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ATMOSPHERIC CYCLES OF NITROGEN OXIDES AND AMMONIA

A. Böttger, D.H. Ehhalt, G.Gravenhorst

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16. Abstract

The atmospheric cycles of nitrogenous trace compounds for the Northern and Southern Hemispheres are discussed. Source strengths and destruction rates for the nitrogen oxides: NO, NO_2 and HNO_3 (NO_x) and ammonia (NH_3) are given as a function of latitude over continents and oceans. The global amounts of NO_x-N and NH_3-N produced annually in the period 1950-1975 ($34 \pm 5 \times 10^{12}$ g NO_x-N/yr and $29 \pm 6 \times 10^{12}$ g NH_3-N/yr) are much less than previously assumed. Globally, natural and anthropogenic emissions are of similar magnitude. The NO_x emission from anthropogenic sources is 1.5 times that from natural processes in the Northern Hemisphere, whereas in the Southern Hemisphere, it is a factor of 3 or 4 less. More than 80% of atmospheric ammonia seems to be derived from excrements of domestic animals, mostly by bulk deposition: $24 \pm 9 \times 10^{12}$ g NO_3^--N/yr and $21 \pm 9 \times 10^{12}$ g NH_4^+-N/yr. Another fraction may be removed by absorption on vegetation and soils.

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1. Introduction

A number of trace substances are given off into the atmosphere. They mix with the main components of the air and form a heterogeneous chemical system in which gaseous, liquid and solid components interact. Nitrogen components participate in an important fraction of these chemical processes in the atmosphere. Of the eight different gaseous oxides of nitrogen, dinitrogen oxide (N_2O) appears with the greatest volume mixing ratio of about 300 ppb (parts per billion). For N_2O in the troposphere, no significant reaction mechanisms are known, so that in this reservoir, it has a relatively long life of decades. The oxides nitrogen monoxide (NO), nitrogen dioxide (NO_2) and nitric acid (HNO_3) have concentrations in the range of several ppb, since they are much more reactive than N_2O and thus do not concentrate in the troposphere. In spite of this relatively low concentration, under the influence of solar radiation in the lower troposphere, a number of new, partly dangerous gaseous pollutants forms from nitrogen oxides and hydrocarbons in photochemical smog. From the gas phase, nitrogen oxides can be converted to the solid phase by settling on existing aerosol particles or by a new nucleus formation. In the liquid phase of cloud or rainwater, they are converted from the gas phase by incorporation of these water particles or by direct absorption. In the rainwater they contribute to its acid effects. The acid content of rainwater has been studied recently in anthropogenic regions due to the harmful effects on populated and unpopulated areas (Likens et al., 1972, Gorham 1976).

In the stratosphere, nitrogen oxides have an important share in the natural balance of stratospheric ozone. Changes in its concentration thus affect the equilibrium determining the stratospheric ozone concentration.

Another reactive nitrogen component is the gaseous ammonia (NH_3) with concentrations in the range of several ppb. It can deposit on existing aerosol particles or be converted into the solid phase by new nucleus formation. It gets into the liquid phase of cloud or rainwater by incorporation of these particles or by direct absorption from the gas phase. It acts there as a base component.

Atmospheric nitrogen components are also interacting with ecologic regions. Thus, losses of gaseous nitrogen-containing components affect the nitrogen supply of the soil. At the same time, plants and soil can receive nitrogen components from the atmosphere by precipitation and dry deposition of gases and aerosols. The type and size of the transport of nitrogen-containing components between atmosphere and earth's surface are thus important not only for atmospheric processes, but also for soil and biologic questions.

In the cycle of atmospheric nitrogen components, possible routes and mechanisms which they can run through, are generally known and are presented in figure 1. Here, the ammonia components of gaseous NH_3 and ammonium NH_4^+ in the aerosol and in clouds and rainwater, as well as the gaseous components NO, NO_2 and HNO_3--often called NO_x below--as well as nitrate ions in aerosol and cloud and rainwater, are taken into account. The gas N_2O was only included inasmuch as it forms NO_x-components by reaction with excited O-atoms in the stratosphere.

The relative significance of the various routes for the individual nitrogen componnets can only be determined if we know how much of the converted quantity is due to each specific reaction route.

This cycle can be disrupted by man since anthropogenic produced NO_x and NH_3 are emitted into the atmosphere. In order to be able to judge the importance of this change due to man, the particular trace cycle must be understood quantitatively. A balance in which the anthropogenic and natural trace substances emitted into the atmosphere are compared to those removed from the atmosphere, can show the degree of human influence on the nitrogen cycle.

In order to be able to set up a balance, numerous attempts were made to quantify the cycle of atmospheric nitrogen components (Eriksson, 1959; Robinson and Robbins, 1968, 1970a, b, 1971, 1975; McConnell, 1973; Söderlund and Svensson, 1976, McElroy et al., 1976; Lie et al., 1977). The basis for these atmospheric nitrogen cycles was in most cases, data on the nitrate and ammonium quantities deposited in the rain. Many of these estimations relate to a survey by Eriksson (1952), which summarizes results of precipitation analyses from the period from 1864 to 1947. In that paper, analysis data from ca. 90 stations is cited; these lay mostly in Europe and the USA. Tropical regions are rarely cited. The European and American values of rain analysis were thus extrapolated to the entire world. Since at tropical latitudes and in the Southern hemisphere, different meteorologic and ecologic conditions prevail, the extrapolation of precipitation data from continental, central latitudes to global relations, is doubtful. The Cast report (1976) and Pratt et al. (1977) used data more than 70 years old for their estimation. Thus it is questionable whether realistic number values are obtained for the deposited quantities. Large differences in the estimations of different authors (table 1) for the global, ground-deposited nitrate and ammonium nitrogen quantities reinforce this supposition. Conclusions drawn from this data are thus largely uncertain. For instance, the natural fraction of NO_x and ammonia quantities given to the atmosphere was computed from the difference between the anthropogenic emitted quantity and the quantity deposited by total deposition (Robinson and Robbins, 1968, 1970a, b, 1971, 1975; Liu et al., 1977). Total deposition of a trace substance is the sum of aerosol deposition and gas absorption on the earth's surface, and deposition by rain. According to these comparisons, natural sources should emit 6 to 1400 times more NO_x and NH_3 than anthropogenic ones (Robinson and Robbins, 1968, 1970a, b, 1971, 1975; Liu et al., 1977). The fraction of human activities of the atmospheric sources of these components would thus have to be small and an increase in the anthropogenic source intensity would still not cause any significant changes. But these conclusions are based on estimates of source intensity which were obtained only by closing the cycle balances; balances which did not use chronologically and spatially representative data. Since 1950 many precipitation analyses have been conducted at numerous locations, but these values were seldom used in the above papers; thus it was an objective of this paper to re-determine the NO_3^- and NH_4^+ quantities removed by total deposition from the atmosphere. The geographic locale of the precipitation analyses was to be taken into account in order to get spatially representative data.

The resulting, total deposition will be compared to the total source strength for the nitrogen components NO_x and NH_3. In order to do this, the anthropogenic and natural sources of these N-components were estimated independently. From them we can already derive the size of emission caused by man, of the total sources for these nitrogen components. Comparisons between sources and size of the sinks then give an indication of uncertainties in the estimations and can necessitate the use of previously ignored production and destruction mechanisms.

2. Sources of Atmospheric Nitrogen Components NO_x and NH_3

Atmospheric nitrogen components are formed by many different processes and emitted to the atmosphere. Georgii (1963) supposed that NO_x can get into the troposphere by the following processes: By anthropogenic combustion processes, oxidation of ammonia, electric discharges and by diffusion of NO from the stratosphere. NH_3 gets into the atmosphere through the decomposition of organic material, losses from the soil and combustion processes (Georgii, 1963).

But very different information is found regarding the intensity of the individual sources: The liberation of NH_3 from metabolic products of animals for example, is the greatest NH_3-source according to Healy et al. (1970), whereas Dawson (1977) explained atmospheric NH_3 only through the release from unfertilized soils. In table 2.1, some estimations of source strength of atmospheric NO_x and NH_3 are compiled. The directly estimated sources of NO_x emitted from anthropogenic combustion lie quite closely together (15 to 18 x 10^{12} g N per year), except for the value of Robinson and Robbins (1971). The NO_x-losses from the soils exhibit large differences: from 5 x 10^{12} g N per year (Chameides et al., 1977) to 305 x 10^{12} g N per year (Robinson and Robbins, 1968). These estimations were not verified by measurements, but were calculated from balances by subtracting the directly estimated sources (sec. 1) from the very different data on the trace quantities removed from the atmosphere. The difference should represent the natural sources, since no chemical decomposition of N-components was assumed in the atmosphere. Like the natural NO_x-sources, the natural NH_3-sources were determined, with all data being "balance values" and not estimations.

Other possible sources like NO_x-production by electric discharge, radiation or oxidation of NH_3, were largely ignored (tab. 2.1).

Since the estimation of natural sources has such large differences and the fractions of individual sources of the total emission of NO_x and NH_3 are unknown, in this section the sources are estimated directly and not with "balance values".

All sources cited in this section are averages for the years 1950 to 1977, since these values are to be compared with the quantities of NO_3^- and NH_4^+-N removed from the atmosphere per year during this period.

2.1 NO_x-Sources

The nitrogen in the earth's atmosphere is largely composed of molecular nitrogen (N_2). A very high energy is needed to form NO from N_2 and O_2.

$$N_2 + O_2 + 1.8 \times 10^5 \text{ Joules} \rightarrow 2\ NO$$

At a temperature of 3000 K, 5%-vol. NO, at 2000 K, 1%-vol. of NO is in equilibrium with synthetic air. The NO-equilibrium concentration decreases quickly with decreasing temperature. By "quenching" and diluting hot gases, the NO-reverse reaction can be reduced. At temperatures below 1000 K, nitrogen oxide practically does not break down--it is a metastable substance.

The energy for NO-formation from atmospheric nitrogen and oxygen can be provided by electric discharge, by chemical reactions--especially combustion. The majority of resulting NO is converted to NO_2 by the production process itself, and in the atmosphere by further reactions; this in turn can react with OH to form HNO_3.

2.1.1 Combustion Processes

The NO_x given off to the atmosphere by combustion processes is computed from the quantity of consumed fuel and an emission factor. But the emission factor is defined for vehicles and gives the emitted NO_x per driven km, but not as a function of burned fuel.

The nitrogen content of the burned material does not define the produced NO_x-quantity, since the fuel itself does not provide the nitrogen of the formed NO_x, but the molecular nitrogen of the atmosphere itself. Different emission factors for different materials essentially reflect different temperatures of the combustion processes. In similar combustion, the same temperatures do not always occur, so then even for the same fuel, differing emission factors are found. The U.S. EPA has given averages for emission factors from various measurements (EPA, 1973 and 1977). In this paper, emission factors are used which are based on many measurements (EPA, 1973 and 1977).

Table 2.2 presents some emission factors from the literature. The reason for the large fluctuations among the emission factors of a fuel is due to the fact that there are various combustion processes for a fuel each having a different emission factor, e.g. for coal combustion, the emission factor of a power plant is much greater than for a household furnace. NUKEM Co. published an emission cadistry for the FRG (Blumenthal and Schöner, 1974). In table 2.2, both the individual emission factors and average emission factors for coal, oil and gas are presented. The averages were calculated by weighting the fuel quantities consumed in power plants, industry or household. The average emission factors thus tell how much NO_x-N is released per mass unit of burned coal, oil or gas in the FRG. Thus, they can reflect conditions in the highly industrialized countries, but these averages do not apply for production conditions in the whole world. Since the fraction of combustion processes for a certain fuel worldwide is unknown, large fluctuations in used values are taken into account in this paper. Extreme emission factors were omitted. The data on consumed quantities of coal, oil or the number of vehicles and domestic animals were taken from the statistic annual of the UNO (1976). Averages for the years from 1950 to 1977 were calculated from the numbers given in the annual, since the following deposition estimation to be compared to these sources, includes this period.

2.1.1.1 Forest-Clearing in Tropical Regions

Annually, large areas of the tropical forest are cleared. Since the beginning of the century, forest regions of the earth have been reduced by 20-25% (Bolin, 1977). The cleared wood is burned in situ (Sioli, 1978).

Estimations of the annual forest destruction in tropical regions fluctuate between 1.2×10^{11} m^2 (Bolin, 1977) and more than 2×10^{11} m^2 (Hampicke, 1977). Sioli (1977) gives a forest reduction due to clearing of 1×10^{11} m^2 per year for the Amazon region alone. These values are averages for the time after 1950.

If a forest stand of 30×10^3 g/m^2 (Hampicke, 1977b) to 40×10^3 g/m^2 (Rodin et al., 1974) is assumed, then the mass of destroyed forest is $3.6 - 9 \times 10^{15}$ g/yr. Since the combustion is incomplete with residual charcoal left over, only ca. 75% of the wood, corresponding to $2.7 - 6.7 \times 10^{15}$ g, is burned (Adams et al., 1977).

The EPA (1973) gives an emission factor of 0.3 - 0.5 g NO_x-N/kg of wood determined from an evaluation of various studies on the combustion of wood. With this emission factor, $0.8 - 3.4 \times 10^{12}$ g NO_x-N per year is released to the atmosphere in the destruction of the primeval forest.

Figure 2.1 shows the zonal distribution of NO_x-N emissions from this source. It was computed from the distribution of tropical forest (Woodwell, 1978) by assuming that at all latitudes, the same fraction of forest is being destroyed by clearing and burning.

2.1.1.2 Grass-fires

Next to burning of cleared wood, grass-fires in tropical regions are another NO_x-source. Large savanna areas burn--intentionally or not--usually in the second half of the dry season (Sarmiento and Monasterio, 1975).

It can be assumed that the plant material produced in one year is destroyed by fire, since the fires appear regularly every one to two years (Sarmiento and Monasterio, 1975). If there is no fire in one year, then the quantity of combustable material doubles (Scott, 1974) and then burns the following year. Annually, an average of 0.4 - 0.8 g combustable material per m^2 of Savanna is formed (Bach, 1976; Woodwell, 1978; Murphy, 1975). World-wide, the Savanna regions are given as 15 x 10^{12} m^2 (Woodwell, 1978) to 18 x 10^{12} m^2 (Bach, 1976). Bach's value is based on data from the UN Food and Agricultiral Organization which gives the Savanna areas for the individual countries in tropical areas. With an emission factor (EPA, 1973) of 0.3 x 10^{-3} g NO_x-N per g of burned material, using the above values, 1.8 - 4.3 x 10^{12} g NO_x-N/yr is given off to the atmosphere. Figure 2.2 shows the zonal distribution of these sources. It was calculated from a geographic distribution of the Savanna (Woodwell, 1978).

2.1.1.3 Forest Fires

Besides clearing, forest is also destroyed directly by forest fires. Yamate (1975) estimates than a world annual wood stock of 210 x 10^{12} g corresponding to an area of 1.1 x 10^{11} m^2 of forest is destroyed by fire. Thus, 0.15 - 0.23 x 10^{12} g NO_x-N is released into the atmosphere according to his data.

Compared to other NO_x-production in vegetation burning, this source is small. Due to the burning of cleared wood in the tropics and Steppe fires, 30 times more NO_x-N is produced world-wide than by forest fires.

2.1.1.4 Fossil Fuels

The anthropogenic combustion of soft coal, hard coal, light and heavy oil and natural gas, represent other significant NO_x-N sources.

The world consumed quantities of these fossil fuels was taken from the Statistics Annual of the UNO (1976). Table 2.3 shows the burned quantities, the used emission factors (from table 2.2) and the computed NO_x-N quantities released to the atmosphere.

The combustion of these fossil fuels with 4.5 - 13.6 x 10^{12} g NO_x-N/yr represents a significant source. In order to get a latitude-dependent distribution of NO_x-production from burning fossil fuels, the consumed quantities of soft and hard coal, light and heavy oil and natural gas was taken from the compilation of the UNO (1976) for individual countries and then ordered according to the geographic location of the countries. Figures 2.3 - 2.7 represent the zonal dependencies of these sources. In contrast to the previous sources, the emission maxima for fossil fuels lies in the middle latitudes between 30 and 60° N. In tropical regions and in the Southern hemisphere, much less NO_x-N is emitted from the combustion of fossil fuels.

2.1.1.5 Vehicular Traffic

The operation of internal combustion engines represents another important NO_x-source. In 1965, a passenger vehicle emitted an average ca. 0.9 g NO_x-N/km in its exhausts (EPA, 1973). In following years, the emission factor increased temporarily, since the emphasis had been placed on reducing CO-emissions from the engines. The NO_x-emission was thus increased. Now, the analysis values for NO_x-concentrations in auto exhausts are again lower. An emission factor of 0.9 - 1.2 g NO_x-N/km (EPA, 1973) seems representative. This average value includes emissions from trucks. The emission factor for vehicles does not give the NO_x-N emissions as a function of consumed fuel, but of the driven distance. Thus, it is defined differently than in sec. 2.1.1. With an average driving of 15,000 - 20,000 km per year (EPA, 1973; Umweltbundesamt, 1976), 13.5 - 18 x 10^3 g NO_x-N per auto per year is determined. Given a number of 27.2 x 10^7 vehicles in the world (UNO, 1976), then 3.7 - 4.9 x 10^{12} g NO_x-N/yr is released to the atmosphere world-wide. These values increase the NO_x-emission from fossil fuels by ca. 25%.

Figure 2.8 shows the zonal distribution of this source; it was computed on the basis of vehicle stocks of individual countries (UNO, 1976). This figure shows the heavy vehicle density in the middle latitudes of the Northern hemisphere. 90% of the vehicle-generated NO_x-N is released between 65 and 30° N.

2.1.2 Thunderstorms

Due to electric discharges during a storm, approximately 10^5 Joules per meter is released in lightening (Chameides et al., 1977). This energy is sufficient to dissociate N_2 and O_2 and form NO_x. However, for a long time it was impossible to detect the NO_x-production due to lightening. Initially, measurements were taken to detect NO_x-production during thunderstorms through increased NO_3^--concentrations. It was assumed that the formed NO_x was removed from the atmosphere as NO_3^- during the rain. But studies have shown no correlation betweeen individual thunderstorms and higher nitrate concentrations in the rain (Viemeister, 1960; Visser, 1961; Wetzelar and Hutton, 1963). There was also no correlation of nitrate concentration in the rain with the temporal distribution of storm activities (Viemeister, 1960). In fact, the conversion of NO and NO_2 into HNO_3 lasts about 1 day*. Thus it cannot be expected that NO formed during a storm will be transported as NO_3^- to the ground immediately with the rain. For this reason, no correlation between individual thunderstorms and higher nitrate concentrations was found.

In the rainy season, greater storm activities are expected (Trewartha, 1968). Thus, higher HNO_3-concentrations in the air are postulated. A higher nitrate concentration in the thunderstorm can be reduced since the increased instability and greater water vapor content

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*Computed from the characteristic time for the reaction $NO_2 + OH + M \rightarrow HNO_3 + M$ with reaction constants of Hampson and Garvarin (1978) and concentrations at M = 2.4 x 10^{19} molecules/cm^3 and OH 5 x 10^5 molecules/cm^3.

causes a higher water vapor condensation with formation of precipitation thus reducing the concentration. Thus, no correlation in time is found between storm activities and nitrate concentration. But the NO_3^- deposition in the storm season should be higher, as has been observed (Viemeister, 1960). The increased NO_3^- deposition does not necessarily permit the conclusion that NO_x is formed by lightening, but it is also not contradicted. This ambiguity can be overcome if NO_x concentrations are known in the air during storms, compared to other situations. Noxon (1976) found an average NO_x mixing ratio in the air of 60 ppbv during a storm. It is near the value of 100 ppbv computed by Griffing (1977) for storm conditions, but is much higher than the value of ca. 0.1 ppbv found without storm activity (Noxon, 1976).

If the number of observed flashes is a measure for the intensity of electric discharges, then in this case ca. 10^{26} NO_x-molecules per flash are formed.

With the assumption that ca. 100 flashes occur per second worldwide (Mühleisen, 1977; Mattern, 1977), and that these contribute to the NO_x production through similar electric discharges (as measured by Noxon in Colorado, 1976), then world-wide 7.4×10^{12} g NO_x-N/yr is produced through storm activity. From laboratory measurements of NO_x formation in electric discharges, Chameides et al. (1977) found a three to four times smaller NO_x production per flash. But they assumed 1600 flashes per sec. on the earth--a significantly greater storm activity--and thus calculated $30 - 40 \times 10^{12}$ g NO_x-N per year produced by lightening flashes. Assuming that the newer value of 100 flashes per second (Mühleisen, 1977) comes closer to atmospheric conditions than 1600 flashes per second, and that the uncertainty is 200 flashes per second, storms produce a global $7.5 - 15 \times 10^{12}$ g NO_x-N/yr. This source is thus on the level of fossil fuel combustion, even ignoring vehicle traffic. The geographic distribution (fig. 2.9) has its maximum in tropical latitudes, whereas fossil fuels contribute almost exclusively to middle latitude NO_x emission. The geographic distribution of this source is based on the distribution of thunderstorms (Trewartha, 1968). Since storms on the oceans are rare, it can be assumed that the formation of NO_x due to electric discharge of lightening is a land source.

2.1.3 NO-Production through NH_3-Oxidation

NO_x can be formed not only by combustion and electric discharge, but also from chemical reactions in the atmosphere. The most important reactions in the atmosphere of ammonia (its atmospheric sources are estimated in sec. 2.2) and its decomposition products are shown in fig. 2.10. The particular reaction partners and attendant constants are also shown. With the assumed concentrations (table 2.4), under steady state conditions,

$$NH_3 \xrightarrow{OH} NH_2 \xrightarrow{O_2} HNO \xrightarrow{O_2} NO$$

is the main reaction sequence.

Only 1 NH_2-molecule in 4000 reacts with NO and contributes in a very limited extent to the NO-decomposition in the atmosphere. Nearly all other NH_2 react with O_2 and form NO-molecules via HNO as intermediate. The reactions of NH_2 with OH or O are even less important than that with NO.

In order to calculate the max. NO-production through NH_3-oxidation it is sufficient to determine the nitrogen quantity participating in the reaction of NH_3 with OH-radicals to NH_2. The vertical distribution of ammonia concentration over land and oceans was taken from section 8, the OH-concentration was taken from model calculations (Fishman and Crutzen, 1978). With these concentrations, world-wide 1.2 - 4.9 x 10^{12} g NO_x-N/yr is produced by the oxidation of NH_3. The latitude-dependence of this source was computed under consideration of the distribution of land and ocean (fig. 2.11).

2.1.4 Diffusion of NO_x from the Stratosphere into the Troposphere

In the troposphere, N_2O is nearly inert and can decompose very slowly. Due to turbulent exchange, 15 x 10^{12} g N_2O-N per year move into the stratosphere (Schmeltekopf et al., 1977). There N_2O can be converted:

I. $N_2O + h\nu\ (\lambda < 230\ \text{nm}) \rightarrow N_2 + O^*$

A large part of the N_2O is broken down via this mechanism. N_2O can also react with an excited oxygen atom O^*:

IIa. $N_2O + O^* \rightarrow 2\ NO$

IIb. $N_2O + O^* \rightarrow N_2 + O_2$

The NO formed in equation IIa can react again to form NO_2 or HNO_3 and moves via turbulent exchange back into the troposphere. Schmeltekopf et al. (1977) state that annually, 1.6 x 10^{12} g NO_x-N formed from N_2O in the stratosphere, is transported back into the troposphere. The latitude distribution of tropospheric deposition of this stratospheric NO_x-source (fig. 2.12) was adapted to the strontium-90 deposition distribution (Junge, 1963), since Strontium-90 is also transported from the stratosphere into the troposphere, and in the troposphere, no additional strontium-90 sources are present. The NO_x-source of other stratospheric processes like cosmic radiation and solar proton events are at least one order of magnitude less than the NO production through decomposition of N_2O (NASA, 1977).

2.1.5 NO_x-Flux from the Ground into the Atmosphere

The nitrogen removed from the atmosphere by biologic fixing is mostly replaced by liberation of N_2O and N_2 in the biologic decompositions in soils and oceans. Besides these nitrogen components however, ammonia and in principle, NO and NO_2 can be released from the earth's surface to the atmosphere. The size of these nitrogen sources is not definitely known. Gaseous NO and NO_2 can be formed in the soil by the chemical reactions:

$$2\,H^+ + 3\,NO_2^- \rightarrow 2\,NO + NO_3^- + H_2O$$

$$H^+ + 2\,NO_2^- \rightarrow NO + NO_2 + OH^-$$

and possibly also in the atmosphere. According to van Cleemput and Baert (1976), for purely thermodynamic reasons, the first reaction should predominate, whereas Nelson and Bremner (1969) can better explain their results with the second reaction. A part of the formed NO is oxidized to NO_2 in the presence of oxygen. If the partial pressures of NO and NO_2 in the soil-air lie above those of the outside air, then NO and NO_2 will escape into the atmosphere. Laboratory experiments on this question can only show whether NO, NO_2 escape from the soil is possible in principle. Thus, a statement on NO_x sources for natural conditions based on laboratory measurements is restricted. Smith and Clark (1960) and Tyler and Broadbent (1960) were not able to find any NO-production in chamber experiments. Nelson and Bremner (1969) explain this that in the used, closed systems, the liberated NO is again absorbed by the soil, and thus cannot be detected in the air. The pH of the soil proved to be an important parameter in laboratory tests detecting NO_x volatility. Gerritsen and de Hoop (1957), Bremner and Nelson (1968), Nelson and Bremner (1969), van Cleemput et al. (1975) were able to show that with decreasing pH from neutral, NO is increasingly formed in the soil containing nitrite. Metal ions however, do not occur in sufficiently high concentration in the soil to contribute much to NO-production through reduction of the nitrite to NO (Nelson and Bremner, 1970).

The percentage nitrogen loss as NO or NO_2 from moss-covered humus is determined by Mahendrappa (1974) on the average as 0.005% of the nitrogen added in various forms.

Under natural conditions, Makarov (1969) found a loss of ca. 0.4 kg NO_x-N/hectare from unfertilized soil (pH 5.0 - 5.2) during the growth period. Of the applied nitrate fertilizers, an additional 0.2 kg N/hectare is lost as NO_2--this corresponds to 0.2% of the N-fertilizer. The value of Makarov (1969) for the NO_x-loss of applied N-minerals of 0.2% lies in the range of Wagner and Smith (1959) who measured NO_x-volitalization of 0.3 - 1.2% of urea-treated clay and loam soil samples (pH 6.0 or 5.6). It does not seem very useful to extrapolate the value for the NO_2-production from natural, unfertilized soil in the experiment, to the entire world. The values for NO_2-formation are certainly determined by the low nitrogen content and the pH-value of the soils in the tropics and subtropics. In regions of low rainfall, the pH-value of the soil is also above 7 (Dawson, 1977), so that the chemical decomposition of nitrite is almost completely suppressed. Wagner and Smith (1959) were not able to find any NO_x release from moss-covered natural humus samples in the laboratory over a period of 8 weeks, even though the soil samples with pH-values between 5.4 and 6.0 were in the favorable range. Thus, in the absence of additional data and due to the high pH-value of natural soils, as an approximation, one-tenth of the value given by Makarov (1969) is assumed for the average NO_x source from natural soils. This corresponds to a global 0.6×10^{12} g NO_x-N per year. It is supposed that the true amount is still less.

If the NO_x-loss from the soil nitrogen fertilizer is assumed to be 1% world-wide, then as an upper limit, 0.2×10^{12} g NO_x-N/yr is emitted into the atmosphere from this source.

Under these assumptions, the NO_x-sources for the natural and fertilized soil contribute at most a few percent to the atmospheric NO_x-content.

The loss of nitrogen from soil samples heated to 55 to 110 °C--interpreted as vaporization of HNO_3 due to interaction of clay minerals, nitrate and iron ions (Thomas and Kissel, 1970)--can only be viewed as speculation and is of no importance, at least not for atmospheric questions.

The ocean, not the land surface, represents the predominant part of the earth/atmosphere interface. Since the chemical decomposition of NO_2^- into gaseous NO_x becomes active in the acidic range below pH 6 and the ocean surface waters have a pH-value of 8.1 - 8.3, a NO_x production by the ocean through this mechanism seems to be impossible.

2.1.6 Additional NO_x-Sources

Two other NO_x sources belong here; they contribute to regional NO_x-emission.

Waste incineration facilities are being constructed on an increasing scale. Annually in the FRG, about 5.4×10^{12} g of waste is burned, in England, ca. 2×10^{12} g and in Canada, ca. 0.7×10^{12} g. World-wide a value of 20×10^{12} g of waste/yr seems reasonable (Federal Environmental Agency, Germany, 1978). With an emission factor of 0.5 g NO_x-N/kg of waste (EPA, 1977), about 10^{10} g NO_x-N/yr is emitted to the atmosphere from this source.

In 1975 about 25×10^{12} g HNO_3 per year was produced industrially (UNO, 1976). With an emission factor of 0.05 - 8.5 g NO_x-N/kg of produced HNO_3 (EPA, 1977), 1.25×10^9 - 0.2×10^{12} g NO_x-N/yr is emitted.

The contribution of this source compared to the NO_x from burning fossil fuels is at least 100 times less. Thus, it is of lesser importance for a global balance, but near incineration facilities or HNO_3-factories, it can make a contribution to atmospheric NO_x.

2.1.7 Summary of NO_x-Sources

In table 2.5, the various NO_x-sources are summarized according to their estimations. The values are averages for the years 1950 to 1977; present values for the anthropogenic fractions are sometimes much greater (sec. 9). Averages are presented for this period, since the quantities removed from the atmosphere through total deposition estimated in sections 4-6, are also averages for this period. In table 2.5, the anthropogenic and natural sources are presented. Anthropogenic NO_x-sources in this report are the combustion of fossil fuels, vehicle traffic and forest clearing. Storms, N_2O-N from the stratosphere and NH_3 oxidation are defined as natural sources. Since grass fires are caused naturally and by man, its contribution is split equally between anthropogenic and natural. World-wide, according to this estimation, anthropogenic and natural sources are about equal in size. In the Northern hemisphere the anthropogenic sources predominate (9 - 20 x 10^{12} g NO_x-N/yr) compared to natural sources (6 - 13 x 10^{12} g NO_x-N/yr), whereas in the Southern hemisphere, the anthropogenic sources are less (1 - 4 x 10^{12} g NO_x-N/yr) than the natural sources (5 - 11 x 10^{12} g NO_x-N/yr. Figure 2.13 shows the zonal dependence of the fraction of anthropogenic NO_x-N emission of the total NO_x-N emission in percent. The solid curve gives the distribution computed from the average values for anthropogenic and natural values. The figure shows that in the highly industrialized belt between 30° and 60° N, the fraction from anthropogenic sources is on the average between 70 and 85%. In the other regions, natural sources predominate according to these estimations.

The total quantity of NO_x-nitrogen given off to the atmosphere from anthropogenic sources of 10 - 24 x 10^{12} g NO_x-N/yr corresponds to the estimations of Robinson and Robbins (1968, 1970a, b, 1975) of 16 x 10^{12} g NO_x-N/yr, Burns and Hardy (1975) of 19 x 10^{12} g NO_x-N/yr, Söderlund and Svensson (1976) of 15 x 10^{12} g NO_x-N/yr and Chameides et al. (1977) of 15 x 10^{12} g NO_x-N/yr. The natural sources in table 2.5 are much less than in Robinson and Robbins (1968, 1970a, 1970b, 1971, 1975) and Söderlund and Svensson (1976). These authors did not estimate the natural sources, but computed it from the balance between the deposited quantity and the anthropogenic sources. Robinson and Robbins (1975) obtain a ratio between natural and anthropogenic sources of 15:1, whereas in this investigation, a global ratio of 4:3 was found, in the industrialized region from 30 - 60° N, it is 1:8.

2.2 NH_3-Sources

Besides oxides and molecular nitrogen, it also appears in the atmosphere as ammonia.

2.2.1 Ground Sources

This is the case in the soil when the ammonia vapor pressure via the ammonium ions contained in soil solutions, is above that in the outside air. Conversely, gaseous ammonia is absorbed from the atmosphere.

Ammonia is formed in the soil mainly by two biologic mechanisms: Mineralization of organic substances and ammonification of nitrate. In addition, it is fed to the soil from the atmosphere in rain and by absorbed aerosols. These formation mechanisms are opposed by two decomposition processes, which again convert ammonia into nitrate (nitirfication) and organic substances (immobilization) with the action of micro-organisms. In addition, ammonium ions are highly absorbed at the surface of soil particles (fixing). The simultaneous evolution of all these processes leads to ammonium concentrations in the soil solution which determine the ammonia vapor pressure in the soil air via the physical, dissolved NH_3-fraction.

From previous investigations (Allison, 1955), the following trend of biologic ammonium production and destruction is found as a function of temperature and pH of the soil. The ammonium formation (mineralization, ammonification) increases in the atmosphere with increasing temperature and pH. The trend toward higher NH_3-release to the atmosphere due to the higher NH_3-content in the soil at higher temperatures and pH-values, is enhanced by a simultaneously higher NH_3-partial pressure. The fraction of physical, dissolved ammonia of the total ammonia in the solution is greater at higher pH-values, whereas the solubility of NH_3 is less at higher temperatures.

2.2.1.1 NH_3-Release to the Atmosphere from Unfertilized Soils and Oceans

From all these relations, Dawson (1977) calculated a world-wide flux of 38 x 10^{12} g NH_3-N per year from unfertilized soils into the atmosphere. According to his model calculations, the quantity of ammonia found in precipitation world-wide, can be explained by this one source. To integrate the complex processes into a generally valid model does not yet seem possible, since the individual ammonium settling rates are unknown. In addition, they usually begin at microcenters whose properties do not necessarily have to agree with the characteristics of a macrosystem. Thus, the ammonia ground source in this report will be quantified more on the basis of measurements of NH_3-losses, even though their interpretation is still controversial. From the nitrogen balance of a semi-arid soil, West and Skujins 1977) concluded a NH_3-source of 10 $\mu g/m^2h$. The advantage of such material balances lies in the fact that they can be integrated over a number of various conditions and thus give a representative value. Their disadvantage consists in the indirect measurement of the NH_3-flux by subtraction of all other nitrogen fluxes.

This NH_3-production rate of 10 $\mu g/m^2h$ is assumed for soils in semi-arid regions, which the authors designate as an open system in which considerable fractions of the nitrogen conversions proceed via the atmosphere. For a forest characterized as a closed system, they assume no ammonia vaporization. Directly measured ammonia sources from soils are available only from Hooker et al. (1973) and Lenhard (1977). The ammonia release from freshly cleared or cultivated soil was measured (Hooker et al, 1973) by sucking ammonia-free air through a closed chamber over the soil and finding the increase in the NH_3-concentration. Over 160 days, production rates of ~ 1 $\mu g/m^2h$ were measured. This is considered an upper limit since in reality, no ammonia-free air comes into contact with the soil and thus there is a smaller or no difference between soil and outside air ammonia concentrations. Ammonia sources from natural soils with different pH-values were measured by Lenhard (1977) in a closed chamber in field experiments at various temperatures. At low temperatures, even soils with higher pH-values exhibit no ammonia release.

As a representative value from these measurements, an ammonia production of 1 $\mu g/m^2h$ is concluded. From the above measurements it seems likely that the real ammonia output from natural, unfertilized soil is in the range of 1 x 10^{12} g NH_3-N/yr world-wide. With this extrapolation it must be remembered that it is based only on a few studies relating only to a small part of the earth's surface (West Europe, USA).

The pH-value of the oceans is at 8.2 (Dietrich et al., 1976). Georgii and Gravenhorst (1977) calculated the NH_3-sources of the oceans for two individual cases as 3×10^{-2} μg $NH_3/m^2/h$. World-wide, this production rate gives 0.1 x 10^{12} g NH_3-N/yr from the oceans to the atmosphere. If this value is close to the actual value, then it is an order of magnitude less than the value estimated for natural, unfertilized soil.

2.2.1.2 NH_3-Losses to the Atmosphere from Fertilized Soils

To increase agricultural yields, fields are fertilized with large quantities of nitrogen-containing substances. In intensive cultivation, sometimes several 100 kg N-fertilizers per year per hectare are consumed in order to increase the N-content of the soil. Basically two types of fertilizer are used: Mineral fertilizers and natural fertilizers. In the chemical and biological conversions of the fertilizer on and in the soil, ammonium ions can be formed as under natural conditions; this causes an ammonia vapor pressure via a solution. The conversions in the soil described in sec. 2.2.1.1 are thus intensified by a larger reservoir of nitrogen-containing nutrients.

2.2.1.2.1 Mineral Fertilizers

Mineral fertilizers are inorganic substances containing essential nutrients and manufactured by the chemical industry for fertilization. Urea is also counted as a mineral fertilizer since it is also produced artificially and used like other mineral fertilizers. The liberation of ammonia depends mainly on the chemical and physical parameters of the soil. The pH-value proved to be an important characteristic, since the NH_3-equilibrium concentration increases via a solution with increasing pH-value. Thus, no NH_3-losses from acid soils were found (Gerritsen and de Hoop, 1957; Kresge and Satchell, 1959), whereas with increasing pH-value, vaporization of up to 87% of the fertilizer nitrogen occurred (Jewitt, 1942). Increasing temperatures caused a similar increase in NH_3-losses (Fenn and Kissel, 1974; Allison, 1955). The losses were reduced through a larger water content of the soil (Musa, 1968), since the soil solution was diluted and soil ventilation reduced. Thus, the length of time between fertilizer application to the soil and the next rainfall has a great influence on the fertilizer action (Förster and Lippold, 1975). The shorter this time, the smaller the losses (fig. 2.14), since the fertilizers were moved by the rain down from the surface into deeper soil layers where the NH_3 vaporization was less probable. Similarly, NH_3-losses are reduced if the fertilizers are not applied directly to the soil surface, but some centimeters below the surface. A smaller vaporization rate can also be attained by using larger, instead of smaller, urea granules, due to the smaller surface-volume relation (Nommik, 1973a).

In tables 2.6 and 2.7, experimental determinations of NH_3-losses are presented for mineral fertilizers and artificial urea. Urea investigations are presented separately since urea is used in the FRG to a much smaller extent than mineral fertilizers (about 2% of N-fertilizers applied in the FRG).

From the data given in the tables it is hardly possible to draw conclusions about the generally-valid nitrogen fraction which gets into the atmosphere after application of mineral fertilizers and urea. Laboratory measurements can only show whether NH_3-losses are possible, since the natural conditions in the field cannot be reproduced. In measurements in the field there is the difficulty of judging how representative they are. Nonetheless, we shall attempt to quantify the general loss of fertilizer nitrogen as ammonia. The pH-value of agricultural soils lies normally at 6 to 7. Since in middle latitudes where most of the N-fertilizer is consumed, there is rainfall on the average every 2 to 3 days, about 5% of the urea fertilizer is lost an NH_3 (Förster and Lippold, 1975). Based on this information, the NH_3-losses are assumed to be 5 - 10% of the applied fertilizer nitrogen. World-wide between 1950 and 1977, ca. 24×10^{12} g nitrogen per year has been consumed of mineral fertilizers (UNO, 1976). The NH_3-N losses according to the above estimations lie at $1.2 - 2.4 \times 10^{12}$ g NH_3-N/yr. Figure 2.15 shows the zonal distribution of this source in 5^{o} intervals. The figure shows that the predominant part of the N-fertilizer is consumed in the intensively cultivated medium latitudes of the Northern hemisphere. Thus, in these zones, the greater quantity of NH_3-N is lost to the atmosphere through vaporization of fertilizer.

2.2.1.2.2 Animal Fertilizers

Besides mineral fertilizers and urea, the excrement of cattle, sheep, pigs and other animals is used to fertilize soil. In the excrement, the nitrogen is present in hard-to-unlock protein compounds, thus it is difficult for bacteria to break it down (Gisiger, 1968). But in urine, 83% of the nitrogen is bound to the easily decomposed urea and 5% to ammonia (Mangold, 1929).

55% of the nitrogen excreted by domestic animals is bound in the feces, according to Gisiger (1968), 45% in urine. A part of this nitrogen is lost to the atmosphere in the form of ammonia. Urea can be converted into ammonia and carbon dioxide by an enzyme reaction (Gisiger, 1968).

$$(NH_2)_2 CO + H_2O \rightarrow 2 NH_3 + CO_2$$

Under anaerobic conditions, a considerable part of the nitrogen in barnyard fertilizer is converted into ammonium carbonate. The formed ammonium carbonate is stable in a CO_2-excess, but otherwise breaks down into NH_3 and CO_2 (Roemer - Scheffer, 1959). Ammonia from excrement is given off to the atmosphere in animal stalls, during storage and after application onto the field. Buchner and Sturm (1973) assume total NH_3 losses of 45% from urine and feces in their nitrogen balance for Germany: 3% vaporization in the stall, 32% during storage and 10% on the field.

Losses of ammonia from animal fertilizers were determined both in the laboratory and in field tests in the stall, during storage, on the field and pasture.

Hall (1915) measured N-losses from animal excrement in stalls. For horses and cattle, the losses are between 25 and 35%, for feeder sheep it is even ca. 55%. Hall assumed that the nitrogen is released to the atmosphere primarily as ammonia. According to Lauer et al. (1976), 85% of the ammonia nitrogen from animal excrement is lost to the atmosphere.

In laboratory experiments with temperatures between 5 and 23 °C, vaporization losses of 1.8 - 34% of the applied N is lost as NH_3-N (Doak, 1952). The losses increase with rising temperature. From slightly dilute liquid manure--a mixture of feces and urine, a little dust and a lot of water (Roemer-Scheffer, 1959), up to 33% of the nitrogen vaporizes as ammonia. Watson and Lapins (1969) obtained different NH_3-losses from soils, depending on whether they were vegetated or not. On vegetated soild, 31 - 45% of the N vaporized as NH_3, from barren soils, 47 - 74%. In winter, the losses were less than in summer. Conseqeuntly, plant growth and low temperatures seem to prevent NH_3-losses to the atmosphere.

Denmead et al. (1976) gave the NH_3-flux from a sheep pasture to the atmosphere at 13 g NH_3/hectare/hour. This value was measured on a 4 hectare pasture holding 90 sheep. It corresponds to NH_3-losses of 25 to 50% of the excreted nitrogen, if ground sources are neglected. McGarity and Rajaratman (1973) conducted measurements of NH_3-N losses with a chamber on the pasture. After 6 days, 7% of the urine nitrogen had vaporized as ammonia. MacDiarmid and Watkin (1972) measured the NH_3-N losses from cow dung: After 13 days, the nitrogen content of the dung was reduced by 5%, with the nitrogen being lost mainly as ammonia.

Söderlund and Svensson (1976) estimate the fraction of nitrogen given off to the atmosphere from excrement as NH_3-N at 10-50%.

