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Potential canopy influences on the isotopic composition of nitrogen and sulphur in atmospheric deposition

Abstract Isotopic studies of nitrogen and sulphur inputs to plant/soil systems commonly rely on limited published data for the $^{15}N/^{14}N$ and $^{34}S/^{32}S$ ratios of nitrate, ammonium and sulphate in rainfall. For systems with well-developed plant canopies, however, inputs of these ions from dry deposition or particulates may be more important than rainfall. The manner in which isotopic fractionation between ions and gases may lead to dry deposition and particulates having $^{15}N/^{14}N$ or $^{34}S/^{32}S$ ratios different from those of rainfall is considered. Data for rainfall and throughfall in coniferous plantations are then discussed, and suggest that: (1) in line with expectations, nitrate washed from the canopy has $^{15}N/^{14}N$ ratios higher than those in rainfall; (2) the $^{15}N/^{14}N$ ratios of ammonium washed from the canopy are variable, with high ratios being found for canopies of higher pH in conditions of elevated ambient ammonia gas concentrations; and (3) in accord with expectations and previous work, $^{34}S/^{32}S$ ratios of sulphate washed from the canopy are not substantially different from those in rainfall. The study suggests that if atmospheric inputs are relevant to isotopic studies of the sources of nitrogen for canopied systems, then confident interpretation will require analysis of these inputs.

Key words Nitrogen sulphur isotopes · $^{15}N/^{14}N$ $^{34}S/^{32}S$ ratios · Atmosphere · Trees

Introduction

Isotopic data for atmospherically-derived nitrogen and sulphur are now being increasingly used in assessing the sources of inputs to a wide variety of soil/plant environments (Vitousek et al. 1989; Krouse et al. 1991; Van Stempvoort et al. 1991; Abbadie et al. 1992; Nriagu and Gooschenko 1992; Evans and Ehleringer 1993; Garten 1993; Durka et al. 1994; Gebauer et al. 1994; Nadelhoffer and Fry 1994; Poulson et al. 1995). In many cases these studies make assumptions as to the isotopic composition of atmospheric inputs based on published analyses from other areas. For nitrogen isotopes this may be especially problematic, because data for atmospherically derived nitrate and ammonium are relatively scarce and show a wide range in $\delta^{15}N$ values (Freyer 1978, 1991; Heaton 1987). These data, moreover, largely relate to rainfall, from which many authors have assumed that the total atmospheric inputs of nitrate and ammonium have negative $\delta^{15}N$ values. Where plant canopies are present, however, the interception of particulates or cloud droplets, and dry deposition of gases, may constitute a significant additional source of N – possibly greater than that from rainfall alone (Fowler et al. 1989; Hanson and Lindberg 1991). These additions to the canopy are dissolved in rainwater and washed down as "throughfall" to the below-canopy environment; but, apart from one data set (Garten 1992), no attempt has been made to assess their probable $^{15}N/^{14}N$ composition. While data from one study suggested that the canopy had little influence on the $\delta^{34}S$ value of sulphate in throughfall (Van Stempvoort et al. 1991), the general use of published data for the $\delta^{34}S$ values of rainfall must also be assessed.

It is acknowledged that biological processes relating to the absorption or emission of gases at leaf surfaces may have an effect on the isotopic composition of ions washed off the canopy in throughfall (Hanson and Lindberg 1991; Gebauer et al. 1994; Nommik et al. 1994). In interpreting isotopic comparisons of throughfall versus rainfall for natural canopies, however, the possible influences of these biologic processes is difficult to predict. They are therefore not considered here. Instead we examine how purely atmospheric influences on isotopic fractionation may lead to likely differences be-

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tween the isotopic compositions of material deposited on canopies compared to those of rainfall. Data for a small number of rainfall and throughfall samples are then examined in this light.

Materials and methods

Experiments simulating dry deposition

Quartz filter papers loaded with either sulphuric acid (0.1 mmol), ammonium sulphate (0.15 mmol, initial $\delta^{15}N = +2.7‰$), or ammonium nitrate (0.15 mmol, initial $\delta^{15}N = -0.1‰$), were allowed to dry (25°C, 45% humidity) and then exposed for different times to NH_3 and HNO_3 gases. Three experiments were conducted:

1. *Experiment 1a* Filters with sulphuric acid exposed in a polyethylene glove bag to an atmosphere of laboratory air + *c.* 1% ammonia gas (initial $\delta^{15}N = -5.0‰$), with the final gas/salt phase distribution of N (total mass of N as NH_3 divided by total mass of N as NH_4^+) being *c.* 4/1
2. *Experiment 1b* Filters with ammonium sulphate exposed to an atmosphere of laboratory air + *c.* 2% ammonia gas (initial $d^{15}N = -5.0‰$), with the final gas/salt phase distribution of N being *c.* 10/1
3. *Experiment 2* Filters with ammonium nitrate exposed in a glass Winchester bottle to atmospheres of dry N_2 + *c.* 1–2% nitric acid vapour, with the final gas/salt phase distribution of NO_3-N being between *c.* 1.5:1 and 10:1, and with the HNO_3 vapour being sampled for analysis after each exposure (separate experiments for each exposure time)

