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Seasonal trends of NH_4^+ and NO_3^- nitrogen isotope composition in rain collected at Jülich, Germany

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ABSTRACT

Data are presented on nitrogen isotope composition in ammonium and nitrate from rain-water collected over 2 years in an interior area at Jülich, Germany. The seasonal trends in these data are discussed relative to natural and anthropogenic emissions of nitrogen compounds which additionally have been measured or estimated in their isotope composition, e.g. ammonia from animal urine, fuel combustion, fertilizer use and organic soil nitrogen, and natural and anthropogenic nitric oxides from automobile exhausts as well. The ^{15}N content of Jülich rain ammonium is found to be different from values of Hoering (1957) and Moore (1974) and from other rain samples collected in coastal areas.

1. Introduction

Recently the method used by Kohl et al. (1971) to identify fertilizer excess in surface waters has been under discussion. The method is based on differences in the nitrogen isotope ratios of commercial fertilizers and the nitrogen compounds of natural soils. The most commonly used fertilizers have nearly the same nitrogen isotope composition as atmospheric molecular nitrogen, while the natural soil-derived nitrogen compounds (nitrate, organic nitrogen) are sometimes enriched in the heavier ^{15}N isotope (cf. Fig. 5). The method has been criticized by Hauck et al. (1972) and others, mainly because the fertilizer applied to soil loses its isotopic identity by mixing with natural soil-derived nitrogen compounds. Under some circumstances, however, the principal findings of Kohl et al. (1971), i.e. a negative correlation between a fertilizer-derived nitrate content and its $\delta^{15}N$ value, are to be expected (Freyer and Aly, 1975).

According to estimates of Delwiche (1970) the amount of industrially fixed fertilizer nitrogen ($30 \cdot 10^6$ tons N/year) is comparable with the total amount of fixed nitrogen delivered to the earth by rainfall ($25 \cdot 10^6$ tons N/year); 70% of this total, however, is previously fixed nitrogen cycling through the biosphere. It was found that even in cultivated soils the amounts of available nitrogen from fertilizers (without manure) and rainfall are of the same order of magnitude (Keeney and Gardner, 1975). Therefore, in nitrogen isotope balances the contribution of rainfall must not be neglected. For many years the only nitrogen isotope data known for ammonium and nitrate in rain were the measurements of Hoering (1957). Recently, however, Moore (1974) found results contrary to Hoering's in regard to the ^{15}N content of ammonium.

In this paper the contributions of various sources of nitrogen compounds (e.g. combustion, agricultural fertilizers, animal urine, natural biological action) are discussed as they affect the seasonal nitrogen isotope composition of ammonium and nitrate in rain-water. The ^{15}N content of ammonium from rain samples at Jülich is shown to be different from the values of Hoering and Moore and others from coastal areas.

2. Experimental procedure

Rain-water samples were collected via a clean PVC-funnel of 4 m^2 area in plastic containers. The samples were filtered and immediately processed or conserved for storage by addition of 1 ml concentrated sulphuric acid/litre water to prevent microbiological activity. The samples were con-

centrated by evaporation (vacuum, 30 °C) at pH 3 (or pH > 7) for isolation of ammonium (or nitrate). The samples were steam distilled and worked up to ammonium sulphate, which was converted into nitrogen gas in a manner described earlier (Freyer and Aly, 1975).

Nitrogen compounds from soil were isolated as described earlier (Freyer and Aly, 1975). For collection of atmospheric ammonia (including aerosolic ammonium) and ammonia from different sources as well, air was sucked at a rate of about 1 m^3/h through three large-sized (2 l) impingers connected one after another and containing 0.01 N sulphuric acid. For previous measurements of anthropogenic nitric oxides, automobile exhausts were sampled in 10-l-sized glass tubes and shaken overnight with 100 ml 0.1 N sodium hydroxide and 25 ml hydrogen peroxide (30%) for oxidation and absorption. All compounds were worked up as described above.

The nitrogen gas was isotopically analysed with a Micromass 602 C mass spectrometer giving a precision of better than ± 0.05 $\delta^{15}N$. The mean reproducibility of the chemical conversion process for ammonium and nitrate in the samples was better than ± 0.2 $\delta^{15}N$, even between immediately processed and conserved samples. Tests of the whole procedure showed neither a chemical loss nor an isotopic shift of ammonium or nitrate nor an interference with organic nitrogen compounds. The $\delta^{15}N$ values reported were calculated as per mil deviation from atmospheric nitrogen as standard.

