

Seasonal variation of $^{15}\text{N}/^{14}\text{N}$ ratios in atmospheric nitrate species

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ABSTRACT

Nitrate in rain sampled in moderately polluted areas at Jülich/Germany and Ahrensburg/Germany, as well as in a rural area at Deuselbach/Germany and in a coastal area at Le Conquet/France, shows a pronounced seasonal variation in its $^{15}\text{N}/^{14}\text{N}$ ratio with lower data in summer ($\delta^{15}\text{N} = -(5 \pm 1)\text{‰}$; mean between the stations) than in winter ($\delta^{15}\text{N} = (0 \pm 2)\text{‰}$). Particulate nitrate trapped in low- and high-volume sampling at Jülich shows a similar seasonal $^{15}\text{N}/^{14}\text{N}$ variation ($\delta^{15}\text{N}$ of about $+3\text{‰}$ and $+7\text{‰}$ in summer and winter, respectively); the absolute data however differ from those in the rain samples. Nitric acid vapour, on the other hand, exhibits nearly constant $^{15}\text{N}/^{14}\text{N}$ data over the seasons ($\delta^{15}\text{N} = -(2-3)\text{‰}$). The data are discussed considering isotope exchange reactions and kinetic fractionations involved in transformations of atmospheric oxidized nitrogen species. Full explanations must await further measurements.

1. Introduction

At almost every stage of any process involving compounds of light elements such as hydrogen, carbon, nitrogen, oxygen and sulphur, kinetic and equilibrium isotope fractionation effects take place. Therefore, measurements of isotope ratios in atmospheric trace gases have been performed in the hope of distinguishing and identifying different sources and sinks as well as physical and chemical reactions. Isotope transformations of nitrogen compounds in soils have been studied by several authors. Isotope measurements on atmospheric nitrogenous trace gases, however, are scarce. For many years, the only nitrogen isotope data known for ammonium and nitrate in rain water had been the measurements of Hoering (1957). Later, Moore (1974, 1977) published isotope data on tropospheric and stratospheric N_2O , NO_2 , NO_3^- and NH_4^+ and on NO_3^- and NH_4^+ in rain water. Freyer (1978a, b) also reported nitrogen isotope data for NH_4^+ and NO_3^- in rain sampled at Jülich and found a seasonal variation in the data for rain-nitrate. Quite recently, Heaton and Collett (1985) and Heaton (1986, 1987) confirmed this seasonal

variation by corresponding measurements of nitrate in rain from Pretoria, South Africa.

This paper gives additional $^{15}\text{N}/^{14}\text{N}$ data for rain-nitrate. Furthermore, $^{15}\text{N}/^{14}\text{N}$ data for particulate nitrate and nitric acid vapour sampled by a low- and high-volume filter technique are presented. Interpretation effects are proposed, whose significance must be studied by further analysis. An abstract of the data has been published elsewhere (Freyer, 1985).

2. Experimental procedure

Rain was sampled during individual events in moderately polluted areas at Jülich/Germany (located about 50 km west of Cologne) from autumn 1979 to winter 1984/85 and at Ahrensburg/Germany (at the northeast periphery of Hamburg) from spring 1980 to winter 1982/83, and also in rural air at Deuselbach (Hunsrück)/Germany (about 150 km southwest of Cologne) from autumn 1979 to autumn 1984 and in Le Conquet (Bretagne) (about 20 km west of Brest) at the French Atlantic coast from winter 1981/82 to

autumn 1983. The samples were collected in plastic containers with a PVC-funnel of 4 m² surface area. The samples were filtered and either immediately processed or conserved for storage and shipment by addition of 1 ml concentrated sulphuric acid/liter of rain water to prevent microbial activity. In the laboratory, the samples were neutralized and concentrated in a rotating evaporator (vacuum, 30°C) for isolation of nitrate. The concentrated solution was made alkaline with MgO. After evaporation of ammonia from sampled ammonium, the nitrate was reduced with Devarda's alloy to ammonia, which was steam distilled and absorbed in diluted sulphuric acid. The ammonium concentration was measured photometrically using Nessler's reagent. Finally, the ammonium sulphate solution was freeze dried and the ammonium converted into nitrogen gas by oxidation with LiOBr in a manner described earlier (Freyer and Aly, 1975).

Particulate nitrate and nitric acid vapour were collected at Jülich during summer 1978 and autumn 1980 with a low-volume filter technique similar to that described by Okita et al. (1976). A glass fiber filter (Satorius; dia. 293 mm) was connected in series upstream to three NaCl-impregnated cellulose acetate filters (Satorius; pore size 0.8 μm) within a large-size Satorius filter holder. Air was sampled through the filter pack at a flow rate of about 4.5 m³ h⁻¹ for collection of particulate nitrate and nitric acid vapour on the glass fiber and the NaCl-impregnated filters, respectively. The volume was measured by a gas-meter. The sampling time was sometimes more than one month. The nitrate amounts found on the last downstream NaCl-impregnated filter were very often in the blank range of the chemical determination (<0.05 mg N).

In another experiment, particulate nitrate was sampled at Jülich during summer 1982 and autumn 1984 by a one stage Andersen high-volume impactor. Some samples were also collected at Deuselbach during April to June 1983. The impactor separated particles with a cutoff diameter of 3.5 μm. The collection plate (diameter 305 mm) and the backup filter holder (203 × 254 mm²) were loaded with glass fiber collection disks (Gelman Type A). The air flow rate was about 68 m³ h⁻¹; the volume was measured by a mass-flow meter. Sampling times ranged from 2 to 5 days. In both filtering techniques, the nitrate was extracted

ultrasonically from the filter media with deionized water and the solution was worked up as described for the rain samples.

The nitrogen gas was analyzed with a Micromass 602 C mass spectrometer. The $\delta^{15}\text{N}$ values were calculated as per mil deviation from atmospheric nitrogen as standard:

$$\delta^{15}\text{N}(\text{‰}) = \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}} - (^{15}\text{N}/^{14}\text{N})_{\text{standard}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} \times 1000.$$

The reproducibility of the $\delta^{15}\text{N}$ data for nitrate in the samples was $\pm 0.3\text{‰}$ (1 S.D.). The amount of nitrogen required for isotope analysis was between 0.6 and 1.0 mg N.

3. Results

3.1. Rain Samples

Seasonal mean concentrations of nitrate in rain collected at Jülich during the years 1975/1976 (Freyer, 1978a) and 1979/1984 are given in Table 1. Despite the scatter, mean concentrations obtained during both sampling periods corresponded to each other and ranged from 0.4 to 1.0 mg N liter⁻¹. The concentrations during spring and summer were higher than during autumn and winter. The annual wet deposited nitrate calculated from the data amounted to 0.39 and 0.68 g N m⁻² yr⁻¹ for the 1975/1976 and 1979/1984 periods, respectively. The latter value corresponds very closely to estimates of 0.7 g N m⁻² yr⁻¹ as given by Bonis et al. (1980) for wet depositions of nitrate over Central Europe.

Table 1 also gives seasonal concentrations of nitrate in rain collected at Ahrensburg, Deuselbach and Le Conquet. Nitrate concentrations in rain from Ahrensburg were in the range of the Jülich data, but showed no seasonality. Rain from Deuselbach gave lower nitrate concentrations. The lowest concentrations were found in rain from Le Conquet. At both latter sites, the concentrations during spring and summer were somewhat higher than during autumn and winter. Similar seasonal nitrate concentrations in rain from Jülich, Deuselbach and Hamburg (a nearby site of Ahrensburg) were observed from daily rain sampling by Georgii et al. (1983) during the 1979/1981 period (Table 1).