Collection of rainfall and throughfall

Rainfall and throughfall samples were collected at three coniferous plantations near the village of West Witton, in lower Wensleydale, Yorkshire, England (54°13′N, 01°54′W). Site and collection details are summarised in Table 1. Groups of collectors were placed within a plantation and in open ground less than 100 m away. Samples were recovered weekly and represented throughfall and rainfall, respectively, collected over the same time interval. Samples visibly contaminated by bird droppings were discarded, and most samples

were also screened on the basis of phosphate content. During one collection interval at Witton Fell, throughfall samples were also collected from a separate part of the plantation which had been subjected to fumigation by ammonia gas released from a cylinder sited upwind. For all samples the contents of different groups of collectors were combined to provide two or three separate samples.

Analysis and notation

Rainfall and throughfall samples were stored at ≤ 5°C prior to acidification and concentration by rotary evaporation. Ammonium and nitrate were recovered by distillation with MgO and Devarda's alloy into H_2SO_4, and the $(NH_4)_2SO_4$ dried and converted to N_2 by combustion with CuO. Sulphate was precipitated with $BaCl_2$, and the $BaSO_4$ converted to SO_2 by combustion with Cu_2O. Isotopic analysis of the gases were performed in VG SIRA II and Optima mass spectrometers, with the results being reported as $\delta^{15}N$ and $\delta^{34}S$ values in per mil (‰), where:

$$\delta(‰) = [(R_{sample}/R_{standard}) - 1] \cdot 1000$$

For $\delta^{15}N$ or $\delta^{34}S$, $R = {}^{15}N/{}^{14}N$ or ${}^{34}S/{}^{32}S$, and the standard is atmospheric dinitrogen or CDT, respectively. Analyses of samples of rainfall and throughfall from separate groups of collectors yielded δ values typically within ± 0.3‰ (exception below).

For simplicity nitrate, ammonium and sulphate – whether as solids or in solution – will be referred to as "ions". Discussion of the effects of isotopic fractionation between ions and gases will be referred to in terms of the isotopic enrichment factor, ε (Fritz and Fontes 1980; Heaton 1986), where:

$$\varepsilon_{ion\text{-}gas}(‰) = [(R_{ion}/R_{gas}) - 1] \cdot 1000 \approx \delta_{ion} - \delta_{gas}$$

Results

Experiments simulating dry deposition

The $\delta^{15}N$ value of $(NH_4)_2SO_4$ formed on filters initially holding H_2SO_4, and exposed to air + ammonia gas (experiment 1a), are shown as open circles in Fig. 1. For

Table 1 Site, sampling, and selected chemical data for rainfall and throughfall collected in lower Wensleydale

Plantation site (Trees; altitude; distance from pig farm)	Sample	Collection interval	Rainfall (mm)	pH		$NH_4^+/(NO_3^- +SO_4^{2-})^a$	
				Rain.	Through.	Rain.	Through.
Fleets Wood (Norway spruce;100 m; 0.5 km WNW)		26/5–12/6/92	19	4.0	[6.5][b]	0.38	[0.81][b]
The Willows (Norway spruce; 100 m; 1 km E)		26/5–12/6/92	25	4.0	5.6	0.39	0.59
Witton Fell (Scots pine; 350 m; 2 km SW)	1	25/2–26/4/93	18	4.3	3.5	0.47	0.39
	2	11/5–21/5/93	81	4.2	3.6	0.27	0.13
	3	25/3–25/4/94	38	4.8	3.6	0.34	0.20
	3, NH_3-fumigated canopy	25/3–25/4/94			4.9		1.0

[a]Meq/l
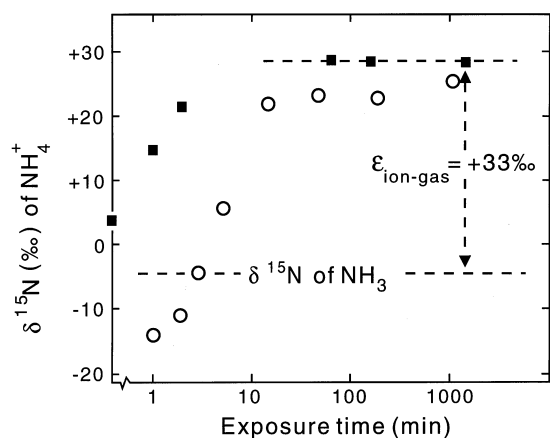[b]Possible bird contamination of ammonium in throughfall at Fleets Wood