3. Characterization of the sample collection area

Samples were collected at Jülich (50°56N, 6°20E) which is located in North Rhine Westphalia in a triangle between Aachen, Düsseldorf and Köln near the Dutch and Belgium borders of Germany.

The Jülich area, as most of the left-hand area of the river Rhine, is characterized by cultivated and fertilized farm land. Cattle breeding is practised less than in the neighbouring Netherlands. Around the big cities industrial and urban areas exist; in the northeast the highly industrialized Ruhr district is located.

For a region of about 10^5 km^2 round the Jülich area, the anthropogenic and natural emissions of nitrogen compounds in 1973–74 were estimated and will be given in detail in a special report (Freyer, 1977). The NH_3 emissions (in t $NH_3/km^2 \cdot yr$) estimated according to a scheme given by Healy et al. (1970) range between 0.11–0.42 for fuel combustion, 0–0.46 for NH_3 and fertilizer factories, 0.13–0.25 for fertilizer use and 0.21–0.69 for animal urine. The anthropogenic NO_x emissions (in t $NO_x/km^2 \cdot yr$), estimated after Meinecke and Bonnenberg (1972) range between 9–46. Estimations on natural emissions of nitric oxides are not available. All primary data are from Statistiches Jahrbuch Nordrhein-Westfalen 1975, Statistisches Jahrbuch 1975 für die Bundesrepublik Deutschland and United Nations Statistical Yearbook 1974.

The natural emissions of nitrogen compounds from soil nitrogen, fertilizer use and animal urine as well depend mainly on the pH values and conditions of soil, which is a modified loess type in this area. Acid and alkaline soils, with minimum and maximum values of pH 3.5 and 7.8, respectively, are present in the sampling area (Schalich, 1968, 1972a, b).

4. Results and discussion

The individual concentrations and $\delta^{15}N$ values of ammonium and nitrate in rain collected at Jülich from winter 1974–75 to autumn 1976, as well as meteorological parameters during sample collection will be published in a special report (Freyer, 1977). In Table 1 the seasonal quarterly mean values for 1975 and 1976 are given.

The chemical concentrations of ammonium and nitrate vary to a large extent. Nevertheless the seasonal quarterly mean values correspond to each other and slight maxima in spring for ammonium and in summer for nitrate are found (cf. Fig. 1), as observed by Ångström and Högberg (1952) in Swedish rain. The concentrations of both compounds are higher than the U.S. network data (Junge, 1958), but in the range of the Dresden (Germany) values measured by Mrose (1966). The mean molar ratio between both compounds is nearly the same (2:1) as reported by several authors (Ångström and Högberg, 1952; Virtanen, 1952; Syers, 1966) in precipitation in temperate regions. The ratio is shifted to lower values (i.e. higher portions of nitrate) in summer. The pH values seem to show the trend as the ratio between both compounds (cf. Fig. 2).

Table 1. *Quarterly mean values of pH, $\delta^{15}N$ and chemical concentration of ammonium and nitrate in rain collected at Jülich from winter 1974–75 to autumn 1976*

	No. of measurem.	mg NH_4^+–N/litre	$\delta^{15}N$–NH_4^+ (‰)	mg NO_3^-–N/litre	$\delta^{15}N$–NO_3^- (‰)	mg NH_4^+–N/ mg NO_3^-–N	($\delta^{15}N$–NH_4^+)–($\delta^{15}N$–NO_3^-)	pH*
Winter 74–75	6	0.74	−9.1	0.28	+0.8	2.34	−9.6	4.2
Winter 75–76	5	1.28	−13.7	0.61	+0.3	2.19	−14.1	4.3
Winter mean	11	0.98	−11.2	0.43	+0.6	2.27	−11.9	4.3
Spring 75	3	1.89	−12.5	0.81	−4.4	2.27	−8.1	3.9
Spring 76	13	1.84	−13.3	0.93	−5.1	2.08	−8.1	3.5
Spring mean	16	1.85	−13.1	0.90	−5.0	2.12	−8.1	3.6
Summer 75	5	1.33	−8.8	1.25	−5.1	1.27	−3.4	3.5
Summer 76	10	1.79	−12.4	0.93	−6.4	2.00	−6.0	3.3
Summer mean	15	1.63	−11.2	1.03	−6.0	1.75	−5.2	3.3
Autumn 75	5	0.91	−13.4	0.34	−0.1	2.44	−13.3	4.8
Autumn 76	6	1.11	−12.7	0.53	+0.1	2.31	−12.7	3.7
Autumn mean	11	1.02	−13.0	0.44	0.0	2.37	−13.0	4.0
Total mean	53	1.44	−12.1	0.75	−3.1	2.10	−9.1	3.6

