Nitrate leaching from a sub-alpine coniferous forest subjected to experimentally increased N deposition for 20 years, and effects of tree girdling and felling

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Abstract Increased nitrogen (N) deposition rates were simulated for 20 years (1995–2015) by sprinkling rain water enriched with NH_4NO_3 ($+22 \text{ kg ha}^{-1} \text{ year}^{-1} \text{ N}$) in a small headwater catchment within a spruce (*Picea abies*) forest at Alptal (central Switzerland). The added N was labelled with $^{15}\text{NH}_4^{15}\text{NO}_3$ during the first year. A control catchment was labelled in years 6 and 8. NO_3^- leaching doubled in the N-addition catchment during the first year, resulting almost entirely from loss of ^{15}N -labelled NO_3^- . The proportion of added N leached as NO_3^- -N reached 1/3 after 5 years, then remained stable for the next 10 years, at $6.6\text{--}10 \text{ kg ha}^{-1} \text{ year}^{-1}$ compared with $1.4\text{--}2.9 \text{ kg ha}^{-1} \text{ year}^{-1}$ in the control catchment. In each catchment, half of the large trees were girdled during the 15th year and felled 1 year later to assess their role in soil N retention. Girdling and felling resulted in a strong increase in NO_3^- -N leaching from the N-addition catchment (up to $19 \text{ kg ha}^{-1} \text{ year}^{-1}$). The

increase was significantly smaller in the control (up to $4 \text{ kg ha}^{-1} \text{ year}^{-1}$). NO_3^- leached after tree girdling contained only 0.18% of the originally applied tracer in the control and none detectable in the N-addition catchment. The increased leaching was thus mainly from new N and due to reduced N immobilisation by trees rather than to increased N mineralisation and nitrification in the soil. Dissolved organic N leaching (average $6.1 \text{ kg ha}^{-1} \text{ year}^{-1}$), in contrast, was unaffected by the treatment.

Keywords Forest ecosystem · Nitrate leaching · Nitrogen deposition · Paired-catchment experiment · Tree girdling · ^{15}N isotope

Introduction

Nitrogen (N) is essential to any form of life and one of the major plant nutrients. The Earth's atmosphere is 78% N and is therefore the main pool of this element, but it exists in a form (N_2) that is not directly usable for most living organisms. It becomes biologically available only through the process of biological N fixation performed by symbiotic and non-symbiotic N-fixing bacteria, and, to a smaller extent, through oxidation by lightning (Galloway et al. 1995). Nowadays, however, N deposition is mainly the consequence of emissions from human activities. On the one hand, N is purposely converted to ammonium (NH_4^+) by the industrial Haber–Bosch process to produce fertilisers (Fields 2004; Galloway et al. 2003). The use of

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fertilisers is accompanied by an enrichment of entire agricultural ecosystems and thus also by emissions to the atmosphere, mainly by the volatilisation of ammonia (NH_3) (Bouwman et al. 2002). On the other hand, N oxides are emitted by all combustion processes, like those used in transport and industry (e.g., EPA 2010). Once in the atmosphere, these reactive N compounds can be transported at a regional to continental scale before being deposited on the surface as dry deposition of gases or aerosols or as wet deposition by precipitation. Emissions of reactive N and thus also N deposition have increased, especially from the 1950s to 1990s in Europe and North America. In the 1990s, inorganic N deposition (wet and dry) ranged from less than 1 to more than $75 \text{ kg N ha}^{-1} \text{ year}^{-1}$ over Europe (Dise and Wright 1995). Since then, it has slowly decreased there but increased strongly in regions with fast economic development like China.

Temperate forests are generally considered naturally N deficient and highly conservative in N use (Aber et al. 1989; Vitousek and Howarth 1991; Zhang et al. 2013). According to Aber et al. (1998), most of the nitrogen added to N-limited systems is taken up by organisms: by plant roots and their associated mycorrhizal symbionts, and comparatively less by soil microbes. In contrast, Stark and Hart (1997) hypothesised that microbial immobilisation is the primary mechanism of N retention. The seasonality of litter decomposition also plays a role in N immobilisation by the soil in deciduous forests (Goodale et al. 2015). Other studies have emphasised the role of non-biotic processes and of the C pool size in the incorporation of inorganic N into soil organic molecules (Davidson et al. 2003; Morier et al. 2010; Lewis et al. 2014). Overall, the relative importance of these processes is still controversial.

Forest canopies can intercept wet deposition in various forms (rain, snow, fog, or rime ice) (Bytnerowicz and Fenn 1996). Positive effects, such as enhanced tree growth, can result as long as N deposition is not excessive for a given ecosystem (Tamm 1991; Bytnerowicz and Fenn 1996). Further inputs of inorganic N, however, can lead to the eutrophication or N saturation of previously N-limited ecosystems (Aber et al. 1989; Dise and Wright 1995; Borken and Matzner 2004). A forest is generally considered N saturated when the vegetation no longer shows a positive growth response to further additions

of N (Nilsson 1986). Besides a levelling-off in foliar N concentrations, an increased leaching of nitrate (NO_3^-) is generally considered the main symptom of N saturation (Aber et al. 1995; Stoddard 1994; Gundersen et al. 1998; MacDonald et al. 2002). Atmospheric deposition of more than $9 \text{ kg N ha}^{-1} \text{ year}^{-1}$ can lead to significant NO_3^- losses in many European forests (Dise and Wright 1995) and this phenomenon is widespread for inputs greater than $25 \text{ kg N ha}^{-1} \text{ year}^{-1}$, showing that N deposition at such rates exceeds the retention capacity of the ecosystems. NO_3^- leaching from forest soils may thus contribute to contamination of groundwater in many regions, even if not as strongly as from agricultural soils (Borken and Matzner 2004; Rothe and Mellert 2004).

The relationship between N inputs and NO_3^- leaching is, however, not so tight. Other factors, like the C/N ratio of the soil, appear to play a role in NO_3^- leaching as well and can be used as a measure of the degree of N saturation (Gundersen et al. 1998; Lovett and Goodale 2011). The mechanisms by which deposited N is retained in the soil are thus decisive for its fate, both in the short and in the long term.