Fig. 1 Results of experiment 1 (*Open circles* Experiment 1a, $\delta^{15}N$ values of ammonium sulphate formed on filters containing sulphuric acid exposed to excess atmosphere of 1% ammonia, *solid squares* experiment 1b, $\delta^{15}N$ values of ammonium sulphate exposed to excess atmosphere of 2% ammonia)

exposures of 1–3 min the amount of NH_4^+ was only 40–90% of that of stoichiometric $(NH_4)_2SO_4$, and $\delta^{15}N$ values were lower than that of the ammonia gas. For exposures of more than 6 min NH_4^+ contents were *c*. 100% stoichiometric $(NH_4)_2SO_4$, with $\delta^{15}N$ rapidly stabilising at values higher than that of the ammonia gas.

Results of the similar experiment with filters initially containing $(NH_4)_2SO_4$ (experiment 1b) are shown as solid squares in Fig. 1. NH_4^+ contents of all filters were consistent with $(NH_4)_2SO_4$ stoichiometry. The higher final $\delta^{15}N$ values for these filters (compared to those of experiment 1a) reflect a lesser modification of the original $\delta^{15}N$ value of the ammonia gas owing to the higher gas/salt phase distribution of N in experiment 1b. The estimated NH_4^+-NH_3 isotopic enrichment factor, $\varepsilon_{NH4-NH3}$, is +33‰.

Results of experiment 2 – nitrate on filter papers exposed to HNO_3 vapour – are shown in Table 2. For the first series of experiments, using an initial *c*. 2% HNO_3 vapour producing final nitrate/gas ratios of 2:3, the isotopic enrichment factor, $\varepsilon_{filter-HNO3}$, stabilised at a presumed equilibrium value of *c*. +5‰ within a few hours. The nitrate contents of these filters, however, were *c*. 3 times the amount expected for stoichiometric NH_4NO_3 (Table 2). Nitrate was not detectable when empty filters were exposed in the same manner, and the amount of ammonium on the filters did not change during exposure. The total nitrate on the filters at the end of exposure is therefore presumed to represent ammonium nitrate plus a larger amount of additional nitrate, possibly adsorbed HNO_3. Using an initial *c*. 1% HNO_3 vapour resulted in a lower final nitrate content on the filters, and higher $\varepsilon_{filter-HNO3}$ (Table 2). Combining the results from these different exposure conditions al-

Table 2 Results of experiment 2: isotopic fractionation for filters containing ammonium nitrate exposed to nitric acid vapour, and estimate of isotopic enrichment factors[a–h]

Exposure (minutes)	HNO_3/nitrate (final ratio)[b]	Filter nitrate (mg NO_3^--N)[c]		$\delta^{15}N_{filter}$ ‰ [d]	$\delta^{15}N_{HNO3}$ ‰ [e]	$\varepsilon_{filter-HNO3}$ ‰ [f]
		Initial (A_{AN})	Final (A_f)	(δ_f)	(δ_g)	(ε_{f-g})
0				−0.1		
2	10	1.9	2.6	+8.7		
10	3	2.0	4.6	+10.3	+6.3	+4.0
105	2.5	1.9	5.2	+10.5	+5.8	+4.7
1470	2	2.0	5.7	+10.1	+5.1	+5.0
14160	2	1.9	5.9	+11.2	+6.1	+5.1
2880[g]	1.5	1.9	4.0	+9.6	+0.9	+8.7

[a]The isotopic enrichment factor, $\varepsilon_{ammonium\ nitrate-HNO3}$, is estimated to be *c*. +21‰, see below
[b]Approximate ratio of HNO_3 gas-N to filter nitrate-N at end of exposure
[c]Amount of nitrate on filter: as stoichiometric ammonium nitrate at beginning of exposure (A_{AN}); and as total filter nitrate at end of exposure (A_f)
[d]$\delta^{15}N$ value of total filter nitrate at end of exposure (δ_f). The value for the 0-min exposure is the initial $\delta^{15}N$ of the ammonium nitrate used in all the exposures
[e]$\delta^{15}N$ value of HNO_3 gas at end of exposure (δ_g)
[f]Isotopic enrichment factor between total filter nitrate and HNO_3 gas (ε_{f-g})
[g]Results of the 2880-min exposure experiment are means from two filters with precisions of ± 0.06 mg NO_3^--N for A, and ± 0.1 ‰ for $\delta^{15}N$
[h]Calculation of isotopic enrichment factor: the total filter nitrate at the end of exposure (with $\delta^{15}N = \delta_f$ and amount = A_f) is assumed to be composed of: (1) nitrate bound as stoichiometric ammonium nitrate (with $\delta^{15}N = \delta_{AN}$ and, since amount of ammonium on filters did not change during exposure, amount = A_{AN}) formed with an ammonium nitrate-gas isotopic enrichment factor, $\varepsilon_{AN-g} \approx \delta_{AN}-\delta_g$; and 2) adsorbed nitrate (with $\delta^{15}N = \delta_{adN}$ and amount = A_{adN}) formed with a nitrate-gas isotopic enrichment factor, $\varepsilon_{adN-g} \approx \delta_{adN}-\delta_g$. For isotopic mass balance:

$\varepsilon_{AN-g} = \varepsilon_{adN-g} + (\varepsilon_{f-g} - \varepsilon_{adN-g}) \cdot (A_f/A_{AN})$

Solving as simultaneous equations for the 14160 and 2880 min exposure experiments yields: $\varepsilon_{AN-g} = c. +21‰$, and $\varepsilon_{adN-g} = c. -2‰$.

lows estimation of the value for $\varepsilon_{\text{ammonium nitrate-HNO3}}$ as $c.$ +21‰ (Table 2).

Rainfall and throughfall in Wensleydale

The concentrations and isotopic compositions of nitrate, ammonium and sulphate in rainfall and throughfall for five collection intervals are shown in Table 3. Samples of throughfall collected from three separate groups of collectors in Fleets Wood yielded very different $\delta^{15}N$ values for ammonium (+5.1, +9.0 and +15.7‰), though $\delta^{34}S$ values for sulphate were similar (1 SD = 0.3‰). Since perching birds were common in this wood, and might have led to random contamination of throughfall samples with ammonium, the mean ammonium values for Fleets Wood are shown in Table 3, but are not discussed further.

With the exception of ammonia in Witton Fell sample 2, the concentrations of all species were higher in the throughfall. The throughfall therefore represents rainfall to which ions from the tree canopy have been added, and the isotopic composition of this canopy-derived contribution can be calculated from isotopic mass balance:

$$\delta_c = [C_t.\delta_t.(1 - E) - C_r.\delta_r]/[C_t.(1 - E) - C_r] \quad (1)$$

For each ion (NO_3^-, NH_4^+ or SO_4^{2-}): δ_c = the isotopic composition of the canopy-derived ion, excluding ions derived from evaporation of rainfall on the canopy; C_t and δ_t = the concentration and isotopic composition in

throughfall; C_r and δ_r = the concentration and isotopic composition in rainfall; and E = fraction of rain water to the canopy which is lost by evaporation. On the basis of the relative volumes of rainfall and throughfall samples collected for a separate, chemical survey, values for E are estimated to be typically 0.4–0.6. Calculated δ_c values for the canopy are shown in Table 3 for $E = 0$ (no evaporation) to $E = 0.6$; the true value does not have a marked influence on δ_c for the purpose of this discussion.

Comparison of the calculated canopy contributions, δ_c, with the composition of rainfall indicates (Table 3) that: (1) $\delta^{15}N$ values of nitrate from the Witton Fell canopy were in all three cases higher than those of rainfall; (2) $\delta^{15}N$ values of ammonium from the canopy were lower than those of rainfall at Witton Fell, but higher than those in rainfall at The Willows and at the ammonia-fumigated canopy of Witton Fell; and (3) $\delta^{34}S$ values of sulphate from the canopy are similar to those of rainfall.

Discussion

Nitrogen

Ion-gas isotopic fractionation

The formation of atmospheric nitrate and ammonium from NO_x (NO and NO_2), HNO_3 and NH_3 gases can be

Table 3 Concentrations and isotopic compositions ($\delta^{15}N$, $\delta^{34}S$)[a] of nitrate, ammonium and sulphate in rainfall and throughfall in plantations in Wensleydale; with the calculated isotopic composition of material derived from the canopy

Species	Site, sample	Rainfall		Throughfall		Calculated canopy-derived δ (‰)[b]		
		meq/l	δ (‰)	meq/l	δ (‰)	(E = 0.0)	(E = 0.4)	(E = 0.6)
Nitrate								
	Witton Fell, 1	0.063	+0.9	0.16	+4.7	+7	+12	
	Witton Fell, 2	0.047	−1.5	0.063	+0.3	+6		
	Witton Fell, 3	0.026	+0.9	0.16	+4.6	+5	+6	+7
	Above, NH₃-fumigated[c]			*0.13*	*+3.4*	*+4*	*+5*	*+6*
Ammonium								
	Fleets Wood	0.13	−7.6	[0.93][d]	[+9.9][d]	[+13][d]	[+15][d]	[+19][d]
	The Willows	0.13	−5.6	1.50	+2.6	+3	+4	+5
	Witton Fell, 1	0.073	−7.8	0.36	−13.2	−15	−16	−19
	Witton Fell, 2	0.039	−7.0	0.039	−5.5			
	Witton Fell, 3	0.025	−8.6	0.13	−10.5	−11	−11	−12
	Above, NH₃-fumigated[c]			*0.75*	*+6.2*	*+7*	*+7*	*+8*
Sulphate								
	Fleets Wood	0.23	+4.6	0.81	+4.8	+5	+5	+5
	The Willows	0.20	+5.2	1.56	+5.2	+5	+5	+5
	Witton Fell, 1	0.094	+6.4	0.75	+5.5	+5	+5	+5
	Witton Fell, 2	0.10	+3.5	0.23	+4.7	+6	+8	
	Witton Fell, 3	0.048	+5.6	0.50	+6.4	+7	+7	+7
	Above, NH₃-fumigated[c]			*0.60*	*+9.8*	*+10*	*+10*	*+11*