* Calculations on basis of mean $[H^+]$-concentrations.

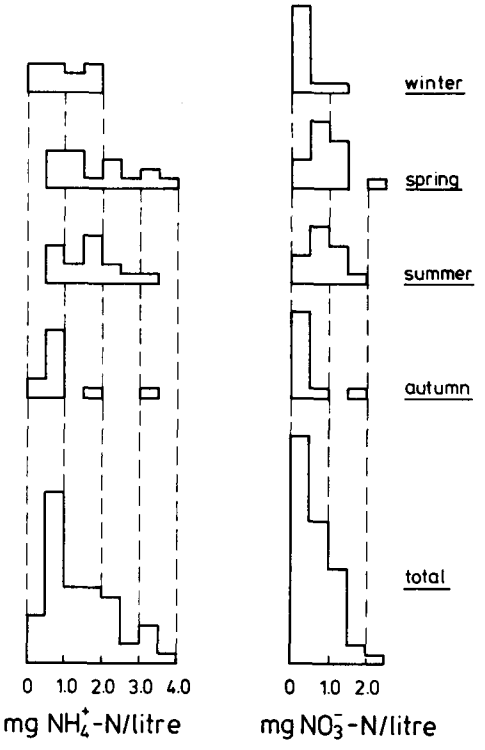

Fig. 1. Histograms of seasonal NH_4^+ and NO_3^--concentrations in Jülich rain.

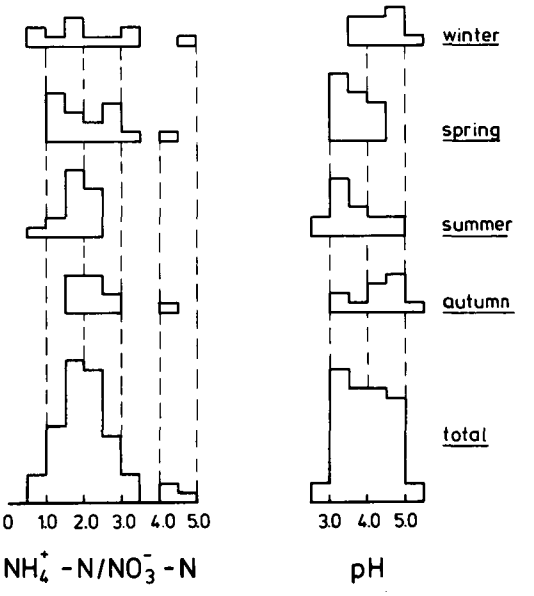

Fig. 2. Histograms of seasonal NH_4^+/NO_3^- molar ratios and pH values in Jülich rain.

The variations in the isotope data within a quarter are lower than those in the chemical ones and a distinct seasonal trend is observed for nitrate with characteristic minima of $\delta^{15}N$ values

in spring and summer (cf. Fig. 3). The values for ammonium on the other hand are nearly uniform, with the exception of the higher values in winter 1974–75 and summer 1975, which cannot be easily interpreted. The mean difference between the δ-values of both nitrogen compounds shows the seasonal trend, too. Consistently the ^{15}N content of ammonium is lower than that of nitrate.

