

# RETENTION AND LEACHING OF ELEVATED N DEPOSITION IN A FOREST ECOSYSTEM WITH GLEYSOLS

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**Abstract.** The responses of nitrogen transformations and nitrate ( $\text{NO}_3^-$ ) leaching to experimentally increased N deposition were studied in forested sub-catchments (1500 m<sup>2</sup>) with Gleysols in Central Switzerland. The aim was to investigate whether the increase in  $\text{NO}_3^-$  leaching, due to elevated N deposition, was hydrologically driven or resulted from N saturation of the forest ecosystem. Three years of continuous N addition at a rate of 30 kg  $\text{NH}_4\text{NO}_3\text{-N ha}^{-1} \text{ yr}^{-1}$  had no effects on bulk soil N, on microbial biomass N, on  $\text{K}_2\text{SO}_4$ -extractable N concentrations in the soil, and on net nitrification rates. In contrast, N losses from the ecosystem through denitrification and  $\text{NO}_3^-$  leaching increased significantly. Nitrate leaching was 4 kg N  $\text{ha}^{-1} \text{ yr}^{-1}$  at an ambient N deposition of 18 kg N  $\text{ha}^{-1} \text{ yr}^{-1}$ . Leaching of  $\text{NO}_3^-$  at elevated N deposition was 8 kg N  $\text{ha}^{-1} \text{ yr}^{-1}$ . Highest  $\text{NO}_3^-$  leaching occurred during snowmelt. Ammonium was effectively retained within the uppermost centimetres of the soil as shown by the absence of  $\text{NH}_4^+$  in the soil solution collected with micro suction cups. Quantifying the N fluxes indicated that 80% of the added N were retained in the forest ecosystem. Discharge and  $\text{NO}_3^-$  concentrations of the outflow from the sub-catchments responded to rainfall within 30 min. The water chemistry of the sub-catchment outflow showed that during storms, a large part of the runoff from this Gleysol derived from precipitation and from water which had interacted only with the topsoil. This suggests a dominance of near-surface flow and/or preferential transport through this soil. The contact time of the water with the soil matrix was sufficient to retain  $\text{NH}_4^+$ , but insufficient for a complete retention of  $\text{NO}_3^-$ . At this site with soils close to water saturation, the increase in  $\text{NO}_3^-$  leaching by 4 kg N  $\text{ha}^{-1} \text{ yr}^{-1}$  through elevated N inputs appeared to be due to the bypassing of the soil and the root system rather than to a soil-internal N surplus.

**Keywords:** catchment, end-member mixing analysis, forest ecosystem, gleysol, nitrate leaching, nitrogen deposition, nitrogen transformation

## 1. Introduction

Until the 1950's nitrogen acted as a growth-limiting nutrient in most coniferous forests in the Northern Hemisphere. Forest soils were low in exchangeable nutrients and characterised by a close cycling of N (Miller *et al.*, 1979). Due to the high atmospheric N deposition of the last decades, the closed N cycle, in which inputs and outputs of the ecosystems are small compared to the internal cycling, became uncoupled, which led to high leaching losses of N (Berg and Verhoef,



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1998). When the available inorganic N is in excess of total plant and microbial nutritional demand, the ecosystem is called 'N saturated' (Aber *et al.*, 1989). Enhanced  $\text{NO}_3^-$  leaching is usually regarded as the main symptom of N saturation (Ågren and Bossata, 1988; Aber *et al.*, 1989).

In recent years, many studies have experimentally manipulated the N deposition to forest ecosystems (Adams *et al.*, 1997; Aber *et al.*, 1998; Wright and Rasmussen, 1998). They showed an immediate response of  $\text{NO}_3^-$  leaching within the first year of treatment, whereas the responses in vegetation and soil were delayed (Gundersen *et al.*, 1998). This suggests that a part of the  $\text{NO}_3^-$  leaching from the forest ecosystem due to elevated N inputs is hydrologically driven and not an expression of N saturation. Field studies, mainly conducted on agricultural land, have shown that in most soils a substantial fraction of the surface applied solutes bypass the soil matrix (Luxmoore *et al.*, 1990; Flury *et al.*, 1994). This indicates that the travel time of solutes is shorter than expected based on the convective-dispersive flow assumption (Stamm *et al.*, 1998). Secondly, only a small proportion of the reactive sites within the soil comes in contact with the infiltrating rainwater. Thus,  $\text{NO}_3^-$  leaching may increase before the elevated N input exceeds the assimilation capacity of the ecosystem.

In most studies focussing on the effects of increased N depositions on forest ecosystems, the response of soil solution chemistry and of N mineralisation was measured (McNulty and Aber, 1993; Emmet *et al.*, 1998; Gundersen *et al.*, 1998). Only a few experiments have examined changes in runoff chemistry (Kahl *et al.*, 1993; Adams *et al.*, 1997; Moldan and Wright, 1998). In this study, we investigate the relationship between the N transformation and runoff processes in response to elevated N deposition in a subalpine forest Gleysol. The fate of added N was studied seasonally and during single rainfall events at different spatial scales: (i) at the  $\text{mm}^2$  scale with micro suction cups; (ii) in plots of  $20 \text{ m}^2$  by sampling soil solution, measuring net nitrification, and denitrification; and (iii) in the runoff from experimentally delineated forested sub-catchments of  $1500 \text{ m}^2$ . Our hypothesis was, that the increased  $\text{NO}_3^-$  leaching from this forest ecosystem due to elevated N deposition is mainly hydrologically driven and not caused by a change in nitrogen saturation.

## 2. Materials and Methods

### 2.1. STUDY SITE

The study area is located in the Alptal ( $47^\circ 03' \text{N}$ ,  $8^\circ 43' \text{E}$ ) in the Prealps of central Switzerland. Mean air temperature is  $6^\circ \text{C}$  and precipitation averages  $2300 \text{ mm}$  per year. The parent rock material is Flysch, consisting of alternate calcareous sandstones with argillite and bentonite shists. Major soil types are clayey Gleysols

TABLE I  
Selected soil properties

Horizon (depth)	pH (CaCl <sub>2</sub> )	Redox potential <sup>a</sup> (mV)	C content <sup>b</sup> (g kg <sup>-1</sup> )	N content <sup>b</sup> (g kg <sup>-1</sup> )	C/N	Texture <sup>c</sup> % clay/ silt/sand
Mound						
LFH (0–5 cm)	3.3		423	19	22	
A (5–10 cm)	4.6	+600 to +800	70	4.1	17	47/47/6
Bw1 (10–20 cm)	5.2	+400 to +700	27	1.8	15	
Bw2 (20–50 cm)	5.9	+200 to +600	14	0.9	15	46/46/5
Depression						
LF (0–2 cm)			423	19	22	
A (2–10 cm)	5.4	+100 to +600	156	8.5	18	51/45/4
BwA (5–10 cm)	6.1	0 to +400	86	4.8	19	44/44/11
Bg (10–50 cm)	6.9	–250 to +100	16	0.8	21	43/42/15

<sup>a</sup> Measured with Pt electrodes (n = 20 per depth).

<sup>b</sup> Measured with a Carlo Erba C/N analyser.

<sup>c</sup> From Schleppe *et al.* (1998).

of low permeability with a water table close to the surface throughout the year. Usually, the soils are covered with snow from mid November to April.

Vegetation and soil types form a mosaic pattern, which reflects the micro-topography. The mounds with a water table exceeding 40 cm depth have an oxidised Bw horizon and a forest floor, consisting of an Oi, an Oe, and an Oa-layer (umbric Gleysol). In the depressions, the water table frequently reaches the surface, leading to a muck topsoil with a high carbonate content (mollic Gleysol). The mineral soil consists mainly of a permanently reduced Bg horizon, overlain by a BwA horizon in better drained spots. Selected soil properties are given in Table I.

Norway spruce (*Picea abies* (L.) Karst.) grow on the better drained mounds and *Vaccinium sp.* (L.) is the dominating plant species of the understory vegetation. The depressions are waterlogged and too wet for tree growth. Here, the ground vegetation is dominated by *Caltha palustris* (L.) and *Petasites albus* (L.) Gaertner under a dense tree canopy, and by *Poa trivialis* (L.) and *Carex ferruginea* (SCOP.) in open patches (Muller, 1997).

## 2.2. EXPERIMENTAL DESIGN OF NITREX SUB-CATCHMENTS (1500 m<sup>2</sup>)

This study was part of the NITREX project (NITrogen saturation EXperiments, Wright and Rasmussen, 1998). Two forested sub-catchments (1500 m<sup>2</sup>) were hydrologically delineated by 80 cm deep trenches to collect the exported N (Schleppe

*et al.*, 1998). Ambient N deposition in throughfall was about  $18 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . The N deposition of one of the sub-catchments was increased by adding  $30 \text{ kg NH}_4\text{NO}_3\text{-N ha}^{-1} \text{ yr}^{-1}$  to rainwater. The other sub-catchment received the same amount of untreated rainwater, which increased the total precipitation by about 10%. The additional rainwater, with and without N, was applied by an automated sprinkling system simultaneously and proportionally to the precipitation. During the winter, concentrated  $\text{NH}_4\text{NO}_3$  solution was applied manually onto the snow using a backpack-sprayer. The water discharge from the sub-catchments was measured continuously by recording the water level of a V-notch weir with an ultrasonic device. Runoff proportional samples, bulk deposition and throughfall were collected weekly (Schleppi *et al.*, 1998). Nitrogen export from the sub-catchments was estimated by multiplying N concentrations and discharge.