A number of investigations have been conducted in forest ecosystems in an attempt to evaluate the complex interactions in the N cycle processes and to measure the impact of N deposition by experimentally manipulating N input rates (Wright and Rasmussen 1998; Nadelhoffer et al. 1999a, b; Lamontagne et al. 2000; Elvir et al. 2006; Dail et al. 2009; Mineau et al. 2014). In Europe in the late 1980s, two research networks of field-scale manipulation experiments in coniferous forest ecosystems were established with this purpose in mind. The first network, NITREX, was used to investigate the direct and indirect effects of N inputs on soils, trees and other organisms and on processes in forest ecosystems, including NO_3^- leaching. In another network, EXMAN, the ecosystem sensitivity to NO_3^- leaching was studied, along with a number of other important environmental factors like N production and consumption (Tietema et al. 1997). These studies confirmed the role of the interaction between deposition rates and soil C/N ratio in determining how much N is lost in the form of NO_3^- leaching (e.g., Curtis et al. 2004).

NO_3^- leaching can additionally be affected by silvicultural practices. Rothe and Mellert (2004) affirmed that forest management can substantially

alter N cycling and thus N leaching. Ring (1995) observed increased N leaching after clear-felling of experimental plots that had been treated previously with ammonium nitrate over a 20-year period at a total rate ranging from 360 to 1800 kg N ha⁻¹. Clear-felling and soil preparation modify site conditions and can influence run-off water quality (Kubin 1998). However, the cutting of trees can reduce evapotranspiration and thereby significantly increase runoff, which may result in a dilution of water pollutants.

An N manipulation experiment was started in 1994 at the site of Alptal (Switzerland) as part of the NITREX research network. At this site, N was added as NH₄NO₃ to a small catchment in a *Picea abies* forest (Schleppi et al. 1998). In a paired-catchment approach, this treatment was compared to a control catchment receiving only unaltered rainwater. Under ambient conditions, NO₃⁻ leaching was observed throughout the year even though the trees were still slightly deficient in N (1.24% in current-year needles, Schleppi et al. 1998, 1999b). This finding was explained by the clay-rich soils and their preferential water flow paths (Hagedorn et al. 1999, 2001a). A hydrological end-member analysis showed that runoff water chemistry is similar to that of soil water in the mineral horizon during low flow, but it resembles a mixture of water from the topsoil and from precipitation when discharge is high (Hagedorn et al. 2000). As a result, NO₃⁻ concentrations in runoff water are similar to those in soil water, both in magnitude and in temporal patterns. Deeper in the soil, nitrate concentrations decrease due to denitrification (Hagedorn et al. 2001b). Denitrification at the site amounts to approximately 1 kg ha⁻¹ year⁻¹ (Mohn et al. 2000). The analysis of further rain and snow-melt events led to the conclusion that water enters the soil mainly through macropores, flows down to a depth of only 5–25 cm, reaches the water table on the gleyic horizon, and then flows laterally (Schleppi et al. 2004). This rapid subsurface flow enables the retention of NH₄⁺ but only a partial absorption of NO₃⁻ from rain or snow-melt.

In the first year of treatment, the added N was labelled with ¹⁵NH₄¹⁵NO₃. During this time, NO₃⁻ leaching approximately doubled in the treated catchment, corresponding to 12% of the tracer amount, while more than 60% of it was recovered in the soil pool (Schleppi et al. 1999a). Over the following 4 years, NO₃⁻ losses increased to 30% of the added N,

indicating that the ecosystem became progressively less able to retain further inputs, i.e., it became N saturated (Schleppi et al. 2004).

Even if trees took up only one tenth of the applied ¹⁵N (Schleppi et al. 1999a), their importance in N cycling in the ecosystem should not be neglected. To gain more insight into this topic, after 15 years of N addition, half of the trees >30 cm in diameter were girdled in both the control and the N-treated catchment. One year later, these trees were felled. Following this girdling and felling intervention, the main purposes of the present study were:

- (a) to determine the long-term effect of the N addition on nitrate leaching after the 7th year of treatment, i.e., 13 years after the results published by Schleppi et al. (2004);
- (b) to investigate if tree girdling and subsequent felling affected nitrate leaching, if possible to separate in time the effects of ceased active nutrient uptake after girdling from those due to the removal of trees by felling;
- (c) to compare the magnitude of effects of tree girdling and felling between the control catchment (ambient N deposition) and the catchment with long-term N addition, i.e., to assess if the N status of the forest interacted with the girdling and subsequent felling of trees;
- (d) to use the time series of NO₃⁻ leaching and the corresponding ¹⁵N signal to understand the underlying mechanisms of this leaching.

Materials and methods

Site description

The research site of the present study is located in the Alptal valley, in central Switzerland (47°03'N, 8°43'E), at 1200 m a.s.l. The parent rock material is Flysch, which is composed of sedimentary conglomerates with clay-rich schists. The main soil types are very heavy Gleysols, with an average of 48% clay, characterized by a low permeability and a water table close to the surface throughout the year (on average 23 cm deep, Krause et al. 2013). The slope is about 20% with a west aspect. The distinct microtopographical features are associated with different soil types: on mounds, umbric Gleysols with mor (raw

humus), Ah and an oxidized or partly oxidized Bw horizon are found, whereas mollic Gleysols are found in depressions, with an anmoor (muck humus) topsoil, a thin LF horizon and an almost permanently reduced Bg horizon (Hagedorn et al. 2001b). The gleyic Bw or Bg horizons start on average at 25 cm depth. Mounds and depressions are typically around 10 m in size. The pH increases with depth from 4.6 to 5.9 in the mineral soil of the mounds and from 5.4 to 6.9 in the depressions. Depending on the locations, annual net nitrification rates (down to 15 cm depth) are either positive or negative (N immobilisation). Overall, the net rate is not significantly different from zero (Hagedorn et al. 2001b).