Table 1. Seasonal data (\pm S.D.) of concentrations and $\delta^{15}\text{N}$ of nitrate in rain collected at Jülich (I and II, during the years 1975/76 and 1979/84, respectively), Ahrensburg, Deuselbach, and Le Conquet; comparison with relevant data reported by Heaton and Collett (1985) and Georgii et al. (1983)

	No. of measurements	mg $\text{NO}_3^- - \text{N}$ liter $^{-1}$	$\delta^{15}\text{N} - \text{NO}_3^-$ (‰)
<i>Jülich</i>			
Spring ^{a)} I	16	0.90 \pm 0.48	-5.0 \pm 1.8
Spring II	26	0.88 \pm 0.71	-2.6 \pm 3.0
Summer I	15	1.03 \pm 0.75	-6.0 \pm 1.8
Summer II	23	0.85 \pm 0.62	-4.9 \pm 2.4
Autumn I	11	0.44 \pm 0.45	0.0 \pm 2.9
Autumn II	24	0.78 \pm 0.63	-0.9 \pm 1.9
Winter I	11	0.43 \pm 0.33	+0.6 \pm 2.8
Winter II	22	0.58 \pm 0.37	0.0 \pm 2.4
<i>Jülich (after Georgii et al.)</i>			
Summer (mean)		0.9 - 1.0	
Winter (mean)		0.5	
<i>Ahrensburg</i>			
Spring	10	1.00 \pm 0.58	-2.7 \pm 3.0
Summer	8	0.60 \pm 0.26	-4.3 \pm 2.5
Autumn	10	0.70 \pm 0.50	-0.9 \pm 3.9
Winter	3	0.59 \pm 0.04	+2.4 \pm 1.4
<i>Hamburg (after Georgii et al.)</i>			
Summer (mean)		0.7	
Winter (mean)		0.7 - 0.8	
<i>Deuselbach</i>			
Spring	16	0.26 \pm 0.13	-2.2 \pm 2.7
Summer	13	0.37 \pm 0.24	-4.5 \pm 2.5
Autumn	14	0.21 \pm 0.25	-3.1 \pm 3.2
Winter	15	0.13 \pm 0.09	-0.1 \pm 1.4
<i>Deuselbach (after Georgii et al.)</i>			
Summer (mean)		0.5 - 0.6	
Winter (mean)		0.2 - 0.3	
<i>Le Conquet</i>			
Spring	13	0.11 \pm 0.07	-5.4 \pm 2.3
Summer	4	0.21 \pm 0.20	-6.5 \pm 3.7
Autumn	5	0.07 \pm 0.05	-3.6 \pm 2.2
Winter	8	0.06 \pm 0.05	-1.7 \pm 1.0
<i>Pretoria (after Heaton and Collett)</i>			
Spring	38	0.65 \pm 0.57	-5.0 \pm 5.2
Summer	32	0.57 \pm 0.49	-4.9 \pm 3.0
Autumn	21	0.49 \pm 0.38	-3.3 \pm 5.1
Winter	5	0.26 \pm 0.23	+0.3 \pm 3.6

^{a)} The seasons in this study were defined as successive three month periods starting on the first of March, June, September and December, respectively.

The mean $\delta^{15}\text{N}$ data for nitrate in the rain samples, given in Table 1 and Fig. 1, ranged from +2 to -6‰. A seasonal variation of data with characteristic minima during summer was evident at all sites. The difference between winter and summer data was in the range from about 4 to 7‰. Quite recently, a seasonal $^{15}\text{N}/^{14}\text{N}$ effect for the Southern Hemisphere was also found in rain-nitrate from Pretoria (Heaton and Collett, 1985; Heaton, 1987). Seasonal data calculated from these measurements are given in Table 1.

3.2. Filter samples

Seasonal concentrations and $\delta^{15}\text{N}$ data for particulate nitrate (NO_3^-) and nitric acid vapour (HNO_3) collected at Jülich from August 1978 to November 1980 with the low-volume technique are given in Table 2, showing that the concentrations for NO_3^- and HNO_3 ranged from 0.9 to 1.4 $\mu\text{g N m}^{-3}$ and from 0.2 to 0.5 $\mu\text{g N m}^{-3}$, respectively. The NO_3^- concentrations showed no seasonality. The concentrations of HNO_3 , on the other hand, were higher during spring and summer than during autumn and winter, and a seasonal shift in the molar $\text{NO}_3^-/\text{HNO}_3$ ratio from about 3 (spring and summer) to higher values of about 6 (autumn and winter) was observed. For the $\delta^{15}\text{N}$ data of NO_3^- , a similar seasonal variation was found as for rain nitrate with values of about +4‰ during summer and about +9‰ during winter. $\delta^{15}\text{N}$ data for HNO_3 by comparison showed no seasonal variation and gave a mean of about -2.5‰ (Fig. 2). Statistical proof of this observation, however, is not possible, because only few $\delta^{15}\text{N}$ measurements for HNO_3 have been performed.

Table 3 gives the corresponding seasonal data obtained with the high-volume technique. The seasonal concentrations of NO_3^- (sum of fine and coarse particles) collected at Jülich from August 1982 to December 1984 ranged from 2.2 to 3.9 $\mu\text{g N m}^{-3}$ with higher concentrations of fine than of coarse particles. The concentrations of NO_3^- found at Deuselbach from April to June 1983 were lower than those found at Jülich, similar to the different nitrate concentrations in rain observed at both sites. The $\delta^{15}\text{N}$ data for the fine and coarse fraction of NO_3^- also showed a seasonality with the lowest values being found in summer. The $\delta^{15}\text{N}$ data obtained at Deuselbach were in the range of the Jülich data.