The water balance, calculated on a yearly basis for the sub-catchments, showed differences between inputs and outputs not exceeding 7% (Schleppi *et al.*, 2000). The budget of  $\text{Cl}^-$ , a conservative tracer negligibly interacting with the soil solids, was balanced. Prior to the treatment, both sub-catchments exhibited the same annual N export (Schleppi *et al.*, 1998).

During four runoff events in the summer 1998, discharge was sampled with higher temporal resolution using flow proportional automatic sampling devices (ISCO 2900, Lincoln, NE, U.S.A.). The sampling devices were connected to the permanent discharge measurements. The sampling rate was adjusted to collect one sample per 0.9 mm runoff.

### 2.3. NITROGEN TRANSFORMATION IN SOIL PLOTS ( $20 \text{ m}^2$ )

Nitrogen transformation was studied in detail in 5 plots ( $20 \text{ m}^2$ ) with and in 5 plots without increased N deposition in a block design. The ten plots, located close to the NITREX sub-catchments, received simultaneously with the sub-catchments additional rainwater either untreated or enriched with N. Soil solution was sampled using horizontally installed porous glass filter plates ( $\varnothing 90 \text{ mm}$ , max. pore radius  $<16 \mu\text{m}$ ) at 5 and 10 cm depths, and with suction cups at 30, 50 and 100 cm depths. To avoid a steady flow towards the suction devices, which would alter the redox conditions in their vicinity, the suction was applied only once a week, to collect a volume sufficient for the analyses. In the waterlogged depressions, a suction of 5 kPa was applied to the suction plates, and 15 kPa to the suction cups. In the mounds, suction plates were evacuated with 10 kPa, and suction cups with 300 kPa. Sampling was performed weekly and bulked bi-weekly per depth and plot on a volume weighted basis.

Denitrification was measured every two weeks by the acetylene inhibition technique using a static core system ( $\varnothing 6.3 \text{ cm}$ , 10 cm) (Ryden *et al.*, 1987). Two cores per plot, inserted several weeks before the sampling, were used for each measurement (details see Mohn *et al.*, 2000).

#### 2.4. MINERALISATION MONITORING BOXES

Mineralisation and net nitrification were investigated with mineralisation monitoring boxes (MMB) in the ten soil plots. The MMBs were designed (1) to allow *in situ* field incubation, (2) to warrant hydraulic conductivity similar to that of the surrounding soil, avoiding water logging or excess drainage and (3) to prevent the  $\text{NO}_3^-$  containing solution from the shallow groundwater to penetrate the MMB.

The MMB consisted of two parts, a soil core on top of an ionic exchange layer (Figure 1). The soil core was obtained by pushing a PVC tube (length 15 cm, inner  $\varnothing$  10.5 cm) gently into a precut circle in the soil. During each incubation period, three soil cores per soil plot were sampled. Two cores were taken to the laboratory for immediate extraction for initial inorganic N determinations. The third core was installed on top of the exchange resin layer and placed back into the original hole in the soil.

The exchange resin layer consisted of two PVC-tubes, an outer tube containing a uniform mixture of silt and ion exchange resin and an inner tube with a sand-resin mixture. The resin (DOWEX 50WX4,  $\text{H}^+$  form; DOWEX 1X8,  $\text{Cl}^-$  form saturated with  $\text{OH}^-$ ) was intended to capture any  $\text{NO}_3^-$  and  $\text{NH}_4^+$  percolating through the column. Two different mixtures of resin with either sand or silt were used to obtain hydraulic conditions similar to those of the B horizon. The B horizon has a clayey texture with a low permeability. Macropores are common in the subsoil and lead to preferential flow phenomena (Feyen *et al.*, 1999). The artificially packed silt-resin mixture had a low hydraulic conductivity ( $K_s < 0.2 \text{ cm hr}^{-1}$ ), whereas the sand-resin mixture had a high conductivity ( $K_s \approx 80 \text{ cm hr}^{-1}$ ). From the similar water contents of the soil inside and outside of the MMB throughout the measuring period, we assume that the exchange resin part had a drainage similar to that of the surrounding soil. The silt-resin tubes were prepared by mixing 25 mL of each resin with industrial pure  $\text{SiO}_2$  silt. For the sand-resin, 20 mL of each resin were mixed with industrial pure  $\text{SiO}_2$  sand. Both silt and sand were rinsed with deionised water before use.

In order to distinguish between  $\text{NO}_3^-$  derived from the incubated soil and  $\text{NO}_3^-$  entering from the groundwater, the resin cores were separated in three vertical sections. The upper section (0 to 4 cm) captured the downward flux of N, whereas the upward N flux was adsorbed by the lower section (8 to 10 cm). The middle section was used as a check to ensure that all N was adsorbed by the upper and lower section. Inorganic N in the middle section was indeed always close to the detection limit. As an internal standard,  $\text{NH}_4\text{NO}_3$  equivalent to  $30 \text{ kg N ha}^{-1}$  was added to 5 MMBs. These standard MMBs were then installed in one of the plots during August 1996. 92 to 110% of the added N was found adsorbed by the resin.

The MMBs were incubated in four week intervals in the field throughout the snowfree season (May to November 1996). During the winter, MMBs were sampled only once in December and once in April. Net nitrification was estimated by the following equation:

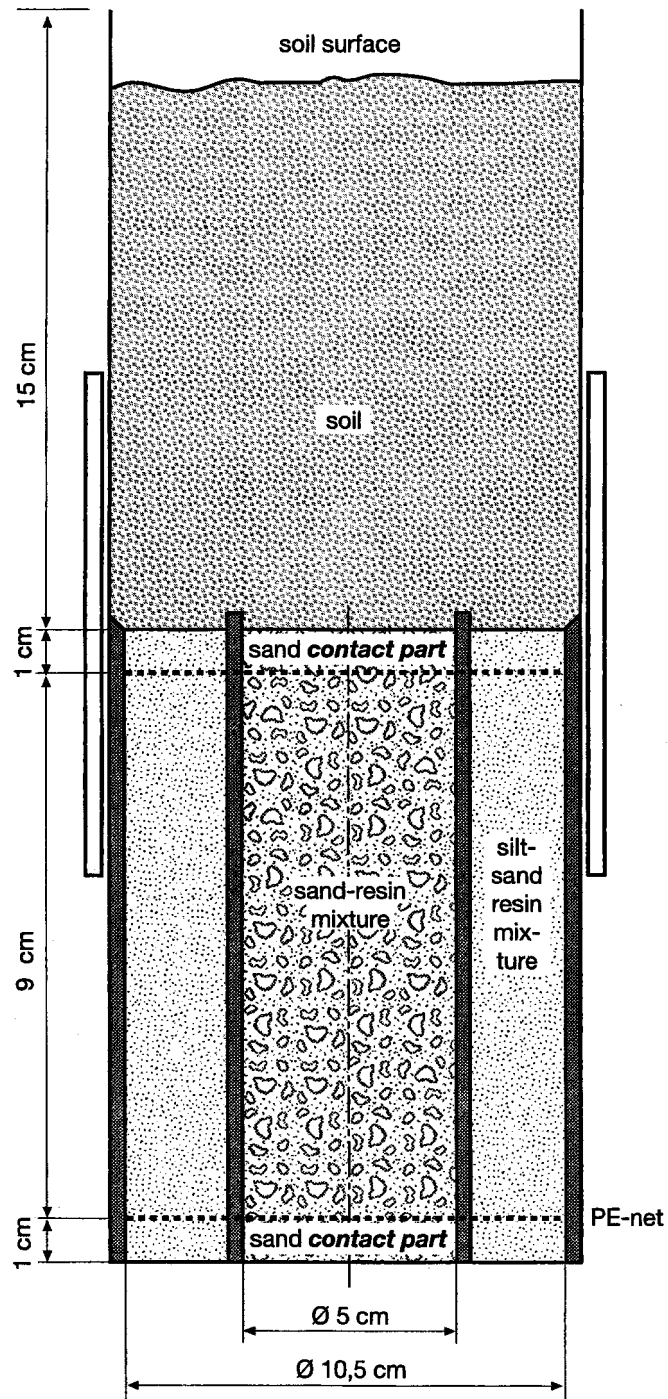


Figure 1. Construction of mineralisation monitoring boxes.

Net nitrification =

$$(\text{NO}_3^-_{t1} - \text{NO}_3^-_{t0}) + (\text{NO}_3^-_{\text{leached}} + N_{\text{denitr}} - \text{NO}_3^-_{\text{input}}) \quad (1)$$

where  $\text{NO}_3^-_{t1}$  is the  $\text{NO}_3^-$  content of the soil after the incubation,  $\text{NO}_3^-_{t0}$  is the  $\text{NO}_3^-$  content of the soil before the incubation,  $\text{NO}_3^-_{\text{leached}}$  represents the amount of resin-absorbed  $\text{NO}_3^-$ ,  $N_{\text{denitr}}$  is the loss through denitrification, and  $\text{NO}_3^-_{\text{input}}$  is the  $\text{NO}_3^-$  input from throughfall.

## 2.5. TRANSFORMATION OF $\text{NH}_4^+$ AND $\text{NO}_3^-$ ON THE SMALL SCALE

Fifty micro suction cups (surface 12 mm<sup>2</sup>) were installed at 1, 2, 3, 4, and 5 cm depths in one of the plots located in a depression and receiving N additions (details see Hagedorn *et al.*, 1999). After 10 weeks of equilibration with the surrounding soil,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were added one after the other to investigate the transformation of both N forms.