[a] $\delta^{15}N$ in per mil vs. atmospheric N_2 for nitrate and ammonium, $\delta^{34}S$ in per mil vs. CDT for sulphate
[b] Canopy-derived δ values (calculated from Equation 1) for evaporative losses, E = 0%, 40%, and 60% (for values of E where denominator in Eq. 1 is positive)
[c] Throughfall samples collected with Witton Fell 3 from part of plantation fumigated with ammonia. The $\delta^{15}N$ values of the NH_3, at the beginning and end of fumigation, were −3.6 and −0.3‰, respectively
[d] Possible bird contamination of ammonium in throughfall at Fleets Wood

considered in terms of kinetically controlled "uni-directional" processes, and "equilibrium" exchange processes. Both processes are illustrated by experiment 1a. At the onset of ammonia reaction with sulphuric acid the process is essentially uni-directional, $NH_3 \rightarrow NH_4^+$. Isotopic enrichment factors for such uni-directional reactions are invariably negative; kinetics favouring diffusion and reaction of the lighter isotope. The first-formed NH_4^+ therefore has $\delta^{15}N$ values lower than that of the NH_3 gas (Fig. 1). When chemical equilibrium in the form of $(NH_4)_2SO_4$ stoichiometry had been achieved, for which $NH_3 \leftrightarrow NH_4^+$ exchange may be anticipated, the $\delta^{15}N$ of NH_4^+ stabilises at values higher than that of the NH_3 gas (Fig. 1). The isotopic enrichment factor estimated for these conditions in Experiment 1b, $\varepsilon_{NH4-NH3} = +33‰$ (Fig. 1), is in fact essentially identical to that determined experimentally for equilibrium at 25°C by Kirshenbaum et al. (1947).

Large positive enrichment factors, $\varepsilon_{NO3-NOX} > +50‰$, have also been demonstrated for the equilibrium formation of nitrate from the NO_x gases (Mahenc 1965). Formation of nitrate from HNO_3 may be an even more important reaction (Hanson and Lindberg 1991), but there are no published data for the accompanying isotopic fractionation. While noting that the conditions of experiment 2 preclude accurate determinations, however, its results suggest that $\varepsilon_{NO3-HNO3}$ is also large and positive (c. +21‰ from Table 2).

In addition to the value for $\varepsilon_{ion-gas}$ the relationship between the $\delta^{15}N$ values of ions and the *original* precursor gas from which they formed will also depend on the ion/gas distribution in the final mixture. For isotopic mass balance in a well-mixed closed system:

$$\delta_{ion} = \delta_{gas}^{0} + \varepsilon_{ion\text{-}gas} \cdot (1 - f) \tag{2}$$

where δ_{gas}^{0} is the isotopic composition of the initial atmospheric gas, and f is the fraction of the initial gas converted to the ion phase. The effect of f on δ_{ion} for negative values of $\varepsilon_{ion-gas}$, resulting from uni-directional reactions, is shown in Heaton (1987). Studies of atmospheric chemistry, and isotopic work (Heaton 1987; Freyer 1991), however, generally support assumptions of equilibrium. The experimental and published data above suggest that for equilibrium we must expect large positive values for $\varepsilon_{ion-gas}$. The effect of f on the δ value of ions for positive $\varepsilon_{ion-gas}$ is shown schematically in Fig. 2a.

