

- Ajayan, P. M. et al. *Nature* **362**, 522–525 (1993).
- Seraphin, S., Zhou, D., Jiao, J., Withers, J. C. & Loutfy, R. *Nature* **362**, 503 (1993).
- Ajayan P. M. et al. *Phys. Rev. Lett.* **72**, 1722–1725 (1994).
- Subramoney, S. et al. *Carbon* **32**, 507–513 (1994).
- Tsang, S. C., Chen, Y. K., Harris, P. J. F. & Green, M. L. H. *Nature* **372**, 159–162 (1994).
- Seraphin, S., Zhou, D., Jiao, J., Withers, J. C. & Loutfy, R. *Appl. Phys. Lett.* **63**, 2073–2075 (1993).
- Audier, M., Oberlin, A. & Coulon, M. *J. Cryst. Growth* **55**, 549–556 (1981).
- Baker, R. T. & Harris, P. S. in *Chemistry and Physics of Carbon* Vol. 14 (ed. Thrower, P. A.) 83–165 (Dekker, New York, 1978).
- Audier, M. & Coulon, M. *Carbon* **23**, 317–323 (1985).
- Saito, Y. & Yoshikawa, T. *J. Cryst. Growth* **134**, 154–156 (1993).
- Cowley, J. M. & Liu, M. *Micron* **25**, 53–61 (1994).
- Ruoff, R. S., Lorents, D. C., Chan, B. C., Malhotra, R. & Subramoney, S. *Science* **259**, 346–347 (1993).
- Murakami, Y. et al. *J. Phys. Chem. Solids* **54**, 1861–1870 (1993).

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Effects of forest decline on uptake and leaching of deposited nitrate determined from ^{15}N and ^{18}O measurements

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ATTEMPTS to understand how atmospheric nitrogen deposition affects forest ecosystems^{1,2} have been hampered by the lack of a direct method to trace the fate of the deposited nitrogen. Nitrate originating in the atmosphere has natural abundances of nitrogen and oxygen isotopes that differ measurably from those of soil nitrate³. Here we present an analysis of the isotope ratios of nitrate in spring waters from eight forested watersheds, ranging from apparently healthy spruce plantations to those in decline owing to acidification. We find that for the healthy, slightly declining and limed sites, only 16–30% of the nitrate in spring water originates directly from the atmosphere without being processed in the soil, whereas for more severely damaged sites almost all of the atmospheric nitrate finds its way directly into the spring water. This suggests that acid-induced forest decline significantly inhibits nitrate consumption by soil microorganisms and trees, and that liming to ameliorate soil acidification restores the consumption of atmospheric nitrate. Nevertheless, in limed ecosystems total nitrate output remains high because of internal nitrate production by the ecosystem.

Nitrate concentrations of forest spring waters in northeast Bavaria (Germany) are correlated with forest decline, liming and net nitrification of forest soils^{4,5}. Although nitrification is generally regarded as a prerequisite for nitrate (NO_3^-) leaching², other studies found that the NO_3^- outputs in spring water seemed to be related to nitrogen deposition from air pollution^{6,7}. However, it has previously not been possible to determine whether nitrate in surface waters originated from nitrification processes or from deposited nitrate that was leached through the soil.

The fate of nitrate deposited from the atmosphere into an ecosystem ($\text{NO}_3^-_{\text{atm}}$) is determined in general by the interplay between nitrification, (which dilutes atmospheric nitrate), NO_3^- consumption through plant uptake, immobilization by uptake in microbial biomass, and denitrification. Depending on the degree of dilution by nitrification, NO_3^- consumption will decrease the recovery of $\text{NO}_3^-_{\text{atm}}$ in spring water. Low recovery of $\text{NO}_3^-_{\text{atm}}$ can be due to a low ratio of NO_3^- input to nitrification

and/or a high ratio of NO_3^- consumption to nitrification. High recovery of $\text{NO}_3^-_{\text{atm}}$ is possible only if NO_3^- consumption is low compared to nitrification.