First, a pulse of 2.5 mmol  $(\text{NH}_4)_2\text{SO}_4$  m<sup>-2</sup> was applied with a backpack sprayer during a simulated rainfall event of 14 mm. Then, after a drainage period of ten days, 5 mmol  $\text{KNO}_3$  m<sup>-2</sup> was added onto the plot with an automatic sprinkling device (described in detail by Flury *et al.*, 1994). Simultaneously with the  $\text{NO}_3^-$ , 5 mmol  $\text{KCl}$  m<sup>-2</sup> was applied as a tracer for the water transport. Since this experiment was designed to study the  $\text{NO}_3^-$  transformation in the topsoil, rapid leaching was avoided by applying  $\text{NO}_3^-$  at the end of the simulated rainfall of 18 mm. The addition of both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  corresponded approximately to a mean N input of 2 weeks (= 18 kg N ha<sup>-1</sup> yr<sup>-1</sup>). After the additions, the field plot was covered with a plastic sheet to avoid an additional N-input by rainfall.

A suction of 30 kPa was applied to the micro suction cups. To obtain sufficient volume for the analysis, the sampled soil solutions from each depth were bulked (50  $\mu\text{L}$  per cup) except the first and the last sampling date, where the micro cups yielded sufficient water for separate analysis. All samples were immediately frozen until analysis.

## 2.6. SAMPLE PREPARATION AND ANALYSES

Within 36 hr after sampling of the soil cores, the roots were removed from the soil, the soil was homogenised, and shaken for 1 hr with 0.5 M  $\text{K}_2\text{SO}_4$  at a 1:4 soil/solution ratio. All fractions of the exchange resin layer from the MMB were extracted with 0.5 M  $\text{K}_2\text{SO}_4$ . The upper section of the sand-resin mixture was shaken with 200 mL for 12 hr, followed by an 1 hr extraction with another 100 mL. The middle and the lower section of the sand-resin column were shaken for 12 hr with 100 mL, and finally all silt-resin columns with 200 mL for 12 hr. Microbial biomass in the soil was estimated with the chloroform fumigation-extraction procedure according to Brooks *et al.* (1985).

Determination of  $\text{NO}_3^-$  in the filtrates (filter: Schleicher and Schuell 589/3) was conducted photometrically at 210 nm according to Norman and Stucki (1981) with a Shimadzu UV-160 spectrophotometer. Water samples of soil solution and catchment runoff were collected and stored in acid-washed polyethylene bottles, passed through a  $0.45 \mu\text{m}$  filter (Schleicher and Schuell ME25) within the next 48 hr and were stored at  $4^\circ\text{C}$ . Subsamples were acidified to 2.5%  $\text{HNO}_3$  by volume for cation analyses. Water samples were analysed for major cations by induced-coupled plasma atomic emission spectrometry (Perkin Elmer ICPAES OPTIMA 3000), and anions by ion chromatography (DIONEX DX-120). Ammonium in both salt extracts and sampled waters was measured colorimetrically by automated flow injection analysis (PE FIAS-300). Dissolved organic carbon (DOC) was measured with a Shimadzu TOC-500 analyser. Total dissolved N (TDN) in soil water and chloroform extracts was estimated by alkaline peroxodisulfate digestion converting all nitrogen to nitrate (Hagedorn and Schleppei, 2000). Dissolved organic N (DON) was obtained by subtracting the concentration of inorganic species from the total dissolved N.

Soil solutions sampled by micro suction cups were analysed with capillary electrophoresis (BioFocus 3000, BioRad). Major anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) were measured using a pyromellitic acid buffer system adjusted to pH 8 with TEMED (Fluka). Analysis of  $\text{NH}_4^+$  was performed with a metol buffer system (5 mM metol, 5 mM ascorbic acid, 2 mM 18-crown-6). Separation was conducted at  $20^\circ\text{C}$  with 20 kV voltage. Samples were injected by vacuum, detection wavelength was 230 nm for anions and 220 nm for cations. Detection limits were  $5 \mu\text{M}$  for  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , and  $10 \mu\text{M}$  for  $\text{NH}_4^+$ . Due to the minimal available volumes, samples were not filtered prior to analysis.

## 2.7. STATISTICAL AND END-MEMBER MIXING ANALYSIS

Effects of elevated N deposition on N concentrations of the soil solution, on exchangeable N of the soil, and on leached N measured by the MMBs were tested by 2-way ANOVA with STATISTICA.

To obtain information about the origin of the runoff, an end-member mixing analysis (EMMA) (Christophersen *et al.*, 1990; Mulder *et al.*, 1995) was performed. The EMMA enables the identification of the contribution of observed sources (the so called end-members) to runoff based upon their water chemistry using a least-square regression technique. Here, the end-members are the B horizon, the topsoil at 5 cm depth, and precipitation. EMMA is applicable (i) when the concentrations of the individual solutes differ significantly between end-members and (ii) when each of the end-members has at least one solute being at maximum concentration. During the monitored storm, this were  $\text{Ca}^{2+}$  in the B horizon, DOC in the topsoil and  $\text{Cl}^-$  in precipitation.

The EMMA procedure relies on the assumption that end-member chemistry is constant in time (Christophersen *et al.*, 1990). To explain runoff chemistry at peak



discharge, we had to use precipitation as one end-member. Element concentrations in precipitation change drastically over time. However, the storm was short compared to the subsequent runoff (Figure 9), which allowed us to consider the precipitation as a short pulse with constant element concentrations.

The relative contribution of the end-members to the runoff was estimated by solving the following set of simultaneous equations:

$$f_1 c_{i,1} + f_2 c_{i,2} + f_3 c_{i,3} = c_{i,r} \quad (2)$$

$$f_1 + f_2 + f_3 = 1 \quad (3)$$

where  $c_i$  is the concentration of the variables  $i = (\text{Ca}^{2+}, \text{Cl}^-, \text{DOC})$ , the subscripts 1, 2, and 3 refer to the end-members (flow paths),  $r$  refers to runoff sample; and  $f$  refers to the runoff fraction contributed by the end-members. Solute concentrations were normalised relative to their standard deviations. Calculations were performed with the non-negative least square fitting procedure of MATLAB.

### 3. Results and Discussion

#### 3.1. SOIL MINERAL N AND NET NITRIFICATION

Increased N deposition caused no increase of  $\text{K}_2\text{SO}_4$ -extractable N in the soil, neither of  $\text{NO}_3^-$  nor of  $\text{NH}_4^+$  (Figure 2). Nitrate contents in the N-treated plots were even lower than those of the control plots, which was probably due to their higher water tables, consequently lower redox potentials and stimulated denitrification (Mohn *et al.*, 2000). Elevated N deposition had no significant impact on net nitrification. The annual net nitrification rate was  $1.2 \pm 2.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the control plots and  $-0.5 \pm 2.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the N addition plots, indicating that the net production of  $\text{NO}_3^-$  in the soil was low. Contents of  $\text{NO}_3^-$  were equally low on the mounds and in the depressions, while net nitrification was slightly higher on the mounds than in the depressions (data not shown). Ammonium contents peaked in the winter. This can either be attributed to a stimulated mineralisation during frost and thaw cycles (DeLuca *et al.*, 1992) or to a increased  $\text{NH}_4^+$  assimilation by plants and soil microbes during the growing season.

#### 3.2. SOIL SOLUTION

Nitrate concentrations of the soil solution were low (Figure 3). At 30 cm soil depth,  $\text{NO}_3^-$  concentrations were already below the detection limit of  $0.8 \mu\text{M NO}_3^-$ , except during snowmelt periods. Concentrations of  $\text{NO}_3^-$  were highest during the winter, probably as a result of a reduced biological assimilation. They coincide with the smallest denitrification rates and the highest redox potentials during these periods (Mohn *et al.*, 2000).  $\text{NH}_4^+$  concentrations of the soil solution were even lower than