The formation of nitrate and ammonium is greatly enhanced by the availability of water. In Fig. 2a, therefore, "wet atmosphere" and "dry atmosphere" conditions are regarded as typifying conditions of high f and low f, respectively. In a wet atmosphere – e.g. with gases being efficiently washed out by rainfall – high f would result in the final bulk value for δ_{ion} becoming similar to that for δ_{gas}^{0}. In contrast, for ions formed as aerosols or by dry deposition of gases at lower f, we may anticipate that δ_{ion} will differ from δ_{gas}^{0} by an amount up to $\varepsilon_{ion-gas}$ (Fig. 2a).
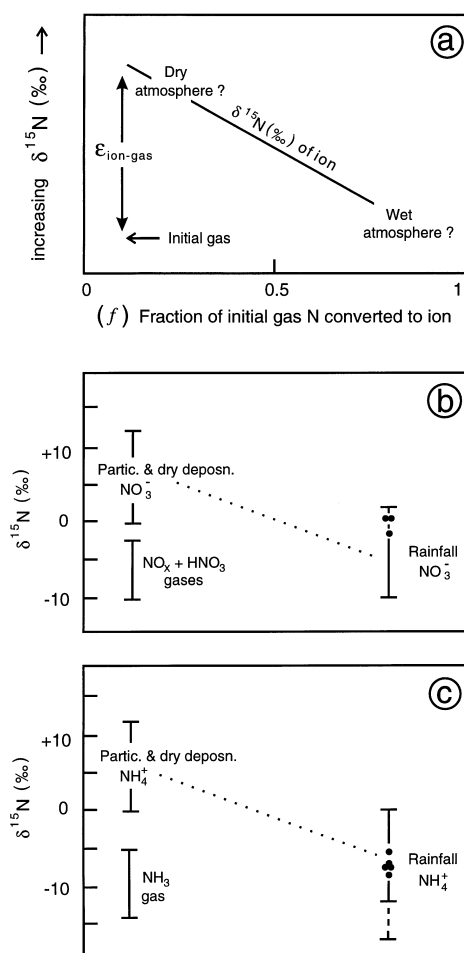

Fig. 2 a Hypothetical change in the $\delta^{15}N$ values of ions formed from gas by process involving large positive isotopic separation factor, $\varepsilon_{ion-gas}$, as a function of the fraction of the total initial gaseous N converted to ion (f). $\delta^{15}N$ value of initial gas is shown. Dry and wet atmospheric conditions are suggested as typifying systems of low and high f, respectively. **b** Typical ranges of published $\delta^{15}N$ values for atmospheric NO_x and HNO_3 gases, nitrate in particulates and dry deposition, and nitrate in rainfall (Moore 1977; Freyer 1978, 1991; Heaton 1987; Freyer et al. 1993) (*solid circles* represent data for rainfall from this study). **c** Typical ranges of published $\delta^{15}N$ values for gaseous NH_3 emissions, ammonium in particulates and dry deposition, and ammonium in rainfall (Moore 1977; Freyer 1978; Heaton 1987) (*broken line* represents lower range of $\delta^{15}N$ values for ammonium in rainfall in Germany (Freyer 1978), *solid circles* represent data for rainfall from this study)

The limited amount of published $\delta^{15}N$ data for atmospheric compounds, shown in Fig. 2b,c, supports this prediction. $\delta^{15}N$ values for nitrate and ammonium ions in rainfall tend to be reasonably similar to the probable composition of the precursor gases. In contrast, aerosol particulates and dry deposition have $\delta^{15}N$ values which tend to be higher than those of the precursor gases (Fig. 2).

This analysis, based on considerations of isotopic fractionation supported by published data, suggests that the $\delta^{15}N$ values of nitrogen ions in aerosols, or formed by dry deposition, will tend to be higher than those in rainfall. Dry deposition and the capture of particulates

constitute important sources of nitrogen input to canopies. These inputs should therefore be reflected by higher $\delta^{15}N$ values for throughfall collected below a canopy, compared with rainfall collected in the open.

Canopy-derived nitrate

The $\delta^{15}N$ values for nitrate in the three samples of rainfall from Witton Fell, between −1.5 and +0.9‰ (Table 3), are within the range of other published values for Western Europe (typically −6 to +2‰, Freyer 1991; Fig. 2b). The calculated $\delta^{15}N$ values for the canopy-derived nitrate at Wensleydale, however, are between 4 to 11‰ higher than those for nitrate in rainfall collected over the same period (Table 3). The canopy-derived nitrate has isotopic similarities to nitrate in particulates and dry deposition (Fig. 2b).

The only previous isotopic comparisons between nitrate in rainfall and throughfall were based on samples from Tennessee (Garten 1992). The mean $\delta^{15}N$ values for throughfall beneath deciduous and pine stands were only 0.4 and 2.2‰ higher, respectively, than the mean value for rainfall. This was regarded as not statistically significant (Garten 1992). These mean values, however, appear to have been based on all rainfall and throughfall samples, some of which were not collected over the same time intervals. An analysis of the graphical data of Garten (1992) suggests that for the 12 sets of rainfall and throughfall samples which were collected over the same intervals, the throughfall nitrate had higher $\delta^{15}N$ values in 11 of these 12 sets. Without information on the concentrations of nitrate in these samples it is difficult to assess the probable isotopic composition of the canopy-derived nitrate in the study of Garten (1992). It nevertheless appears that the canopy-derived nitrate from the Tennessee canopies probably had $\delta^{15}N$ values higher than the nitrate in the rainfall over the same period. If this analysis is true, then the pattern in Tennessee is consistent with that observed for the Wensleydale samples.