These processes can be investigated by using natural isotope ratios of nitrogen ($\delta^{15}\text{N}_{\text{NO}_3^-}$) and oxygen ($\delta^{18}\text{O}_{\text{NO}_3^-}$) in nitrate as tracers to investigate the flux of nitrate through an ecosystem (Fig. 1). Although the interpretation of the nitrogen isotope ratios is problematical because of their narrow range^{8–10}, the oxygen isotope ratios are more informative owing to the large difference in $\delta^{18}\text{O}$ between atmospheric nitrate ($\text{NO}_3^-_{\text{atm}}$) and nitrate from microbial nitrification in the soil ($\text{NO}_3^-_{\text{nit}}$)¹¹. The $\delta^{18}\text{O}$ values of atmospheric nitrate cover a range³ of $\delta^{18}\text{O}_{\text{NO}_3^-_{\text{atm}}} = 52.5\text{--}60.9\text{‰}$; this is different to the $\delta^{18}\text{O}$ atmospheric sulphate which is closer to atmospheric oxygen¹². In contrast, $\delta^{18}\text{O}_{\text{NO}_3^-_{\text{nit}}}$ ranges¹¹ from 0.8 to 5.8‰ because one oxygen atom of microbial nitrate originates from atmospheric O_2 ($\delta^{18}\text{O}_{\text{O}_2} = 23.5\text{‰}$) and two atoms from soil water ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = -10.5$ to -3‰)^{11,13}. Denitrification leads to an increase of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in the remaining NO_3^- at a constant ratio^{3,11,14} of 2:1.

This study quantifies the impact of nitrate deposition on nitrate leaching by measuring natural isotope ratios of NO_3^- oxygen and NO_3^- nitrogen in atmospheric deposition as ecosystem input and spring water as ecosystem output. We interpret

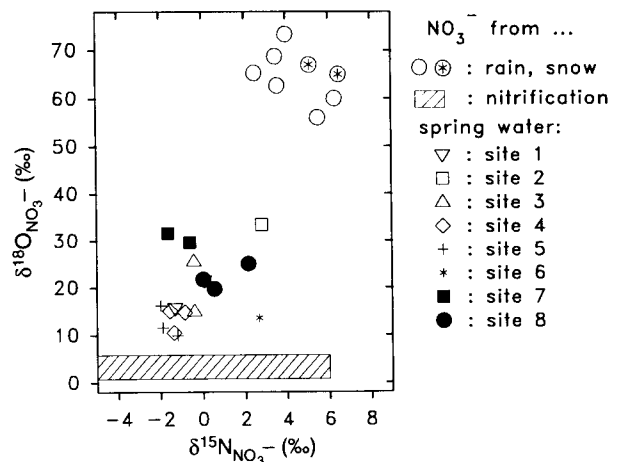


FIG. 1 Natural isotope ratios of nitrate oxygen ($\delta^{18}\text{O}_{\text{NO}_3^-}$) and nitrate nitrogen ($\delta^{15}\text{N}_{\text{NO}_3^-}$) of precipitation nitrate and springwater nitrate from the Fichtelgebirge. Details of sites are given in Table 1. The shaded area represents the range of $\text{NO}_3^-_{\text{nit}}$ produced by nitrification of soil nitrogen^{3,11}.

METHODS. Spring water was sampled in November 1991, and March and May 1992. Atmospheric input was collected as rain or snow in autumn and spring below the tree canopy. Natural isotope ratios were analysed following filtration with charcoal, cation exchange (Merck Kationenaustauscher I) and neutralization with KOH. After elimination of sulphate and phosphate by precipitation with BaCl_2 , the water samples were evaporated to dryness. For oxygen isotope analyses aliquots were heated with $\text{Hg}(\text{CN})_2$ in an evacuated sealed tube to 550°C for 6 h. The CO formed was converted to CO_2 by slowly cooling the tube^{3,14}. Carbon dioxide was analysed on a Finnigan MAT delta E gas isotope mass spectrometer. Nitrogen isotope abundances were measured directly from the residue with a system combining an elemental analyser (Heraeus CHN-O Rapid) for Dumas combustion, a Finnigan MAT Trapping Box HT and a Finnigan MAT delta D gas-isotope mass spectrometer⁹. The isotope ratios are reported in delta notation ($\delta^{18}\text{O}$, $\delta^{15}\text{N}$ in ‰) relative to standard mean ocean water or to air nitrogen as the standard⁹. Repeated measurements of standard substances yielded means and standard deviations of $-1.03 \pm 0.12\text{‰}$ for $\delta^{15}\text{N}$ (acetanilide, $n=105$)⁹ and $22.44 \pm 0.55\text{‰}$ for $\delta^{18}\text{O}$ (NH_4NO_3 , $n=7$)³.