The N-losses as NH_3 to the atmosphere from the metabolic products of domestic animals are assumed in this report to be 30%. This value should include losses in the stall, during storage, on the field and pasture, under consideration of temperature and plant growth. The value is not an average from the above figures, but rather an attempt to extrapolate the above information world-wide.

To calculate the total N-quantity lost to the atmosphere annually as NH_3 from the metabolic products of animals, in addition to the percentate N-loss, the quantity of N excreted per animal and the total number of animals need to be known.

In tables 2.8 and 2.9, the daily excreted nitrogen quantities for domestic animals are summarized for middle latitudes and tropical regions. The nitrogen content in tropical regions had to be estimated separately since the animals in these regions have a lower weight and they thus excrete less excrement (Festerling, 1968; Steinbach, 1978) and thus less nitrogen. Whereas information on animal weights by different authors for middle latitudes has only little variation, for tropical zones, the differences are considerable. In estimation I (See table 2.9), the daily excreted N-quantity is computed directly from the live weight LM [in kg] of the animals and an additional factor K by the empiric formula:

$$A = K \times LM^{0.75} \qquad \text{(Steinbach, 1978)}$$

The values of estimation II (see table 2.9) are based on excrement quantities and the percentage nitrogen in this exrement.

For an estimation of the NH_3-quantities released annually to the atmosphere from the metabolic products of domestic animals, the following quantities were assumed:

Cattle	170 - 250 g N/day
Sheep	20 - 40 g N/day
Pigs	20 - 30 g N/day

In order to account for the smaller weight of animals in the tropics, the N-content of cattle excrement between 30° North and 30° South latitude was assumed as 80 - 120 g N/day-animal. The number of animals in the world was taken from the Statistics Annual of the UNO (1976). An average value was used for the years 1950 to 1977, since the data on the NH_3-sinks also includes this period (sec. 4-6). It is assumed that on the average in the period between 1950 and 1976, 1080 x 10^6 cattle, 1012 x 10^6 sheep and 575 x 10^6 pigs were on the earth.

With these values on the numbers of animals, the per-animal excreted nitrogen quantities and an assumed NH_3-N loss of 30% of the total nitrogen quantity, the following annual amounts are given off to the atmosphere:

by cattle	14.4 - 21.3 x 10^{12} g NH_3-N/yr
by sheep	2.2 - 4.4 "
by pigs	1.3 - 1.9 "

The remaining animals are included by a factor of 10% of the above value, since they excrete much less N.

World-wide, according to this estimation, 19.7 - 30.4 x 10^{12} g NH_3-N/yr is given off to the atmosphere. This source is thus about 20-30 times greater than the NH_3-losses from mineral fertilizer, according to this study. Figure 2.16 shows the zonal distribution of this source. The distribution was computed from the number of animals in the individual countries (UNO, 1976).

2.2.2 Combustion of Fossil Fuels

Even in the combustion of fossil fuels, ammonia can be released into the atmosphere.

Before the Haber-Bosch method for production of ammonia was developed, coking plants were the main source for industrially produced ammonia. 15-20% of the nitrogen of coked coal, or about 2.8 kg/t, is present as NH_3 in the coking gas (Powell, 1945). The coking gas does not get into the atmosphere, but is used and burned. Freyer (1978) measured the NH_3-emission in the combustion of hard coal as 12 g NH_3-N/t. At an average consumption of 21 x 10^8 t hard coal per year (derived from UNO, 1976), 0.026 x 10^{12} g NH_3-N/yr is given off to the atmosphere. Thus, this source is about 100 times smaller than the release of NH_3 from animal excrement.

The emission factor for ammonia in the combustion of soft coal was measured as 6 - 9 g NH_3-N/t (Freyer, 1978). According to these values, at an average soft coal consumption of 8 x 10^8 t/yr (derived from UNO, 1976), 0.005 - 0.008 x 10^{12} g NH_3-N/yr is emitted. This quantity is about 300 times less than the release of NH_3-N from animal metabolic products.

The NH_3-N quantities released to the atmosphere in the burning of hard and soft coal are ca. 200 times less than the emitted NO_x-N quantities over the same period. Assuming that at least 100 times more NO_x-N as NH_3-N gets into the atmosphere in the combustion of fossil fuels, then ca. 0.1 x 10^{12} g NH_3-N/yr is emitted by this source. This source is at least 100 times less than the NH_3-N quantities evaporating from the metabolic products of animals, according to these results.

2.2.3 Automobile Exhausts

Harkins and Nicksic (1967) found 1 - 6 ppm NH_3 in automobile exhausts. Thus, about 25 mg NH_3-N/driven km is emitted, and globally 0.2 - 0.3 x 10^{12} g NH_3-N/yr assuming 15,000 - 20,000 km/vehicle and a world total of 27.2 x 10^7 vehicles (derived from UNO, 1976). This amount is very low world-wide. It is about 100 times less than the production from animals.

2.2.4 Summary of NH_3-Sources

In table 2.10 the NH_3-sources are summarized. The sum of the given sources is 22 - 35 x 10^{12} g NH_3-N/yr. These values are far below the estimations of Robinson and Robbins (1970b, 1975). They give the NH3-N sources as 955 x 10^{12} g N/yr. These authors do not determine the sources directly, but compute them from their NH_3-balance.

In this estimation, domestic animals are the main source for atmospheric ammonia, and cattle provide the greatest share of this. This result agrees with the ammonia balance prepared by Healy et al. (1970) for England.

The distribution of NH_3-N sources between Northern and Southern hemisphere seems to be more extreme from this work, than the NO_x-N; 4/5 of the NH_3-N is emitted on the Northern hemisphere (tab. 2.10).

3. Analysis Results for an Estimation of Deposited NO_3^- and NH_4^+-N Quantities

After the type and size of sources of atmospheric NO_x-nitrogen and NH_3-nitrogen had been estimated, we had to find those sinks which will absorb them.

The first sink is the total deposition on the soil. By this, we mean the deposited amount of a trace substance deposited in rain collection vessels during dry and rainy periods. Thus, it includes not only the quantity contained in the rainwater, but also the amount which gets into the vessels through dry deposition of aerosols and gases. In spite of this, measurements of total deposition are often discussed as rain analyses. Only in a very few studies (Eriksson, 1957; Gambell and Fisher, 1964; Junge, 1958; Larson and Hettick, 1956; Weinmann, 1955; Wetselaar and Hutton, 1963; Wolaver and Lieth, 1972) are the quantities deposited exclusively in the rainwater determined. Below, total deposition and precipitation, which also includes the dry fraction, are used synonymously. If the discussion is about rain analyses or rain samples, then reference is made only to the rainwater itself, the wet precipitation.

Ammonium ions can get into rainwater through incorporation of ammonia-containing aerosols and by absorption of gaseous ammonia.

Since the ammonium in the aerosol is also formed of gaseous ammonia, the ammonium quantity in the rain represents a part of the ammonia emitted into the atmosphere. Other atmospheric sources for the ammonium found in the rainwater are unknown.

The nitrate ion can get into rainwater through incorporation of aerosol nitrate and by absorption of gaseous nitric acid (HNO_3). In addition, it is possible that NO, NO_2 and PAN (Peroxy acetyl nitrate) absorbed in the water, are detected as nitrate. Since the aerosol nitrate and gaseous nitric acid were formed from gaseous NO, NO_2, the nitrate quantity found in the rainwater indicates a decomposition product of NO and NO_2 present in the atmosphere. Other atmospheric sources for nitrate in rainwater are unknown.

For an estimation of the ammonium and nitrate deposited on both hemispheres, precipitation analyses from the period from 1950 to 1977 were used. An intensive literature survey was performed to find all information on concentrations in rain and deposited quantities and to integrate this into a common picture. But the available data had to be examined for its method of collection and analysis and type of preservation.

To evaluate correctly the data on atmospheric measurements solely based on knowledge of published information is a difficult undertaking.

3.1 Chemical Analysis

Nitrate and ammonium ions are detected by several different methods whose general principles will be described briefly. In the individual investigations, various modifications of these methods were used, but the details cannot be reported here. A subsequent evaluation of the chemical analyses is very difficult. Even the effects of any cross-sensitivity (e.g. Taras, 1958) in atmospheric samples can hardly be evaluated. The derived deposition values do show a useful spatial distribution which will be discussed below. In spite of skepticism toward measurements of trace substances in atmospheric samples--this skepticism is based on our own experiences--the analysis results were not discarded.

3.1.1 Nitrate Detection Method

For a chemical detection of nitrate in rain, four photometric and one polarographic method was used.

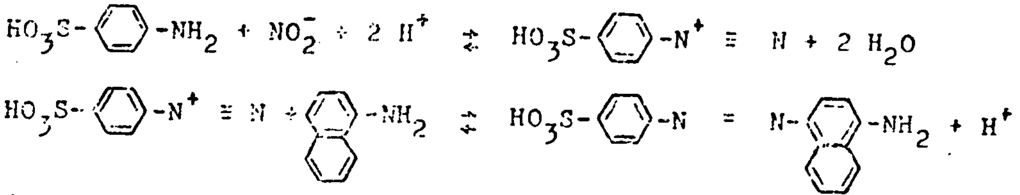
3.1.1.1 Reduction

Nitrate is reduced and then detected in a precipitate as ammonium or nitrite.

Devardas alloy is an often-used reducing agent which consists of an aluminum-copper-zinc alloy (Böttger, 1925). In alkaline solution, it will reduce nitrate via hydrogen, to ammonium (Ohlmüller and Spitta, 1931), which is then detected (see sec. 3.1.2).

The reduction to nitrite occurs with soda lye and powdered zinc (Freier, 1964) or with alkaline copper sulfate and hydrazine sulfate solution (Kamphake and Hannak, 1967) or with cadmium (Technicon, 1974/76). The formed NO_2^- is then detected with the Griess reaction.

The reactions causing the dissociation of sulfaniline acid and the bonding with 1-naphthylamine can be represented as follows:



(Taras, 1958)

In acid solution, nitrite reacts with a primary aromatic amine to form a diazonium salt. The salt, when treated with an aromatic component, then acts on amino- or hydroxy-substituents and forms an azo-dye which can be measured photometrically.

3.1.1.2 Brucine Method

Nitrate reacts with brucine in sulfuric acid medium and forms a red color which can turn yellow over time (e.g. Taras, 1958).

3.1.1.3 Phenol Disulfonic Acid Method

Phenol disulfonic acid forms a dye with ammonium hydroxide and nitrate which has its maximum absorption at 410 nm (e.g. Taras, 1958).

3.1.1.4 Polarographic Detection Method

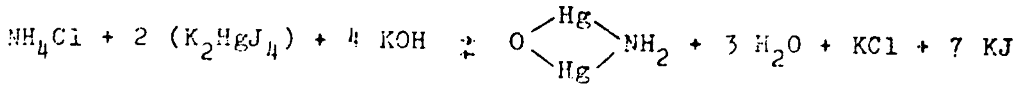
This method was used in rain analysis only in Czechoslovakia (Macku et al., 1959 a, b). It is inferior to the other methods since its lower detection limit lies at the upper limit of atmospheric concentrations. The trace substances to be analyzed must then be concentrated before the analysis.

3.1.2 Ammonium Detection Method

Ammonium ions are detected in rain analyses by two methods: With Nessler's reagent and with the Berthelot reaction.

3.1.2.1 Nessler's Reagent

Nessler's reagent (Nessler, 1856) is an alkaline solution of potassium-mercury-4-iodide (K_2HgI_4), which gives a red-brown precipitate with ammonium, or at very low NH_4^+ concentrations, a reddish-brown color. The precipitate or color is generated as follows:



$$NH_4Cl + 2\ (K_2HgJ_4) + 4\ KOH \rightleftharpoons O\begin{smallmatrix}\diagup Hg \diagdown \\ \diagdown Hg \diagup\end{smallmatrix}NH_2 + 3\ H_2O + KCl + 7\ KJ$$

(Böttger, 1925; Teichert and Greifenhagen, 1954)

The precipitate or color formation of this reaction is not an actual colorimetric method, but colloids are formed. Temperature, time, pH, purity of used chemicals and the nature of the reagents affect the color formation (Taras, 1958). Nessler's reagent is sensitive to organic substances which are always contained in the precipitation. Teichert and Greifenhagen (1954) thus drive the ammonium out of the solution by adding sodium carbonate. The driven ammonia is captured in an acid solution and then detected with Nessler's reagent. The organic substances remain in the first solution. This method is used frequently.

3.1.2.2 Berthelot Reaction

Berthelot discovered a color reaction of ammonia in 1859. Ammonium ions react with phenol and an active halogen compound to form an intense, blue dye. The conversion of the ammonium ions into the indophenol complex probably proceeds as follows (Weichselbaus et al., 1969):

$$Na_2\,[Fe\,(CN_5)\,NO] + NaOH \rightleftharpoons Na_4\,[Fe\,(CN)_5\,ONO] + H_2O$$

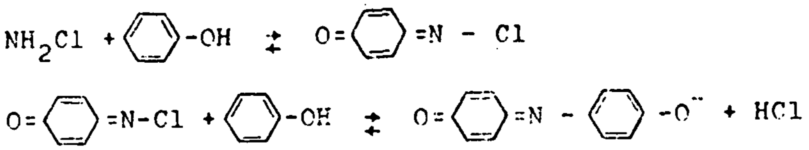
Disodium pentacyanonitrosyl ferrate and soda lye form a catalyst and water.

Since the reactions proceed in an alkaline medium, we have:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

$$NH_3 + OCl^- \overset{\text{Catalyst}}{\rightleftharpoons} NH_2Cl + OH^-$$

The resulting ammonia reacts with hypochlorite under the action of the catalyst (see above).



The reaction of NH_2Cl with two phenol molecules then gives the indophenol complex.

The central nitrogen atom comes from the ammonium ion. Weichselbaum et al. (1969) write that the reaction equations do not fully reproduce the Berthelot reaction. But the action and proportionalities of the ammonium concentration with the color formation are important.

3.1.3 Valuation of the Analysis Methods

In the used methods for nitrate and ammonium detection, two basic problems occur:

1. For each method there is a number of special "cooking regulations" which were partly worked out by the individual laboratories. Thus, their applicability to atmospheric samples cannot be checked. Often, the exact procedures are not reported. The applicability depends on the used chemicals as well.
2. The matrix of examined deposition samples have unknown composition. Above all, the organic constituents are unknown. Some examples:

1. Devardas alloy can reduce NO_3^- and organic compounds to ammonium.

2. The Brucine method for NO_3^- analysis is cross-sensitive to chloride.

3. The Nessler reaction for NH_4^+ detection is cross-sensitive to organic N-compounds. Thus, before the analysis the solution is often distilled over to separate the organic from the inorganic components. The type and manner and duration of distillation determine whether or not organic compounds are distilled over with the NH_4^+.

Due to the used method of analysis alone, those investigations were omitted in which no distillation was used for the Nessler detection of ammonia (Leland, 1952; Drover and Barrett-Lennard, 1956; Herman and Gorham, 1957; Georgii and Weber, 1960; Georgii, 1965; Holden, 1966; Nucciotti and Rossi, 1968).

This small number of discarded studies due to the used method of analysis seems quite optimistic on the basis of comparison measurements initiated by the World Organization for Meteorology (WMO, 1976). Four synthetic rain samples of various concentrations were produced by the National Bureau of Standards (NBS) and sent to 25 laboratories. They were examined for ammonium and nitrate by various colorimetric methods. In the report of the WMO (1976) it was found that poor agreement prevailed between the individual laboratory analyses and the NBS vlaues, and for nitrate analysis a certain agreement was found only at the highest concentration. The size of the deviations was not given, however. But it can be assumed that at low concentrations(< 0.05 μg NH_4^+-N or NO_3^--N/ml) the deviations are greater than at higher concentrations. But rain with low concentrations contributesrelatively little to the total deposition compared to rain with higher concentrations, so that the error for nitrogen components removed from the atmosphere by total deposition is probably not so great as indicated by the comparison of the WMO.

3.1.4 Frequency of the Used Analysis Methods

In table 3.1 the various detection methods and frequency of their use are listed. The reduction methods are used frequently for nitrate detection. The Griess reaction and polarography are seldom used.

Ammonium was determined almost exclusively with Nessler's reagent. 6% of the NH_4^+ analyses were performed with Nessler's reagent without distillation. These results were not taken into account since they are significantly higher than the values with distillation.

A part of the stations of the WMO Background Air Pollution Monitoring Network (BAPMoN, 1975/76) cites only "colorimetric" as analysis method. Since no conclusion of a specific method can be made, these results are presented separately.

3.2 Sampling

Samples of precipitation to be examined for their content of atmospheric trace substances, can be collected by two different methods:

1. The collection device is exposed only to rain; in dry periods it is closed with a cover. With this device, the nitrogen quantity deposited directly with the rain can be determined.

2. This device collects both during rainy and dry times. Besides the quantity deposited directly with the precipitation, the dry

deposited aerosols and gases absorbed at the collector are taken into account. With this device, the total deposition is measured. The dry deposition will not correspond to real conditions, since the surface nature of the collector does not correspond to the natural conditions (see sec. 3.). Galloway and Likens (1978) have investigated the differences for NH_4^+ and NO_3^- between total deposition and direct precipitation deposition by comparing measured results of collectors type 1 and 2 (see above). They define:

$$R = \frac{\text{monthly total deposition}}{\text{monthly direct rain deposition}}$$

For $R > 1$ we have: Dry deposition has occurred or wet deposited material has been lost. $R = 1$: There was no dry deposition. If $R < 1$, then the dry deposited material has reduced the measurable components or material has been lost from the total precipitation collector.

Figure 3.1 shows their results. For both substances, increased values result for the total deposition. The annual average total deposition values were increased by ca. 20% for NO_3^- and ca. 30% for NH_4^+. The dry deposition of aerosols and absorption of gases thus provide an important contribution to the settling of N-components, even though gas absorption is not fully taken into account.

In addition, it seems unlikely that the used collection vessels equal the real, natural interface between ground and atmosphere, and thus the direct deposition of gases and aerosols in these vessels does not represent the deposition rates on barren and vegetative soils, on plants and water areas. The resulting corrections must be estimated however.

The dry deposited quantities of trace substance on a vegetated surface can be determined for natural conditions in two different ways:

1. Above the top of a tree, the total precipitation deposition is less than the sum of deposited quantities in the precipitation below the top of the tree and in the branches. This additional quantity can be washed off leaves. But it can also represent the trace substance filtered out of the atmosphere by vegetation and then washed off by rain. Only field measurements could show that about 20 - 30% of the N-components removed from the atmosphere by total deposition are filtered out through the forest (Mayer and Ulrich, 1975; Ulrich, 1978). These values were measured in Solling (Central Europe, 140 km East of the Ruhr Valley) in a cohesive forest area under clumps of trees. Certainly they apply only for forested areas of similar precipitation characteristics. This small difference can be taken into account in a comparison of sources and total deposition as an additional sink.

2. For an ecosystem, a conclusion can be drawn about vegetation filtration from the difference in feed through total deposition, accumulation in the system and the quantities transported off in the surface water. In the analysis of trace substance fluxes in the Hubbard Brook Experimental Forest, New Hampshire, for SO_2 there resulted a deposition rate (Garland, 1977) considered reasonable if a deposition rate for sulfate of 0.1 cm/sec is assumed (Eaton et al., 1978). This value for SO_4^{--} under natural conditions agrees with results measured with a conventional collector (Koch, 1978).

Both examples show that the deposited quantities measured with the standard collectors come close to the trace quantities removed from the atmosphere by a natural, larger stand of trees. Within the frame of the existing uncertainties, they can be considered to be approximately the total deposition rates. Individual trees or groups of trees, hedges or bushes are more effective at removing trace substances from the atmosphere than larger, cohesive forests, since the transport of substances to the plants is not affected by other plants. At this time it is premature to give quantitative data on these additional trace substance sinks. But it is possible to draw a conclusion about the extent of this filtering effect from a comparison of known sources and sinks.

Galloway and Likens (1978) have also investigated the differences in collection efficiency of six total precipitation collectors having a 149 m^2 surface area. For 15 deposition measurements, the individual samples of the 6 collectors were analyzed. The variation in sampling (the quotient of standard deviation and average value) thus also includes that of the chemical analysis. For the sampling, the variation of NO_3^- was ca. 6%, for NH_4^+, ca. 15% according to the results of Galloway and Likens (1978). The variation of the chemical analyses was included with 1% for NO_3^- and 2% for NH_4^+.

In order to be able to determine the deposited quantities, the spatial variation of precipitation must be known. The spatial variation is practically the variation in collection efficiency on a large area. The collectors are distributed over a larger region, then as above, the variation determined: Galloway and Likens (1978) distributed 3 collectors over a region of 20 km^2. They computed from 12 rainfalls, variations for NO_3^- of 9% and for NH_4^+ of 13%. They are not significantly greater than the variations of sampling.

Granat (1976) distributed ∿ 50 collectors in Scandinavia over an area of 7600 km^2. From 7 rainfalls, variations of 32% result for NO_3^- and 87% for NH_4^+. The larger the areas under consideration, the larger the influences due to the variation of meteorologic parameters and the geographic distribution of the sources.

In spite of certain reservations due to these comparisons and error estimations, the obtained data from the collectors will be set in a meaningful relation to the atmospheric sources and other sinks for nitrogen-containing trace substances.

3.3 Storage of the Samples

If rainfall samples are stored, nitrogen compounds can be converted by biologic processes. Microbiologically active bacteria, fungii, algae can ammonify, nitrify, denitrify and change the chemical composition of rain samples. These biologic activities are intensified by two external factors: light and heat.

We distinguish between two types of storage:

1. Storage in collection vessels, if collection extends over a longer period. The samples of the European Atmospheric Chemistry Network stay in the collector for up to one month because monthly samples are collected (Egner et al., 1955). In order to protect these samples against changes caused by biologic activities, the samples have added reagents or acids.

2. The storage after sampling in the laboratory is usually done in the absence of light and at temperatures just above freezing. Galloway and Likens (1978) have investigated possible changes in concentrations during this storage. They used samples from winter for their tests; thus probably less biologic activity was in the rainwater.

At room temperatures with and without light, the samples showed no changes over 7 months. Only the samples frozen at -10 °C exhibited a decrease in NH_4^+ concentration from 0.12 µg/ml to 0.02 µg/ml .

Galloway (1975) finds no differences in the chemical composition of precipitation samples stored at 21 °C, 4 °C and -4 °C. He attributes this to the low pH-value of the samples of < 4.5.

The deposition data used in this investigation came from samples stored not longer than one month in the collector vessel or laboratory. It is assumed that the changes due to biologic activities are relatively small and the chemical composition of the rain samples is not affected too much.

3.4 valuation of Analyses, Sampling, Storage

The discussion of collection methods, of storage and analysis methods has shown that difficulties can occur in all steps.

The measured data cannot be interpreted as if they corresponded to real conditions. Studies with apparent inconsistencies were omitted of course, but the quality of the individual, used data is uncertain. Nonetheless, there resulted a useful, spatial distribution of deposition rates once the data of individual stations was entered on a geographic map of the Northern hemisphere. In geographically neighboring regions with similar air chemistry and meteorologic conditions, nearly equal deposition rates were measured (see sec. 3.8). This was taken as an indication that in spite of all possible differences in the individual measurements, comparable results were obtained.

Regions with few deposition measurements presented a special problem. The tropics covers about 40% of the earth's surface, but only about 5% of the stations are in this area. The measured-value comparison with neighboring stations is only conditionally possible. In addition, in these regions, measurements are taken under extreme conditions: During sampling, insects can contaminate the sample. The increased temperatures prevailing there promote the biologic conversion of the sample. In addition, higher concentrations of organic material can occur in the sample. These three difficulties were observed in precipitation samples collected by members of the "Mt. Kenya Baseline Air Pollution Station Projects" and analyzed at the Institute for Atmospheric Chemistry of the Nuclear Research Center, Jülich. The deposition data in the tropics are thus taken with more reservations than for middle and higher latitudes. In spite of these reservations, it can be assumed that extreme errors in individual investigations will not be so noticable in the size of the total deposition, since in this report at least 5 times more analysis results were used (500 measuring locations) than in previous estimations.

3.5 Evaluation of Literature Data

In the literature, the analysis results are published in various ways, depending on what factors gave rise to the investigations. In order to determine the nitrogen balance of an ecosystem, the deposited quantities per year are given (e.g. Borman et al., 1968). Somewhat more detailed data are presented by the European Atmospheric Chemistry Network (EACN). The rain quantities and their content of nitrate and ammonium-nitrogen are published on the basis of monthly samples. Sometimes, the results of the investigations of individual precipitations are given over longer periods (Visser, 1961) like the values for Mount Vernon in Iowa (see sec. 14.4). If possible, the deposited quantities D_g of a year were computed from the data of individual rainfall or monthly values.

$$D_g = \Sigma P_i \times K_i$$

P_i = the precipitation quantity of a single rainfall or the monthly sample in l/m^2.

K_i = the concentration in mg/l in the rain P_i.

The average concentration $\bar{K}$ of a year is then:

$$\bar{K} = \frac{D_g}{\Sigma P_i}$$

From the product of the arithmetic mean of the single concentration and the annual amount of precipitation, the deposited quantity of trace substance cannot be calculated, since the precipitation P_i and the concentrations K_i are correlated. Average trace concentrations in the rain which were not computed from concentrations which were weighted with the particular rain quantity (BAPMoN, 1976/77; Georgii, 1960), lead to irreal deposition rates. The differences between weighted and unweighted average annual concentrations are sometimes twice as large as the weighted values. From table 3.2 for the presented stations, we see that the unweighted concentrations are larger on the average by a factor of 1.3.

In this report, the deposition rates are computed from individual rainfall or monthly data. The cited concentration values were weighted with the particular precipitation values. Only the data for the oceans is based on individual, unweighted concentrations, since there is no better data available.

3.6 Geographic and Chronological Distribution of Rainfall Analyses

3.6.1 Chronological Distribution of the Analyses

Figure 3.2 shows the number of places where precipitation analyses were performed in individual years between 1950 and 1977. First, we take the locations on the Northern hemisphere, since only a few investigations were performed on the Southern hemisphere.

3.6.2 Spatial Distribution of Measurement Sites

The geographic location of the measurement positions is another reason for considering the data from the years 1950 to 1977. For a shorter time it is not possible to cover the Northern hemisphere with sufficient measurements of multi-year averages in order to begin an estimation of the deposited quantities. Figure 3.3 shows the geographic position of the stations. In Europe and North America, the individual stations were not marked, but only their number is given. The stations on the oceans are the positions of research ships collecting rain samples (Tsunogai, 1971; Gravenhorst, 1975). They cannot be assigned the same predictive force as the land values, since they are the results of individual samples and are not multi-year averages. Only the value for 8°30' W is based on an average of 104 samples collected from 6/28 - 9/14/74 during GATE (GARP Atlantic Tropical Experiment; GARP: Global Atmospheric Research Program; Gravenhorst, 1975). Possible seasonal fluctuations could not be taken into account in all ocean values. In fig. 3.4, the zonal distribution of stations is presented. They illustrate the lack of data in tropical areas, whereas the middle latitudes are much better represented.

3.7 Our Measurements

Due to insufficient data, we sent some of our own total-precipitation collectors into various regions. For example, rainwater samples were collected in Bermuda, Kenya, Elba island (Italy), Southwest France and in Austria. various snow samples from the South Pole were examined. With this additional data, the literature values were supplemented (table 3.3).

3.8 Differences in Nitrogen Quantities removed from the Atmosphere via Total Deposition in Cities and Rural Areas

The majority of measuring stations where total precipitation samples were collected and whose analysis results were used in this report, are in rural areas and not in the immediate vicinity of cities. Thus, potentially higher deposition rates at locations near the sources of atmospheric NO_x and NH_3 might not be taken into account on a representative basis in this report.

There was no difference in ammonia between rural and city areas, although the sources are almost exclusively in rural regions. A study by Koch (1978) also shows this; he measured the differences in deposition rates of NH_4^+ in Deuselbach (Hunsrück) and in the botanical gardens of Frankfurt/Main for one year. Whereas the weighted average concentrations of NH_4^+ in the rain water were equal, in the botanical garders, an additional 150 mg NH_4^+-N/m^2-year and in Deuselbach 120 mg NH_4^+-N/m^2-yr were dry deposited. According to these results, the difference between the total NH_4^+ deposition rates (the sum of precipitation and dry deposition) in Frankfurt and Deuselbach is about 30 mg NH_4^+-N/m^2-yr, if equal amounts of rain fell at both places. This difference of 30 mg NH_4^+-N/m^2-yr makes up at most 10% of the total NH_4^+ deposition rate in the FRG. Since the annual variation of total deposition rates is often 30% and more, the results of Koch (1978) show that the differences in total NH_4^+ deposition rates between cities and rural areas is less than the annual variations and thus of lesser significance.

Unfortunately, these investigations did not include nitrate. A comparison of NO_3^- total deposition rates measured at various places in the FRG (fig. 3.5), shows that these values too, lie close together. Thus, for NO_3^- too, the difference between total deposition rates measured in cities and rural regions seem to be of lesser importance.

These suppositions are confirmed by studies by Georgii (1965, 1966). In 1960 in Frankfurt/Main, NO_3^- total precipitation concentrations of 0.63 μg NO_3^--N/ml were measured. On the Small Tower in Taunus, an average 0.59 μg NO_3^--N/ml was measured at the same time (Georgii, 1965). On the Zugspitze Mountain [S. Germany], 0.18 μg NO_3^--N/ml was measured. Since average precipitation in Frankfurt is about 650 mm, at the Small Tower about 1000 mm and on the Zugspitze about 2200 mm, less NO_3^--N is deposited in Frankfurt than on the Small Tower or on the Zugspitze.

4. Estimation of the Nitrate and Ammonium Quantities Removed from the Atmosphere via Total Deposition on the Northern Hemisphere

In order to estimate the nitrogen quantities removed from the atmosphere by total deposition on the Northern hemisphere, precipitation analysis results of more than 500 different locations were used. Previously, to estimate the global deposited nitrogen by precipitation, analysis results were used which were measured mainly in Europe and North America. Tropical regions and the oceans were not taken into account separately. The geographically differing distribution rates do not permit omission of some areas in estimating

N-quantities deposited on the Northern hemisphere, while overestimating others. In order to equalize this geographically unrepresentative distribution of measuring stations, we tried to derive a synoptic picture of world-wide deposition rates from previously known studies. For this reason, analysis results of precipitation were collected from as many different places as possible where precipitation had been studied over several years (appendix data 1950-1977). With this data, average deposition rates, the quantities of nitrate and ammonium-nitrogen deposited per surface area per year through total deposition, were determined (see also sec. 3.5). After these deposition rates had been entered onto world maps in accord with their geographic coordinates, we tried to bring together regions of equal NO_3^- or NH_4^+ fluxes from the atmosphere to the earth by means of lines of constant deposition rates. For large areas of Asia, America and especially the oceans, there is no data on total precipitation analyses. But in order to get a deposition distribution for the entire Northern hemisphere, the isolines were extrapolated from regions with known deposition rates.

The following considerations were taken into account:

1. With increasing distance from source regions, the quantities of trace substance deposited on the earth decrease.

2. The atmospheric circulation determines the main transport direction of trace substances. The general wind directions were taken from a compilation by Trewartha (1968).

3. The quantity deposited in the rain increases with increasing level of precipitation (e.g. Georgii, 1965).

In South America, the lines of equal deposition rates were adapted to the contours of the northern part of the continent, with declining deposition quantities toward the North and toward the oceans. In the Asiatic part of the Soviet Union, the deposition rates are surely below those in the European part due to the lower precipitation and greater distance from the main sources. Southeast Asia, Japan--based on our measurements--and the heavy rainfall region near the equator, are characterized as regions with increased deposition rates. In arid regions of Africa and Near East, from assumed aerosol concentrations for NO_3^--N and NH_4^+-N of 0.1 $\mu gN/m^3$ and a deposition rate of 0.1 cm/sec, upper limits of dry deposition rates of about 3 mgN/m^2-yr are estimated and thus, the neighboring isolines are run accordingly. For the North Atlantic and Pacific, the rainwater analyses of Gravenhorst (1975) and Tsunogai (1971) were taken as base values; they showed a decrease in trace concentration in the rain with increasing distance from land. Under additional consideration of atmospheric transport conditions, a transition to maritime conditions was interpolated for the isolines from the continents. The lowest deposition rates over the oceans can be at about 5 mgN/m^2-yr for both NO_3^- and NH_4^+. But they were not included in the isoline presentation since the values are uncertain and no concrete indications of quantifiable data were available. Future measurements in this unresearched region can show how much reality agrees with the assumptions.

Previously, only for some regions were distribution maps of deposition rates of nitrate or ammonium-nitrogen published. Probably Emanuelsson et al. (1954) published the first maps with lines of constant deposition rates. They drew maps for Sweden. From the geographic distribution of nitrate and ammonium concentrations in the precipitation, as prepared by Junge (1958) for the USA, one each for Spring, Summer, Autumn and Winter, no accurate conclusions can be drawn about the deposited quantity or about the sources, since the attendant precipitation characteristic was omitted. Isoline presentations of deposition rates of N-components were drawn by Wolaver and Lieth (1972) for the USA, by Söderlund (1967a) for Northwest Europe. In this report for the first time, the deposition of nitrate and ammonium is presented for the entire Northern hemisphere in distribution maps. From these maps of deposition rates, integral deposition rates are derived, separated for land and ocean, in 5°-latitude intervals. The sum of these integrations gives the quantity deposited as total deposition.

4.1 Nitrate

Figure 4.1 shows the distribution map of the deposition rates for nitrate-nitrogen. The unit of the values is 100 mg N/m^2-yr $\hat{=}$ 1 kg N/hectare-yr. Thus, in Europe, North America and Japan with values over 300 mg N/m^2-yr, large quantities of NO_3^--N are removed from the atmosphere by total deposition. Also in tropical regions, the deposition rates are higher. The values in Africa are based on results of Mayer and Pampfer (1959), Nye (1961), Visser (1961, 1964), Jones and Bromfield (1970) and Jones 91971) (tab. 4.1). According to some concentration measurements in samples collected during 1977 in Kenya, the nitrate concentrations (about 0.1 μg NO_3^--N/ml) are 5 times less than given in the above papers. The reason may be that here only precipitation--or wet deposition--and not the total deposition was measured. Microbiologic processes probably did not change the samples, since samples treated with sulfuric acid show only slightly lower concentrations than the untreated ones. By adding acid to the rain samples, the bacteria can be killed; these could have caused changes in the chemical composition of the rainwater (see sec. 3.).

In the distribution maps (fig. 4.1), an average value is used. The line of 200 mg NO_3^--N/m^2 deposition per year was thus not placed farther to the North. The large values given in the literature could also be due to cross-sensitivity of organic substances.

In South America there are large differences between the data of Ungemach (anonymous, 1972) and Brinkmann (1977) (table 4.2). Since there is no indication for incorrect collection, storage or analysis, an average value was used for this region.

In the remaining areas, on oceans and the polar caps, the deposition rates are very low according to this map.

Figure 4.2 shows the zonal distributions of deposition rates over land and on the oceans. It was determined through integration of the distribution in fig. 4.1. On the abscissa, the sine of the latitude is plotted to represent the area distribution of the earth. In the tropics and middle latitudes, are the greatest deposition rates. On the oceans, they are 5-10 times less by comparison. The zonal dependence of deposition rates for NO_3^--N computed by Robinson and Robbins (1970b) from the data of Eriksson (1952), but without making a distinction between land and ocean, shows only one maximum in the middle latitudes. Their curve is doubled in tropical regions and in middle latitudes, it is three times as high as the values obtained in this report.

For the zonal distribution of average deposition rate, the deposition rates for land and ocean were weighted in accord with their respective areas in the individual latitude intervals. The error belt of the "land" curve shows the standard deviation of the deposition rates in the individual 5°-latitude intervals (see sec. 4.3).

Figure 4.3 shows the distribution of NO_3^--N concentrations in the total precipitation. In middle latitudes over land, an increase in concentration is found which explains the larger deposition rates. It is not caused by larger amounts of rainfall, as in the tropics. See also fig. 4.4 which shows the zonal distribution of rainfall over land and oceans according to Baumgartner and Reichel (1975).

The distribution of deposition rates was determined again by a second method. From an isoline presentation of the weighted nitrate-nitrogen concentrations in the total precipitation (fig. 4.5) and the average amount of precipitation (Baumgartner and Reichel, 1975), a second map with an isoline presentation of deposition rates was produced (fig. 4.6). These used quantities of precipitation are averages over several years, but which do not need to be representative for the period in which the trace concentrations were determined in the rain. The resulting map (fig. 4.6) shows the same pattern as in fig. 4.1.

The deposited quantity was computed from the weighted concentration and precipitation quantity at the particular site. Other concentration data were taken into account (e.g. Handa, 1969b), but no deposition rates could be calculated from it because the attendant precipitation rates were missing. This deposition distribution was also integrated in 5° latitude intervals. Figure 4.7 presents the zonal relations found from the map "Concentrations x average amount of precipitation", compared to those from the deposition map (fig. 4.1). Both curves show the same behavior for land and ocean: large values at both middle and tropical, continental latitudes. Although there must a great degree of freedom in the drawing of isolines of both distribution maps of the deposition rates, the results still agreed well. This is an indication that they are not unrealistic.

4.2 Ammonium

As for nitrate, also for ammonium, distribution maps of the deposition rates on the Northern hemisphere were drawn (fig. 4.8). According to these maps, in the USA, Europe, Japan and the tropical areas of South America and Africa, the greatest quantities are deposited (> 300 mg N/m^2 per year). The remaining areas and oceans have significantly lower deposition rates. The zonal distributions of deposition rates for land and oceans show this (fig. 4.9). They were determined through integration of the distribution in fig. 4.9. Here too, for a comparison, the zonal relationship of deposition rates of Robinson and Robbins (1970b) from Eriksson (1952) are included. It has the same profile as for nitrate. The deposition rates are higher by a factor of 1.5. The latitude dependence of Robinson and Robbins (1970b) has only one maximum in the middle latitudes. But the deposition rates in tropical latitudes are three times higher, and in middle latitudes, four times higher than those from the results of this work. The error belts give the standard deviation of the land deposition rates in the individual intervals (sec. 4.3). The higher deposition rates for ammonium, like nitrate, in the middle latitudes, are attributable to high concentrations in the total precipitation (fig. 4.10) and not to larger amounts of precipitation. The increased deposition rates in the tropics over land and oceans can be explained by the greater amounts of rain.

The deposition map was drawn for ammonium in another manner as well. From a map with the lines of equal precipitation concentration (fig. 4.11) and a precipitation distribution from Baumgartner and Reichel (1975), the map (fig. 4.12) was drawn. It shows the same pattern as the map drawn directly from the deposition rates of the individual measurement points (fig. 4.8). The comparison of zonal dependencies of deposition rates confirms this (fig. 4.13). The curves nearly coincide--except for deviations between 15° N and 30° N. Both distribution maps of the deposition rates for NH_4^+ (fig. 4.8 and 4.12) resulted, like those for nitrate, largely from different starting data. Nevertheless, they agree relatively well.

4.3 Fluctuations in Deposition Rates or Quantities

The fluctuations for the deposition rates of nitrate and ammonium nitrogen over land (fig. 4.2 and 4.9) and for the estimation of total deposited quantities (sec. 4.4) were calculated from the standard deviations σ_i from the multi-year average $\bar{x}_i$ of the deposition rates of each individual measuring station. The standard deviation σ_i of a station was computed from the measured annual averages $x_{j,i}$:

$$\sigma_i = \sqrt{\frac{\sum_{j=1}^{n_i} (x_{j,i} - \bar{x}_i)^2}{n_i\,(n_i-1)}}$$

n_i is the number of years in which precipitation analyses were performed at the particular station. Each standard deviation was assigned a weighting factor w_i which takes into account the relative size of the region. The sum of w_i is 1.

The standard deviation σ_i of the average deposition rate of a latitude interval or of the deposited quantity, is then calculated as follows:

$$\sigma = \sum_{i=1}^{n} w_i \sigma_i^2$$

n is the number of measuring stations in the latitude intervals or on the Northern hemisphere.

Measuring errors occurring in the determination of deposition rates were not included in the calculation of σ. σ gives the annual variation of deposition rates due to the changing meteorologic parameters and trace substance concentrations in the atmosphere.

4.4 Estimation of Annual Quantities Deposited in the Northern Hemisphere

An integration of the deposition rates based on isoline figures gives the quantities of NO_3^--N or NH_4^+-N removed from the atmosphere per year onto the Northern hemisphere by total deposition. Thus, $15 \pm 6 \times 10^{12}$ g NO_3^--N/yr results both from the deposition map (fig. 4.1) and from the map produced from the product of weighted concentration and average precipitation (fig. 4.6). About 5×10^{12} g NO_3^--N/yr (ca. 30%) of this quantity is deposited in the oceans. For ammonium-nitrogen, the integrations give $17 \pm 5 \times 10^{12}$ g NH_4^+-N/yr (fig. 4.8) or $19 \pm 6 \times 10^{12}$ g NH_4^+-N/yr (fig. 4.12), of this, $4.5 - 5 \times 10^{12}$ g NH_4^+-N/yr (ca. 25%) falls on the oceans. The results of the integrations for NO_3^--N and NH_4^+-N are not close together, although for both components, different sources are responsible.

A comparison with other estimations shows that the values calculated here are very low. In table 4.3 there are some literature values for comparison. Partly, the numbers were computed from global estimations, where it was assumed that of the world deposited quantities, 2/3 of the nitrate and 4/5 of the ammonium-nitrogen was deposited on the Northern hemisphere. These figures are based on the conditions of source strengths of NO_x-N and NH_3^--N between Northern and Southern hemisphere (see sec. 2).

The large results of other estimations can be explained by unrepresentative data, as used for instance, in the CAST report. Many estimations refer to Eriksson (1952) who compiled the precipitation analyses. He cites ca. 90 measuring stations where precipitation analyses had been made for several years between 1864 and 1947. These values related primarily to Europe and North America. But this caused the high deposition rates in these countries to be over-estimated. Robinson and Robbins (1968, 1970a, b, 1971, 1975) do not distinguish between land and oceans, although the deposition rates on the oceans is much less (see fig. 4.2 and 4.9).

4.5 Ratio of Deposition Rates of Ammonium and Nitrate-Nitrogen

From the ratio of deposition rates of ammonium and nitrate-nitrogen, it can be concluded that certain N-components predominate in the total deposition. Robinson and Robbins (1970b) give this ratio world-wide as 1.5:1. According to the results of this work, the ratio of NH_4^+-N : NO_3^--N on the Northern hemisphere is about 1.1:1. Figure 4.14 shows this ratio as a function of the geographic latitude. In middle latitudes, according to this figure, more ammonium nitrogen than nitrate nitrogen is removed from the atmosphere through total deposition, whereas South of 30° N, more nitrate nitrogen is deposited. This distribution seems realistic since the sources of atmospheric NO_x and NH_3 are different (see sec. 2) and thus also, the distributions of the quantities removed from the atmosphere are different.