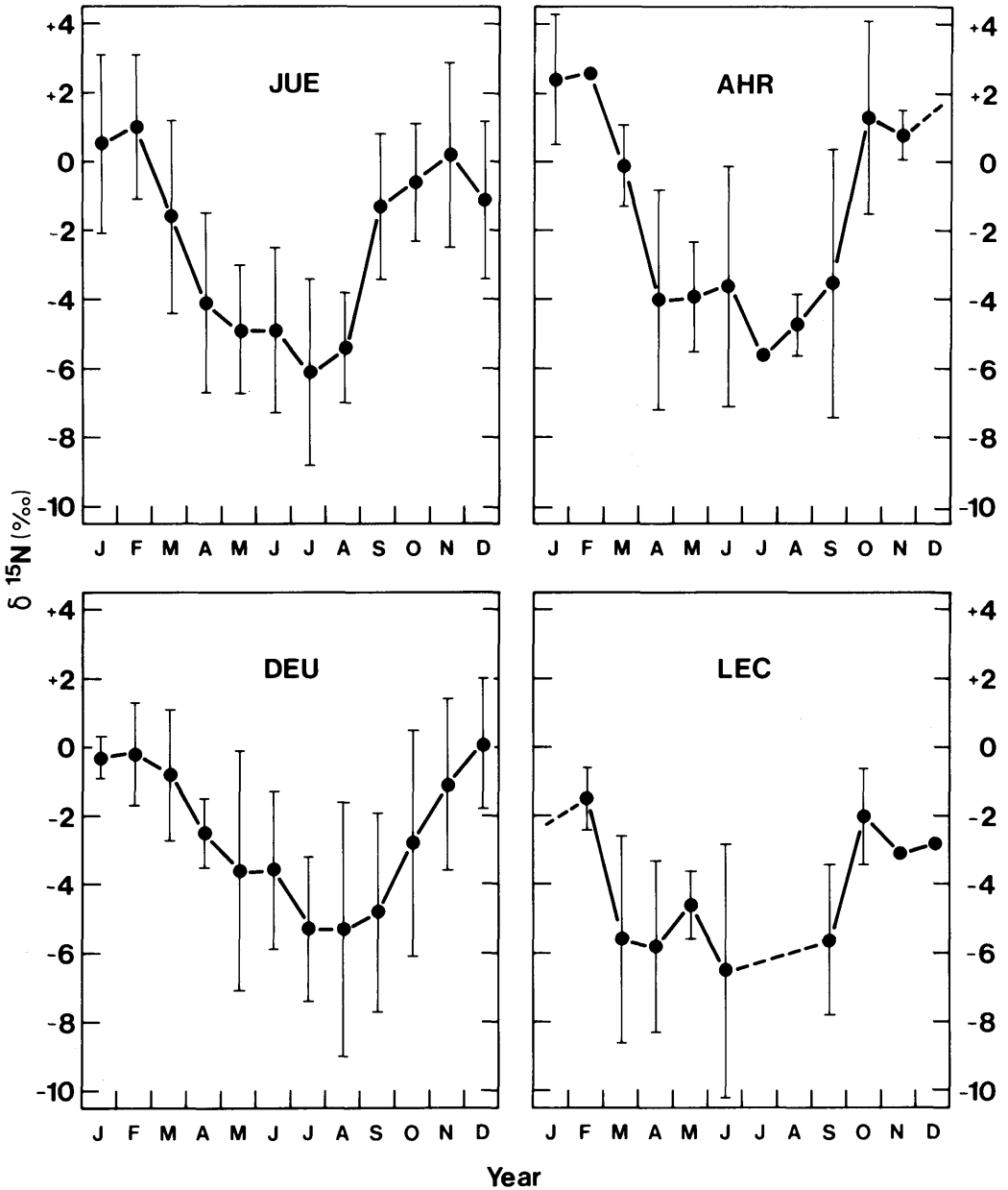


Fig. 1. Monthly $\delta^{15}\text{N}$ data (\pm S.D.) of nitrate in rain collected at Jülich (JUE; 1975/76 and 1979/84 data), Ahrensburg (AHR), Deuselbach (DEU) and Le Conquet (LEC).

Table 2. Seasonal data (\pm S.D.) of concentration and $\delta^{15}\text{N}$ of particulate nitrate (part. NO_3^-) and nitric acid vapour (HNO_3 vap.) collected at Jülich with the low-volume technique

	part. NO_3^- ($\mu\text{g N m}^{-3}$)	$\delta^{15}\text{N}(\text{NO}_3^-)$ (‰)	HNO_3 vap. ($\mu\text{g N m}^{-3}$)	$\delta^{15}\text{N}(\text{HNO}_3)$ (‰)	conc. (NO_3^-)/ conc. (HNO_3)
Spring	1.29 ± 0.59 (13) ^{a)}	$+5.5 \pm 2.7$ (9)	0.47 ± 0.24 (8)	-2.2 ± 0.5 (5)	3.4 ± 1.7 ^{b)}
Summer	0.93 ± 0.46 (14)	$+3.7 \pm 0.9$ (10)	0.46 ± 0.24 (8)	-3.0 ± 1.5 (2)	3.0 ± 1.4
Autumn	1.37 ± 0.60 (16)	$+6.8 \pm 2.9$ (14)	0.26 ± 0.10 (14)	-2.6 ± 1.1 (5)	5.7 ± 2.5
Winter	1.35 ± 1.06 (12)	$+9.2 \pm 2.0$ (10)	0.25 ± 0.17 (7)	-2.7 ± 1.0 (5)	6.2 ± 2.4

a) The number of measurements is given in parenthesis.

b) The molar $\text{NO}_3^-/\text{HNO}_3$ ratios were calculated from individual measurements.

The mean concentrations of NO_3^- in the high-volume experiment (Table 3) were significantly higher (confidence limit: $P < 0.01$) than those in the low-volume experiment (Table 2), with a greater difference of concentrations during summer than during winter. At first sight, this fact might be explained by a volatilization loss of NO_3^- in the low-volume experiment, particularly during the warmer summer months. A larger loss of NO_3^- during summer would also explain the higher HNO_3 concentrations and lower molar $\text{NO}_3^-/\text{HNO}_3$ ratio during summer (Table 2),

because volatilized NO_3^- would be collected as HNO_3 on the after-filters. The $\delta^{15}\text{N}$ data of NO_3^- , shown in Fig. 3, seem to support this NO_3^- loss. On average, $\delta^{15}\text{N}$ data found with the low-volume technique were about 1‰ higher than corresponding data (mean data for total NO_3^-) found with the high-volume technique. If NO_3^- loss has occurred, the heavier isotope will be enriched in the residual fraction on the filter media.

Another interpretation came from the measurements of Meixner et al. (1985), who have per-

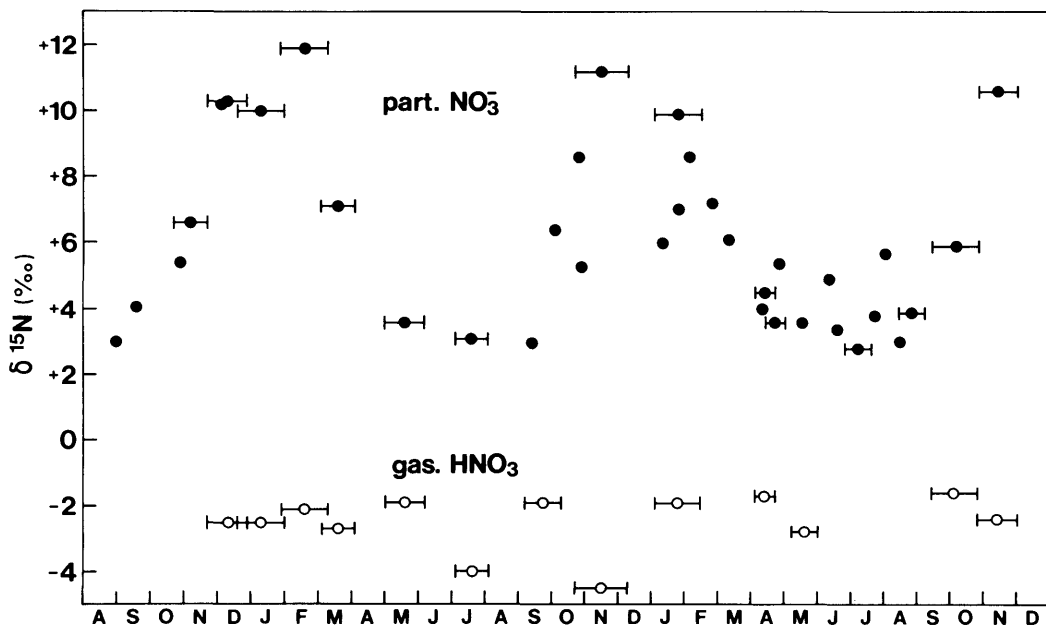


Fig. 2. $\delta^{15}\text{N}$ data of particulate nitrate (full dots) and nitric acid vapour (open dots) collected at Jülich with the low-volume technique. The bars represent the sampling times.