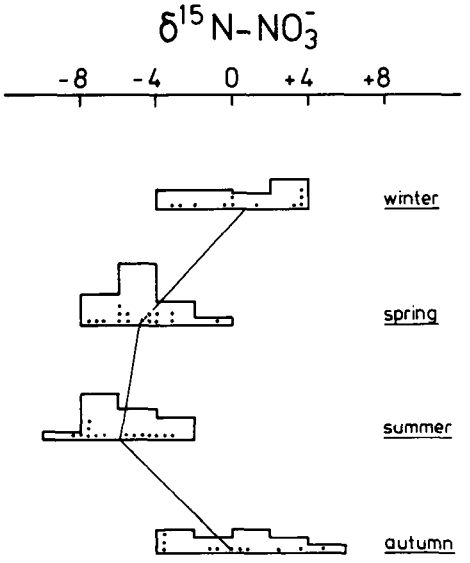

Fig. 3. Histograms of seasonal nitrogen isotope composition in Jülich rain-nitrate.

No dependence of the nitrogen isotope data on the type of rainfall or other meteorological parameters is detected. A slight increase in $\delta^{15}N$–NH_4^+, however, is found during thunderstorms in correspondence with lower NH_4^+/NO_3^- ratios [rain during thunderstorms: $\delta^{15}N$–$NH_4^+ = -(9.7 \pm 1.7)‰$, $NH_4^+/NO_3^- = 1.56 \pm 0.40$ (9 measurements); normal rain and rain shower; $\delta^{15}N$–$NH_4^+ = -(12.6 \pm 2.5)‰$, $NH_4^+/NO_3^- = 2.21 \pm 0.83$ (43 measurements); both sets of values are significantly different at the 95% confidence level]. This fact may be an indication of partial atmospheric oxidation of ammonia, in which the lighter isotope is kinetically favoured, whereas the heavier isotope is enriched in the unreacted ammonia.

Georgii (1960) has found that atmospheric gas concentrations of nitric oxides and ammonia are approximately proportional to the concentrations of nitrate and ammonium in rain. Therefore, it is supposed that the nitrogen isotope data found in rain reflect those of gaseous nitrogen compounds released from local sources (without considering the possible isotope fractionation processes in rainout and washout of nitrogen compounds or the minor effect during thunderstorms). The main sources of atmospheric ammonia are from animal urine, fuel combustion, fertilizer factories and fertilizer use. On the other hand, the main source of atmospheric nitric oxides in the sampling area should be from fuel combustion only (cf. Table 7).

About 40–60% of total ammonia production by animal urine in the sampling area stems from cattle breeding. $\delta^{15}N$ values of ammonia from cattle urine are given in Table 2. It is seen that the $\delta^{15}N$ values vary with the amount of ammonium formed in animal urine by hydrolysis of urea, which is kinetically controlled and favours the lighter nitrogen isotope. The lower values for the initially formed ammonium correspond to values of ammonia found in ambient air in cowsheds. Emitted ammonia from sewage treatment plants should be depleted in ^{15}N, too, while the remaining ammonium in the effluent of these plants is found to be enriched to $\delta^{15}N = +(7–16)‰$ (Freyer and Aly, 1975).

Combusted fuels in the sampling area (North Rhine Westphalia) are hard coal to about 25% and brown coal to about 10% (in units of coal equivalents); in the near surrounding of Jülich (Eschweiler, Bergheim) the contribution of brown coal increases to about 95% due to large power plants. Ammonia emission data and $\delta^{15}N$ values from combustion of these fuels in domestic furnaces are given in Table 3. The emission data are in the range of <60 g NH_3 emission/metric ton of coal, given by Healy et al. (1970), but far away from calculations of Söderlund and Svensson (1976) of 1.9–5.8 kg NH_3/metric ton of coal. The δ-values correspond to $\delta^{15}N = -9‰$ for ammonia from coke-oven gas (Bokhoven and Theeuwen, 1966). Due to the nitrogen isotope variations in coal ($\delta^{15}N = -3$ to $+3‰$; Wlotzka, 1972), it is assumed that the δ-values of ammonia emitted during combustion or dry distillation of coal are within $\delta^{15}N = -(9 - 3)‰$.

The release of ammonia or nitric oxides from fertilizer use depends mainly on the pH values of soil. Both types of soils, acid and alkaline, exist in the sampling area, favouring the release of nitric oxides and ammonia as well. Moreover, the spring

Table 2. *Concentrations and $\delta^{15}N$ values of ammonia produced from cattle urine*

Ambient air in cow-sheds

Conc. (mg NH_3–N/m³ air)	$\delta^{15}N$–NH_3 (‰)	Livestock
4.1	−10.3	8 cows
0.63*	−11.5	12 cows, 5 calves
4.5	−12.6	10 calves

Incubation of cow urine at room temperature

Time of incubation (days)	Conc. (mg NH_4^+–N/l urine)	$\delta^{15}N$–NH_4^+ (‰)
2	43	−9.6
2	48	−9.1
3	61	−7.7
5	116	−5.9
9	395	−4.4
12	1562	−4.6

* Measurement in a well-ventilated cow-shed.