5. Estimation of Nitrate and Ammonium Quantities Removed from the Atmosphere as Total Deposition

Although the precipitation on the Southern hemisphere has seldom been examined for nitrate and ammonium-nitrogen, in this section we shall attempt to draw conclusions about the quantity of nitrogen deposited on the Southern hemisphere.

In order to do this, two different methods are used: First, we try to estimate the deposited quantity from analysis data of the precipitation; second, we proceed from the known source strengths.

1) Isolines of deposition rates were extrapolated from the Northern hemisphere to the Southern. The little analysis data existing for the Southern hemisphere was taken into account (Ingham, 1950; Weinmann, 1955; Miller, 1955, 1963; Drover and Barrett-Lennard, 1956; Wilson, 1959a, b; Wilson and House, 1963; Wetselaar and Hutton 1963; BAPMoN, 1976, 1977; Parker et al., 1978) (fig. 5.1 and 5.2). After integration of these distribution maps, 5×10^{12} g NO_3^--N/yr on land and 2×10^{12} g NO_3^--N/yr on oceans is deposited as total precipitation. For ammonium nitrogen, the integration gives 6×10^{12} g NH_4^+-N/yr on land and 2×10^{12} g NH_4^+-N/yr on oceans. The deposited quantities on oceans were computed at a deposition rate of 10 mg N/m^2/yr for both NO_3^--N and NH_4^+-N.

2) It was assumed that both in the Northern and Southern hemispheres, the ratio of the sum of sources and of the quantities removed from the atmosphere are the same. The sources were estimated for the Southern and Northern hemispheres (sec. 2) and are thus available. Also, the deposited quantities for the Northern hemisphere are known. Thus, a deposited quantity for the Southern hemisphere can be calculated. With these assumptions, 8.5×10^{12} g NO_3^--N/yr and 3.5×10^{12} g NH_4^+-N/yr are deposited on the Southern hemisphere through total deposition.

If we also consider that even on the Northern hemisphere, less NO_3^--N and NH_4-N is deposited on the oceans than on the land, then we can draw conclusions about the distribution of this Southern hemisphere deposition on continents and seas. But the larger ocean areas and necessarily smaller deposition rates with increasing distance from land, must be taken into account. With these prerequisites, we can calculate about 5.5 x 10^{12} g NO_3^--N/yr on land and about 3 x 10^{12} g NO_3^--N/yr on the oceans; for ammonium, we have 2.3 x 10^{12} g NH_4^+-N/yr on land and 1.2 x 10^{12} g NH_4^+-N on the oceans.

The results of the two independent estimations agree fairly well; only the deposited NH_4^+-N quantities differ by a factor of 2.6. They show that these results can be realistic. But the isoline displays will have to be completed by more measurements.

6. Estimation of World-wide Deposited Nitrogen Quantities

With the data for the total deposition of nitrate and ammonium-nitrogen from sections 4 and 5, it turns out that world-wide, 17 $\pm$ 7 x 10^{12} g NO_3^--N/yr is deposited on land, 8 $\pm$ 6 x 10^{12} g NO_3^--N/yr on the oceans, and 15 $\pm$ 7 x 10^{12} g NH_4^+-N/yr on land, and 6 + 6 x 10^{12} g NH_4^+-N/yr is deposited on the oceans. These values were determined as averages for the period from 1950 to 1977 and thus cannot reflect the situation in the year 1978.

Although these results exhibit fluctuations of 40-100% due to the lack of data, especially the small number of rain analyses in tropical regions and on the oceans, they still are up to 2 orders of magnitude less than most previous figures (table 6.1).

Most estimations of this table relate to a compilation of analysis results from the years 1864-1947 (Eriksson, 1952): Emery, 1955; Eriksson, 1959; Robinson and Robbins, 1968, 1970a, b, 1971, 1975; McConnell, 1973; Warneck, 1974; Burns and Hardy, 1975; Söderlund, 1976b; Söderlund and Svensson, 1976; Liu et al., 1977; Hanh and Junge, 1977; Dawson, 1977. Sometimes the reference is not found directly. Liu et al. (1977) relate to Burns and Hardy, 1975, who is cited by Robinson and Robbins, 1968. Only Robinson and Robbins (1968) refer back for the first time to the original work by Eriksson. In Eriksson's compilation (1952) mainly data from Europe and the USA is mentioned. Thus, we get the impression that the world deposition rates are as high as those in Europe and the USA. Perhaps Robinson and Robbins (1968, 1970a) let an error slip in when converting units, since the cited deposition rates of 9000 mg/m^2-yr for NO_3^- and 5000 mg/m^2-yr for NH_4^+ are not given by Eriksson. These values are at least a factor of 10 greater then those of Eriksson (1952). Later, Robinson and Robbins (1970b, 1971, 1975) derived the zonal distribution of deposition rates for ammonium and nitrate from Eriksson (1952) (see sec. 4.1 and 4.2). Since no difference was made between land and ocean, world-wide there is much too large a deposited quantity.

In other papers, the Eriksson data were supplemented by more recent values, especially for regions which had been under-represented (McConnell, 1973; Warneck, 1974; Liu et al., 1977; Hahn and Junge, 1977). From the data, attempts were often made to derive average deposition rates for N-components or average total precipitation concentrations. With these values, or with an average rainfall rate, the deposited quantities could be calculated. Warneck (1974) gives average nitrate concentrations of 1 mg/l over land and 0.15 mg/l over ocean. Tsunogai (1971) derives from the literature (Junge, 1963) a land (NO_3^- + NH_4^+)-N-concentrations of 0.5 mg/l and from his own measurements over oceans, 0.07 mg/l in the precipitation. These assumptions seem to be too high globally, by a factor of at least 2 according to the results of this work.

Deposition rates to be applied world-wide have been cited in the CAST Report (1976) and by Pratt et al. (1977) for NO_3^--N as 230 mg/m^2-yr and for NH_4^+-N as 470 mg/m^2-yr. It is a mystery how these values were obtained. Also, the other papers refer back to literature data, but do not describe how the results were obtained. In no paper were the deposited quantities obtained from the integration of distribution maps in which the relations are given in regions which reflect their size. The results of this present paper thus seem realistic, even though the used data contain uncertainties. In addition, in this paper, the data from more than 500 measuring stations is used, but in other estimations, the values of at most 100 places are used.

7. Other Sinks

Before we can look at the atmospheric cycle of the nitrogen components NO_x and NH_3, other possible sinks for these trace substances mentioned in the literature, must be discussed and estimated.

7.1 Reactions in the Gas Phase

In section 2.1.3 the oxidation of NH_3, a possible destruction mechanism of atmospheric NH_3, was described as a NO_x-source. The quantity of NH_3 oxidized to NO is determined by the reaction with OH:

$$NH_3 + OH \rightarrow NH_2 + H_2O \qquad k = 1{,}57 \times 10^{-13} \frac{cm^3}{\text{molecules second}}$$

(Stuhl, 1973).

With this reaction, 1.2 - 4.9 x 10^{12} g NH_3-N/yr is converted. These values are based on measured NH_3-profiles (sec. 8) and calculated vertical OH-distribution (fishman and Crutzen, 1978). According to these results, the NH_3-oxidation is a second NH_3 sink, in addition to total deposition. Total deposition is at least 4 times greater than oxidation.

The outline of possible reaction by which ammonia can be converted into nitrogen monoxide (fig. 2.10) also includes reactions which will decompose NO. But calculations under steady state conditions at average concentrations (sec. 2.1.3) have shown that of 4000 produced NO-molecules, only one is destroyed by reactions with NH_2 or NH. Thus, the decomposition of NO by this mechanism is very small.

In the oxidation of higher hydrocarbons, besides other products, peroxy acetyl nitrate (PAN) is formed. The formation of PAN was already related to photochemical smog in cities like Los Angeles.

Investigations in the North Atlantic have shown however, that PAN can be formed on appropriate surfaces under the influence of solar radiation, if the substances needed for PAN production are present in the surrounding air (Lovelock, 1976). From reaction-kinetic calculations, the NO_x-quantity used annually for PAN formation cannot be obtained. In section 7.2.4 the deposited quantity will be calculated with the deposition rate of PAN. Since the nitrogen in PAN comes from NO_x and the deposition is an important PAN sink, from the deposited quantity we can conclude how much NO_x-N has been converted into PAN-N and deposited, if this is the only PAN sink.

7.2 Absorption of Gases

The absorption of gas depends on the surface characteristics, thus, total precipitation collectors as used to collect precipitation samples, cannot reflect natural conditions. The extraction of trace substances by vegetation or absorption by the ground or water are probably determined incompletely by total precipitation collectors. In order to evaluate these sinks in comparison to total deposition, they will be discussed in this section.

7.2.1 Absorption of Ammonia by Soil and Ocean Surfaces

Robinson and Robbins (1968, 1970a) considered the absorption of NH_3 in soil to be an important sink. They calculated that 740 thousand g NH_3-N/yr is absorbed by the ground. This value is based on the assumption that ammonia has the same deposition rate as SO_2. It was given as 1 cm/sec. An average ammonia concentration of 6 ppbv was assumed.

Söderlund and Svensson (1976) referred back to a deposition rate of 0.8 cm/sec for SO_2 to calculate the absorbed NH_3-quantities. There resulted a quantity of 67 - 134 x 10^{12} g NH_3-N/yr absorbed by the earth's surface.

Whereas Robinson and Robbins do not distinguish between land and ocean, Söderlund and Svensson computed absorbed NH_3-N-quantities of 57 -114 x 10^{12} g/yr on land, and 10 - 20 x 10^{12} g/yr on the oceans.

Malo and Purvis (1964) measured the absorption of NH_3 in the ground. According to their data, up to 570 µg $NH_3/m^2/h$ is absorbed by the soil. But they performed their measurements on acid soil which easily absorbs NH_3, but which is seldom found in the natural state.

Lenhard (1977) measured a source strength or absorption rate of natural, unfertilized soils in Central Europe for NH_3 (see sec. 2.2.1). According to his results, ± 1 µg $NH_3/m^2/h$ is given off or absorbed by the soil. Soil can thus be an NH_3-source or an NH_3-sink. If Lenhard's values are extrapolated to the entire world, then max. 1 - 1.2 x 10^{12} g NH_3-N/yr can be absorbed. The absorbed ammonia in the soil would be much less with this data, than from the estimations of Robinson and Robbins (1968, 1970a, b, 1971, 1975) and Söderlund and Svensson (1976).

Georgii and Gravenhorst (1977) calculated the relationship between atmospheric NH_3-concentration and that of ammonia and ammonium ions dissolved in ocean water. In fig. 7.1, the calculated dependence between temperature and the ammonia-air concentration at a pH-value of 8.2 and various quantities of ammonia and ammonium dissolved in the surface water is illustrated. 8.2 is an average pH for oceans (Kalle-Dietrich, 1975).

From fig. 7.1 is follows that: For NH_3 concentrations of more than 0.1 μg NH_3/m^3, a flux into the ocean is possible. But higher concentrations are probably only in coastal regions, since NH_3-concentrations are still encountered here like those prevailing over land. Georgii and Gravenhorst (1977) assume that the ammonia in maritime air is essentially of continental origin, as also follows from estimations in this report (sec. 2). At greater distances from land, the NH_3-concentrations decrease quickly (see tab. 8.6), so that the absorbed quantities are very small.

7.2.2 Absorption of Nitric Acid

Another NO_x-component which can be absorbed by soil, is HNO_3. The deposition rate is still unknown. But let us assume a deposition rate of 0.5 cm/sec^{-1} and an HNO_3-N concentration over land of 0.15 μg/m^3, then on the land in the Northern hemisphere, about 4 x 10^{12} gN is deposited, and over sea, 0.2 x 10^{12} g N at a concentration of 0.01 μg/m^3. This is naturally a very rough estimation, but it does describe the potential strength of this sink.

7.2.3 Absorption of Nitrogen oxides NO and NO_2 by Soil and Water

Robinson and Robbins (1968) also calculated the absorbed quantity of NO_2. Again, the deposition rate of SO_2 is used and a global NO_2 concentration of 1 ppbv. Accordingly, 107 x 10^{12} g NO_2-N/yr on land and oceans is absorbed. In their work from 1970(a), they calculate the same value, but with a deposition rate of 0.5 cm/sec and an NO_2 concentration of 2 ppbv. Robinson and Robbins (1975) correct the absolute NO_2-quantity under the same assumptions, to 145 x 10^{12} g NO_2-N per year. They give (1970b) the absorbed NO_x-N quantity likewise as 145 x 10^{12} g NO_x-N/yr. This time they use a deposition rate of 1 cm/sec. Söderlund and Svensson (1976) compute absorbed NO_2 quantities on land as 19 - 50 x 10^{12} g N/yr. They refer to NO_2-concentrations of 0.5 - 4 ppbv. At a concentration of 0.3 ppbv, 6 - 17 x 10^{12} g NO_2-N/yr is said to be absorbed in the oceans. Their calculations used deposition rates of 0.3 - 0.8 cm/sec.

According to these theoretical works, the absorption of NO_x in soil is an important sink. These estimations are contradicted by measurements of deposition rates for NO and NO_2. Abeles et al. (1971) have measured the decrease in concentration of ethylene, sulfur dioxide and nitrogen dioxide in a glass vessel whose base was covered with soil. According to their measurements, the concentration of SO_2 in the container decreased 60 - 100 times faster than that of NO_2.

Thus, SO_2 could have a 60 - 100 times faster deposition rate than NO_2 over the used soil. Garland and Cox (1977) measured the concentrations of NO and NO_2 at altitudes of 0.2 and 2 m in order to determine the vertical flux of these substances. No significant variation of concentration with altitude was found from which a flux of NO and NO_2 to the ground can be calculated. This means that even after these measurements, no surface absorption of NO and NO_2 can be demonstrated. From measurements at a 120 m tall tower, there was still no flux of NO_2 into the soil (Platt, 1977).

In order to get a more accurate conception of the deposition rate for NO and NO_2 for bare soil and water areas, we conducted some of our own tests. In a closed plexiglass container (100 x 150 x 30 cm), the concentration decrease of NO and NO_2 was determined over time. The soil in the container was covered with seawater, fresh water, acid water (pH = 1), forest soil, moist or dry sand as absorbing material. For a mixing of air in the container, a ventilator was provided. The NO and NO_2-concentrations were determined with a chemiluminescence analyser. The deposition rate was calculated as follows: The concentration $C_{(t)}$ after time t [sec] can be expressed as:

$$(1) \quad C_{(t)} = C_o \, e^{-v \cdot \frac{F}{I} \cdot t}$$

C_o is the concentration in the container at time t = 0;
F is the absorbing surface in cm^2
I is the volume of the container in cm^3
v is a proportionality factor with a velocity in cm/sec (if t is in sec) sec) and is called the deposition rate.

Since not only earth or seawater, but also the walls of the chamber absorb NO or NO_2, we have:

$$(2) \quad C_{(t)} = C_o \, e^{-(v \cdot \frac{B}{I} + V_o \cdot \frac{R}{I}) \, t}$$

B is the base area of the container which is covered with the absobing material, in cm^2.
R is the remaining surface area of the container in cm^2
V_o is the deposition rate in cm/sec at which NO or NO_2 is absorbed if no absorbing material is present in the container.

From (2) we can compute the deposition rate:

$$(3) \quad v = \frac{I}{B} \left[\frac{1}{t} \ln \frac{C_o}{C_{(t)}} - V_o \frac{R}{T} \right]$$

In table 7.1, some deposition rates computed in this manner are presented for various surfaces. They were determined with ambient air (50 ppbv) and also with higher concentrations (up to ca. 700 ppbv NO_x).

From the measurements there result deposition rates for NO of about 10^{-3} cm/sec and for NO_2 of about 0.1 - 0.3 cm/sec on barren soil. Repeat measurements taken 3 months later gave about the same values. With the results of these tests, the absorption of NO is insignificant, since the NO concentrations are lower than those of NO_2. In figures 7.2 and 7.3, the measured results are presented graphically. The illustrative exponential curves were adapted to the measured values. The used method to determine deposition rate was already applied to other substances, e.g. by Lenhard (1977), Beilke and Payrassat (1975), Seiler (1974) etc.

The natural transport in chamber experiments does not necessarily reflect conditions in the atmosphere. The validity of such tests is thus restricted. It would then be useful, to measure the concentration decrease of a substance whose atmospheric deposition rate is known. Here, we can use SO_2 for comparison measurements. From the ratio of NO or NO_2 to SO_2 concentration decrease in the chamber, we can then draw conclusions with greater certainly about the atmospheric deposition rate of NO and NO_2. The NO and NO_2-deposition rates over water were so low that the transport resistance of the atmospheric interface cannot be the limiting factor. The same applies for the absorption of NO on the soil. The different turbulence conditions in the chamber and in the atmosphere can affect the NO_2 uptake by soil. But if we assume that the deposition rates for NO_2 measured here correspond to the natural conditions, then the world-wide dry deposited NO_2-N quantities can be calculated. With concentrations of 1 - 2.5 μg NO_2-N/m^3 over land and the determined deposition rates, about 2.4 - 18 x 10^{12} g NO_2-N/yr is absorbed on barren land areas. It is assumed that half the land areas are barren.

According to these measurements, at concentrations of 0.03 - 0.2 μg NO_2-N/m^3 , about 0.03 - 1 x 10^{12} g NO_2-N/yr is absorbed by oceans. According to these calculations, on barren soil and water areas, about two times less NO_x-N is deposited as by total deposition. A part of this NO_x-N quantity is already contained in the total deposition. This value is based on only a few measurements which cause this large range of uncertainty. Additional, more accurate measurements taken for example, simultaneously with comparison measurements of SO_2, can promote a better estimation of this sink than is given here.

7.2.4 Absorption of PAN by Soil, Plants and Water Surfaces

Peroxy Acetyl Nitrate (PAN) [$CH_3C(O)\ OO\ NO_2$] is generated by photochemical processes. But at present, little is known about the mechanisms by which PAN is removed from the atmosphere.

In laboratory tests in which the PAN concentration decrease was measured in a chamber with planted clover using an average concentration of 15 ppb, 0.2 mg PAN-N per m^2h was absorbed (Hill, 1971).

This value corresponds to a deposition rate of about 0.6 cm/sec. The clover is a widely used fodder plant. Measurements of PAN concentration decrease were also taken in a wind tunnel, in which the air was not exchanged (Garland and Penkett, 1976). These experiments showed than PAN has a deposition rate of about 0.25 cm/sec over grass and over wet, moist and dry soils, whereas over water, the rate is insignificant. These values are probably more representative than the results of Hill (1971), since the values for grass surfaces more likely reflect average conditions.

Measurements in St. Louis, Missouri and in West Covina, CA showed that the PAN mixing relations of 1.8 or 8.8 ppbv during a period of July-August 1973 or August-Sept. 1973 resp., were about 20 times less than those of NO_x (Spicer, 1971). In Delft on 12/2/73 an average of 3 ppbv PAN was found, this is about 10 times less than NO_x. During two days in August, 0.9 ppbv PAN was measured in Harwell, England (Garland and Penkett, 1976). These values were measured when the production prerequisites for PAN were optimum: In the summer under strong solar radiation. But in Winter, the PAN concentrations will be lower since the radiation intensity is less so that less PAN can be produced.

Assuming that the PAN concentration is 20 times less than NO_x (about 0.05 - 0.12 μg PAN-N/m^3 derived from average values, see sec. 8) and the deposition rate is 0.25 cm/sec, then 0.6 - 1.5 x 10^{12} g PAN-N/yr is deposited on the land. Thus, with this mechanism 0.6 - 1.5 x 10^{12} g NO_x-N/yr can be removed from the atmosphere worldwide, if we presume that the nitrogen of PAN comes originally from the NO_x. This NO_x-sink is about 20 times weaker that total deposition.

7.2.5 Absorption of NH_3 and NO_x by Vegetation

Another possible sink for NH_3 and NO_x can be the uptake by leaves of plants. The pH-value of plant juices and the exchange capacity of the stomata of the leaves with the surrounding air, probably determine the absorption.

Porter et al. (1972) measured the NH_3-absorption of plants by using N^{15}-tagged isotopes in ammonia. Their results are not representative since they used 100 - 1000 times greater concentrations than occur in the atmosphere.

Hutchinson et al. (1972) measured the NH3-uptake by soybean plants. The absorbed quantity was determined by measuring the uptake of ammonia from air flowing through a chamber containing one plant. The NH_3-absorption according to these tests, follows the daily cycle of CO_2 uptake. During the day, when plants absorb large quantities of CO_2, the absorption of NH_3 also increases, at night, when the leaf stomata are closed, it is much less. Cotton plants absorb an average 350 μg NH_3/m^2 h at an NH_3 concentration of 44 $\mu g/m^3$, soybeans absorb 410 μg NH_3/m^2 h at 26 μg NH_3/m^3, sunflowers 490 μg NH_3/m^2 h at 31 μg NH_3/m^3 and corn, 560 μg NH_3/m^2 h at 24 μg NH_3/m^3 (Hutchinson et al., 1972). The deposition rates used to calculate this data lie between 0.2 and 0.6 cm/sec. All results relate to the leaf surface. From this data, an average absorption rate of NH_3 by vegetation of 2000 mg NH_3/m^2-yr is derived, related to the land surface (Hutchinson et al., 1972). But this value seems very high, since this sink alone would require 10 times greater NH_3 sources to be valid world-wide. With an ammonia concentration of about 25 μg NH_3/m^3, as used for the above tests, there results with this absorption rate of 2000 mg NH_3/m^3 per year, a deposition rate of about 0.25 cm/sec. With a global average concentration of about 1.5 - 3 μg NH_3-N/m^3 and this deposition rate, world wide, 4.5 - 8 x 10^{12} g NH_3-N/yr can be absorbed by plants. This presumes that only about half the land surface has plants (Woodwell, 1978) and plants can absorb for only half a year, when they are biologically active. This is an initial, rough estimation of this sink for atmospheric ammonia, which is about 6 times weaker than total deposition. Measurements by Lemon (1978) also led to similar, large NH_3-absorption rates for plants. A part of the absorbed NH_3 is released directly from the soil under the plant (Lemon, 1978), so that there is an internal cycle between soil and vegetation. A part of the NH_3 liberated from the soil thus does not get into the free atmosphere via the plants.

Also, the uptake of NO and NO_2 by clover, a widely-used fodder plant, was measured (Hill, 1971, Bennett and Hill, 1975). The tests were conducted in a chamber planted with clover (lucern). By day, the NO_2-absorption proceeded parallel to that of CO_2: In the morning, when the leaf stomata opened, the absorbed quantities increase and stay constant all day, and then decline at night to 20 to 35% of the quantities absorbed by day (Hill, 1971). At concentrations of 80 ppbv, by day absorption rates of 37 μg NO_2-N/m^2-min were measured. From this data, a daily average of deposition rate can be derived for the absorption of NO_2 by lucern as 0.4 - 0.6 cm/sec. Since only about 50% of the land surface is planted (Woodwell, 1978) and the absorption only occurs during that time when the plants are biologically active, or in the summertime, with the above deposition rates and concentrations of 1 - 2.5 μg NO_2-N/m^3, world-wide about 4.7 - 18 x 10^{12} g NO_2-N/yr is absorbed by vegetation. This assumes of course, that the absorption of NO_2 by lucern is representative for global vegetation.

According to the above discussion, the absorption of NH_3 and NO_2 by plants is possible. However, the estimations of these fluxes are based on very few measurements. The caculated numbers are thus very uncertain. Other investigations of this sink are needed to be able to give a better estimation of it and to understand the processes by which the molecules are absorbed by leaves.

7.3 Impaction of Aerosols

This sink was already mentioned in section 3.2. Vegetation can comb out trace substances from the atmosphere which are then washed from the plants by subsequent rainfall (Mayer and Ulrich, 1977, 1978; Ulrich, 1978). This sink is not included by total precipitation collectors. A quantification of this sink has not been possible, since measurements are available only for Central Europe at Solling. The fraction of total deposition depends on the precipitation characteristic and the vegetation. This sink can serve to explain possible differences between source strengths and total deposition.

7.4 Conclusions

From the preceeding discussion on the sinks which can remove the nitrogen components NO_x and NH_3 from the atmosphere (in addition to total deposition), there results:

1. Except for chemical reactions and impaction of aerosols on vegetation, all other sinks for NO_x and NH_3 are already partly contained in the total deposition. Their fractions of total deposition are unknown.
2. Due to absorption of NO_x and NH_3, up to 18 x 10^{12} g N/yr can be removed by land from the atmosphere.
3. According to this research, much less N-quantities are absorbed by water surfaces, since the trace concentrations on the oceans are smaller, and NO_x is not very soluble in water.
4. Through oxidation of NH_3, annually a world total of about 1.2 - 4.9 x 10^{12} g NO_x-N is produced.
5. The impaction of aerosols on plants cannot yet be estimated.

8. Atmospheric Dwell Times of Nitrogen Components

Besides the estimation of source strengths and decomposition rates, atmospheric dwell times are important to describe the nitrogen cycle. With them, possible transport processes can be explained, e.g. trace substance transport in regions having weak sources, but powerful sinks. The dwell time τ is defined as follows:

$$\tau = \frac{\text{quantity in the atmosphere}}{\text{quantity removed from or given to the atmosphere per time unit}}$$

Both the annual quantity of nitrogen given to the atmosphere (sec. 2) and that deposited through total deposition (sec. 4-6) have been estimated. Thus, the mass of N-components in the atmosphere must be determined in order to calculate the dwell time τ. In tables 8.1 - 8.6, concentrations of NO_3^- and NH_4^+ in aerosols, and of the gases NO, NO_2, HNO_3 and NH_3 are summarized. This data shows large differences in concentrations on the ground between land and ocean values.

In order to be able to determine the mass of the components in the atmosphere, it is also necessary to know the concentration relationship with elevation. This information was taken from measurements of the vertical concentration distributions and model calculations. In table 8.7, the used profiles are presented. Figures 8.1 - 8.4 show the graphic illustrations of these profiles.

Since the oceans are weak sinks and sources for the gases NO, NO_2, HNO_3,NH_3, no vertical decrease of mixing relations was assumed there. Gravenhorst (1975) measured a relatively constant ammonia profile over the Bay of Biscay (fig. 8.4) It is further assumed that the vertical concentration gradient of aerosols shows no difference between land and oceans.

For each component, average profiles were computed from the measured values by adapting the data to an e-function.

$$C_{(z)} = C_o \cdot e^{b \cdot z}$$

$C_{(z)}$ is the concentration at elevation z
C_o is the ground concentration
b determines the decrease of concentration with altitude.

In figures 8.1 - 8.4, the average profiles are also drawn in.

The integration of the vertical profiles gave the column densities of the individual nitrogen components. Data up to 3,000 m was included, since more than 95% of the N-components are found here (derived from the profiles). In table 8.8 are the used concentrations and the quantities of the various components in the Northern hemisphere.

With these values, there results for ammonia and ammonium-nitrogen, a dwell time of 15 $\pm$ 9 days, since total precipitation and ammonia oxidation are the sole sinks (sec. 7). The dwell time for NO_x-nitrogen is 5 $\pm$ 4 days, and is thus shorter than that for (NH_3^- + NH_4^+)-N. This time also relates to total precipitation, since this is the most important NO_x-sink (sec. 7).

If the dwell times are related to the quantities released to the atmosphere, then for NO_x-N, 4 $\pm$ 2 days results, and for (NH_3^- + NH_4^+)-N, 11 $\pm$ 6 days results. These figures are somewhat smaller than those calculated due to the deposited quantities, since there are other, possible sinks (sec. 7) which were not taken into account in the calculation of dwell time. The dwell time of (NH_3^- + NH_4^+)-N will be on the order of about two weeks, according to the results of this research, and that of NO_x-N will be about one week.

According to the measurements of Tsunogai (1971) and Gravenhorst (1975), the precipitation concentrations of N-components decrease with increasing distance from land.

The analysis results in table 8.9 indicate a relationship between NO_3^--N concentrations in the rain and the origin of the air masses. The samples were collected in Sept. 1976 by U. Schmidt in SW France. For air masses which crossed the British Isles, the NO_3^--N concentrations in the rain were about five times higher than that in samples measured in a maritime air mass.

These results confirm that the quantities removed from the atmosphere over oceans is not replaced by maritime sources, because the oceans are very weak NO_x and NH_3 sources--if at all.

9. Comparison of NO_x and NH_3 Quantities Emitted into and Removed from the Atmosphere

Now that sources for atmospheric NO_x and NH_3 have been estimated (sec. 2) and then the effectiveness of possible sinks for these components have been discussed, these independently-determined quantities of source strength and sink functions will be compared to each other.

World-wide, according to results of this research, anthropogenic and natural sources emit about $34 \pm 5 \times 10^{12}$ g NO_x-N/yr, whereas through the primary sink, total deposition, $24 \pm 9 \times 10^{12}$ g NO_3^-/yr is removed from the atmosphere. In fig. 9.1, the zonal dependencies of annual nitrogen quantities given to the atmosphere as NO_x-N and that removed by total deposition as NO_3^--N, are plotted for the Northern hemisphere. Whereas in tropical regions, the fluxes into and from the atmosphere are about equal, in middle latitudes the emitted NO_x-N quantities cannot be removed by total deposition alone. This difference between the emitted and deposited quantities (due to total precipitation in middle latitudes), must be explained by other sink mechanisms not already contained in the total deposition. In sec. 7, such other possible NO_x-sinks were discussed and their sizes were partly estimated. It turned out that through conversion of NO_x into PAN and absorption of NO_x by plants, soil and water, about $20 \pm 10 \times 10^{12}$ g NO_x-N/yr is removed from the atmosphere. The extent to which these sinks are already included in the total deposition cannot be estimated, since the absorption of the gas components depends greatly on the surface characteristics of the collection apperatus (sec. 3). We also do not know to what extent dry deposition of HNO_3 is included in total precipitation samples. Especially in the vicinity of NO and NO_2-sources, increased HNO_3 concentrations can occur, which may lead to non-negligible deposition rates. A part of this HNO_3 can even be contained in the total deposition, since the collection vessels can absorb HNO_3. The size of this absorption cannot be estimated at present because the absorption coefficient of the collection is unknown. If we assume that HNO_3 is not absorbed in the collector, that it has a deposition rate of 0.5 cm/sec and occurs world-wide over land at an average concentration of 0,15 µg HNO_3-N/m^3, then through this process, an additional ca. 4×10^{12} g HNO_3-N/yr can be absorbed by the ground. This 4×10^{12} g N/yr is surely an upper limit, since the collection apperatus will absorb at least a part of the occurring HNO_3-molecules. If the NO_x-fluxes from the atmosphere are compared with the emitted NO_x-quantities, then it can be assumed that there is a balance of sources and sinks, even though the estimations used here were performed independently of each other.

In sections 3 and 7, an additional sink for NO_x and for NH_3 was described--the removal of aerosols and gas by vegetation. An estimation of this sink is not possible given the present level of knowledge, but it can be assumed that this flux from the atmosphere is included by the large range of the other fluxes.

The main sink for atmospheric ammonia is the total deposition of $21 \pm 9 \times 10^{12}$ g NH_4^+-N/yr. Annually, about $29 \pm 6 \times 10^{12}$ g NH_3-N is given off to the atmosphere. In fig. 9.2, the zonal dependencies of the nitrogen quantities are entered for NH_3 to the atmosphere, and that deposited on the Northern hemisphere as NH_4^+ through total precipitation. As for the figures for global estimation, there are also differences in the comparison of zonal dependencies.

Transport processes probably cause the greater quantity deposited by total precipitation between 0° and 10° N. The otherwise low amounts of deposited NH_4^+-N compared to the emitted amount, can be explained by the oxidation of NH_3 (sec. 7.1) in part: $3.1 \pm 1.8 \times 10^{12}$ g NH_3-N/yr is oxidized to NO_x (sec. 2.1.3). Another $7.8 \pm 2.4 \times 10^{12}$ g NH_3-N/yr is removed by absorption on plants, soil and water. Here too, the fraction already contained in the total deposition, is unknown. However, it can be assumed that for NH_3, the balance of sources and sinks is in order.

Sources and sinks for atmospheric NO_x and NH_3-cycles can be estimated independently in this report. No values have to be determined from balances, but all values can be derived directly. The strength of the sources and sinks for the N-components NO_x and NH_3 show good agreement.

10. Chronological Trends of NO_3^- and NH_4^+ Quantities Removed from the Atmosphere by Total Deposition

The change in annual quantities of NO_3^- and NH_4^+ removed from the atmosphere will permit conclusions about the differing conversion of these two N-components in the atmosphere. If we assume that the natural sources are not subject to any chronological development, then the changes caused by anthropogenic influences can be discovered. Thus, we shall attempt to estimate the NO_3^- and NH_4^+ N-quantities removed from the atmosphere through total deposition around the year 1900. Furthermore, the trends at several stations will be presented.

10.1 NO_3^- and NH_4^+ Quantities Deposited in the Northern Hemisphere around 1900 by Total Deposition

With data on the deposition rates of NO_3^--N and NH_4^+-N from the period around 1900 (see annex "Old precipitation data"), as described in section 4, maps were drawn for the Northern hemisphere with lines of equal deposition rates (fig. 10.1 and 10.2). No data was discarded since there would then be insufficient measured values available. Therefore, we had to use possibly incorrect analysis results. Since there are no values for oceans from this period, the maps relate only to the continents. The deposited quantities were also taken into account in the estimation: It was assumed that the ratio of total deposited quantity to that quantity deposited on the land has not changed on the Northern hemisphere. With these assumptions, according to data published around the year 1900, about 17 x 10^{12} g NO_3^--N/yr and 22 x 10^{12} g NH_4^+-N/yr is removed from the atmosphere by total deposition. Both values lie within the confidence interval for N-quantities deposited annually from 1950 to 1977 (16 ± 6 x 10^{12} g NO_3^--N/yr or 17 ± 5 x 10^{12} g NH_4^+-N/yr). These values permit no conclusions about chronological changes.

10.2 Chronological Trends of Deposition Rates of NO_3^- and NH_4^+-N

Analyses of precipitation for nitrogen components lasting over several decades are unknown at any location. With a few interruptions, there is data for Rothamsted in England since 1856 (see sec. 14.3). From 1910 to 1938 in Mount Vernon, Iowa, the precipitation concentrations were measured (see sec. 14.4). Finally, longer measured series are available from Ithaca, New York (see sec. 14.5). Figure 10.3 shows how the deposition rates of nitrate and ammonium nitrogen have changed at these three locations over time. The increase in deposited NO_3^--N can probably be explained by the increased comsumption of fossil fuels. Also, the sources located around measuring stations can have changed and thus changed the deposition rates. In 100 years, the nitrate-nitrogen deposition rate at Rothamsted has quadrupled. At the other stations as well, the NO_3-N deposition rates have risen. The rates for NH_4^+-N decreased at all three stations. The cause of this decrease in deposition rate can be due to the decreased NH_3-emission, but also to the defective detection methods which resulted in excessive NH_4^+ concentrations being measured in the rain.

In table 10.1, averages of deposition rates and of concentrations of NO_3^--N and NH_4^+-N are presented for different times. The values were determined in Europe from chronologically differing series. The old values of Erikson (1952) were cited; the data from 1955 was measured by Stations of the European Atmospheric Chemistry Network (EACN, 1973a, b, 1975). Also, no trend for NH_4^+ deposition rates can be derived from this data. The deposited quantity of nitrate-nitrogen has doubled within 50 years. The increase in nitrate deposition rates is probably due to increased anthropogenic sources, yet no statement is yet possible about a chronological trend of the ammonium deposition rates.

10.3 Conclusions on the Chronological Trend

From global estimations of deposited NO_3^--N and NH_4^+-N quantities, no chronological trend can be derived. But for nitrate, at individual stations, a trend is found. The deposition rates at some locations have doubled within 50 years.

Additional investigations are needed in order to find any global, chronological development of the deposition rates. Precise data could be obtained from accurately datable ice samples from glaciers and polar caps. In ice samples, the ion concentrations of aqueous solutions are preserved from the time in which they were frozen.

Indications of a chronological development of emitted quantities of NO_x^--N and NH_3-N can also cause changes in trace substance concentrations in the atmosphere. Whereas the SO_2-concentration in Frankfurt decreased for instance, between 1962 and 1977 (pilot station of the Federal Environmental Agency, Germany, near the city center), the NO_x concentration (fig. 10.4) increased 7-fold. This station in Frankfurt is certainly not representative for large areas. But the results do indicate that in built-up areas a sharp increase in the near-ground concentration of NO_x can be found in recent years. Thus, atmospheric nitrogen components assume a growing importance.

In the results of this work, this increase in NO_x-concentration, caused by higher NO_x-emissions, does not appear. The deposition rates of this research are averages for the years 1950 to 1977 and not current values. For instance, even in 1974 the emitted NO_x quantities were 15% above the average value assumed for this study. This increase alone was caused by the increase in anthropogenic sources; they grew by 44%, whereas the natural sources stayed constant. The NH_3-sources even rose by 19%. The reasons for this are increased cattle raising and a higher consumption of N-fertilizers. Both the increase in NO_x-N and NH_3-sources indicates that the deposited NO_3^--N and NH_4^+-N quantities probably also grew by the indicated percentages. Only future, world-wide deposition measurements will be able to determine this increase in anthropogenic emissions.

11. The Essential Results of the Work

The results of this research are based primarily on the published analysis results of others. In spite of our willingness to view this data as accurate, it is possible that it does not reflect real conditions. With this reservation, the results of the work can be summarized:

1. World-wide, $34 \pm 5 \times 10^{12}$ g NO_x-N/yr is emitted. The ratio of natural to anthropogenic NO_x-sources in this report is world-wide about 1:1. Previously, relations of 6:1 (Liu et al., 1977) to 1400:1 (Robinson and Robbins, 1968) were assumed.

2. World-wide, $29 \pm 6 \times 10^{12}$ g NH_3-N/yr is emitted. NH_3 is given off to the atmosphere mainly by liberation from the metabolic products of cattle ($18 \pm 4 \times 10^{12}$ g NH_3-N/yr.

3. According to this research, world-wide $24 \pm 9 \times 10^{12}$ g NO_3^--N and $21 \pm 9 \times 10^{12}$ g NH_4^+-N is removed from the atmosphere by total deposition. These values are lower than all other, previously published estimations.

4. Total deposition is the most important sink for the atmospheric nitrogen components NO_x and NH_3.

5. There are strong latitudinal dependencies of deposition rates: Over land in middle and tropic latitudes, much more nitrate and ammonium-nitrogen is deposited than in the other regions. The same trend of latitude dependence is found over the oceans.

But there, 3 times less is deposited than over the land.

6. The absorption of NO_x and NH_3 by the soil seems to be important for the atmospheric nitrogen cycle. However, measurements are still needed for an accurate estimation of this sink.

7. The estimated fluxes of NO_x and NH_3-components to and from the atmosphere agree within the frame of accuracy dictated by the data, even though they were determined independently of each other.

8. The atmospheric dwell times of NO_x-N are 5 ± 4 days, if calculated on the basis of quantities removed from the atmosphere through total deposition, 4 ± 2 days, if the emitted NO_x-N quantities are taken as the basis. For NH_3-N, atmospheric dwell times of 15 ± 9 days result on the basis of quantities removed through total deposition, and 11 ± 6 days if the quantities given off to the atmosphere are used. The small differences in atmospheric dwell times of NO_x-N and NH_3-N resulting if the quantities removed by total deposition or the emitted quantities are used for the calculation, show that the other fluxes of these N-components from the atmosphere are of subordinate importance compared to the total deposition.

9. From the existing data, no global chronological change in deposition rates can be found. Only for individual stations can trends for NO_3^--N be cited: The NO_3^--N deposition has doubled within the last 50 years according to the data from individual stations. An increase in emitted NO_x-N and NH_3-N quantities to 1974 compared to the value in this report for the years 1950 to 1977 does indicate higher deposited NO_3^--N and NH_4^+-N quantities.

10. The annual N-quantities converted in the atmosphere according to this research are less by a factor of 100 that previously published estimations of the atmospheric cycles of NO_x and NH_3.

With the results of the work, the atmospheric nitrogen cycle can be quantified (fig. 11.1).

It is possible that new precipitation investigations will shift the position of the isolines in the maps at some locations. But the basic pattern of the maps will not be changed.