TABLE 1 Characteristics of sites studied

Site no.	Site condition*	Atmospheric input†		Springwater output	
		NO ₃ ⁻ (mmol m ⁻² yr ⁻¹)	NH ₄ ⁺ (mmol m ⁻² yr ⁻¹)	NO ₃ ⁻ concentration‡ (μmol l ⁻¹)	Total NO ₃ ⁻ output§ (mmol m ⁻² yr ⁻¹)
1	Healthy	46	92	53	29
2	Declining, peaty soil	57	107	43	30
3	Slightly declining	74	108	98	69
4	Healthy	74	81	225	90
5	Slightly declining, limed	45	91	361	90
6	Slightly declining, limed	60	81	191	96
7	Strongly declining	88	96	167	117
8	Strongly declining	36	59	274	137

Site conditions, atmospheric inputs of nitrogen to the watersheds, and NO₃⁻ output characteristics of eight forest springs in the Fichtelgebirge (northeast Bavaria, Germany).

* Definitions: slightly declining, single trees affected by needle yellowing and crown thinning; strongly declining, all trees affected.

† Extrapolated from measurements of throughfall sampled between 15 April and 15 December 1992 with ten funnels per site.

‡ Volume-weighted mean of monthly measurements in 1991 and 1992.

§ Modelled from volume-weighted mean NO₃⁻ concentration and seepage¹⁷.

the observations in relation to soil hydrology and nitrate uptake in these forests.

Eight springs in the Fichtelgebirge (northeast Bavaria; 50° 5' N, 11° 51' E; 700–1,051 m above sea level) were selected from a total of 200 springs under investigation^{4,5}. They represent the observed range of NO₃⁻ concentration in spring water, a wide range of nitrogen inputs and all stages of forest decline (Table 1). All watersheds are dominated by Norway spruce (*Picea abies* [L.] Karst.) forests growing on acid brown earth soils covering granitic and phyllitic bedrock. Locally, hydromorphous peat soils have developed. Springs are mainly fed by interflow with discharge of 0.05–1 l s⁻¹. Nitrogen and sulphur deposition rates greatly exceed critical loads¹⁵. Forest decline due to magnesium deficiency is widespread in the area¹ and liming is widely used for soil amelioration.

We measured δ¹⁵N and δ¹⁸O in atmospheric nitrate. Values of δ¹⁵N were 2.6–6.3‰ with a mean of 4.3 ± 1.1‰; δ¹⁸O reached values between 60.3 and 73.4‰ with a mean of 64.5 ± 4.8‰ (Fig. 1).

Springwater nitrate had δ¹⁵N values between -2 and +2‰, with δ¹⁸O between +11 and +33‰ (Fig. 1). Neither nitrification nor denitrification can explain these isotope ratios, as nitrification leads to δ¹⁸O_{NO₃⁻} values¹¹ between 0.8 and 5.8‰. If the observed isotope ratios were caused by kinetic isotope effects accompanying nitrification of nitrate, a hypothetical NO₃⁻ substrate with δ¹⁵N between -63 and -19‰ has to be postulated, which is outside the range observed in terrestrial ecosystems¹⁶. However, a small influence of denitrification is possible in samples from sites 2, 6 and 8 (Fig. 1) with δ¹⁵N of +2‰. These samples have started at δ¹⁵N = 0 with an accompanying rise in δ¹⁸O of +1‰ due to denitrification.