Table 3. *Specific emissions and $\delta^{15}N$ values of ammonia from combustion of brown and hard coal in domestic furnaces*

Fuel	Specific emission (g NH_3–N/tons fuel)	$\delta^{15}N$–NH_3 (‰)
Brown coal	8.64	−6.9*
	6.14	−4.3
Hard coal	11.76	−7.2

* During sample collection with 0.01 N sulphuric acid the lighter isotope is absorbed stronger than the heavier isotope. The ^{15}N contents and relative amounts of total ammonia in three impingers connected one after another were: first impinger: 97.5% of total ammonia, $\delta^{15}N = -7.3$‰; second impinger: 2.2%, $\delta^{15}N = +6.6$‰; third impinger: 0.3%, $\delta^{15}N = +21.0$‰.

maxima of ammonium concentrations in rain refer to a stronger ammonia emission, at a time when fertilizer is applied to land. In the same way the summer maxima of nitrate concentrations in rain can be explained by increased biological activity at higher temperatures and more acid conditions of soil in summer, favouring denitrification reactions and the release of nitric oxides. For calculations of the ^{15}N content of soil-emitted nitrogen compounds, the mixing of fertilizer nitrogen with the organic nitrogen pool has to be considered. Mineralized soil-ammonium and -nitrate have lower $\delta^{15}N$ values than the soil nitrogen, because of kinetical favouring of the lighter ^{14}N isotope in the degradation reaction. Data for this relationship in loess soils sampled in the surroundings of Jülich and processed immediately after sampling are presented in Fig. 4. Even from incubation experiments of soils, it has been shown that

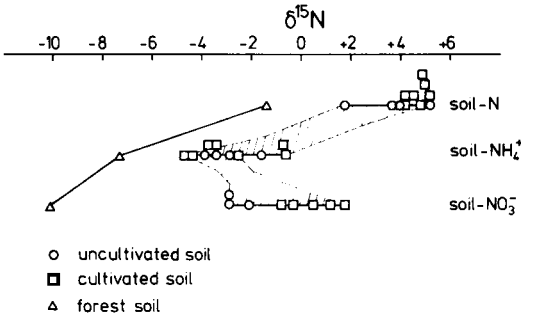

Fig. 4. Nitrogen isotope relationship between total soil nitrogen, soil ammonium and soil nitrate in loess soils (surface samples) sampled in the surroundings of Jülich (measurements by H. D. Freyer and G. Kasten, unpublished).

ammonium (Cheng et al., 1964) and nitrate (Feigin et al., 1974) compared to the organic soil nitrogen are either depleted in ^{15}N or have the same isotopic content. Therefore, the $\delta^{15}N$ values of ammonia and nitric oxides released from soil must be lower than those of soil nitrogen and, possibly, even lower than those of fertilizer nitrogen. For an ammonia assimilation by soil bacteria the reverse effect has been found (Delwiche and Steyn, 1970). The final product of denitrification is nitrogen, which is depleted to $\delta^{15}N = -19$‰ (Wellmann et al., 1968; Delwiche and Steyn, 1970). It is assumed that the liberated intermediates of nitrate reduction, N_2O and NO, are depleted in ^{15}N, too. Even liberated nitric oxide intermediates during nitrification reactions have to be depleted in ^{15}N due to the large kinetic isotope effects involved (Freyer, 1975). All available data on fertilizer and soil nitrogen are summarized in Fig. 5. For estimation of the ^{15}N content of soil-released ammonia in the sampling area, at least the values for mineralized ammonium given in