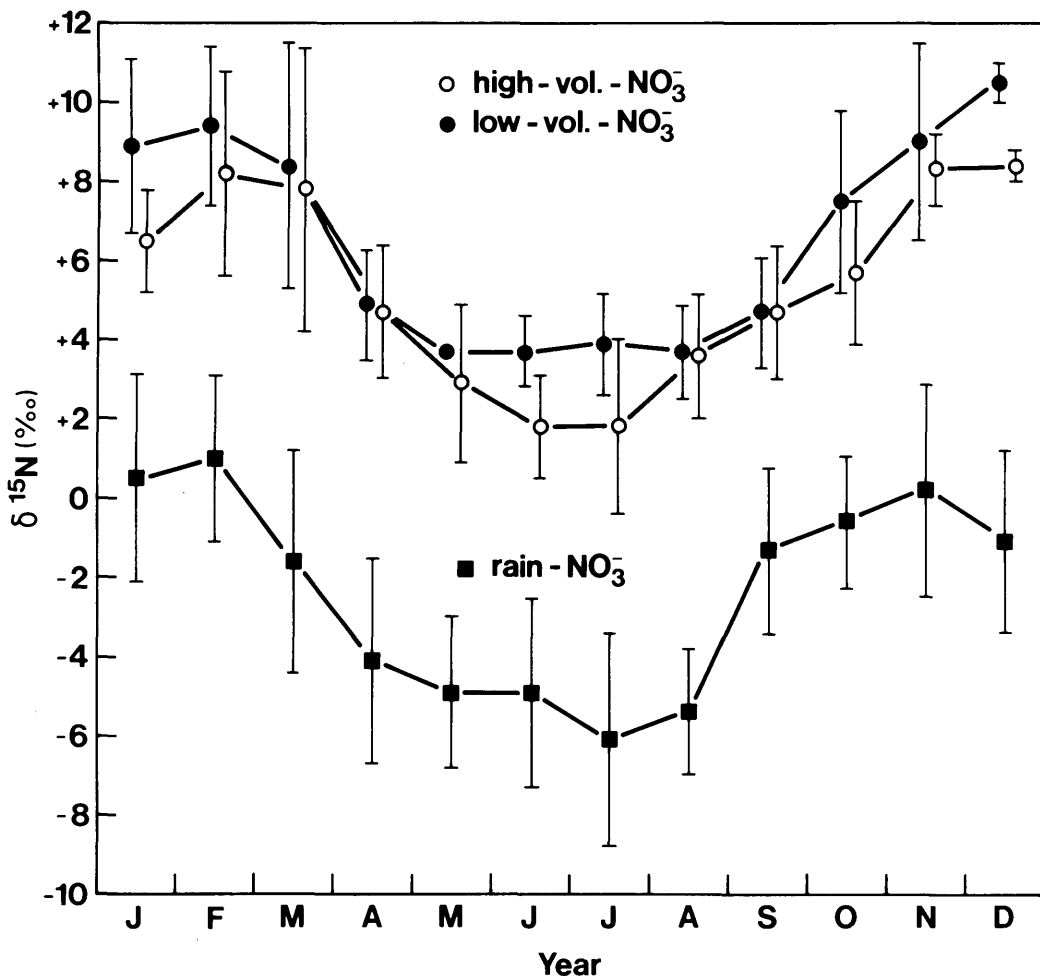


Fig. 3. Monthly $\delta^{15}\text{N}$ data (\pm S.D.) of rain (full squares) and particulate nitrate (high-volume: open dots; low-volume: full dots) collected at Jülich.

formed similar collections of NO_3^- and HNO_3 at Jülich from January 1982 to January 1984 with a total of 710 samples. In those measurements, a filter pack (diameter 90 mm) was also used. The filter media, however, differed from those used in this study. NO_3^- was collected on a PTFE prefilter. HNO_3 was collected on 3 following non-impregnated nylon filters. The sampling times ranged from 0.5 to 2 h instead of sometimes more than a month in the low-volume experiment of this study. The data of Meixner et al., taking standard deviation and inter-annual variation into account, are in the range of the data

found in the low-volume experiment of this study. Also, a seasonal shift in the molar $\text{NO}_3^-/\text{HNO}_3$ ratio from about 2 during summer to about 10 during winter is observed in the measurements of Meixner et al. (1985), which is larger than that found in the present study (Table 2).

Accidentally, the measurements of Meixner et al. (1985) overlap in their sampling period with the high-volume measurements of this study. Due to the short-time sampling of Meixner et al. (1985) the difference between extreme data (maximum and minimum) for NO_3^- is larger than in our high-volume measurements. Mean monthly

Table 3. Seasonal data ($\pm S.D.$) of concentration and $\delta^{15}N$ of fine ($<3.5 \mu m$) and coarse ($>3.5 \mu m$) particulate nitrate collected at Jülich and Deuselbach (DEU; only data for April to June) with the high-volume technique

	No. of measurements	Fine		Coarse		Total	
		part. NO_3^- ($\mu g N m^{-3}$)	$\delta^{15}N(NO_3^-)$ ($‰$)	part. NO_3^- ($\mu g N m^{-3}$)	$\delta^{15}N(NO_3^-)$ ($‰$)	part. NO_3^- ($\mu g N m^{-3}$)	$\delta^{15}N(NO_3^-)^{a)}$ ($‰$)
Spring	10	3.39 ± 1.76	$+6.9 \pm 4.6$	0.49 ± 0.29	$+2.1 \pm 4.2$	3.88 ± 2.04	$+6.3 \pm 4.5$
Spring (DEU)	14	0.80 ± 0.50	$+5.7 \pm 2.3$	0.28 ± 0.11	-0.5 ± 1.6	1.08 ± 0.58	$+4.0 \pm 1.8$
			$+6.2 \pm 3.4$		$+0.6 \pm 3.2$		$+4.9 \pm 3.4$
Summer	21	1.72 ± 1.00	$+4.3 \pm 1.9$	0.54 ± 0.24	-1.2 ± 2.4	2.26 ± 1.15	$+2.8 \pm 1.8$
Summer (DEU)	4	0.74 ± 0.43	$+3.7 \pm 2.1$	0.39 ± 0.18	-2.3 ± 2.2	1.13 ± 0.55	$+1.7 \pm 1.8$
			$+4.2 \pm 1.9$		-1.4 ± 2.4		$+2.7 \pm 1.8$
Autumn	32	1.87 ± 1.02	$+6.6 \pm 1.9$	0.50 ± 0.29	$+0.6 \pm 2.8$	2.37 ± 1.26	$+5.4 \pm 2.0$
Winter	17	1.92 ± 1.20	$+8.0 \pm 2.2$	0.30 ± 0.14	$+5.5 \pm 2.6$	2.22 ± 1.30	$+7.7 \pm 2.0$

^{a)} $\delta^{15}N$ data for total particulate nitrate were calculated from the data of fine and coarse particles weighted for their concentrations.

NO_3^- concentrations are, however, significantly lower ($P < 0.01$) than the data obtained from our measurements. Positive and negative artefacts in measurements of atmospheric particulate nitrate have been described by several authors (e.g., Appel et al., 1981). Teflon filters, as used in the study of Meixner et al. (1985), yield very low levels of artefact particulate nitrate; They can give, however, negative errors because of evaporation of NH_4NO_3 particles and reactions of particulate nitrate with strong acids on the filter media, liberating HNO_3 . Gelman A glass fiber filters, as used in the present study, tend to give positive errors because of simultaneous collection of nitric acid vapour and, in fact, Appel et al. (1981) have used these filters for collection of total inorganic nitrate (i.e., HNO_3 plus particulate nitrate). From these observations, it is concluded that our measurements of particulate nitrate using the high-volume technique are slightly high owing to the contribution of nitric acid vapour. This would also explain the lower $\delta^{15}N$ values (by 1 to 2‰) found for particulate nitrate in the high-volume as compared with the low-volume technique. These features should not have a significant effect, however, on the observed seasonal variation in the $\delta^{15}N$ values of the particulate nitrate.

4. Comparison of $\delta^{15}N$ data for nitrate species

The available information on $\delta^{15}N$ in rain and particulate nitrate is plotted in Fig. 4. It is apparent that all sites show similar ranges of $\delta^{15}N$ values, which indicate nitrate sources of similar composition and origin. In each case, however, $\delta^{15}N$ values of rain nitrate are lower than those of particulate nitrate.