The isotope ratios observed in spring water can only be explained by a contribution of unmodified atmospheric

NO₃⁻ to the NO₃⁻ output. The fraction of atmospheric nitrate in spring water averaged 26%, with 74% originating from nitrification (Table 2). No consistent seasonal trend of the NO₃⁻ fraction was observed. This corresponds to the absence of seasonal trends in NO₃⁻ concentration of these springs.

The δ¹⁸O values of atmospheric nitrate from summer precipitation has been determined previously³ to be 57.5 ± 2.9‰, which is lower than that measured here. Therefore a seasonal variation cannot be excluded, which could affect our data analysis. Nevertheless our calculations are conservative. Assuming atmospheric nitrate to be at δ¹⁸O = 58‰ instead of 65‰, the calculated fraction of leached atmospheric nitrate would even increase by 2–6%. By using the highest value of atmospheric nitrate (73‰) the fraction of leached atmospheric nitrate would decrease by 1–5%.

Hydrological transport processes in the hilly terrain can influence leaching of NO₃⁻. In the site with peaty waterlogged soils (site 2, Table 1), direct input of NO₃⁻ by surface flow cannot be ruled out as a contributor to the high fraction of NO₃⁻. In all other sites no surface flow occurred, so that NO₃⁻ leaching is regulated only by biological processes in the soil.

The lowest fraction of NO₃⁻ was found in forest stands treated by liming, whereas highest values occurred at sites of forest decline (Table 2). Thus, even in apparently healthy forest stands, nitrate from air pollution may leach through the soil profile without any biological interaction. This implies that adverse effects of high NO₃⁻ outputs from ecosystems, such as cation leaching, soil acidification and eutrophication of surface waters, can be linked directly to NO₃⁻ deposition.

In the healthy, slightly declining or limed sites the amount of NO₃⁻ recovered in spring water is equivalent to 16–30% of the NO₃⁻ input (Table 2, Fig. 2). On these sites NO₃⁻ consumption by plants and soil microflora is still large enough to absorb a high proportion of the deposited nitrate, but not active enough

FIG. 2 Absolute amount of NO₃⁻ in springwater output originating from air pollution (NO₃⁻_{atm} in output ± min, max) as a function of atmospheric NO₃⁻ input (± standard error) (a) and total NO₃⁻ output (b). Dashed lines in a indicate percentage recovery of NO₃⁻_{atm} in springwater output (Table 2).

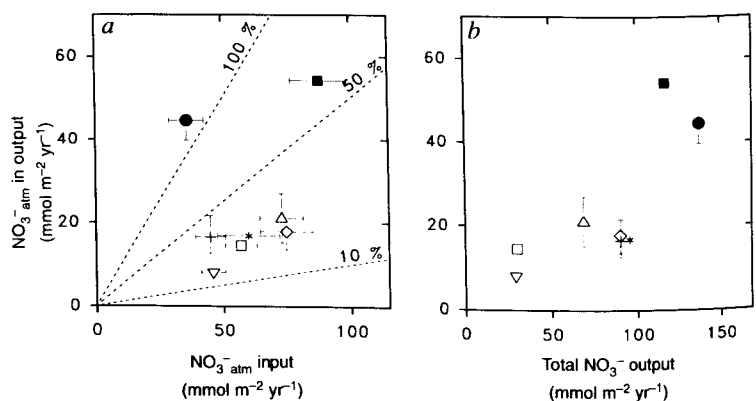


TABLE 2 Nitrate in spring water

Site no.	Output of NO_3^- in spring water		
	Fraction of total NO_3^- output (%)	Absolute flux ($\text{mmol m}^{-2} \text{yr}^{-1}$)	Fraction of NO_3^- input (%)
1	25	8	16
2	46	15	24
3	28	21	26
4	16	18	20
5	15	16	30
6	14	16	23
7	44	54	59
8	30	45	114*