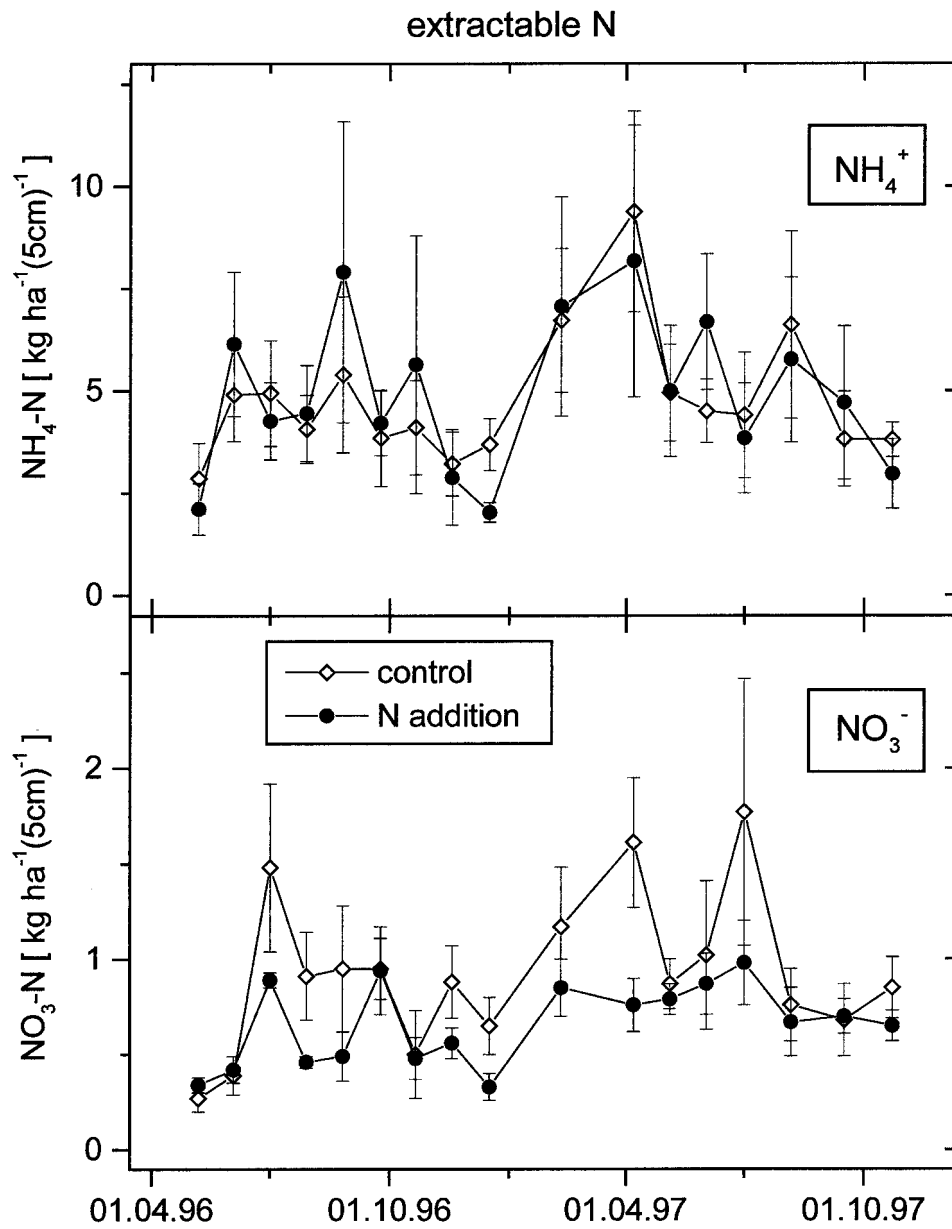


Figure 2. Contents of  $K_2SO_4$ -extractable  $NH_4^+$  and  $NO_3^-$  in the soil. Means and standard errors of 5 plots per treatment. Please note that the y-axis of  $NH_4^+$  and  $NO_3^-$  contents have different scales.

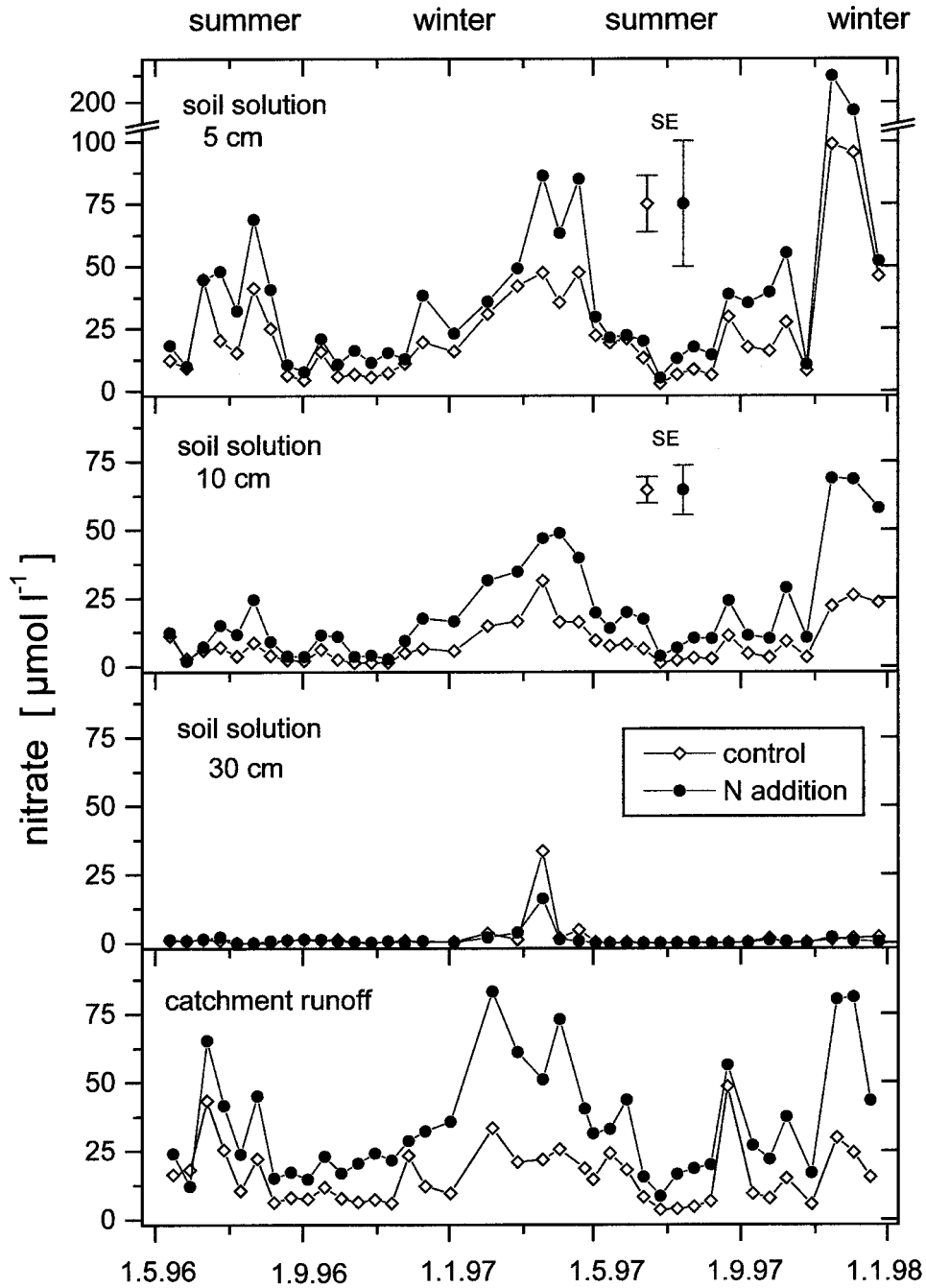


Figure 3. Nitrate concentrations in the soil solution and in the sub-catchment runoff. Means of 5 plots per treatment. Error bars indicate the mean standard errors of all sampling dates.

$\text{NO}_3^-$  concentrations (data not shown). Below the 5 cm depth,  $\text{NH}_4^+$  concentrations were below the detection limit of  $0.9 \mu\text{M NH}_4^+$ . Increasing the N deposition increased  $\text{NO}_3^-$  concentrations in the soil solution at 5 and 10 cm depths (Figure 3). However, the effect was only significant during the winter ( $p < 0.05$ ) and not during the growing season.

### 3.3. TRANSFORMATION OF $\text{NH}_4^+$ AND $\text{NO}_3^-$ ON A SMALL SCALE

To study the dynamics of *in situ* transformation and transport of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the soil, both N forms were applied separately onto one of the plots in a depression. Sampling of the soil solution with micro suction cups enabled the identification of the transformation of the added N with a high spatial and temporal resolution. The breakthrough of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  demonstrates that the form of N deposition is important for the N fluxes and the N transformation in the soil. The  $\text{NH}_4^+$  pulse addition was not reflected in the soil solution at all (Figure 4), not even at the 1 cm depth. Concentrations of  $\text{SO}_4^{2-}$ , which was applied simultaneously with  $\text{NH}_4^+$ , responded rapidly to the addition. This indicates that  $\text{NH}_4^+$  is immediately removed from the percolating rainwater. The extremely rapid retention of  $\text{NH}_4^+$  suggests that abiotic rather than biotic processes dominate. Abiotically,  $\text{NH}_4^+$  is either exchanged as a cation to negatively charged surfaces and/or incorporated into organic matter through chemical reactions (Nommik, 1970; Schimel and Firestone, 1989; Thorn and Mikita, 1992).

In contrast to  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  applied at the end of a rainfall event was leached beyond the 20 cm depth (data not shown, see Figure 5 for 5 cm depth). The dynamics of  $\text{NO}_3^-$  and the inert  $\text{Cl}^-$  were similar at 1 cm soil depth. Concentrations of both increased rapidly after the application, dropped during the next 3 days and increased again after 5 days of drying. The increase during drying was more pronounced for  $\text{NO}_3^-$  than for  $\text{Cl}^-$ , suggesting that  $\text{NO}_3^-$  was produced in the soil (Figure 5). At 5 cm depth,  $\text{NO}_3^-$  and  $\text{Cl}^-$  concentrations peaked rapidly. During the next 3 days, concentrations of  $\text{Cl}^-$  remained constant, while those of  $\text{NO}_3^-$  declined. This decrease in  $\text{NO}_3^-$  relative to the inert  $\text{Cl}^-$  suggests a net  $\text{NO}_3^-$  consumption in the soil, which was partly due to denitrification as indicated by low redox potentials and increased denitrification rates during this period (Hagedorn *et al.*, 1999). Net nitrification, here indicated by an increase of  $\text{NO}_3^-$  compared to  $\text{Cl}^-$ , was low at 5 cm depth and it did not commence until 5 days of drainage. These results suggest that in the depressions, net nitrification was mainly restricted to a thin aerobic soil layer. Since the research site receives 2300 mm of rain per year and there were only 2 rainless weeks during the summers 1996 and 1997, net nitrification was of minor importance in the depressions. The findings of low net nitrification rates with the MMBs support this conclusion.