The study area has a cool and wet climate, with an average annual temperature of 6 °C and average annual precipitation of 2300 mm, reaching a maximum of 270 mm in June and a minimum of 135 mm in October (averages over the duration of the experiment, 1994–2015). No trend in air temperature, precipitation amount or vapour pressure deficit was detected over these 21 years. However, a drier period occurred in the middle of the experiment, with the years 2003–2008 receiving 10% less precipitation than the overall average (Fig. 2). The site's forest is a naturally regenerating mature Norway spruce stand (*Picea abies* (L.) Karst., with 15% silver fir (*Abies alba* Mill.). The trees are up to 270 years old, have a dominant height around 30 m and a low leaf area index (LAI) of 3.8 (Schleppi et al. 1999b). Stems >10 cm in diameter are 430 ha^{-1} , corresponding to a total basal area of $41 \text{ m}^2 \text{ ha}^{-1}$. Under these trees, the ground vegetation is dominated by *Vaccinium myrtillus* and *Vaccinium vitis-idaea*. The waterlogged depressions are too wet for tree growth, and ground vegetation there is dominated by *Caltha palustris*, *Petasites albus*, *Poa trivialis* and *Carex ferruginea*. Rooting depth of all plants is limited to 10–25 cm depending on the microtopography (Schleppi et al. 1999b). Atmospheric deposition of inorganic N is 12 and $17 \text{ kg N ha}^{-1} \text{ year}^{-1}$ in bulk and throughfall, respectively (Schleppi et al. 1998).

Experimental catchments and N addition

Two forested catchments, each with a surface area of approximately 1500 m^2 , were delimited by trenches. These trenches were dug 1 year before measurements began and reach into the gleyic sub-soil, ensuring the

capture of sub-surface water flow (Schleppi et al. 1998). Polyethylene geotextiles were used to cover the inside and borders of the trenches to prevent erosion. No change of the vegetation along the trenches has been observed that would indicate an enhanced drainage of the soil along the trenches. Both catchments feature a similar proportion of mounds (approx. 40%) and depressions (approx. 60%). Overland flow has only been observed on very rare occasions during intensive thunderstorms. Water level is measured continuously in V-notch weirs at the bottom of the catchments. Water discharge is calculated from these measurements and averaged over 10-min periods (Schleppi et al. 1998). During 8% of the time (average over 21 years), the small experimental catchments did not produce any discharge. Both catchments always showed a rapid response to rain events and exhibited similar discharge peaks (Schleppi et al. 2004).

One year of measurements with weekly water analyses served as a calibration period. Increased N deposition was then simulated in one of these catchments by sprinkling NH_4NO_3 dissolved in rain water collected into a water tank (2000 L) from a polyethylene sheet (300 m^2) spread outside the forest. N addition occurred automatically when the tank was full, i.e., in small but frequent amounts: approximately 200 times per year for an average of $22 \text{ kg N ha}^{-1} \text{ year}^{-1}$. In a paired-catchment design, the other catchment served as a control and received the same amount of rain water without any added N (Fig. 1).

The automatic irrigation was replaced during winter by the occasional application of a concentrated NH_4NO_3 solution on the snow cover with a backpack sprayer. During the first year of treatment (April 1995–March 1996), the added N was labelled with $^{15}\text{NH}_4^{15}\text{NO}_3$. The amount of added tracer was $219 \text{ mmol } ^{15}\text{N m}^{-2}$ yielding an enrichment of 0.88 at.%. The control catchment was also labelled with ^{15}N , but $^{15}\text{NH}_4$ and $^{15}\text{NO}_3$ were added separately (Providoli et al. 2005). First, K^{15}NO_3 (0.17 mmol m^{-2} ; 99 at.%) was applied between July 2000 and June 2001. $^{15}\text{NH}_4\text{Cl}$ (0.7 mmol m^{-2} ; 99 at.%) was then applied from July 2002 to June 2003. These tracers, dissolved in deionised water (10 L per catchment and application), were applied with a backpack sprayer, weekly during the vegetation period and fortnightly in winter. The different application forms ($^{15}\text{NO}_3$ and $^{15}\text{NH}_4$ together or separately) and methods (automatic irrigation or backpack sprayer) would not

Fig. 1 Setup of the nitrogen addition experiment at Alptal, central Switzerland. Catchment 3 (control, wet grassland) is not part of the present report

allow a direct comparison of the labelling in the two catchments in the short term. However, Providoli et al. (2006) showed that differences in recovery rates in the different soil pools practically disappeared within 1 week after the application of either $^{15}\text{NO}_3^-$ or $^{15}\text{NH}_4^+$, thus enabling comparison of the fate of the tracer in the long term.

In June 2009 (15th year of the N treatment), 15 trees per forested catchment, all with a diameter at breast height >20 cm, were girdled by the complete removal of a 30-cm wide strip of the bark and cambium around the stem (Krause et al. 2013). The trees were chosen across each catchment as representing a heavy selective cutting by 38% of the total basal area of all trees >10 cm at breast height. One year later, the girdled trees became infested by bark beetles (*Ips typographus*). To prevent spreading of the infestation, trees were felled in August 2010. The branches (with needles still attached) were left on site, while the boles were removed by helicopter. Within 2 years after girdling, neither soil temperatures (7.1°C on average) nor soil water depths (23 cm on average) were affected. (Krause et al. 2013).

Sampling and analyses

Runoff samples were collected proportionally to the discharge at the V-notch weirs (1 aliquot every 200 L), bulked and analysed fortnightly for NO_3^- and NH_4^+ by ion chromatography and by flow injection, respectively (Schleppi et al. 1998). Total dissolved N was analysed as NO_3^- after persulfate oxidation (Hagedorn and Schleppi 2000) and dissolved organic N (DON) was calculated as total minus inorganic N. For ^{15}N analyses, water samples were further pooled proportionally over 3 months. $^{15}\text{NO}_3^-$ in the obtained samples was analysed by a modified ammonium diffusion technique (Downs et al. 1999; Schleppi et al. 2006a). Shortly, NO_3^- was reduced to NH_4^+ with Devarda's alloy, and NH_4^+ was converted to NH_3 and captured in fibreglass filters drenched with citric acid and enclosed in PTFE membranes. The filters were analysed by mass spectrometry. Total ^{15}N in runoff water was measured by lyophilisation followed by mass spectrometry analysis. The same analytical procedures were applied to precipitation and through-fall samples collected from an open area and from the

forested catchments, respectively (Schleppi et al. 1998). These samples were obtained from two rain collectors (snow buckets in the winter) per catchment, except for throughfall samples from before 2006, which were obtained from four collectors. While NH_4^+ concentrations were too low in runoff water to allow for isotope analyses, such analyses were completed for precipitation water by inserting a diffusion without Devarda's alloy before a diffusion with this alloy.