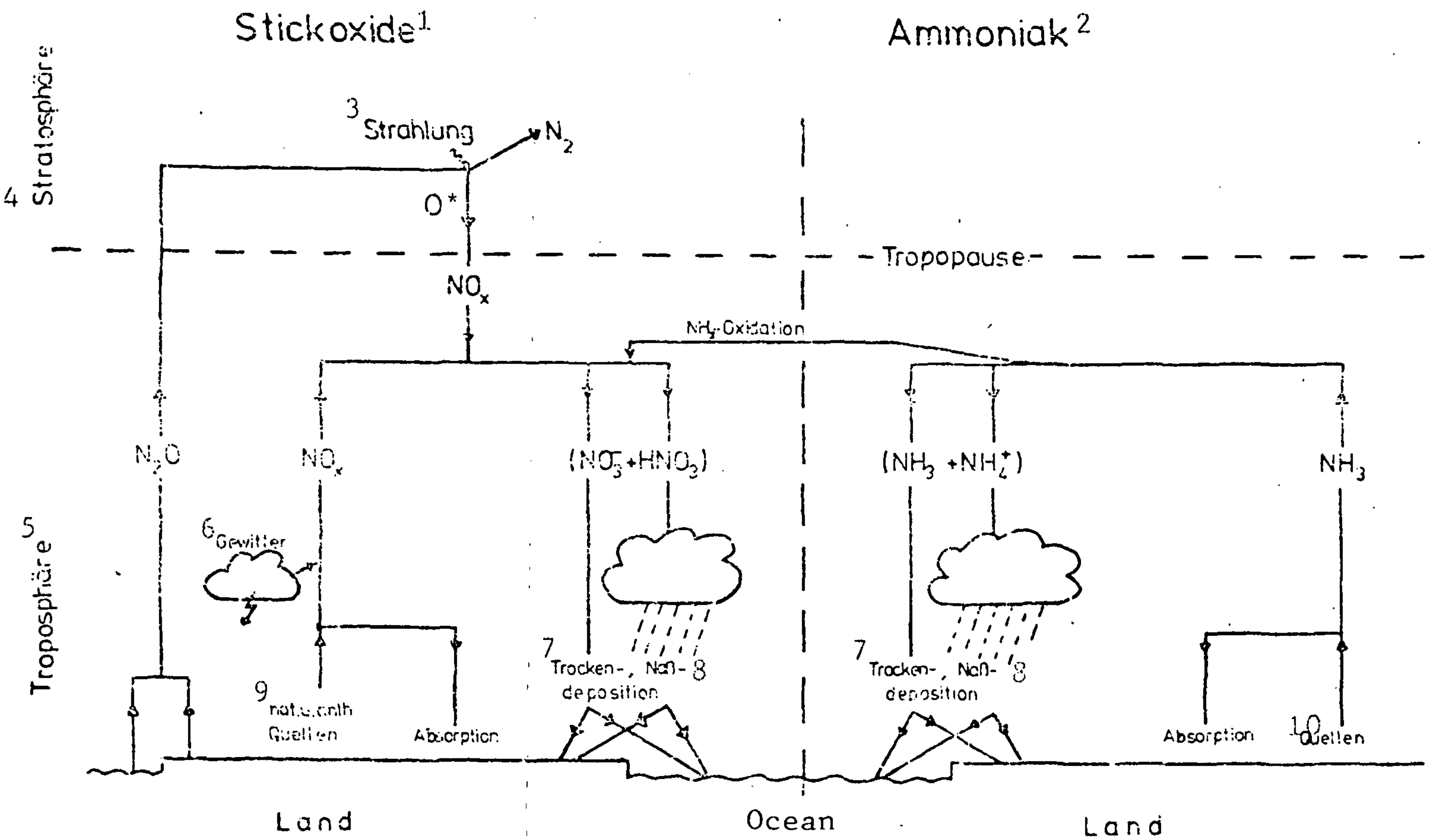


Figure 1: Schematic Illustration of the Atmospheric Nitrogen Cycle

1-nitrogen oxides 2-ammonia 3-radiation 4-stratosphere 5-troposphere 6-thunderstorm 7-dry 8-wet 9-natural and anthropogenic sources 10-sources

Table 1: ESTIMATIONS OF NITROGEN QUANTITIES DEPOSITED ON THE EARTH THROUGH TOTAL DEPOSITION

		[10^{12}g N/a]		
		NH_4^+-N	NO_3^--N	$(NH_4^+ + NO_3^-)$-N
Eriksson	1959	99	48	147
Robinson & Robbins	1968	2700	1400	4100
	1970a,b 1971,1975	210	105	315
Tsunogai & Ikeuchi	1968	-	-	350
Tsunogai	1971	-	-	70
McConnell	1973	100	90	190
Warneck	1974	-	38	-
Burns & Hardy	1975	116	49	165
CAST	1976	240	117	357
Chameides et al	1977	-	60-90	-
Pratt et al	1977	240	117	357
Söderlund & Svensson	1976	110-236	43-116	153-352
McElroy et al	1976	-	-	240
Liu et al	1977	-	-	220
Hahn and Junge	1977	-	-	200

Table 2.1: COMPILATION OF ESTIMATIONS OF GLOBAL SOURCES FOR ATMOSPHERIC NO_x AND NH_3 FROM VARIOUS AUTHORS IN 10^{12} g N PER YEAR. A PART OF THE VALUES WAS COMPUTED DIRECTLY (a), THE REST FROM THE DIFFERENCE OF NITROGEN QUANTITIES REMOVED FROM THE ATMOSPHERE MINUS THE DIRECTLY CALCULATED RESULTS (b)

		NO_x-Sources					NH_3-Sources		
		Losses from the soil	Thunderstorms	NH_3-oxidation	Diffusion from the stratosphere	Anthropogenic combustion	Losses from metabolic products	Losses from the soil	Anthropogenic combustion
Robinson & Robbins	1968	305 (b)	?	n.b	v.b	16(a)	5500(b)		3,5 (a)
"	1970a	112 (b) 150 (b)	?	n.b	v.b	16(a)	4900(b)		3,5 (a)
"	1970b	234 (b)	?	n.b	v.b	16(a)	957(b)		v.b
"	1971	182 (b)	?	n.b	v.b	45(a)	870(b)		v.b
"	1975	234 (b)	?	n.b	v.b	16(a)	560(b)		3,5 (a)
Burns & Hardy	1975	n.b	10(a)	30 (a)	5(a)	19(a)	165(b)		v.b.
Söderlund & Svensson	1976	21-89(b)	?	3-8(a)	0,3	15(a)	22-41(a)	87-191 (b)	4-12 (a)
Chameides et al	1977	5-15(b)	30-40(a)	0-20(a)	< 1	15(a)	-	-	

n.b. not considered
v.b. omitted since less than other sources
? possible sources, but not estimates

(a) estimated
(b) computed from balance!

Table 2.2: NO_x NITROGEN QUANTITIES FROM SOME FOSSIL FUELS EMITTED INTO THE ATMOSPHERE FOR VARIOUS COMBUSTION PROCESSES PER FUEL QUANTITY (kg OR m^3)

Autoren[1] Brennstoffe/ Verbrennungsprozess		Söderlund (1976a)	Robinson & Robbins (1968)	EPA (1973/1977)	NUKEM (1974)	[2]mit in der Bundesrepublik verbrannten Mengen gewichteter Mittelwert (NUKEM, 1974)	[3]hier verwendete Werte
Steinkohle[4]	gNO_x-N/kg						0,9 - 2,75
[5]Kraftwerke	"	0,61-2,43	2,71	2,7	2,99		
[6]Industrie	"		2,71	0,91 - 2,7	(3,36)		
[7]Haushalte	"		0,67	0,3 - 0,9	,61	[13]Kohle 2,5	
Braunkohle[8]	"						1 - 2,8
[5]Kraftwerke	"	0,61-1,81			2,85		
[6]Industrie	"				(3,36)		
[7]Haushalte	"				0,39		
Öl[9]	"					1,9 - 2,6	
[10]leicht	"	6,1	2,59	1,7 - 3,5	1,18 - 1,84		1,5 - 3
[11]schwer	"		3,53	1,6 - 3,1	3,67		1,5 - 3,1
[5]Kraftwerke	"	0,46-0,91		3	5,51		
Erdgas[12]	gNO_x-N/10^3m^3					1,62	0,6 - 3,0
[5]Kraftwerke	"	0,3 -0,91	1,9	2,9	3,5		
[6]Industrie	"	0,18-0,91	1,04	0,6 - 1,1	1,56		
[7]Haushalte	"	0,15-0,3	0,57	0,4 - 0,6	0,62		

1-authors 2-average value weighted with quantities burned in the FRG
3-values used here 4-hard coal 5-power plants 6-industry 7-households
8-soft coal 9-oil 10-light 11-heavy 12-natural gas 13-coal
[Commas in tabulated material are equivalent to decimal points]

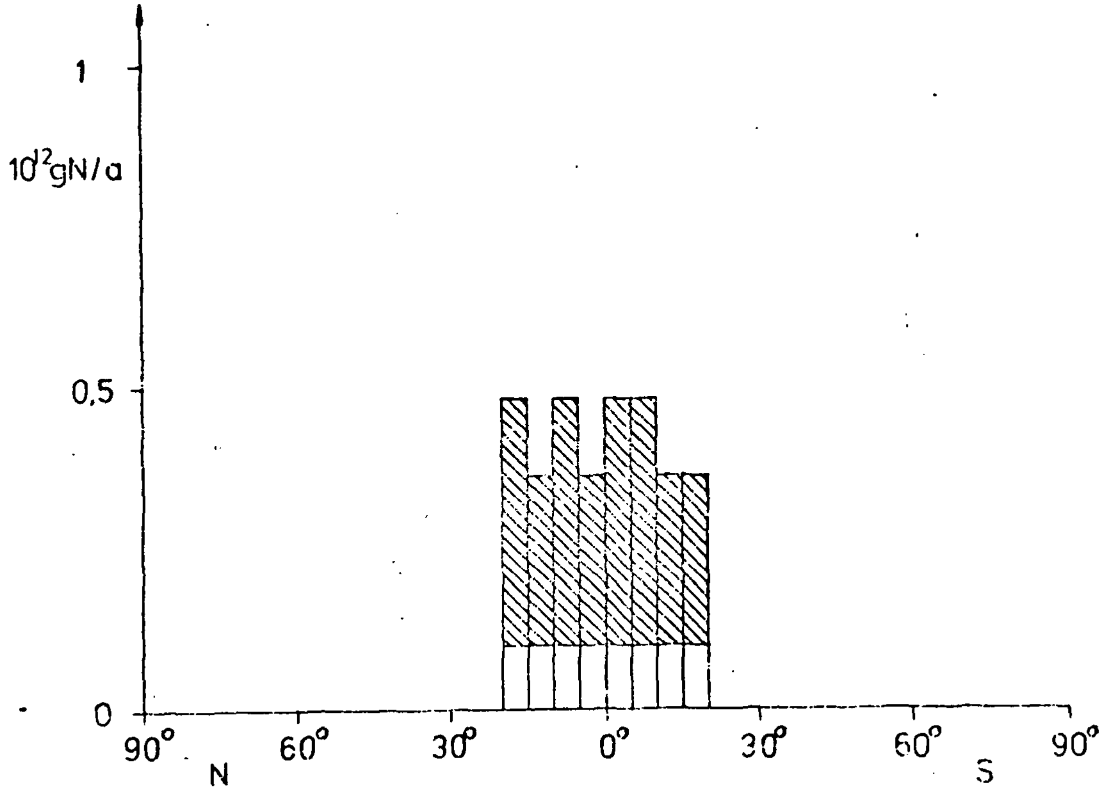


Figure 2.1: Zonal Distribution in 5° Intervals of NO_x-Quantities Emitted to the Atmosphere in Tropical Regions through the Combustion of Cleared Wood. The shaded Region shows the Fluctuation of this Source

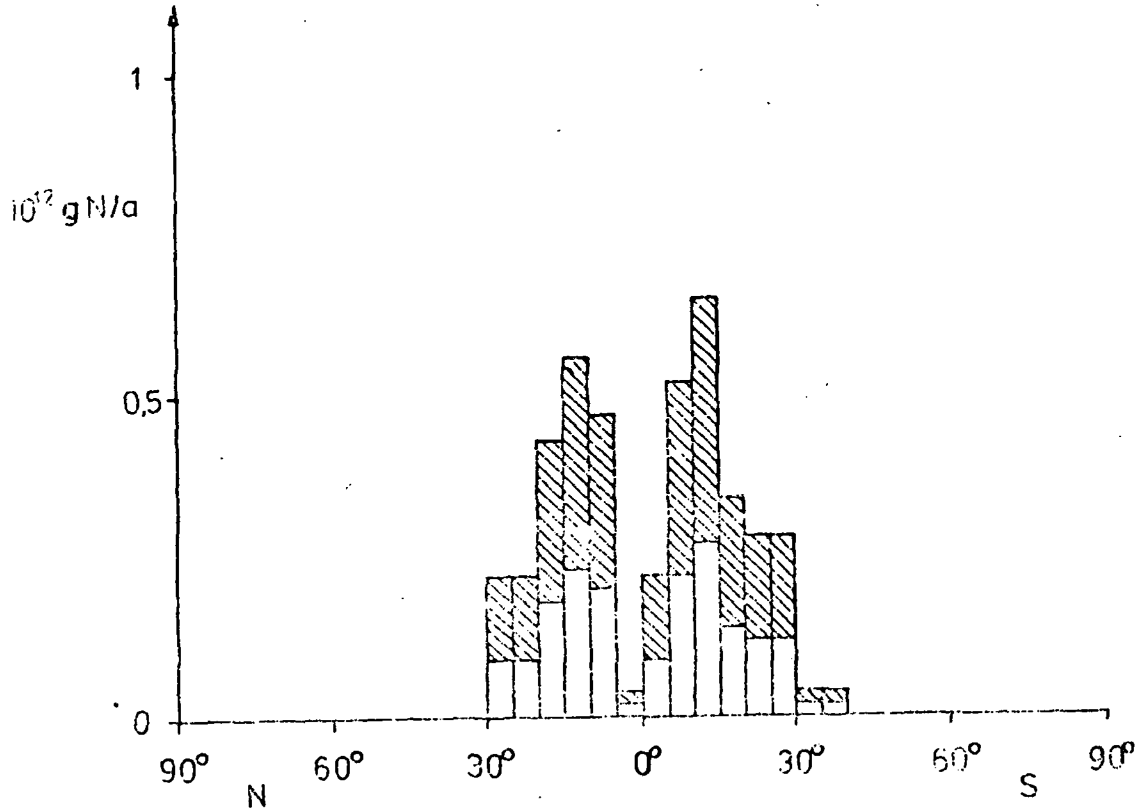


Figure 2.2: Zonal Distribution in 5° Intervals of NO_x-Quantities Emitted to the Atmosphere through Grassfires. The Shaded Region shows the Fluctuation of this Source

Table 2.3: EMISSION FACTORS FOR FOSSIL FUELS, QUANTITIES BURNED ANNUALLY AND NO_x-N QUANTITIES EMITTED ANNUAL TO THE ATMOSPHERE THROUGH COMBUSTION

	Emission factor	Consumption	Emitted quantities (10^{12} g NO_x-N/yr
Soft coal	1,0-2,8 g NO_x-N/kg	$8,1 \times 10^8$ t	0,8 - 2,3
Hard coal	0,9-2,75 "	21,5 "	1,9 - 5,8
Light oil	1,5-3 "	3,0 "	0,5 - 0,8
Heavy oil	1,5-3,1 "	4,7 "	0,7 - 1,5
Natural gas	0,6-3,0 g NO_x-N/$10^3 m^3$	$10,4 \times 10^{14} m^3$	0,6 - 3,2
NO_x-N total emission from fossil fuels			4,5 -13,6

[Commas in tabulated material are equivalent to decimal points]

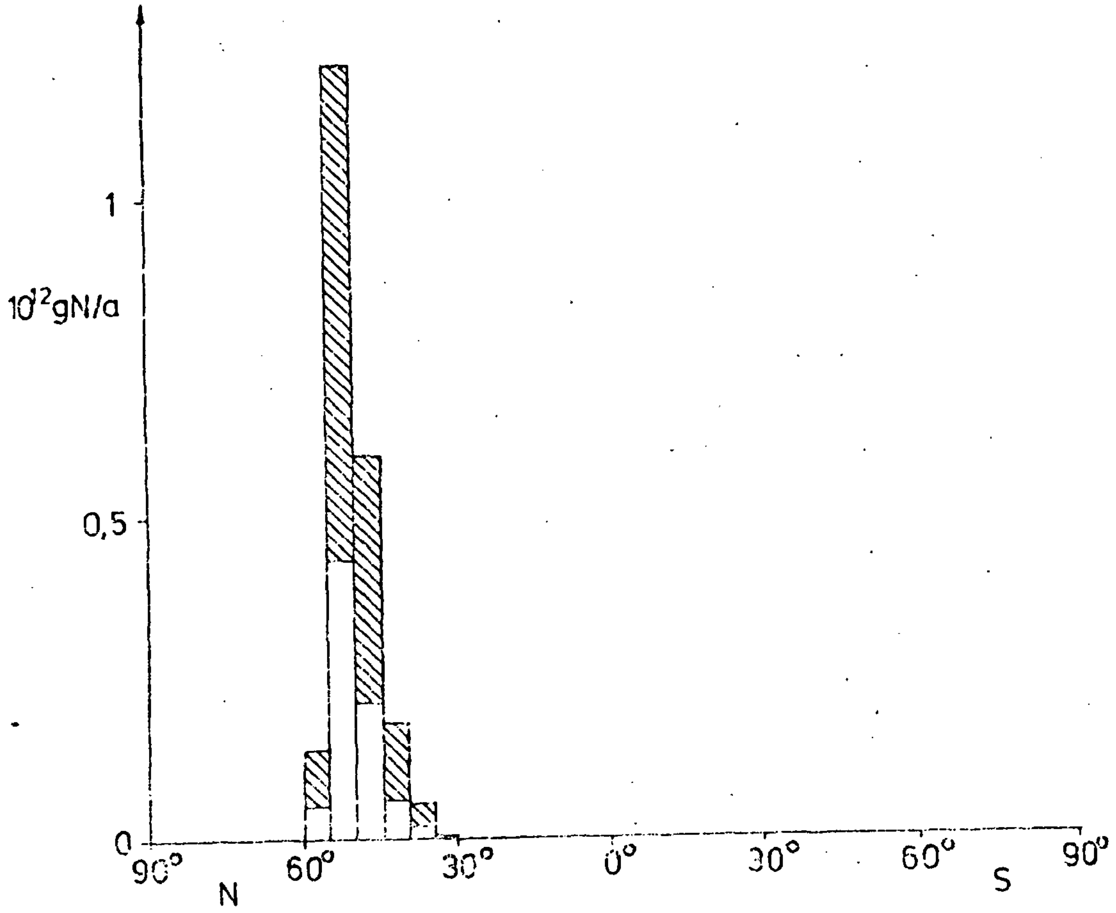


Figure 2.3: Zonal Distribution in 5° Intervals of the NO_x Quantities given off to the Atmosphere through the Combustion of Soft Coal. The Shaded Region shows the Fluctuation of this Souce.

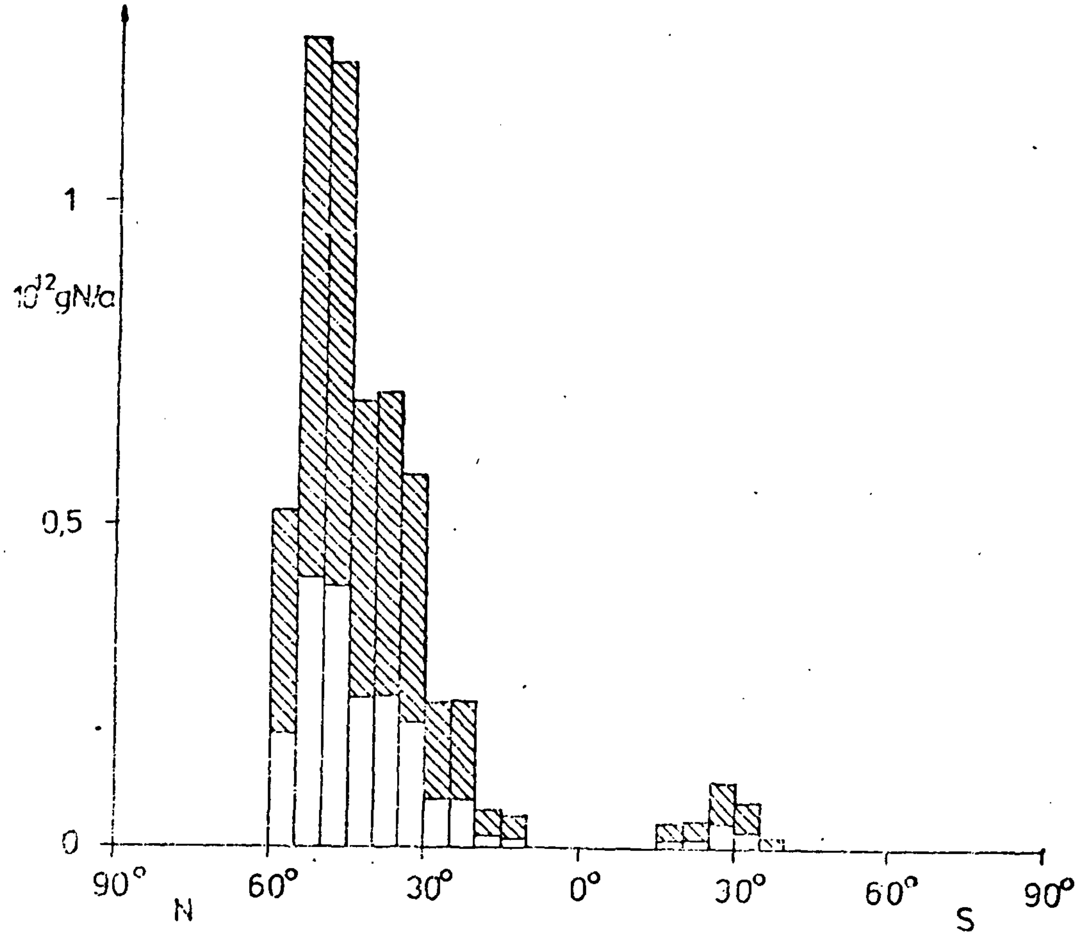


Figure 2.4: Zonal Distribution in 5° Intervals of the NO_x-Quantities given off to the Atmosphere through the Combustion of Hard Coal. The Shaded Region shows the Fluctuation of this Source.

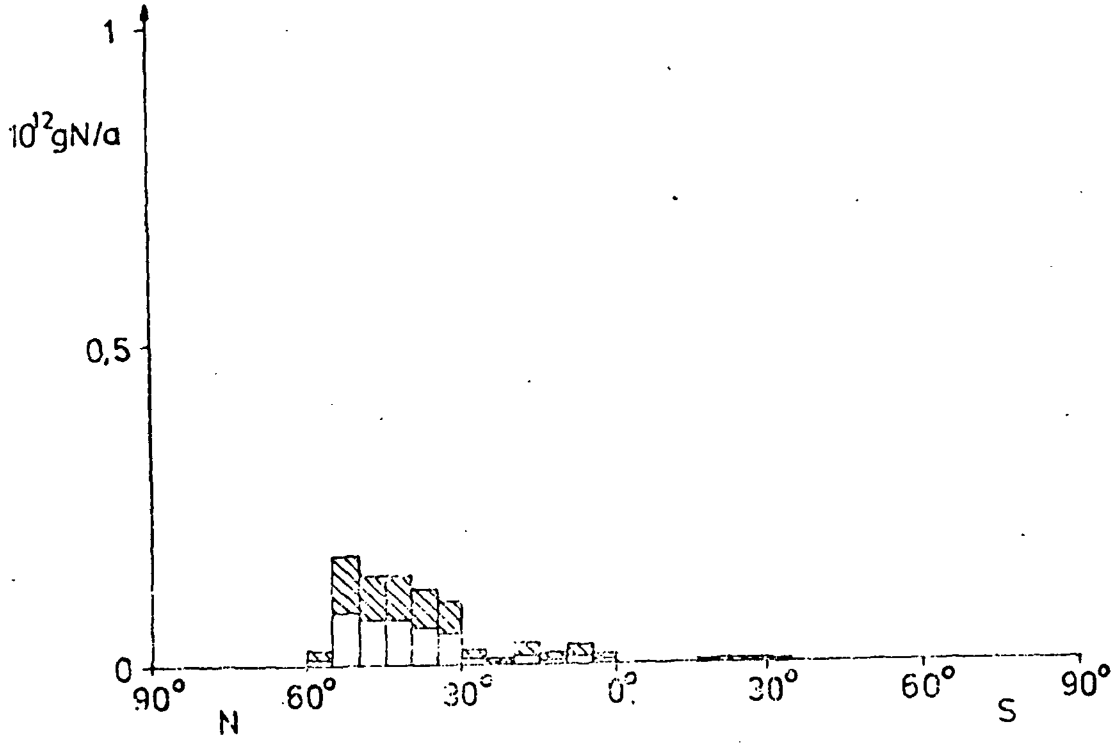


Figure 2.5: Zonal Distribution in 5°-Intervals of the NO_x-Quantities given off to the Atmosphere through the Combustion of Light Oil. The Shaded Region shows the Fluctuation of this Source.

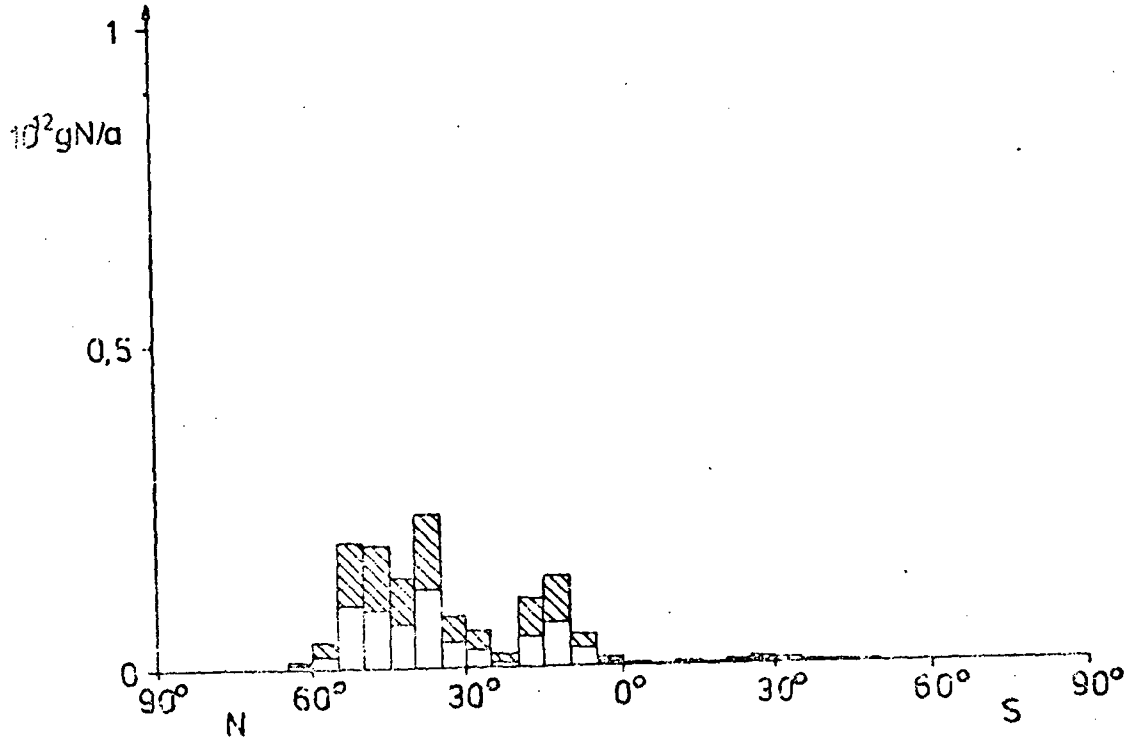


Figure 2.6: Zonal Distribution in 5° Intervals of the NO_x-Quantity given off to the atmosphere through the Combustion of Heavy Oil. The Shaded Region shows the Fluctuation of this Source.

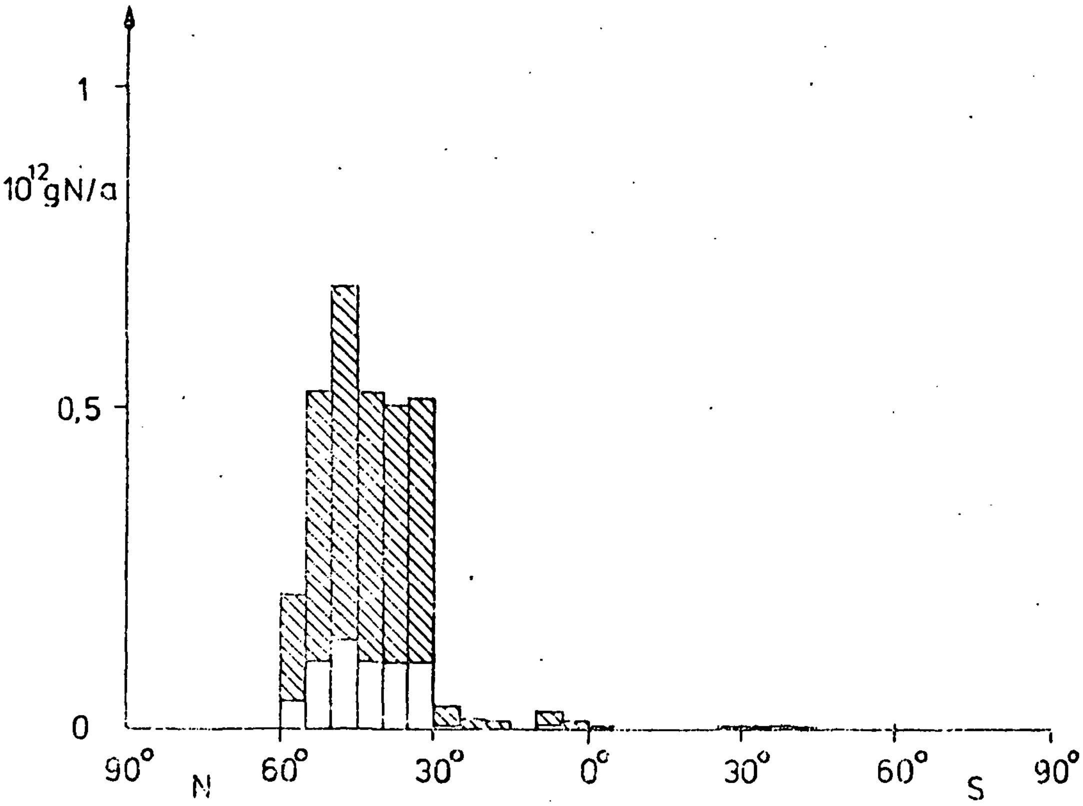


Figure 2.7: Zonal Distribution in 5° Intervals of the NO_x-Quantity given off to the Atmosphere through Combustion of Natural Gas. The Shaded Region shows the Fluctuation of this Source.

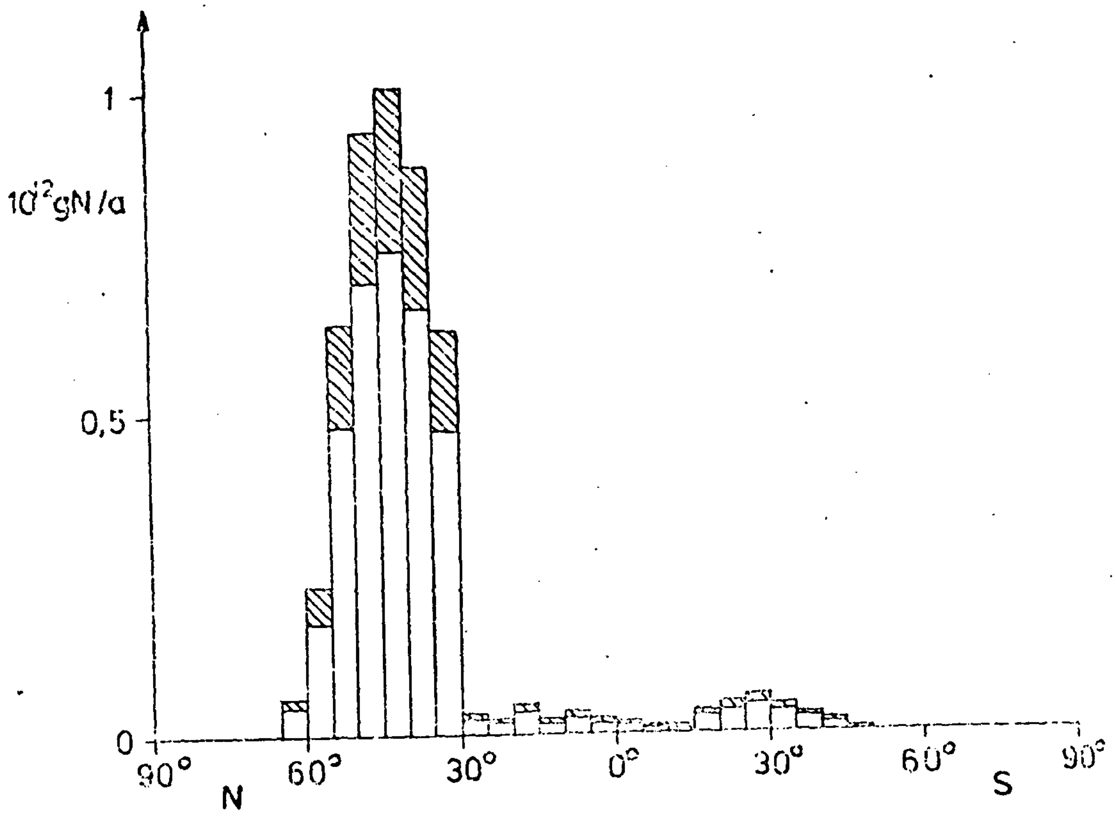


Figure 2.8 Zonal Distribution in 5° Intervals of the NO_x-Quantities given off to the Atmosphere through Vehicles. The Shaded Region shows the Fluctuation of this Source.

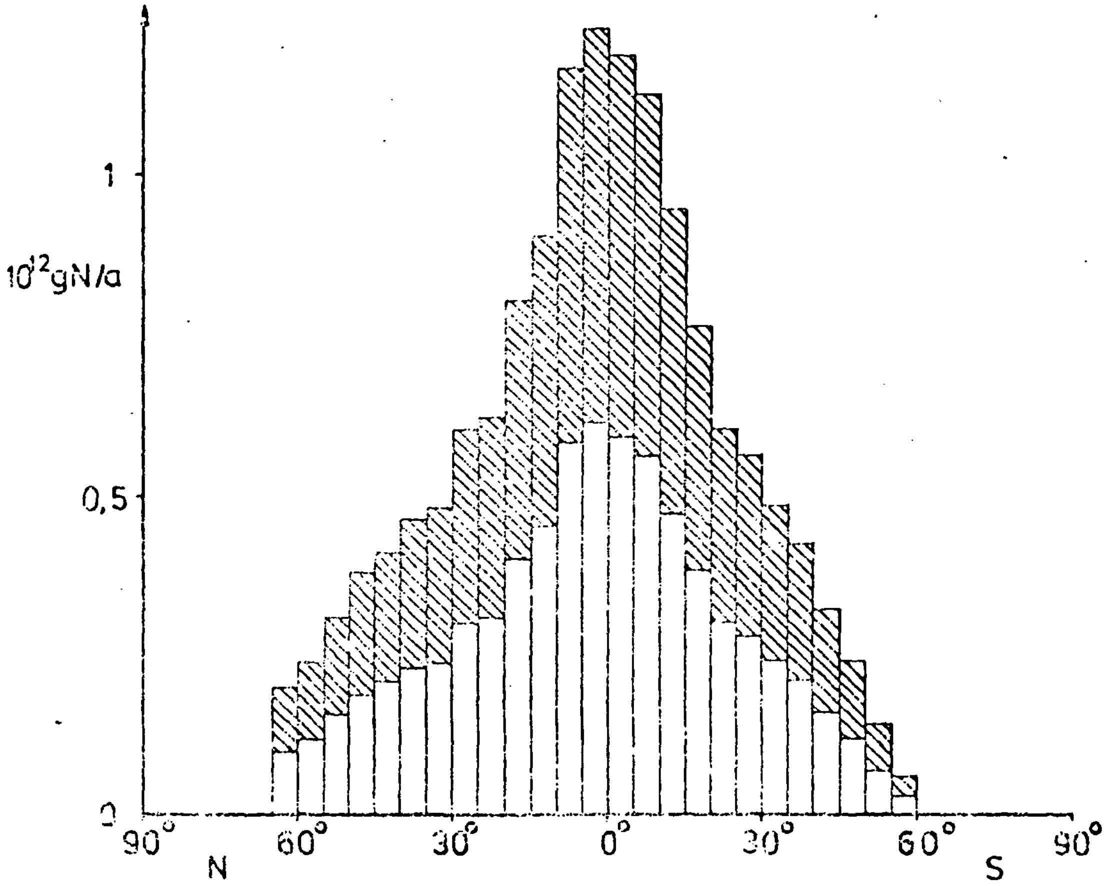
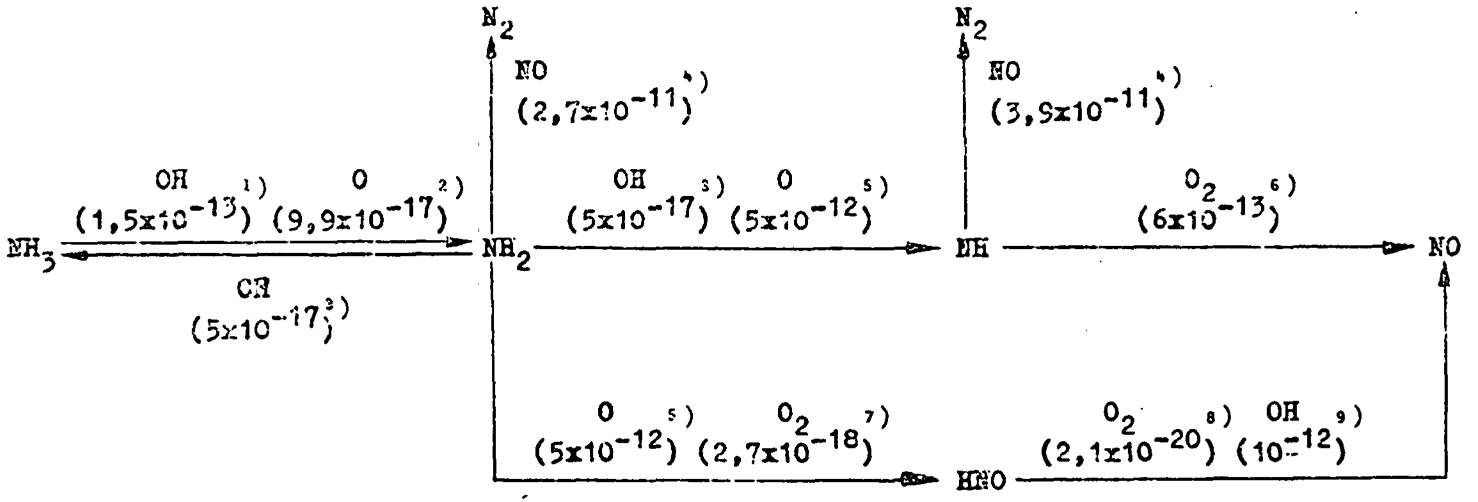


Figure 2.9: Zonal Distribution in 5° Intervals of NO_x-Quantities Produced during Thunderstorms. The Shaded Region shows the Fluctuation of this Source.

Table 2.4: CONCENTRATIONS (MOLECULES/cm^3) WHICH WAS USED TO CALCULATE THE FIGURE 2.10 UNDER STEADY STATE CONDITIONS

$NH_3 = 10^{10}$ $OH = 10^6$ $O_2 = 4 \times 10^{18}$

$NO = 10^8$ $O = 10^4$



( ) =Reaction constant in $\frac{cm^3}{molecules \cdot sec}$

[1] Stuhl (1973)

[2] Garvin (1973)

[3] **Garvin** and **Hampson** (1974)

[4] Gordon et al (1971)

[5] Albers (1963)

[6] McConnel (1973)

[7] Röth (1978)

[8] **Demerjian et al** (1960)

[9] **Halstead** and **Jenkins** (1968)

Figure 2.10: Outline of Important Ammonia Gas-Phase Reactions in the Troposphere

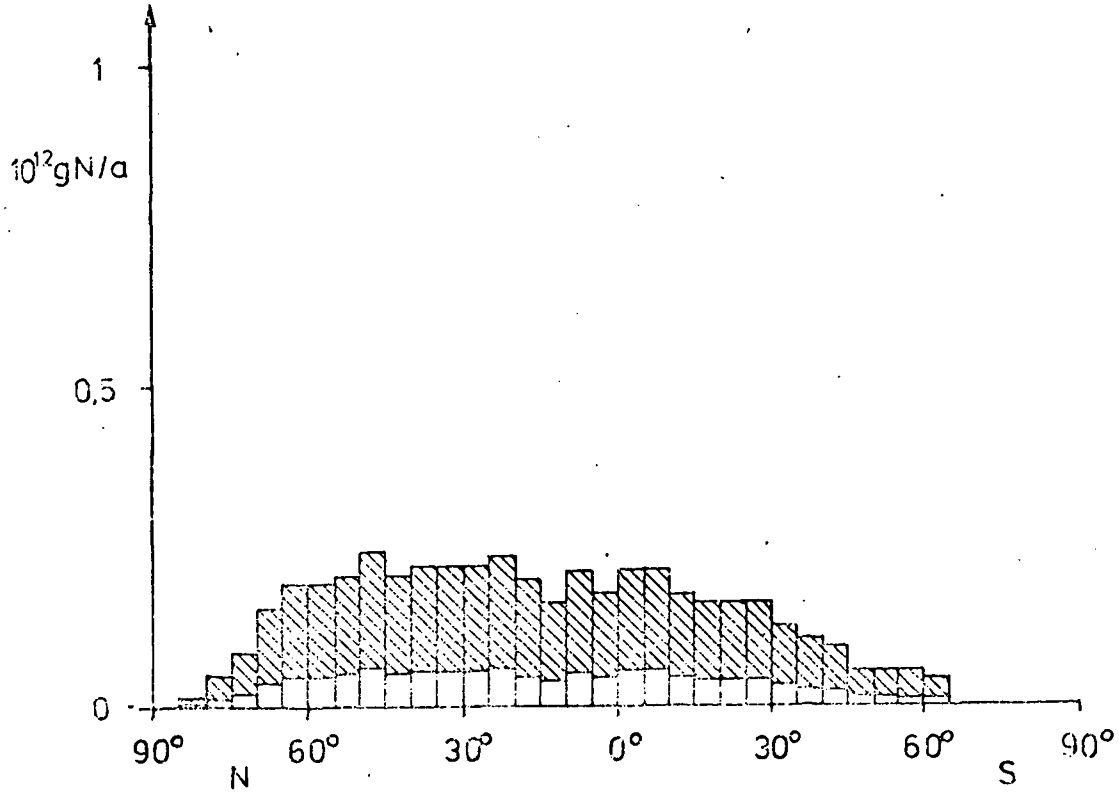


Figure 2.11: Zonal Distribution in 5^o Intervals of the NO_x-Quantities Produced through the Oxidation of Ammonia. The Shaded Region shows the Fluctuation of this Source

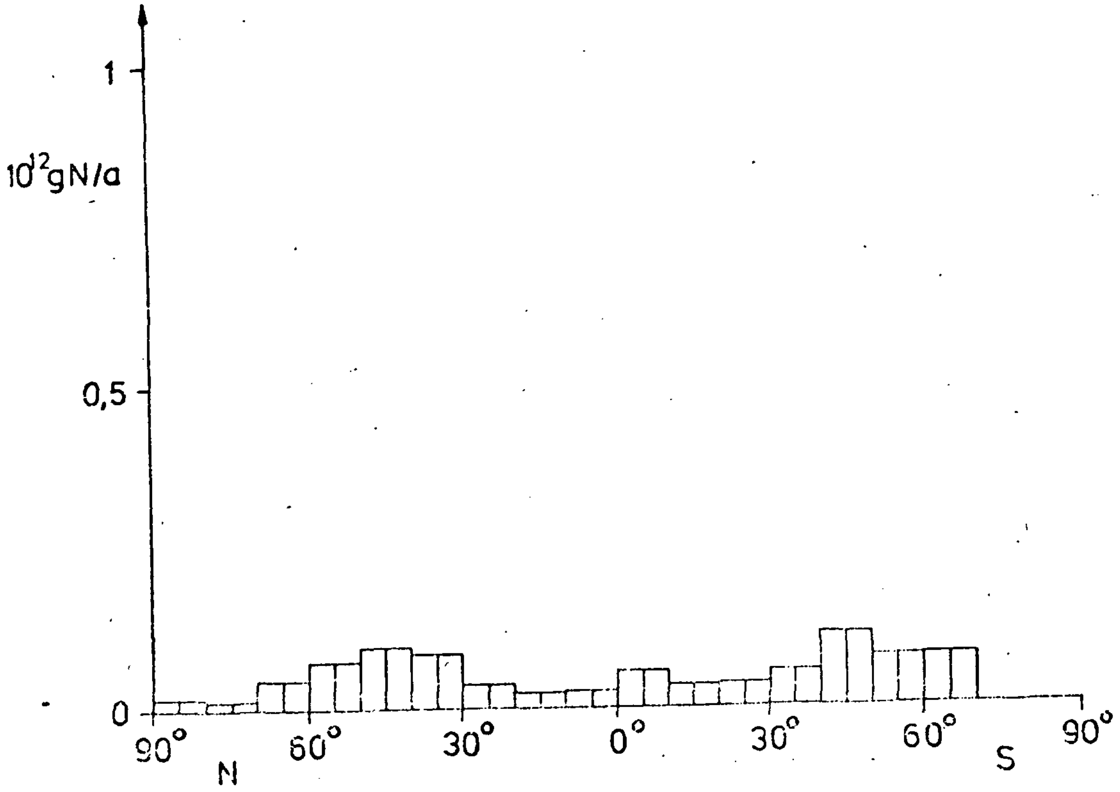


Figure 2.12: Zonal Distribution in 5° Intervals of the N-Quantities Transported as NO_x back into the Troposphere after the Decomposition of N_2O in the Stratosphere.