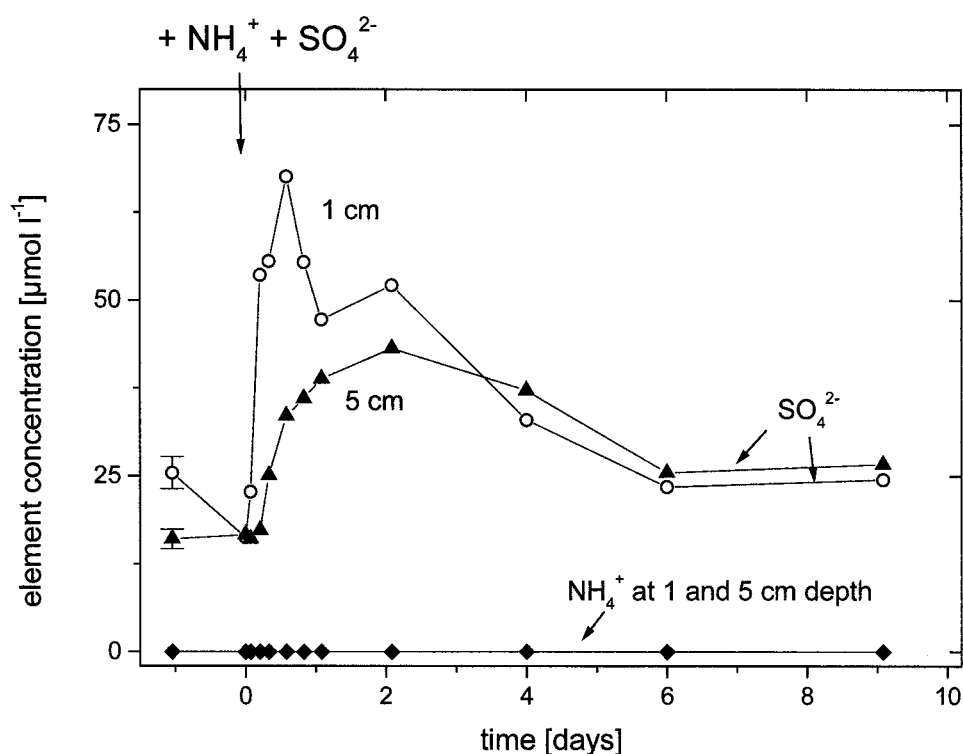


Figure 4. Ammonium and  $\text{SO}_4^{2-}$  concentrations in the soil solution at 1 and 5 cm depth of one depression plot after applying  $2.5 \text{ mmol } (\text{NH}_4)_2\text{SO}_4 \text{ m}^{-2}$  during a rainfall. Soil solution was sampled with micro suction cups. Standard errors were estimated from 10 micro suction cups at the beginning of the experiment.

### 3.4. NITRATE LEACHING

Cumulative  $\text{NO}_3^-$  leaching was measured by the MMBs and based on the concentrations of the runoff from the NITREX sub-catchments (Figure 6). Both methods yielded a similar  $\text{NO}_3^-$  export. The addition of  $30 \text{ kg } \text{NH}_4\text{NO}_3\text{-N ha}^{-1} \text{ yr}^{-1}$  caused an increase of  $\text{NO}_3^-$  export from the sub-catchment by about  $4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  during the second year of treatment. Based on the MMBs arranged in a block design, the increase of  $\text{NO}_3^-$  leaching below 10 cm depth was significant and accounted for  $3.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  ( $p < 0.05$ ). Within the MMBs,  $\text{NO}_3^-$  was only captured by the coarser sand-resin mixture with its higher saturated conductivity. As with  $\text{NO}_3^-$  concentrations in the soil solution,  $\text{NO}_3^-$  export and the effect of N-addition was highest during the winter (Figures 3 and 6). This is consistent with other N manipulation experiments at Bear Brook (Maine, U.S.A.) and at Gårdsjön (Sweden), which received similar N inputs (Kahl *et al.*, 1993; Moldan and Wright, 1998). Chronic  $\text{NO}_3^-$  export during the nongrowing season and  $\text{NO}_3^-$  leaching during the growing season is considered to be the incipient stage of N saturation (Stoddard,

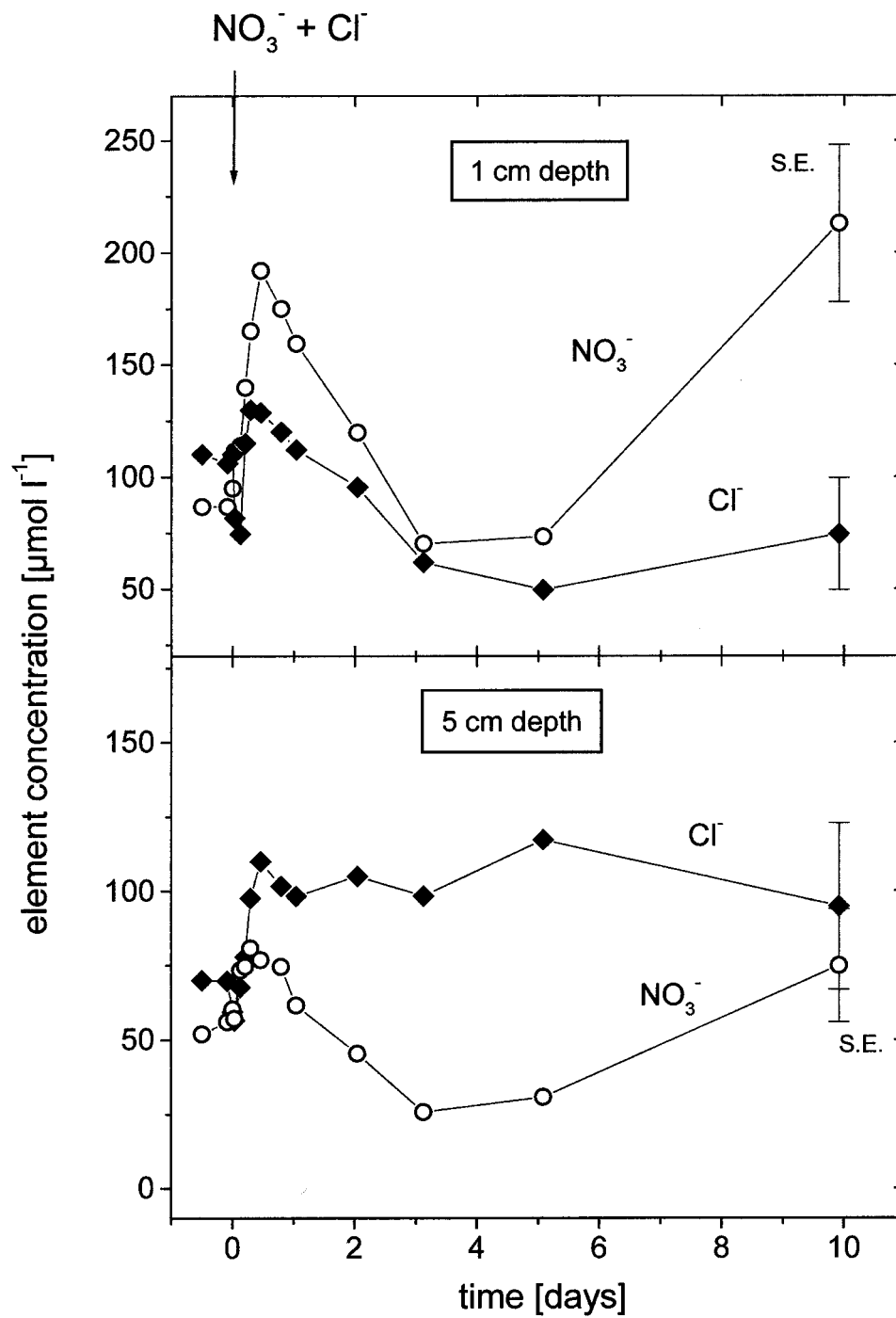


Figure 5. Nitrate and  $\text{Cl}^-$  concentrations in the soil solution sampled at 1 and 5 cm depth of one depression plot after applying  $5 \text{ mmol KNO}_3 \text{ m}^{-2}$  and  $5 \text{ mmol KCl m}^{-2}$  at the end of a rainfall. Soil solution was sampled with micro suction cups. Standard errors were estimated from 10 micro suction cups per depth at the end of the experiment.

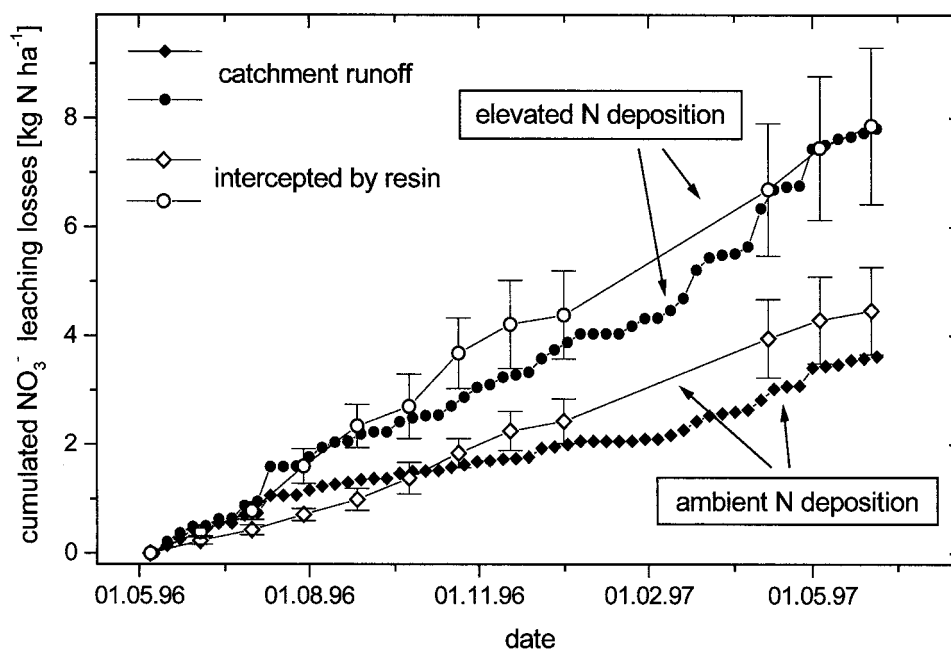


Figure 6. Cumulative  $\text{NO}_3^-$  leaching losses measured by the sub-catchment runoff and by the resin in the mineralisation monitoring boxes at 10 cm depth. In the case of the mineralisation monitoring boxes, means and standard errors of 5 plots per treatment are shown.