Soil cores were taken from the nodes of a grid of 8 m mesh size, separated by horizon, recombined by morphological type (corresponding to the microtopography) and analysed for total C, N and ^{15}N contents as described in Providoli et al. (2005). This sampling was done in 1997, 2001, 2003 and 2009 for the control catchment and in 1997, 2002 and 2009 for the N-addition catchment (Krause et al. 2012).

Calculation of recovery rates

The N pools of the ecosystem were calculated from their masses and N concentrations according to Providoli et al. (2005). Tracer fractions of the pools and fluxes were calculated as the molar ratio of tracer N to total N content, and the tracer recovery was calculated as the proportion of the applied tracer found in any particular pool or flux. For details see Eq. 4 for the tracer fraction (X) and Eq. 5 for the recovery rate (Z) in Providoli et al. (2005).

Statistical analyses

Two-way analyses of variance were performed comparing three selected periods and four seasons per year. Starting 2 years after the last labelling (to let ^{15}N partitioning reach stable values), the periods examined were before girdling (2005–2009), between girdling and felling (summer 2009 to spring 2010) and after felling (since summer 2010). The specified seasons were winter (January–March), spring (April–June) summer (July–September), and autumn (October–December). The means presented here are all least-squares means from such analyses.

Multiple regressions based on time series were conducted to assess which factors controlled the variability of NO_3^- concentrations in runoff water from each catchment. All fortnightly measurements falling entirely between 21 May and 28 October were

considered; thus periods with snow cover were excluded. The following independent variables were considered: NO_3^- concentration in throughfall, discharge volume, soil temperature (at 20 cm below ground) and leaching ratio of Cl^- (concentration in runoff/concentration in precipitation). NO_3^- concentrations and discharge volume were log-transformed to improve their normality. The basal area of the trees was also tested as a further independent variable.

Results

Soil C/N ratio and N leaching

The C/N ratio in the soil of the treated catchment decreased over time, both in the organic LF and in the mineral A horizons (Table 1). In spite of an apparent increase in the LF horizon between 2002 and 2009, there was no significant non-linearity in this trend.

Over the 21 years of the experiment, the correlation between the discharges of the two catchments (at a 10-min frequency) was 0.987. The runoff coefficient of the control catchment (0.71) was slightly lower than that of its N-addition counterpart (0.74). A sharp increase in NO_3^- leaching during the first year of NH_4NO_3 treatment (1995–1996) was followed by a progressive increase during the 6 subsequent years (1996–2002). From the 8th to 14th year of N addition, NO_3^- -N leaching decreased from 9.2 to 6.6 $\text{kg ha}^{-1} \text{ year}^{-1}$, while the control catchment lost between 1.5 and 2.0 $\text{kg ha}^{-1} \text{ year}^{-1}$ (Fig. 2). In spite of a decreasing trend in absolute numbers, the difference between the two catchments (i.e., the extra NO_3^- -N leached due to the treatment) remained stable at approximately 1/3 when expressed as a proportion of the added N. In this regard, 2003 was an exception: NO_3^- leaching itself remained at a level similar to that in previous years and occurred mainly during the spring and following winter, but because of summer drought conditions there was much less rain water available for the automatic N addition by irrigation. The added N amount was thus low and the ratio of extra leaching to added N was higher. Other differences between years in the amount of added N occurred because of total precipitation amounts, proportions of snow, occurrence of frost and some irregularities in the functioning of the technical equipment. Over the period from the pre-treatment year to the 14th year of N addition

Table 1 C/N ratio in the upper soil horizons of the catchment with NH_4NO_3 addition

Horizon	Depth (cm)	C/N 1997	C/N 2002	C/N 2009	Yearly change	P value
LF	0–5	20.3	17.7	18.4	−0.16	0.074
A	5–10	17.4	17.3	16.2	−0.10	0.026
LF + A	0–10	18.4	17.4	17.1	−0.10	0.017

Standard error is 0.66, $n = 8$ samples out of 20 soil cores in an $8 \text{ m} \times 8 \text{ m}$ grid

Fig. 2 Nitrate and DON leaching from the experimental catchments, from 1 year before and during 20 years of NH_4NO_3 addition (on average $22 \text{ kg N ha}^{-1} \text{ year}^{-1}$), including ^{15}N in the first year. Leaching of $^{15}\text{NO}_3^-$ is indicated by hatching (visible only during two years in the N-addition catchment at the scale of the graph). The black line represents the extra NO_3^- N output (as a difference between both catchments) divided by the experimental N addition. Discharge (in the top panel) is indicated as average of both catchments

(1994–2009), yearly precipitation showed a decreasing trend ($P = 0.066$) and NO_3^- leaching from the control plot decreased significantly ($P < 0.0001$).

Girdling trees in the 15th treatment year (June 2009) and felling them the year after (August 2010) affected NO_3^- leaching in both catchments (Fig. 3).

Compared to the 4 preceding years, NO_3^- leaching strongly increased starting in autumn 2009 (control catchment: $P < 0.0001$, N-addition catchment: $P < 0.0003$). Analysing the different seasons separately also showed significant increases, except for winter, when there was only a tendency in this direction. After a peak in summer 2010 when the trees were felled, NO_3^- -N leaching remained high for the next 3 years, between 12 and 15 $\text{kg ha}^{-1} \text{ year}^{-1}$ in the N-addition catchment and between 2.5 and 4.5 $\text{kg ha}^{-1} \text{ year}^{-1}$ in the control (Fig. 2). In all 5 years following tree girdling, the difference between the catchments amounted to 10 $\text{kg ha}^{-1} \text{ year}^{-1}$ or more and was thus larger than in the treatment years before girdling ($P < 0.0001$). Expressed as a proportion of the added N, this extra leaching from the treated catchment peaked at 79% in the 16th year (2010–2011) then decreased again to reach approximately 50% in the 18th and 19th years (2012–2014).