Table 2.5: NO_x-N Sources in 10^{12} g/yr broken down according to this study into Natural and anthropogenic Production mechanisms.

	N-hemisphere	S-hemisphere	World
Forest clearing	.4 - 1.7	.4 - 1.7	.8 - 3.4
Grassfires	0.8 - 1.9	1.0 - 2.4	1.8 - 4.3
Burning hard coal	1.8 - 5.5	.1 - .3	1.9 - 5.8
Burning soft coal	.8 - 2.2	<.1	.8 - 2.3
Burning light oil	.4 - .9	<.1	.5 - .9
Burning heavy oil	.7 - 1.4	<.1	.7 - 1.5
Burning natural gas	.6 - 3.1	<.1	.6 - 3.1
Vehicle traffic	3.4 - 4.4	.3 - .5	3.7 - 4.9
Thunderstorms	3.9 - 8.0	3.5 - 7.0	7.4 - 15.0
N_2O from the stratosphere	.8	.8	1.7
NH_3 oxidation	.7 - 3.0	.5 - 1.9	1.2 - 4.9
Total sources	14.3 - 32.9	6.6 - 15.0	20.9 - 47.8
Anthropogenic production mechanisms	8.5 - 20.0	1.3 - 4.0	9.8 - 24,0
Natural production mechanisms	5.8 - 12.8	5.3 -11.0	11.1 - 23.8

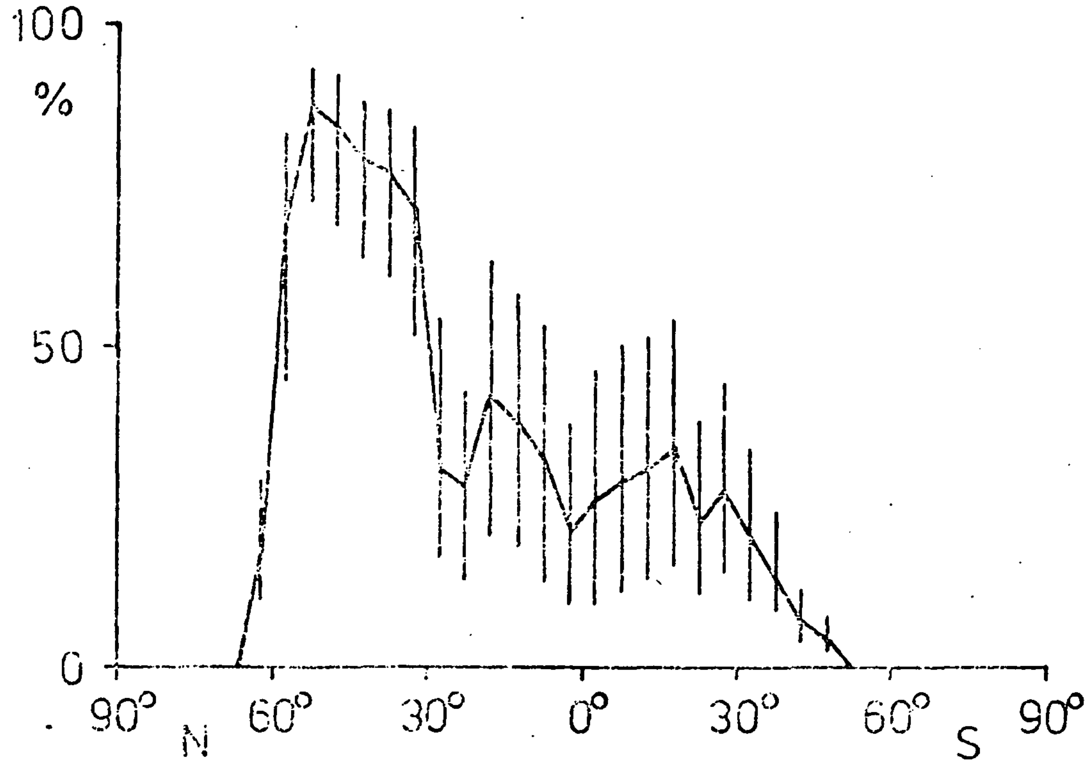


Figure 2.13: Zonal Distribution in 5° Intervals of the Anthropogenic Fraction of total NO_x Emission in percent. The Error bars result from the Fluctuation of Sources, the Solid Curve was Computed from the Average Values of the Emitted Quantities

Natural sources:	Anthropogenic sources:
Thunderstorms	Combustion of fossil fuels
N_2O-N from the stratosphere	Vehicle traffic
NH_3 oxidation	Combustion of cleared wood
50% of grassfires	50% of grassfires

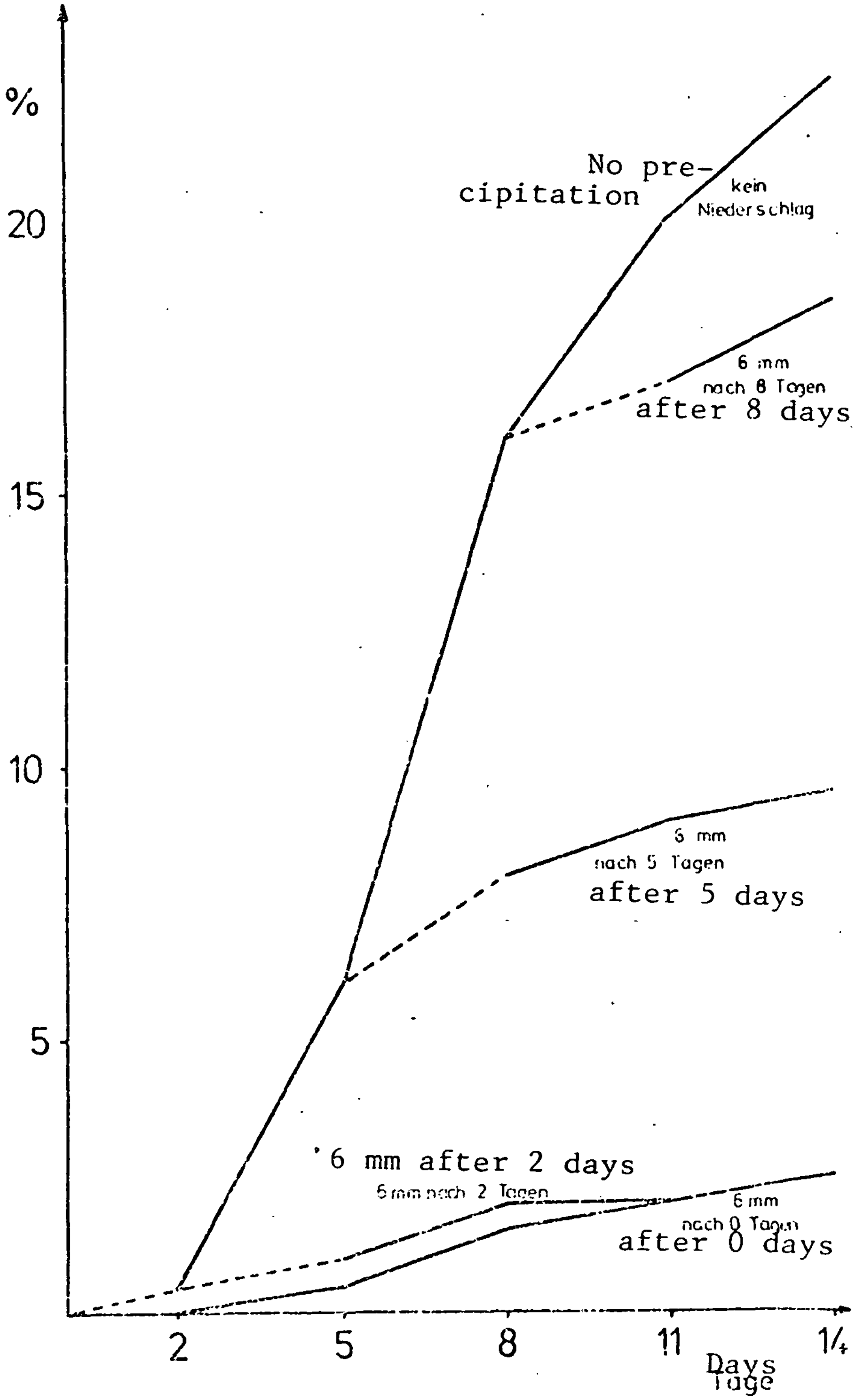


Fig. 2.14: Cumulative NH_3-Losses from Soils after Application of Urea. The shorter the time between application of fertilizer and the beginning of rainfall, the smaller the ammonia losses (derived from Förster and Lippold, 1975).

Table 2.6: NH_3-EMISSIONS FROM MINERAL FERTILIZERS TO THE ATMOSPHERE (IN % OF APPLIED NITROGEN)

Autoren[a]		Bemerkungen[b]	Labor[c]	Feld[d]
Jewitt	(1942)	(Sudan)	28 - 39	
Tovberg-Jensen und[e] Kjar	(1950)		5	
Kresge und[e] Stachell	(1959)	[f]saure Böden		[g]nicht erkennbar
Gerritsen und[e] de Hoop	(1957)	[f]saure Böden		[g]nicht erkennbar
Wagner und[e] Smith	(1959)	[h]Gesamt N-Verlust!	12	
Acquaye und[e] Cunningham	(1965)	[i]Wald (Tropen)	1.9 ± .75	8 ± .12
Musa	(1958)	[j]25% Wassersättigung des Bodens		49
		50% "		30
		75% "		27
Nommik	(1966)	(4 Tage[k]) ($NaNO_3$)		16
		($CaNH_4NO_3$)		25
		($(NH_4)_2SO_4$)		21
Förster und[e] Lippold	(1975)			14 - 28
Buchner	(1977)			1 - 2

a-authors b-comments c-laboratory d-field e-and f-acid soils g-not known h-total nitrogen loss i-forest (tropics) j-25% water saturation of soil k-four days

Table 2.7: NH_3-EMISSIONS FROM UREA TO THE ATMOSPHERE (IN % OF APPLIED NITROGEN QUANTITY)

Autoren[a]		Bemerkungen[b]		[c]Labor-	[d]Feld-Messungen
Acquaye und[e] Cunningham	(1965)		[f]tropischer Wald	21 ± 8	18 ± 8
Bernier et. al.	(1969)	23 Tage[g]		20 - 70	
Volk	(1970)	4 Tage[g]		3	
McGarity und[e] Hoult	(1971)	14 Tage[g]		6 - 17	
Nommik	(1973b)	13 Tage[g]	Granulat[h] groß[i]	12	
			klein[j]	22	
		34 Tage[g]	groß[i]	34	
			klein[j]	48	
Mahendrappa und[e] Salonius	(1974)			3.2-4.2	
Nommik	(1966)	4 Tage[g]			46
Musa	(1968)		Sudan; 25% Wassersättigung[k] des Bodens		35
			50% "		13
			75% "		6
Overrein	(1968)				3.5
Förster und[e] Lippold	(1975)	24 Tage[g]			29 ± 7
Buchner	(1977)				6 - 7

a-authors b-comments c-laboratory d-field measurements e-and f-tropical forest g-days h-granulate i-large j-small k-25% water saturation of soil

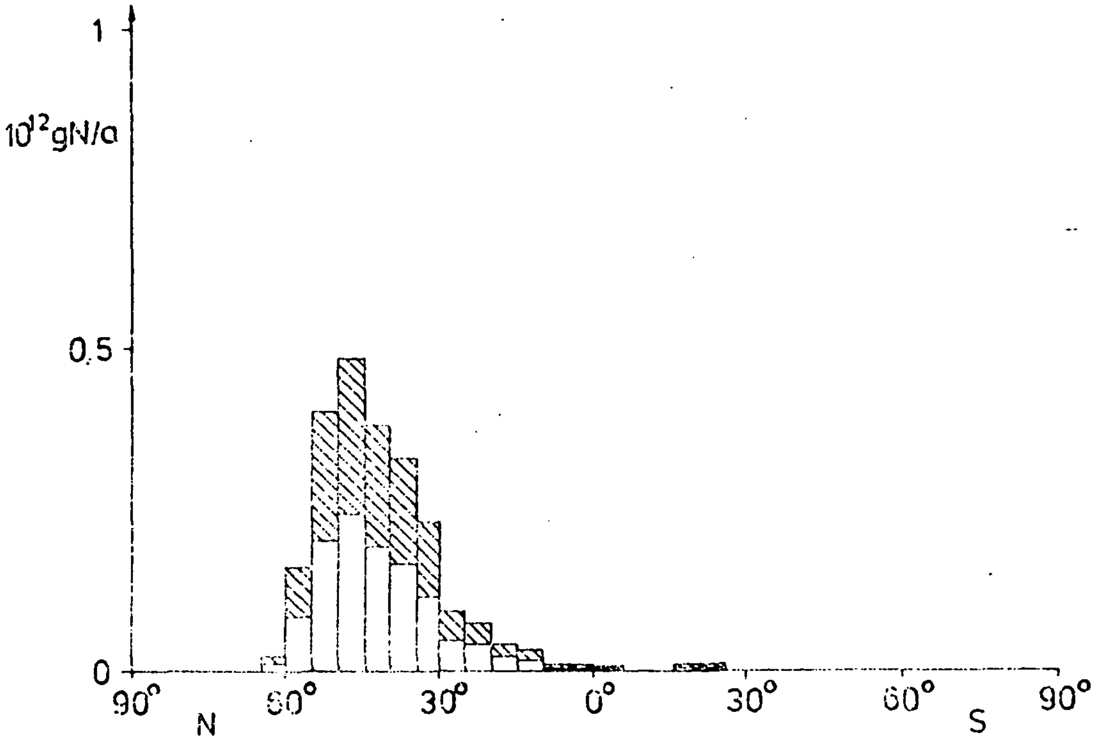


Figure 2.15: Zonal Distribution in 5° Intervals of NH_3-Losses from Soils after Application of Mineral Fertilizers. The Shaded Region denotes the Fluctuation of this Source.

Table 2.8: NITROGEN QUANTITIES IN g N/ANIMAL/DAY IN THE EXCREMENT OF *DOMESTIC* ANIMALS IN MIDDLE LATITUDES

(g N/day	Feces N	Urine N	Total N	slightly soluble nitrogen in feces	
Cattle	70	59	129		from Haselhoft, citen in Roemer-Scheffer, 1959
Horses	86	39	125		
Sheep	28	10	38		
Cattle	118 - 148	100	218 - 248	12 - 15	from Nehring, 1963 Mangold, 1929
Horses	34 - 78	80	114 - 158	3 - 7	
Sheep	5 - 7	15	20 - 22	0,4 - 0,6	
Pigs	12 - 18	10	22 - 28	1.6 - 2.4	

Table 2.9: NITROGEN QUANTITIES IN g N/DAY/ANIMAL EXCRETED BY DOMESTIC ANIMALS IN TROPICAL REGIONS

I	[a]Lebensgewicht (LM)[+] (kg)		[b]K[++] (empirische Konstante)	[c]Gesamt N berechnet aus $KxLM^{0.75}$[++]
[d]Rind	400 - 600		0.4 - 1	36 - 121
Schaf[e]	35 - 70		0.4	6 - 10
Schwein[f]	70 - 100	(Afrika)[g]		
	170 - 200	(Asien)[h]		
	130 - 170	(gewichtet)[i]	1.3 - 1.7	50 - 80

II[+]	[j]Kot N	[k]Harn N	[l]Gesamt N
[d]Rind	112 - 189	112 - 168	224 - 357
[e]Schaf	20 - 43	2 - 4	22 - 47
[f]Schwein	16 - 45	18 - 50	34 - 93

[+] Festerling (1978)

[++] Steinbach (1978)

a-weight b-empirical constant c-total N, computed as d-cattle e-sheep f-pigs g-Africa h-Asia i-weighted j-feces k-urine l-total N

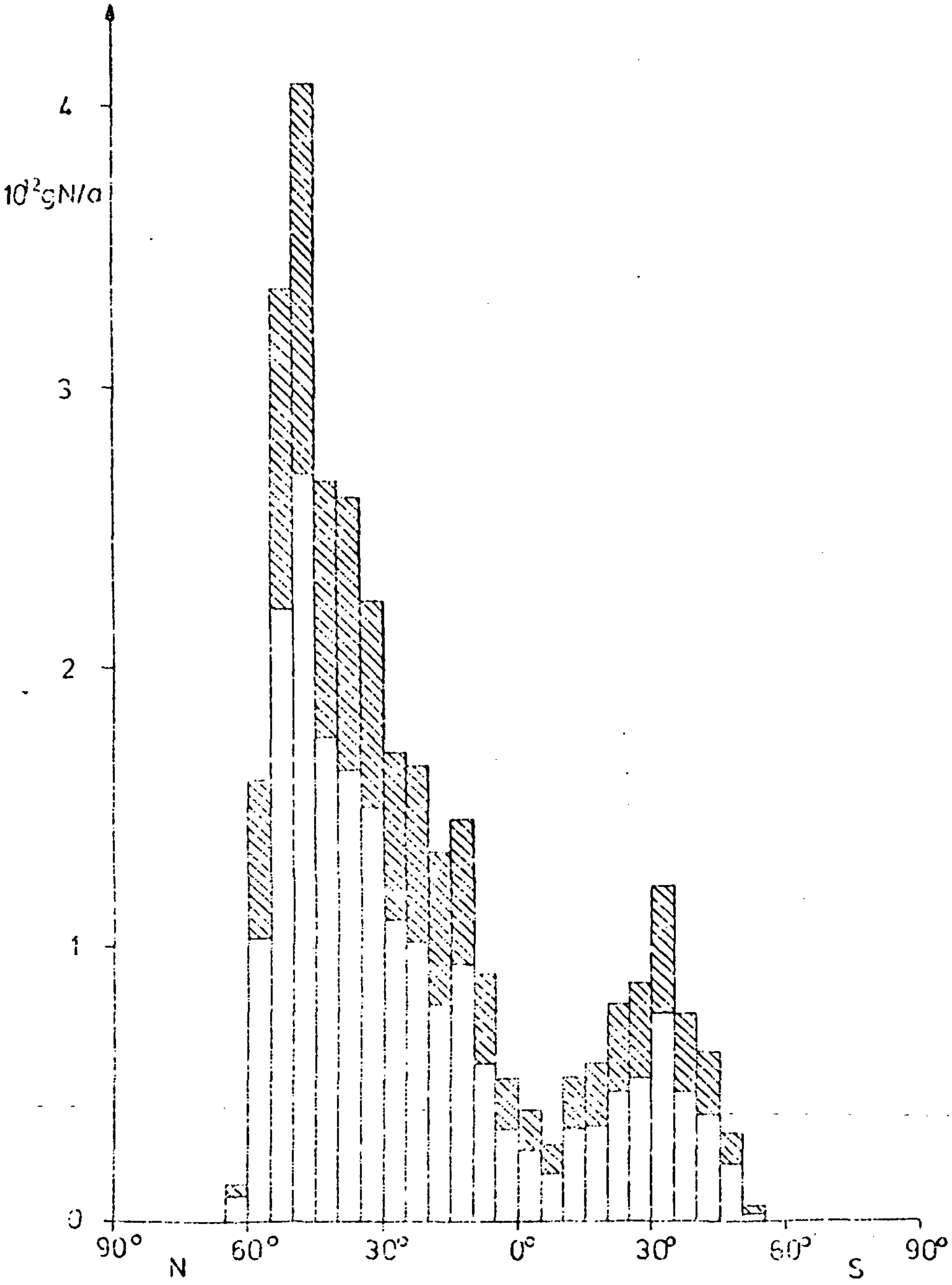


Figure 2.16: Zonal Distribution in 5° Intervals of the NH_3-Quantities given off to the Atmosphere in Animal Excrement. The Shaded Regions denote the Fluctuation of this Source

Table 2.10: NH_3-N SOURCES (DATA IN 10^{12} g N/yr)

	N-hemisphere	S-hemisphere	World
Unfertilized soil	0.6 - 1.3	0.3 - 0.8	1 - 2
N-containing mineral fertilizers	1,2 - 2,3	0.04 - 0.07	1,2 - 2,4
Domestic Animals			
Cattle	11,8 - 17,5	2.6 - 3.8	14.4 - 21.3
Sheep	1,3 - 2,6	0.9 - 1,8	2,2 - 4,4
Pigs	1,2 - 1,7	0,1 - 0,2	1,3 - 1,9
Other animals	1,4 - 2,2	0,4 - 0,6	1,8 - 2,8
Vehicles	0,2 - 0,3	0,1	0,2 - 0,3
Fossil fuels	0,1	0,1	0,1
Total Sources	18 - 28	4 - 7	22 - 35

[Commas in tabulated material are equivalent to decimal points]

Table 3.1: FREQUENCY OF EMPLOYED DETECTION METHODS (IN %)

1. NO_3^--N

Brucine	18	
Colorimetric*	7	
Devardas alloy or copper-zinc	47	
Griess reaction	6	
Phenoldisulfonic acid	17	
Polarography	5	

2. NH_4^+-N

Berthelot	6	
Colorimetric*	6	
Nessler after distillation	82	
Nessler without distillation	6	(not taken into consideration)

* A part of the BAPMoN stations gave no precise data on the method of determination.

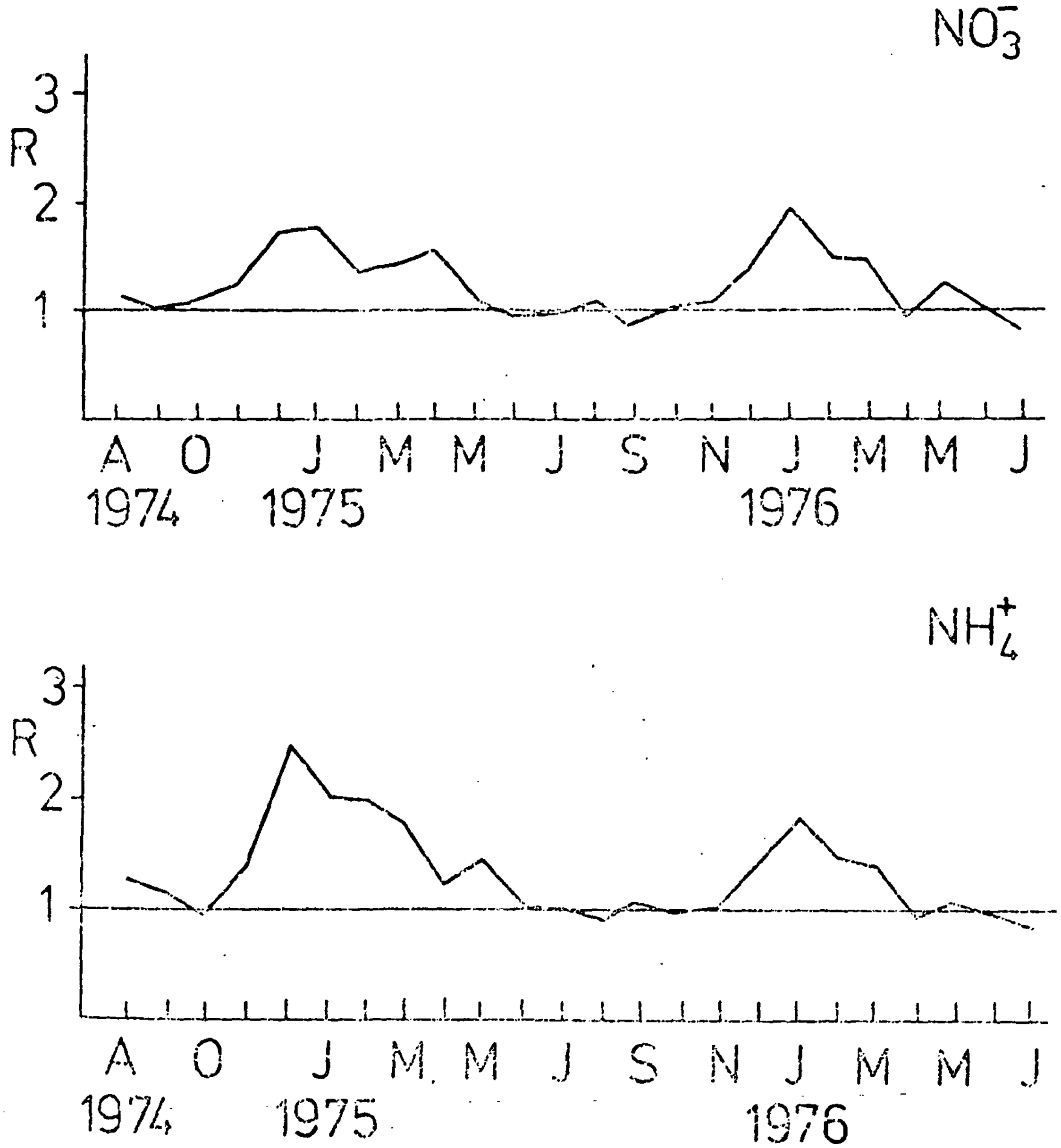


Figure 3.1:The Influence of dry Deposition on Total Deposition. R is the Quotient of Monthly Total Deposition and Monthly Wet Deposition (Galloway and Likens, 1978). In Winter, the Fraction of dry deposited N-components in Ithaca, New York, is greater than in Summer.

Table 3.2: AVERAGE CONCENTRATIONS FROM MONTHLY OR INDIVIDUAL VALUES WEIGHTED WITH THE PARTICULAR PRECIPITATION QUANTITY, COMPARED TO UNWEIGHTED AVERAGES. n IS THE NUMBER OF INDIVIDUAL RAINFALLS.

	$\bar{K} = \frac{\Sigma P_i \times K_i}{\Sigma P_i}$ [b](gewichtet)	$\bar{K} = \frac{\Sigma K_i}{n}$ [c](ungewichtet)
100 km südlich von Prag[a] (Monatsmittelwerte) (Moldan, 1977)		
NO_3^--N	.59 ± .25	.65 ± .28
NH_4^+-N	.85 ± .47	.86 ± .06
Jungfraujoch[d] (Sterzky, 1977) (Einzelwerte)[e]		
NO_3^--N	.52 ± .32	.69 ± .72
NH_4^+-N	.37 ± .15	.55 ± .48
Pajerne (Sterzky, 1977) (Einzelwerte)[e]		
NO_3^--N	1.26 ± .97	1.39 ±1.6
NH_4^+-N	.91 ± .71	1.68 ±1.57
Kampala (Visser, 1961) (Einzelwerte)[e]		
NO_3^--N	.38 ± .21	.55 ± .35
NH_4^+-N	.52 ± .28	.61 ± .38

a-100 km South of Prague (Monthly averages) b-weighted c-unweighted d-Jungfrau (Mt. in Switz.) draw e-individual values

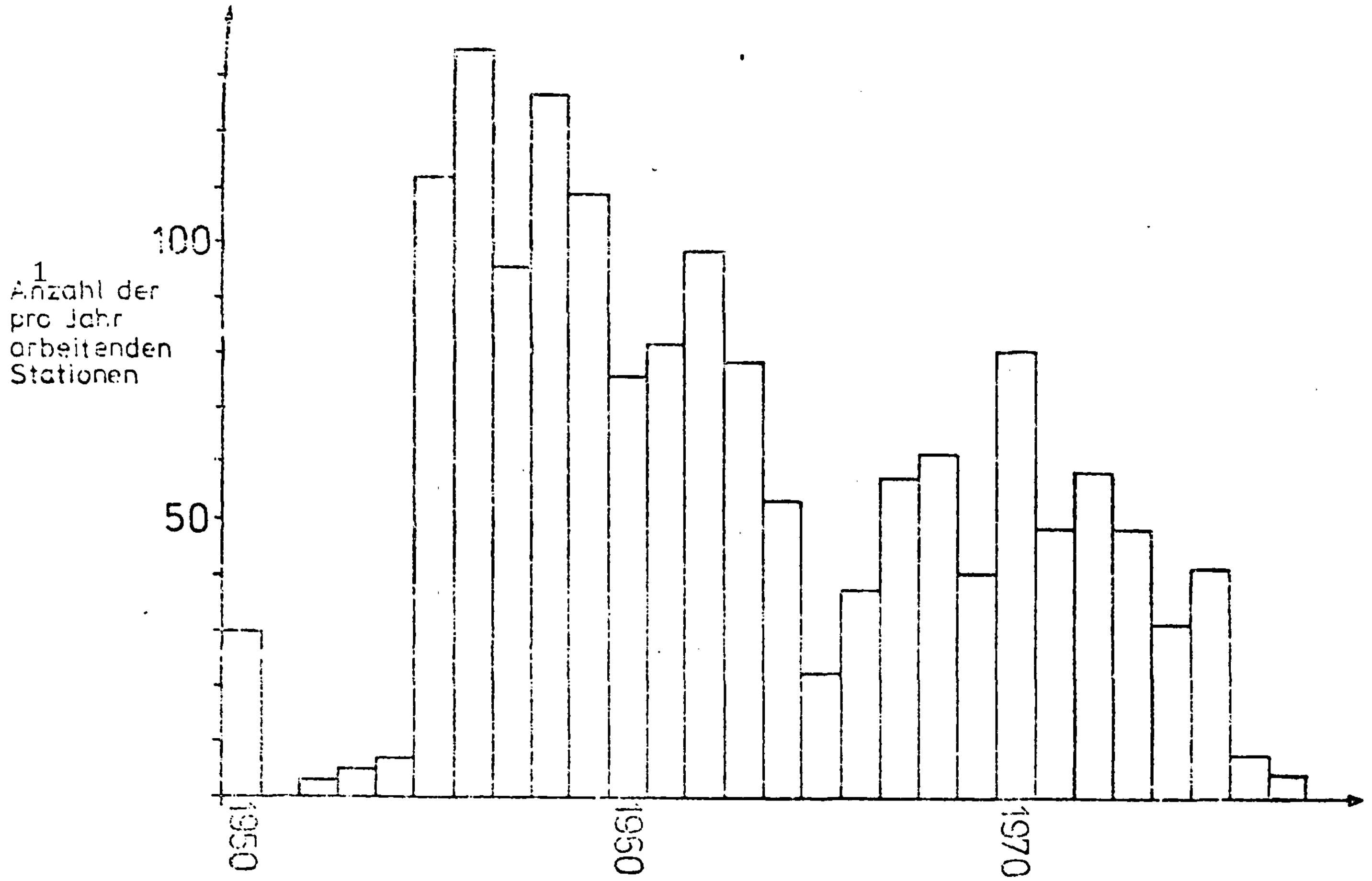


Figure 3.2: Number of Stations with annual Precipitation Analyses in the Northern Hemisphere in the Period between 1950 and 1977; their results were used in this Report.

1-number of stations operating annually

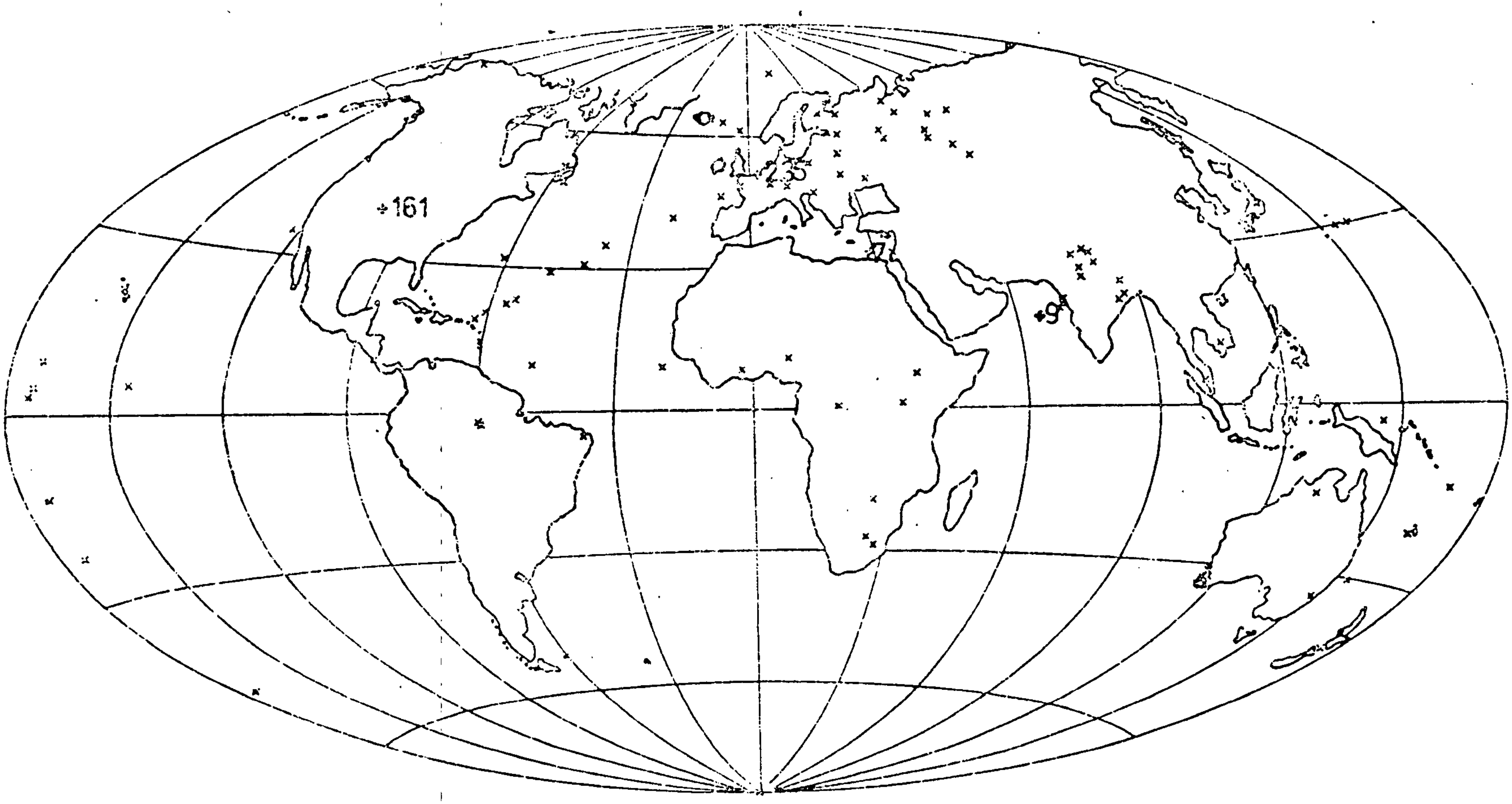


Figure 3.3: Geographic Location of the Used Measuring Stations. In Europe, USA and Bombay, the Number of Stations is shown, and not their Positions.

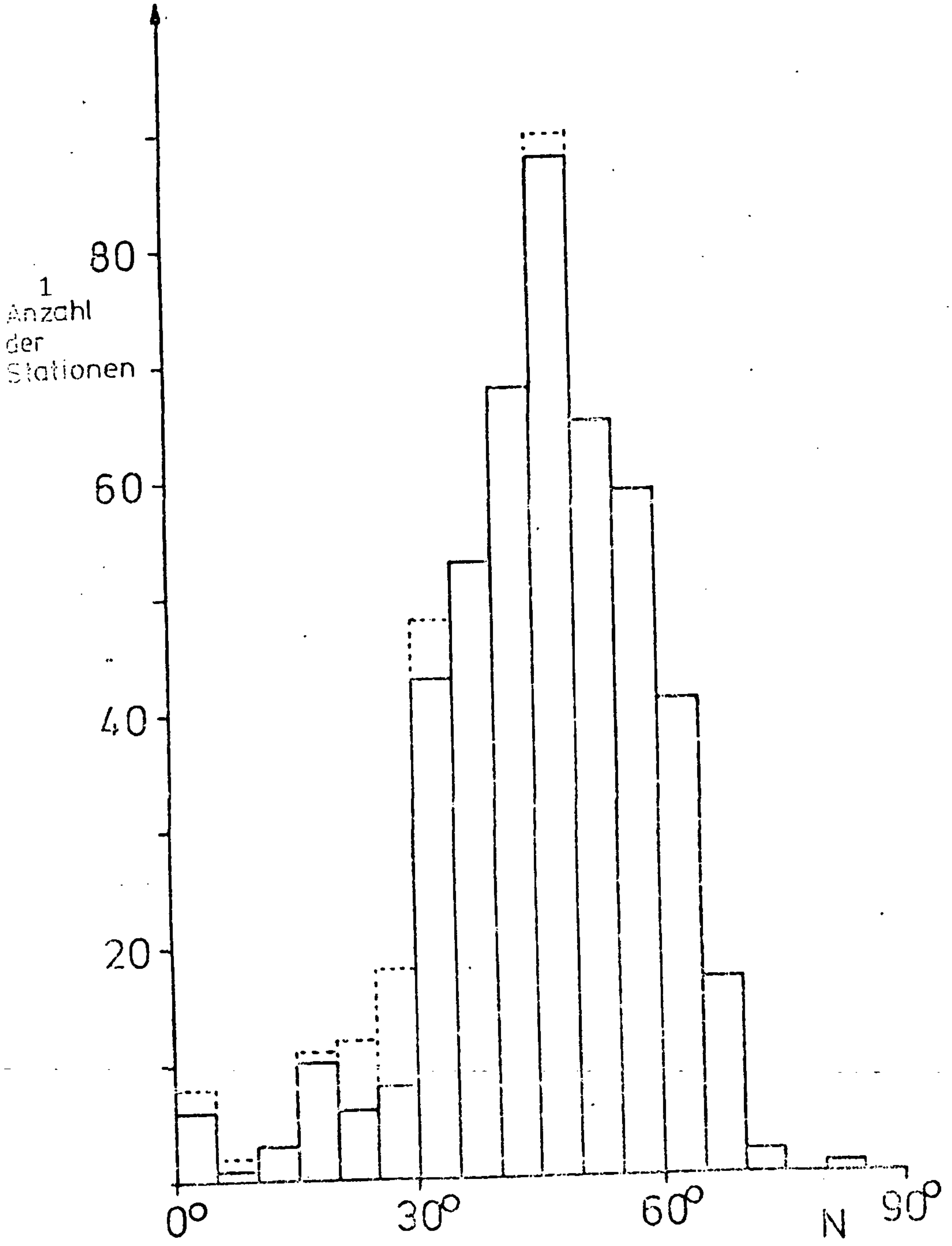


Figure 3.4: Zonal Distribution in 5° Intervals of the Number of Locations on the Northern Hemisphere where Precipitation Analyses were Performed for several years during the Period from 1950 to 1977. Ocean Stations are dashed-in, but only Invididual Samples were collected there, thus no Annual Averages were Determined.

Key: 1-number of stations

Table 3.3 Summary of Precipitation Analyses examined at the Institute for Atmospheric Chemistry of the KFA, Jülich.

Location	Time	NO_3^--conc. μgN/ml
Burmuda	July 1977	0.06
Kenya (Nairobi)	June 1977	0.1
Elba (Capoliveri)	Sept.-Oct. 1977	0.3
SW France (Aire Sur l-Adour)	8/31 - 9/15/76	0.1 - 0.9
Austria (St. Johann)	Sept. 10-16, 1976	0.1 - 0.5
South pole (snow)		0.3 (contaminated)
Paciifc		0.002 - 0.003 (two samples)

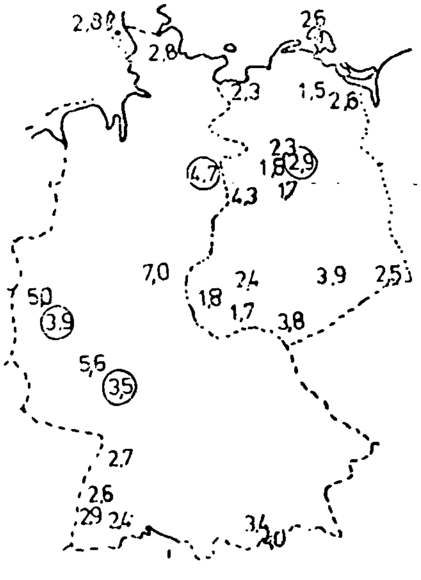


Fig. 3.5: NO_3^- Total Deposition Rates in the FRG and GDR (EACN, 1973a, b, 1975; Georgii 1965, 1966; Reiter and Carnuth, 1965; Mayer and Ulrich, 1875; Mrose, 1961; Reiter, 1966). The values measured in Cities (denoted with 0) were not significatnly higher.

Table 4.1: COMPILATION OF DEPOSITION RATES OF NITRATE AND AMMONIUM NITROGEN PREVIOUSLY MEASURED IN AFRICA (100 mg N/m^2/yr ≙ 1 kg N/ha/yr).

[a]Autor Meßart[b]	NO_3^--N	NH_4^+-N
	mg N/m^2 a	
Ingham (1950a, b) Natal (Südafrika)[c]	124	1.070 [g](falsche Analyse?)
Weinmann (1955) Salisbury (Rhodesien)[d]	95	277
Meyer und Pampfer (1959) Yangambi (Kongo)[e]	220	320
Nye (1961) Kade (Ghana)	247	1.081 [g](falsche Analyse?)
Visser (1961, 1964) Kampala (Uganda)	488	660
Jones (1971) Jones und Bromfield (1970) Samaru (Nigeria)	200	250
eigene Messungen (1977)[f] Kenia (aus einigen Werten auf ein Jahr extrapoliert trockene Deposition ist nicht enthalten)	140	200

a-author b-type of measurement c-South Africa d-Rhodesia e-Congo f-our measurements (1977) Kenya (dry deposition extrapolated to one year from our values, is not included) g-wrong analysis?