1994). In contrast to  $\text{NO}_3^-$ , leaching of  $\text{NH}_4^+$  was not detected, which supports the findings of the small scale experiment that  $\text{NH}_4^+$  is effectively retained in the soil.

### 3.5. RUNOFF PROCESSES

Considering soil solution data only (as done in most studies), it seems that N deposition affected only the topsoil, and that  $\text{NO}_3^-$  leaching from the deeper soil layers was not increased by elevated N inputs (Figure 3). The runoff data show, however, that  $\text{NO}_3^-$  export from the sub-catchments ( $1500 \text{ m}^2$ ) was increased. Absolute concentrations and seasonal variations of  $\text{NO}_3^-$  in the outflow from the sub-catchments corresponded closely to that of the soil solution at 5 cm depth (Figure 3). The  $\text{NO}_3^-$  leaching from 10 cm depth, as measured with the MMBs, was equal to that from the whole sub-catchment. Both findings are first indications that the runoff from this Gleysol site most likely consists of topsoil rather than subsoil water.

To obtain more information about the origin of the runoff, samples were taken with a high temporal resolution during storm events. Subsequently, the contribution of precipitation, soil water from 5 cm depth and from the B horizon to the runoff were estimated with an end-member mixing analysis (EMMA).

The sub-catchments discharge responded rapidly to storm events (Figure 9), which points to a rapid water movement through the soil system and/or surface run-

off. The headwater catchment, in which the experimentally sub-catchments were embedded, exhibited a similar runoff dynamics and hydrochemistry (Schleppi *et al.*, 1998; Feyen, 1999), suggesting that the 80 cm deep trenches, used to delineate the sub-catchments, did not alter runoff processes substantially. EMMA indicated that the proportion of precipitation at peak discharge was approximately 58% in the control sub-catchment and 51% in the N-treated sub-catchment (Figure 7). It rapidly declined within the following 10 hr. On average, the estimated proportion of precipitation at discharge was 24 and 18% in the control and N-treated sub-catchment, respectively. The largest contribution of all end-members came from the topsoil water, particularly at later stages of the discharge event. In both sub-catchments, 12 hr after the rainfall, the proportion of topsoil water reached up to 85%. The Bg horizon contributed substantially only to base flow. During the storm, the proportion of soil water from the Bg horizon in the runoff was low.

To check the EMMA predictions against independent information, the estimated topsoil contribution was compared with piezometer readings. They were significantly positively correlated ( $r^2 = 0.93^{***}$ ,  $n = 22$ ), which supports the findings of EMMA. Finally, the contributions of end-members using  $\text{Ca}^{2+}$ , DOC, and  $\text{Cl}^-$  concentrations were used to predict  $\text{NO}_3^-$  concentrations in the runoff. Predicted and measured  $\text{NO}_3^-$  concentrations were significantly correlated, but predicted concentrations were about 40% lower than measured concentrations (Figure 8). The underestimation of  $\text{NO}_3^-$  concentrations in the runoff based on EMMA was probably due to lower  $\text{NO}_3^-$  concentrations in the soil end-members, as measured with suction devices, than in the aerobic macropores, which are relevant for solute transport. Flow paths can have substantially higher  $\text{NO}_3^-$  concentrations than the rest of the soil, particularly under reducing conditions (Hagedorn *et al.*, 1999).

EMMA clearly shows that a large proportion of the runoff had limited contact with the subsoil and originated mainly from the precipitation and topsoil. This is consistent with the results from tracer experiments conducted in soil plots in the immediate vicinity of the sub-catchments. They demonstrated rapid solute transport through a network of macropores (Feyen *et al.*, 1999). Since  $\text{NO}_3^-$  concentrations were highest in the rainwater and decreased with depth in the soil, the highest  $\text{NO}_3^-$  concentrations occurred at peak flow when precipitation had the largest contribution to the runoff (Figure 9). The consequence was that most of the  $\text{NO}_3^-$  was exported directly after rainfalls. Concentrations of  $\text{NH}_4^+$  during the runoff event did not exceed  $5 \mu\text{mol L}^{-1}$ , which shows that the contact of the infiltrating rain water with the soil was sufficient to retain all  $\text{NH}_4^+$ .

The comparison of the duration of the  $\text{NO}_3^-$  peak – hours – with the time scale of N transformations measured with the micro suction cups – days – is a further indication that the  $\text{NO}_3^-$  export from the sub-catchments was mainly hydrologically driven (Figures 5 and 9). Net nitrification rates may influence the ‘boundary conditions’ of each runoff event, the concentrations of  $\text{NO}_3^-$  concentrations in the base flow and those of the end-members, topsoil and subsoil, but the temporal pattern of  $\text{NO}_3^-$  concentrations in the catchment outflow will remain the same. This is



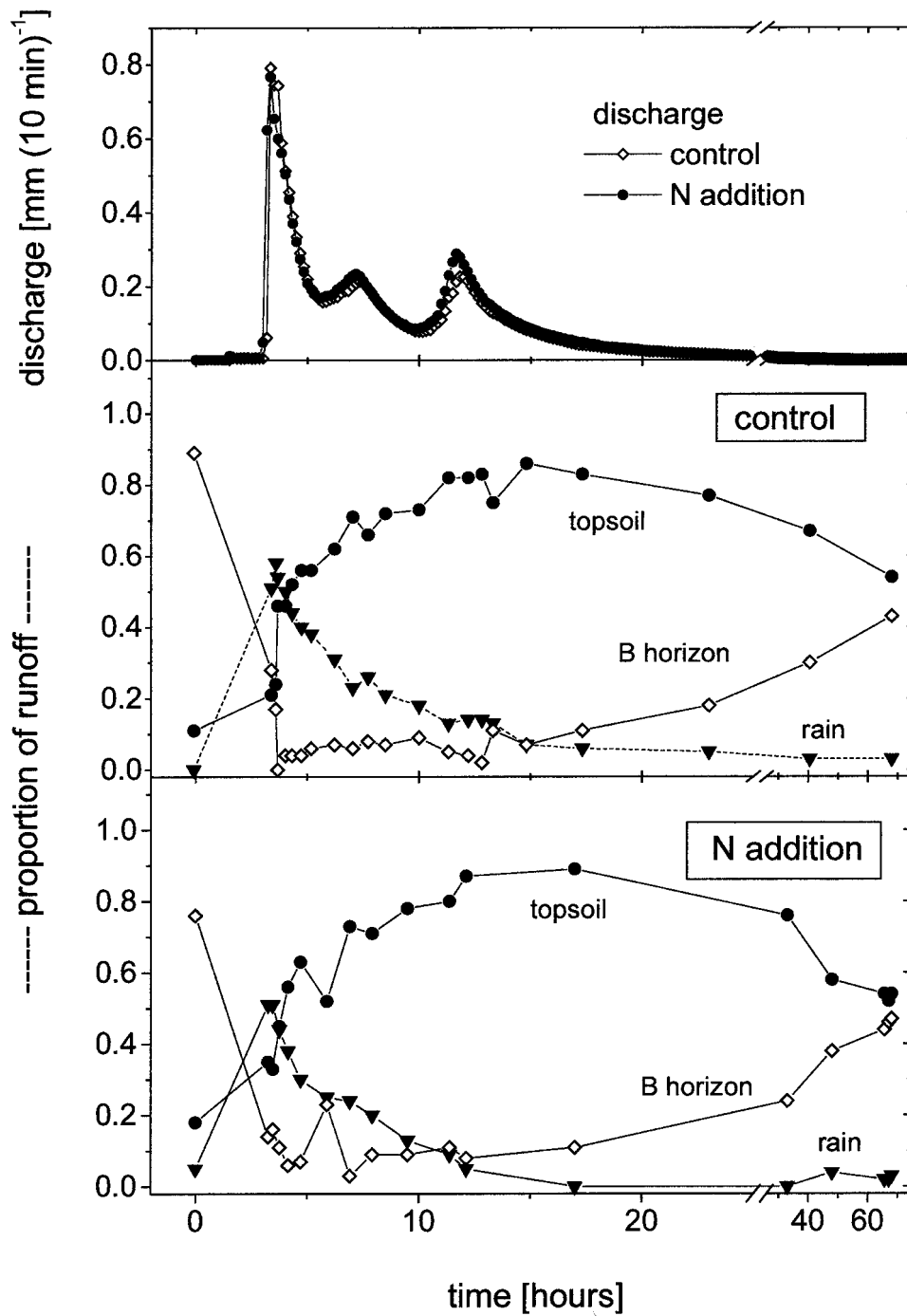


Figure 7. Discharge and contribution of end-members (rain, topsoil at 5 cm depth, B horizon) to the runoff from the control and N addition sub-catchment during the storm of July 13–16, 1998. The EMMA was calculated with  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and DOC concentrations.