In 54% of the runoff samples, NH_4^+ concentrations were below the detection limit of 0.012 mg/L. Therefore, only a rough calculation of NH_4^+ leaching can be given: 0.18–0.27 $\text{kg ha}^{-1} \text{ year}^{-1}$ for the control (i.e., roughly 1/10 of NO_3^- leaching) and 0.27–0.35 $\text{kg ha}^{-1} \text{ year}^{-1}$ for the N-treated catchment over the whole duration of the experiment. A random intervention analysis of the time series did not reveal any effect of the N addition, of tree girdling or

of tree felling. DON leaching showed large differences between years, but only small differences between catchments (Fig. 2). Unfortunately, analytical blanks were too high during the first months of the experiment (Hagedorn and Schlegli 2000). Therefore, reliable DON measurements could only be obtained for the last 8 weeks of the calibration period. These results had thus to be extrapolated to a whole year by taking the seasonality of concentrations into account. In comparison with this truncated calibration period, the N-addition treatment did not appear to increase DON leaching (Fig. 2). Over the 20 years of N addition, the difference between the two catchments was remarkably constant and showed neither a significant trend over time nor an effect of girdling and felling trees.

Due to the small number of rain gauges in the catchments, it was not possible to estimate if through-fall N deposition (average 17 $\text{kg ha}^{-1} \text{ year}^{-1}$ before girdling) changed after tree felling. However, a comparison with N deposition in open-land precipitation (12 $\text{kg ha}^{-1} \text{ year}^{-1}$) indicates that it may have decreased by up to 2 $\text{kg ha}^{-1} \text{ year}^{-1}$.

Recovery of ^{15}N tracer in N leaching

The $\delta^{15}\text{N}$ signal in NO_3^- was between -10 and $+4\text{‰}$ in the years before tree girdling in the runoff water from the control catchment (Fig. 4). In the N-addition

Fig. 3 Nitrate concentrations (lines) and fluxes (bars) in discharge-proportional runoff samples from the experimental catchments from 2005 to 2013 (years 11–19 of N addition)

catchment, values between -6 and $+3\text{‰}$ were measured. Starting in the autumn after tree girdling (2009), $\delta^{15}\text{N}$ in the control catchment remained above -2‰ for almost 4 years. The increase from pre-girdling to post-felling was significant (Tukey test: $P = 0.007$). The calculated tracer recovery was also significantly higher after felling than before girdling ($P = 0.0002$, Fig. 5). The accumulated ^{15}N recovery over the 4 years following girdling was 0.18% of the tracer applied between 2000 and 2003. In the N-addition catchment, however, no trend in $\delta^{15}\text{N}$ could be observed (Figs. 4, 5) and there was no difference in tracer recovery between the reference (pre-girdling) period and the post-felling years.

The $\delta^{15}\text{N}$ in leached NO_3^- can also be compared with ^{15}N abundances in precipitation and soil. Precipitation water analysed between 1994 and 2002 showed, on average, -4.1‰ $\delta^{15}\text{N}$ in NO_3^- and -7.0‰ in NH_4^+ (Table 2). Soil analyses done in 2009 revealed a tracer accumulation in the LF and A soil horizons. If we compare the $\delta^{15}\text{N}$ values in leached NO_3^- with those in precipitation NO_3^- and in the LF horizon, a mixing ratio between these two potential sources can be estimated (Table 2). NO_3^- in runoff appears to come mainly (68–98%) from NO_3^- in precipitation, even if some contribution from the soil

can be seen in the N-addition catchment as well as in the control catchment after tree girdling and felling.

No changes due to girdling and felling were detected in the $\delta^{15}\text{N}$ values of total dissolved N. Over 6 years from 2007 (before girdling) to 2013 (after felling), $2.2 \pm 1.1\text{‰}$ were measured in the control, $1.3 \pm 1.1\text{‰}$ in the N-addition catchment. Reduced ^{15}N amounts (DO^{15}N and, to a much smaller extent, $^{15}\text{NH}_4^+$) can be calculated by subtracting $^{15}\text{NH}_3^-$ from total dissolved ^{15}N . This calculation gave $3.2 \pm 1.6\text{‰}$ for the control and $4.0 \pm 4.5\text{‰}$ in the N-addition catchment.

Fortnightly time series

In a regression analysis, NO_3^- concentration integrated fortnightly in discharge water from the control catchment was significantly affected by the NO_3^- concentration in throughfall in the same periods (Table 2). Further significant variables were the basal area of the trees, the leaching ratio of Cl^- , and the discharge volume. The soil temperature did not have a significant effect. With all variables included, the model had a coefficient of determination (R^2) of 0.55. Applying the same analysis to the N-addition catchment gave a similar model but with a lower R^2 of 0.36.

Fig. 4 $\delta^{15}\text{N}$ in nitrate from runoff water of the experimental catchments from 2005 to 2013 (years 11–19 of N addition). Dashed lines connect data across a missing value

Fig. 5 ^{15}N tracer recovery in nitrate from runoff water of the experimental catchments from 2005 to 2013 (years 11–19 of N addition). Dashed lines connect data across a missing value

Table 2 ^{15}N abundance in pools and fluxes, and mixing ratio of NO_3^- derived from the two potential sources (soil LF horizon and precipitation NO_3^-)

Pool/flux	N species	Period	$\delta^{15}\text{N}$		Precipitation mixing ratio	
			Control	N addition	Control	N addition
Runoff (leaching)	NO_3^-	2005–2009 ^a	−3.8	−0.5	0.98	0.72
Runoff (leaching)	NO_3^-	2009–2010 ^b	−1.5	−1.4	0.82	0.79
Runoff (leaching)	NO_3^-	2010–2013 ^c	0.4	−0.7	0.68	0.73
Yearly litterfall	Total	2009	8.5	4.0		
LF horizon	Total	2009	10.1	8.7		
A horizon	Total	2009	0.5	2.7		
B horizon	Total	2009	1.0	1.7		
Precipitation	NO_3^-	1994–2002	−4.1			
Precipitation	NH_4^+	1994–2002	−7.0			

