EXCHANGES OF ORGANIC NITROGEN

Large transfers of organic nitrogen compounds are found within the aquatic and terrestrial systems rather than between them. The latter flows are shown in Fig. 7. The magnitude of the flows between these systems and the atmosphere is much less than the internal circulations. The total nitrogen incorporated in terrestrial net primary production, obtained from data by Rodin *et al.* (1974), Bazilevich (1974) and Lieth (1975), was $1.8–2.6 \cdot 10^3$ Tg N yr^{-1}. Parallelly, there is a transfer of organic nitrogen from plant biomass to litter, which has been estimated at $1.4–2.4 \cdot 10^3$ Tg N yr^{-1} according to figures given by Reiners (1973) and Bazilevich (1974). From these two estimates, which agree with each other quite well, there are no indications of a non-steady state for the plant biomass. Turnover times for the various terrestrial reservoirs are given by Rosswall (1976).

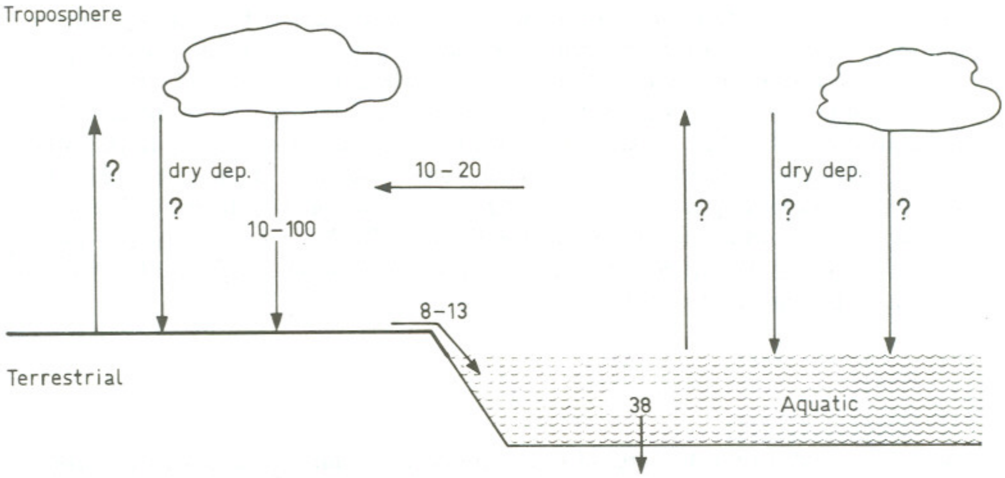

Figure 7. The flows of organic nitrogen in Tg N yr^{-1}. A net flow to terrestrial areas due to sea-spray is indicated.

The nitrogen uptake in primary production in the oceans was estimated at about $4.3 \cdot 10^3$ Tg N yr^{-1} (see paragraph on organic nitrogen sedimentation below). The inventory of phytomass in the oceans was calculated at about 300 Tg N, hence a turnover time of 0.07 yr is indicated for this reservoir. This is obviously much shorter than the corresponding figure for land (4.9 yr) given by Rosswall (1976).

The examples given show that the internal flows of organic nitrogen in terrestrial and aquatic systems exceed their mutual exchanges and those between them and the atmosphere by a factor of more than ten.

Depletion of organic matter in soil due to man's activities has been the subject of several articles. Stanford (1969) emphasized the variation in nitrogen loss from soils due to different kinds of crops. Reinhorn & Avnimelech (1974) reported high losses of organic nitrogen from newly worked virgin soils. In an article on nitrogen in terrestrial ecosystems, Paul (1976) reported losses of 165 and 440 g N m^{-2} due to agricultural activities from two different Canadian grassland soils over a period of 60–70 years. He estimated 20 % as removed in the form of grain or animal protein and another 20 % lost as nitrate nitrogen below the root zone. The rest was attributed to denitrification, erosion, leaching or volatilization of ammonia.

Taking 300 g N m^{-2} as the average of Paul's figures above, and scaling with the area of agricultural land of $44 \cdot 10^{12}$ m^2 (Burns & Hardy, 1975), a global loss of soil nitrogen of the order of $13 \cdot 10^3$ Tg N is indicated. A figure of $6 \cdot 10^3$ Tg for nitrogen losses from the terrestrial system due to man's activities was calculated by using the estimated figure of about $1.7 \cdot 10^5$ Tg C for man-made changes of the carbon reservoir given by Whittaker & Likens (1973) and assuming a C/N ratio of 30: 1 for the nitrogen content of plant biomass. Several objections can be raised to these methods of estimating the global depletion of soil organic nitrogen due to man's activity – the validity of scaling to all types of soil, the length of time for which soils have been cultivated, the paucity of the data used, etc. The authors of the present paper are aware of these objections but believe that the figure reflects the order of magnitude for these losses due to agricultural activity. Since the losses occurring in conjunction with forest cutting were not taken into consideration they may be even higher on a global scale.