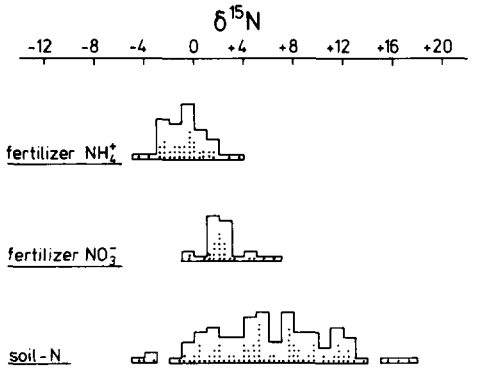

Fig. 5. Histograms of nitrogen isotope composition in commercial fertilizers and in total soil nitrogen. Fertilizer data are from Shearer et al. (1974) and Freyer and Aly (1974); total soil nitrogen data are from Cheng et al. (1964), Bremner and Tabatabai (1973), Shearer et al. (1974), Rennie and Paul (1975) and this work (Fig. 4).

Fig. 4 are supposed. Emitted ammonia from synthesis plants or fertilizer factories, possibly, has a similar ^{15}N content as fertilizer ammonium (Fig. 5), i.e as atmospheric nitrogen.

Table 4 summarizes the estimated $\delta^{15}N$ values of emitted ammonia from different sources. Unfortunately, due to the overlapping range of values, the different sources can hardly be distinguished. Only a mean isotopic content of atmospheric ammonia in the sampling area can be calculated. This content corresponds to data resulting from direct measurements of gaseous (and aerosolic) atmospheric ammonia given in Table 5. If the following isotope exchange equilibrium has been established during rainout and washout of atmospheric ammonia,

$$^{15}NH_3 + {}^{14}NH_4^+ \rightleftharpoons {}^{14}NH_3 + {}^{15}NH_4^+$$

$$\alpha_{25°C} = \frac{^{15}NH_4^+/^{14}NH_4^+}{^{15}NH_3/^{14}NH_3} = 1.031 \quad \text{(Scalan, 1959)}$$

the ^{15}N content within ammonium has to be higher than that within ammonia. The reverse effect—lower values within rain ammonium than in atmospheric ammonia—has been found in the Jülich samples. Even Moore (1974) has shown that tropospheric aerosolic ammonium is enriched in ^{15}N compared to rain ammonium. Therefore the isotope fractionation between gaseous ammonia (including aerosolic ammonium) and dissolved rain ammonium is not determined by the isotope exchange reaction, but by kinetic resolution and absorption effects in which the lighter ^{14}N isotope is preferred (see additionally note to Table 3).

Table 4. *$\delta^{15}N$ values of emitted ammonia from different sources and calculated mean value of emitted ammonia in the sampling area*

NH_3 emission from sources	Percentage in the sampling area	Range in $\delta^{15}N$ (‰)
Fuel combustion	10–35 %	−9 to −3
NH_3 factories	0–35 %	−3 to +2
Fertilizer use	10–35 %	−5 to 0
Animal urine	30–50 %	−12 to −4
Mean of emitted ammonia in the sampling area		$\delta^{15}N = -(5 \pm 3)$‰

Table 5. *Concentrations and $\delta^{15}N$ values of atmospheric ammonia (including aerosolic ammonium)* collected at Jülich*

Date (1976)	Conc. (μg NH_3–N/m³ air)	$\delta^{15}N$–NH_3 (‰)	mm rainfall during collection
Apr. 4–9	7.06	−5.8	4.4
Sept. 8–10	5.36	−4.8	2.1
Sept. 10–15	4.14	−5.2	1.0
Sept. 16–23	5.89	−3.3	2.5

* The NH_3/NH_4^+ ratio of atmospheric ammonia in this area is contrary to older measurements of Georgii (1960) about 1 (G. Gravenhorst, personal communication).

From global emission data of nitric oxides (Table 6) the portions of anthropogenic and natural emissions in the sampling area (North Rhine Westphalia, Kr. Düren incl. Jülich) have been calculated and given in Table 7. As a rough estimation it has been assumed that the natural emissions are proportional to the effective agricultural area, whereas the anthropogenic ones are proportional to the energy consumption data. Other areas and the area of the ocean are neglected because of their possibly lower contributions to the natural emissions (Junge, 1963).

According to the data of Söderlund and Svensson (1976) the main source of nitric oxides in the sampling area is only an anthropogenic one.