^a Before tree girdling

^b Between girdling and felling

^c After tree felling

Discussion

During the first 3 years of the experiment, NO_3^- leaching from the control catchment was relatively high compared to subsequent years (Fig. 2). This observation may be due to digging the trenches 1 year earlier, but it does not impair the comparison with the treated catchment because both were established in the same way at the same time. The slightly lower runoff coefficient measured in the control catchment (0.71 vs. 0.74 in the N-addition catchment) is likely due to the fact that its south and east borders are not delimited by trenches but by soft hills on which the water divide

cannot be determined very precisely. Both small experimental catchments are in this regard very similar to a natural forested catchment in the same valley (Vogelbach, size 155 ha, runoff coefficient 0.73) (Burch et al. 1996).

With an overall average of $6.1 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Fig. 2), DON represented a large fraction of N leaching from our experimental catchments. DON leaching did not respond to the long-term addition of NH_4NO_3 or to tree girdling and felling. However, large differences were observed between years, with largest amounts measured in 1995 and 2001. In both cases, March to August were the months with the

Table 3 Regressions of NO_3^- concentration in runoff water from the experimental catchments (in mg L^{-1} , after log-transformation) against five independent variables

Independent variable	Control catchment ($R^2 = 0.55$)			N-addition catchment ($R^2 = 0.37$)		
	Coefficient	Standard error	P value	Coefficient	Standard error	P value
NO_3^- -N concentration in throughfall (mg L^{-1}) ^a	0.88	0.10	<0.0001	0.52	0.08	<0.0001
Tree basal area ($\text{m}^2 \text{ha}^{-1}$) ^b	−0.115	0.015	<0.0001	−0.101	0.015	<0.0001
Cl^- leaching ratio	0.069	0.016	<0.0001	0.065	0.017	0.0001
Discharge volume (mm) ^a	−0.146	0.046	0.0017	−0.222	0.034	<0.0001
Soil temperature ($^{\circ}\text{C}$)	−0.014	0.011	0.19	−0.013	0.011	0.24

Fortnightly data falling entirely between May 21 and October 28 of each year (1994–2014) were considered. For the N-addition catchment, NO_3^- in throughfall includes NO_3^- from the treatment

^a Log-transformed

^b Living trees >10 cm diameter at breast height

highest DON fluxes. They resulted from the combination of high concentrations with high discharges (1200–1300 mm in 6 months). In a detailed study on the same catchments, Hagedorn et al. (2001a) already noted that DON concentrations do not decrease much or even increase with water discharge, unlike most other solutes. No decrease was found either in the present study. From qualitative analyses of DON, Hagedorn et al. (2001a) concluded that DON leaching is due both to DON from throughfall and from flushing from the soil, especially when the water table rises to the upper soil layers. A significant correlation between concentrations in throughfall and in runoff could also be found in the present study ($R = 0.55$). Because DON concentrations and fluxes did not change with girdling and felling, it is not surprising that their ^{15}N labelling was not affected either.

As shown by the analysis of precipitation events (Hagedorn et al. 2001b; Schleppi et al. 2004), including $^{15}\text{NO}_3^-$ labelling (Providoli et al. 2005), NO_3^- leaching at the Alptal site is largely due to the preferential flow of NO_3^- from precipitation through the upper soil and then laterally as subsurface flow towards water channels. As a consequence of the experimental N addition, NO_3^- leaching increased compared with the control and with the calibration period. Even if a single calibration year is short for a paired-catchment experiment, this increase was highly significant (random-intervention analysis: $P < 0.00001$). In the 6 following years, the potential of the forest ecosystem to retain N appeared to decrease in parallel with the C/N ratio of the upper soil. This

pattern was interpreted as a progressive N saturation of the ecosystem (Schleppi et al. 2004, 2006b), in line with the results of Emmett et al. (1998a), who showed that the N retention capacity of coniferous forests is linked to the C/N ratio of the forest floor. The ability of soils to retain mineral N has also been related to the C pool size in hardwood forests (Lewis et al. 2014; Lovett and Goodale 2011). In our study, the previously observed trend of more and more NO_3^- leaching was thus expected to continue as N accumulated further in the soil. Soil C and N concentrations themselves were too variable to show any tendency (data not shown), but a decreasing C/N ratio of $0.1 \text{ kg kg}^{-1} \text{ year}^{-1}$ in the 10 upper cm (Table 1) is a clear sign of such an accumulation. If we suppose a constant C pool size, the measured decrease corresponds to an average increase of the N pool size of $16 \text{ kg ha}^{-1} \text{ year}^{-1}$, or 3/4 of the added N amount. In spite of the relatively low precision of such a calculation, it is nevertheless in line with our reported ^{15}N retention in the soil (Schleppi et al. 1999a).

Given this ongoing decrease in the C/N ratio (Table 1), it was unexpected that NO_3^- leaching decreased slightly between the 7th and 14th years of N addition. This result can partly be explained by the fact that these years were relatively dry: first, because this reduces leaching overall (as shown also in the control catchment) and second, because there was less rain water available for N addition via sprinklers. In fact, during 5 out of the 6 years starting in the 9th treatment year, the amount of N added was below 20 kg ha^{-1} compared to the long-term average of 22 kg ha^{-1} .

Accounting for the variability between yearly precipitation amounts and other meteorological parameters, NO_3^- leaching can thus be considered stable over a 10-year period. In other words, the N saturation level reached after 5 years of N addition was sustained for the next 10 years. Based on the fast $^{15}\text{NO}_3^-$ immobilisation in the Alptal soil (30% within 1 h reported by Providoli et al. 2006), it seems that part of the deposited N in this system is rapidly chemically bound to the soil organic matter and that this process is the first to saturate as the C/N ratio decreases, reducing the availability of binding sites. According to this interpretation, uptake by microbes and roots would be more constant over time, which would explain why the N retention of the forest stabilised at around 1/3 of the deposition after a few years. In this regard, our results are in agreement with the review by Aber et al. (1998), which underlined the importance of mycorrhizal roots for the retention of N in soils.