Output of NO_3^- derived from deposition ($\text{NO}_{3\text{atm}}$) in forest spring water in the Fichtelgebirge; means of 1–3 measurements. Because deposited nitrate ($\text{NO}_{3\text{atm}}$) and nitrate originating in the soil ($\text{NO}_{3\text{nit}}$) are the only two sources of nitrate, the fraction of nitrate in spring water originating directly from the atmosphere can be calculated as: $(\delta^{18}\text{O}_{\text{NO}_{3\text{spring}}} - \delta^{18}\text{O}_{\text{NO}_{3\text{atm}}}) / (\delta^{18}\text{O}_{\text{NO}_{3\text{atm}}} - \delta^{18}\text{O}_{\text{NO}_{3\text{nit}}})$ per cent. For $\delta^{18}\text{O}_{\text{NO}_{3\text{atm}}}$, the mean of the measured values (65‰) was used; for $\delta^{18}\text{O}_{\text{NO}_{3\text{nit}}}$, the published value^{3,11} of 3.3‰ was employed in the calculation.

* This value (>100% recovery) could have been caused by errors in the input–output balance, or by temporal $\text{NO}_{3\text{atm}}$ storage in the aquifer.

to metabolize all of it. Generally, one would expect nitrate to be rapidly turned over by microorganisms and vegetation under healthy undisturbed conditions, as well as under disturbed conditions like clear felling or forest decline. But in declining sites with a loss of closed canopy, recovery of $\text{NO}_{3\text{atm}}$ in spring water increases and reaches 59% and 114% of the respective NO_3^- -input (sites 7 and 8, Table 2). An almost complete throughflow of $\text{NO}_{3\text{atm}}$ seems to take place due to a significant reduction of NO_3^- consumption by soil microorganisms and trees.

The results from the limed sites can clarify the possible role of soil microorganisms. Liming results in higher soil pH, and stimulates microbial activity and nitrification in these acidic soils. The limed declining sites (sites 5 and 6) showed reduced recovery of $\text{NO}_{3\text{atm}}$ compared to unlimed declining sites (sites 7 and 8). Thus soil internal NO_3^- cycling by microorganisms is the most sensitive process determining the fate of deposited nitrate. Nevertheless, in limed sites total nitrate output remains at a high level because of ecosystem internal nitrate production.

The fraction of $\text{NO}_{3\text{atm}}$ in nitrate output, as calculated from the natural isotope abundances, still underestimates the total effect of nitrogen deposition on groundwater quality. Even if only a part of the atmospheric nitrate percolates through the soil without microbial interaction, more nitrate in spring water will originate from air pollution, because our measurements do not account for nitrification of deposited ammonium. Atmospheric deposition contains even more ammonium than nitrate (Table 1). Ammonium from deposition will be partially assimilated and nitrified by microorganisms and contribute to nitrate in runoff. It is presently not possible to quantify this fraction from isotopic abundances. □

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- Schulze, E.-D. *Science* **244**, 776–783 (1989).
- Gundersen, P. *NORD Miljørapport* 1992: 41, 55–110 (Nordic Council of Ministers, Copenhagen, 1992).
- Voerkelius, S. thesis, Tech. Univ. Munich (1990).
- Durka, W. & Schulze, E.-D. *UWSF. Z. Umweltchem. Ökotox.* **4**, 217–226 (1992).
- Durka, W. *Bayreuther Forum Ökologie* **7**, 1–197 (1994).
- Grennfelt, P. & Hultberg, H. *Wat. Air & Soil Pollut.* **30**, 945–963 (1986).
- Driscoll, T., Schaefer, D. A., Molot, L. A. & Dillon, P. J. *NORD Miljørapport* 1989: 92, 1–45 (Nordic Council of Ministers, Copenhagen, 1989).
- Handley, L. L. & Raven, J. A. *Plant Cell Envir.* **15**, 965–985 (1992).
- Handley, L. L. & Schulze, E.-D. *Oecologia* **87**, 198–207 (1991).
- Gebauer, G. & Schulze, E.-D. *Oecologia* **29**, 35–44 (1993).
- Gebauer, G. & Dietrich, P. *Isotopenpraxis Envir. Health Stud.* **29**, 2699–2705 (1987).
- Amberger, A. & Schmidt, H. L. *Geochim. cosmochim. Acta* **51**, 2699–2705 (1987).
- Holt, B., Cunningham, P. T. & Kumar, R. *Envir. Sci. Technol.* **15**, 804–808 (1981).
- Holt, B., Cunningham, P. T. & Kumar, R. *Envir. Sci. Technol.* **15**, 804–808 (1981).
- Förstel, H. & Hütten, H. *Nature* **304**, 614–616 (1983).
- Böttcher, J., Strelow, O., Voerkelius, S. & Schmidt, H. L. *J. Hydrol.* **114**, 413–424 (1990).