Because of different $\delta^{15}N$ data for particulate and rain nitrate, Moore (1974) concluded that most of the particulate nitrate is from airborne soil and that rain nitrate originates directly from atmospheric NO or NO_2 . Also Heaton (1987) assumed that the bulk of nitrate in rain is not derived from particulate nitrate. On the other hand, it is assumed from chemical studies that nitrate is incorporated in rainwater mainly by capture of particulate nitrate and by absorption of gaseous nitric acid in cloud and raindrops (e.g., Altwicker, 1983). In addition, reactions of gaseous precursors in the dispersed phase may lead to formation of more nitrate, a process which should not be discussed here. At one of our stations in Deuselbach, Kins (1987) has found that the washout of particulate nitrate and gaseous precursors below cloud basis by rain-

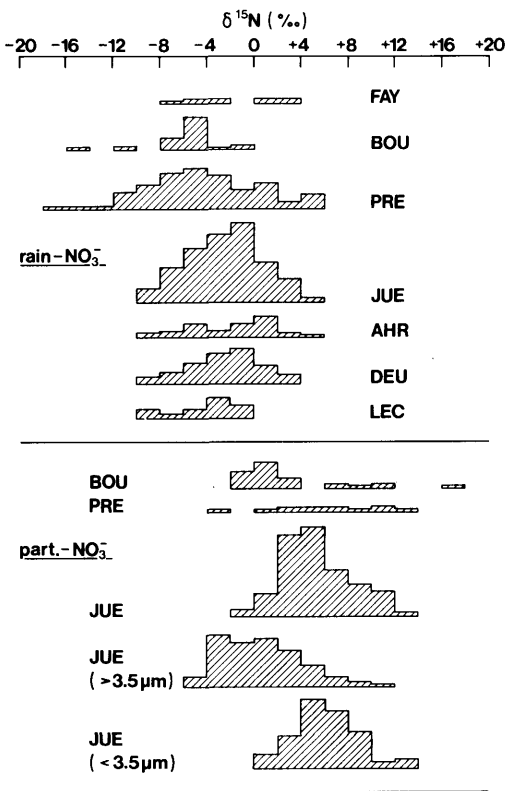


Fig. 4. Histograms of $\delta^{15}\text{N}$ data of rain and particulate nitrate from Fayetteville, Arkansas (FAY; Hoering, 1957), Boulder, Colorado (BOU; Moore, 1974, 1977), Pretoria, South Africa (PRE; Heaton and Collett, 1985), Jülich, Germany (JUE; Freyer, 1978a, and this work), Ahrensburg, Germany (AHR; this work), Deuselbach, Germany (DEU; this work) and Le Conquet, France (LEC; this work). $\delta^{15}\text{N}$ data of particulate nitrate from Jülich are given for the coarse ($>3.5\ \mu\text{m}$) and the fine fraction ($<3.5\ \mu\text{m}$) from the high-volume experiment of this work (both lower histograms) and for the weighted sum of data from both fractions with inclusion of the data set from the low-volume experiment of this work (upper histogram).

drops (below-cloud scavenging) could amount to up to 50% of total nitrate found in rain water; the washout of gaseous nitric acid alone could be up to 50% of that of particulate nitrate. Due to the similar seasonal variation of $\delta^{15}\text{N}$ values found in both particulate and rain nitrate, it is expected that the bulk of rain nitrate stems from particulate nitrate, which could not be of airborne soil origin. The isotope fractionation

between particulate and rain nitrate, however, has not been fully resolved. For nitric acid, nearly constant $\delta^{15}\text{N}$ values in the range of $-(2-3)\text{‰}$ have been found in this study. Therefore, $\delta^{15}\text{N}$ values of a mixture resulting from capture of particulate nitrate and from additional absorption of nitric acid by cloud and raindrops would be lower than those of particulate nitrate alone. Kinetic effects may further lower the $\delta^{15}\text{N}$ values of the nitrate species in rainwater, which could occur during absorption of gaseous nitric acid and other gaseous precursors, but scarcely during capture of particulate nitrate.

Another aspect results from the $\delta^{15}\text{N}$ data of the coarse and fine fraction of particulate nitrate found in our high-volume experiment. Table 3 and Fig. 4 show lower $\delta^{15}\text{N}$ values for the coarser particulate nitrate than for the bulk of particulate nitrate, which is in the fine fraction, indicating populations of particulate nitrate of different origin (see Subsection 5.4). The $\delta^{15}\text{N}$ values of the coarse nitrate fraction correspond closer to those of rain nitrate and it has been found that atmospheric concentrations of coarse, especially highly soluble particles, showed large decreases during rainfall (Tanaka et al., 1980). A dependence of $\delta^{15}\text{N}$ values on the size of atmospheric nitrate particles would partly explain also the observations of Heaton (1987), who has found a systematic ^{15}N enrichment combined with a decline in concentration for rain nitrate during the course of rain events. Coarser particles are removed more efficiently than fine particles by cloud and raindrops in the rainout and washout process. It is therefore expected that the fraction of larger particles becomes smaller in favour of fine particles during the course of rain events with a decrease in rain-nitrate concentrations and an increase in their $\delta^{15}\text{N}$ values. This effect could be amplified by the simultaneous washout of nitric acid vapour (with low $\delta^{15}\text{N}$ values of $-(2-3)\text{‰}$), which also shows a decline in atmospheric concentrations during rainfall (Kins, 1987).

The chemical form of particulate nitrate is of further importance. Nitrate in the coarse fraction is mainly associated with Na^+ or Mg^{2+} ions, while nitrate in the fine fraction consists mainly of volatile NH_4NO_3 (Harrison and Pio, 1983). Evaporation of part of the NH_4NO_3 due to a shift in the dissociation equilibrium would prefer

the lighter ^{14}N isotope leading to a ^{15}N enrichment in the residual fraction of sampled nitrate. Also, nitrogen isotope exchange effects between oxidized atmospheric nitrogen species may occur, which enrich the ^{15}N isotope in the more oxidized form (see Subsections 5.3 and 5.4). If heterogeneous exchanges are involved, only fine particles have to be considered. Higher $\delta^{15}\text{N}$ values for particulate nitrate by artefact caused by isotopic exchange or evaporation loss during sampling on the filter media cannot be excluded. However, the similar seasonal amplitude in the $\delta^{15}\text{N}$ data for rain and particulate nitrate as well as the similar range of data by active sampling of this study and by passive sampling of Heaton (1987) of dry deposited nitrate, contradicts this possibility.

5. Possible interpretation of the seasonal $\delta^{15}\text{N}$ effect

5.1. Correlation of data with climate parameters

The annual march of climate parameters at Jülich (suboceanic, cool-temperate climate) and at Pretoria (dry-winter, warm-temperate subtropical climate) is illustrated in Fig. 5. Without regard to higher temperature and solar radiation data, and also higher duration of sunshine and lower cloudiness at Pretoria in comparison to Jülich, the main climatic difference between both sites is the annual march of rainfall. Whereas rainfall at Jülich shows no seasonality, rainfall at Pretoria occurs mainly in the summer half-year from October to March. The annual pattern of cloudiness is comparable to that of rainfall at both sites. The sunshine duration at Jülich follows the annual march of solar radiation. At Pretoria, the rainfall and cloudiness pattern is similar to the annual march of solar radiation, from which a small variation in the monthly duration of sunshine results. Temperatures at both sites are self-evidently correlated with solar radiation data.