Our analysis of the fortnightly concentration time series (Table 3) confirms a strong link from the atmospheric deposition to the leaching of NO_3^- . This result contradicts findings of Berger et al. (2009), also on Flysch parent material, that NO_3^- production in the topsoil was a dominant process. At the Alptal site, no net nitrification occurs in the topsoil (Hagedorn et al. 2001b) and it is thus not surprising that soil temperature (as a determinant of its biological activity) does not appear to play a substantial role in NO_3^- leaching during the snow-free season. The negative sign of the corresponding coefficients could even be a indication that immobilisation would increase with soil temperature. A highly significant factor in our regression was the basal area of the trees (with a negative sign). Contrary to the other time series variables considered here, basal area does not vary stochastically from one time point to the next but only with tree growth, tree mortality (one tree lost in each catchment during the Lothar storm in December 1999) and especially tree felling. A negative regression parameter can thus be interpreted as extra leaching due to the reduced tree N uptake after our girdling and felling treatments (2009–2010). This finding underlines the importance of functioning roots with their rhizosphere relative to free-living soil microorganisms in the retention of NO_3^- . Further significant factors in the regressions were the Cl^- leaching ratio and the discharge volume. As another anion, but practically without biological interactions, Cl^- is indicative of the hydrological

behaviour of NO_3^- . These two factors can thus be considered linked to the movements of water in the soil, including temporary storage and dilution effects. In summary, the fortnightly data suggest that NO_3^- deposition is the dominant factor driving NO_3^- leaching, tree uptake (represented by basal area) and soil hydrology (represented by Cl^- leaching) also matter, but bulk-soil biology (represented by soil temperature) has no significant effect. Overall, with R^2 values of 0.55 and 0.37, the considered factors explain a large part of the variability in NO_3^- concentrations in the discharge from our experimental catchments.

Other long-term N-addition experiments in forested headwater catchments have been conducted in Gårdsjön, Sweden, Bear Brook, Maine, USA and Fernow, West Virginia, USA (Moldan and Wright 2011; Fernandez et al. 2010; Adams et al. 2006). At all three of these sites, NO_3^- leaching increased and then more or less stabilised, with variations from year to year ascribed to the timing of N addition and to weather conditions. NO_3^- leaching was the smallest at Gårdsjön, where the ambient N deposition is the lowest and the soil C/N ratio is the highest. In that experiment, NO_3^- -N losses slowly increased from 0 to approximately 10% of the N input over 15 years. NO_3^- leaching was greatest in Fernow, both in terms of absolute fluxes and in proportion to the N input (approx. 30%). This site is subjected to an ambient N deposition comparable to that at Alptal. Bear Brook showed a response that was intermediate between Gårdsjön and Alptal. Together, these studies confirm that NO_3^- leaching is a function of the history and N status (with soil C/N ratio as an indicator) of the site and of the current N deposition (Dise and Wright 1995; Gundersen et al. 1998).

As also observed by Moldan and Wright (2011) at Gårdsjön, NO_3^- concentrations at Alptal were higher during the dormant season. Until girdling and felling (years 15 and 16, respectively), the largest losses of NO_3^- occurred during snowmelt (Schleppi et al. 2004). After girdling, however, NO_3^- concentrations in runoff remained high during the growing season, especially in fall 2009 and summer 2010. The increase in nitrate leaching was much larger in the N-addition catchment but was also significant in the control catchment. However, measurements of soil CO_2 efflux from the soil before and after girdling and felling did not show any sign of increased mineralisation (Krause et al. 2013). Edwards and Ross-Todd (1979) found

increased concentrations of NO_3^- in soil water after girdling tulip poplar (*Liriodendron tulipifera* L.) trees, resulting in losses of NO_3^- below the root zone. Likewise, elevated concentrations and fluxes of NO_3^- were measured after girdling eastern hemlocks (*Tsuga canadensis* (L.) Carrière) (Yorks et al. 2003). Zeller et al. (2008) reported increased N mineralisation after girdling Norway spruce trees, resulting in higher NO_3^- concentrations in the soil. Similar effects were reported by Falxa-Raymond et al. (2012) after girdling oaks (*Quercus rubra* L. and *Q. prinus* L.). Dannenmann et al. (2009) also observed increased NO_3^- concentrations in small plots where beech trees (*Fagus sylvatica* L.) had been girdled, but with no significant difference in gross N mineralisation. In the study by Trahan et al. (2015), however, NH_4^+ concentrations increased, but there was no effect on NO_3^- , and dissolved organic N (DON) decreased after girdling. Together, these studies suggest that different microbial N transformations may be affected differently but that concentrations of inorganic N generally increase in the soil after girdling trees. Tree death after insect outbreaks has been reported to have similar effects (Huber 2005; Trahan et al. 2015).

In our experiment, root starch concentrations started to decrease within 1 month after girdling had interrupted the transport of photosynthates from the canopy to the roots (Krause et al. 2013). This change certainly affected the whole root and rhizosphere metabolism, including N uptake and the energy-consuming NO_3^- assimilation. Tracer applications to the experimental catchments resulted in the presence of a ^{15}N signal in the soil, which can help us propose mechanisms involved in the NO_3^- leaching observed after girdling (see Providoli et al. 2005; Krause et al. 2012, for further details about the fate of the tracer before girdling). Because the $\delta^{15}\text{N}$ signal in the soil was a difference of only a few ‰, it is in the same order of magnitude as discrimination effects expected as a result of the changing N saturation of the forest (Emmett et al. 1998b). For this reason, we do not compare the abundances measured after girdling or felling with those measured prior to the experiment but with those obtained in the few years just before girdling. In the N-addition catchment, the large increase in NO_3^- leaching after girdling and felling was not accompanied by a change in $^{15}\text{NO}_3^-$ abundance, which means that no increase in mineralisation from the soil was detectable compared to the 4 years