Canopy-derived ammonium

$\delta^{15}N$ values for ammonium in rainfall in Wensleydale are low, between −8.6 and −5.6‰. These are within the range reported for other parts of the world (Fig. 2c), though not quite as low as the majority of samples from the only other European study (typically −16 to −8‰ for Germany; Freyer 1978). Canopy influences were variable. In Witton Fell samples 1 and 3, where the throughfall had higher NH_4^+ concentrations than the rainfall, the calculated $\delta^{15}N$ values of the canopy-derived ammonium were markedly negative – between 2 to 11‰ lower than the values for rainfall (Table 3). In contrast, for the ammonia fumigation experiment of the canopy at Witton Fell, and in the samples from the Willows, canopy-derived ammonium had $\delta^{15}N$ values

which were higher than the values for rainfall. An analysis of the Tennessee study of Garten (1992) suggests similar variable canopy influences.

Low $\delta^{15}N$ values for canopy-derived ammonium are contrary to the pattern expected if the canopy gained ammonium by $NH_3 \leftrightarrow NH_4^+$ exchange processes, with positive $\varepsilon_{ion\text{-}gas}$, under relatively dry conditions of low f. As noted above, the availability of water should have a major influence on f. The acidity of water or canopy surfaces, however, will also exert a control, and some of the variability in the calculated isotopic compositions of the canopy-derived ammonium in Table 3 may be related to acidity or other aspects of the chemistry. The ammonium contents of throughfall at Witton Fell are much lower than those of the major acidic components – a feature reflected in the low pH values (Table 1). The solubility of ammonia is enhanced by low pH. A strongly acidic canopy may promote either the more complete removal of ammonia gas (high f), or partial removal by predominantly unidirectional uptake (negative $\varepsilon_{NH4\text{-}NH3}$). These factors could favour the formation of canopy ammonium with low $\delta^{15}N$ values, as is found for Witton Fell samples 1 and 3.

As expected, ammonia fumigation had a pronounced effect on the throughfall at Witton Fell, and resulted in ammonium concentrations which were c. 6 times higher than those in throughfall from the non-fumigated canopy (Table 3). The higher ammonium concentrations in the fumigated throughfall, however, were not balanced by substantially higher sulphate or nitrate concentrations (Table 1); as a consequence, the pH in throughfall from the fumigated canopy was significantly higher than from the non-fumigated canopy (Table 1). Under these conditions ammonium saturation, with $NH_3 \leftrightarrow NH_4^+$ exchange and positive $\varepsilon_{NH4\text{-}NH3}$, is more likely to occur. The high concentrations of ammonia resulting from fumigation, moreover, would ensure lower values of f. These factors would favour the formation of canopy ammonium with high $\delta^{15}N$ values.

The high $\delta^{15}N$ value for canopy-derived ammonium at the Willows (Table 3) was also associated with throughfall having much higher pH and ammonium concentrations (Table 1). The high ammonium concentrations are believed to reflect the location of this plantation down wind of a pig farm in an area of high concentrations of atmospheric ammonia (Table 1; ITE 1993). Both the environment and the isotopic patterns found at The Willows therefore have similarities to the ammonia-fumigated section of the Witton Fell plantation.

Sulphur

Ion-gas isotopic fractionation

In contrast to the volatility and ready exchange of ammonium and nitrate species, the formation of involatile sulphate from SO_2 is essentially irreversible. Thus, although thermodynamic calculations predict a large

positive equilibrium ion-gas isotopic enrichment factor, $\varepsilon_{SO4-SO2} \approx +30‰$ at 25°C (Sakai 1957), this equilibrium is not attained. The effective isotopic fractionation appears to be controlled by the combination of two processes (Saltzman et al. 1983): a positive equilibrium enrichment factor for the exchange process $SO_2 \leftrightarrow HSO_3^-$, and a negative kinetic enrichment factor for the uni-directional process $HSO_3^- \rightarrow SO_4^{2-}$. Analysis of co-existing atmospheric SO_2 and particulate SO_4^{2-} suggest that the effective isotopic enrichment factor, $\varepsilon_{SO4-SO2}$, is probably small – possibly ranging from *c.* 0‰ to only +3‰ (Saltzman et al. 1983; Newman et al. 1991).

In contrast to nitrogen isotopes, with their large $\varepsilon_{ion-gas}$ values, changes in *f* (Equation 2) should therefore have relatively less effect on $\delta^{34}S_{ion}$. This is born out by available data for atmospheric sulphur compounds shown in Fig. 3. Unlike nitrogen, $\delta^{34}S$ values for sulphate in aerosol particulates are generally similar to those for gases (SO_2) and for sulphate in rainfall. One may therefore anticipate that dry deposition and captured particulates on a canopy, washed off in throughfall, will have $\delta^{34}S$ values which are not substantially different to those in rainfall.