$\delta^{15}\text{N}$ values and concentrations in nitrate species found at Jülich and Pretoria were checked for correlation with each other and with climate parameters. The following main features were obtained. A negative correlation between $\delta^{15}\text{N}$ data and nitrate concentrations in rain is observed for the Jülich data ($r = -0.76$; confidence limit

$P < 0.005$), which expresses the relation between lower $\delta^{15}\text{N}$ data and higher nitrate concentrations during summer and vice-versa during winter. By contrast, no correlation between the mean data is observed for Pretoria ($r = +0.28$), though a negative correlation is expected from observations of Heaton (1987) at Pretoria during the course of single rain events (see Section 4). $\delta^{15}\text{N}$ and monthly rainfall data correlate highly for Pretoria ($r = -0.76$; $P < 0.005$), and it has been found that rainfall intensity of single events influences rain nitrate concentrations and their $\delta^{15}\text{N}$ data systematically due to the degree of removal of rain-nitrate forming precursors (Heaton, 1987). However, these effects must not have an influence at Jülich, where mean $\delta^{15}\text{N}$ and monthly rainfall data do not correlate at all ($r = +0.04$). Significant negative correlations for both sites are observed between $\delta^{15}\text{N}$ data and both temperatures and solar radiation data; the regressions are given below. Because of correlations between $\delta^{15}\text{N}$ data in particulate nitrate and rain nitrate at Jülich ($r = +0.87$; $P < 0.001$), $\delta^{15}\text{N}$ data in particulate nitrate also correlate significantly with temperatures and solar radiation data. No correlations are observed between $\delta^{15}\text{N}$ data and concentrations of particulate nitrate ($r = +0.48$ and $+0.10$ for the low- and high-volume experiment, respectively).

The regression of $\delta^{15}\text{N}$ data for rain and particulate nitrate on temperature (temperature in $^{\circ}\text{C}$) and solar radiation (radiation in $\text{kW m}^{-2} \text{day}^{-1}$) are represented by the following equations:

$$\begin{aligned} \text{Jülich data, particulate } \text{NO}_3^- : \\ \delta^{15}\text{N} = (9.70 \pm 0.52) - (0.38 \pm 0.05) \text{ temp.} \\ (r = -0.87; P < 0.001) \end{aligned}$$

$$\begin{aligned} \delta^{15}\text{N} = (9.86 \pm 0.45) - (0.024 \pm 0.003) \text{ rad.} \\ (r = -0.91; P < 0.001) \end{aligned}$$

$$\begin{aligned} \text{Jülich data, rain } \text{NO}_3^- : \\ \delta^{15}\text{N} = (1.39 \pm 0.91) - (0.35 \pm 0.08) \text{ temp.} \\ (r = -0.69; P < 0.01) \end{aligned}$$

$$\begin{aligned} \delta^{15}\text{N} = (1.95 \pm 0.62) - (0.026 \pm 0.003) \text{ rad.} \\ (r = -0.86; P < 0.001) \end{aligned}$$

$$\begin{aligned} \text{Pretoria data, rain } \text{NO}_3^- : \\ \delta^{15}\text{N} = (8.77 \pm 4.34) - (0.69 \pm 0.24) \text{ temp.} \\ (r = -0.69; P < 0.01) \end{aligned}$$

$$\begin{aligned} \delta^{15}\text{N} = (10.34 \pm 5.57) - (0.039 \pm 0.016) \text{ rad.} \\ (r = -0.62; P < 0.05). \end{aligned}$$

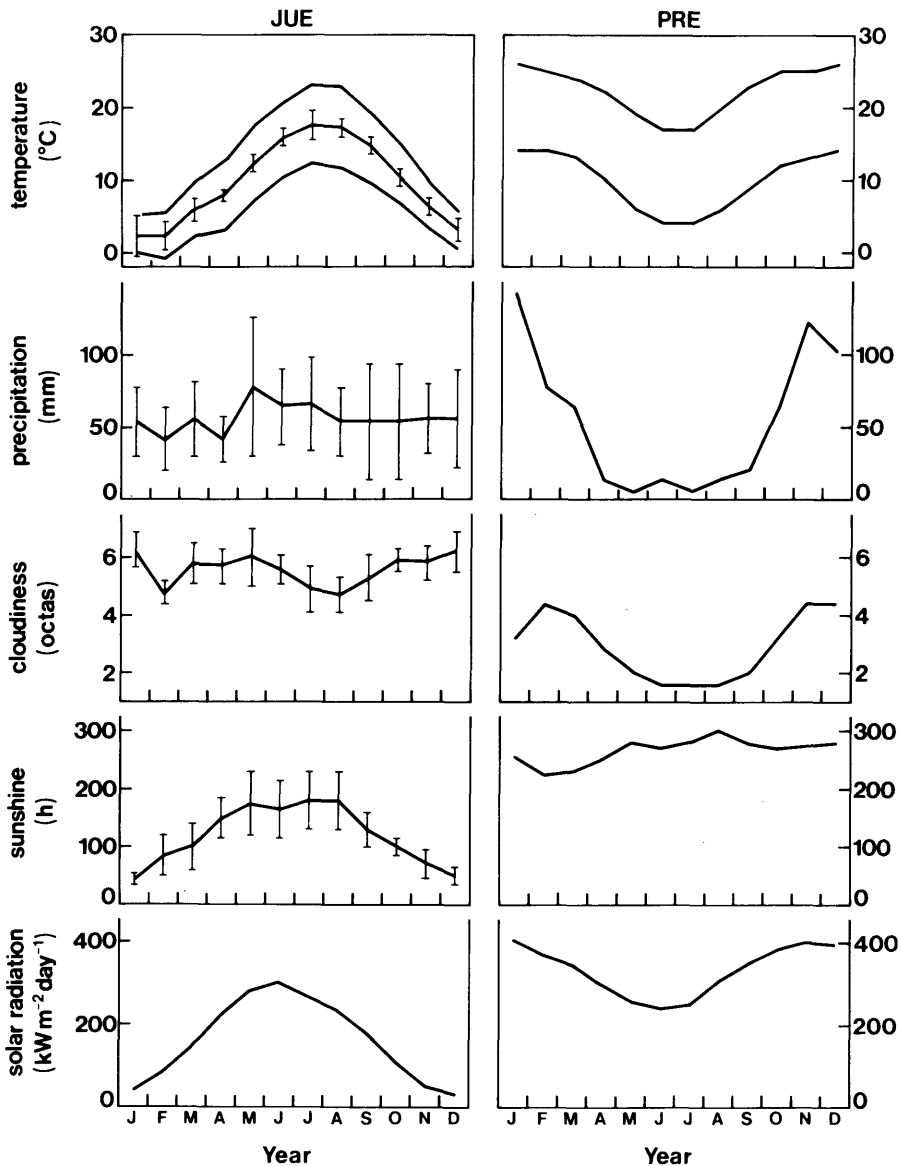


Fig. 5. Annual march of monthly data (\pm S.D.) for temperature (incl. mean maximum and minimum temperature), amount of rainfall, cloudiness, hours of sunshine and solar radiation during the years 1975 to 1984 at Jülich and corresponding data at Pretoria. Detailed climate parameters (except for solar radiation data) were available for Jülich (1975–1979 data: Bergs et al., 1980; 1980–1984 data: Geiss and Polster, personal communication, 1985). For the solar radiation data at Jülich ($50^{\circ}55' \text{N}$, $6^{\circ}25' \text{E}$), the mean from two more distant stations of similar latitude, De Bilt, The Netherlands ($52^{\circ}06' \text{N}$, $5^{\circ}11' \text{E}$) and Uccle-Brussels, Belgium ($50^{\circ}48' \text{N}$, $4^{\circ}21' \text{E}$) were taken (Arléry, 1970). For Pretoria, only 5-year averages of rainfall data for the period 1980–1984 were on hand (Heaton and Collett, 1985). For mean monthly (maximum and minimum) temperatures and hours of sunshine at Pretoria ($25^{\circ}45' \text{S}$, $28^{\circ}12' \text{E}$), 30-year and 10-year averages, respectively, from Germiston, South Africa ($26^{\circ}15' \text{S}$, $28^{\circ}09' \text{E}$) a nearby station, were used (Schulze, 1972). The solar radiation data used were 11-year averages from measurements at Pretoria (Schulze, 1972).