Table 4.2: RESULTS OF PRECIPITATION INVESTIGATIONS IN MANAUS, SOUTH AMERICA

	NO_3^--N	mg/m^2 a	N_4^+-N
Brinkmann (1977)	9		140
Ungemach (Anonymous, 1972)	237-267		294-335
Used here	150		>200

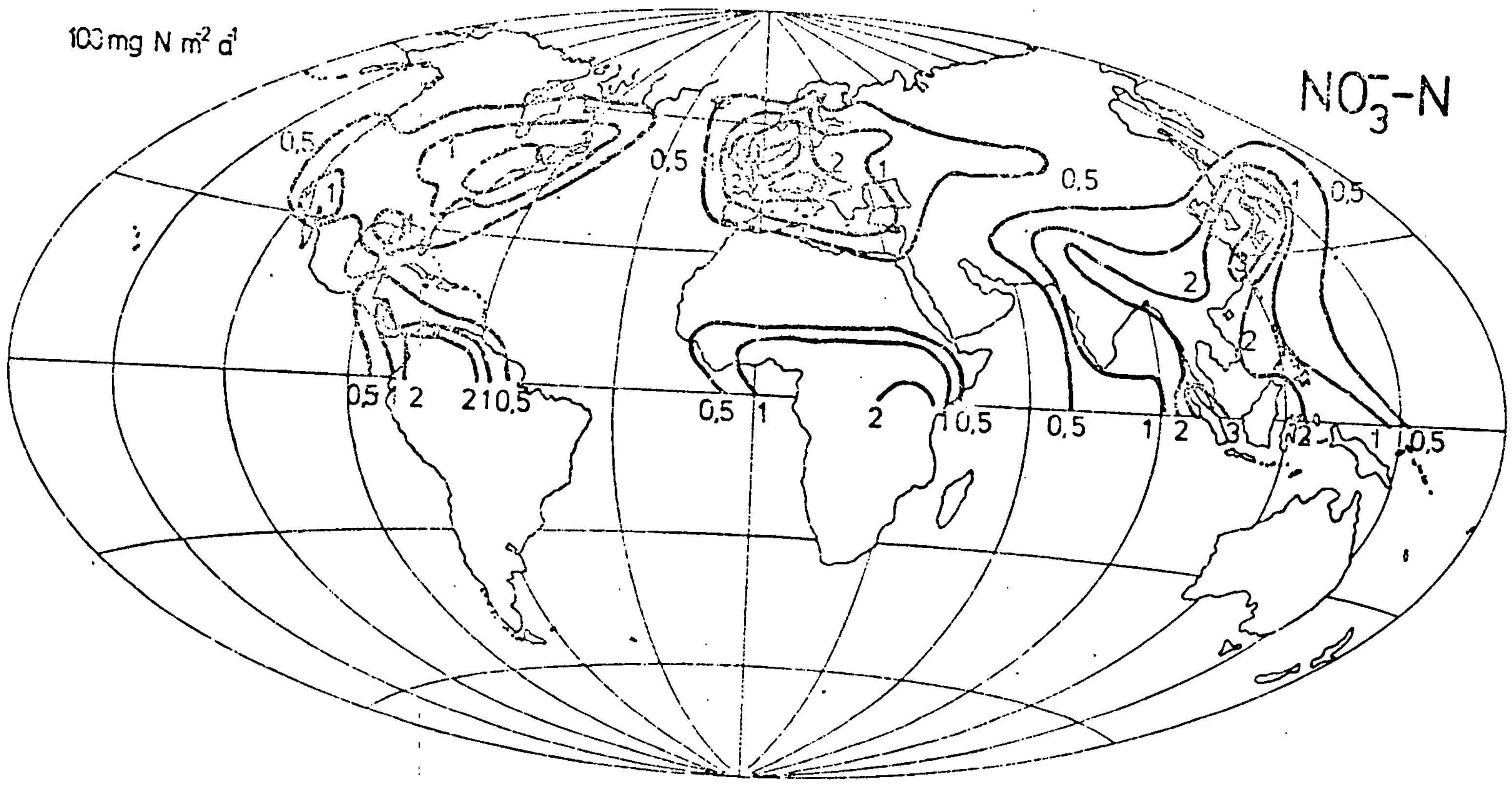


Fig. 4.1: Distribution Map of NO_3^--N Total Deposition Rates on the Northern Hemisphere. It is based on the Results of Precipitation Analyses from the Period 1950 to 1977. Some Measurements in Central Europe gave Values up to 700 mg/m^2-yr (100 mg N / m^2-yr $\hat{=}$ 1 kg / hectare-yr).

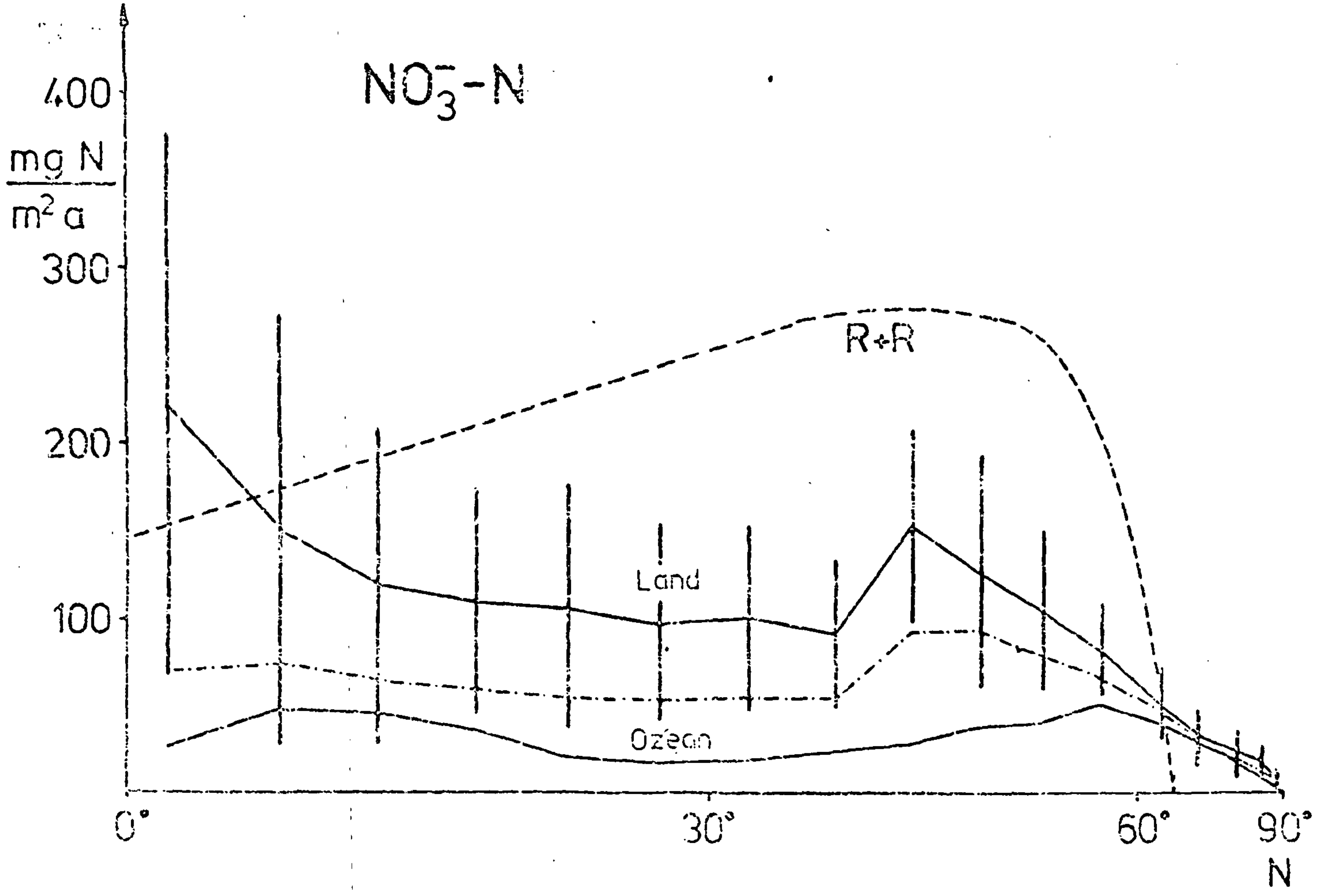


Fig. 4.2: Zonal Distribution in 5° Intervals of the NO$_3^-$-N Total Deposition Rates over Land and Ocean derived from the Distribution Map (fig. 4.1). The error bars of the "Land" curve show the fluctuation range of deposition rated in the Invididual Intervals (see sec. 4.3). (·—·–·–·) shows the zonal distribution of deposition rates weighted with the Particular Land and Ocean surface-areas. For comparison, the Zonal Distribution of Deposition Rates from Robinson and Robbins (1970b) (R+R) are drawn in.

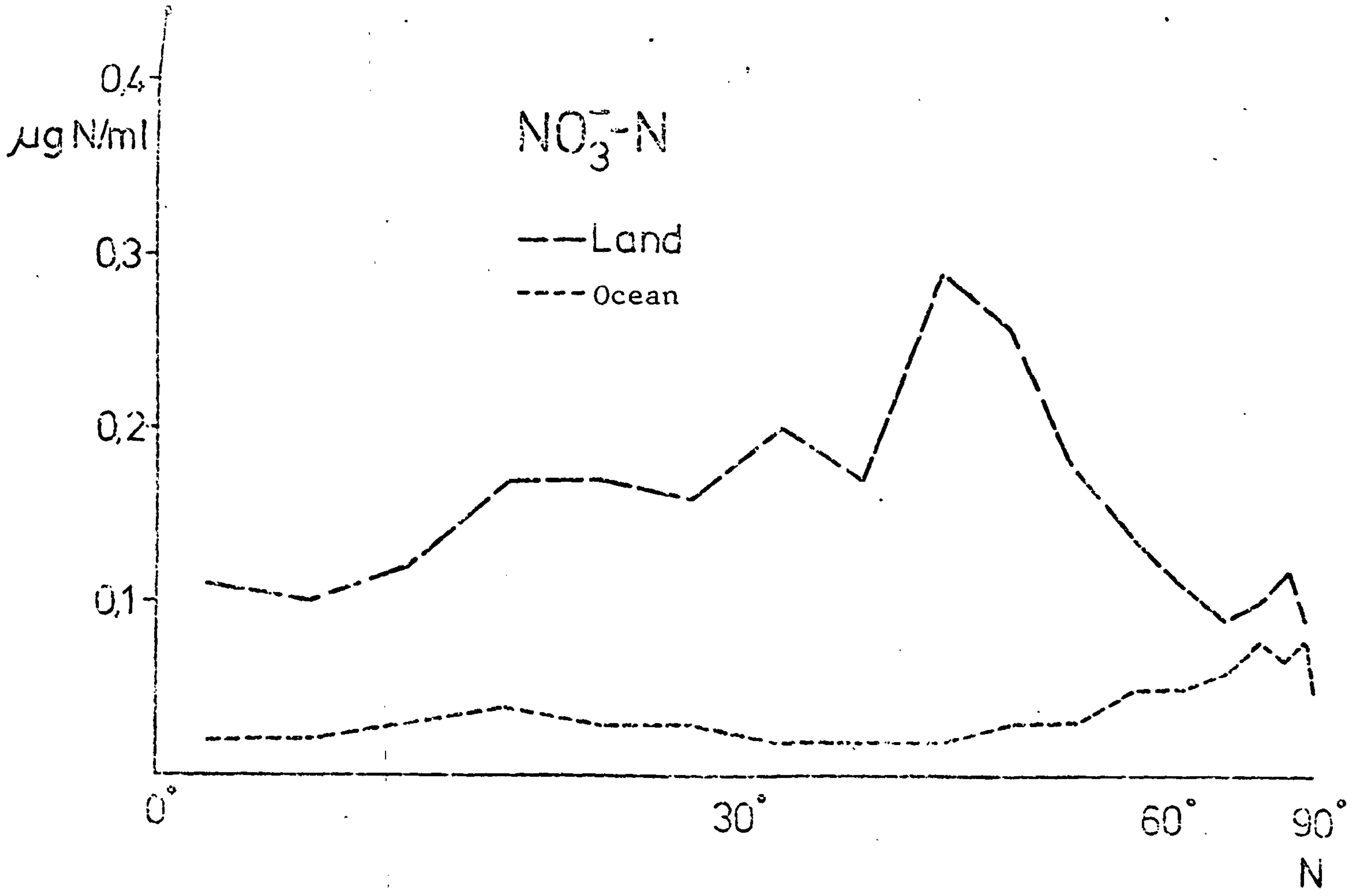


Fig. 4.3: Zonal distribution in 5° Intervals of NO_3^- Total Precipitation Concentration over Land and ocean on the Northern Hemisphere

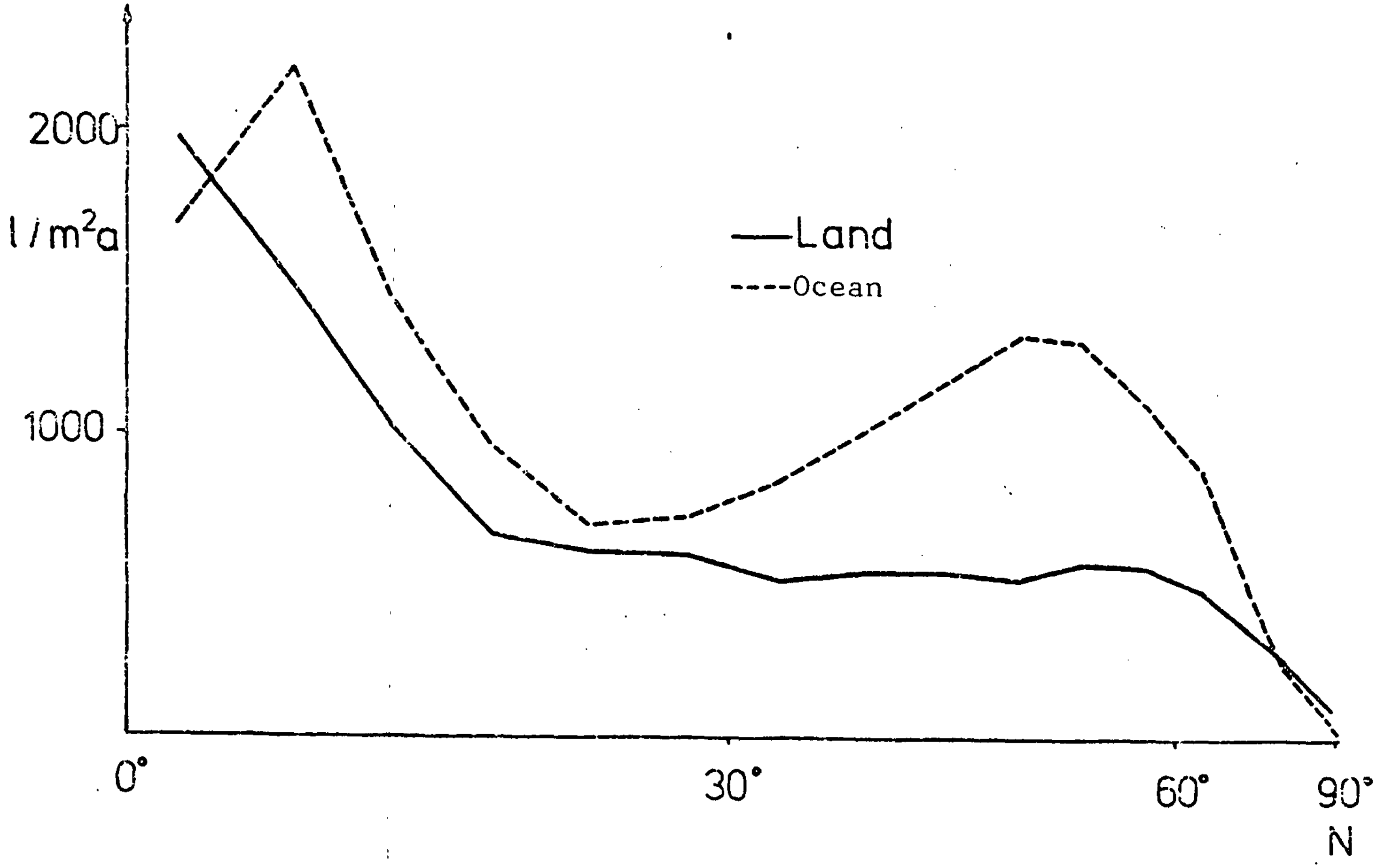


Fig. 4.4: Zonal Distribution in 5° Intervals of the Precipitation Rates on the Northern Hemisphere (Baumgartner and Reichel, 1975).

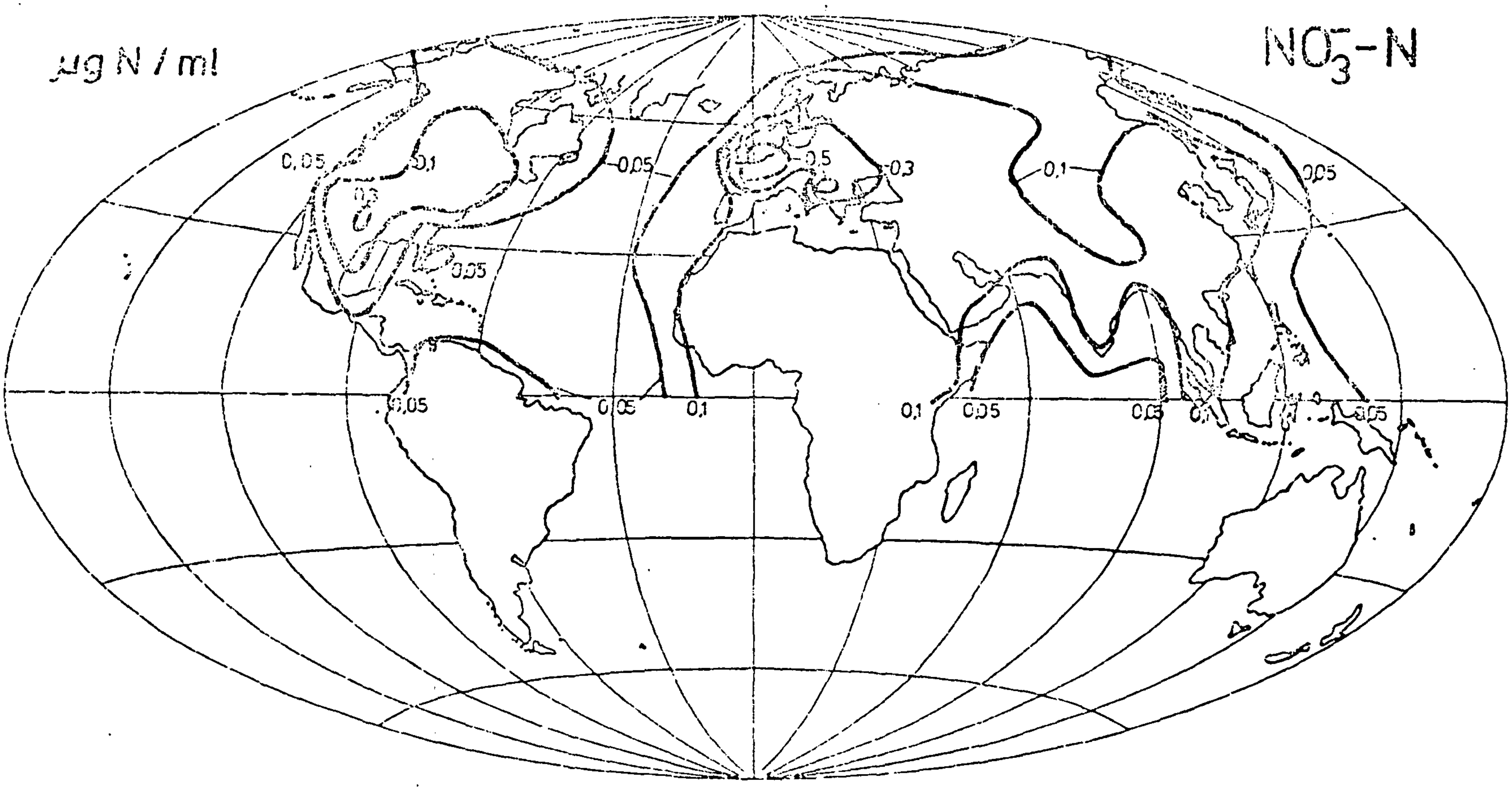


Fig. 4.5: Distribution Map of NO_3^--N Total Precipitation Concentrations on the Northern Hemisphere. It is based on Precipitation Analyses from the period from 1950 to 1977.

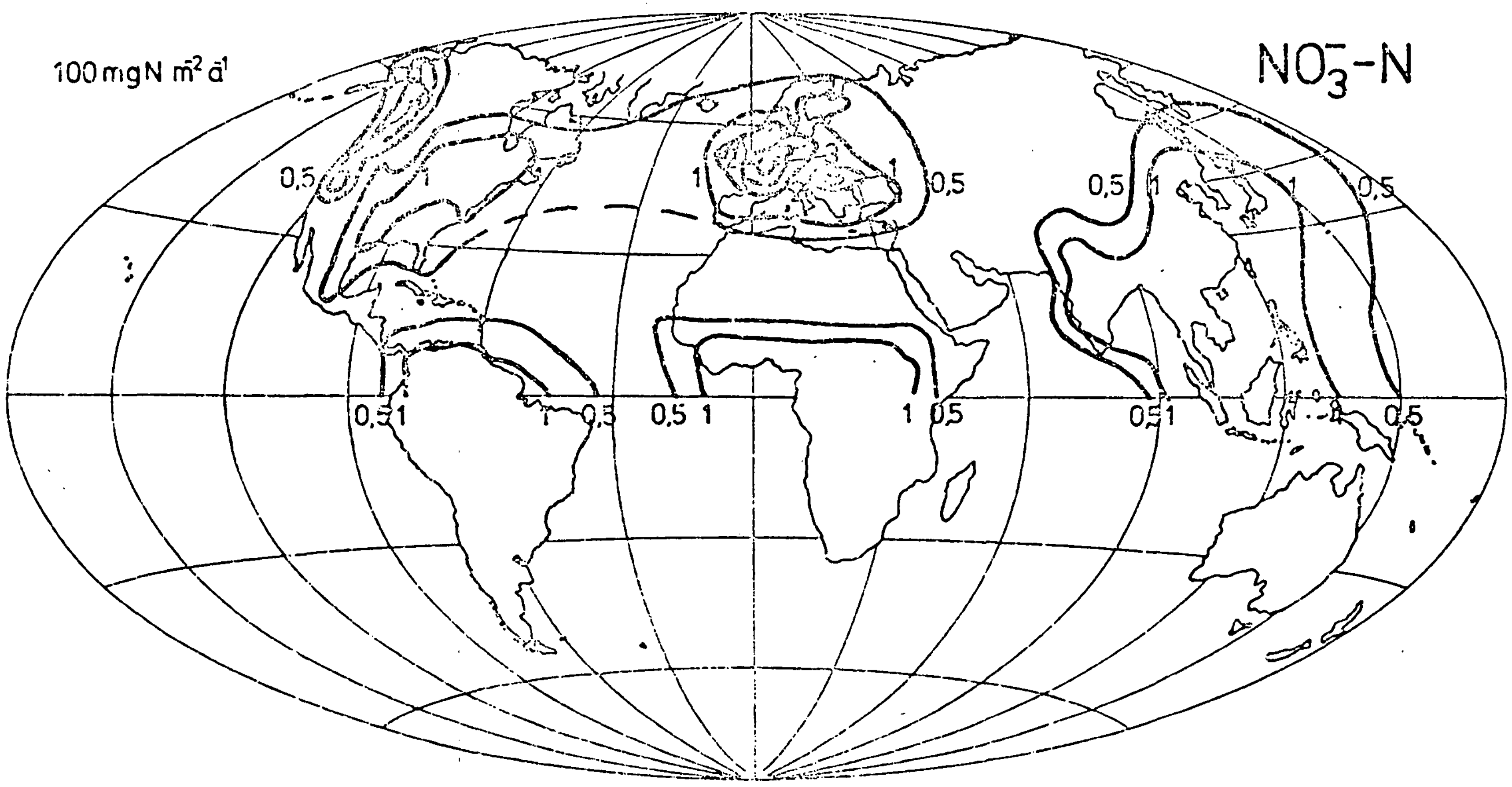


Fig. 4.6: Distribution Map of NO_3^--N Total Deposition Rates on the Northern Hemisphere Calculated from the product of NO_3^--N Total Precipitation Concentrations and the Average Precipitation Rates (Baumgartner and Reichel, 1975) for the Particular Sites.

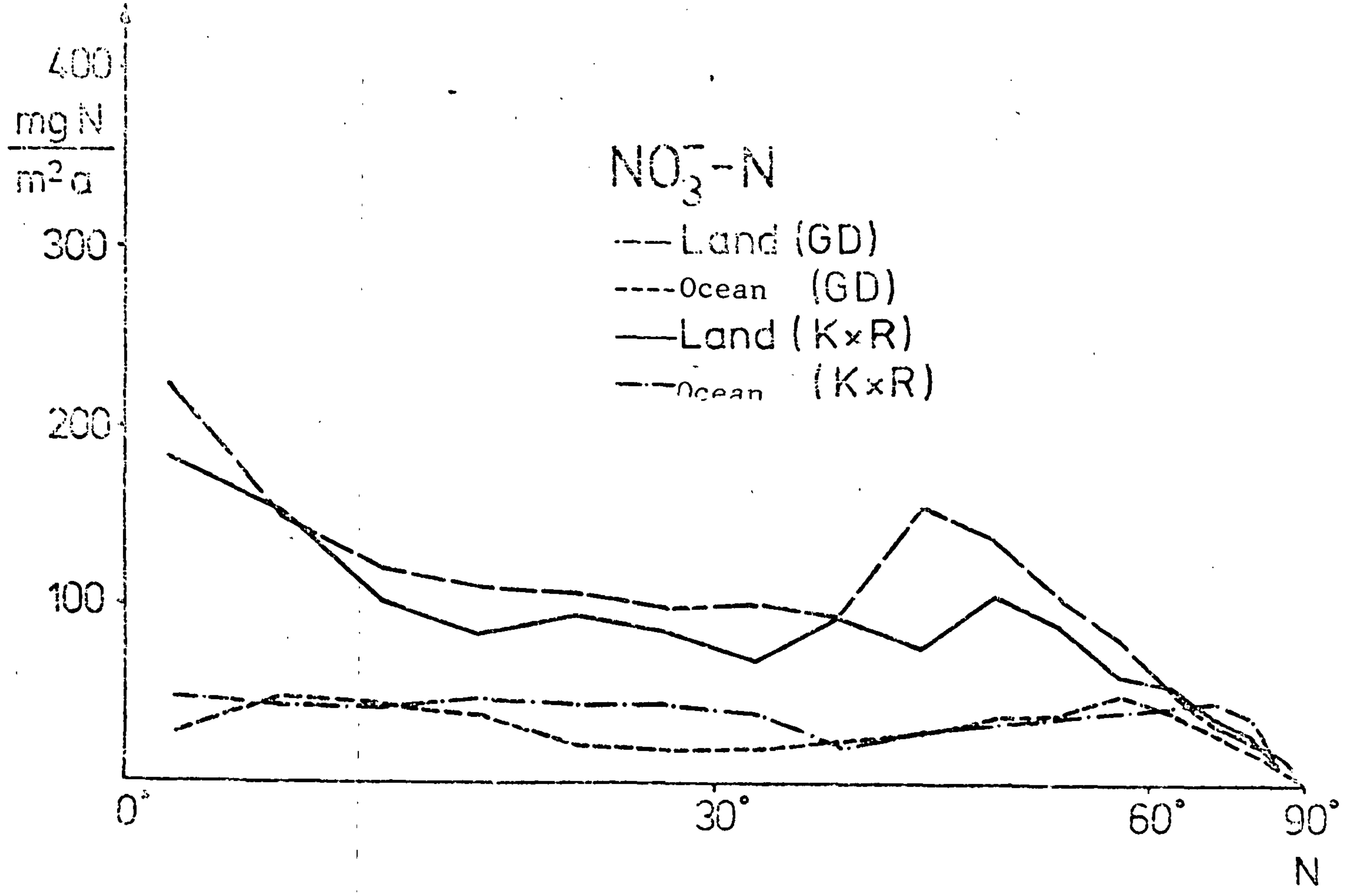


Fig. 4.7: Comparison of the Zonal Distribution of NO_3^--N Total Deposition Rated (GD) with the Deposition Rates from the Products of Total Precipitation Concentrations with the particular, Average Precipitation rates (K x R).

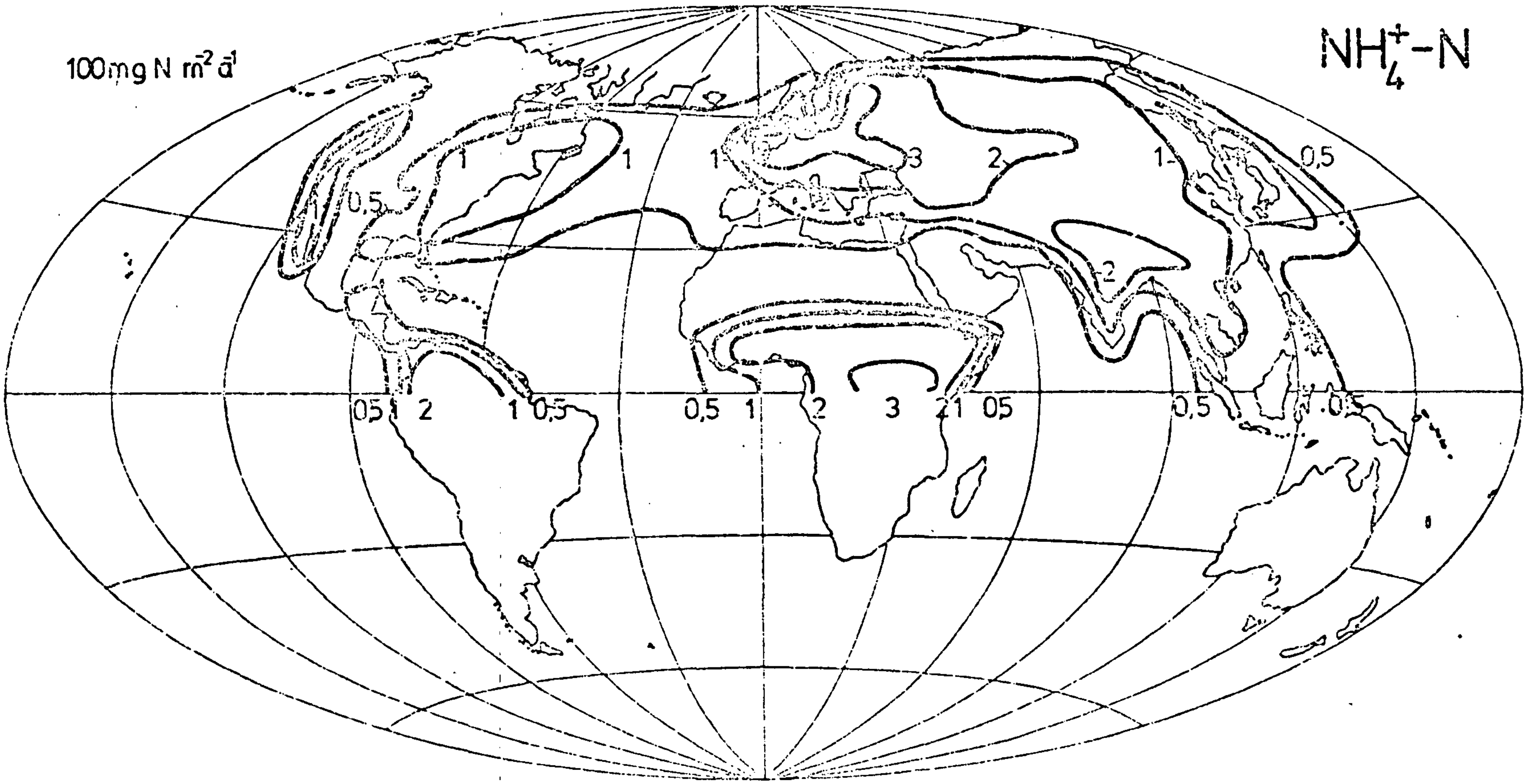


Fig. 4.8: Distribution Map of the NH_4^+-N Total Deposition rates on the Northern Hemisphere. It is based on the Results of Precipitation Analyses from the Period from 1950 to 1977. Some measurements in Central Europe gave Values up to 700 mg/m^2-yr (100 mg N / m^2-yr $\hat{=}$ 1 kg / hectare-year)

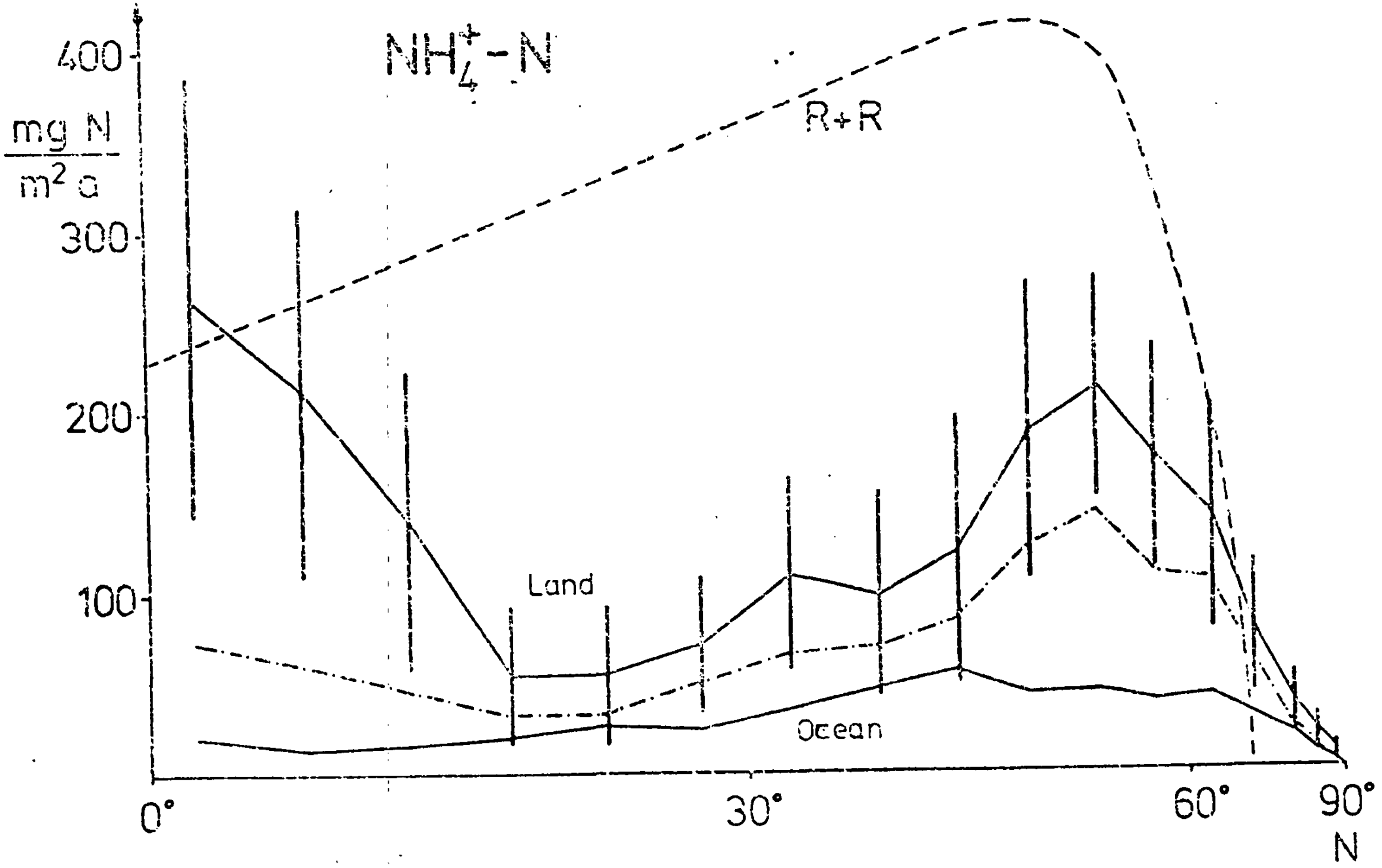


Fig. 4.9: Zonal Distribution in 5° Intervals of the NH$_4^+$-N Total Deposition Rates over Land and Ocean, derived from the Distribution map (Fig. 4.8). The error bars of the "Land" Curve shows the fluctuation range of deposition rates in the Individual Intervals (see sec. 4.3). (–·–·–·–·) shows the zonal distribution of deposition rates weighted with the particular land and ocean surface areas. For comparison, the zonal distribution of deposition rates from Robinson and Robbins (1970b), R+R, is shown.

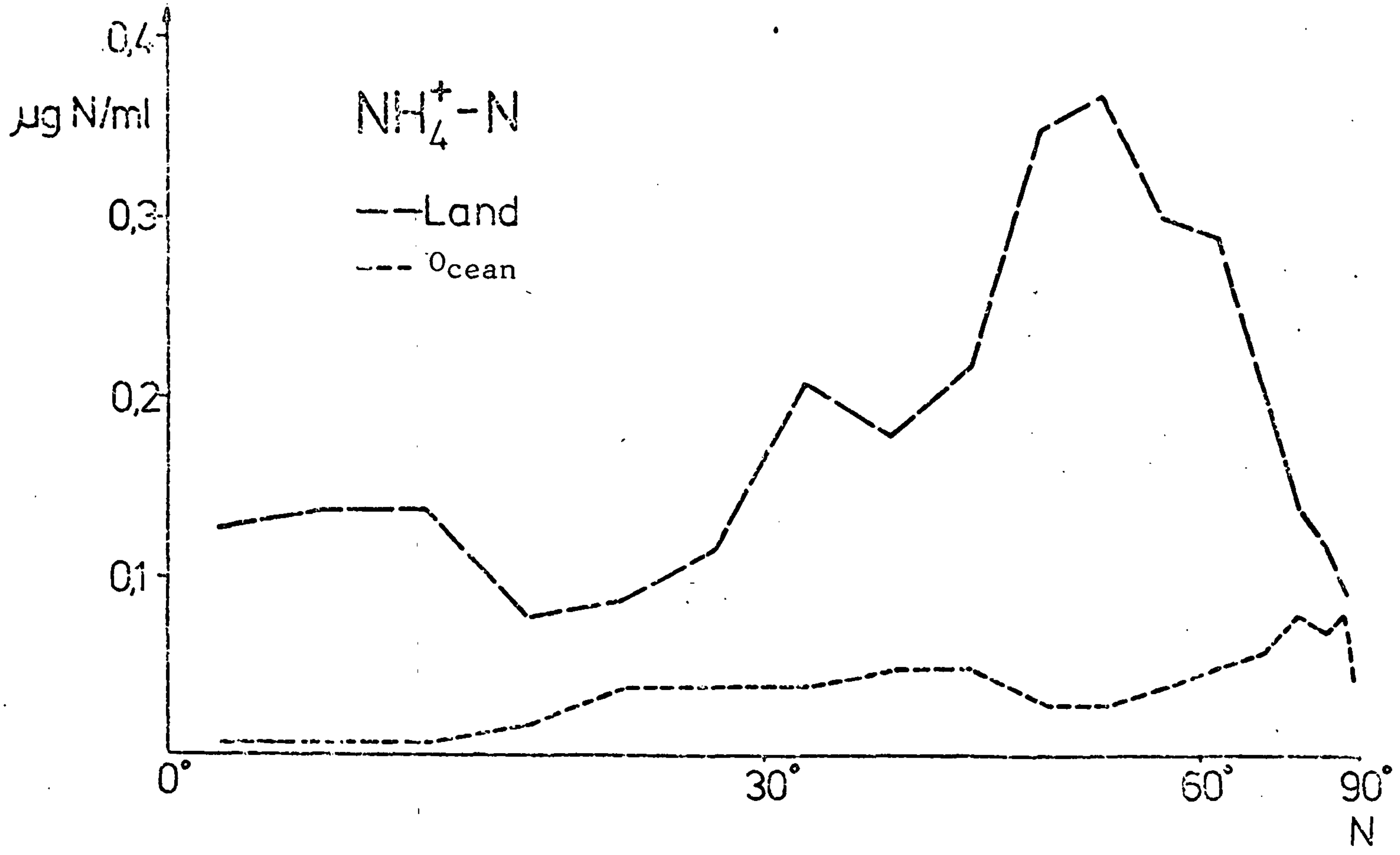


Fig. 4.10: Zonal Distribution in 5^o Intervals of the NH_4^+-N Total Precipitation Concentrations over land and ocean on the Northern Hemisphere

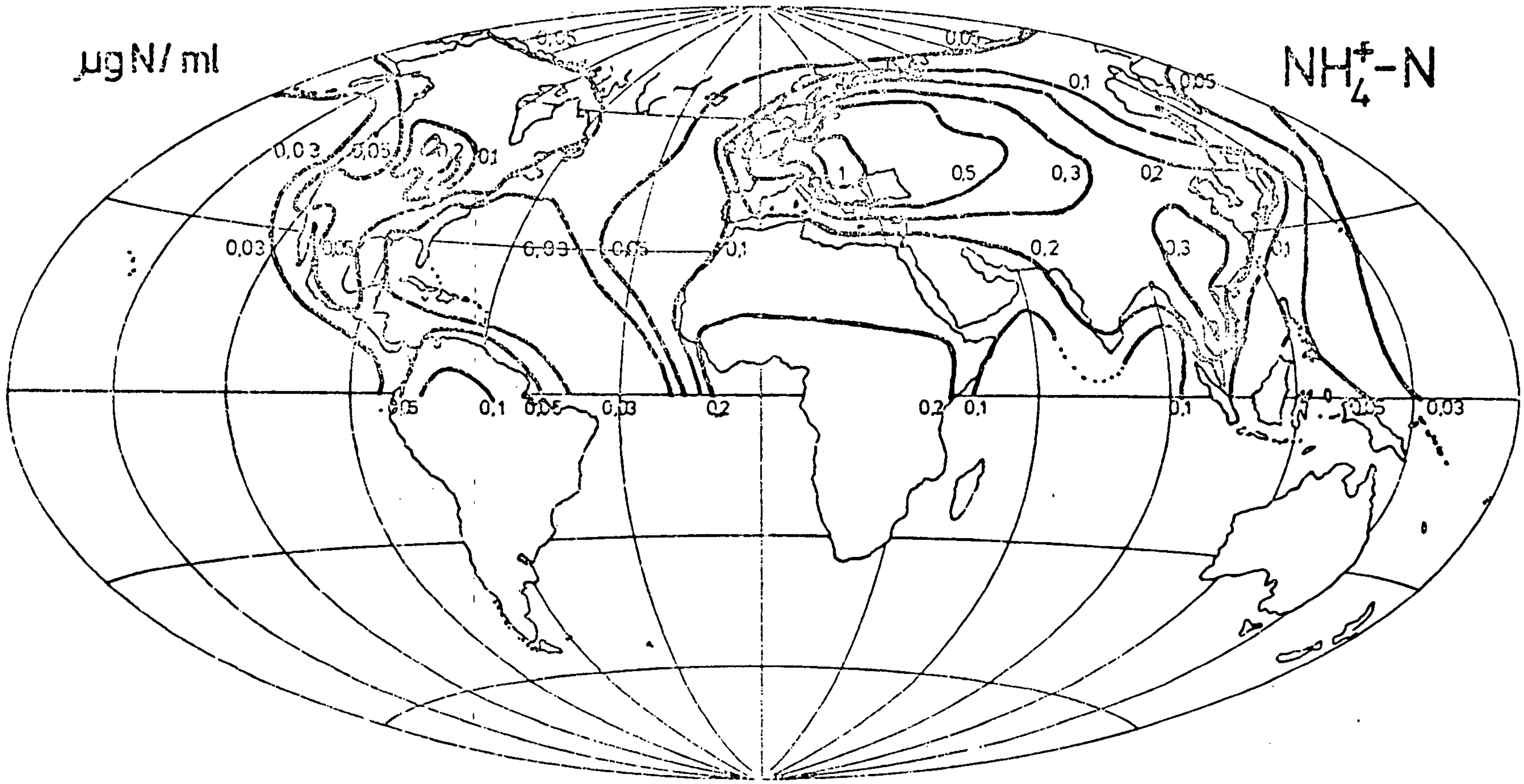


Fig. 4.11: Distribution Map of the NH$_4^+$-N Total Precipitation Concentrations on the Northern Hemisphere from Precipitation analyses from the Period 1950 to 1977.