Canopy-derived sulphate

Wensleydale is some 80 km from the sea (in the direction of the prevailing wind) and the $\delta^{34}S$ values for sulphate in rainfall, +3.5 to +6.4‰ (Table 3), fall within the published range of values for rainfall in non-coastal areas (Fig. 3). The calculated $\delta^{34}S$ values for canopy-derived sulphate range from +5 to not more than +8‰, and for most samples are not significantly different from those of rainfall (Table 3). This supports the study of Van Stempvoort et al. (1992) in a forest in Ontario, where sulphate in rainfall and throughfall also had very similar $\delta^{34}S$ values.

Conclusions

Equilibrium isotopic enrichment factors, $\varepsilon_{ion-gas}$, for formation of nitrate and ammonium from atmospheric
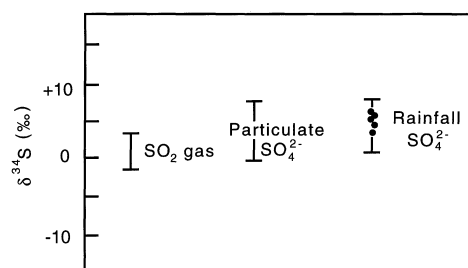

Fig. 3 Typical ranges of published $\delta^{34}S$ values (in non-coastal and non-industrial areas) for atmospheric SO_2, sulphate in particulates, and sulphate in rainfall (Chukrov et al. 1980; Saltzman et al. 1983; Caron et al. 1987; Newman et al. 1991; Nriagu et al. 1991; Van Stempvoort et al. 1991) (*solid circles* represent data for rainfall from this study)

gases – HNO_3, NO_x ($NO + NO_2$) and NH_3 – are positive and large. Nitrate and ammonium formed where the atmospheric gas phase concentrations remain high should therefore have higher $\delta^{15}N$ values than under conditions where most of the gas is removed by solution. This probably accounts for the observation, based on limited data, that nitrate and ammonium collected as dry deposition or particulates have $\delta^{15}N$ values higher than those in rainfall. The former components are important sources of N inputs to canopies. We therefore suggest that throughfall deposition to the below-canopy environment – representing rainfall plus dissolved canopy deposits – may have $\delta^{15}N$ values which are higher than those of rainfall alone. Data from a small number of throughfall samples from coniferous plantations in Wensleydale, together with an appraisal of published data (Garten 1992), support this prediction for nitrate. For ammonium, canopy-effects appear to variable, and may be particularly sensitive to the influence of pH and ammonia gas concentrations.

With one exception (Garten 1993) these possible canopy effects have not been considered in isotopic studies of nitrogen inputs to soil/plant environments. The data above, however, cast doubt on the validity of the general assumption that the $\delta^{15}N$ values for rainfall may be considered as representative of the input of atmospheric nitrate and ammonium. Whilst sampling of rainfall on typical collectors will often include a component of dry deposition (Heaton 1987), this will be substantially less than the amount collected by a plant canopy; particularly by trees. The $^{15}N/^{14}N$ ratio of the total atmospheric deposition to a canopied system, moreover, will not only depend on canopy influences on the proportion of "dry" and "wet" inputs. Other factors include: (1) the proportion of nitrate and ammonium – $\delta^{15}N$ values for these ions are often quite different; (2) effects of chemistry on gas/ion distribution (e.g. for ammonium); and (3) localised differences in the $\delta^{15}N$ values of atmospheric NO_x and NH_3 resulting from differences in emission source or the effects of gas-gas isotopic fractionation (Freyer 1978; Heaton 1987, 1990; Freyer et al. 1993).

The nitrogen compounds considered here have lifetimes of only a few days. For large regional studies it may therefore be realistic to assume that the isotopic composition of the total deposition of nitrogen is similar to the total emission of NO_x and NH_3 into the atmosphere. The sparse data for these gases suggests that, on balance, their $\delta^{15}N$ values are negative (Fig. 2). If nitrogen isotope studies are to be used in assessing the role of atmospheric inputs to a local system, however, then confident interpretation will almost certainly require actual isotopic analysis of this input.

Isotopic enrichment factors for the formation of sulphate from SO_2, $\varepsilon_{SO2-SO4}$, are effectively small (Saltzman et al. 1983; Newman et al. 1991). It is probably for this reason that sulphates in atmospheric particulates and rainwater, in areas unaffected by marine sources, have generally similar $\delta^{34}S$ values. Data for all

five collection periods in Wensleydale support a previous study (Van Stempvoort et al. 1991) in indicating that there is similarly little difference between the $\delta^{34}S$ values for sulphate formed on the canopy and that in rainfall. This might not hold in certain environments where different primary sources of S exist – e.g. where the canopy's capture of marine-derived sulphate aerosols is important. It is probable, however, that assumptions of the $\delta^{34}S$ value of atmospherically deposited S to a canopy, based on the $\delta^{34}S$ value of rainfall, are more likely to be valid than similar assumptions for the $\delta^{15}N$ values of atmospherically deposited N.

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