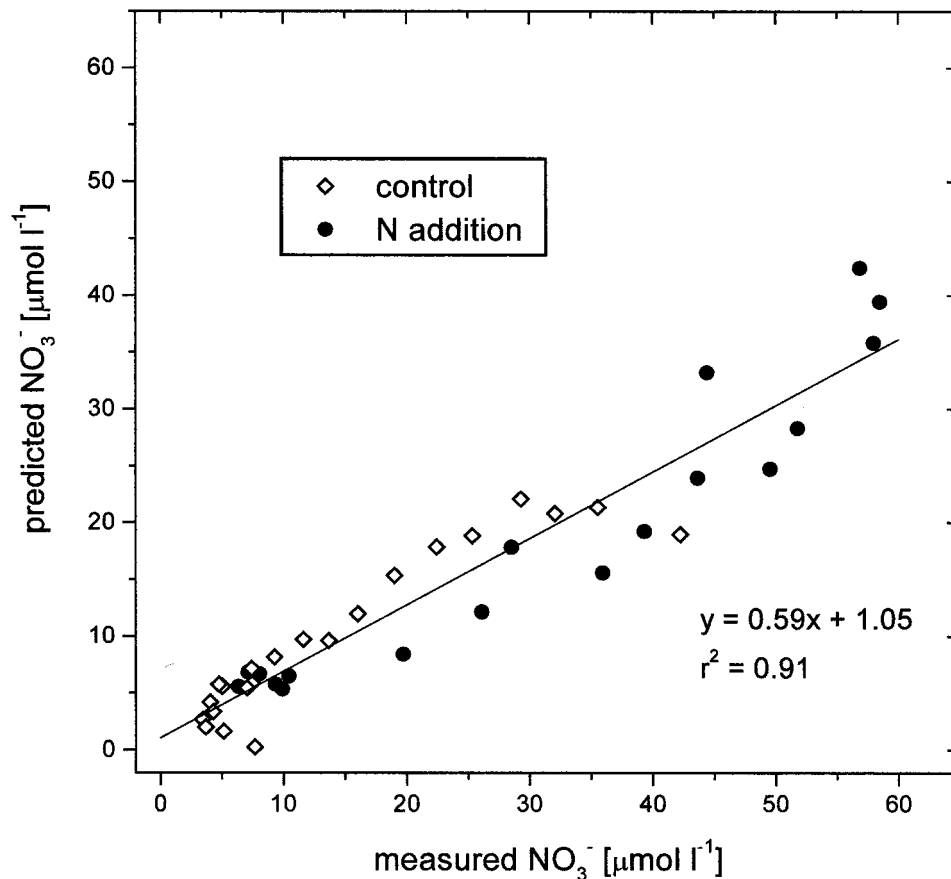


Figure 8. Predicted (y) on measured (x)  $\text{NO}_3^-$  concentrations in the outflow of the sub-catchments during the storm of July 13–16, 1998. Predictions were performed on the basis of estimated contributions of the end-members (rain, topsoil at 5 cm depth, B horizon) to the runoff.

supported by the similar  $\text{NO}_3^-$  dynamics during all of the four monitored events (data not shown).

The pronounced impact of hydrological processes on  $\text{NO}_3^-$  leaching was also observed on a larger temporal scale. The weekly  $\text{NO}_3^-$  export from the sub-catchment, expressed as percentage of the weekly  $\text{NO}_3^-$  input, was closely related to the discharge of the sub-catchment (Figure 10). The higher the discharge, the more  $\text{NO}_3^-$  was exported. However, the relative effect of discharge on the  $\text{NO}_3^-$  export was lower in summer when significant losses through denitrification occurred (Mohn *et al.*, 2000) and plant uptake was highest.

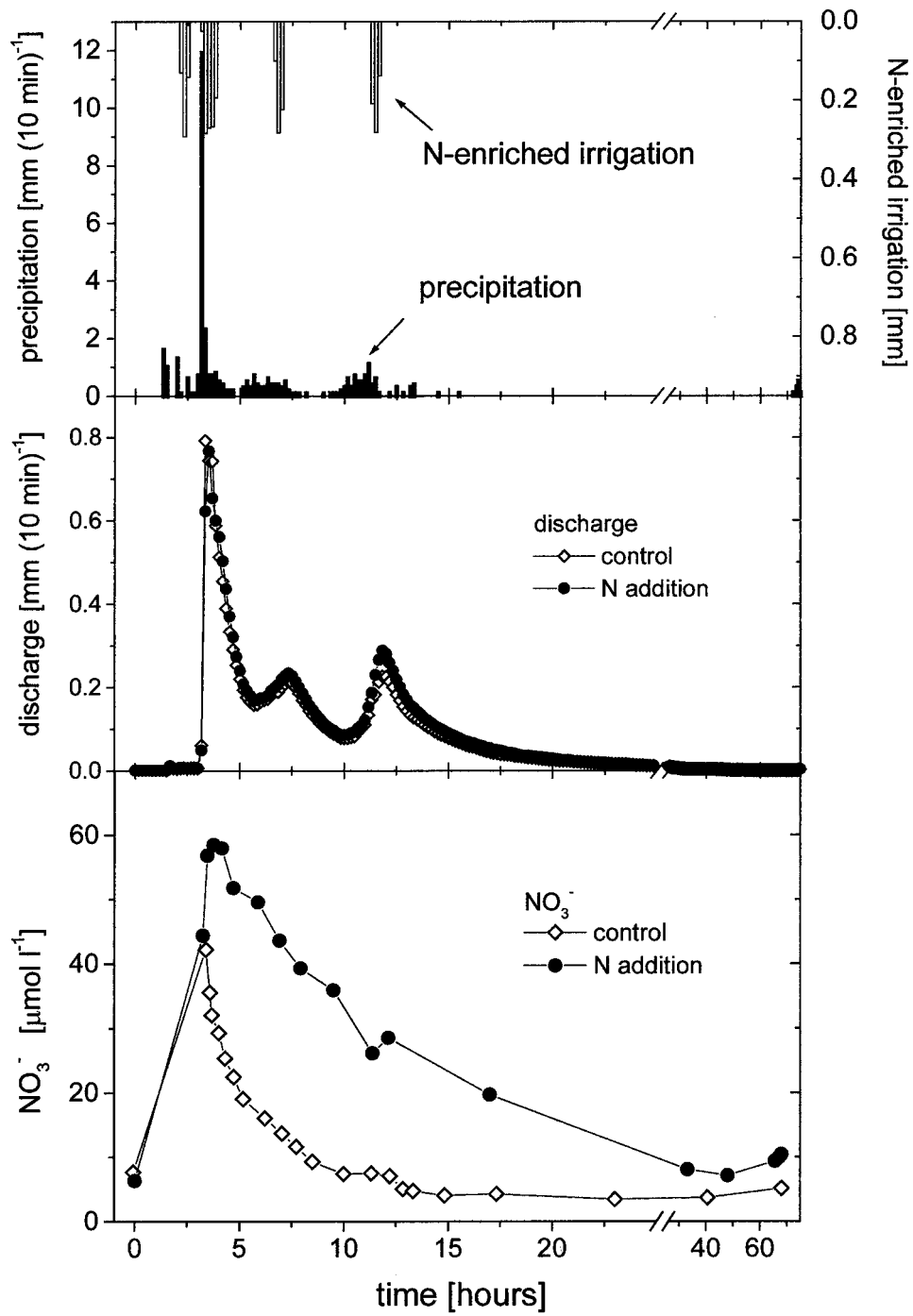


Figure 9. Precipitation, N-irrigation, discharge, and nitrate concentrations of the sub-catchments runoff during the storm of July 13–16, 1998.