Fluxes to and from the atmosphere

This part of the nitrogen cycle has been poorly investigated and only fragmentary information is available. In the nitrogen cycle presented by Eriksson (1959a), an annual turnover of 36 Tg N yr^{-1} as organic nitrogenous compounds in the atmosphere was estimated from a few measurements of the organic-N in precipitation. The sink term was estimated from a limited number of measurements hence no great precision was claimed for this estimate.

Sinks

A few measurements of the content of organic nitrogen compounds in precipitation have been reported in the literature: Neuman *et al.* (1959) found an average of 1.4 mg N l^{-1} in snow samples collected in Sweden. Semenov *et al.* (1967) analyzed rain and snow from various localities of the European USSR, obtaining averages of 2.2 and 1.8 mg org.-N l^{-1} respectively. These authors identified free amino acids, proteins and amines in their samples. Dean (1963) reported an average content of 0.17 mg org.-N l^{-1} in rainwater collected in New Zealand. Carlisle *et al.* (1967) reported an annual deposition of 0.13 g org.-N m^{-2} yr^{-1} for a site in England, which corresponds to a concentration of approximately 0.2 mg l^{-1}. The sampling techniques for liquid precipitation were not reported, hence the possibility of local cyclic dust as a significant contribution to the observed concentrations cannot be ruled out. An estimate for the annual wet deposition of organic nitrogen with precipitation would be 10–100 Tg. This was calculated from an average organic nitrogen content of 0.1–1 mg N l^{-1} for terrestrial precipitation.

Oceanic sources

Wilson (1959) suggested that the ocean surface is a source of atmospheric organic nitrogenous material. Organic nitrogen in the form of bacteria in jet drops from bursting bubbles emanating from the sea surface may contribute to this flux to the atmosphere (Blanchard & Syzdek, 1972). The size distribution of organic material collected in an oceanic location by Barker & Zeitlin (1972) indicated that the major mass of the organic material was associated with small particles which could have a substantial transit time in the atmosphere, and could thus show up in terrestrial precipitation. This is one of the few natural mechanisms for a net transfer of fixed nitrogen from the aquatic to the terrestrial system; the net flux was estimated to be not more than 20 % of the terrestrial wet deposition (Fig. 7). Other mechanisms are fishing by man, and guano deposition by sea birds.

Terrestrial sources

A few reports deal with atmospheric organic nitrogen in areas with large population densities of domestic animals and also discuss the fluxes of these substances in these regions. Mosier *et al.* (1973) detected about 15 different aliphatic amines in samples close to a cattle feedlot over an extended period. In a large dairy area Luebs *et al.* (1973) observed that approximately 20 % of the total nitrogen sampled was not ammonium. Amines were specifically determined in some cases and about 10 % of the total nitrogen was found to be of the amine-type.

Denmead *et al.* (1974) determined the ammonia flux by measuring different nitrogen fractions in a gradient over a grazed pasture. In some experiments 50 % of the total nitrogen volatilized was not ammonia, indicating the presence of volatile amines. In laboratory experiments with urea-treated soils, a decrease in methyl content was found by Steen & Stojanovic (1971) and they suggested that methyl nitrite was evolved.

The residence times and chemical conversions in the atmosphere of these organic nitrogenous compounds are unknown, as are also other possible sources for their occurrence.

River discharge

The transfer of organic nitrogen by rivers from terrestrial to aquatic systems was calculated by using data from Ahl & Odén (1972). Mean areal runoff values for northern and southern Sweden for organic-N were 82 and 124 mg org.-N m^{-2} yr^{-1} respectively. The organic-N was mainly of humic character. By applying the same areal distribution as when calculating the corresponding discharge of nitrate into the oceans (see above) to the values for organic nitrogen runoff (Table 18), 9.9 Tg org.-N yr^{-1} was obtained for organic nitrogen discharge.