$\delta^{15}\text{N}$ data found at Jülich correlate at the highest confidence limit first of all with solar radiation data, then with temperature. The confidence limit for correlation of Pretoria data is lower, but the correlations are significant. The regression coefficients, $\delta^{15}\text{N}/\text{temp.}$ and $\delta^{15}\text{N}/\text{rad.}$, however, differ for both sites.

5.2. Anthropogenic and natural NO_x sources

In view of correlations of $\delta^{15}\text{N}$ data in atmospheric nitrate species with temperatures and solar radiation data, the seasonal $\delta^{15}\text{N}$ effect could possibly be interpreted by temperature-dependent or photochemical mechanisms. Before considering these mechanisms, some aspects of $\delta^{15}\text{N}$ data for the gaseous precursors of nitrate should be discussed first.

Anthropogenic nitric oxides produced by combustion processes originate from oxidation of atmospheric N_2 ($\delta^{15}\text{N} = 0\text{‰}$) for mobile sources and from fuel nitrogen more for stationary sources ($\delta^{15}\text{N}$ for total nitrogen in coal: -3 to $+7\text{‰}$ (range), $+2 \pm 2\text{‰}$ (mean); in crude oils: -2 to $+13\text{‰}$ (range), $+3 \pm 4\text{‰}$ (mean); e.g., Wlotzka, 1972; Drechsler and Stiehl, 1977; Rigby and Batts, 1986). Hoering (1957) reported $\delta^{15}\text{N}$ data for spark-formed NO_x of $+1.4$ and -0.5‰ . Moore (1977) and Freyer (1978a) gave values of $+3.7\text{‰}$ and -1.8‰ , respectively, for nitric oxides from automobile exhausts. Heaton (1987) found $+5.2\text{‰}$ for NO_x from a coal-fired power station and -1.6‰ for NO_x from a diesel engine under load. More negative data for NO_x from idling diesel and petrol cars (with emissions being more than one order of magnitude lower than those from an engine under load) were reported by Heaton (1987), which amounted $-(13.2 - 11.5)\text{‰}$ and -7.3‰ for diesel and petrol cars, respectively. More detailed data within the same range with possible interpretations were given recently by Heaton (1990). Only of marginal importance to the atmospheric NO_x burden are emissions from stacks of nitric acid plants, which can show extremely low $\delta^{15}\text{N}$ data of -150‰ due to isotope exchange reactions (Heaton, 1987). Neglecting the data for the minor emissions, it is assumed for the following discussions that the overall $\delta^{15}\text{N}$ value for emitted anthropogenic NO_x from combustion is close to 0‰ .

$\delta^{15}\text{N}$ data for mineralized soil-ammonium and

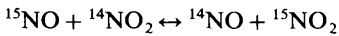
-nitrate sampled in the Jülich area have been found in the range of -7 to -1‰ and -10 to $+2\text{‰}$, respectively (Freyer, 1978a, b). $\delta^{15}\text{N}$ data for fertilizer-ammonium and -nitrate cover a similar range from -5 to $+4\text{‰}$ and -1 to $+7\text{‰}$, respectively (Freyer and Aly, 1974; Shearer et al., 1974). Nitric oxides emitted from soils (Slemr and Seiler, 1984; Johansson, 1984; Williams et al., 1987) occur as intermediates in the nitrification reaction of ammonia to nitrate or denitrification reaction of nitrate to molecular nitrogen and nitrous oxide. During both reactions, large kinetic isotope effects in the order of 1.02 are involved (Freyer, 1978b; Létolle, 1980; Medina and Schmidt, 1982; sometimes 1.03 to 1.035, Mariotti et al., 1981), which means that the first formed products are depleted in ^{15}N by -20‰ compared to the initial material. If it is assumed that the intermediate nitric oxides formed during these processes are depleted in ^{15}N too, then they should differ from the $\delta^{15}\text{N}$ data of the anthropogenic nitric oxides. Measurements by Moore (1977), who has found $\delta^{15}\text{N} = +3.7\text{‰}$ for NO_x from automobile exhaust and $\delta^{15}\text{N} = -9.3 \pm 3.5\text{‰}$ for NO_2 in clear air, would confirm this difference.

Gravenhorst (1985) has estimated the annual natural NO_x emissions (emissions from soils derived from fertilizers were considered in this case as natural) for the Federal Republic of Germany (FRG) to be in the range of $(2 - 22) \cdot 10^3 \text{ t N yr}^{-1}$ emitted from unfertilized soils and in the range of $(0.7 - 26) \cdot 10^3$ and $13 \cdot 10^3 \text{ t N yr}^{-1}$ emitted from mineral and organic nitrogen fertilized soils, respectively. The anthropogenic NO_x emissions from burning of fossil fuels for the FRG amounted to $940 \cdot 10^3 \text{ t N yr}^{-1}$ in 1982 (Beilke, 1984). Using these emission data and assuming for a rough estimate that natural and anthropogenic nitric oxides have $\delta^{15}\text{N}$ data of about -20‰ and 0‰ , respectively, and that natural NO_x is emitted only during spring and summer, the spring and summer $\delta^{15}\text{N}$ data for NO_x would be lower than the winter data (i.e., anthropogenic NO_x with $\delta^{15}\text{N} = 0$) by maximally -2.3‰ . According to this result, variable natural and anthropogenic NO_x sources during the seasons could potentially contribute to the observed seasonal variation in $\delta^{15}\text{N}$ of atmospheric nitrate species. On the other hand, the very similar range of $\delta^{15}\text{N}$ values of

rain nitrate from different areas and environments (with expected different anthropogenic/natural NO_x emissions) in Europe, the USA and Africa is inconsistent with a significant difference between $\delta^{15}\text{N}$ values of natural and anthropogenic NO_x . Proof of such a difference must await actual measurements.

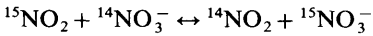
5.3. Isotope exchange equilibria between oxinitrogen species

An interpretation of the seasonal $\delta^{15}\text{N}$ effect due to temperature variations could be based on the fact that isotope exchange equilibria between gaseous NO and NO_2 and NO_3^- ions in aqueous solution exist with enrichment of the heavier nitrogen isotope in the more oxidized form. The equilibrium constants K are temperature-dependent and amount according to Begun and Fletcher (1960):



$$K_{25^\circ\text{C}} = \frac{^{15}\text{NO}_2/^{14}\text{NO}_2}{^{15}\text{NO}/^{14}\text{NO}} = 1.040$$

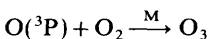
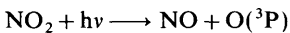
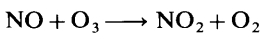
$$K_{0^\circ\text{C}} = 1.046;$$



$$K_{25^\circ\text{C}} = \frac{^{15}\text{NO}_3^-/^{14}\text{NO}_3^-}{^{15}\text{NO}_2/^{14}\text{NO}_2} = 1.039$$

$$K_{0^\circ\text{C}} = 1.045.$$

Our own preliminary isotope measurements on atmospheric NO_2 show that the $\delta^{15}\text{N}$ data (mean range: $\delta^{15}\text{N} = -2$ to $+2$ ‰) depend on the NO_2/NO ratio (higher $\delta^{15}\text{N}$ data for lower NO_2/NO ratios and vice-versa) which would confirm isotope exchange equilibria. Besides, these processes between NO and NO_2 in the atmosphere are most probable because both species are close to equilibrium during the day through the oxidation of NO with O_3 and the photolysis of NO_2 to NO (Leighton relationship; Leighton, 1961):



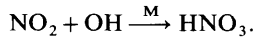
Another exchange in the gas phase might occur

between NO_2 and N_2O_5 (see Subsection 5.4) in a pathway, by which finally particulate nitrate, especially in the fine fraction is formed. Observed $\delta^{15}\text{N}$ data for atmospheric NO_2 (range: -15 to -5 ‰) and particulate NO_3^- (range: -2 to $+18$ ‰) from the measurements of Moore (1977) and this study indicate that NO_3^- is enriched in ^{15}N with respect to NO_2 , which is consistent with isotope exchange reactions in the atmosphere between oxinitrogen species.