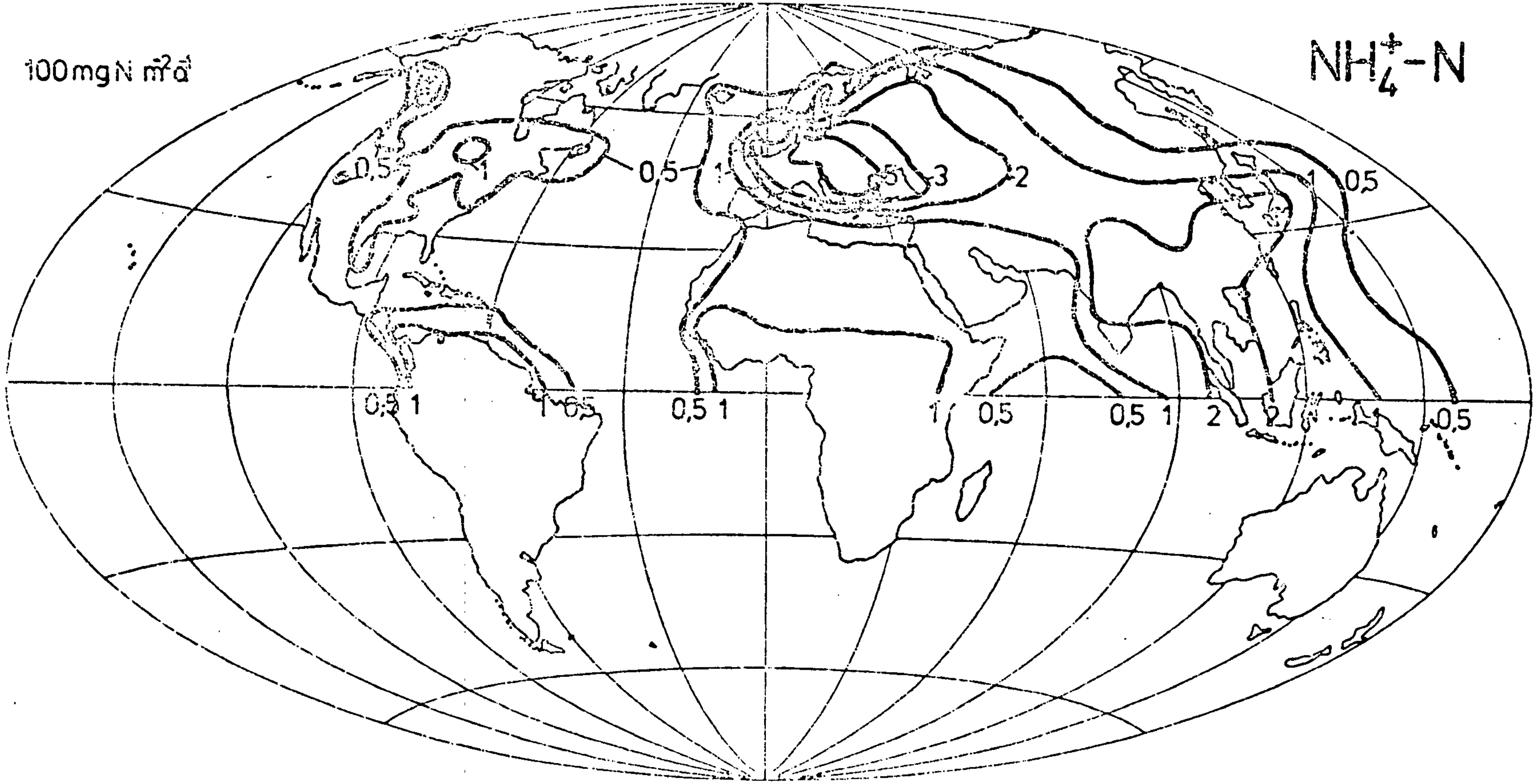


Fig. 4.12: Distribution Map of the NH_4^+-N Total Deposition Rates on the Northern Hemisphere Calculated from the Product of the NH_4^+-N Total Precipitation Concentrations and the Average Precipitation Rates (Baumgartner and Reichel, 1975) for the particular location.

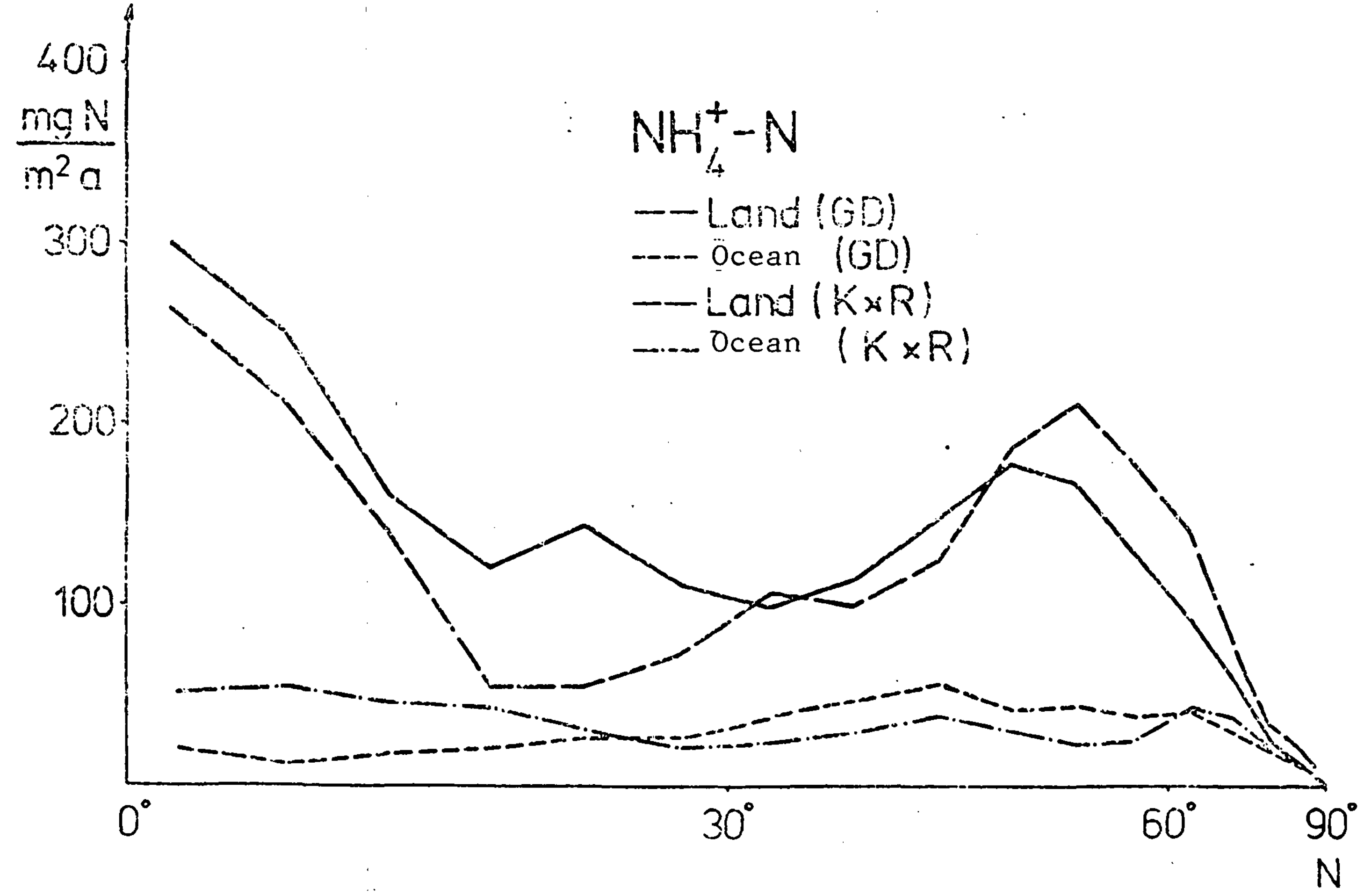


Fig. 4.13: Comparison of the Zonal Distribution of the NH_4^+-N Total Deposition Rates (GD) with the deposition rates from the Products of the total Precipitation Concentrations with the particular average precipitation rates (K x R).

Table 4.3: ESTIMATION OF TOTAL DEPOSITION OF NO_3^--N AND NH_4^+-N FOR THE NORTHERN HEMISPHERE (* THESE VALUES WERE ASSUMED TO BE 2/3 FOR NO_3^--N, AND 4/5 FOR NH_4^+-N OF QUANTITIES DEPOSITED ON THE ENTIRE WORLD). [UNITS 10^{12} g N|yr $\hat{=}$ 10^6 t N/yr].

		NH_4^+-N	NO_3^--N	$(NO_3^-+NH_4^+)$-N
Eriksson	1959	79*	32*	111*
Robinson and Robbins	1968, 1970a	1300	650	1950
" "	1970b, 1971 1975	168*	70*	238*
McConnell	1973	80*	60*	140*
Warneck	1974	--	21	--
Commission on nat. resources	1975	--	71	--
CAST	1976	120	60	180
Pratt et al	1977	120	60	180
Söderlund and Svensson	1976	88-190*	29-77	117-267*
McElroy	1976	--	--	160-190*
Liu et al	1977	--	--	150-180*
Hahn and Junge	1977	--	--	130-160*
Chameides et al	1977	--	40-60*	--
This estimation		17±6	16±6	33±9

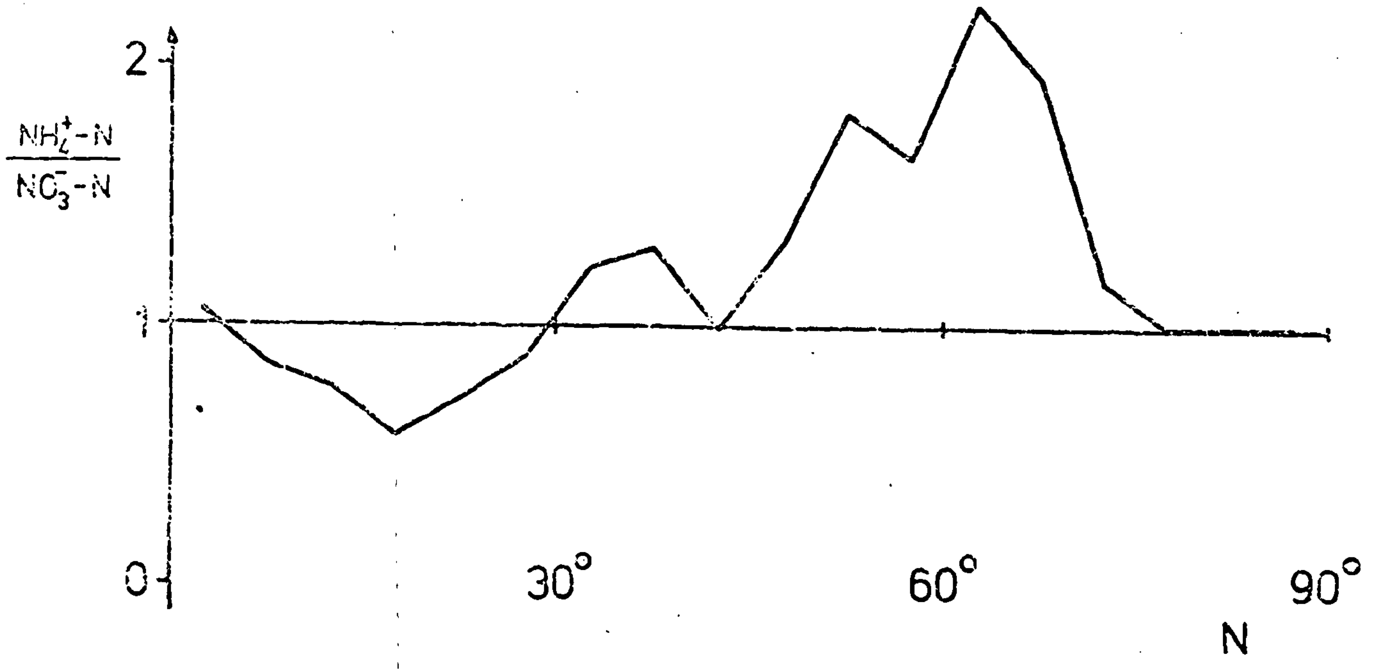


Fig. 4.14: Zonal Distribution in 5° Intervals of the Ratio NH_4^+-N/NO_3^--N" of the Total Desposition Rates.

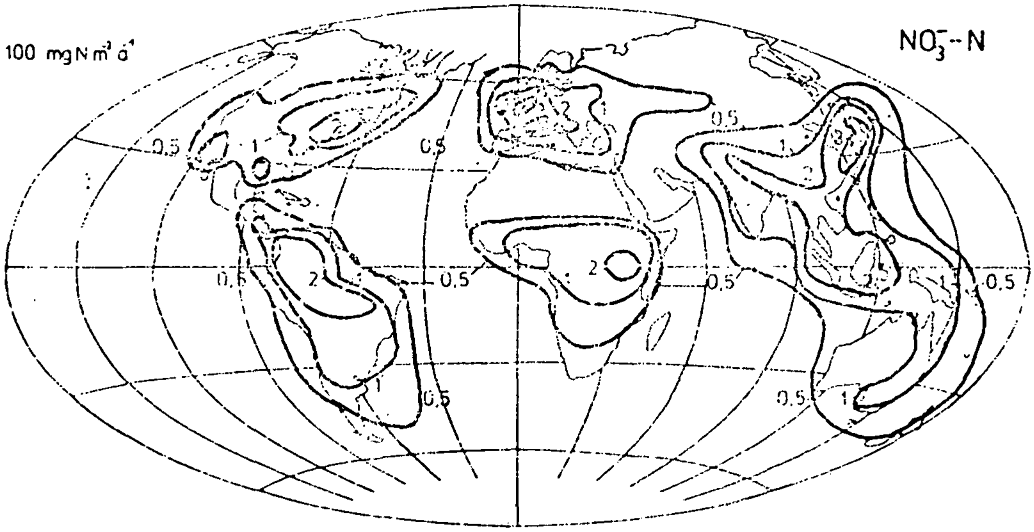


Fig. 5.1: Distribution Map of the NO_3^--N Total Deposition Rates. The distribution map of total deposition rates for the Northern Hemisphere (fig. 4.1) was extrapolated to the Southern Hemisphere

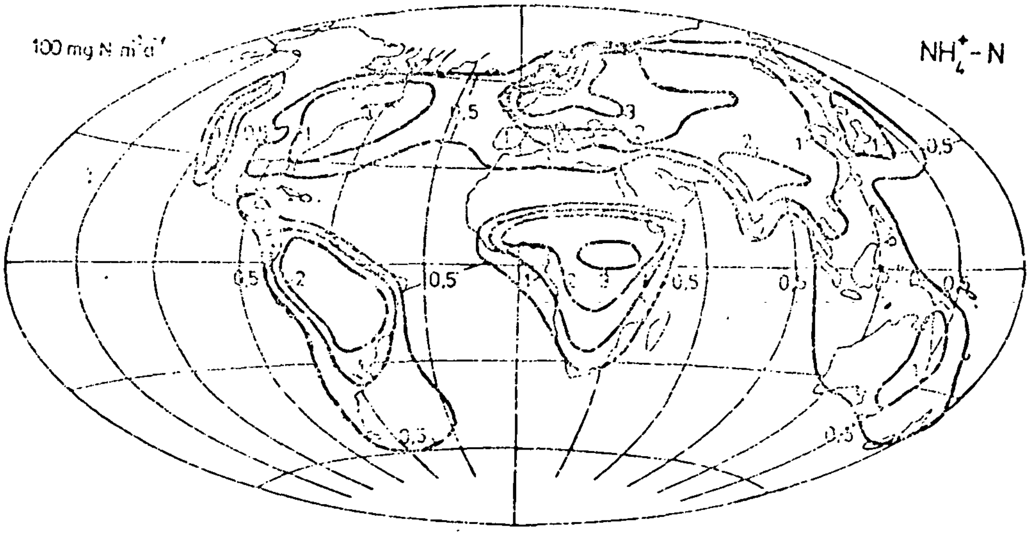


Fig. 5.2: Distribution Map of NH_4^+-N Total deposition Rates. The Distribution map of the total deposition rates for the Northern Hemisphere (fig. 4.8) was extrapolated to the Southern hemisphere.

Table 6.1: Estimations of the N-Components Deposited on the World as Total Deposition in 10^{12} g N/yr.

		NH_4^+-N Land	NH_4^+-N Ozean[a]	NH_4^+-N gesamt[b]	NO_3^--N Land	NO_3^--N Ozean[a]	NO_3^--N gesamt[b]	(NO_3^-+NH_4^+)-N Land	(NO_3^-+NH_4^+)-N Ozean[a]	(NO_3^-+NH_4^+)-N Land + Ozean[a]
Emery	1955	-	-		-	-		--	59	-
Eriksson	1959	44	55		21	27		65	82	147
Robinson and Robbins	1968,1970			2700			1400			4100
Robinson and Robbins	1970b,1971,1975			210			105			315
Tsunogai and Ikeuchi	1968			-			-	140	210	350
Tsunogai	1971			-			-	49	21	70
McConnell	1973			100			90			190
Holland	1973			-				-	10	-
Warneck	1974			-	25	13		-	-	-
Burns and Hardy	1975	74	42		31	18		105	60	165
Commission on nat. resources	1975			-			106	-		-
CAST-Report	1976			240			117			357
Pratt et al	1977			240			117			357
Söderlund and Svensson	1976	91-186	19-50		32-83	11-33		123-269	30-83	153-352
Söderlund	1976b		8-25			9-16			18-41	-
McElroy	1976			-			-	220	20	240
Liu et al	1977			-			-	160	60	220
Hahn and Junge	1977			-			-	160	40	200
Dawson	1977			35			-	-		-
Chameides et al	1977			60-90			-	-		-
Diese Abschätzung[c]		15±7	6±6	21±9	17±7	8±6	24±9	32±10	14±8	46±13

a-ocean b-total c-this estimation

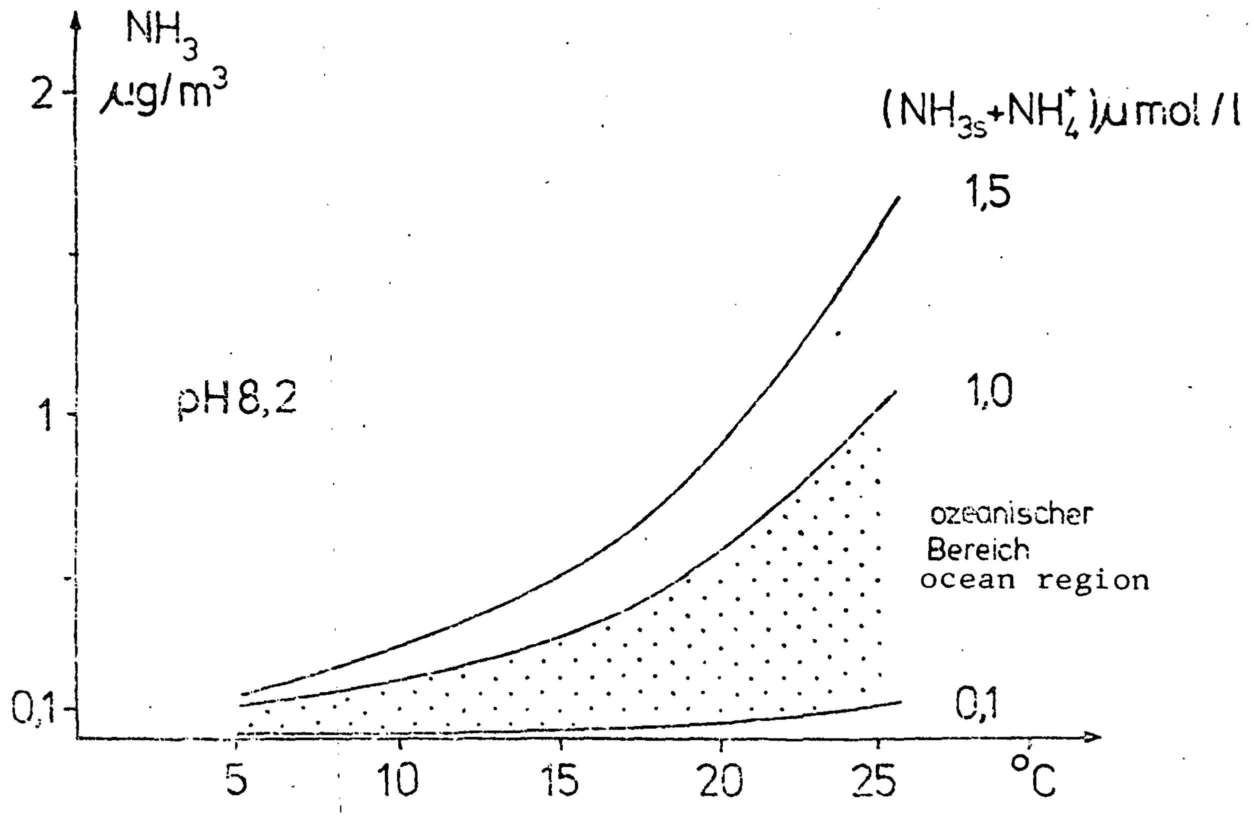


Fig. 7.1: Computed Equilibrium Concentration NH_3 over the Ocean as a Function of Temperature and Total Ammonia Concentration in Ocean Water at a pH-value of 8.2 (Georgii and Gravenhorst, 1977). NH_{3s} is the physical ammonia dissolved in the ocean water.

	v_{NO} (cm/sec)	v_{NO_2} (cm/sec)
Blind value	5×10^{-6}	2×10^{-3}
Sea water	1450×10^{-6}	15×10^{-3}
Fresh water	720×10^{-6}	10×10^{-3}
Water (pH=1)	620×10^{-6}	-0.3×10^{-3} *)
Forest soil	$<10 \times 10^{-6}$	300×10^{-3}
Sandy soil (dry)	$<10 \times 10^{-6}$	600×10^{-3}
Sandy soil (moist)	$<10 \times 10^{-6}$	280×10^{-3}

*Accuracy probably causes negative value.

Table 7.1: DEPOSITION RATES COMPUTED FROM THE CONCENTRATION DECREASES OF NO OR NO_2 IN A PLASTIC CONTAINER FROM EQUATION (3). THE SOIL OF THE CONTAINER WAS COVERED WITH VARIOUS ABSORBING MATERIALS. AIR IN THE CHAMBER WAS MIXED BY A VENTILATOR.

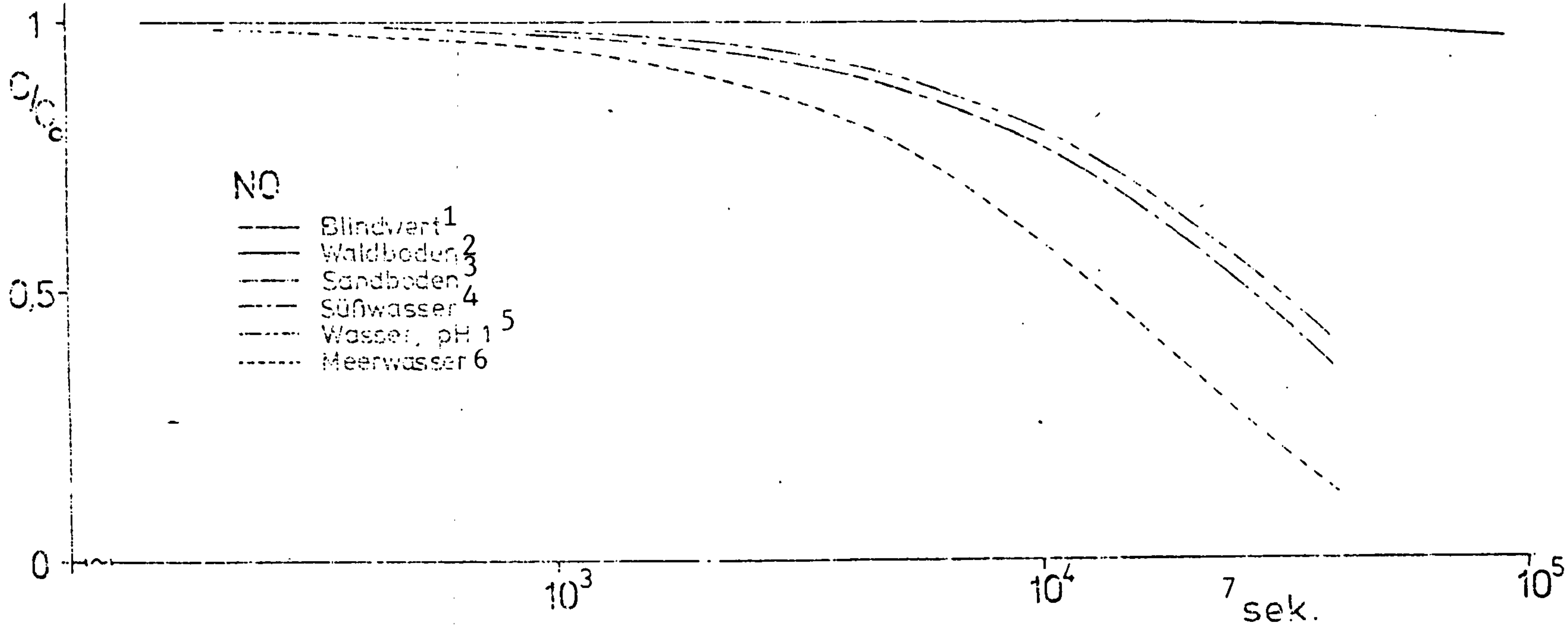


Fig. 7.2: Decrease in the NO Concentration in a Plexiglass Vessel as a Function of Time. The Base of the Vessel was covered with Various Absorbing Materials. An e-function was adapted to the measured values.

Key: 1-blind value 20forest soil 3-sandy soil 4-fresh water 5-water, pH 1 6-sea water 7-sec.

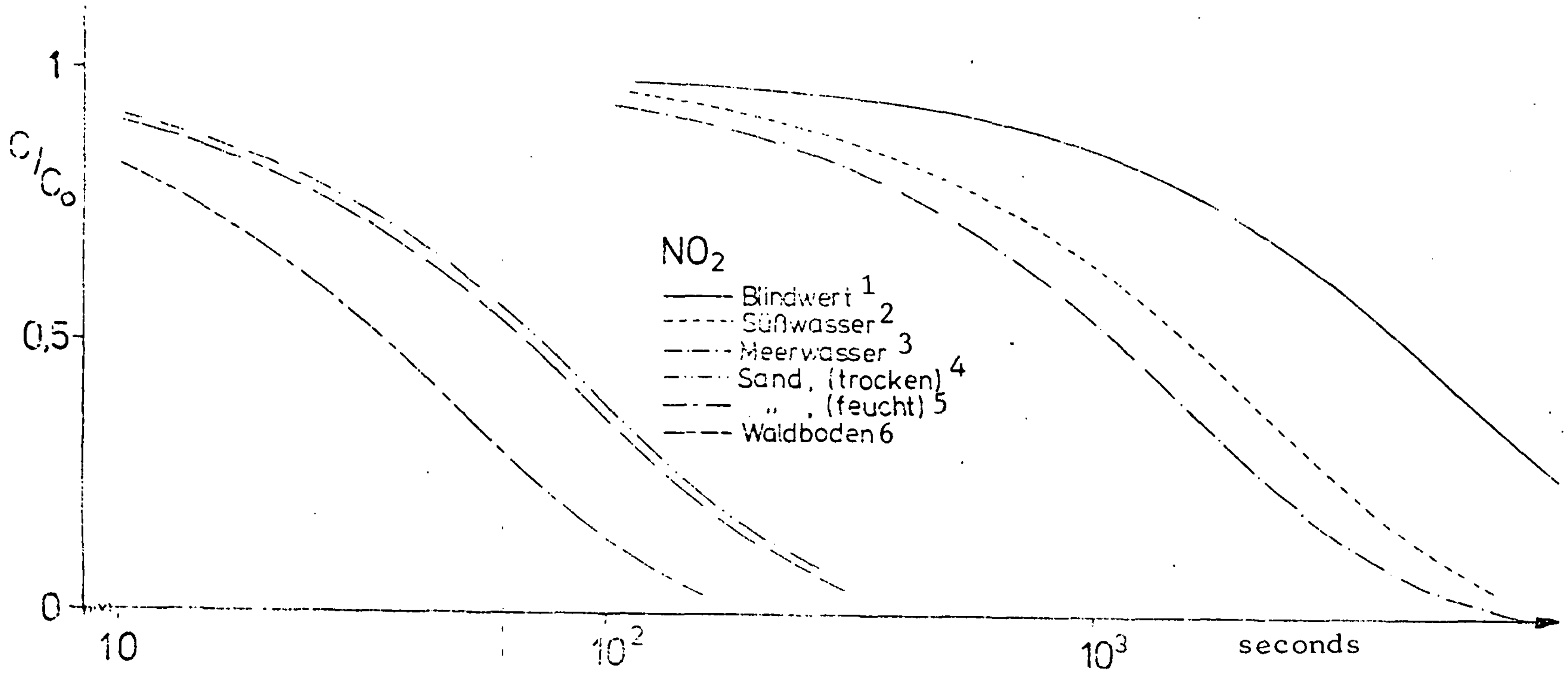


Fig. 7.3: Decrease in the NO_2-Concentration in a Plexiglass Vessel as a Function of Time. The base of the vessel was Covered with Various Absorbing Materials. An e-function was adapted to the measured values.

Key: 1-blind value 2-fresh water 3-sea water 4-sand (dry) 5-(moist) 6-forest soil

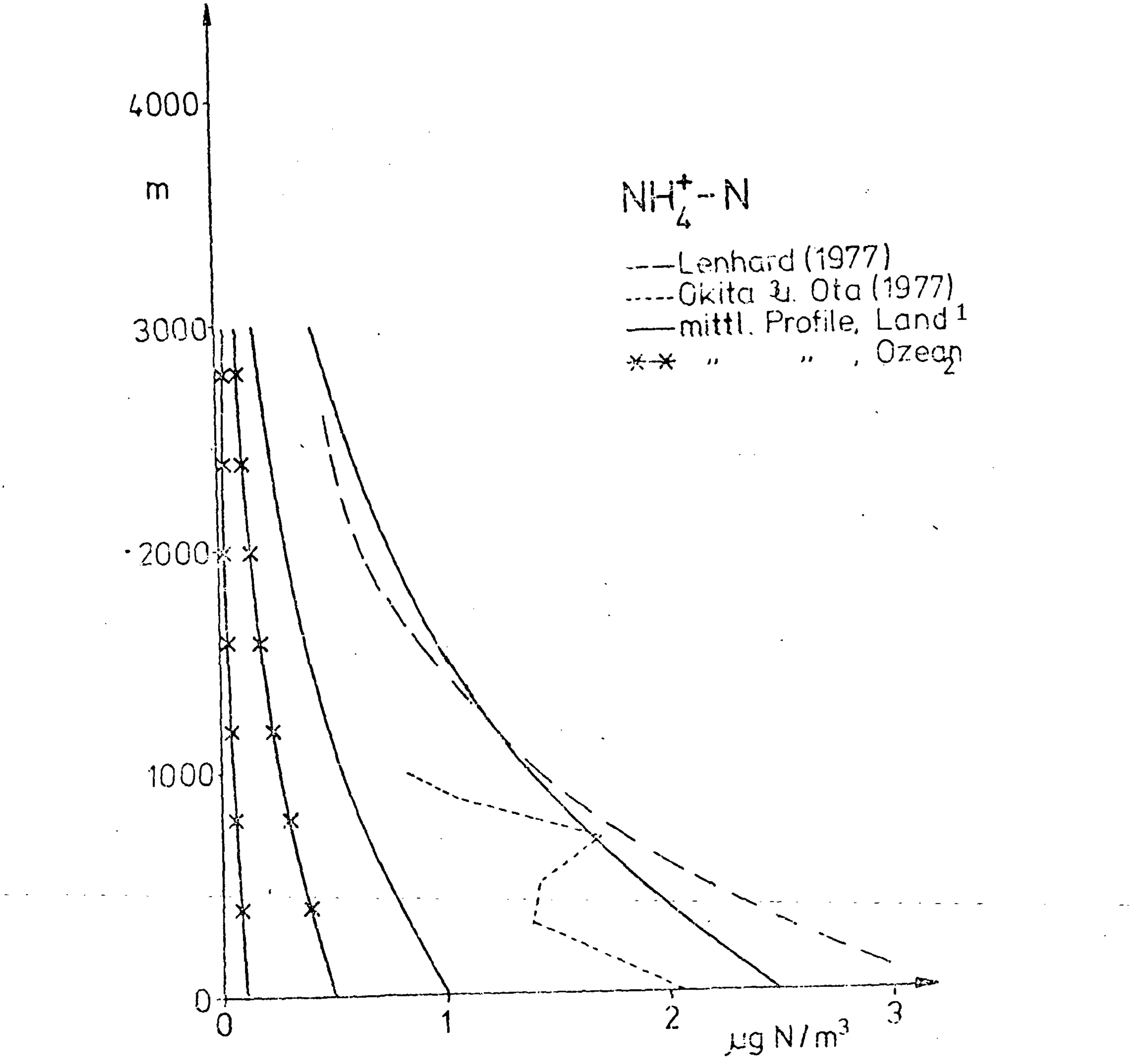


Fig. 8.1: Vertical Profiles of Atmospheric NH_4^+-Concentrations. The middle profiles show a Concentration Decrease of a Trace substance for two assumed Soil Concentrations. By using these, the nitrogen mass in the atmosphere was calculated in this work.

Key: 1-middle profiles, land 2-ocean 3-and

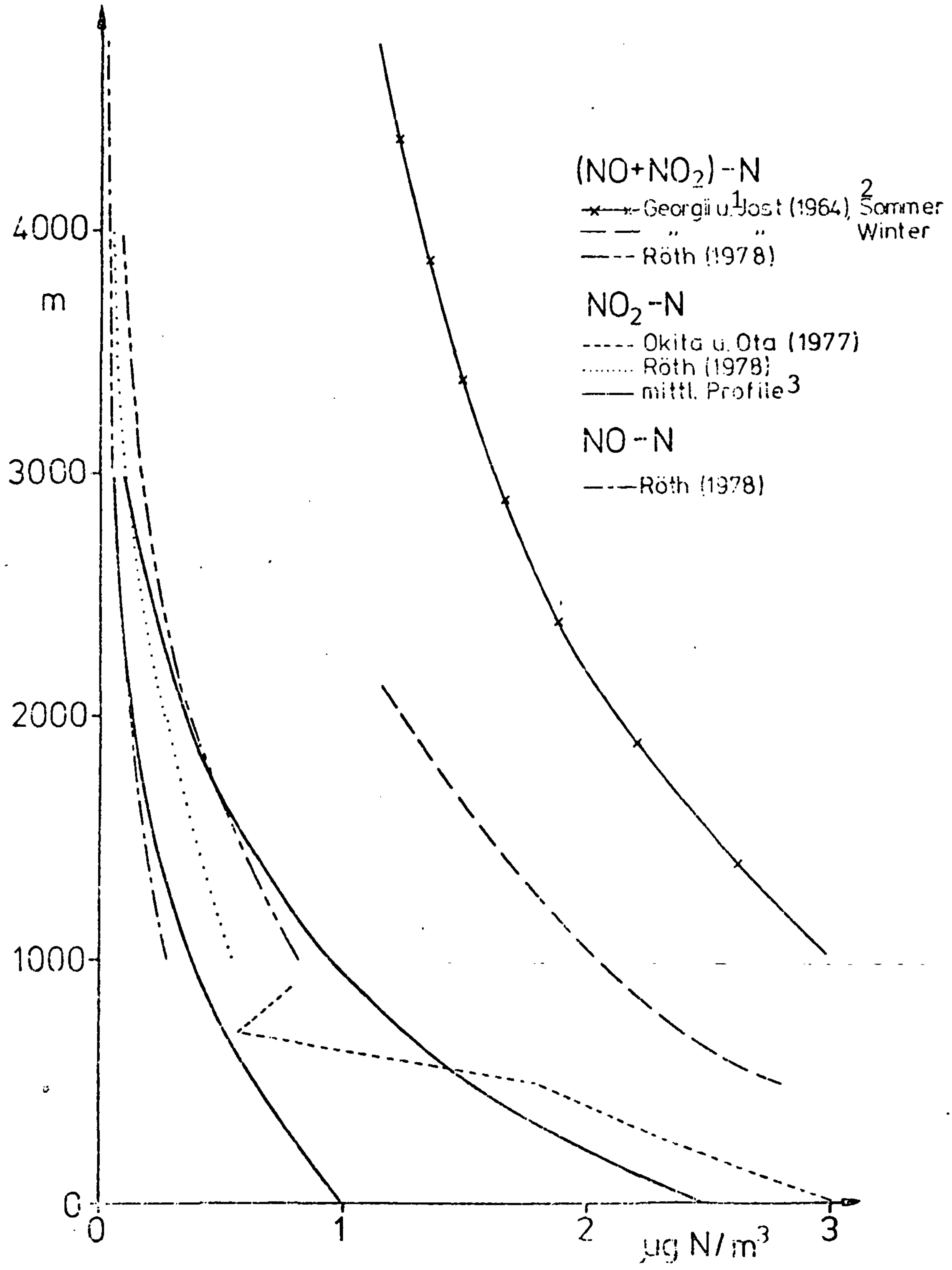


Fig. 8.2: Vertical Profiles of Atmospheric NO and NO_2 Concentrations The profiles of Röth (1978) are based on model calculations. The middle profiles show concentration decreases of a trace substance for two assumed soil concentrations. By using these, the nitrogen mass in the atmosphere was calculated in this work.

Key: 1-and 2-summer 3-middle profiles

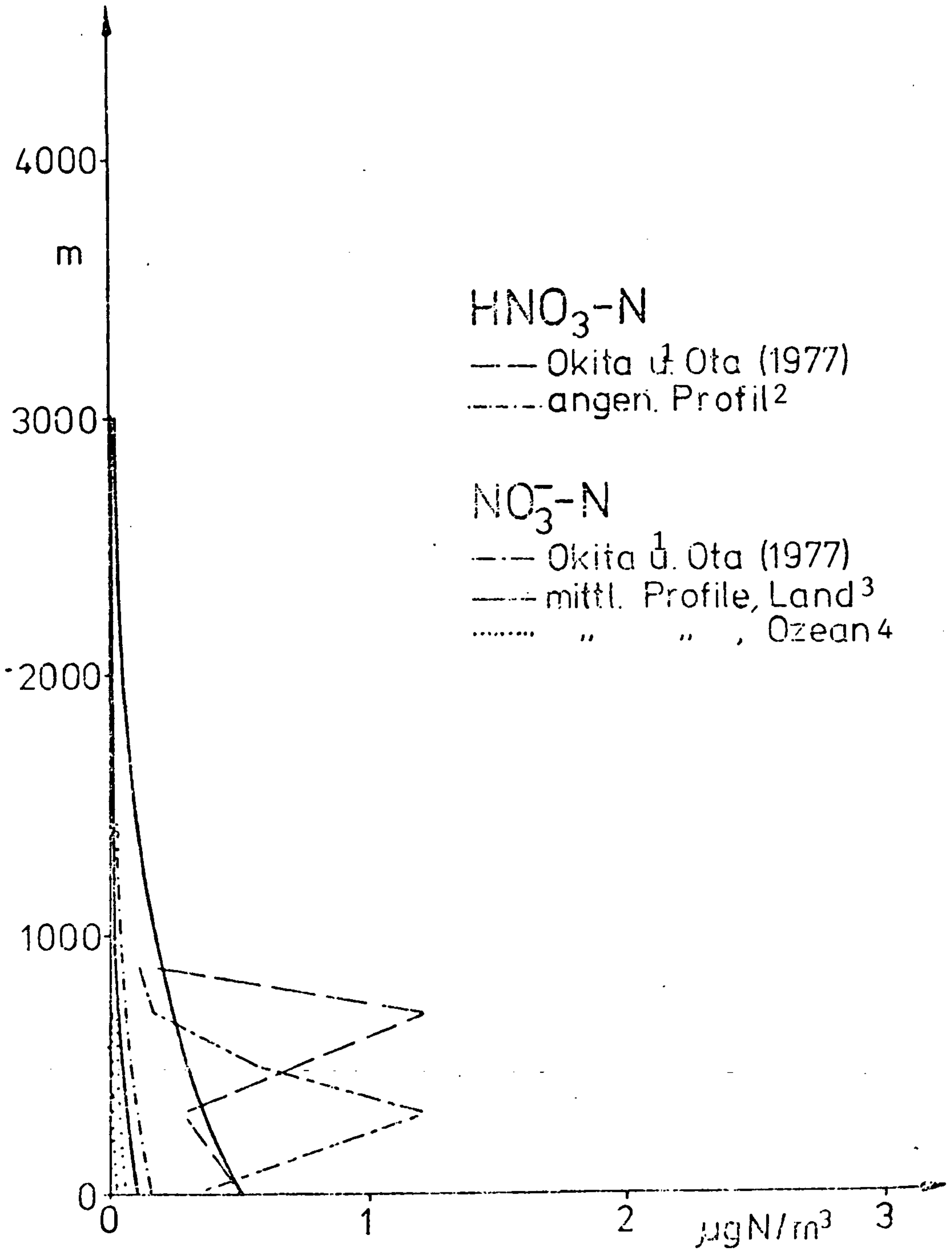


Fig. 8.3: Vertical Profiles of Atmospheric HNO_3 and NO_3^- concentrations. The assumed HNO_3-profile was derived from the vertical conc. decrease of HNO_3 from model calculations (Röth, 1978). The middle profiles for NO_3^- show assumed conc. decreases for a higher and lower soil concentration. The assumed profile for HNO_3 was determined at only one soil concentration.