Table 18. **Total global river discharge of organic nitrogen based on rates given by Ahl & Odén (1972) excluding polar and desert areas.**

Origin	Area (10^{12} m^2)	Rate (mg N m^{-2} yr^{-1})	Total annual rate (Tg N)
Agricultural	44.0	124	5.5
Non-agricultural tropical	33.9	82	1.6
Non-agricultural other than tropical	19.1	82	2.8
Total	97.0		9.9

Extrapolating the concentration given for the Amazon River by Williams (1968) to global runoff gave a discharge of 8 Tg N yr^{-1} for dissolved and particulate organic nitrogen. In the same way the data from the Mississippi-Missouri are (Horne, 1969) resulted in 13 Tg N yr^{-1}. An average of 10 Tg N yr^{-1} was used as reasonable value for the flow of organic nitrogen into the sea. The mean figure given by Livingstone (1963) for organic nitrogen concentrations in rivers was based on the extrapolation of a few determinations of the ratio of organic nitrogen to total dissolved matter. The ratio used was probably too high and consequently the annual global discharge of 37 Tg yr^{-1} based on his value was disregarded.

Organic nitrogen transferred to sea sediments

Net primary productivity in the sea has been estimated at about 70 g C m^{-2} yr^{-1} (Whittaker & Likens, 1973). Assuming a C/N ratio of 6:1 for marine phytoplankton (Redfield *et al.*, 1963), there will be a production of about 12 g org.-N m^{-2} yr^{-1}. This represents an annual organic nitrogen production of $4.3 \cdot 10^3$ Tg for the entire ocean. As a conservative estimate, about 95 % of the annual production is recycled within the euphotic zone (E.T. Degens, pers. comm.), i.e. $4.1 \cdot 10^3$ Tg. The rest (about 200 Tg N) settles to the ocean floor as tripton. A small part, however, becomes oxidized during the transport to the water/sediment interface.

A substantial amount of organic matter is dissolved, forming a mixture of recycled organic compounds and metabolites of planktonic origin. The organic nitrogen in dissolved organic matter was $5.3 \cdot 10^5$ Tg (Table 2). The age of dissolved organic matter of about 3000 years given by Williams *et al.* (1969), together with this amount, gives a transfer of 177 Tg org.-N yr^{-1} through this pool. The removal is accomplished by particles, the material then ending up in the sediment.

From a total of 377 Tg organic nitrogen annually added to the sediment, about 10 % or 38 Tg N is believed to become permanently trapped (E.T. Degens, pers. comm.), while the rest is returned to the aquatic environment principally by microorganisms and benthic communities. The fate of organic nitrogen during diagenesis within the sediments is rather complex and will not be discussed here.

TURNOVER TIMES FOR NITROGENOUS MATTER IN THE TROPOSPHERE

As pointed out by Bolin & Rodhe (1973), the turnover time is a simple indicator of the time spent by a substance in an environmental reservoir. Although a more relevant parameter would be the distribution of transit times for the various compounds in different reservoirs, the information on transit times for nitrogen compounds in the various systems is scanty, and more work needs to be done on this subject. Differences in turnover times reflect the differences in efficiency of sink processes for the compounds studied.

Since turnover times for the nitrogen compounds in the terrestrial system have been delt with in a separate article (Rosswall, 1976) and since too few data were available for the compounds in the aquatic system, these are just briefly treated here. The estimates for the turnover times for the various compounds in Table 19 were based on the fluxes and inventories given in previous sections.

Table 19. Approximate estimates of tropospheric turnover times.

Compound	Years	Days
N_2	$2 \cdot 10^7$	–
N_2O	$< 2 \cdot 10^2$	–
NH_3	–	1–4
NO_x(g)	–	2–8
NH_4	–	7–19
NO_x(s)	–	4–20
Organic-N	–	~ 10

Gases

Molecular nitrogen

Compared with the vast amount of nitrogen gas in the atmosphere (79 % by volume), the fraction annually converted into nitrogenous compounds is extremely small. The turnover time was calculated from the annual amounts of nitrogen fixed biologically and abiologically, and from the inventory of nitrogen gas within the troposphere. The inventory given corresponds to a turnover time of the order of 20 million years. If industrial and anthropogenic fixation is excluded, the turnover time increases by approximately 30 %.

Nitrous oxide

The estimate given by Junge (1974) of a tropospheric turnover time in the range of 4–16 years for N_2O was mainly based on the total sources for N_2O given by Seiler & Schmidt (1974). In this inventory ocean sources were believed to be the major sources of N_2O. For reasons discussed in a previous section (denitrification in the oceans), this source – estimated in the same way as by Hahn (1974, 1975) – was believed to be too high. It is at present impossible to give an accurate figure for the turnover time of tropospheric N_2O; all that can be said is that it is less than 200 years.