before girdling, which is in line with the absence of any change in soil respiration reported by Krause et al. (2013). In the control catchment, the increase in NO_3^- leaching was much smaller but contained a significant amount of tracer. This difference may be explained by the timing of the labelling, which was 14 years before girdling in the N-addition catchment but only 8 years (for the most part) in the control. This interpretation cannot be directly tested, but it would be in line with the fact that the $\delta^{15}\text{N}$ signal of the control catchment varied more with time than that of the N-addition catchment, which points to a further stabilisation of the tracer during this 6-year shift in the timing of labelling. As proposed by Morier et al. (2010) for this site, such a stabilisation may arise from the biological recycling of N in the soil, which leads to a progressive shift from available towards recalcitrant N. In the control catchment, the mixing model that we applied showed an increase in the proportion of soil-derived N in leached NO_3^- , from almost nothing before girdling to about 1/3 after tree felling. Even if this mixing model with only two sources is over-simplified, it shows that tree girdling and felling remobilised some of the N that had entered the soil as deposition a few years before. If the A mineral horizon had been taken as an end-member instead of the LF layer, the estimated contribution from the soil would have been higher (details not shown). Because of the low redox potentials in the mineral soil (Hagedorn et al. 2001b), however, nitrification is limited to a thin soil layer, at least in microtopographic depressions. Further, the NO_3^- concentrations in soil water at 5 cm depth are very similar to those in runoff, while at 10 cm depth they are clearly lower. For these reasons, the LF horizon is certainly a better end-member than the A horizon. Nonetheless, it appears that most of the leached N was recent, as was the case before girdling in this experiment (Schleppi et al. 1999a; Providoli et al. 2005) and in the Gårdsjön study (Moldan and Wright 1998; Kjonaas and Wright 2007). Girdling and felling trees thus appear to further reduce the immobilisation of newly deposited N. The most likely explanation is the reduced or lack of N uptake by roots and mycorrhizae, as this is the most direct effect that girdling has below ground. The duration of the leaching peak observed here (6 years) is in line with other studies (Schleppi 2011). It is certainly related to the development of shrubs and herbaceous species under the new canopy gaps, especially blackberries

(*Rubus fruticosus* and *R. saxatilis*) in the N-addition catchment (data not shown).

Felling trees has often been reported to increase NO_3^- leaching in catchment studies (review by Schleppi 2011). There are, however, studies in which no such effect was found. Fukuzawa et al. (2006), for example, did not find a significant increase in NO_3^- concentration in stream water during the growing season after tree cutting of a cool-temperate forested watershed. Comparing and interpreting tree-felling experiments is more difficult than it is for girdling experiments because their impact depends on which parts of the trees are removed or left on site and because the soil is disturbed to varying degrees depending on the machines used. In our case, bole wood was removed by helicopter and the soil disturbances were thus kept minimal. This fact probably explains why NO_3^- leaching barely increased further when the (previously girdled) trees were cut and removed.

The predominance of recently deposited N in leached NO_3^- in our experiment, both after N addition and after tree girdling, is in the upper range compared with studies on natural abundances of both ^{15}N and ^{18}O isotopes in NO_3^- (Mayer et al. 2002; Stoewer et al. 2015; Rose et al. 2015a, b). In the streams, rivers or groundwater bodies studied or reviewed by these authors, most NO_3^- appeared to be derived from nitrification. The high proportion of precipitation-derived, unprocessed NO_3^- in our site can be explained by a combination of several factors, all of which were mentioned by Rose et al. in their review (2015a) or in their study at the Fernow experimental site (2015b). First, because precipitation-derived NO_3^- is higher during storm-flow than during baseflow, the discharge-proportional sampling that we used takes this NO_3^- better into account than less frequent and non-proportional sampling schemes (Schleppi et al. 2006c). Further, the small size of the experimental catchments and the absence of a riparian zone essentially prevent any in-stream denitrification. The importance of preferential water flow paths in the gleyic soils of our site (Hagedorn et al. 1999, 2001b) also physically limits the contact between water and soil. Finally, the large proportion of precipitation falling as snow (one third) concentrates a large input of NO_3^- into a short period of snow-melt when biological uptake by soil microbes and roots is low.

Conclusions

Our previous observations from the Alptal N-addition experiment have always highlighted the importance of preferential water flow paths in the soil, with associated rapid leaching of NO_3^- derived directly from deposition. This interpretation was confirmed in the present study by a strong relationship between concentrations in leaching and atmospheric deposition. A fast (probably partly abiotic) immobilisation appeared to be a key process in counteracting this direct leaching, but its effectiveness decreased with time and with the C/N ratio of the upper soil as the N addition continued. In the additional N treatment years reported here, however, NO_3^- leaching remained more or less stable over a decade, until roughly half of the large trees were girdled then felled. Girdling induced a marked increase in NO_3^- leaching in both the control and the N-addition catchment. This increase was expected because it has been reported in other comparable studies, but the present experiment revealed a new aspect: an interaction between girdling and N status resulting from the N deposition history. Indeed, the increase in NO_3^- leaching was much more pronounced in our N-addition catchment, i.e., in the catchment that had experimentally reached a higher level of N saturation. This difference between the two catchments highlights that both the N uptake by the trees and the N status of the soil control the N retention of the forest. In other words, a higher degree of N saturation makes the ecosystem much more susceptible to NO_3^- leaching in the case of a disturbance.

The importance of living roots was demonstrated by the fact that girdling and then felling the trees led mainly to leaching of ^{15}N -unlabelled, thus new, NO_3^- . Only a small proportion of N was remobilised from the previously ^{15}N -labelled soil in the control catchment, and no measurable N was remobilised from the N-addition catchment. The increased NO_3^- leaching was thus caused more by a lack of immobilisation rather than by an increased mineralisation and nitrification in the soil (which would have caused an enrichment in $^{15}\text{NO}_3^-$). It must be noted, however, that the direct disturbance of the soil was minimal in our girdling and felling experiment. In commercial harvest operations and in the case of windthrow, the direct impact on the soil would be larger and may expose soil N to increased mineralisation.

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