5.4. Pathways of formation for atmospheric nitrate species

The seasonal $\delta^{15}\text{N}$ effect might also reflect seasonal differences in the chemical reactions by which nitrate ions are formed (Calvert et al., 1985). The dominance of these reactions depends as much as on temperature as on solar radiation and these reactions may exhibit different isotope effects.

Nitric acid vapour in the atmosphere is mainly formed by oxidation of NO_2 with OH radicals:



The magnitude of kinetic isotope fractionation that might occur during this reaction is roughly estimated by the following equation:

$$\frac{k_{15}}{k_{14}} = \left(\frac{\mu_{14}}{\mu_{15}} \right)^{1/2},$$

where k_{15} and k_{14} are the rate constants of the isotopically labelled NO_2 species, and μ_{14} and μ_{15} are the reduced masses in the transition complex defined as:

$$1/\mu = 1/m_{\text{NO}_2} + 1/m_{\text{OH}}.$$

With the masses of the reactants, an effect in the order of

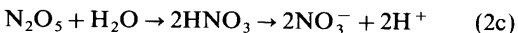
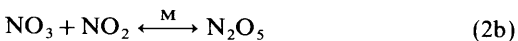
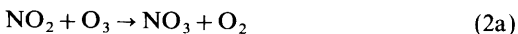
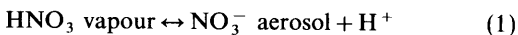
$$\frac{k_{15}}{k_{14}} = \left(\frac{46 \cdot 17 \cdot 47 + 17}{46 + 17 \cdot 47 \cdot 17} \right)^{1/2} = 0.9971$$

is expected, which means that the isotopic value for the nitric acid formed is $\delta^{15}\text{N}(\text{HNO}_3) \approx -3$ ‰, assuming $\delta^{15}\text{N}(\text{NO}_2) = 0$ ‰ for NO_2 . In fact, $\delta^{15}\text{N}(\text{HNO}_3) \approx -2.5$ ‰ was found for nitric acid vapour in the low-volume experiment of this study. This agreement may be entirely

fortuitous, especially when considering the uncertainty in assuming $\delta^{15}\text{N}(\text{NO}_2) = 0$.

The formation of nitric acid vapour from dissociation of the fine mode NH_4NO_3 aerosol is furthermore neglected. This aerosol exists in equilibrium with ammonia and nitric acid and is formed mainly by another pathway (see below). The dissociation constant for the aerosol is extremely temperature-sensitive and the equilibrium mass concentration in the gas phase of HNO_3 increases from about 0.25 (at 0°) to about $25 \mu\text{g HNO}_3 \text{ m}^{-3}$ (at 30°C), by two-orders of magnitude at relative humidities $< 60\%$ (Stelson and Seinfeld, 1982). Provided that an NH_4NO_3 dissociation contributes to the observed increased HNO_3 concentrations during the warmer summer months, then a possible seasonal effect for $\delta^{15}\text{N}$ in HNO_3 vapour (similar to that in the NO_3^- aerosol) could be masked because the NH_4NO_3 aerosol is enriched in ^{15}N .

The formation mechanism for particulate nitrate in the atmosphere is very uncertain and only two possible paths should be discussed. One includes the direct absorption of HNO_3 vapour into an aerosol droplet giving particulate nitrate mostly in the coarse fraction (Wolff, 1984). The other pathway may result from oxidation of NO_2 with O_3 to NO_3 , which can react with NO_2 to form N_2O_5 . This N_2O_5 may thermally decompose. It may also react heterogeneously with water surfaces forming nitrate particles, such as NH_4NO_3 (Harrison and Pio, 1983), mostly in the fine mode.



Assuming no isotope fractionation for absorption of HNO_3 vapour ($\delta^{15}\text{N}(\text{NO}_3^-)$ from (1)) $\approx -3\text{‰}$, it is expected due to the positive $\delta^{15}\text{N}$ data for total particulate nitrate that the isotope fraction of the reaction sequence (2a–c) is positive. This positive fraction (with respect to assumed $\delta^{15}\text{N} \approx 0$ for initial NO_2) does not reflect kinetic effects, because kinetic fractionation resulting from uni-directional reactions is

negative or zero. These effects could be explained, however, by an equilibrium fractionation associated with the exchange reaction (2b). NO_2 , NO_3 and N_2O_5 are in thermal equilibrium at night (Russell et al., 1984) and the isotope exchange between these species is very fast (half-life 1–2 min; Amell and Daniels, 1952).

The reactions discussed could account for the $\delta^{15}\text{N}$ values in particulate nitrate with respect to the size effect as well as to the seasonal effect. A seasonal variation of the molar $\text{NO}_3^-/\text{HNO}_3$ ratio from about 3 (for summer) to about 6 (for winter) was observed in the low-volume experiment of this study. Obviously, the formation of particulate nitrate from absorption of HNO_3 vapour is larger in summer than in winter and a shift in the $\delta^{15}\text{N}$ data from higher values in winter to lower values in summer would result, which is actually observed.

The importance of the reaction sequence (2a–c) for winter nitrate generation (cooler temperatures favour the storage of the N_2O_5 product) and the higher contribution of reaction (1) for summer nitrate generation (higher solar radiation gives higher OH-concentrations) has been pointed out by Calvert et al. (1985). These different formation mechanisms may partly explain the seasonal variation of $\delta^{15}\text{N}$ data in particulate nitrate; another part could result from a temperature dependence of the exchange reaction (2b). Thus, seasonal variations in both solar radiation and temperature could be responsible for the seasonal $\delta^{15}\text{N}$ effect.

6. Conclusions

Nitrate in rain as well as atmospheric particulate nitrate show seasonal variations in their $\delta^{15}\text{N}$ data with the lowest values being found in summer, though their absolute data differ, a fact, which has not been fully resolved. For nitric acid vapour, which on the other hand exhibits nearly constant $\delta^{15}\text{N}$ data, a possible seasonal effect could be masked due to dissociation of the NH_4NO_3 aerosol, especially during the warmer summer months. Three effects were discussed which could partly contribute to the observed seasonal variations: (1) variable anthropogenic and natural NO_x sources during the seasons;

(2) temperature-dependent isotope exchange equilibria between atmospheric oxinitrogen species; (3) effects due to seasonal variations of formation mechanisms for particulate nitrate.

Due the similarity of $\delta^{15}\text{N}$ data for atmospheric nitrate species in general, in different environments, a significant difference between nitrogen isotope data for anthropogenic and natural NO_x can be excluded. Because of seasonal variations in the molar $\text{NO}_3^-/\text{HNO}_3$ ratio and correlations of $\delta^{15}\text{N}$ data for particulate nitrate with temperature and solar radiation, variations of formation mechanisms (which depend on temperature and solar radiation) for particulate nitrate associated with temperature dependent isotope exchange equilibria are favoured for explanation of the seasonal $\delta^{15}\text{N}$ effect in nitrate species. This explanation would also require seasonal $\delta^{15}\text{N}$ variations in NO_x due to the assumption of isotope exchange equilibria.

The significance of these conclusions has to be studied by further measurements. These measurements have to include seasonal $\delta^{15}\text{N}$ data for NO_x , $\delta^{15}\text{N}$ data for NO_x from different sources, detailed studies of the size-dependent $\delta^{15}\text{N}$ effect

in particulate nitrate and determinations of isotope effects for reactions in the atmospheric nitrogen cycle.

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