Ammonia

In the calculation for the turnover time of tropospheric ammonia, the inventory and annual fluxes estimated in this work were used together with the following assumption. All ammonia in the estimated annual fluxes was considered to pass through the gaseous phase, and direct emissions of particulate ammonium into the atmosphere were considered to be unimportant. The resulting range for the turnover time was 1–4 days. This short transit time in the atmosphere is consistent with the highly variable wet-deposition patterns for ammonium over the continents (Junge, 1958; Eriksson, 1959a).

NO_x

In analogy with the assumption made for the calculation of the tropospheric turnover time for ammonia, it was assumed that the emissions of nitrate particulate matter were of minor importance, and that all the NO_x annually deposited passed through the gaseous phase. From the ranges for the NO_x fluxes given, a turnover time of 1–20 days was calculated. The reactions between different compounds generically termed NO_x in the atmosphere due to photochemical reactions were not regarded as fluxes when calculating this range.

Particulate matter

Ammonium

In the calculation of the turnover time of ammonium compounds, a fraction (20 %) of the total amount of ammonium annually found in natural precipitation was assumed to be directly scavenged as gaseous ammonia, and consequently not passing through the particulate phase. The range for the turnover time calculated from the fluxes and estimated inventories given in previous sections falls within a range of 7–19 days. The lower value was considered as the more likely, since a recent estimate of aerosol transfer times in the troposphere was of the order of one week (Martell & Moore, 1974).

Nitrates

A direct gaseous scavenging of 20 % of the total NO_x by precipitation was also used when calculating the turnover time for nitrate-containing aerosols. Using the estimated fluxes given in previous sections, the turnover time was found to be in the range 4–20 days. The lower figure was considered as being more likely, as, in the atmosphere, nitrates are preferentially associated with larger particles than are ammonium compounds. Large particles are more easily scavenged than small ones (Junge, 1963), hence size distribution is an important parameter which determines the efficiency of the dry and wet deposition processes.

Organic nitrogen

The turnover time of atmospheric organic nitrogen was assumed to be somewhat longer than that of ammonium. This assumption was mainly based on the observations by Baker & Zeitlin (1972) on the size distribution of particulate organic matter found in the atmosphere. The small particles contained by far the largest fraction of the total amount of organic compounds.

Organic substances are generally less soluble in water than inorganic substances. Scavenging by natural precipitation and deposition on wet surfaces would therefore be less efficient, and therefore a longer turnover time for organic-N as compared with inorganic compounds is consistent. The turnover time was believed to be about 10 days. This value, together with an assumed total deposition of 40 Tg of organic-N, was used to calculate the atmospheric inventory of 1 Tg (Table 2). It must be stressed that these estimates for organic nitrogen compounds are uncertain, indicating more the order of magnitude of the inventory and fluxes than providing accurate figures.

SOME CONCLUDING REMARKS – MAN-MADE CONTRIBUTIONS

The man-made contributions can be roughly calculated from the data given in previous sections. Nitrogen fixation by the fertilizer industry amounts to 26 % of the present biological terrestrial fixation (including fixation in agricultural areas). The annual growth rate for the fertilizer industry is at present 7–9 % (UN, 1975). If this high growth rate is maintained, the industrial fixation will be as large as the biological by 1989. The implications of such a change are at present not clear.

As regards the anthropogenic fixation of NO_x, the high demand for energy and increased prices of fossil fuels will result in the use of higher combustion temperatures. This in turn implies that the amount of nitrogen fixed by combustion will increase rapidly – more rapidly than the increase in fossil fuel consumption. This increase of NO_x released into the atmosphere must be considered a serious problem in the context of acidification of natural precipitation and freshwater systems with low buffering capacity. The greater amount of fixed nitrogen compounds circulating through the atmosphere due to man's activities will also increase the amount transferred to aquatic systems. The effect of such perturbations is not known at present.

ACKNOWLEDGEMENTS

The authors especially wish to thank K. Gundersen for great help in preparing the parts on oceanic nitrogen fixation and denitrification and E.T. Degens for valuable advice in structuring the organic sedimentation calculations. We are also indebted to B. Bolin, D.R. Keeney, T. Rosswall and W.D.P. Stewart for their critical reading of the manuscript and their valuable suggestions.

The financial support of UNEP, the Swedish Natural Science Research Council (NFR) and Shell is gratefully acknowledged. This work has also been sponsored by NFR under contract No. G 0223-065.

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