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 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 nitrate. 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. Although nitrate is generally regarded as a prerequisite for nitrate (NO$_3^-$) leaching, other studies found that the NO$_3^-$ outputs in spring water seemed to be related to nitrate deposition from air pollution. 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 (NO$_3^-$$_{atm}$) is determined in general by the interplay between nitrification, (which dilutes atmospheric nitrate), NO$_3^-$ consumption through plant uptake, immobilization by uptake in microbial biomass, and denitrification. Depending on the degree of dilution by nitrification, NO$_3^-$ consumption will decrease the recovery of NO$_3^-$$_{atm}$ in spring water. Low recovery of NO$_3^-$$_{atm}$ can be due to a low ratio of NO$_3^-$ input to nitrification and/or a high ratio of NO$_3^-$ consumption to nitrification. High recovery of NO$_3^-$$_{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 ($\delta^{15}$N$_{atm}$) and oxygen ($\delta^{18}$O$_{atm}$) 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$^{10}$, the oxygen isotope ratios are more informative owing to the large difference in $\delta^{18}$O between atmospheric nitrate (NO$_3^-$$_{atm}$) and nitrate from microbial nitrification in the soil (NO$_3^-$$_{nm}$)$^{11}$. The $\delta^{18}$O values of atmospheric nitrate cover a range of $\delta^{18}$O$_{atm}$$\approx$$52.5$–$60.9%$, this is different to the $\delta^{18}$O atmospheric sulphate which is closer to atmospheric oxygen$^{12}$. In contrast, $\delta^{18}$O$_{nm}$ ranges$^{13}$ from 0.8 to 5.8% because one oxygen atom of microbial nitrate originates from atmospheric O$_2$ ($\delta^{18}$O$_{atm}$$=23.5%$) and two atoms from soil water ($\delta^{18}$O$_{water}$$=\approx$$-10.5$ to $-3%$)$^{11,13}$. Denitrification leads to an increase of $\delta^{15}$N and $\delta^{18}$O in the remaining NO$_3^-$ at a constant ratio$^{10,11}$ 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

![Graph showing the isotopic analysis of nitrate](https://example.com/graph.png)

**FIG. 1.** Natural isotope ratios of nitrate oxygen ($\delta^{18}$O$_{atm}$) and nitrate nitrogen ($\delta^{15}$N$_{atm}$) of precipitation nitrate and springwater nitrate from the Fichtelgebirge. Details of sites are given in Table 1. The shaded area represents the range of NO$_3^-$$_{atm}$ produced by nitrification of soil nitrogen$^{13}$. **METHODS.** Spring water was sampled in November 1991, and March and May 1992. Atmospheric input was collected as rain or snow in a subset of sites and below the tree canopy. Natural isotope ratios were assessed following filtration with charcoal, cation exchange (Merck Kationenaustauscher l) 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 Hg(CN)$_2$ in an evacuated sealed tube to 550°C for 6 h. The CO$_2$ formed was converted to CO$_2$ by slowly cooling the tube.$^{14}$ 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 spectrometer.$^9$ The isotope ratios are reported in delta notation ($\delta^{15}$N, $\delta^{18}$O in %) relative to standard mean ocean water or to air nitrogen as the standard.$^8$ Repeated measurements of standard substances yielded means and standard deviations of $\pm0.3\%$ for $\delta^{15}$N (acetanilide, n = 105) and 22.4±0.55% for $\delta^{18}$O (NH$_4$NO$_3$, n = 7).
TABLE 1  Characteristics of sites studied

<table>
<thead>
<tr>
<th>Site no.</th>
<th>Site condition*</th>
<th>Atmospheric input†</th>
<th>Springwater output‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Healthy</td>
<td>NO₃ (mmol m⁻² yr⁻¹)</td>
<td>NH₄⁺ (µmol l⁻¹)</td>
</tr>
<tr>
<td>2</td>
<td>Declining, peaty soil</td>
<td>46</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>Slightly declining</td>
<td>57</td>
<td>107</td>
</tr>
<tr>
<td>4</td>
<td>Healthy</td>
<td>74</td>
<td>108</td>
</tr>
<tr>
<td>5</td>
<td>Slightly declining, limed</td>
<td>74</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>Slightly declining, limed</td>
<td>45</td>
<td>91</td>
</tr>
<tr>
<td>7</td>
<td>Strongly declining</td>
<td>88</td>
<td>96</td>
</tr>
<tr>
<td>8</td>
<td>Strongly declining</td>
<td>36</td>
<td>59</td>
</tr>
</tbody>
</table>

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.
§ Modelled from volume-weighted mean NO₃ concentration and seepage flow.

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; 700–1051 m above sea level) were selected from a total of 200 springs under investigation. 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 0.05–11 l s⁻¹. Nitrogen and sulphur deposition rates greatly exceed critical loads. Forest decline due to magnesium deficiency is widespread in the area 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 ± 8.8% (Fig. 1).

Springwater nitrate had δ¹⁵N values between −2 and +2‰, with δ¹⁸O between +1 and +33‰ (Fig. 1). Neither nitrification nor denitrification can explain these isotope ratios, as nitrification leads to δ¹⁸O of NO₃⁺ values of 8.8 and 5.8‰. The observed isotope ratios were caused by kinetic isotope effects accompanying denitrification of nitrate, a hypothetical NO₃⁻ substrate with δ¹⁵N between −63 and −19‰ has to be postulated, which is outside the range observed in terrestrial ecosystems. 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 have been determined previously 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 with 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.

![Graph](image-url)
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 zone. 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-queenschalced CaSiO₃ perovskite, stishovite and a sodic, aluminium 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 magnesium silicate perovskite nor magnesiowüstite, but instead consists of garnet rich in pyrope and almandine endmembers, stishovite, CaSiO₃ perovskite and an alumino phase with the Ca-ferrite structure.2 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 predictions2 that garnet might survive to depths of ~1200 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 iron3. 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 iron5. 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 ferro iron at pressures above 10 GPa. No such phenomena have subsequently been observed in multi-anvil experiments.5,7 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