Table 6. *Estimated annual global emissions of nitric oxides*

	Emission (10^6 tons N yr^{-1})		
	Anthropogenic	Natural	References
NO, NO_2, NO_3^-	18	—	McConnell (1973)
	—	30 ± 20*	Galbally (1975)
	16.1	234	Robinson and Robbins (1975)
	19	21–89	Söderlund and Svensson (1976)

* Values given for the Northern Hemisphere.

Table 7. *Portions of anthropogenic nitric oxides in the sampling area calculated from global emission data after (a) Robinson and Robbins (1975) and (b) Söderlund and Svensson (1976). (Portions of anthropogenically + naturally emitted compounds = 1.0)*

	World	North Rhine Westphalia	Kr. Düren
Area (10^3 km^2)	135 897	34.1	0.92
Effective agricultural area (10^3 km^2)	44 440	18.8	0.59
Energy consumption (10^6 tons of coal equiv./yr)	7 608	141	1.53
Anthropogenic NO, NO_2, NO_3^- (portion)			
(a)	0.064	0.75	0.51
(b)	0.18–0.48	0.90–0.98	0.76–0.93

In that case the $\delta^{15}N$ values of nitrate expected in rain have to be positive and nearly constant. Anthropogenic nitric oxides should have similar isotopic composition as atmospheric nitrogen, from which the nitric oxides are originated. Nitric acid and nitrate formed from these oxides should be enriched in ^{15}N due to isotope exchange reactions exhibiting the following equilibrium constants:

$$\alpha_{25°C} = \frac{^{15}NO_3^-/^{14}NO_3^-}{^{15}NO/^{14}NO} = 1.096 \quad \text{(Spindel, 1954)}$$

$$\alpha_{25°C} = \frac{^{15}NO_3^-/^{14}NO_3^-}{^{15}No_2/^{14}NO_2} = 1.053$$

In previous studies of anthropogenic nitric oxides from automobile exhausts a value of $\delta^{15}N\text{–}NO_x = -1.8‰$ has been found, which corresponds to data ($\delta^{15}N\text{–}NO_x = +1.4$ and $-0.5‰$) given by Hoering (1958) for fixation of atmospheric nitrogen with electric sparks. Natural nitric oxides formed by denitrification or nitrification reactions, on the contrary, should be depleted in ^{15}N as stated above and differ from the anthropogenic ones.

The pronounced seasonal trend found in the $\delta^{15}N$ values of rain nitrate (Fig. 3) can be explained, therefore, by the different contributions of natural and anthropogenic nitric oxides. Moreover, it indicates a heavier contribution of natural emissions taking place preferentially at higher temperatures and more acid conditions of soil in summer. Due to these results the higher natural emissions of nitric oxides given by Robinson and Robbins (1975) seem to be more probable than those of Söderlund and Svensson (1976). For quantitative estimations the isotope data of naturally and anthropogenically emitted nitric oxides, as well as possible isotope fractionations during rain- and washout of these compounds, have to be measured in further studies.

5. Comparison with the data of Hoering and Moore

All available NH_4^+ and NO_3^- nitrogen isotope data found in rain are plotted in Fig. 6. It is seen that although the nitrate data correspond to each other, the ammonium data deviate considerably from the data measured by Hoering and Moore. These deviations cannot be explained, because it is supposed that the sources of atmospheric ammonia in the interior U.S. sampling areas—Fayetteville, Arkansas (Hoering), and Boulder, Colorado (Moore)—are similar to those discussed in this investigation. Even the chemical ammonium concentrations or the NH_4^+/NO_3^- ratio found in rain by Moore and us are in the same range. Perhaps the sample preparation may be of importance. We have checked our experimental technique and have found neither a chemical loss nor an isotopic shift during sample preparation. We have prepared our samples by vacuum evaporation of rain-water, while Hoering and Moore have extracted the ammonium in rain by ion exchange. If amonium is lost by bacterial oxidation during storage of the samples, or by any other kinetic process during sample preparation, the values of the remaining ammonium have to be higher than those of the initial material, as can be seen by similar reactions taking place in soil (Freyer, 1975).