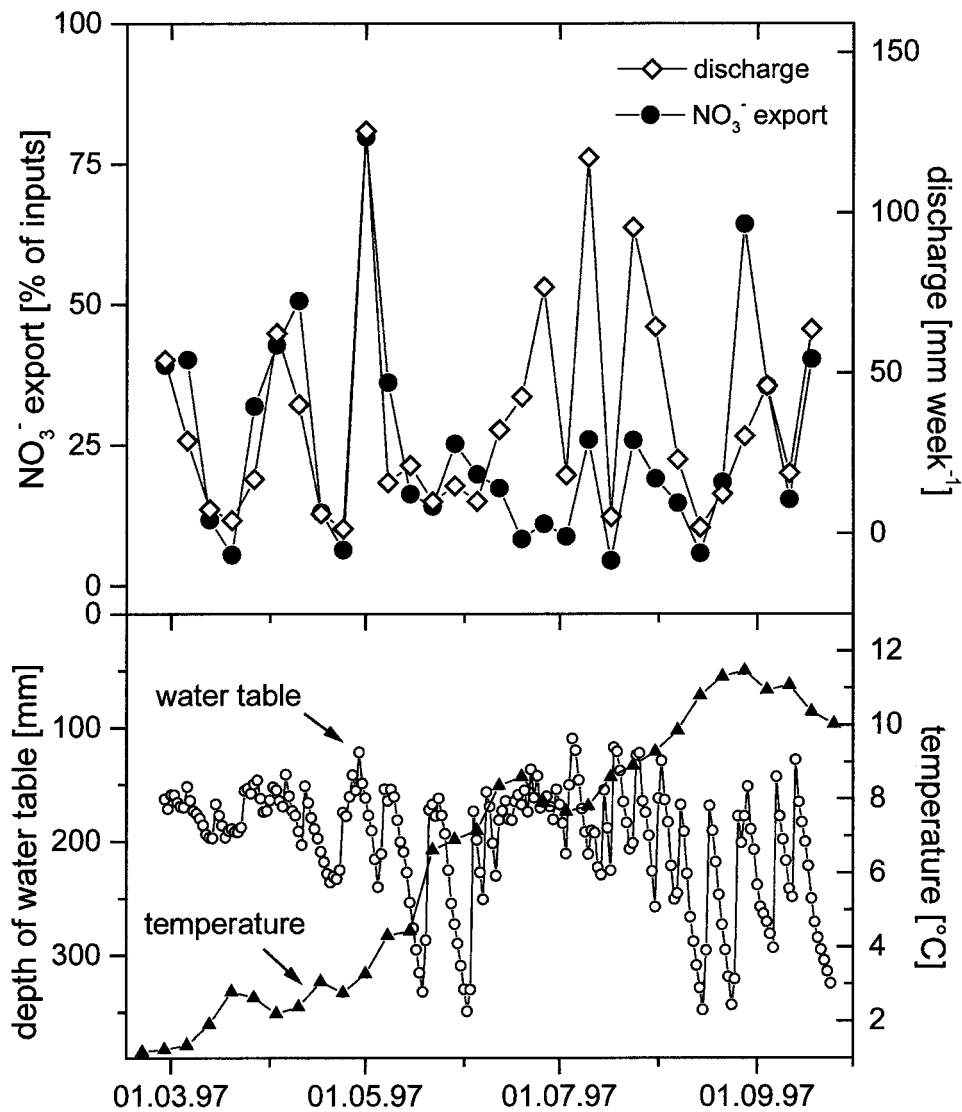


Figure 10. Weekly nitrate export, expressed as the percentage of the weekly nitrate inputs, from the sub-catchment receiving elevated N deposition during the 3rd year of treatment. Runoff and throughfall samples were bulked weekly. Water table and soil temperature at 20 cm depth were measured within the sub-catchment.

### 3.6. N BALANCE

During the monitored storm event, 18% of the applied N was exported by the catchment outflow. On an annual basis, about 80% of the added N was retained in the forest ecosystem (Table II). These values agree well with the results of a <sup>15</sup>N study,

which showed that one year after the 12 months of continuous  $^{15}\text{N}$  addition, 75% of the applied N was still present in the organic layer and the upper soil horizons (Schleppi *et al.*, 1999a). The above-ground vegetation took up only 12% of the added  $^{15}\text{N}$ . The high N retention in the soil at the Alptal site is consistent with other N manipulation experiments (Aber *et al.*, 1998; Bredemeier *et al.*, 1998; Tietema *et al.*, 1998). N retention in the soil is generally related to (1)  $\text{NH}_4^+$  adsorption to cation exchange sites and fixation by clay minerals, (2) microbial immobilization (Clinton *et al.*, 1995; Tietema, 1998), (3) abiotic incorporation of inorganic N into organic matter through chemical reactions (Nommik, 1970; Schimel and Firestone, 1989; Thorn and Mikita, 1992), or (4) mycorrhizal assimilation (Aber *et al.*, 1998).

The negligible effect of N deposition on  $\text{K}_2\text{SO}_4$ -extractable  $\text{NH}_4^+$  (Table II) suggest that adsorption to cation exchange sites was not – or at most only temporarily – a major sink for deposited N. As indicated by the immediate retention of  $\text{NH}_4^+$  in the organic layer, the direct fixation of deposited  $\text{NH}_4^+$  by clay minerals is hindered by the minimal travel distance of  $\text{NH}_4^+$ , but it is probably responsible for the non-detectable  $\text{NH}_4^+$  concentrations in the subsoil. Nor was microbial biomass a dominant sink for the added N (Table II), which is in accordance with the minimal effects of manipulated N inputs on soil fungi and bacteria at other NITREX sites (Boxmann *et al.*, 1998). Since none of these N-pools was affected by the increased N inputs, most of the added N was likely to have been incorporated into soil organic matter. This is supported by various laboratory experiments demonstrating a very high potential of forest floors to incorporate inorganic N (Nommik, 1970; Clinton *et al.*, 1995; Thorn and Mikita, 1995).

Assuming a retention of about 70% of the additional N-inputs into the organic matter of the uppermost 5 cm of soil, the C/N ratio will decrease by about 1 approximately every 3 yr. Since the C/N ratio of the organic layer at Alptal (about 22) is close to that of N saturated forest stands in The Netherlands and Wales (20–22; Gundersen *et al.*, 1998) long-term effects on nitrogen pools in the ecosystems and an additional increase in  $\text{NO}_3^-$  leaching can be expected.

#### 4. N saturation?

The Alptal site receiving a moderate ambient N deposition of  $18 \text{ kg NH}_4\text{NO}_3\text{-N ha}^{-1} \text{ yr}^{-1}$  was in the proximity of the critical threshold for  $\text{NO}_3^-$  leaching from forest ecosystems (Dise and Wright, 1995). Thus,  $\text{NO}_3^-$  leaching of  $4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  under ambient N deposition was within the range of leaching losses from other forest sites exposed to a similar N deposition in Europe (Dise and Wright, 1995; Bredemeier *et al.*, 1998; Moldan and Wright, 1998). The experimental increase of N-inputs by  $30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  raised the N deposition above the critical threshold at which cycling of N is thought to become uncoupled. However, after the first 3 yr of N additions, trees were still slightly deficient in N and no effects on vegetation were observed (Schleppi *et al.*, 1999b). Nitrogen pools in the soil and net nitrifica-

TABLE II

Pool sizes and N-fluxes during the second and third year of treatment. Numbers in parenthesis represent the percentage of N exported relative to the total N-input

	Control	N-addition	Difference
	(kg N ha <sup>-1</sup> yr <sup>-1</sup> )		
Bulk deposition			
NO <sub>3</sub> <sup>-</sup>	6.0	19.9	13.9
NH <sub>4</sub> <sup>+</sup>	6.6	20.5	13.9
DON	2.5	2.5	0.0
Dry deposition <sup>a</sup>	4.6	4.6	0.0
Total N input	19.7	47.4	27.7
Soil N pools (0–5 cm)			
Total nitrogen	1400.0±180	1230.0±150	-170.0 (n.s.)
<sup>2</sup> Exchangeable NH <sub>4</sub> <sup>+</sup> <sup>b</sup>	4.8±1.5	5.1±2.2	0.3 (n.s.)
<sup>2</sup> Exchangeable NO <sub>3</sub> <sup>-</sup> <sup>b</sup>	1.1±0.4	0.8±0.1	-0.3 (n.s.)
<sup>3</sup> Microbial biomass N <sup>c</sup>	68.1±15	62.4±13	-5.7 (n.s.)
N output			
Denitrification <sup>d</sup>	2.2 (11%)	3.8 (8%)	1.6 (6%)
NO <sub>3</sub> <sup>-</sup> export	4.0 (20%)	8.0 (17%)	4.0 (14%)
NH <sub>4</sub> <sup>+</sup> export	0.0	0.0	0.0
DON export	5.5 (28%)	5.5 (11%)	0.0
Total N output	11.7 (59%)	17.3 (36%)	5.6 (20%)
Apparent N retention	8.0 (41%)	30.1 (64%)	22.0 (80%)

<sup>a</sup> According to Fischer-Riedmann (1995).

<sup>b</sup> Average of 16 samplings in 1996–1997.

<sup>c</sup> Measured by chloroform fumigation extraction using a  $k_{en} = 0.54$  (Brooks *et al.*, 1985), mean of 6 samplings in 1996–97.

<sup>d</sup> 0–10 cm.

n.s.: Not significant.

tion were not affected by increased N-inputs. Nevertheless, NO<sub>3</sub><sup>-</sup> leaching, usually regarded as the main symptom of N saturation (Aber *et al.*, 1989; Gundersen *et al.*, 1998), was increased due to elevated N deposition. This is consistent with findings of other NITREX experiments which have shown that NO<sub>3</sub><sup>-</sup> leaching responded within the first year of manipulating N inputs, whereas responses in vegetation and soil were delayed (Gundersen *et al.*, 1998). Nitrate leaching of 8 kg ha<sup>-1</sup> yr<sup>-1</sup> under elevated N deposition of 47 kg N ha<sup>-1</sup> yr<sup>-1</sup> was still lower than that from forest sites in Germany and in The Netherlands receiving similar N input

as ambient deposition over longer periods (Bredemeier *et al.*, 1998). The relative small increase subsequent to the drastic change in N deposition suggests that the forest ecosystem at Alptal is not yet N saturated and that the retention capacity for N is still high. About 80% of the added N was retained in the ecosystem. However, all of the  $\text{NH}_4^+$  was retained and the production of  $\text{NO}_3^-$  in the soil was negligible, which shows that the forest ecosystem was less retentive for  $\text{NO}_3^-$ : about 30% of the additionally applied  $\text{NO}_3^-$  was leached. Our results demonstrate that the increase in  $\text{NO}_3^-$  leaching was mainly hydrologically driven at this site with soils usually close to water saturation. The rapid response of discharge and  $\text{NO}_3^-$  concentration to rainfall and the large contribution of precipitation and topsoil water to the catchment runoff suggest the occurrence of preferential flow through near-surface or subsoil pathways. As a consequence, the contact time of the water with the soil matrix was insufficient for a complete retention of  $\text{NO}_3^-$ . Enhanced  $\text{NO}_3^-$  leaching was caused by the bypassing of the soil and root system rather than by a soil-internal N surplus. Thus, the increase in  $\text{NO}_3^-$  leaching due to elevated N deposition was hydrologically driven and did not reflect a change in nitrogen saturation of the forest ecosystem at Alptal.

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