Key: 1-and 2-assumed profile 3-middle profiles, land 4-ocean

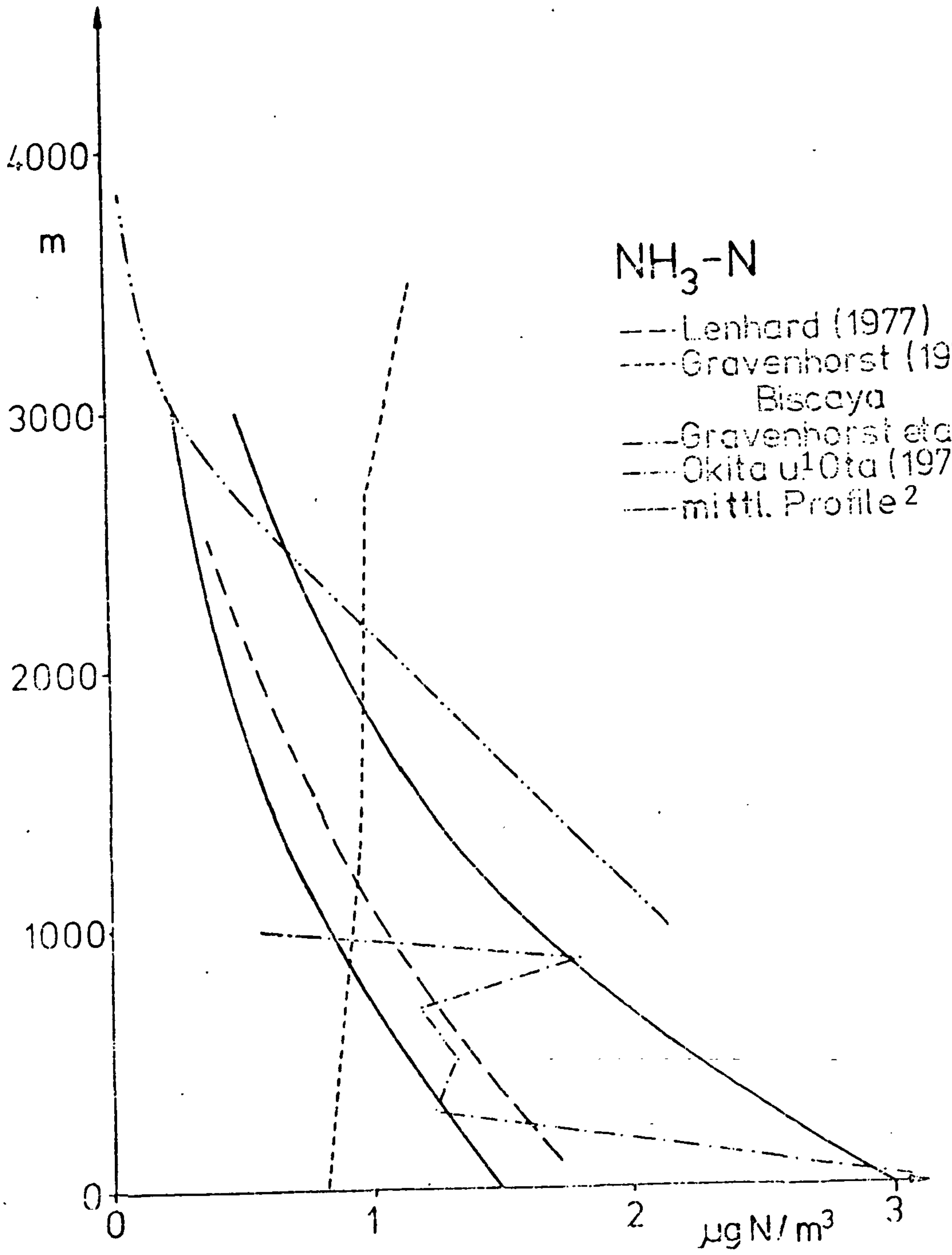


Fig. 8.4: Vertical Profiles of Atmospheric NH_3-Concentrations. The profile of Gravenhorst et al. (1977) is the result of model calculations. The middle profiles show conc. decreases of a trace substance for two assumed soil concentrations. By using these, the nitrogen mass in the atmosphere was calculated in this work.

Key: 1-and 2-middle profiles

Table 8.1: CONCENTRATIONS OF NO_3^--N IN AEROSOLS NEAR THE GROUND

Crt[a]	μg NO_3^--N/m^3	
Sudan	0.41	Penkett et al (1977)
Harwell	0.97	
Florida	0.07	Junge (1956)
Hawaii	0.02	
USA Stadt[b]	0.54	Bach (1976)
stadtnahes Gebiet[c]	0.32	
ländliches Gebiet[d]	0.19	
abgelegenes Gebiet[e]	0.10	
Mt. Tsukuba, Japan, 870 m ü. NN	0.33	Okita et al (1976)
Wank, Alpen[f], 1670 m ü. NN	0.21	Reiter et al (1976)
Stadt (Mittelwerte)[g]	0.43	Moyers et al (1977)
Land[d] "	0.19	
Göteborg	0.06	Brosset (1977)
Onzala	0.03	
Nagoja, Japan	0.7	Kadowacki (1976)
Atlantik[h] N-E-Passat	0.09	Gravenhorst (1975)
[i]kontinentaler Einfluß	0.06	
[j]ohne kontinentalen Einfluß	0.01	
Catalina Island, Pazifik[k]	0.38	Hidy et al (1974)

Key: a-location b-city c-near city d-rural e-remote area f-Alps
g-city (averages) h-Atlantic i-continental influence
j-no continental influence k-Pacific Ocean

Table 8.2: CONCENTRATION OF NH_4^+-N IN AEROSOLS NEAR GROUND

Ort[a]		µg NH_4^+-N/m^3	
Florida		.07 - .08	Junge (1956)
Hawaii	Küste[b]	.02 - .03	
	Mauna Kea (3200 m ü. NN)[c]	.003	
USA	Stadt[d]	.7	Bach (1976)
	stadtnahes Gebiet[e]	.95	
	ländliches Gebiet[f]	.22	
	abgelegene Gebiete[g]	.12	
Bundesrepublik[h]		.88	Georgii und Müller (1974)
"		2.00	Süßenguth (1976)
"		3.00	Lenhard (1977)
Wank, Alpen[i], 1670 m ü. NN		1.01	Reiter et al (1976)
Stadt[d]		.86	Moyers et al (1977)
Land[f]		.6	
Nagoya, Japan		2.49	Kadowacki (1976)
Teaside, England		3.73	Junge (1963)
Chilton, "		6.53	
Cataline Island, Pazifik[j]		.51	Hidy et al (1974)
Irische Atl. Küste[k]		.01 - 1.9 .008- .35	o'Connor (1963) zitiert nach Robinson u. Robbins (1970)
Nord-Atlantik[l]		.21	Gravenhorst (1975)
"		.78	Georgii u. Gravenhorst (1977)

Key: a-location b-coast c-elevation d-city e-near city f-rural g-remote regions h-FRG i-Alps j-Pacific k-Irish Atlantic coast l-North Atlantic

Table 8.3: CONCENTRATION OF NO_2-N NEAR THE GROUND

Ort [a]	µg NO_2-N/m^3	
Panama karibische Luftmassen, trocken [b]	.56	Lodge und Pate (1966)
Regen [c]	2.25	
Wald unter Baumkronen [e]	.81	
über [d] "	1.38	
Bucht von Panama (Pazifik) [f]	1	
Wald: unter Baumkronen [e]		Lodge et al (1974)
Duke Forest Res.(Brasilien) [g]	.13	
Albrook Forest (Panama)	.25	
anderes Panama [h]	.19	
über Baumkronen [d]		
Albrook Forest (Panama)	.31	
anderes Panama [h]	.19	
Über Flüssen: [i]		
Rio Turuma/Solimos (Bras.)	.19	
Chagges R (Panama)	.38	
Savanne Panama	.38	
Maritime Luft: [j]		
Karibik: [k] Ft. Sherman (Panama)	.31	
anderes Panama [h]	.25	
Barbados	.19	
Pazifik: Bucht von Panama [l]	.44	
Bombay ($NO+NO_2$ in der Stadt) [m]	1.25-6.25	Zutschi et al (1973)
Hawaii Küste [n]	.81	Junge (1956)
Mauna Kea (3200 m ü.NN)	.53- .76	
Colorado	2.56	
North Carolina	2.88	Robinson u. Robbins (1970)
Mittelwert Land [o] 65°N-65°S	2.5	
[p] Rest Land und Ozean	.31	
Colorado	.06	Noxon (1976)
Irland [q]	.05- .65 .21	o'Connor (1962) zitiert [t] bei Robinson u. Robbins(197
Bundesrepublik (Mittelwert) [r]	4.0	Fricke (1978)
Stadt [s]	23.75	EPA (1972) zitiert [u] nach Bach (1976)

Key: a-location b-Panama Carribean air mass, dry c-rain d-forest above tree crown e-under f-Panama bight g-Brasil h-other Panama i-over rivers j-maritime air k-Carribean l-Pacific: Panama bight m-in the city n-coast o-average value, land p-remaining land and ocean q-Ireland r-FRG (average) s-city t-O'Connor (1962) cited in R & R (1970) u-EPA (1972) cited in Bach (1976).

Table 8.3 [Continued]

Background	.31-2.5	Hidy (1973) zitiert nach[a] Bach (1976)
	2.5 -13.13	
Florida	.41	Junge (1956)
Hawaii Küste[b]	.59	
Mauna Kea	.32	
Ipswich. Mass.	.59	
Ozean Nordatlantik[c]	.03	Gravenhorst u. Müller[d] (unveröffentlichte Daten 1974)
"	.09- .4	Kühme (1968)

Key: a-Hidy (1973) cited by Bach (1976) b-coast c-ocean, North Atlantic d-Gravenhorst & Mueller (unpublished data 1974)

Table 8.4: CONCENTRATION OF NO-N NEAR THE GROUND

Ort[a]	µg NO-N/m^3	
Colorado	1.69	Robinson u. Robbins (1970)
Mittelwert[b] 65°N-65°S Land	1.25	" " "
Rest + Ozean[c]	.13	
Panama	3.75	Lodge und Pate (1966)
Wald: unter Baumkronen[d]		Lodge et al (1974)
Duke Forest Res. (Brasilien)[e]	.06	
Albrook Forest (Panama)	.31	
anderes Panama[f]	.19	
über Baumkronen[g]		
Albrook Forest (Panama)	.25	
anderes Panama[f]	.19	
über Flüssen:[h]		
Rio Turuma/Solimos (Bras.)	.19	
Charges R (Panama)	.44	
Savanne Panama	.31	
Maritime Luft:[i]		
Karibik:[j] Ft. Sherman (Panama)	.44	
[f] anderes Panama	.19	
Barbados	.19	
Pazifik: Bucht von Panama[k]	.38	
urban camp station	31.25	[l] EPA (1972) zitiert nach Bach (1976)
Background	.13-1.3	[m] Hidy (1973) zitiert nach Bach (1976)
Bundesrepublik[n]	2.0	Fricke (1978)

Key: a-location b-average value c-remainder + ocean d-forest: below tree crowns e-Brasil f-other Panama g-above tree crowns h-over rivers i-maritime air j-Carribean k-Pacific: Panama Bight 1-EPA (1972) cited by Bach (1976) m-Hidy (1973) cited by Bach (1976) n-FRG

Table 8.5: CONCENTRATION OF HNO_3-N NEAR THE GROUND

Location	ug HNO_3-N/m^3	
Mt. Tsukuba	0.9	Okita et al (1976)
West Covina and St. Louis	1 - 30	Spicer (1977)

Table 8.6: CONCENTRATION OF NH_3-N NEAR THE GROUND

[a]Ort	µg NH_3-N/m^3		
Bombay (Stadt, Mittelwert)[b]	62.5 - 12.5 31	Zutschi et al (1973)	
Ipswich, Mass.	5.0	Junge (1956)	
Florida	4.2		
Hawaii Küste[c]	1.9		
Mauna Kea (3200 m[d] ü. NN)	.8		
Wald: unter Baumkronen[e]		Lodge et al (1974)	
Duke Forest Res.(Brasilien)[f]	5.6		
Albrook Forest (Panama)	10.0		
anderes Panama[g]	8.1		
über Baumkronen[h]			
Albrook Forest (Panama)	9.4		
anderes Panama[g]	9.4		
über Flüssen:[i]			
Rio Turuma/Solimos (Bras.)	15.6		
Charges R (Panama)	3.1		
Savanne Panama	9.4		
Maritime Luft[j]			
Karibik:[k] Ft. Sherman (Panama)	19.4		
[g]anderes Panama	5.6		
Barbados	9.4		
Advances II	10,0		
Pazifik:[l] Bucht von Panama	11.4		
Bundesrepublik[m]	2.5 - 12.5	Georgii u. Müller (1974)	
"	2.0	Süßenguth (1976)	
"	1.8	Lenhard (1977)	
Background	6.25 6.25	[n]Lovelock (1971) Williamson (1973) Hidy (1973)	zitiert nach Bach (1976)
Land	4.12 (Februar)[o] 1.0 (August)	Tsunogai (1968)	
Pazifik[p]	.16		
Pazifik[p]	.04	Tsunogai (1971)	
Nordatlantik[q]	.8	Georgii u. Gravenhorst (1977)	

Key: a-location b-city, average value c-coast d-elevation e-forest, below tree crowns f-Brasil g-other Panama h-above tree crowns i-over rivers j-maritime air k-Carribean l-Pacific: Panama Bight m-FRG n-Lovelock (1971) cited by Bach 91976) o-February p-Pacific q-North Atlantic

Table 8.7: USED PROFILES

	NH_4	NH_3	NO	NO_2	$NO+NO_2$	NO_3^-	NO_2+NO_3
Lenhard (1977)	x	x					
Okita and Ota (1977)	x	x		x		x	x
Georgii and Müller (1974)		x					
Gravenhorst et al (1977) (Modell)		x					
Gravenhorst (1975)		x					
Georgii and Jost (1974)					x		
Fricke (1973)					x		
Röth (1978)			x	x	x		

Table 8.8: AVERAGE GROUND CONCENTRATION OF THE N-COMPONENTS AND THEIR MASS IN THE NORTHERN HEMISPHERE

		Assumed conc. on the ground in $\mu g\ N/m^3$	Mass in the atmosphere of the Northern Hemisphere in 10^{12} g N
NH_4^+-N	Land	1 - 2.5	0.14 - 0.35
	Ocean	0.05 - 0.1	0.01 - 0.02
NH_3-N	Land	1.5 - 3.0	0.21 - 0.42
	Ocean	0.1 - 0.2	0.05 - 0.09
			0.41 - 0.88
NO_3^--N	Land	0.1 - 0.5	0.01 - 0.05
	Ocean	0.01 - 0.05	0.00 - 0.01
NO_2-N	Land	1.0 - 2.5	0.1 - 0.24
	Ocean	0.03 - 0.2	0.01 - 0.09
HNO_3-N	Land	0.15	0.015
	Ocean	0.01	0.005
			0.14 - 0.41

Table 8.9: NO_3^--N CONCENTRATIONS IN THE RAIN IN SW-FRANCE (Sept. '76)

Probe[a]	Datum[b]	NO_3^--N (µg/ml)	Herkunft der[c] Luftmassen
1	31.8.76	0.4	Spanien[d]
2	9.5.	0.3	nur schwache Winde[e]
3	12.9.	0.7	England
4	12.9.	0.3	England
5	14./15.9.	0.1	Nordatlantik[f]
6	15.9.	0.6	England
7	15.9.	0.8	England
8	15.9.	0.9	England

Key: a-sample b-date c-origin of air masses d-Spain e-slight wind f-North Atlantic

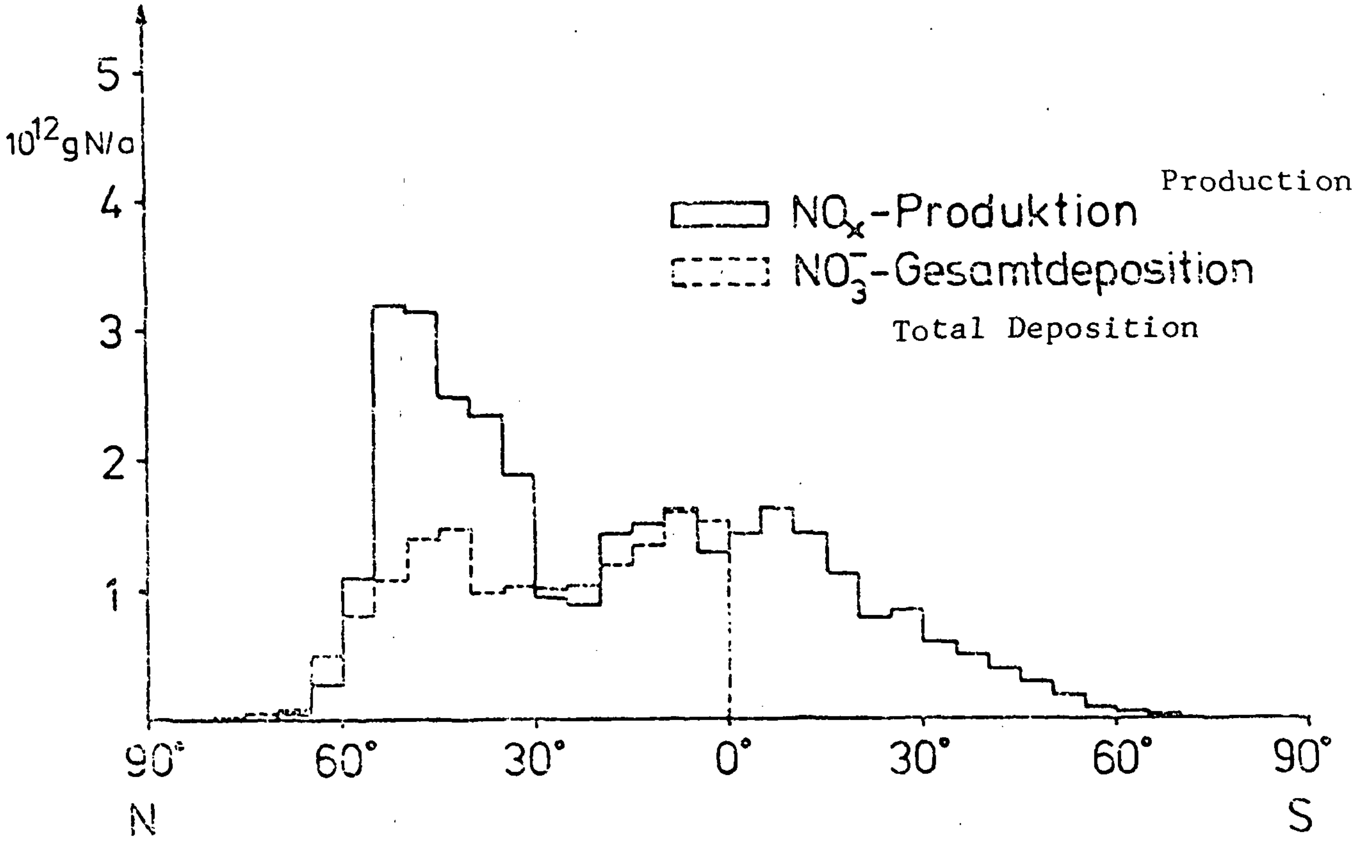


Fig. 9.1: Zonal Distribution in 5^o Intervals of NO_x-N Quantities given off to the Atmosphere compared to that removed NO_3^--N through Total deposition. *Since the values for* the total deposition on the S. Hemisphere are uncertain, they were not included.

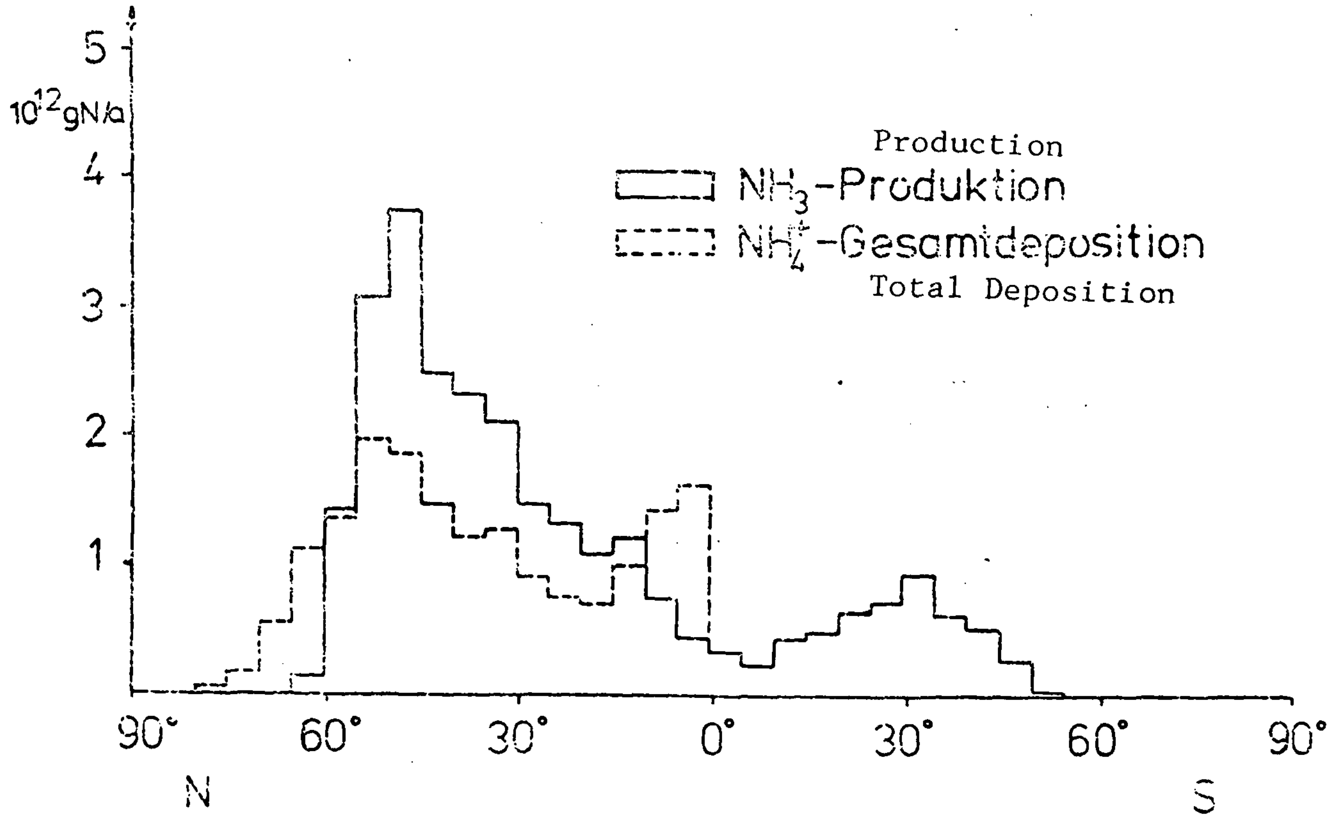


Fig. 9.2: Zonal Distribution in 5^o Intervals of the NH_3-N given off to the Atmosphere Compared to that amount of NH_4^+-N removed by Total deposition. Since the values for Total Deposition on the S. Hemisphere are uncertain, they were not included.

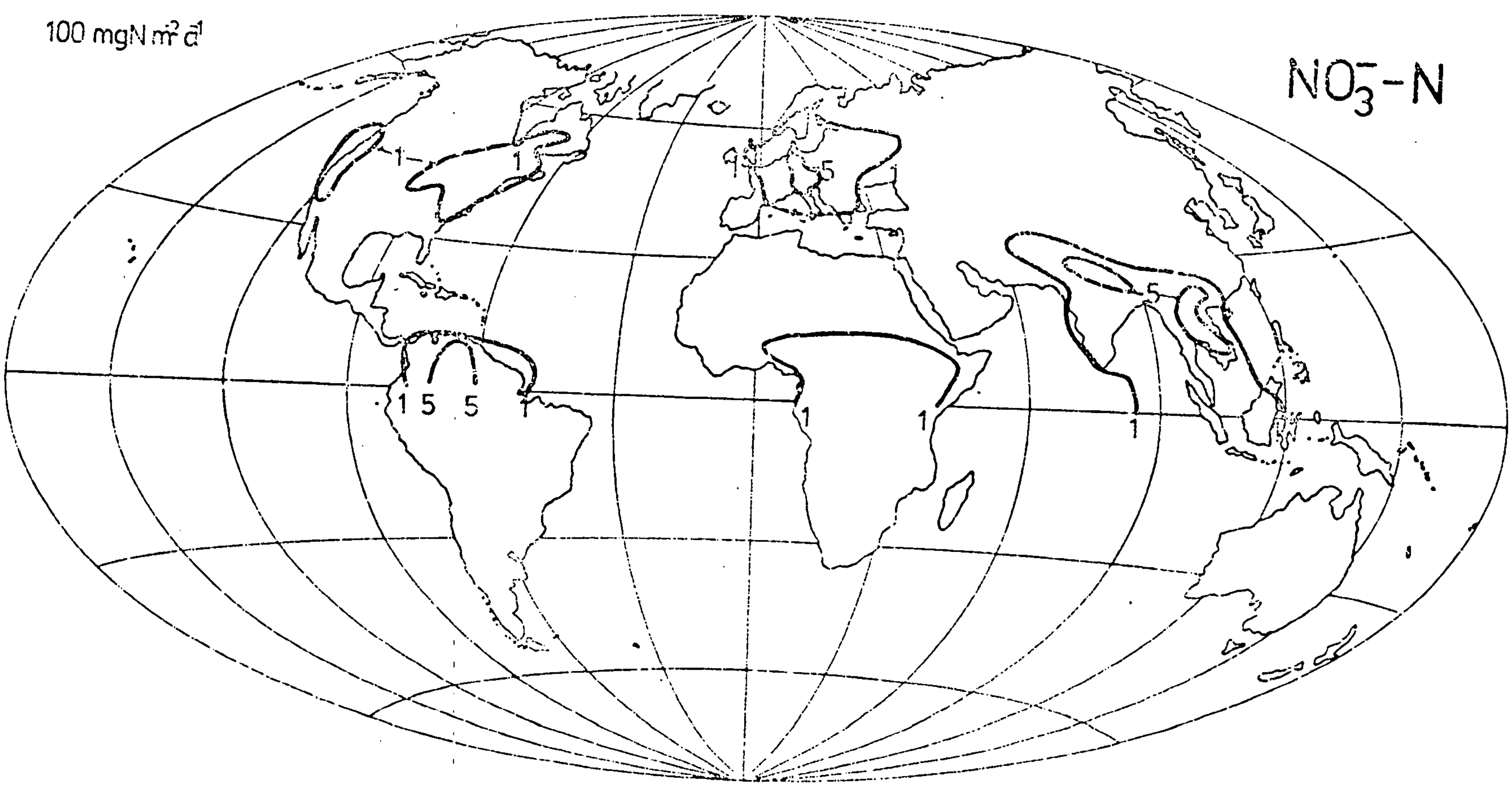


Fig. 10.1: Distribution Map of NO_3^--N Total Deposition Rates on the N.-Hemisphere. It it based on the results of Precipitation analyses from the period around 1900.

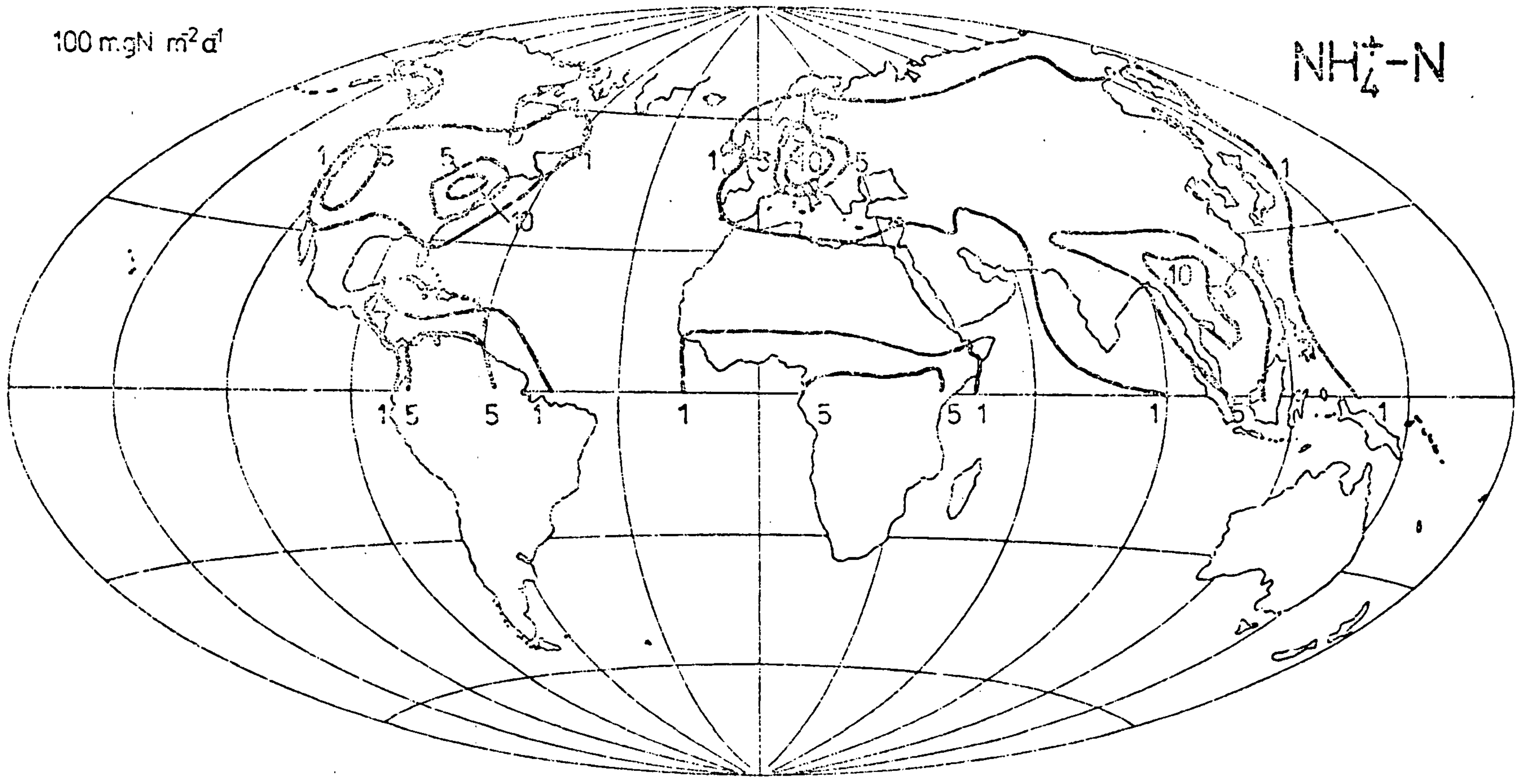


Fig. 10.2: Distribution Map of NH_4^+-N Total Deposition Rates on the N.-Hemisphere. It is based on the results of Precipitation Analyses from the period around 1900.

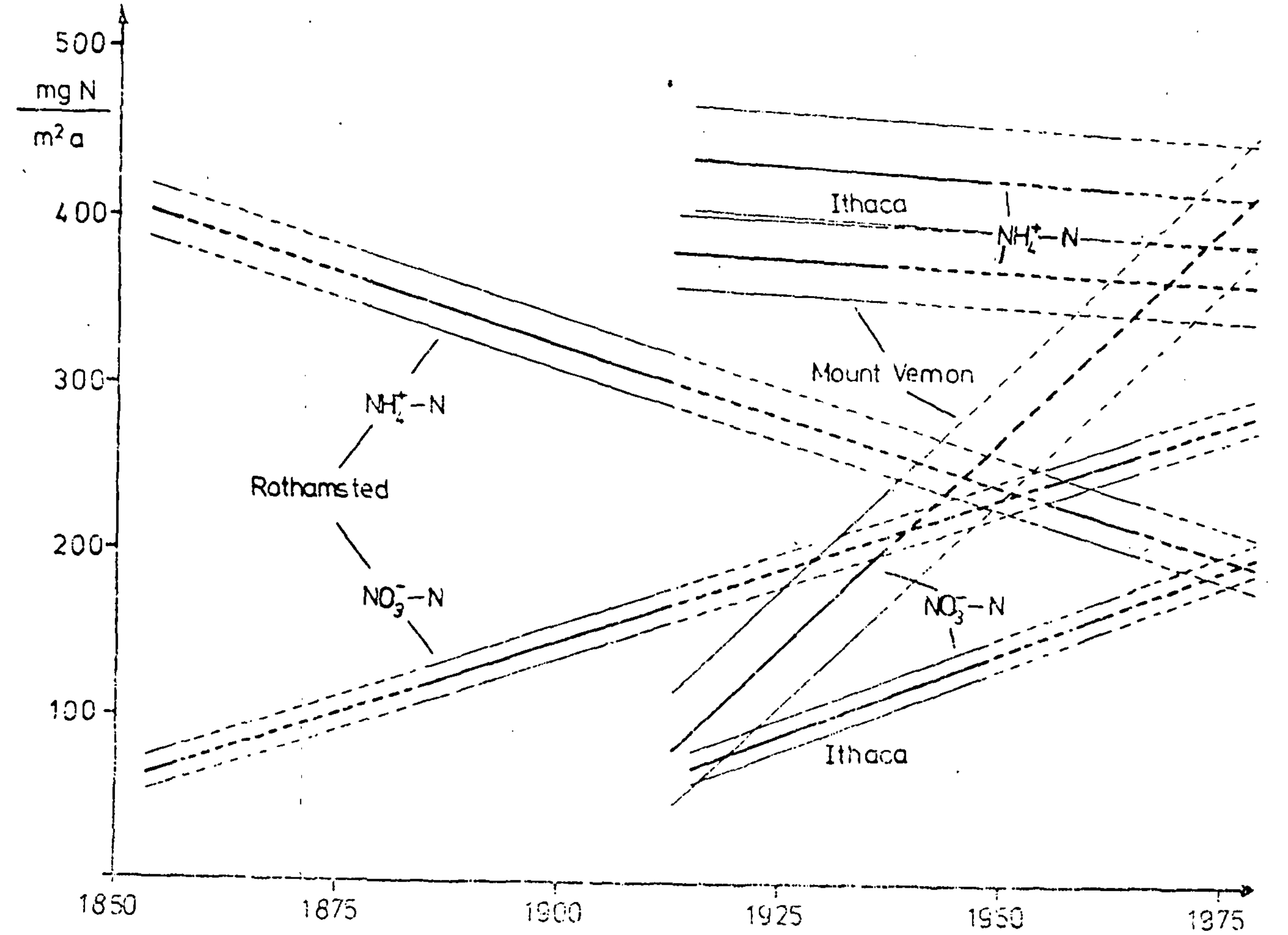


Fig. 10.3: Chronological Development of Total Deposition Rates of NO_3^--N and NH_4^+-N at several Places in the USA and Europe. Analysis results are available for the years having solid lines. The thinner, solid parallel lines give the standard deviation of the analysis results.

Table 10.1: CHRONOLOGICAL CHANGE IN PRECIPITATION QUANTITIES, DEPOSITED NH_4^+-N AND NO_3^--N AND THE CONCENTRATION OF THESE N-COMPONENTS IN THE RAINWATER AT SEVERAL PLACES IN EUROPE (ERIKSSON, 1952; EACN, 1973a, b; 1975).

Location			mg/m^2/a		µg/ml	
		l/m^2/a	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N
Flahult (Sweden)	1909	827	327	146	.7	.18
	1955-1958	650	155	110	.24	.17
	1970-1973	619	297	244	.48	.39
Ås (Norway)	1864	670	210	-	.31	-
	1955-1962	719	156	146	.22	. 2
	1970-1973	554	427	259	.77	.47
Askow (Norway	1922/23-26/27	740	525	263	.71	.36
	1955-1961	696	260	530	.37	.76
	1970	884	617	1069 ?	.70	1.21 ?
Stornoway	1908-1913	1060	40	34	.04	.03
	1958-1959	870	199	109	.23	.13

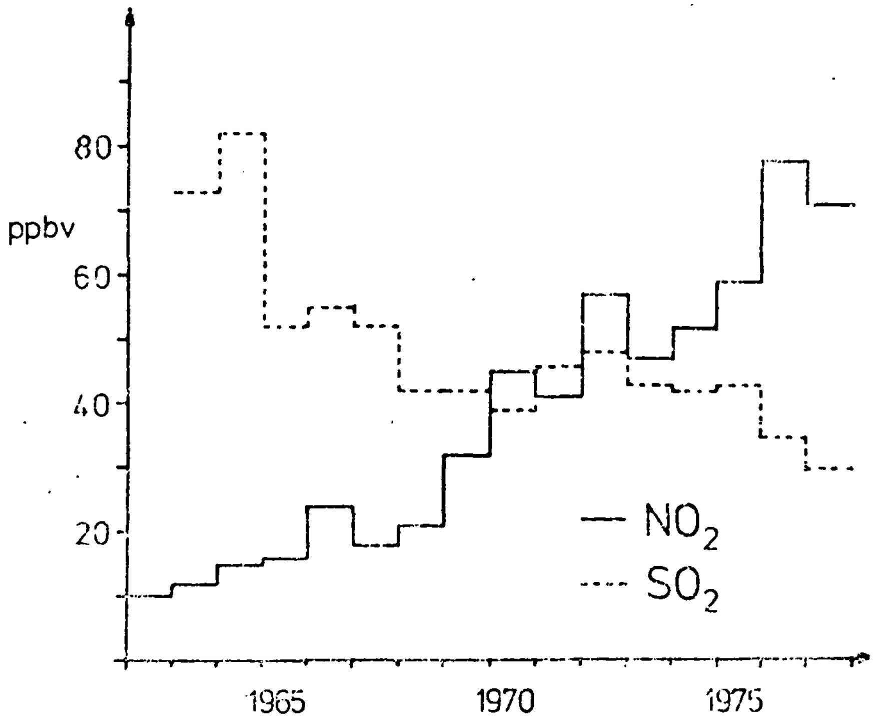


Fig. 10.4: Chronological Development of NO_2 and SO_2 Concentrations in Frankfurt am Main (from data of the Umweltbundesamt, 1978)

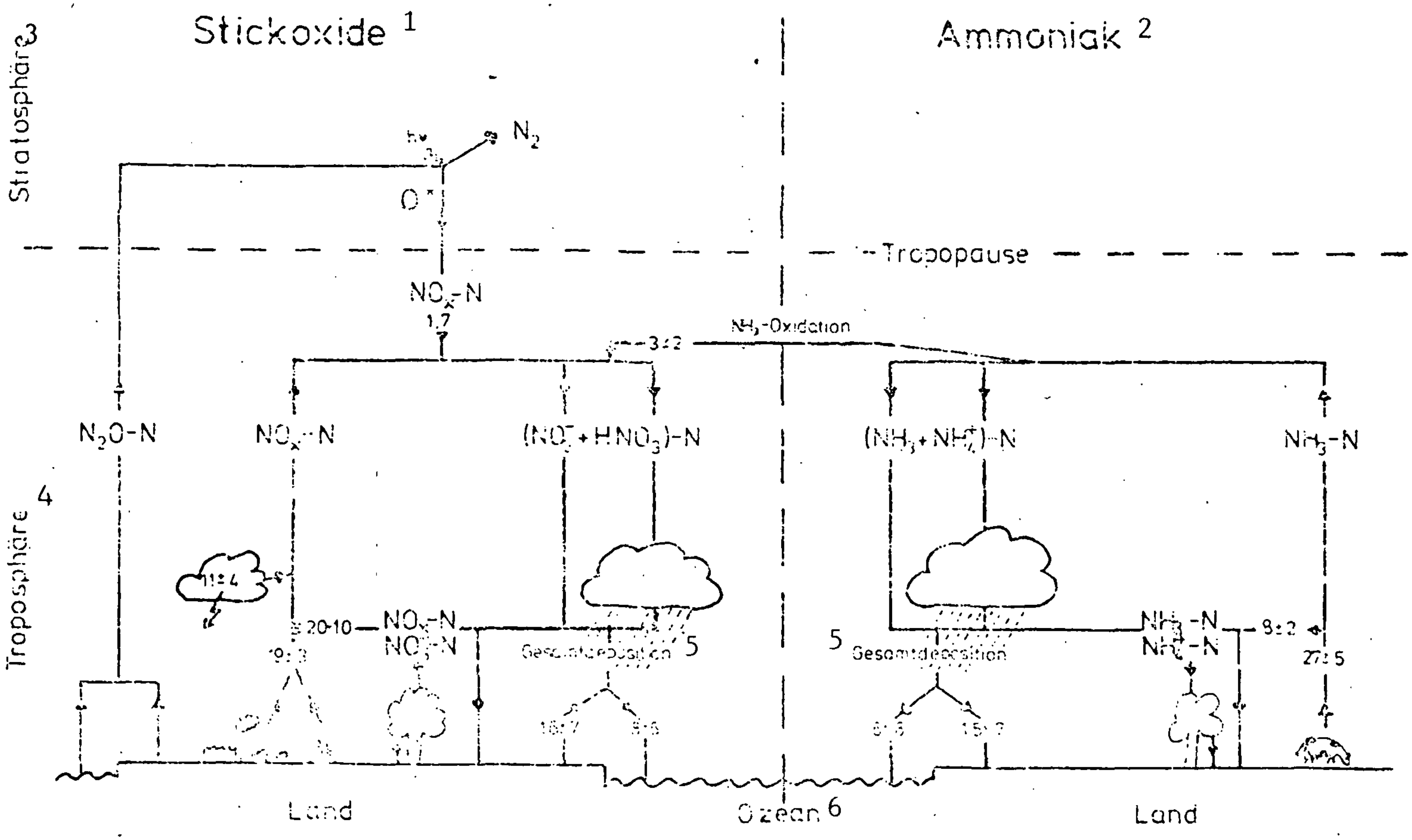


Fig. 11.1: Schematic of Atmospheric Nitrogen Cycle. The numbers denote the fluxes to or from the atmosphere in 10^{12} g N/yr as estimated in this report. The nitrogen quantities removed dry from the atmosphere and cited as 20 ± 10 x 10^{12} g NO_x-N or 8 ± 2 x 10^{12} g NH_3-N represent the N-quantities absorbed by plant, soil and water surfaces and that filtered out by vegetation. An unknown part of this N-quantities can also be contained in the given quantities for the total deposition.

Key: 1-nitrogen oxides 2-ammonia 3-stratosphere 4-troposphere 5-total deposition 6-ocean