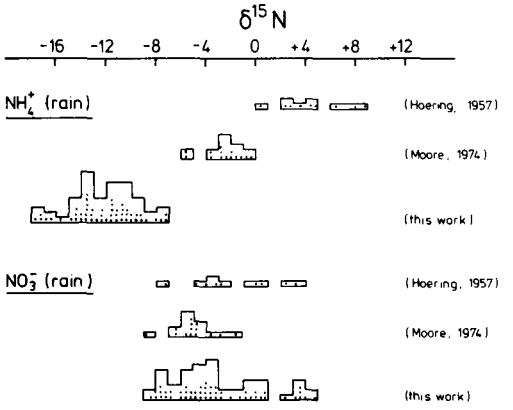

Fig. 6. Histograms of nitrogen isotope composition in rain-ammonium and -nitrate from data of Hoering (1957), Moore (1974) and this work.

According to the values presented the difference between the δ-values of both nitrogen compounds differs very much. Hoering has explained the positive difference (i.e. higher values for ammonium than for nitrate) by atmospheric oxidation of ammonia and formation of nitrate as main processes. This contribution has been called into question (Eriksson, 1958). Our values show an opposite effect, varying with the season, which can be explained only by different sources of nitrogen compounds, while atmospheric processes (lightning, ammonia oxidation) may be of minor importance for the total of these compounds (Junge, 1963).

6. Previous results in rain collected in coastal areas as well as in snow collected in an unpolluted alpine area

Previous NH_4^+ and NO_3^- nitrogen isotope data in rain collected in coastal areas—at Fortaleza/

Table 8. *Concentrations and $\delta^{15}N$ values of ammonium and nitrate in rain and snow samples collected in coastal areas and an unpolluted alpine area*

Location, date	mg NH_4^+–N/ litre	$\delta^{15}N$–NH_4^+ (‰)	mg NO_3^-–N/ litre	$\delta^{15}N$–NO_3^- (‰)	pH
Rain samples					
Fortaleza					
1975, May 3	0.027	(+17.7)	0.020	(+12.0)	7.8
1975, May 16	0.025	+3.6	0.025	—	8.3
Perros Guirec					
1975, Sept. 9	0.42	+2.6	0.59	+6.9	—
1975, Sept. 11	0.38	+3.0	0.54	+6.2	—
Snow samples					
Rettenbachferner					
1976, March	0.065	−8.8	0.27	−3.3	—

Ceará, Brasil (3°35S, 38°35W) and at Perros-Guirec, France (48°48N, 3°29W)—are given in Table 8. The main wind direction at the time of sampling was from the Atlantic Ocean. Additional data are given for powdery snow collected at the Rettenbachferner/Tyrol, Austria, at an elevation of 2800 m.

The isotope data in snow correspond to those found in rain collected at Jülich. The coastal rain data, however, are different. Especially, the coastal ammonium is enriched in ^{15}N, because the sea or the acid latosolic soil at Fortaleza is an absorption sink for ammonia which favours the lighter ^{14}N isotope. Further studies have to be carried out for confirmation.

7. Acknowledgements

The first measurements of the Jülich rain samples from November 1974 to August 1975 have been performed by A. I. M. Aly and are mentioned in his thesis (1975). The co-operation with him is gratefully acknowledged. Further thanks are due to H. Knappe, K. Kobel, H. Musall and R. Pohling for their technical assistance. The rain samples from Fortaleza have been collected and concentrated by R. Pohling; those from Perros Guirec have been collected by G. Haller. The meteorological data are kindly provided by the meteorological staff of the Jülich Nuclear Research Center.

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СЕЗОННЫЕ ТРЕНДЫ В ИЗОТОПНЫХ СОСТАВАХ АЗОТА В NH_4^+ И NO_3^- В ДОЖДЕ, СОБРАННОМ В ЮЛИХЕ, ФРГ

Представлены данные по изотопному составу азота в аммиаке и нитрате в дождевой воде, собиравшейся в течение полных двух лет во внутренней (континентальной) области в Юлихе, ФРГ. Обсуждаются сезонные тренды в этих данных в сравнении с естественными и анторопогенными эмиссиями азотных компонент, измерявшихся дополнительно или оценивавшихся по их изотопному составу, например, аммиак из мочи животных, сжигание топлива, азот из удобрений или органики почвы, а также окислы азота из естественных или антропогенных источников, например, выхлопных газов автомобилей. Найдено, что содержание изотопа ^{15}N в аммиаке дождя в Юлихе отличается от величин, полученных Герингом (1957) и Муром (1974) и от других дождевых проб, собранных в прибрежных областях.