- Schulze, E.-D. *et al. Water Air Soil Pollut.* **48**, 451–456 (1989).
- Fritz, P. & Fontes, J. C. (eds) *Handbook of Environmental Isotope Geochemistry* Vol. 2 (Elsevier, Amsterdam, 1986).
- Schriftenreihe No. 5 (Bavarian Federal Agency of Water Supply Munich, 1973).
- Rundel, P. W., Ehleringer, J. R. & Nagy, K. A. (eds) *Ecological Studies* Vol. 68 (Springer, Berlin, 1989).

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Mineral chemistry and density of subducted basaltic crust at lower-mantle pressures

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SUBDUCTED slabs are less dense than the surrounding mantle near the base of the transition zone (~660 km depth) because of the survival of garnet in former basaltic crust: by this depth mantle peridotite has transformed to denser perovskite^{1,2}. The buoyancy of the former basaltic crust may contribute to the observed accumulation or horizontal displacement of many slabs at the base of the transition zone³. Here we report experimental confirmation of the widely held belief that the basaltic crust of slabs eventually transforms to a dense perovskitic lithology, stable in the lower mantle. Synthetic mid-ocean-ridge basalt (MORB) glass subjected to pressures of 45, 80 and 100 GPa in a laser-heated diamond anvil cell transforms to an assemblage of aluminous Mg,Fe silicate perovskite, non-quenchable CaSiO_3 perovskite, stishovite and a sodic, aluminous phase with the Ca-ferrite structure (Fig. 1). Perovskitic MORB is about 0.06 g cm^{-3} more dense than a model lower mantle (PREM) derived from seismological data. Thus even thermally equilibrated perovskitic slabs should encounter no significant hindrance to subduction and convection in the lower mantle.

At depths below 660 km and to at least 800 km, buoyant former MORB is known to comprise neither magnesian silicate perovskite nor magnesio-wüstite, but instead consists of garnet rich in pyrope and almandine endmembers, stishovite, CaSiO_3 perovskite and an aluminous phase with the Ca-ferrite structure². Our preliminary diamond anvil cell experiments on the high-pressure stability limit of garnet in MORB were conducted using a synthetic glass equivalent in composition to the garnet that Irifune and Ringwood² found still survived in MORB at 27 GPa (~800 km depth). This same garnet could be synthesized only below 30–35 GPa. We find no evidence to substantiate predictions⁴ that garnet might survive to depths of ~1,200 km, and instead propose that transformation of subducted MORB to perovskite should be complete by ~900 km depth.

Past attempts to transform synthetic MORB glass to perovskite have been unsuccessful, with the most recent yielding only glass plus metallic iron⁵. These diamond anvil cell experiments essentially recapitulated earlier attempts by Bell and co-workers, in which the recovered samples showed evidence of extensive melting and also contained metallic iron⁶. We do not agree with the suggestion of Bell *et al.* that metallic iron is stabilized as a consequence of the pressure-induced disproportionation of FeO to metal plus ferric iron at pressures above 10 GPa. No such phenomena have subsequently been observed in multi-anvil experiments^{2,7} on MORB glass at pressures up to 27 GPa, nor have we ourselves induced disproportionation in experiments at pressures as high as 100 GPa. However, intense peak temperatures can be attained during the laser heating of a material with intrinsically strong infrared absorption. Thus our preferred